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1 **The significance of early and late stages of coupled aggregation and**
2 **sedimentation in the fate of nanoparticles: measurement and modelling**

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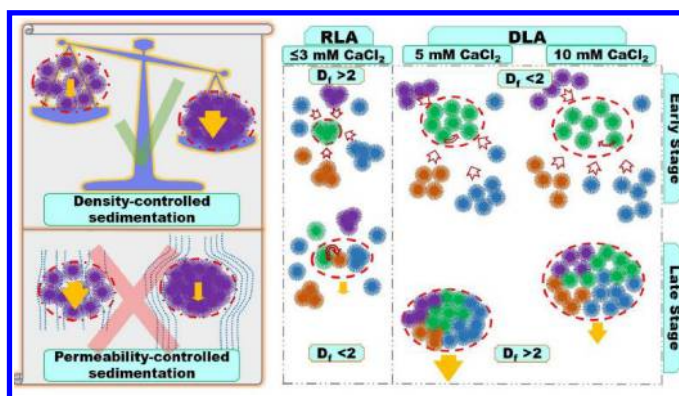
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21 **Abstract.**

22 Despite aggregation's crucial role in
23 controlling the environmental fate of
24 nanoparticles (NP), the extent to which
25 current models can describe the
26 progressive stages of NP



27 aggregation/sedimentation is still unclear. In this paper, 24 model combinations of two
28 population-balance models (PBMs) and various collision frequency and settling velocity
29 models are used to analyse spatiotemporal variations in the size and concentration of
30 hydroxyapatite (HAp) NP. The impact of initial conditions and variability in attachment
31 efficiency, α , with aggregate size are investigated. Although permeability models perform well
32 in calculating collision frequencies, they are not appropriate for describing settling velocity
33 because of their negative correlation or insensitivity in respect to fractal dimension.
34 Considering both early and late stages of aggregation, both experimental and model data
35 indicate overall mass removal peaks at an intermediate ionic strength (5 mM CaCl₂) even
36 though the mean aggregate size continued to increase through higher ionic strengths (to 10 mM
37 CaCl₂). This trend was consistent when different approaches to the initial particle size
38 distribution (PSD) were used and when a variable or constant α was used. These results point
39 to the importance of accurately considering different stages of aggregation in modeling NP fate
40 within various environmental conditions.

41

42 **Keywords:** nanoparticles; early and late stage aggregation; sedimentation; population balance
43 modelling; fractal dimension; settling velocity

44 **Nomenclature**

- 45 a_0 primary particle radius or particle radius in the smallest size class [L]
- 46 a_k aggregate radius in size class k [L]
- 47 D_f fractal dimension [-]
- 48 D_H hydrodynamic diameter
- 49 G shear rate [T^{-1}]
- 50 i, j subscripts used to indicate aggregates size class i and j
- 51 k_b Boltzmann constant
- 52 k_{max} maximum number of classes considered in the numerical model (<100)
- 53 n_k aggregate number concentration in size class k [L^{-3}]
- 54 q geometric factor
- 55 T temperature [K]
- 56 U_k aggregate sedimentation velocity in size class k [LT^{-1}]
- 57 U_0 sedimentation velocity of primary particles [LT^{-1}]
- 58 v_k volume of solids of each aggregate in size class k [L^3]
- 59 v_0 volume of primary particles [L^3]
- 60 Z_s sedimentation depth [L]

- 61 α attachment efficiency [-]
- 62 $\beta_{i,j}$ aggregate collision frequency in size class i and j [L^3T^{-1}]
- 63 β_{Diff} differential settling collision frequency [L^3T^{-1}]
- 64 β_{Orth} orthokinetic collision frequency [L^3T^{-1}]
- 65 β_{Prik} perikinetic collision frequency [L^3T^{-1}]
- 66 $\delta_{j,i}$ Kronecker delta
- 67 μ dynamic viscosity of the suspending medium [$M T^{-1} L^{-1}$]

68 **List of abbreviations.**

- 69 CCC critical coagulation concentration
- 70 DCR derived count rate
- 71 DI deionized
- 72 DLA diffusion limited aggregation
- 73 DLS dynamic light scattering
- 74 DLVO Derjaguin, Landau, Verwey, and Overbeek
- 75 FP fixed pivot
- 76 HAp hydroxyapatite
- 77 IS ionic strength

- 78 MP moving pivot
- 79 NP nanoparticles
- 80 PB population balance
- 81 PSD particle size distribution
- 82 RLA reaction limited aggregation
- 83 SI Supporting Information
- 84
- 85

86 Introduction

87 Nanoparticles, often unintentionally released into the environment, have also shown promise
88 in remediation of hazardous contaminants such as radionuclides.¹⁻³ Effective *in situ* field-scale
89 management of NP is hindered by the lack of adequate models to simulate NP fate and transport
90 in realistic environmental compartments.^{4, 5} Considering the long-established potential for
91 colloids to enhance the mobility of contaminants in groundwater environments^{6, 7} or facilitate
92 their redistribution in surface water bodies,⁸⁻¹⁰ this lack of predictive capability is a critical
93 concern. Aggregation of NP is important because progressive increase in particle size can
94 substantially affect NP mobility, reactivity and hence potential contribution to mobilization of
95 other solute contaminants.^{4, 11-13} Aggregation has complex interactions with other NP transport
96 mechanisms such as sedimentation.^{4, 5, 14, 15} This leads to distinct changes in trends of particle
97 concentration or size over time.^{14, 16} The early stage of aggregation, in which the slope of mean
98 particle size versus time is typically linear, is the subject of many studies.^{15, 17, 18} However, the
99 late stage of aggregation, more common in environmentally-relevant conditions where
100 phenomena such as aggregation and sedimentation occur over longer periods with no clear
101 initial condition, has received relatively little attention to date.^{14, 16}

102 In late-stage conditions, NP aggregate sizes increase sufficiently to induce sedimentation and
103 removal from suspension. This may lead to decreasing concentration of NP dispersion and
104 consequently reduction in aggregation rates. Conversely, differentially-settling aggregates may
105 collect smaller particles more easily during late-stage. Sedimentation-induced movement of
106 aggregates may bring about aggregate restructuring.¹⁹ This may affect the number of collisions
107 among aggregates thereby changing their consequent aggregation rates and settling velocity.^{19,}
108 ²⁰ These complex interacting phenomena may drive localised nonlinearities in slope of mean
109 particle size or concentration versus time. Many established theories and concepts, such as

110 CCC, are invalidated during late-stage aggregation since they are based upon the linear slope
111 of size or concentration versus time at the early stage.^{21, 22}

112 The ability of PB models to account for both stages in tandem while retaining meaningful
113 description of the system in terms of parameters such as attachment efficiency, α , and fractal
114 dimension, D_f is still unclear but is important if PB approaches are to be used to provide
115 description of aggregation processes within larger-scale models of NP fate and transport.^{20, 23}

116 In this study, we measure and model the quiescent aggregation and sedimentation of HAp NP
117 across a range of solution chemistries and at different measurement depths over a period of at
118 least five hours—sufficient in most of the cases for systems to develop late stage conditions.

119 We systematically investigate two numerical approaches to aggregation combined with
120 different settling velocity and collision frequency terms to find the models which best describe
121 observed mean particle size, averaged concentration, and PSD. Using the best-performing
122 model set, we then investigate how the trends of parameters change from early-stage to early-
123 late-stage cases across a range of solution chemistries and at different positions within a short
124 column. The initial PSD is a critical variable in aggregation modelling. We applied models
125 with three approaches: initial PSD observed in each experiment as the initial condition in each
126 model (A); constant initial condition for all experiments/models (B); and the latter approach
127 with variable- α across different size classes, accounting for aggregate size-driven variations in
128 surface interaction energy profiles according to the DLVO theory (C).²⁴ This comprehensive
129 experimental and numerical study yields new insights into both the changing dynamics of
130 aggregation as NP systems evolve over time, and the applicability of model concepts used to
131 describe them.

132 **Modelling**

133 Population balance models such as the Smoluchowski model^{25, 26} are the most widely-used
 134 methods for predicting aggregation-driven PSD of colloidal suspensions.²⁷⁻²⁹ However, the
 135 basic discretised form of these models applies only when each aggregate size class volume is
 136 considered the arithmetic sum of volumes of smaller classes. To span the size range that can
 137 result from early and late stages of aggregation, e.g., 40 nm to 10 μm , over 10^5 size classes are
 138 required, for each of which the PB equation should be solved. This is computationally
 139 impractical, particularly when other transport phenomena are modelled or for iterative
 140 calibration of parameters against experimental data. A geometric size discretization technique
 141 proposed^{30, 31} to mitigate this issue was recently used by Dale et al.³² to simulate aggregation
 142 and dissolution of environmentally-relevant NP. A geometric series of aggregate volumes is
 143 given as $v_{i+1}/v_i = 2^{1/q}$, where q is an integer greater than or equal to one. However, values
 144 of q derived from PSD obtained from experimental techniques such as DLS are typically non-
 145 integer, e.g., varying from $q = 1.574$ for $D_f = 3$ to $q = 2.63$ for $D_f = 1.8$.

146 More flexible approaches include FP and MP techniques.^{33, 34} Fixed-pivot maintains a
 147 minimum number of size classes (bins) via selective refinement of a coarse discretization of
 148 the particle volume dimension. This approach can consider binary or multiple collisions.
 149 Ignoring terms for breakage and adding a sedimentation term, the FP model conserving two
 150 properties of mass and number can be expressed as:³³

$$\frac{dn_k}{dt} = \sum_{\substack{j \geq i \\ v_{k-1} \leq (v_j + v_i) \leq v_{k+1}}} \left[1 - \frac{1}{2} \delta_{j,i} \right] \eta_k \alpha_{j,i} \beta_{j,i} n_j n_i - n_k \sum_{i=1}^{k_{max}} \alpha_{k,i} \beta_{k,i} n_i - \frac{U_k}{Z_s} n_k \quad (1)$$

151 where η_k is given as:

$$\eta_k = \begin{cases} \frac{v_{k+1} - (v_j + v_i)}{v_{k+1} - v_k}, & v_k \leq (v_j + v_i) \leq v_{k+1} \\ \frac{(v_j + v_i) - v_{k-1}}{v_k - v_{k-1}}, & v_{k-1} \leq (v_j + v_i) \leq v_k \end{cases} \quad (2)$$

152 The MP model³⁴ assumes that when the particle number concentration in a size class changes
 153 from sharp-decreasing gradients toward near-uniformity, the 'pivot' (the representative point of
 154 each size class in the particle size distribution) moves from the lower end of that class toward
 155 the middle. Two differential equations need to be solved over time. Omitting the breakage-
 156 relevant terms and considering the sedimentation term, the governing equations for the MP
 157 model become:

$$\frac{dn_k}{dt} = \sum_{\substack{j \geq i \\ v_k \leq (v_j + v_i) \leq v_{k+1}}} \left[1 - \frac{1}{2} \delta_{j,i} \right] \alpha_{j,i} \beta_{j,i} n_j n_i - n_k \sum_{i=1}^{k_{max}} \alpha_{k,i} \beta_{k,i} n_i - \frac{U_k}{Z_s} n_k \quad (3)$$

$$\frac{dv_k}{dt} = \frac{1}{n_k} \sum_{\substack{j \geq i \\ v_k \leq (v_j + v_i) \leq v_{k+1}}} \left[1 - \frac{1}{2} \delta_{j,i} \right] [(v_j + v_i) - v_k] \alpha_{j,i} \beta_{j,i} n_j n_i \quad (4)$$

158 Equations (1-4) can be solved for a given initial PSD, to yield PSDs resulting from aggregation
 159 and sedimentation at any time for a specified sedimentation depth Z_s . From the PSD, other
 160 quantities such as mean D_H and mass concentration can be determined as described in the SI.
 161 Note that, following common practice in this area,³⁵⁻³⁷ sedimentation is not modelled as a mass
 162 transfer process but as a net mass loss rate for each size class which scales linearly with Z_s .

163 The collision frequency for environmental colloids is commonly given as the sum of three
 164 mechanisms: perikinetic collisions (Brownian), orthokinetic collisions (shear-induced

165 aggregation under fluid motion), and differential settling (collection of smaller aggregates by
 166 the larger ones during sedimentation).¹⁷ Expressing collision frequencies based on the volume
 167 (or mass) of aggregates as a representative variable,^{32, 38} using fractal dimension relationships
 168 and considering permeability drag effects,³⁹ the following relationships yield:

$$\beta_{Prik_{i,j}} = \frac{2k_b T}{3\mu} \left(v_i^{\left(\frac{1}{D_f}\right)} + v_j^{\left(\frac{1}{D_f}\right)} \right) \left(\frac{1}{\Omega_i} v_i^{-\left(\frac{1}{D_f}\right)} + \frac{1}{\Omega_j} v_j^{-\left(\frac{1}{D_f}\right)} \right) \quad (5)$$

$$\beta_{Orth_{i,j}} = \frac{G}{\pi} v_0^{\left(1-\frac{3}{D_f}\right)} \left(\eta_{c_i}^{\left(\frac{1}{2}\right)} v_i^{\left(\frac{1}{D_f}\right)} + \eta_{c_j}^{\left(\frac{1}{2}\right)} v_j^{\left(\frac{1}{D_f}\right)} \right)^3 \quad (6)$$

$$\beta_{Diff_{i,j}} = \frac{3}{2} \left(\frac{\pi}{6}\right)^{\frac{1}{3}} v_0^{\left(\frac{2}{3}-\frac{2}{D_f}\right)} \left(\eta_{c_i}^{\left(\frac{1}{2}\right)} v_i^{\left(\frac{1}{D_f}\right)} + \eta_{c_j}^{\left(\frac{1}{2}\right)} v_j^{\left(\frac{1}{D_f}\right)} \right)^2 |U_i - U_j| \quad (7)$$

169 The superposition of the three rates gives the total rate of collisions, $\beta(i, j)$:

$$\beta_{i,j} = \beta_{Prik_{i,j}} + \beta_{Orth_{i,j}} + \beta_{Diff_{i,j}} \quad (8)$$

170 where Ω is the drag coefficient correction factor defined as the ratio of drag force exerted on a
 171 permeable aggregate to drag force exerted on an impervious aggregate with the same size,^{35, 40}
 172 and η_c is the fluid collection efficiency of an aggregate, defined as the ratio of flow through an
 173 aggregate to total flow approaching the aggregate.^{35, 41} To calculate collision frequencies, we
 174 use two permeability models: the Brinkman permeability model^{35, 42} and the Davies
 175 permeability model.⁴³ Additionally, we investigate the use of collision frequencies calculated
 176 based only on fractal relationships without permeability consideration.^{44, 45} Four types of
 177 settling velocity models were investigated for NP aggregates of fractal nature. These include
 178 an empirical power-law equation,^{46, 47} a permeability model based on the Davies correlation,^{43,}
 179 ⁴⁸ a permeability model based on the Brinkman model,^{35, 40, 41} and a fractal model which
 180 considers the effect of the size distribution of primary particles forming each aggregate.^{49, 50}

181 Finally, in the variable α approach, α was calculated based on DLVO theory considering only
182 van der Waals attraction and electrostatic repulsion interaction energies. The Hamaker constant
183 for HAp-water-HAp system was calculated as 2.77×10^{-21} J.⁵¹ All models and their related
184 equations are thoroughly introduced in the SI.

185 **Materials and Methods**

186 *Numerical modelling*

187 Details of MATLAB[®] (Mathworks, USA) codes for all models used in this study are available
188 in the SI. In brief, an explicit forward Euler scheme was used for the time derivative. The
189 explicit approach was chosen due to potential inaccuracy and computational problems of using
190 an iterative implicit approach.⁵² A simple forward Euler approach was selected since higher-
191 order schemes, such as fourth-order Runge-Kutta, were previously found ineffective in solving
192 PB models, which are examples of “stiff” problems.^{32, 53} Potential numerical instability in
193 certain ranges of parameters within the explicit model was mitigated by an adjustable time step
194 and a novel optimization algorithm based on a heuristic approach which, by incrementing a
195 parameter at a time within set ranges, enhanced the fit between observations and model outputs
196 using a parallel processing approach. An automatic increase of initial time step of the ‘slave’
197 numerical model by the ‘master’ optimization algorithm helped prevent unstable runs affecting
198 the optimization process.

199 Parameter calibration was conducted on the Chadwick high performance cluster and the
200 Condor high throughput computational systems at the University of Liverpool. Comparison of
201 numerical model performance with analytical solutions of the Smoluchowski model for both
202 monodisperse¹⁷ and log-normal-distributed initial conditions⁵⁴ is demonstrated in the SI. The
203 Nash–Sutcliffe determination coefficient (a conservative R^2)⁵⁵ was used to assess goodness of

204 fit. In this study, we calibrated the parameters based on the hydrodynamic size as an objective
205 function and investigate how well the fitted model describes concentration variation over time
206 and PSD at certain times.

207 *Experiment procedure*

208 Hydroxyapatite (particle density = 3.16 g/cm^3) was obtained from Alfa Aesar, UK. Evolution
209 of aggregate mean size, PSD and concentration over time were measured by DLS (Malvern
210 Zetasizer Nano ZS, UK). The valid measurement size range reported by the manufacturer is
211 from 1 nm to 10^4 nm. Measurements were carried out with an interval of ~ 3.37 min. For all
212 measurements, the number of runs was 5 (duration 10 s), beam attenuator index was 11,
213 position of measurement was 6.5 mm following pre-tests to establish the least noise and highest
214 reproducibility in the count rate as well as the Z-average data (hydrodynamic diameter, D_H).
215 Zeta potential was measured with the same instrument with an automatic adjustment. To
216 prevent the growth of bacteria in samples during the course of the experiment, we added 10
217 mM sodium azide. This was also beneficial due to its buffering capability to ensure a stable
218 pH, although corollary measurements indicated a potential variation of ± 0.52 at pH 7-10 over
219 24 h.

220 All experiments were conducted for at least 5 hours and in duplicate according to this
221 procedure: (1) prepare particle dispersion in DI water with a final particle concentration 50
222 mg/L, and sodium azide concentration 10 mM; (2) adjust pH at 6, 7, 10, or 11 ± 0.05 with
223 NaOH/HCl (100 mM); (3) ultrasonicate 5 min, add electrolyte (CaCl_2) to reach concentrations
224 of 0, 1, 2.5, 3, 5, 7.5, 10 mM, immediately vortex 5 sec, transfer to a disposable cuvette and
225 immediately start the DLS measurement. The whole process duration, from ultrasonication
226 until the start of the first measurement, was 70 ± 20 sec. Standard sample volume of 3 mL
227 resulted in a measurement depth of ~ 2.33 cm. We also investigated the impact of the

228 measurement depth by varying the sample volume as 1 mL, 3 mL, and 4 mL, corresponding to
229 approximate measurement depths of 0.33 cm, 2.33 cm, and 3.33 cm, respectively. The DCR,
230 which is the measured DLS count rate divided by the attenuation factor was extracted from the
231 DLS data and used as an indicator of mass concentration.⁵⁶⁻⁵⁸ To assess the significance of the
232 relationship between DCR and the mass concentration, DCR was measured at different
233 concentrations (1, 5, 10, 50, 100, 250, and 500 mg/L) of HAp NP.

234 **Results and Discussion**

235 *Experimental results*

236 Figure 1 shows averaged D_H and DCR for HAp at various solution chemistries over 5 hours.
237 DLS measurements of aggregate D_H evolution showed low noise and good reproducibility as
238 indicated by small standard deviations of duplicate experiments (error bars, Fig. 1). However,
239 stability of DCR measurements tended to decrease over time. At constant pH 6, below 3 mM
240 CaCl_2 the slope of D_H versus time is near linear on a semi-log plot throughout the experiment;
241 above 3 mM the slope asymptotes from a steep slope at < 40 min to a gentle slope at greater
242 times, revealing both early and late stages of aggregation/sedimentation (Fig. 1a). This also
243 suggests that the CCC lies between 3 and 5 mM CaCl_2 . Similar behaviour is observed for
244 various pH when the ionic strength is held at 5 mM CaCl_2 (Fig. 1b). Figures 1c,d illustrate
245 DCR data normalized to the initial DCR value of each experiment. This quantity drops below
246 0.5 by the end of the experiments in most cases under the DLA regime (>4 mM CaCl_2).
247 However, normalized DCR increases over time for RLA regime (CaCl_2 concentrations < 4
248 mM). This increasing trend might be interpreted as settling, slow-aggregating particles arriving
249 at the point of measurement from further up the water column, causing increase of mass
250 concentration in this point to above the initial uniform concentration in the sample. Such an
251 increased concentration in the lower positions of the water column has been already reported.⁵⁹⁻

252 ⁶¹ Although DCR data have been used as proxy for colloid mass concentration in multiple
253 studies,^{57, 58, 62, 63} its application in NP studies is less common,⁵⁶ and there have been indications
254 that DCR can be affected by size⁶⁴ or the number of particles⁶¹ in addition to the mass. We
255 assessed the relationship between the DCR and HAp concentration in the ranges 1 to 100, 250,
256 or 500 mg/L in DI water. The result of this investigation revealed a linear correlation ($r^2 > 0.98$
257 and $P \gg 0.05$) between these two factors (Fig. S1, SI). We should note that the use of DLS
258 data like any experimental technique has inherent measurement uncertainties, e.g., mean
259 hydrodynamic size might be affected by the larger fraction of PSD.⁶⁵ However, as shown in
260 PSD results (Figs. S2 and S3) developing a monodisperse PSD toward later times suggests that
261 this impact might not be significant here.

262 ***Model screening***

263 A detailed discussion of the screening of the 24 model combinations is provided as SI (Figs.
264 S4-S6 and Tables S1-S4). Briefly, for both FP and MP models, calculation of collision
265 frequencies using the simple fractal approach or Davies permeability correlation led to poorer
266 matches between the experimental and modelled D_H values (Fig. S4) than when permeability
267 collision frequencies were based on the Brinkman model. In the two former collision models,
268 R^2 of D_H data was below 0.5, whereas for the Brinkman permeability model R^2 increased up to
269 0.71 (Tables S1 and S2). Fits to DCR data were relatively insensitive to model type (Table S3).
270 The simple fractal and Davies permeability correlation approaches led to D_H curve shapes
271 inconsistent with the experimental data. Therefore, we discarded these two collision frequency
272 models. The best among the settling velocity models, using the FP numerical approach, was
273 the power-law formulation in terms of fitting for D_H data ($R^2 = 0.71$). Using the MP scheme,
274 the power law, Brinkman permeability, and size distribution models gave close fitting results

275 with R^2 equal to 0.68, 0.71, and 0.70, respectively, against D_H data and 0.62, 0.58, and 0.87,
276 respectively against DCR data (Table S2).

277 The FP model performs much faster than the MP method in simulating both early and late
278 stages of aggregation. In fact, once the initial stage of the aggregation is passed, a significant
279 increase (e.g., 500 times) in the time step length can be adopted for the FP model without
280 affecting model stability. The MP method, in spite of being originally faster than FP,⁵³ is not
281 as flexible as FP in reducing the number of time steps in the late stage, potentially because of
282 sharp gradients at longer times caused by the additional volume-based equation in the MP
283 model. The final selected model set (FP, Brinkman-permeability-based collision frequency,
284 and power-law settling velocity) based on a case-specific initial PSD (approach A, Table 1) fit
285 the experimental data with mean R^2 of 0.795 (D_H) and 0.670 (DCR) for all cases with various
286 pH and IS except the cases under the RLA regime (Fig. 1, Table S3). The model matched to
287 D_H data could well describe normalized DCR trends under the DLA condition, suggesting that
288 in this regime DCR is an appropriate representative of mass concentration.

289 *Aggregate structure and sedimentation velocity*

290 The model fit results indicate that models assuming bulk density-controlled sedimentation tend
291 to outperform models assuming permeability-controlled sedimentation. The impact of
292 aggregate structure on settling velocity is a disputed subject.⁶⁶ Enhanced sedimentation
293 velocities compared to Stokes' law based on hydrodynamic size have been reported and
294 interpreted as flow through the aggregates reducing the aggregate drag.^{40, 42, 43, 67} Other
295 studies^{47, 68, 69} point to the overestimation of Stokes' law for floc sedimentation velocity. We
296 compared trends in terminal settling velocity versus the size of aggregates resulted from each
297 sedimentation model used in the present study.

298 Figure 2 illustrates, for three values of D_f (1.6, 2.0, and 2.3), that the highest sedimentation
299 velocity is predicted by the Davies permeability model, followed by the Brinkman, size-
300 distribution-based and power-law models, respectively. The Davies permeability model
301 predicts an increase in sedimentation velocity with decrease of D_f in agreement with other
302 studies.^{40, 43, 67} However, this model yields an estimate of settling velocity that is much higher
303 than all the other models.⁷⁰ The Brinkman model exhibits a slight increase of velocity with D_f
304 which is only discernible for particles of less than 1 μm in size—not considerable in the
305 sedimentation process.^{17, 71} This low sensitivity of settling velocity to the aggregate structure
306 contradicts experimental observations.^{40, 42, 43, 47, 67, 68} However, both power-law and size-
307 distribution-based models predict increased velocity with D_f due to the greater bulk density of
308 aggregates (Fig. 2). This variation is more significant for the power-law model compared to
309 the size-distribution-based model, suggesting that the power-law expression is more sensitive
310 to D_f . Overall, simulations incorporating these bulk density-controlled sedimentation terms
311 yielded the best fits against our experimental data.

312 Figure 2 shows that for particles of the same matter and with constant diameter, reducing D_f
313 (i.e. increasing porosity and decreasing mass) results in considerable reduction in the settling
314 velocity according to power-law and size-distribution-based models. Recently, in an insightful
315 study, Emadzadeh and Chiew⁷² showed that for large synthetic particles ($> 1\text{ cm}$ in size and
316 density $\gg 1\text{ g cm}^{-3}$) with identical matter and diameter, increasing porosity corresponding to
317 a decreased mass caused reduction of the terminal settling velocity. However, when particles
318 of different matter were used to maintain the mass constant too, the particles with higher
319 porosity exhibited higher settling velocity. This implies for homogeneous NP aggregates with
320 density of primary particles $\gg 1\text{ g cm}^{-3}$, the impact of the bulk density of aggregates far
321 outweighs permeability or drag effects, in agreement with our analysis based on best fits to
322 early and late stage HAp aggregation data and in contrast to Johnson et al.⁴³

323 *Attachment efficiency and fractal dimension*

324 Table 1 shows the parameters determined from the fitting (optimisation) procedure,
325 demonstrating that with the increase of CaCl_2 concentration above 5 mM the model parameter
326 α increases above one. Classical theories of aggregation^{18, 22} prescribe that attachment
327 efficiency increases until the double layer repulsion is completely screened, where the CCC is
328 met and α is equal to one. Calculation of DLVO profiles, shown in Fig. S7, confirms that at
329 $[\text{CaCl}_2] \geq 5$ mM there is no energy barrier against aggregation. We interpret values greater
330 than one in this model parameter as indicating a mechanism associated with the late-stage
331 aggregation which enhances the *effective* attachment efficiency above its classical limit.
332 Although there have been cases in the literature reporting α above unity,^{67, 73-76} to investigate
333 this further, we fitted the model to D_H data only at the early stage (first 20 min) of the processes.
334 Since we found including D_f as an estimating parameter was not necessary for early-stage
335 fitting, we fixed this at 1.6 (close to the common DLA range) for all cases of pH and high IS.
336 Results, presented in Table S5, reveal that for most of the cases α reduces to below one. The
337 only remaining case with $\alpha > 1$ also reduces to below one if D_f is considered as a free parameter
338 in the optimization process.

339 To scrutinize this issue further, we fixed the initial PSD in all cases based on a single-peaked
340 PSD extracted from the experimental case with no aggregation (approach B, Table 1). In this
341 approach, the very first moments of the aggregation (~ 70 s), which are not captured in
342 experiments, are considered by the model with shear coagulation operating, and the
343 sedimentation process turned off as described in the SI. This approach yields slightly poorer
344 goodness-of-fit (mean R^2 0.736 for D_H and 0.513 for DCR) than approach A (mean R^2 0.763
345 for D_H and 0.64 for DCR) for cases of IS > 5 mM and various pH (Figs. 1, S8 and Table S3).
346 In contrast to approach A, approach B yields α closer to one in all cases of high IS (maximum

347 α is 1.65 which occurs at pH 7, Table 1). We furthermore investigated the condition in which α
348 varies from 0 to 1 with particle/aggregate size according to varying DLVO interaction energies,
349 using a fixed-PSD initial condition (approach C, Table 1). The results (Fig. S8 and Table S3)
350 show that for cases of IS higher than 5 mM and for various pH, mean model fit R^2 is rather
351 lower than that of previous approaches—0.687 and 0.429 for D_H and DCR, respectively.
352 Although this approach could fit experimental data cases at 5, 7.5, and 10 mM CaCl_2 , with only
353 one adjustable parameter (D_f), there was a need for adding another adjustable parameter in
354 other cases, due probably to uncertainties in measurement of factors like zeta potential (with
355 common accuracy on the order of $\pm 10\%$)⁷⁷ as reported in Fig. S9 and Table S3. Even
356 considering two adjustable parameters (D_f and zeta potential), approach C was still unable to
357 fit the case at 3 mM CaCl_2 . Other non-DLVO factors such as specific-ion effects⁷⁸ which have
358 not been considered in this study or some basic assumptions of the DLVO such as perfect
359 sphere⁷⁹ ignored for nonuniform-shaped porous aggregates might be reasons for the
360 discrepancies.

361 Conventionally, open aggregate structures (D_f tends to 1.8) are formed in DLA regime where
362 every contact results in attachment, while more compacted structures (D_f tends to 2.1) are
363 formed under the more selective RLA condition.^{17, 80} As shown in Table 1, models fitted across
364 both early and late stage data indicate that at CaCl_2 concentrations ≤ 3 mM (RLA) D_f is lower
365 than 1.8 while at ≥ 5 mM (DLA) D_f ranges is higher than 2.03 and further increases with pH
366 (up to 2.7 at pH 11). Approach B yielded even larger D_f on average by 11% compared to
367 approach A. This difference was 8% for approach C. Strongly overlapping ranges of D_f for
368 RLA and DLA regimes have been frequently reported in the literature,^{47, 81-85} especially for
369 particles subject to mechanisms other than Brownian diffusion, such as ‘ballistic’
370 aggregation,¹⁷ orthokinetic aggregation,^{81, 86} and differential sedimentation.¹⁹ These can be the
371 result of linear trajectories¹⁷ or restructuring.^{19, 41} It has also been indicated in the literature^{87,}

372 ⁸⁸ that rapid particle-cluster aggregation leads to a denser aggregate ($D_f = 2.5$) than cluster-
373 cluster aggregation ($D_f = 1.8$). Allain et al.¹⁹ reported a D_f value of 2.2 for calcium carbonate
374 colloids within the DLA regime under quiescent sedimentation, and others⁸⁶ reported D_f in
375 range of 2.3 to 2.8 for calcium phosphate in a system with settling and shear. Experimentally-
376 measured D_f reported in the literature are typically limited to the early stage of aggregation or
377 lower aggregation rates than those investigated in the present study.

378 Fitting the model to only the early stage of experiments showed ranges of D_f consistent with
379 conventional expectations (Table S5) under the DLA regime. The contrasting trends obtained
380 when fitting to both stages together suggests the crucial role of late-stage aggregation process
381 in modifying this parameter. Our observation of an increase in the DCR curves under the RLA
382 regime versus decreasing DCR in the DLA regime indicates that sedimentation under the RLA
383 regime is slower than that under the DLA regime (Fig. 1c). This implies that the bulk density
384 and therefore D_f of aggregates in the RLA regime should be lower than that under the DLA
385 condition.

386 We deduce that in the late stage, evolved aggregates formed from mixed particle-cluster
387 populations under the RLA condition are less compact than early-stage aggregates, potentially
388 as a result of irregular packing geometries and inaccessibility of internal pore spaces to incident
389 particles in unfavourable interaction conditions.⁸⁹ Decreasing D_f over the course of experiments
390 has been observed already for fullerene NP under both DLA and RLA regimes.⁹⁰ However,
391 due to uncertainties associated with the DCR data obtained under the RLA regime (discussed
392 below), further experimental/modelling investigations are required to confirm this explanation.
393 Conversely, aggregates formed in late-stage DLA conditions may have higher D_f (compared to
394 less-compact early stage aggregates) as a result of internal reorganisation of particles within
395 each aggregate, aggregate-aggregate collisions, and trapping individual particles in voids of

396 large, open clusters during their downward sedimentation.^{19, 89} It should be mentioned that
397 model-fit parameter values might bear both experimental and model uncertainties. Direct
398 experimental measurement of D_f under the late-stage conditions used in this study is a priority
399 for future work to confirm the model predictions reported here.

400 Although all three modelling approaches are reasonably successful in fitting the experimental
401 data, none of final models does so while maintaining all parameter values simultaneously
402 within the ranges expected from previous literature. The model formulation applied in the
403 present study is not able to reproduce the experimentally observed rise in DCR data under the
404 RLA regime, because the sedimentation term used in these models is a simple decay term (last
405 term in Eqs. 1,3) which avoids the computational expense and potential numerical dispersion
406 problems of solving a spatio-temporal partial-differential equation.⁹¹ Although it was shown
407 that DCR is an appropriate indicator of the mass concentration under DLA, it remains for future
408 studies to validate this conclusion under the RLA regime. The modelled PSDs are shown in
409 Figs. S2 and S3 and discussed in detail in the SI. Overall, approach B demonstrates the best
410 overall match between observed PSD and modelled PSD through late-stage conditions.

411 ***Mass removal rates and measurement depth***

412 Table 1 shows the predicted mean percentage mass removal after 5 h within a 3 cm modelled
413 water column for different pH and IS, using parameter values estimated in both early and late
414 stages. Under the RLA regime (2.5 and 3 mM CaCl_2) a negligible ($\leq 0.5\%$) decrease in mass
415 concentration indicates that sedimentation is minimal, in agreement with our experimental
416 observations (Fig 1c). Under the DLA regime (5-10 mM CaCl_2) and at various pH, for the three
417 approaches A, B and C predicted mass removal reaches 85.4%, 74.5%, and 71.0%,
418 respectively. Figure 3 shows that predicted mass removal is greater in the upper part of the
419 water column. Removal percentage is maximum at pH 7 (86.4%, average of the three modelling

420 approaches, Table 1). With increasing pH above pH 7, mass removal decreases (down to 63.6%
421 on average), consistent with the decrease of α and increase of D_f (Table 1). Surprisingly, as
422 illustrated in Fig. 3 under the DLA condition, the percentage mass removal consistently (under
423 almost all modelling approaches) decreases with increase in the IS from on average 79.5% at
424 5 mM CaCl_2 to 78.3% and 68.9% at 7.5 and 10 mM CaCl_2 , respectively (Table 1, Fig. 3).

425 We examined experimentally how the depth of measurement from the surface of the liquid
426 affects the parameter values obtained using approach A. The results for depths of 0.33, 2.33,
427 and 3.33 cm are presented in Table S6 and Fig. S10. For measurements at short distance below
428 the water surface (0.33 cm), the aggregation is significantly lower than when measured at
429 greater depths (2.33 and 3.33 cm). This might indicate the significance of differential
430 sedimentation in aggregation of HAp NP. This also indicates that the late stage of coupled
431 aggregation-sedimentation processes is less noticeable in the regions just below the surface of
432 water. The model fit results (Table S6) confirm that late-stage influences on both α and D_f
433 increase with the measurement depth. Crucially, α determined for the smallest depth (0.33 cm)
434 assumes a value lower than one and D_f is relatively closer to the common threshold of DLA
435 regime which agrees with fit result of early stage alone (Table S5). This strongly associates
436 parameter values $\alpha > 1$ and D_f outside expected ranges of DLA regime, with the complications
437 of interacting late-stage processes during coupled aggregation and sedimentation.

438 ***Implications for the fate of NP in groundwater and aquatic environments***

439 The combination of experiment and modelling approaches presented here has enabled the
440 complex interactions between aggregation and sedimentation to be investigated in NP systems
441 well inside the late-stage at which the particle-aggregate population has evolved significantly
442 from its initial PSD. These conditions are likely to be the norm in most environmental systems
443 in which NP have been resident for any length of time. We demonstrate that population balance

444 models can be applied to systems at both stages of aggregate evolution. Although the best-
445 performing model suite included permeability-based models for describing collision
446 frequencies, the empirical, density-controlled descriptions for settling velocity were able to
447 better describe the observed trends in experimental data over 5 h of coupled aggregation and
448 sedimentation. Allowing the attachment efficiency to vary with aggregate size did not
449 significantly alter model outcomes compared to assumption of a constant attachment
450 efficiency, but fitted parameters were much more sensitive to the specification of the initial
451 PSD. In terms of reduction in computational effort over the late-stage of the processes, we
452 found the FP aggregation model has a greater capability than the MP technique. These results
453 have significance in developing practical, computationally-efficient models for the fate and
454 transport of NP in the environment.

455 While models fitted to only early stage data showed trends in attachment efficiency and fractal
456 dimension consistent with classical theory, these trends varied as the systems evolved. Our
457 results demonstrate that at lower IS (RLA), aggregation is slow, and sedimentation is negligible
458 in the timescales considered here. At intermediate IS (5 mM CaCl_2) near the CCC, a moderate-
459 rate DLA develops a population of NP clusters which are optimally more efficient at collecting
460 (by aggregation) and removing (by sedimentation) large numbers of smaller particles and
461 aggregates than that at higher IS (7.5 and 10 mM CaCl_2) where the system moves rapidly to
462 fewer, larger, but less-compact aggregates, and overall mass removal rates are reduced due to
463 slower sedimentation. These lower removal rates within high-IS solutions may bring about
464 lifetimes and potential transport distances of NP aggregates in aqueous suspension in settings
465 such as marine environments, coastal aquifers, or in soil pore microenvironments that are
466 longer than expected based on conventional models or extrapolations from experimental data
467 obtained only in early-stage conditions. Although the population balance techniques applied in
468 the present study alleviate computational expenses of using an arithmetic particle size

469 discretization well with a geometric discretization when applied to small-scale laboratory
470 conditions, it remains a question whether such models are efficient when coupled to fate and
471 transport models at larger environmental scales, e.g., aquifer and watershed.

472

473 **Supporting Information.**

474 **PDF File:** Full model equations; details of MATLAB code; DVLO calculations and results;
475 development of the parameter estimation algorithm; results of the comparison between
476 numerical and analytical solutions; further investigations of sedimentation models; fit results
477 to PSD; graphs of approaches B and C, etc.

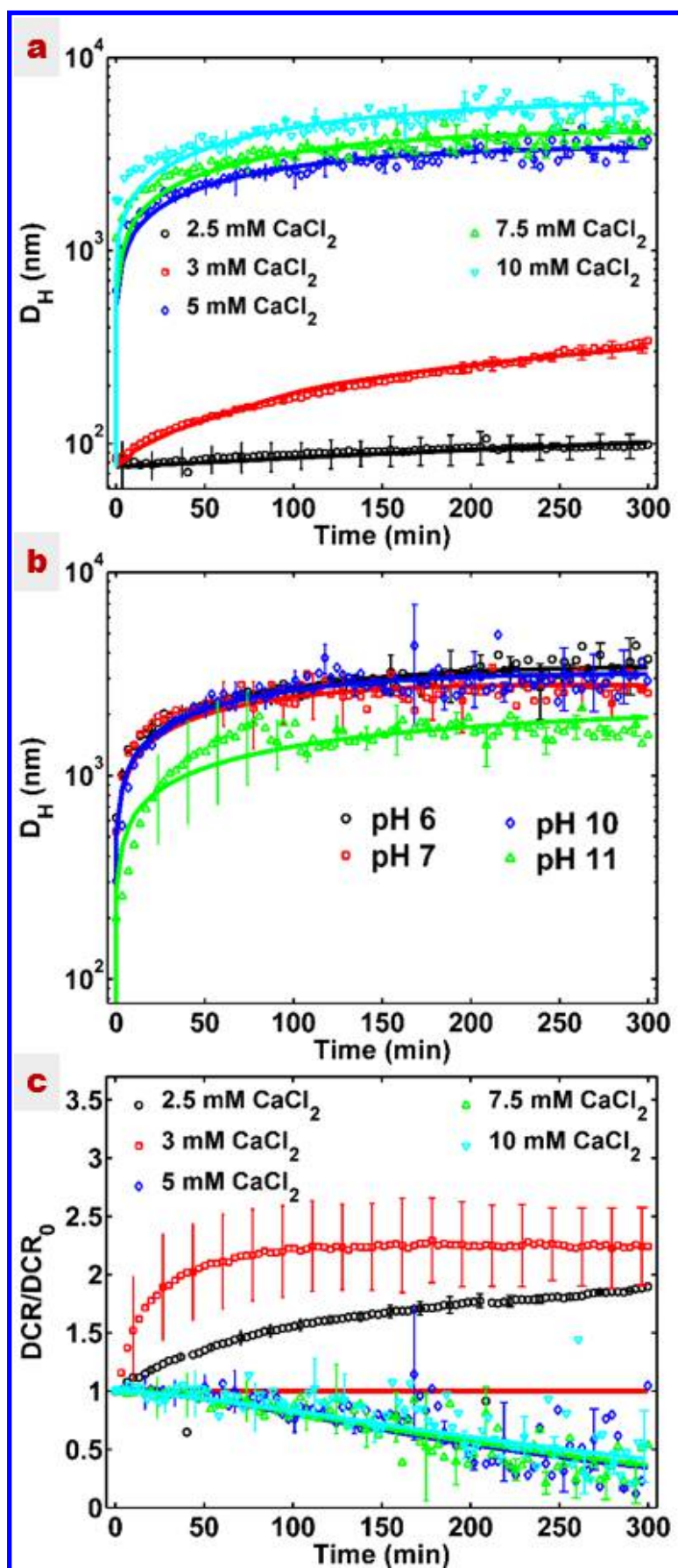
478 **Electronic Supporting Information:** MATLAB codes developed for solution of FP and MP
479 techniques and for parameter estimation of population balance models

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488

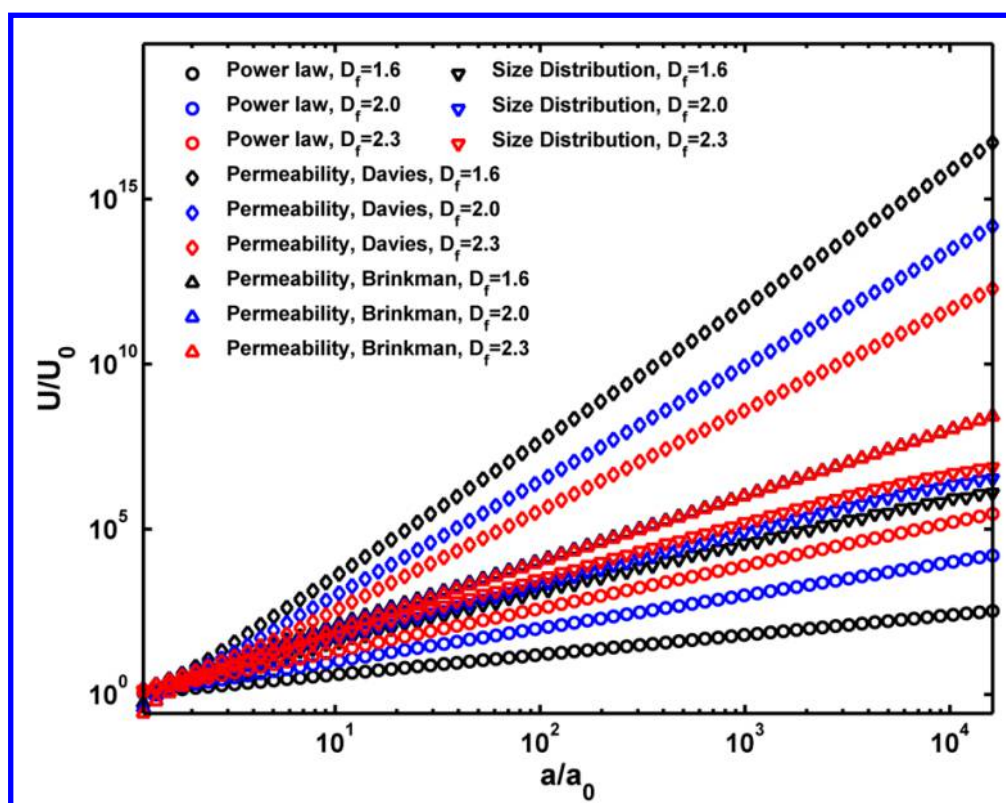
489 **Figures and Tables**



490 **Figure 1.** Evolution of averaged hydrodynamic diameter, D_H , (a,b) and change in mean

491 derived count rate (DCR) normalized to the initial derived count rate (DCR_0) (c) for HAp NPs
 492 at the point of measurement at various IS with a fixed pH at 6 (a,c) and various pH with a fixed
 493 IS at 5 mM $CaCl_2$ (b). The model used here was FP with power law formulation and Brinkman
 494 collision model. The modelling approach includes a fixed initial PSD with considering the pre-
 495 early stage of aggregation and a constant attachment efficacy (approach B).

496

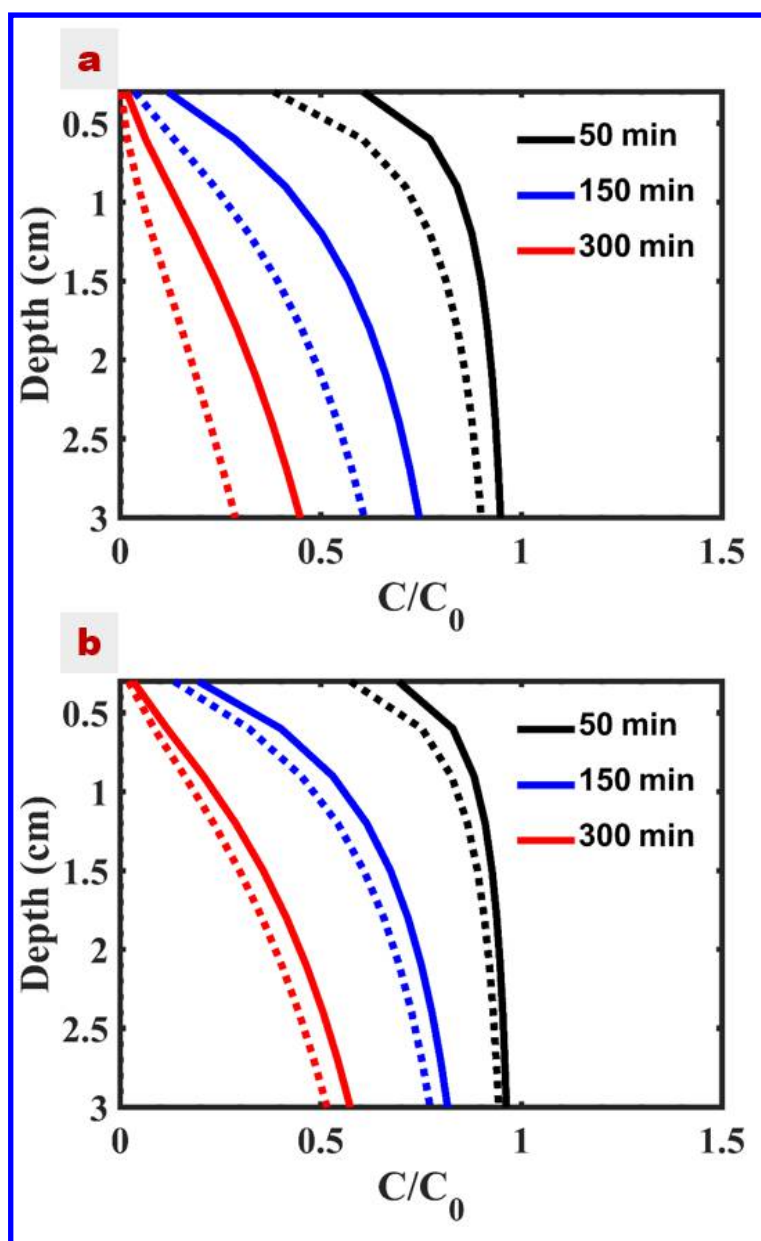


497

498 **Figure 2.** Trends of settling velocity, U , normalized to the settling velocity of primary particles,
 499 U_0 , versus particle radius of each size class, a , normalized by the primary particle radius
 500 (smallest size class), a_0 , calculated by four different types of velocity models. Fractal
 501 dimension is set as 1.6, 2, and 2.3. The primary particle radius used in these models is 40 nm.

502

503



504 **Figure 3.** Modelled mass concentration, C , profiles normalized by the initial mass
505 concentration, C_0 , versus the water column depth at (a) 5 mM CaCl_2 and (b) 10 mM CaCl_2 after
506 50, 150, and 300 min. The continuous lines represent approach A (case-specific initial PSD)
507 and dashed lines represent approach C (fixed initial PSD combined with variable α computed
508 by DLVO).

509

510

511 **Table 1.** Model parameters estimated by fitting FP models to both early and late stages of
 512 aggregation under different electrolyte concentrations (at fixed pH 6) and different pH (at fixed
 513 electrolyte concentration, 5 mM CaCl₂) over 5 h, based on three modelling approaches (A, B,
 514 C), and mass removal results estimated by the models for a sample volume of 3 mL (3 cm water
 515 depth) after 5 h. The power-law model and Brinkman-based permeability model are used to
 516 calculate the sedimentation velocity and collision frequencies, respectively.

Parameter	Modelling approach	Electrolyte Concentration (mM)					pH		
		2.5	3	5	7.5	10	7	10	11
α	A	1.1×10^{-4}	7.1×10^{-3}	11.60	8.10	1.10	15.40	6.33	1.59
	B	2.0×10^{-6}	1.0×10^{-5}	1.13	1.13	1.23	1.65	1.37	0.21
	C	NA	NA	NA	NA	NA	NA	NA	NA
D_f	A	1.53	1.48	2.03	2.12	2.27	2.26	2.32	2.70
	B	1.71	1.38	2.53	2.53	2.45	2.69	2.63	2.66
	C	1.50	1.50	2.50	2.42	2.25	2.60	2.61	2.70
Removal %	A	0.4	1.0	86.1	86.9	70.0	94.9	88.8	84.7
	B	0.1	0.1	77.5	75.8	71.8	86.3	81.6	50.9
	C	0.1	0.1	75.0	72.2	65.0	78.0	76.8	55.1

517 A: initial PSD; B: identical PSD; C: identical PSD, DLVO; NA: not applicable

518

519

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