

1 **Interactions between organic model compounds and ion exchange resins**

2

3 Pascal Finkbeiner^a, Graeme Moore^b, Tebogo Tseka^c, Thabo T.I. Nkambule^c, Lueta De

4 Kock^c, Bruce Jefferson^a, Peter Jarvis^{ac*}

5 ^aCranfield Water Science Institute, Building 52a, Cranfield University, Cranfield,

6 Bedford, MK43 0AL.

7 ^bScottish Water, Castle House, 6 Castle Drive, Dunfermline, KY11 8GG.

8 ^cNanotechnology and Water Sustainability Research Unit, University of South Africa,

9 (UNISA), Johannesburg, Florida, 1709, South Africa.

10 [*p.jarvis@cranfield.ac.uk](mailto:p.jarvis@cranfield.ac.uk)

11

12

13

14

15

16

17

18

19

20

21

22

23 **Interactions between organic model compounds and ion exchange resins**

24

25 **Abstract**

26 Ion exchange (IEX) can successfully remove natural organic matter (NOM) from
27 surface water. However, the removal mechanism is not well understood due to the
28 complexity and variability of NOM in real source waters as well as the influence of
29 multiple parameters on the removal behaviour. For example, this includes the
30 physicochemical properties of the NOM and IEX resin, and the presence of competing
31 anions. Model compounds with a range of physical and chemical characteristics were
32 therefore used to determine the mechanisms of NOM removal by IEX resins. Fifteen
33 model compounds were selected to evaluate the influence of hydrophobicity, size and
34 charge of organic molecules on the removal by ion exchange, both individually and in
35 mixtures. Three different resins, comprising polystyrene and polyacrylic resin of
36 macroporous and gellular structure, showed that charge density (CD) was the most
37 important characteristic that controlled the removal, with CD of $>5 \text{ meq mg}_{\text{DOC}}^{-1}$
38 resulting in high removal ($\geq 89\%$). Size exclusion of compounds with high MW ($\geq 8 \text{ kDa}$)
39 was evident. The hydrophobicity of the resin and model compound was particularly
40 important for removal of neutral molecules such as resorcinol, which was best
41 removed by the more hydrophobic polystyrene resin. Relationships were identified that
42 provided explanations of the interactions observed between NOM and IEX resin in real
43 waters.

44

45 **Keywords:** ion exchange; model compounds; removal; natural organic matter

46 **Introduction**

47 The removal of natural organic matter (NOM) from surface water is known to be of
48 importance, primarily for reduction of the formation of disinfection by-product (DBPs)
49 in drinking water.¹ Ion exchange (IEX) has been shown to successfully reduce the
50 concentration of NOM, particularly when used in combination with coagulation,
51 specifically in the order of IEX followed by coagulation.²

52 Exchange of NOM onto IEX resin occurs through the release of a counter ion into
53 solution.³ The use of strong base anion resins has been found to remove generally
54 more NOM than weak base anion resins due to the lower number of charged sites
55 available at neutral pH.⁴⁻⁶ However, it has not been clearly shown how the physical
56 structure of the IEX resin influences NOM removal. Some studies suggest that
57 macroporous resins remove NOM more efficiently than gellular resins due to their
58 larger pore diameter.⁴ Others have shown a better performance of gellular resins,
59 attributed to the higher degree of swelling and thus access to exchange sites.⁵ There
60 have also been contrasting results when considering how the chemical structure of a
61 resin influences removal behaviour. Styrene resins have been found to have a higher
62 affinity for compounds with an aromatic structure due to stronger hydrophobic
63 interactions.⁷ However, in other work similar or slightly higher NOM removal was
64 achieved by acrylic resins compared to styrene resins and it was reported that the
65 water content of the resin played an important role in controlling removal.⁴ Similarly,
66 Cornelissen et al.⁵ found no differences in NOM removal between resin types when
67 investigating three acrylic and six styrene resins. On the contrary, higher removal was
68 observed for polyacrylic resins in a study by Humbert et al.⁸. The better performance
69 of this resin was linked to its smaller bead size and the resulting higher easily
70 accessible surface exchange sites.

71 These differences reflect the role that the NOM properties have on removal, where
72 charge, hydrophobicity and size have all been shown to be important.⁹⁻¹¹ The most
73 important removal pathway is the electrostatic attraction between functional groups on
74 the resin and the negatively charged moieties of NOM molecules. Regarding only
75 these electrostatic interactions, each exchange is associated with an increase in Gibbs
76 free energy (ΔG) when a larger ion on the exchanger resin is replaced by a smaller
77 ion of equivalent valency from the solution, described by equation 1, based on
78 Coulomb's law:³

$$\Delta G_{el} = -\frac{Ne^2}{4\pi\epsilon_0\epsilon_D}\left(\frac{1}{r_R + r_B} - \frac{1}{r_R + r_A}\right) \quad \text{Equation 1}$$

79 where N is the Avogadro constant, e is the elementary charge, ϵ_0 is the vacuum
80 permittivity, ϵ_D is the dielectric constant of the ion exchanger, r_R is the charge radius
81 of the hydrated fixed ion and r_A or r_B that of the counter ions, where A refers to chloride
82 and B to the ion that is exchanged.

83 The most common anionic groups in NOM are the carboxylate ion with a hydrated
84 radius of 0.304 nm¹² and the deprotonated hydroxyl ion (no data available for hydrated
85 radius). During removal, these groups exchange with the chloride ion ($r_{\text{hydrated}} = 0.332$
86 nm¹³) in a stoichiometrical fashion.¹⁴ A higher number of charged groups relative to a
87 molecules mass should favour the energy balance and a direct correlation between
88 CD and bulk NOM removal has been reported previously.¹⁵ However, this is
89 complicated by other factors such as the molecular weight of organic compounds as
90 large molecules can experience size exclusion and reduced removal.^{10,16} Several
91 studies have reported a preferential removal of UV-absorbing DOC by IEX,^{8,17,18} which
92 indicated that these aromatic compounds are favourably removed by the resin.⁵ The
93 sorption of the non-polar moiety onto the hydrophobic resin leads to an increase in

94 entropy which overcompensates the endothermic desolvation, resulting in an overall
95 negative free energy change, making the process favourable.³

96 The importance and differentiation of these interactions between IEX resin and sorbent
97 is difficult in a diverse mixture such as NOM, where the water matrix can have an
98 effect, such as through complexation with divalent cations and competition with
99 inorganic anions for exchange sites.^{16,21} Accordingly, model compounds can be used
100 to elucidate such interactions as different individual structures can represent the
101 chemical features required for comparison, without the complexity and unknown
102 structure associated with NOM in real water sources. Humic acid, tannic acid and
103 resorcinol have been used as surrogates for hydrophobic NOM, while amino acids and
104 sugars have been used to represent charged hydrophilic and neutral hydrophilic
105 compounds.^{22,23} However, there have been no studies that have considered the
106 combined influence of charge, hydrophobicity and molecular weight when selecting
107 model compounds. This is particularly the case when considering the role of
108 concentration (by mass, molecule and charge), competition and resin property. The
109 aim of this work was to therefore determine the key features of NOM that control
110 removal. This was achieved through investigation of 15 model compounds, spanning
111 a wide spectrum of molecular structure, and three resins of different chemical and
112 physical structure.

113 **Materials and Methods**

114 ***Model compounds***

115 Model compounds of different hydrophobicity, molecular weight and charge were
116 selected to cover a diversity of physicochemical properties, as well as representing
117 constituents of raw water, including humic substances (humic and fulvic acids),
118 breakdown products (referred to as building blocks), carbohydrates, carboxylic acids

119 and amino acids (Table 1). Glucose and xylose were selected as model compounds
120 for neutral small aliphatic molecules; glutamic acid as a surrogate for amino acids with
121 one positively and two negatively charged groups. Resorcinol represented a
122 breakdown product of fulvic acids and is an aromatic compound with almost no
123 charged functionality at neutral pH.²⁴ Aromatic compounds with increasing numbers
124 of carboxylic acid group(s) were chosen to compare the impact of the number of
125 charged moieties: benzoic acid, trimesic acid and mellitic acid. Citric acid represented
126 a charged aliphatic low MW acid. Tannic acid was selected as a large hydrophobic
127 compound. Smaller derivatives of this large molecule with a comparable base
128 structure were studied to show differences in molecular weight and hydrophobicity:
129 pentagalloyl glucose (PGG), monogalloyl glucose (MGG) and corilagin. Three different
130 weight-average molecular weights (M_w) between 1.2-15 kDa of the synthetic polymer
131 poly(acrylic acid) sodium salt (PAA) were used to study the influence of size for a
132 charged aliphatic macromolecule.

133 A solution of $10 \text{ mg}_{\text{DOC}} \text{ L}^{-1}$ was prepared for each model compound. Additionally,
134 solutions of equivalent molar concentration (0.119 mM) and equivalent charge load
135 (0.707 meq L^{-1}) were prepared to compare different concentrations. Equivalence
136 values were chosen to evaluate the influence of equivalent numbers of molecules and
137 charge present in the solution. The working solutions were buffered with 20 mg L^{-1}
138 NaHCO_3 and adjusted using HCl and NaOH to give a final of pH 7. Mixtures of benzoic
139 acid, resorcinol and tannic acid were prepared at both equivalent mass and molar
140 concentrations ($10 \text{ mg}_{\text{DOC}} \text{ L}^{-1}$ and 0.119 mM) to investigate removal kinetics.

141 ***Resin preparation and jar tests***

142 Three strong base anion exchange resins were selected based on their application for
143 NOM removal and the differences in their structure (Table S1). The macroporous

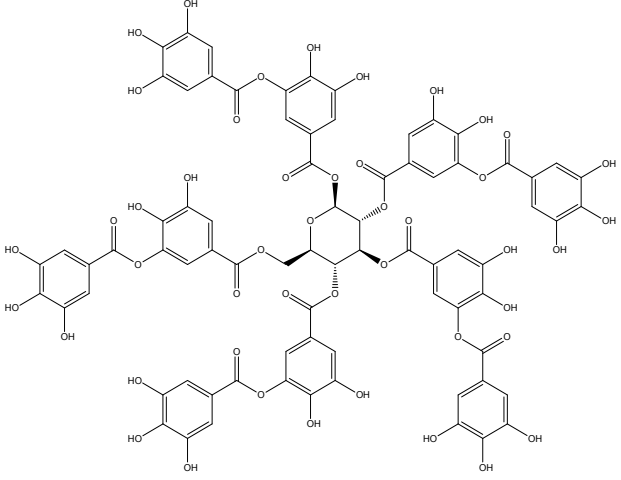
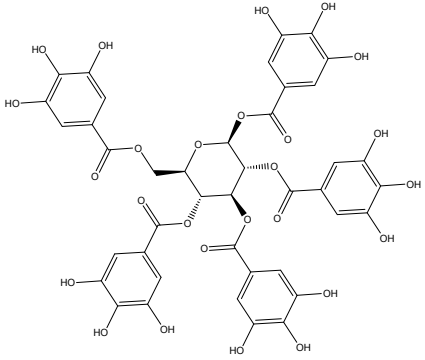
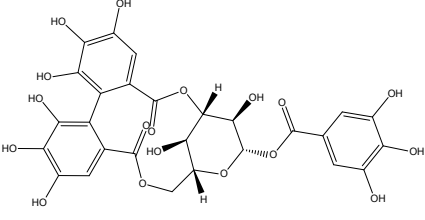
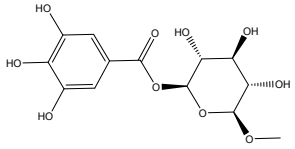
144 polystyrene Dowex Tan-1 resin had a bead size of 420 to 1200 μm and a capacity of
145 0.7 eq L^{-1} . The gellular Lewatit S5128 resin had a polyacrylic backbone with a bead
146 size of 400 to 1600 μm and a capacity of 1.25 eq L^{-1} . The third resin was the magnetic
147 macroporous MIEX®Gold resin which was of polyacrylic nature with a bead size of 15
148 -180 μm and a capacity of 0.52 eq L^{-1} .

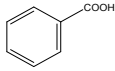
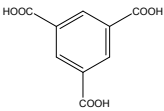
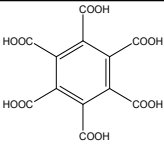
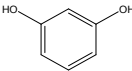
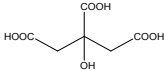
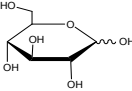
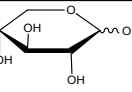
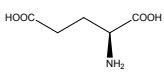
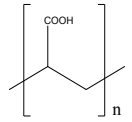
149 Prior to use, each virgin resin was rinsed using 20 times the resin volume (RV) of
150 deionized water to remove any impurities. The resin was regenerated with sodium
151 chloride solution (20 RV, 100 g L^{-1} NaCl) in stirred suspension for 30 min at 150 rpm.
152 The resin was separated from the brine and rinsed with deionized water (10-20 RV).
153 To remove excess NaCl from the resin pores, the resin was stirred for another 30 min
154 in 20 RV of deionized water at 150 rpm. The required volume of resin was measured
155 in a measuring cylinder then transferred into a 1 L beaker where excess water was
156 removed.

157 Previous research has shown that the utilisation of resin capacity is low and did not
158 exceed 1.5% of its equivalence capacity during ion exchange of NOM (Finkbeiner et
159 al., 2018, Mergen 2008). This suggests that the resin surface area is more important
160 for NOM removal than the overall capacity for suspended ion exchange systems.
161 Therefore resin concentrations of equivalent surface areas of idealized monodisperse
162 spherical beads were used, normalised to 20 mL L^{-1} of the Lewatit resin, a
163 concentration typical of that used in practice. This resulted in a resin volume of 4 mL L^{-1}
164 for MIEX and 20 mL L^{-1} for Dowex (see supporting information (SI), S.1). The
165 required volume of the conditioned resin was mixed with 500 mL of the model
166 compound solutions in a 1 L glass beaker and stirred with a paddle jar tester. After a
167 contact time of 15 min at a stirring speed of 150 rpm, the resin was allowed to settle.
168 For MIEX resin the settling was assisted by strong neodymium magnets (15 mm

169 radius, pull force 118 N). Each test was carried out in triplicate. Samples were taken
 170 after the 15 min experimental time.

171 **Table 1: Chemical structure and physicochemical properties of the model**
 172 **compounds.**

Name (constituent)	Structure	Log $K_{ow}^{(b)}$	CD ^(a) (meq mg_{DOC}^{-1})	MW (Da)
Tannic acid (humic substance)		6.2	0.56	1701.2
Penta-galloyl-glucose (humic substance/ building block)		3.6	1.08	940.7
Corilagin (building block)		0.1	4.00	636.5
Mono-galloyl-glucose (building block)		-1.3	0.49	332.3

Benzoic acid (arom. CA)		1.87	11.88	122.1
Trimesic acid (arom. CA)		0.5	27.71	210.1
Mellitic acid (arom. CA)		-0.9	41.23	342.2
Resorcinol (neutral arom.)		0.8	0.08	110.1
Citric acid (aliph. CA)		-1.7	41.23	192.1
Glucose (CH)		-2.6	0.00	180.2
Xylose (CH)		-2.5	0.00	150.1
Glutamic acid (AS)		-3.7	33.27	147.1
Poly (acrylic acid) sodium salt	 $n \approx 14, 28, 85, 158$	n.a.	n.a.	n14 =1200 n28 =8000 n85 =15000

173 (a) Charge density calculated based on pKa values estimated with Chemicalize.com
 174 (May 10, 2018), (b) PubChem XlogP3 values, n.a. = not available; CD = charge
 175 density, Log Kow = Octanol-water partition coefficient, MW = molecular weight, aliph
 176 = aliphatic, arom. = aromatic, AS = amino acid, CH = carbohydrates, CA = carboxylic
 177 acid.
 178

179 Analyses

180 Prior to analysis, all samples were filtered through a 0.45 μm filter. Dissolved organic
181 carbon (DOC) analysis was carried out using a non-purgable organic carbon method
182 on a total organic carbon (TOC) analyser (TOC-V_{CPH}, Shimadzu). Results were
183 reported as an average of triplicates.

184 Model compound mixtures were quantified on an Agilent 1200 Series high
185 performance liquid chromatography (HPLC) equipped with a degasser (G1379B,
186 Tokyo, Japan) and ALS autosampler (G1329A, Waldbronn, Germany). A sample
187 volume of 0.1 mL was injected onto a Gemini C6-Phenyl column (5 μm , 110 Å, 150 x
188 4.6 mm) (further details provided in SI, S.2).

189 A zetasizer connected to an autotitrator (Malvern Nano Series, Worcestershire, UK)
190 was used to measure the charge load and determine the CD of selected model
191 compound solutions (tannic acid and PAA) using a titration against
192 pol(diallyldimethylammonium chloride) according to an adapted method of Kam and
193 Gregory.²⁵ The theoretical CD was calculated based on the molar concentration of the
194 model compound and its proportion of ionised groups at pH 7 according to their
195 logarithmic dissociation constant (the pKa) estimated by chemicalize.com (May 10,
196 2018). Determination of the sDBP-FP was carried out as detailed by Finkbeiner et al.¹⁰
197 In short, the model compound solutions (DOC = 1 mg L⁻¹) were chlorinated with NaOCl
198 (5 mg L⁻¹ of free chlorine) and incubated for 7 days at 25°C. Trihalomethanes (THMs)
199 were quantified with gas chromatograph mass spectrometry (GC-MS) using a
200 headspace method, and haloacetic acids (HAAs) were extracted and derivatised prior
201 to analysis on a GC-MS. The determination of total resin capacity was an adjusted
202 silver nitrate titration method from Harland²⁶ (see SI, S.3).

203 **Results and Discussion**

204 ***Increased removal at higher charge density***

205 At a model compound DOC concentration of 10 mg L⁻¹, a steep increase in removal
206 with increasing CD was observed for all three resins (Figure 1). For example, PGG
207 had a CD of 1.07 meq g_{DOC}⁻¹ and was removed by 74-82%. In comparison, benzoic
208 acid with a CD of 11.88 meq g_{DOC}⁻¹ was removed by 90-93%. This was explained by
209 the higher free energy of the exchange of benzoic acid that occurred due to the
210 increased proportion of charged groups on the molecule. To illustrate, the change in
211 free energy ΔG was -1.7 J mg_{DOC} for benzoic acid, while this was -0.2 J mg_{DOC} for
212 PGG (see S.4 in SI for calculations). Tannic acid, PGG, MGG and corilagin, which
213 share a glucose ring with differing numbers of gallic acid ester groups, followed the
214 same trend of increasing removal with CD. MGG had the lowest CD of the set
215 (0.49 meq g_{DOC}⁻¹) and had a removal efficiency of 29%, while corilagin, with a CD of
216 4.0 meq g_{DOC}⁻¹, was reduced by 80% when using the Lewatit resin. The higher removal
217 for the higher CD molecule was aligned with an increase in the free energy that
218 favoured ion exchange.

219 Large improvements in removal were seen when the CD was increased from 0.4 to
220 4.0 meq mg_{DOC}⁻¹ while there was little or no change above 11.88 meq g_{DOC}⁻¹, where
221 $\geq 89\%$ was seen for all resins. For example, the removal for citric acid (CD
222 41.23 meq g_{DOC}⁻¹), trimesic acid (CD 27.71 meq g_{DOC}⁻¹) and benzoic acid (11.88
223 meq g_{DOC}⁻¹) was 93% for the Lewatit resin. The results show that a maximum removal
224 was reached in the CD range between 5 to 10 meq g_{DOC}⁻¹. Above this threshold, no
225 further increase in removal with higher CD was observed. These results align with
226 observations seen for real surface waters treated by virgin resin that had CDs ranging
227 between 6.2 to 10.5 meq g_{DOC}⁻¹ resulting in removal between 86-89%.²⁷ Mergen²³

228 showed that CD between 5.5 and 6.5 meq g_{DOC}⁻¹ resulted in removal of 50-65% and a
229 CD of 1.9 meq g_{DOC}⁻¹ resulted in removal of 35%. However, one water source of very
230 low CD (0.3 meq g_{DOC}⁻¹) resulted in 65% removal.

231 The exception to the trend was glutamic acid (CD of 33.27 meq g_{DOC}⁻¹), where removal
232 was less than for other compounds of similarly high CD. This was attributed to the
233 zwitterionic nature of the compound. Repulsive forces, originating from the positive
234 charge carried on the nitrogen atom of the amino acid, resulted in a less favourable
235 exchange. Furthermore, Donnan ion exclusion restricts glutamic acid molecules from
236 entering the resin due to the positive charge on the molecule.³

237 Resorcinol was removed by 9 and 29% by the Lewatit and Dowex resin, whereas
238 MIEX resin showed no considerable removal (2%). At pH 7, the molecule was present
239 almost entirely in the protonated form and of no charge; hence ion exchange would
240 not take place. Hydrophobic effects, and π - π interactions have been proposed as
241 alternative removal mechanisms.¹ Sorption of a hydrophobic compound to the resin
242 results in an increase in entropy and hence leads to a negative ΔG . The Dowex resin
243 had stronger interactions with the resorcinol due to the more hydrophobic and aromatic
244 styrenic resin backbone compared to the polyacrylic resins, explaining the increased
245 removal.

246 The removal of tannic acid was principally driven by its moderate CD (0.56 meq g_{DOC}⁻¹
247 ¹). However, differences in removal were observed for the Lewatit and Dowex resin at
248 57 and 71% respectively. This was explained by the hydrophobic/aromatic interaction
249 of the molecules with the resin backbone. The MIEX resin showed a higher removal
250 of tannic acid (78%) than the other two resins. This was unexpected as the resin has
251 a polyacrylic structure, which is less favourable for removal of compounds of high log

252 Kow (Table 1). However, this resin has been developed to target high molecular weight
253 organic compounds between 2 and 5 kDa through having reportedly larger pore sizes
254 than other resins used for DOC removal.²⁸ This would allow tannic acid easier access
255 to more exchange sites in the resin. Additionally, the small bead size allows faster
256 kinetics through improved diffusion into the resin. To quantify these effects further,
257 research is required to determine the resin pore size distribution using porosimetry.
258 The neutral uncharged compounds glucose and xylose were not removed by any
259 resin. These compounds possess no charge that could electrostatically interact with
260 the resin. They are also very hydrophilic molecules (log Kow -2.5 to -2.6) and so have
261 very low adsorption potential.

262 Trimesic, mellitic, glutamic and benzoic acid as well as the sugars glucose and xylose
263 had a negligible sDBP-FP (Figure S1). Tannic acid, PGG and MGG shared a similar
264 sTHM-FP between 33 and 39 mg g_{DOC}⁻¹ and all three had a high HAA-FP of 103, 139
265 and 197 mg g_{DOC}⁻¹, respectively. Citric acid was equally important for both sHAA- and
266 sTHM-FP with values of 117 and 145 mg g_{DOC}⁻¹. Resorcinol had a low sHAA-FP
267 (31 mg g_{DOC}⁻¹) but a very high sTHM-FP of 1142 mg g_{DOC}⁻¹. There was no correlation
268 between the sDBP-FP and the physicochemical characteristics of the compounds
269 (Figure S2), suggesting that the properties that control their removal by IEX do not
270 relate to sDBP-FP.

271



272

273

274

275

276

277

278

279

Figure 1: Removal of model compounds as a function of their charge density for a) Lewatit, b) Dowex and c) MIEX resin; BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC = glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE = resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose.

280 Impact of compound concentration on removal

281 Higher concentrations of organic molecules might influence their removal due to
282 occupation of easy accessible exchange sites, particularly for larger compounds that
283 might block exchange sites. Therefore, solutions of equivalent molar concentration
284 were prepared for eight selected compounds that were well removed by IEX.
285 Additionally, five compounds with CDs $>10 \text{ meq mg}_{\text{DOC}}^{-1}$ were used to prepare
286 solutions of equivalent charge load. Tannic acid was also included here to be
287 representative of a large hydrophobic compound. An increase in charge load (CL) or
288 concentration showed no considerable change in removal for the small molecules
289 ($<350 \text{ Da}$): resorcinol, benzoic acid, trimesic acid, mellitic acid and citric acid (Figure
290 2). For example, 93% of the benzoic acid was removed at 0.13 and 0.70 meq L^{-1} .
291 Glutamic acid was less well removed with increasing CL, decreasing from 78 to 72%
292 for the Lewatit resin. Pore blockage was not thought to be responsible for this decrease
293 because twice as many of the similar sized benzoic acid molecules were removed
294 (0.64 mM) in comparison to glutamic acid (0.26 mM).

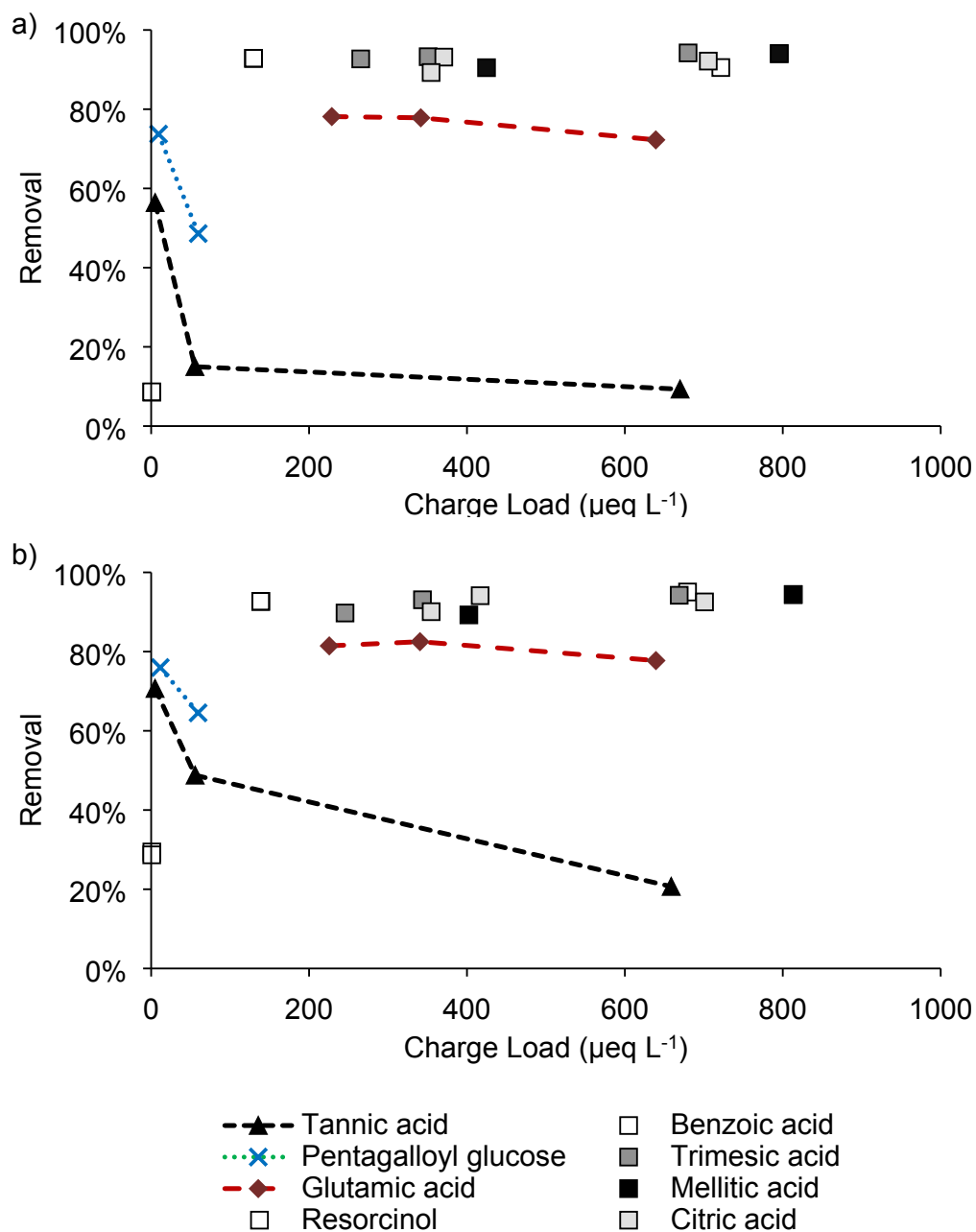
295 A greater change in removal was observed for larger compounds with increasing
296 charge concentration. For example, when the charge load of PGG (941 Da) was
297 increased from 10 to 60 $\mu\text{eq L}^{-1}$ the removal dropped from 74 to 49% and from 76 to
298 65% for Lewatit and Dowex resin, respectively. A similar trend was observed for tannic
299 acid (1701 Da): where the Lewatit resin showed a decrease in removal from 56 to 9%
300 across the gradient of 5 to 670 eq L^{-1} . This was congruent with the hypothesis that
301 compounds of high MW were restricted to the outer surface of the resin due to
302 sterically hindered pore diffusion.^{3,29} As a result, reduced removal was observed as
303 the surface area was occupied. The diameter of tannic acid has been estimated to be
304 3 nm, therefore size exclusion effects were important for the gel type resin with pores

305 of <2-4 nm.^{26,30,31} Also the macroporous resins consist of gel phases that are
306 fragmented by large pores and hence size exclusion can also occur in these resins.^{3,26}

307 ***Molecular weight as a limiting factor***

308 To further study the influence of size while reducing the impact of other
309 physicochemical factors, solutions of PAA of different mass-average molecular weight
310 (M_w) were used. Measurement of PAA solutions resulted in a high CD ranging from
311 21.3 to 24.0 meq g_{DOC}^{-1} . PAA was less well removed with increasing size of the
312 polymer chain for all resins (Figure 3). For a M_w of 1.2 kDa, the concentration of the
313 PAA was reduced by 83, 78% and 81% for Lewatit, Dowex and MIEX resin,
314 respectively. The removal of PAA of 8 kDa was similar when MIEX resin was used
315 (80%). However, the other two resins resulted in removal of 60%, suggesting that size
316 exclusion started to take effect between a M_w of 1.2 and 8 kDa for PAA. While the
317 Lewatit and Dowex showed similar removal efficiencies for low M_w compounds, the gel
318 type resin (Lewatit) had a much lower removal of 28% for the solution containing the
319 largest polymer (15 kDa) compared to the macroporous resin (Dowex) that had a
320 removal of 53%. The macroporous Dowex resin has wider pores, with diameters
321 between 20-100 nm³², which enabled the large molecules to access into the resin.
322 Comparatively, for the microporous Lewatit gel-type resins with pores <2-4 nm access
323 into the resin was restricted and a lower removal observed (Figure 3a and b). Similarly,
324 the macroporous MIEX resin removed 67% of PAA. The improved removal of the large
325 PAA molecule by MIEX was consistent with the high removal of tannic acid and was
326 explained by the large pore size of the resin. While both Dowex and MIEX were
327 macroporous resins, MIEX was able to remove more of the 8 and 15 kDa PAA
328 compounds. This was explained by the higher available accessible resin surface area

329 for the smaller MIEEX in comparison to the Dowex resin when used at equivalent
 330 volumetric doses.



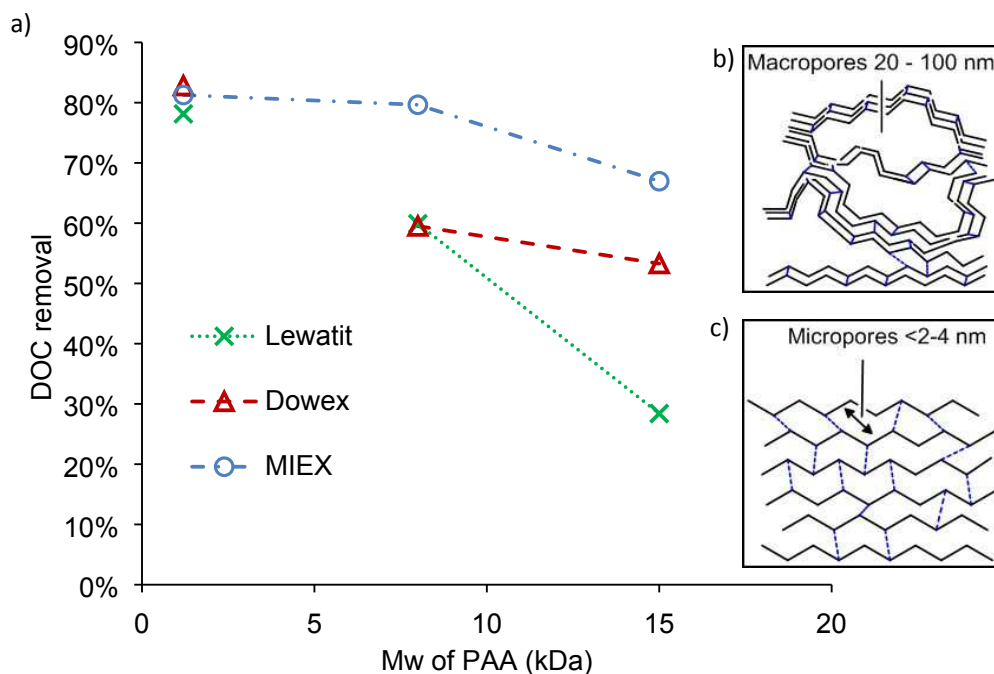
331

332 Figure 2. Removal of model compounds at different initial concentrations expressed
 333 as charge load for a) Lewatit and b) Dowex resin.

334

335

336



337

338 Figure 3: a) Comparison of the removal of PAA (poly(acrylic acid) sodium salt) at
 339 different weight-average molecular weight by Lewatit, Dowex and MIEX resin, b)
 340 structure of the macroporous resin such as Dowex and MIEX, c) structure of gel-type
 341 resin such as Lewatit; (b) and c) were adapted with permission. Copyright 2019
 342 Dardel³²).

343

344 **Stoichiometric exchange of NOM for chloride**

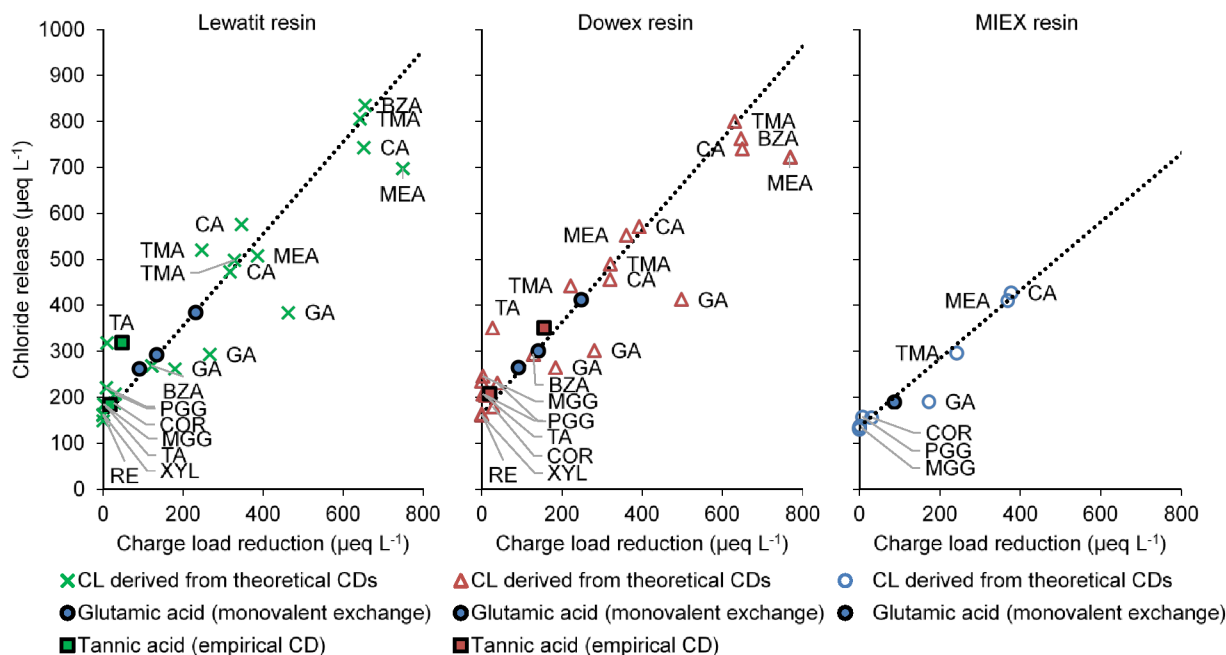
345 The released chloride concentration was plotted against the theoretically exchanged
 346 charge load to evaluate whether a stoichiometric exchange took place (Figure 4). The
 347 data points were clustered around the stoichiometric exchange line, with the exception
 348 of glutamic and tannic acids. The higher values obtained for tannic acid were explained
 349 by an underestimation of the CD calculated from its pKa value ($0.56 \text{ meq g}_{\text{DOC}}^{-1}$). This
 350 was supported by empirical determination of the CD to be $3.2 \text{ meq g}_{\text{DOC}}^{-1}$. When this
 351 CD value was used, the data points were located much closer to the stoichiometric
 352 exchange line (Figure 4).

353 The CL reduction for glutamic acid was higher than the predicted chloride release.
354 This supported the view that glutamic acid binds to the resin with only one of its
355 carboxyl groups. When the CL reduction for the exchange of glutamic acid was based
356 on only one negatively charged group, this corresponded very well with the released
357 chloride equivalence (circular data points, Figure 4). For all resins, mellitic acid at a
358 set concentration of 0.41 meq L^{-1} resulted in a stoichiometric exchange for all six acidic
359 functional groups. At high initial charge loads (0.8 meq L^{-1}), however, a lower than
360 expected chloride release was observed, which was equivalent to an exchange of
361 between 4 and 5 carboxylate groups. Accordingly, it was considered that not all of the
362 available anionic groups attached to the resin exchange sites as the molecular
363 concentration increased.

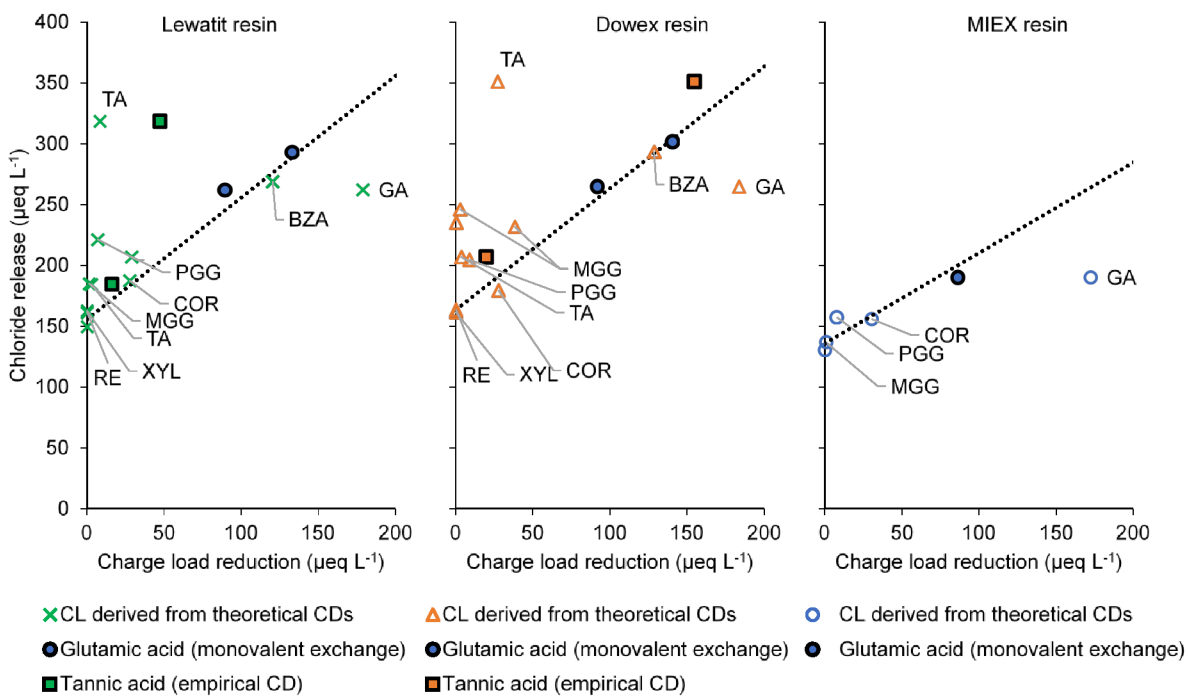
364

365

366



367



368

369 Figure 4: Chloride release as a function of the theoretically removed charge density (CD). The
 370 dotted line indicates the stoichiometric exchange of the charged groups of the molecules for
 371 chloride. BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC =
 372 glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE =
 373 resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose. *Bottom set of figures shows*
 374 *the same data with re-scaled axes to show detail for the low charge load reductions.*

375 ***Competition for exchange sites between contaminants***

376 Where compounds were present at equal DOC concentration (mixture 1), the
377 concentration of benzoic acid showed a rapid decline in the first few minutes and
378 levelled off at concentrations of 0.65, 0.45 and 2 mg L⁻¹ after 15 min for Lewatit, Dowex
379 and MIEX resin, respectively (Figure 5a). The difference between the resins was
380 explained by their chemical structure (styrene vs. acrylic) and the relative occupation
381 of the exchange sites. The same trend was observed for mixture 2, where there was
382 a fixed molar concentration of 0.119 mM for each chemical (Figure 5b). The efficient
383 removal of benzoic acid, even in the presence of a high concentration of tannic acid,
384 indicated that exchange was not inhibited by other components. This was explained
385 by the ability of small aromatic anions to access pores and exchange sites between
386 voluminous anions already exchanged on the resin surface. However, the presence
387 of increased concentrations of tannic acid influences the exchange kinetics. For MIEX
388 resin, the removal kinetics showed a faster rate of removal of benzoic acid in the first
389 few minutes of contact time compared to the other two resins. For instance within 1
390 min the benzoic acid concentration of mixture 1 was reduced by more than 50% by
391 the MIEX resin, whereas Lewatit and Dowex resin required 2.5 min to achieve the
392 same reduction. The smaller diameter and larger pore sizes of the MIEX resin beads
393 enabled faster intraparticle diffusion and enhanced the ion exchange rate.^{3,26} For
394 benzoic acid, the pseudo first order adsorption rate constant was calculated to be 0.32,
395 0.37 and 0.55 min⁻¹ for Lewatit, Dowex and MIEX resin in mixture 1 and 0.30, 0.29 and
396 0.39 min⁻¹ in mixture 2. The higher diffusion rate for Dowex and MIEX resin can be
397 explained by the larger pore size and smaller bead size (MIEX only) which enables
398 faster ion exchange.³⁰ However, at higher tannic acid concentrations (mixture 2) the
399 rate was lower for all resins and can be attributed to the hindrance of benzoic acid

400 removal by the larger organic molecules. When approaching equilibrium, however, the
401 overall removal of benzoic acid was similar for the high and low tannic acid
402 concentration. The benzoic acid removal for MIEX was lower than for the Lewatit and
403 Dowex resin, attributed to the lower frequency of available exchange sites of the MIEX
404 resin. While the total exchange capacity was not exhausted, the relative occupation of
405 the resin was much higher for the MIEX resin (due to its lower charge density)
406 compared to Dowex and Lewatit resin, particularly if removal was limited to the
407 exchange sites near the surface of the resin.

408 The removal of tannic acid by the Dowex resin was shown to be influenced by its initial
409 concentration, but only slightly by the presence of competing compounds. The level of
410 removal was 69 and 46% in mixture 1 and 2 respectively, while in the individual
411 compound solutions it was 71 and 49% (Table S2). Interestingly, there was a higher
412 removal of tannic acid by Lewatit resin in mixture 1 of 64% compared to 56% in the
413 single compound experiment. This was postulated to be due to hydrophobic
414 interactions between the tannic acid and sorbed aromatic benzoic acid molecules on
415 the resin, favouring the removal of tannic acid. The removal of tannic acid by MIEX
416 resin declined when competing compounds were in the solution. Rather than
417 enhancing the removal of tannic acid from the increase in the hydrophobicity of the
418 resin from the sorbed benzoic acid, in this case the competition for exchange sites
419 reduced the sorption of tannic acid to the resin. For mixture 1, the removal was 74%
420 compared to 78% in the single compound experiment. Again, this was ascribed to the
421 overall lower exchange capacity of MIEX resin (0.51 eq L^{-1}) compared to the other two
422 resins ($0.68\text{-}1.15 \text{ eq L}^{-1}$). Resorcinol was removed by up to 8 and 28% for Lewatit and
423 Dowex resin, respectively. The highest removal rate was achieved in the first minute
424 and then declined quickly. The removal of resorcinol in the mixtures was of a similar

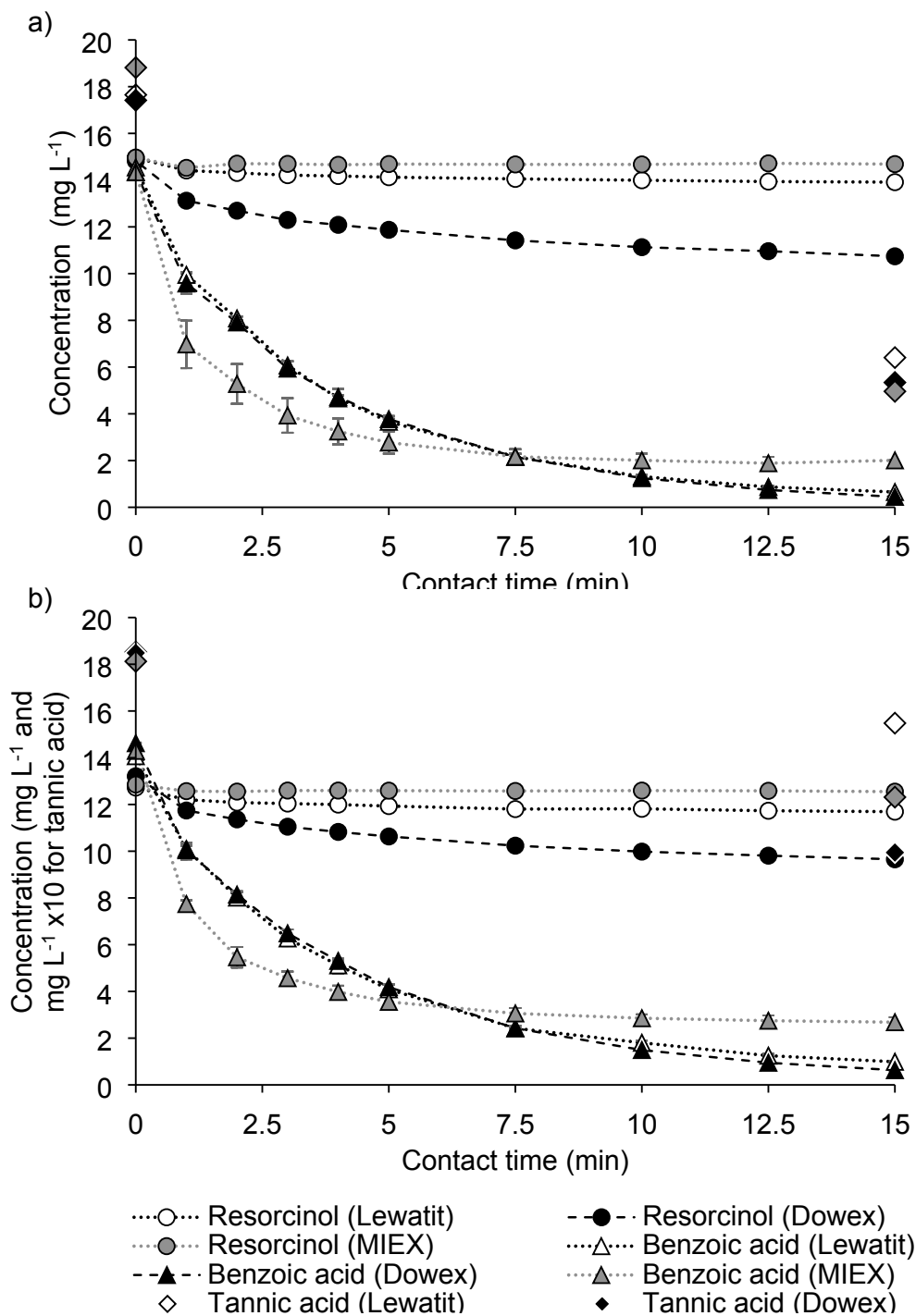
425 magnitude as for the pure compound solutions, and therefore was not considerably
426 impacted by the presence of other compounds. This was explained by the different
427 removal mechanism of this molecule.

428 With respect to the DBP formation, the increased residual concentration of the high
429 THM forming resorcinol resulted in a considerable increase in the sTHM-FP of mixture
430 1 (Table S3). . The Dowex resin gave the highest removal of resorcinol and had the
431 smallest increase in sTHM-FP (69%, 741 mg g_{DOC}⁻¹). Less effective removal of
432 resorcinol by Lewatit and MIEX resulted in a higher sTHM-FP. In mixture 2, the
433 concentration of tannic acid was very high and the proportion of resorcinol was
434 relatively small, hence the sTHM-FP of the untreated and treated water was
435 comparatively low (155 and 194-239 mg g_{DOC}⁻¹ respectively). However, the sHAA-FP
436 was reduced by 60-64% for all resins, which was explained by the removal of tannic
437 acid, a high HAA former. The sHAA-FP was higher than expected based on the
438 concentration and individual formation potential (see SI, S.5 for more detail).

439

440

441



442

443 Figure 5: Removal over time for compound mixtures of tannic acid, resorcinol and
 444 benzoic acid at a) 10 mg L⁻¹ DOC and b) 0.119 mM of each compound; tannic acid
 445 concentration calculated from DOC measurements.

446 ***Relating the results to real waters***

447 The influence of charge, hydrophobicity and MW were evaluated using the known
448 structure and physicochemical properties of model compounds. For individual
449 compound experiments, a relationship between CD and DOC removal was seen, with
450 maximum removal observed as the CD approached $10 \text{ meq mg}_{\text{DOC}}^{-1}$. This was
451 consistent with that seen for treatment of real water sources using virgin resin.²⁷
452 However, while CD is the main driving force behind exchange of NOM onto IEX
453 resins,⁹ when used in multiple cycles, fouling of the resin takes place that limits access
454 of NOM to pores,³³ such that no consistent relationship is seen with DOC removal and
455 CD as hydrophobic interactions and MW contribute to the selectivity.¹⁰

456 Compounds with multiple charged groups do not necessarily exchange all of their
457 anionic groups, resulting in a higher removal of charge compared to the sites occupied
458 on the resin. This explains the high CL removal efficiency seen for waters of high CD.
459 Furthermore, glutamic acid showed that oppositely charged groups on a molecule
460 inhibited its removal, an aspect that has not been considered in investigations treating
461 real water. Studying individual compounds showed that hydrophobic character
462 noticeably improved selectivity for low CD compounds, especially for resins with a
463 styrene backbone. This was shown by the removal of uncharged hydrophobic
464 molecules. In real water the importance of neutral compounds is very hard to establish
465 as bulk charge density measurements provides only information about the overall
466 charge load. Similarly, when real waters are split into fractions of different
467 hydrophobicity, there is no information provided about the charge of the compounds
468 present. The present work has shown that IEX can provide some removal of
469 hydrophobic compounds such as resorcinol, which can be important contributors to
470 DBPs. While not investigated in the present work, understanding the influence of

471 competing ions in real source water, such as sulphate, nitrate and bromide, on DOC
472 removal should also be assessed as this can influence overall removal and DBP
473 formation and speciation.

474 The model compounds provided further insight into the removal of different sized DOC
475 compounds where it was shown that the removal of molecules such as tannic acid
476 (1.701 kDa) and PGG (0.940 kDa) was lower at elevated concentrations. This
477 supports the view that large compounds block resin pores, consistent with
478 observations seen for real waters for compounds in the 1 kDa fraction.²⁷ The use of
479 model compounds identified that the sDBP-FP and its reduction depended on the
480 composition of the mixture. The ratio of different compounds defined the resulting
481 sHAA- and sTHM-FP, and apparent synergistic effects were observed. These
482 observations help explain why some water types are not effectively treated by IEX and
483 provide explanation as to why IEX treatment results in a reduction of sDBP-FP for real
484 water sources in some cases, while in others no change has been observed.²

485 **Supporting Information.** S.1 Calculation of resin concentration; S.2 Analysis of
486 mixtures; S.3 Determination of resin capacity; S.4 Calculation of free energy; S.5
487 Specific HAA-FP; Table S1 Properties of ion-exchange resins; Table S2 Comparison
488 of tannic acid removal; Table S3 sHAA- and THM-FP of mixture 1 and 2; Figure S1
489 DBP formation for model compounds; Figure S2 DBPs as a function of
490 physicochemical properties.

491 **Acknowledgements**

492 The authors would like to thank Scottish Water for their financial support to conduct
493 this research. The resins used in this study were kindly provided by PWNT, DOW and

494 IXOM. The authors thank Adel Abrar from Phenomenex for his support in developing
495 a method for the HPLC analysis.

496

497 **References**

- 498 (1) Zhang, Y.; Zhao, X.; Zhang, X.; Peng, S. A Review of Different Drinking Water
499 Treatments for Natural Organic Matter Removal. *Water Sci. Technol. Water*
500 *Supply* 2015, 15 (3), 442–455.
- 501 (2) Metcalfe, D.; Rockey, C.; Jefferson, B.; Judd, S.; Jarvis, P. Removal of
502 Disinfection By-Product Precursors by Coagulation and an Innovative
503 Suspended Ion Exchange Process. *Water Res.* 2015, 87, 20–28.
- 504 (3) SenGupta, A. K. *Ion Exchange in Environmental Processes*; John Wiley &
505 Sons, Inc.: Hoboken, NJ, USA, 2017.
- 506 (4) Bolto, B.; Dixon, D.; Eldridge, R.; King, S.; Linge, K. Removal of Natural
507 Organic Matter by Ion Exchange. *Water Res.* 2002, 36 (20), 5057–5065.
- 508 (5) Cornelissen, E. R.; Moreau, N.; Siegers, W. G.; Abrahamse, A. J.; Rietveld, L.
509 C.; Grefte, A.; Dignum, M.; Amy, G.; Wessels, L. P. Selection of Anionic
510 Exchange Resins for Removal of Natural Organic Matter (NOM) Fractions.
511 *Water Res.* 2008, 42 (1–2), 413–423.
- 512 (6) Croué, J.-P.; Violleau, D.; Bodaire, C.; Legube, B. Removal of Hydrophobic and
513 Hydrophilic Constituents by Anion Exchange Resin. *Water Sci. Technol.* 1999,
514 40 (9), 207–214.
- 515 (7) Gustafson, R. L.; Lirio, J. A. Adsorption of Organic Ions by Anion Exchange
516 Resin. *Ind. Eng. Chem. Prod. Res. Dev.* 1968, 7, 116–120.
- 517 (8) Humbert, H.; Gallard, H.; Suty, H.; Croué, J. P. Performance of Selected Anion
518 Exchange Resins for the Treatment of a High DOC Content Surface Water.
519 *Water Res.* 2005, 39 (9), 1699–1708.
- 520 (9) Bazri, M. M.; Mohseni, M. Impact of Natural Organic Matter Properties on the
521 Kinetics of Suspended Ion Exchange Process. *Water Res.* 2016, 91, 147–155.

- 522 (10) Finkbeiner, P.; Redman, J.; Patriarca, V.; Moore, G.; Jefferson, B.; Jarvis, P.
523 Understanding the Potential for Selective Natural Organic Matter Removal by
524 Ion Exchange. *Water Res.* 2018, 146, 256–263.
- 525 (11) Rahmani, S.; Mohseni, M. The Role of Hydrophobic Properties in Ion Exchange
526 Removal of Organic Compounds from Water. *Can. J. Chem. Eng.* 2017, 95,
527 1449–1455.
- 528 (12) Degtyarenko, I. M.; Nieminen, R. M. Dynamics of Biomolecules From First
529 Principles. In *Nanoclusters: A Bridge across Disciplines*; Jena, P., Castleman,
530 A. W., Eds.; Elsevier: Oxford, 2010; pp 557–573.
- 531 (13) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier Scientific
532 Publishing Company: Amsterdam, 1981.
- 533 (14) Boyer, T. H.; Singer, P. C. Stoichiometry of Removal of Natural Organic Matter
534 by Ion Exchange. *Environ. Sci. Technol.* 2008, 2008, 42 (2), 608–613.
- 535 (15) Boyer, T. H.; Singer, P. C.; Aiken, G. R. Removal of Dissolved Organic Matter
536 by Anion Exchange : Effect of Dissolved Organic Matter Properties. *Environ.*
537 *Sci. Technol.* 2008, 42, 7431–7437.
- 538 (16) Tan, Y.; Kilduff, J. E. Factors Affecting Selectivity during Dissolved Organic
539 Matter Removal by Anion-Exchange Resins. *Water Res.* 2007, 41, 4211–4221.
- 540 (17) Kitis, M.; Harman, I. B.; Yigit, N. O.; Beyhan, M.; Nguyen, H.; Adams, B. The
541 Removal of Natural Organic Matter from Selected Turkish Source Waters Using
542 Magnetic Ion Exchange Resin (MIEX). *React. Funct. Polym.* 2007, 67, 1495–
543 1504.
- 544 (18) Grefte, A.; Dignum, M.; Cornelissen, E. R.; Rietveld, L. C. Natural Organic
545 Matter Removal by Ion Exchange at Different Positions in the Drinking Water
546 Treatment Lane. *Drink. Water Eng. Sci.* 2013, 6, 1–10.

- 547 (19) Humbert, H.; Gallard, H.; Jacquement, V.; Croué, J.-P. Combination of
548 Coagulation and Ion Exchange for the Reduction of UF Fouling Properties of a
549 High DOC Content Surface Water. *Water Res.* 2007, 41, 3803–3811.
- 550 (20) Fearing, D. A.; Banks, J.; Guyetand, S.; Eroles, C. M.; Jefferson, B.; Wilson, D.;
551 Hillis, P.; Campbell, A. T.; Parsons, S. A. Combination of Ferric and MIEX® for
552 the Treatment of a Humic Rich Water. *Water Res.* 2004, 38 (10), 2551–2558.
- 553 (21) Li, Q.; Elimelech, M. Organic Fouling and Chemical Cleaning of Nanofiltration
554 Membranes: Measurements and Mechanisms. *Environ. Sci. Technol.* 2004, 38
555 (17), 4683–4693.
- 556 (22) Bond, T.; Goslan, E. H.; Parsons, S. A.; Jefferson, B. Disinfection By-Product
557 Formation of Natural Organic Matter Surrogates and Treatment by Coagulation,
558 MIEX and Nanofiltration. *Water Res.* 2010, 44 (5), 1645–1653.
- 559 (23) Mergen, M. R. D. Impact of Magnetic Resin on DOC Removal and Downstream
560 Water Treatment Processes, PhD Thesis, Cranfield University, 2008.
- 561 (24) Christman, R. F.; Ghassemi, M. Chemical Nature of Organic Color in Water. *J. -*
562 *Am. Water Work. Assoc.* 1966, 58 (6), 723–741.
- 563 (25) Kam, S. K.; Gregory, J. The Interaction of Humic Substances with Cationic
564 Polyelectrolytes. *Water Res.* 2001, 35 (15), 3557–3566.
- 565 (26) Harland, C. E. *Ion Exchange: Theory and Practice*, 2nd ed.; The Royal Society
566 of Chemistry: Cambridge, 1994.
- 567 (27) Finkbeiner, P. *Understanding the Removal of Natural Organic Matter Using Ion*
568 *Exchange for Drinking Water Treatment*, Cranfield University, 2019.
- 569 (28) López-Ortiz, C. M.; Sentana-Gadea, I.; Varó-Galvañ, P. J.; Maestre-Pérez, S.
570 E.; Prats-Ricoa, D. Effect of Magnetic Ion Exchange (MIEX®) on Removal of
571 Emerging Organic Contaminants. *Chemosphere* 2018, 208, 433–440.

- 572 (29) Ghossoub, Y. E.; Fares, H. M.; Delgado, J. D.; Keller, L. R.; Schleno, J. B.
573 Antifouling Ion-Exchange Resins. *ACS Appl. Mater. Interfaces* 2018, 10,
574 41747–41756.
- 575 (30) Bhandari, V. M.; Sorokhaibam, L. G.; Ranade, V. V. Ion Exchange Resin
576 Catalysed Reactions - An Overview. In *Industrial Catalytic Processes for Fine
577 and Specialty Chemicals*; Elsevier, 2016; pp 393–422.
- 578 (31) Vinu, A.; Ji, Q.; Hill, J. P.; Ariga, K. Mesoporous Nanoarchitectonics. In
579 *Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics*;
580 The Royal Society of Chemistry: Cambridge, 2012.
- 581 (32) De Dardel, F. Ion Exchange <http://dardel.info/IX/index.html> (accessed Feb 6,
582 2019).
- 583 (33) Gönder, Z. B.; Kaya, Y.; Vergili, I.; Barlas, H. Capacity Loss in an Organically
584 Fouled Anion Exchanger. *Desalination* 2006, 189, 303–307.

