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Author(s)	Ezzati, Golnaz; Healy, Mark G.; Christianson, Laura E.; Fenton, Owen; Feyereisen, Gary; Thornton, Steven; Callery, Oisín
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8 **Use of rapid small-scale column tests for simultaneous prediction of** 9 **phosphorus and nitrogen retention in large-scale filters**

10

11 G. Ezzati^{1,2}, M.G. Healy², L. Christianson³, K. Daly¹, O. Fenton^{1*}, G. Feyereisen⁴, S.
12 Thornton⁵, O. Callery⁶

13

14 ¹Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

15 ²Civil Engineering and Ryan Institute, College of Science and Engineering, National University of
16 Ireland, Galway, Galway, Ireland

17 ³Department of Crop Sciences, University of Illinois at Urbana-Champaign, Urbana, IL, USA

18 ⁴USDA-Agricultural Research Service (ARS), St. Paul, MN, USA

19 ⁵Groundwater Protection and Restoration Group, Kroto Research Institute, University of Sheffield,
20 Sheffield, United Kingdom

21 ⁶Earth and Ocean Sciences and Ryan Institute, College of Science and Engineering, National
22 University of Ireland, Galway, Galway, Ireland

23

24 *Corresponding author: owen.fenton@teagasc.ie

25

26

27 **Abstract**

28 Rapid small-scale column tests (RSSCTs) have been previously used to predict the effluent
29 concentration of a single nutrient in large filters with good accuracy. However, in drainage
30 waters originating from heavy textured soils, where there is a need for in-ditch filters to retain

31 both dissolved reactive phosphorus (DRP) and ammonium (NH₄) simultaneously, the
32 suitability of a RSSCT approach to model both parameters must be proved. In this study, a
33 decision support tool was used to identify appropriate media that may be placed in filters for
34 the removal of DRP and NH₄. The selected media for this study were sand and zeolite. Both
35 media were placed in acrylic tubes each with an internal diameter of 0.01 m and with lengths
36 ranging from 0.1 to 0.4 m, and their performance for simultaneous removal of DRP and NH₄
37 (1 mg DRP and NH₄-N L⁻¹) from water was evaluated. The data generated from the RSSCTs
38 were used to model DRP and NH₄ removals in 0.4 m-long laboratory columns of internal
39 diameter 0.1m, which had the same media configuration as the small columns and were
40 operated using the same influent concentrations. The developed model successfully predicted
41 the effluent concentration of both the DRP and NH₄-N from the large columns. This indicates
42 using RSSCTs to model the performance of filters will produce substantial savings in
43 operational, financial and labour costs, without affecting the accuracy of model predictions.

44

45 **Keywords:** adsorption, phosphorus, ammonium, agriculture, drainage, water

46

47

48 **1. Introduction**

49 Intensification of agriculture through crop growth strategies and increased animal stocking
50 rates has been enacted in many countries of the European Union (EU) (Van Zanten et al., 2016).
51 This may result in unabated diffuse and point-source nutrient (nitrogen (N) and phosphorus
52 (P)) losses to water bodies, causing multiple effects on environmental systems while traveling
53 along biogeochemical pathways and continua from soil to water bodies (Galloway et al., 2003;
54 Sharpley et al., 2011). As surface and subsurface storage components of these mixed nutrients
55 are large, critical and incidental losses which are deleterious for the aquatic system, will occur

56 (Schulte et al., 2014; Ascott et al., 2018). Therefore, alongside existing best management
57 practices to mitigate surface and groundwater nutrient losses, there is a need for a number of
58 additional measures that can intercept and mitigate nutrients before they leave the farm system.
59 Engineered remediation technologies, often referred to as engineered structures, are amongst
60 these measures and have moved beyond proof of concept in recent years (Christianson and
61 Schipper, 2016). These are placed at nutrient pollution delivery points in hydrologically active
62 areas (Penn et al., 2017), where the soil natural attenuation capacity does not exist or has
63 already been exhausted due to accumulation of nutrients (Ezzati et al., 2020). These structures
64 include installation of structures filled with P sorbing materials (Penn et al., 2014a; Sanford
65 and Larson, 2016) to intercept surface runoff, in-ditch control structures designed to remove
66 both P and N in drainage waters (Fenton et al., 2016), and denitrifying bioreactors connected
67 to tile systems that are filled with carbon-based media that convert nitrate (NO_3) to di-nitrogen
68 gas (Christianson et al., 2013; Healy et al., 2014; Fenton et al., 2016). Efforts are now being
69 made to make the use of engineered structures as a sustainable pollution remediation technique
70 that takes local, environmental and financial conditions of the user into consideration.

71

72 Ezzati et al. (2019) developed a decision support tool (DST) to assist users in the selection of
73 locally sourced media for use in mitigating pollution associated with excess nutrients in
74 drainage waters which incorporates several factors important in choosing filter media such as
75 lifespan, hydraulic conductivity, the potential for pollution swapping, attenuation of non-target
76 contaminants (e.g. pesticides, organic carbon, etc.), local availability, and costs associated with
77 transporting media to site. Within this DST, several water contamination scenarios were
78 identified, such as NO_3 only, dissolved reactive phosphorus (DRP) only, or a mixed discharge
79 of ammonium (NH_4) and DRP.

80

81 On heavy textured soils, where land drainage has been installed to extend the grazing season,
82 there is a large body of evidence (e.g. Clagnan et al., 2019) that identifies NH_4 (not NO_3) and
83 DRP as the main nutrients of concern in both shallow and groundwater drainage systems. The
84 aim of the current study is to design and quantify the effectiveness of small filters containing
85 appropriate media capable of retaining both NH_4 and DRP.

86
87 Prior to deployment of filters in field situations, it is advisable to characterise the adsorption
88 capacity of the media using batch experiments. These tests are quick, cheap, and easy-to-
89 perform (Crini and Badot, 2008), but fail to replicate in-field conditions, in which there may
90 be additional variables, such as fluctuating water temperatures, flow dynamics and pollutant
91 loads. Consequently, they often fail to accurately estimate lifespan or effectiveness of the media
92 (Pratt and Shilton, 2009). As the accurate estimation of long-term performance of a medium is
93 only possible under continuous flow conditions in the field (Pratt et al., 2012), the closest
94 simulation to in-field conditions is to allow nutrient-rich water to flow through large-scale
95 adsorption columns which are frequently operated in the laboratory (Nwabanne and Igbokwe,
96 2012; Monrabal-Martinez et al., 2017). However, these tests are costly and may take a long
97 period to reach steady-state conditions (Penn et al., 2014b).

98
99 Rapid small-scale column tests (RSSCTs), which use only a minimum quantity of medium and
100 contaminant solution, have been developed to reproduce the results of large-scale column
101 studies (Poddar, 2013). Callery et al. (2016) used RSSCTs to predict the long-term P retention
102 performance of large-scale, single medium adsorption filters. Callery and Healy (2017)
103 developed the model further to predict medium saturation, as well as filter-pore and effluent
104 concentration data. This RSSCT and modeling approach has never been attempted to examine
105 a mixed contaminant scenario such as that found in heavy textured soils i.e. the simultaneous

106 treatment of DRP and NH₄. Such a scenario would necessitate the presence of more than one
107 medium in a filter that would retain both nutrients of environmental concern in drainage waters.

108

109 Therefore, the objective of the current study is to examine the efficacy of the RSSCT modeling
110 approach in predicting DRP and NH₄ effluent concentration that simultaneously pass through
111 large-scale columns filled with two media. If this methodology proves successful, this approach
112 may provide an accurate and quick method of predicting the performance of filter media that
113 may negate the need for long-term and expensive large-scale column studies.

114

115 **2. Materials and Methods**

116

117 *2.1 Media selection using batch experiments and falling head tests*

118 The DST, developed by Ezzati et al. (2019), was used to generate a list of media capable of
119 mitigating DRP and NH₄ in drainage water (Table 1 - Stage 1). Batch and adsorption isotherm
120 experiments were conducted to identify media with the highest adsorption capacities for DRP
121 and NH₄ (Table 1 - Stage 2). The batch experiments were conducted as follows: 2 g of locally
122 sourced media, identified in Stage 1, were placed in 50 ml-capacity glass containers. Each
123 medium was overlain with 35 ml of distilled water, which was amended with both KH₂PO₄
124 and NH₄Cl to produce mixed DRP and NH₄-N solutions with concentrations ranging from 1
125 mg L⁻¹ to 40 mg L⁻¹. The containers were then sealed and placed in an end-over end shaker for
126 24 h. Following this, the samples were allowed to settle for 1 h and then centrifuged at 3500
127 rpm for 10 min, before the supernatant was withdrawn and filtered using 0.45-µm filters. All
128 water samples were analysed for DRP and NH₄-N within 24 h using a Thermo Konelab 20
129 analyser (Technical Lab Services, Ontario, Canada). A multipoint Langmuir isotherm
130 (McBride, 2000) was used to estimate the adsorption capacity of each medium. The specific

131 adsorption (q_e) (the mass of nutrient adsorbed per unit mass of amendment at equilibrium) (g
132 kg^{-1}) was calculated from the following equation (McBride, 2000):

133

$$134 \quad q_e = (C_0 - C_e) * \frac{V}{M} \quad \text{[Eqn. 1]}$$

135

136 where C_e is the concentration of nutrient (DRP or $\text{NH}_4\text{-N}$) in solution at equilibrium (mg L^{-1}),
137 C_0 is initial concentration, V is the volume of solution (L), and M is the weight of adsorbent
138 medium (g). q_{max} , an estimate of the maximum monolayer adsorption capacity of the media,
139 was calculated by plotting q_e/C_e against C_e and using the slope and intercept from the following
140 equation (McBride, 2000):

141

$$142 \quad \frac{C_e}{q_e} = \frac{1}{b} * q_{\text{max}} + C_e/q_{\text{max}} \quad \text{[Eqn. 2]}$$

143

144 where b is the coefficient associated with adsorption energy (L mg^{-1}) to form a complete
145 monolayer on the surface.

146

147 The average retention efficiency S (%) (Penn et al., 2010) was calculated as follows:

148

$$149 \quad S = \frac{C_e - C_0}{C_0} * 100 \quad \text{[Eqn. 3]}$$

150

151 where C_e and C_0 are as defined above.

152

153 A constant head method (ASTM D2434; ASTM, 2000) was used to measure the saturated
154 hydraulic conductivity (K_{sat} , m d^{-1}) of the media selected in Stage 2 (Table 1 – Stage 3). This

155 parameter helps in avoiding filter clogging and is considered to be one of the factors that
156 ensures effective operation of filters (Segismundo et al., 2017). The elemental composition of
157 selected media was analysed with a Rigaku NEX CG energy dispersive X-ray fluorescence
158 bench-top spectrometer (EDXRF; Rigaku, Austin, USA).

159

160 *2.2 Preparation of filter columns*

161 In this experiment, two sets of filter columns were constructed: small columns, with lengths
162 ranging from 0.1 to 0.4 m (internal diameter 0.01 m), and large columns with lengths of 0.4
163 m (internal diameter 0.1 m) (Figure 1 and Figure S1 in the Supplementary Material). For both
164 scales the selected media for DRP and NH₄ retention was sand and zeolite, respectively. The
165 packing density for sand and zeolite was 1.8 g cm⁻³ and 0.92 g cm⁻³, respectively.

166

167 Each large column was instrumented with an inlet pipe at the base and an outlet pipe, which
168 was positioned 0.38 m from the base (after the second media). The media overlay a fine metal
169 mesh, positioned 0.01 m from the base to prevent clogging and to allow for uniform water
170 distribution. The columns were positioned vertically and fixed on a steel frame, with flow
171 entering the bottom of the columns. For the large columns, two media configurations were
172 used to investigate possible differences in nutrient breakthrough. Such an aspect is important
173 in real world filters, where the first medium acts as a bulk removal medium with a large
174 capacity for the contaminant, and the second medium captures the low concentration of the
175 remaining contaminant (e.g. DRP) before discharge. The media configurations were as
176 follows: sand over zeolite or zeolite over sand (each at n=3) and each layer was 0.19 m deep,
177 giving a total depth of filter media of 0.38 m

178

179 For the small columns, polycarbonate tubes with an internal diameter of 0.01 m and lengths
180 of 0.1, 0.2, 0.3, and 0.4 m were used (Figure 1 (b)). Plastic syringes were connected to either
181 end of the columns, into which acid-washed glass wool (2 g) was placed to retain the media
182 and avoid microbial growth. The columns were positioned vertically and fixed in retort
183 stands, with flow entering the bottom of the columns. As media configuration change made
184 no difference to retention (Section 3.2), a single configuration was chosen i.e. zeolite over
185 sand. To achieve a similar packing density to the large columns for each column length, a
186 mass of 12.4, 24.9, 37.4 and 49.7 g of sand and 6.3, 12.7, 19.1 and 25.5 g of zeolite were used
187 for the 0.1, 0.2, 0.3 and 0.4 m columns, respectively.

188

189 *2.3 Operation of the filter units*

190 Prior to the start of the experiment, potable water was pumped through the small and large
191 columns to remove background concentrations of DRP and NH_4 . When the outlet
192 concentrations were $< 0.01 \text{ mg DRP L}^{-1}$ and $< 0.01 \text{ mg NH}_4\text{-N L}^{-1}$, the experiment
193 commenced. KH_2PO_4 and NH_4Cl were used to produce mixed influent water for the large and
194 small columns with concentrations of 1 mg DRP L^{-1} and $1 \text{ mg NH}_4\text{-N L}^{-1}$. As the objective
195 of the study was to examine the efficacy of the RSSCT modeling approach in predicting DRP
196 and NH_4 effluent concentration, effects such as competitive adsorption between multiple
197 contaminants were not examined.

198

199 Peristaltic pumps were used to pump the influent water to the large columns at a hydraulic
200 loading rate (HLR) of 156 cm d^{-1} , which is similar to the HLR applied in onsite wastewater
201 filtration systems (Hermann et al., 2013). The large columns were operated for 42 d, with the
202 pumps operational for 5 h per day.

203

204 For the small columns, influent water (with a concentration of 1 mg DRP L⁻¹ and 1 mg NH₄-
205 N L⁻¹) was pumped into the base of the columns at a HLR 52.8 cm d⁻¹ for 6 h per day. The
206 HLR was chosen so as the median empty bed contact time (EBCT) of the small columns was
207 similar to the large columns. The duration of the small column experiment was 11 d, which
208 was the length of time over which both DRP and NH₄-N removals dropped below 100% to
209 provide enough data for model generation.

210

211 *2.4 Data collection and analysis*

212 For both column scales, the influent (daily) and effluent (different time points) were sampled
213 in 50 mL tubes and filtered immediately through 0.45 µm filters and analysed for DRP and
214 NH₄-N within 24 h using a Thermo Konelab 20 analyser (Technical Lab Services, Ontario,
215 Canada). During the first 4 days of operation of the large columns, the effluent was sampled
216 after every bed volume. After reaching steady-state conditions (defined as the point at which
217 the effluent concentration began to stabilise), sampling was increased to every 5 bed volumes
218 for another 2 days, and later on increased to every 10 bed volumes. For the small columns,
219 sampling was conducted every two hours. On each sampling occasion, two samples were
220 taken from each column: a sample (5 ml) was taken directly from the effluent (marking the
221 end of the 2-h period and compared with the influent daily concentration) and a sub-sample
222 (50 ml) was taken from the total filtered volume in that 2-h composite period.

223

224 In order to model the effluent concentrations of nutrients leaving the large and small columns,
225 the adsorption model of Callery and Healy (2017) was used, assuming that pseudo-second
226 order kinetics was occurring for both nutrients (Jiang et al., 2013; Olgun et al., 2013; Siczka
227 and Koda, 2016; Riahi et al., 2017; Wasielewski et al., 2018):

228

229
$$C_t = C_0 - [(A V_B^{(\frac{1}{B})} M) / VB] * [t / (t + K)]$$
 [Eqn. 4]

230

231 where C_t is the filter effluent concentration (mg L^{-1}), C_0 is the influent concentration (mg L^{-1});

232 A, B and K are coefficients representing a constant of proportionality (mg g^{-1}), a constant of

233 system heterogeneity (i.e. existence of multiple types of adsorption sites in the medium) (no

234 units), and a time constant (min), respectively; V_B is the empty bed volumes (the volume of the

235 filter without media) of filtered solution (no units), M is the mass of adsorbent (g), V is the

236 volume of filtered solution (L), and t the empty bed contact time (min) (the average retention

237 time in an empty filter). A coded MS Excel™ file is given in the Supplementary Material.

238

239 The coefficients (A, B, and K), determined from the small column study, were fitted using

240 the Levenberg-Marquant algorithm via Solver in Excel to give the least error squared

241 (ERRSQ) of difference between the predicted and the actual effluent concentrations. They

242 were then applied to predict the effluent concentration of the large columns.

243

244 As the concentration of NH_4 effluent in the 0.2 to 0.4 m columns was zero during the early bed

245 volumes of the experiment (i.e. 100% retention was achieved initially), data for the modelling

246 process was taken after 12 bed volumes for all column sizes. From this period onwards, the %

247 retention in the columns dropped below 100%.

248

249 *2.5 Statistics*

250 To assess if there were any differences in % of nutrient retention capacity based on media

251 configuration in the large columns i.e. sand over zeolite or zeolite over sand, a z-test was

252 conducted. A p value of < 0.05 rejected the null hypotheses i.e. no difference in terms of
253 retention based on the configuration.

254

255 **3. Results and discussion**

256

257 *3.1 Selection of media*

258 The final selected media for the small and large column experiments were coarse sand
259 (particle size 1-2 mm) sourced from the south west of Ireland with a high iron (Fe) content
260 and natural Turkish (Yildizeli) zeolite (particle size 1-3 mm). Batch experiment results
261 indicated that both the sand and zeolite had good DRP and NH_4 removals, and had good K_{sat}
262 values for the column experiments (Table 2).

263

264 The sand had a q_{max} of $8.34 \text{ g DRP kg}^{-1}$ with a binding energy, k , of 2.87 L mg^{-1} (Table 2)
265 This q_{max} was higher than other sands commonly used in filter systems (e.g. Danish sands,
266 which have 0.02 to $0.13 \text{ g DRP kg}^{-1}$; Fenton et al., 2008). Zeolite, which is an aluminosilicate
267 mineral, also had good DRP retention, similar to the results of other studies (Lin et al., 2014;
268 Gérard, 2016; Ibrahim et al., 2015).

269

270 Zeolite, used in the current study to target NH_4 removal, had an aluminium (Al) content of
271 12.8% (Table 2), which is within the range of commonly used filter P materials (i.e. 1.3 to
272 over 40%) (Cucarella and Renman, 2009). According to Penn et al. (2017), high Fe and Al
273 content of a P-sorption material indicates ligand exchange (ion binding to a metal) as the main
274 mechanism for DRP retention rather than precipitation, which would occur in high calcium
275 content materials. Zeolite had a q_{max} of $39.5 \text{ g NH}_4\text{-N kg}^{-1}$ with a binding energy of 9.8 L mg^{-1}
276 ¹ (Table 2). The $\text{NH}_4\text{-N}$ retention mechanism was either molecular adsorption or ion exchange

277 (Zhang et al., 2011). Various ranges of q_{\max} for zeolite are found in the literature due to
278 variations in country of origin and chemical element (Wasielewski et al., 2018) e.g. 15.3-25
279 g $\text{NH}_4\text{-N kg}^{-1}$ (Langwald, 2008; Zhang et al., 2010; Kotoulas et al., 2019), 31.9 g $\text{NH}_4\text{-N kg}^{-1}$
280 ¹(Ham et al., 2018), and 40.3 g $\text{NH}_4\text{-N kg}^{-1}$ (Ibrahim et al., 2015). These have resulted in 84%
281 to complete $\text{NH}_4\text{-N}$ removal (99%), depending on operational conditions such as influent
282 concentration, temperature, pH, and adsorbent dosage.

283

284 *3.2 Retention of DRP and $\text{NH}_4\text{-N}$ in the columns*

285 For the large columns, the DRP retention was initially high at >95% for the first two empty
286 bed volumes, V_B , of filtered solution, and decreased gradually to 13% after >100 pore volumes
287 (43 V_B) (Figure 2). One hundred percent $\text{NH}_4\text{-N}$ retention was achieved for the first 25 pore
288 volumes, but decreased to 80% after 120 pore volumes (52 V_B) (Figure 3). Similar trends in
289 $\text{NH}_4\text{-N}$ retention using zeolite were also documented by other studies (Alshameri et al., 2014;
290 Huang et al., 2015; Kotoulas et al., 2019). Clinoptilolite zeolite is known to be a very good ion-
291 exchanger (Wasielewski et al., 2018), and a high adsorption rate has been associated with
292 diffusion of $\text{NH}_4\text{-N}$ ions (Huang et al., 2010) through macropores and mesopores to the surface
293 of zeolite (Shaban et al., 2017).

294

295 The configuration of the media did not affect DRP or NH_4 retentions ($p > 0.05$). The use of
296 dual media, placed side by side in a filter with each designed to adsorb either P or N from
297 different wastewater types has been previously investigated (e.g. Goodwin et al., 2015) and,
298 similar to the current study, other studies have found that configuration of the media (N
299 adsorbing media before P adsorbing media, or vice versa) does not affect P or N removal
300 (Christiansen et al., 2017).

301

302 The small columns were P-saturated after 1 L of filtered volume ($V_B=50$ for the 0.3 m
303 column), whereas the NH_4 saturation of the columns took substantially longer to occur; the
304 0.1 m column was 80% saturated after approximately 10 L filter volumes ($V_B=1550$) and
305 duration of complete removal was related to the length of the column. Unlike many batch
306 adsorption experiments and large-scale column tests examining the NH_4 removal efficiency
307 of zeolite, RSSCTs operated under continuous loading of a few hours per day has never been
308 investigated. However, the results here are in agreement with other studies, which showed a
309 positive relationship between removal efficiency, mass of adsorbent and contact time
310 (Kotoulas et al., 2019).

311

312 *3.3 Predicting DRP effluent concentration in large columns using scale column data*

313 Regardless of media configuration, the model developed using the small column data (Table
314 3, $ERRSQ=5.56$) was able to predict the trend of DRP effluent in the large columns. Figure 2
315 superimposes the modelled data from the small columns onto the measured data from the
316 large columns and Figure 4 presents the observed versus modelled data using coefficients
317 from small column tests for each individual column and configuration.

318

319 The constant of heterogeneity, B , was a dominant coefficient in predicting effluent
320 concentrations. This is indicative of potentially multiple adsorption mechanisms responsible
321 for nutrient removal which can be explained by the fact that the model is predicting combined
322 removal efficiency of two media with different elemental compositions (Table 2), which are
323 packed into one filter column. According to Callery and Healy (2017), the curve produced by
324 Eqn. 4, which is based on second-order kinetics, can indicate the importance of intraparticle
325 diffusion (Ko et al., 2000) for model prediction within small columns at different lengths.
326 This is shown in Figure 2, where the tailing of the breakthrough curve has likely been caused

327 by intra-particle diffusion (Doekar and Mandavgane, 2015). This may become significant as
328 the surface of the medium/media become saturated or as EBCT increases (Callery and Healy,
329 2017).

330

331 *3.4 Predicting NH₄-N effluent concentration from large columns using small columns*

332 Complete NH₄-N removal was observed during the initial operational period of the large and
333 small columns, which is consistent with other studies (Balci and Dince, 2002; Sharifnia et al.,
334 2016; Mazloomi and Jalali, 2016; Kotoulas et al., 2019). Consequently, the small columns were
335 operated for a longer period of time (11 d in total) to generate enough data for the successful
336 prediction of NH₄-N effluent concentrations leaving the large columns.

337

338 Eqn. 4 predicted the behaviour of the filters in retaining NH₄-N (Figure 3) and Figure 5 presents
339 observed versus modelled data using coefficients from small column tests for each individual
340 column. The constant of heterogeneity in NH₄-N adsorption, B, was less than DRP (Table 4),
341 which indicates that zeolite, not sand, was the only medium in the columns capable of NH₄-N
342 retention as also observed in the batch experiment. However, the high K values indicate that
343 the adsorption rate did not follow a linear regression with filter depth, as initially proposed by
344 filter bed depth service time (BDST) (Hutchins, 1973) which has been used by many adsorption
345 studies. The BDST model assumes that intraparticle diffusion is negligible (Ayoob and Gupta,
346 2007), which becomes an important factor as a medium's surface becomes more saturated
347 (Doekar and Mandavgane, 2015; Callery and Healy, 2017). The proposed model in this study
348 is therefore describing a real-world adsorption system in which several factors control the
349 adsorption (Crini and Badot, 2010), meaning that larger amounts of media and increased
350 contact time may not produce directly proportionally higher adsorption. A similar lack of
351 proportionality between the length of columns (amount of adsorbent) and increase in NH₄-N

352 retention has been reported by Sarioğlu (2004). Although the experiments were carefully
353 designed to provide similar environmental conditions for all columns, there was a small
354 difference between data generated from various large-scale columns. In order to avoid any bias,
355 average effluent data were used to generate model parameters.

356

357 *3.6 Implications of study for drainage filters*

358 To date, large-scale columns have been mainly used to estimate nutrient saturation and
359 longevity of media to replicate operational conditions (Peyne et al., 2014; Lopez-Ponnada et
360 al., 2017; Monrabal-Martinez et al., 2017). However, moving from large-scale columns to
361 RSSCTs would gain financial and labour advantages, whilst not sacrificing the accuracy of
362 model outcomes. This may include considerable savings on: time required for constructing and
363 operating the columns, labour hours and number of staff required, space required to house the
364 structure and experimental set up, number/capacity of containers, amount of influent (chemical
365 and distilled water), procurement of adsorbent(s) (media) and sampling equipment e.g. tubes,
366 syringes, filter pours; number of pumps, cost of laboratory analysis of water samples; and
367 overhead costs, including electricity and light.

368

369 The results of this study validated the model, showing that it could upscale RSSCTs accurately
370 to describe the pattern of large-scale column performance. However, it is important to design
371 the experiment carefully so as the media becomes partially saturated over the duration of the
372 experiment. In the current study, the modelling parameters of Eqn. 4 predicted the $\text{NH}_4\text{-N}$
373 effluent concentration in the large columns only after the retention of $\text{NH}_4\text{-N}$ in the small
374 columns dropped to below 100%.

375

376 Figure 6 presents a flowchart which shows steps towards the implementation of an efficient
377 field-scale engineered structure filled with adsorptive media, to treat DRP and NH₄-N in
378 drainage water. In general, a successful implementation includes characterisation of nutrient
379 losses in the farm, correct choice of medium/media with a high nutrient retention capacity (and
380 which does not contribute to pollution swapping; Ezzati et al., 2019), characterisation of the
381 retention capacity, and therefore lifetime, of the selected media, and the identification of an
382 optimal location for installation of structure (Ezzati et al., 2020). This would ultimately provide
383 a sustainable and cost-effective mitigation for the removal of mixed contaminants in
384 agricultural ditches.

385

386 **4. Conclusions**

387 In this study, rapid small scale column tests were used to predict effluent DRP and NH₄-N
388 concentrations from much larger columns with good accuracy. As large-scale laboratory filter
389 column tests are time consuming and expensive, but are considered to replicate in-field
390 conditions well, the methodology used in this study will save operational, financial and labour
391 costs, whilst providing good model predictions of DRP and NH₄-N. Future work should
392 consider modelling biological N removal (e.g. nitrate) in filters containing C-rich media (e.g.
393 woodchip), where adsorption is not the dominant removal mechanism. In addition, research
394 should focus on potential uses for saturated filter media.

395

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398 innovation programme under the Marie Skłodowska-Curie grant agreement No 675120.

399

400

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572 **Captions for Figures**

573

574 Figure 1. Schematic diagram of large columns (a) and small columns (b).

575 Figure 2. Normalised DRP concentration (y-axis) vs. pore volume (x-axis) for both
576 configurations of the large columns. The dashed line is the model fit using coefficients from
577 small columns. Top: sand over zeolite (A, B and C). Bottom: zeolite over sand (D, E, F).

578 Figure 3. Normalised NH₄-N concentration (y-axis) vs. pore volume (x-axis) for both
579 configurations of the large columns. The dashed line is the model fit using coefficients from
580 small columns. Top: sand over zeolite (A, B and C). Bottom: zeolite over sand (D, E, F).

581 Figure 4. Observed DRP concentrations versus predicted DRP concentrations using
582 coefficients from small columns. Left: Configuration 1 (zeolite at the bottom, sand at the top)
583 (A, B, C); Right: Configuration 2 (zeolite at the top and sand at the bottom) (D, E, F).

584 Figure 5. Observed NH₄-N concentrations of large columns versus predicted NH₄-N
585 concentrations using coefficients from small columns. Left: Configuration 1 (zeolite at the
586 bottom, sand at the top) (A, B, C); Right: Configuration 2 (zeolite at the top and sand at the
587 bottom) (D, E, F).

588 Figure 6. Flow chart for the design of an in-ditch field scale engineered structure filled with
589 reactive media for a mixed discharge of NH₄-N and DRP.

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596 **Captions for Tables**

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598 Table 1. Stages of media selection for dual nutrient mitigation. At the end of each selection
599 stage, media failing the criteria are omitted from the table.

600

601 Table 2. Batch experiment and constant head data for maximum adsorption capacity of media
602 (q_{\max} ; g kg^{-1}), binding energy (k ; L mg^{-1}), and selected elemental composition based on XRF
603 analysis of sand and zeolite used in the column experiments

604

605 Table 3. Comparison of model parameters, coefficients and ERRSQ values, obtained when
606 (a) fitting Eqn. 4 to DRP concentration data from large columns using model coefficients
607 determined from small columns, (b) parameters at different depths of small columns.

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609 Table 4. Comparison of model parameters, coefficients and ERRSQ values, obtained when
610 (a) fitting Eqn. 4 to $\text{NH}_4\text{-N}$ concentration data from large columns using model coefficients
611 determined from small columns, (b) model parameters at different depths of small columns.

612

613 Table 1. Stages of media selection for dual nutrient mitigation. At the end of each selection stage, media
 614 failing the criteria are omitted from the table.

Stage 1 Selection of media using a DST ¹	Stage 2 Batch & Adsorption isotherm tests	Stage 3 K _{sat} tests
Peat soil	Peat soil	
Processed Peat (Puraflo peat)	Processed Peat (Puraflo peat)	
Compost	Compost	
Woodchip	Woodchip	
Dewatered alum-sludge		
Soil (air dried at 40 °C)		
Sand	Eight types of sands ²	Five types of sand ²
Turkish (Yildizeli) zeolite (particle size: 1-3 and 3-5 mm)	Turkish (Yildizeli) zeolite (particle size 1-3 and 3-5 mm)	Turkish (Yildizeli) zeolite (particle size 1-3 and 3-5 mm)
Barley straw	Barley straw (cut into 2 mm lengths)	
Maize		
Silage		

615 ¹Ezzati et al. (2019); ² Collected from quarries in the south of Ireland

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629 Table 2. Batch experiment and constant head data for maximum adsorption capacity of media (q_{max} ; $g\ kg^{-1}$), binding energy (k ; $L\ mg^{-1}$);
 630 and selected elemental composition based on XRF analysis of sand and zeolite used in the column experiments.

631

	q_{max} ($g\ kg^{-1}$)		k ($L\ mg^{-1}$)		K_{sat} ($m\ s^{-1}$)	Na	Mg	Al	Si	Fe	K	Ca	Ti	S	Mn	P
	DRP	NH ₄ -N	DRP	NH ₄ -N												
Sand	8.34	0.6	2.87		7.41×10^{-4}	1.3	1.0	11.8	70.9	8.6	4.0	0.1	1.2	0.4	0.2	0.1
Zeolite	6.33	39.52	2.2	9.8	7.39×10^{-4}	-	1.3	12.8	70.0	2.8	7.4	4.3	-	-	0.1	-

632 ¹ Na: Sodium; Mg: Magnesium; Al: Aluminium; Si: Silicon; Fe: Iron; K: Potassium; Ca: Calcium; Ti: Titanium; S: Sulphur; Ms: Manganese;
 633 P: Phosphorus. Elements presented only for those having > 0.1% of total composition.

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637 Table 3. Comparison of model parameters, coefficients and ERRSQ values, obtained when (a) fitting
 638 Eqn. 4 to DRP concentration data from large columns using model coefficients determined from small
 639 columns, (b) parameters at different depths of small columns.

Model Coefficients	(a) Parameters determined using small column data	(b) Parameters at different lengths of small columns			
		Small column depth (m)			
		0.1	0.2	0.3	0.4
A	0.03	280.56	447.05	206.32	669.24
B	2.13	18684.43	18681.93	18687.69	18682.58
K	901	897.99	846.75	972.76	877.25
ERRSQ	5.56	0.04	0.04	0.08	0.052

640 A: Constant of proportionality
 641 B: Constant of system heterogeneity
 642 K: Constant of time

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660 Table 4. Comparison of model parameters, coefficients and ERRSQ values, obtained when (a) fitting
 661 Eqn. 4 to NH₄-N concentration data from large columns using model coefficients determined from small
 662 columns, (b) model parameters at different depths of small columns.

Model coefficients	(a) Parameters determined using small column data	(b) Parameters at different lengths of small columns			
		Small column depth (m)			
		0.1	0.2	0.3	0.4
A	0.057	0.051	0.048	0.11	0.11
B	1.13	1.13	1.10	1.04	1.04
K	1961.61	1961.61	1961.61	1961.63	1961.60
ERRSQ	0.13	0.11	0.12	5.23	1.75

663 A: Constant of proportionality
 664 B: Constant of system heterogeneity
 665 K: Constant of time
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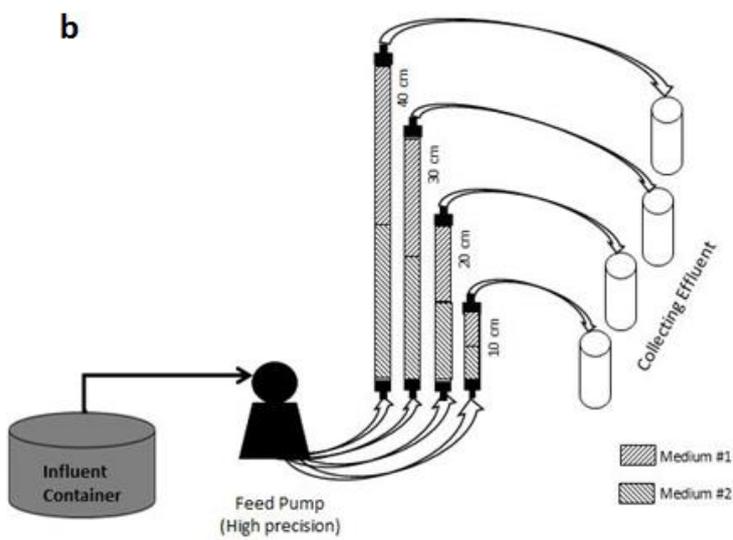
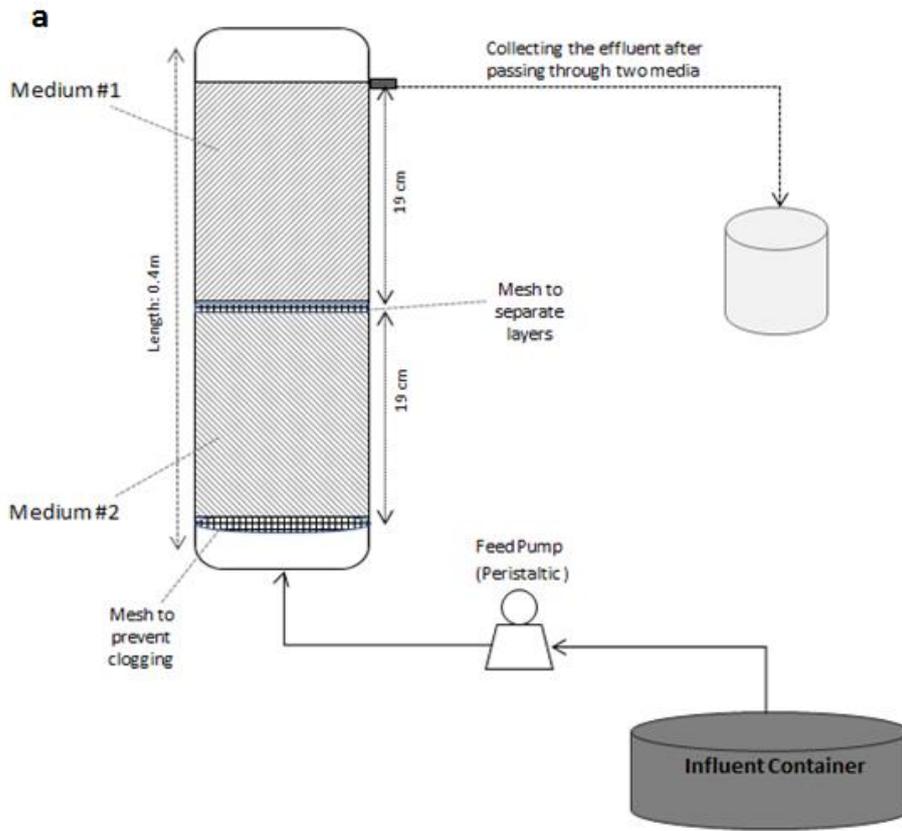
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679 **Figure 1.**

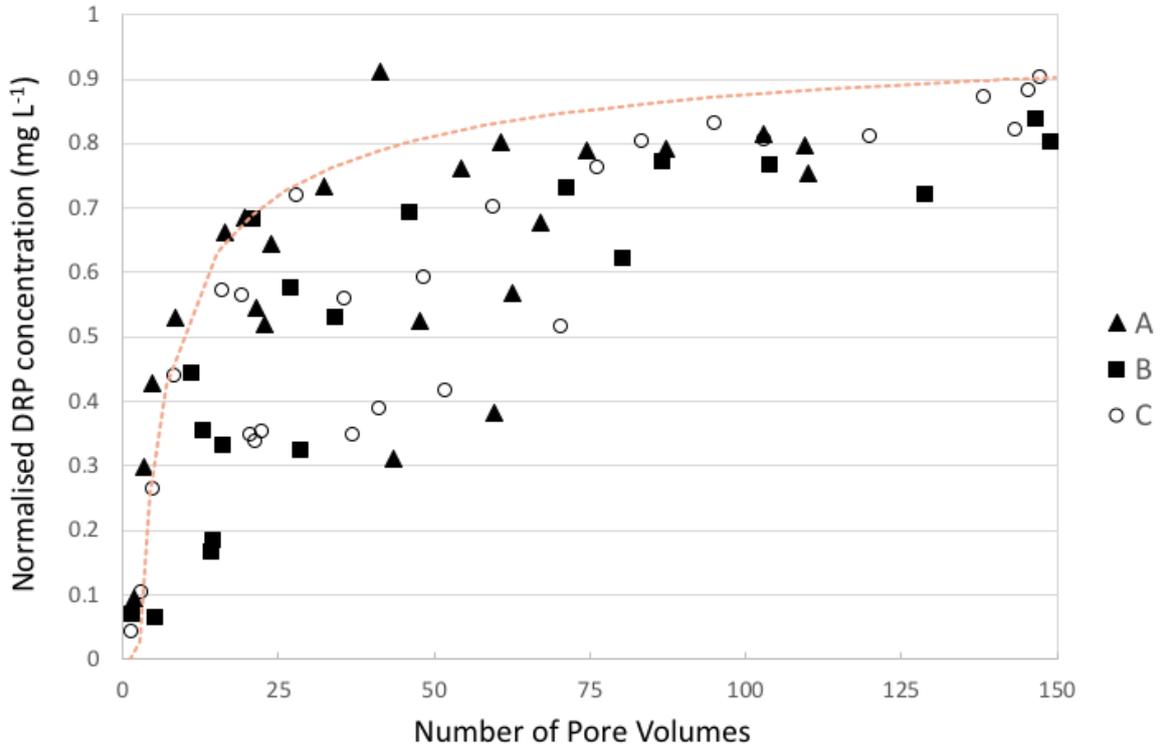


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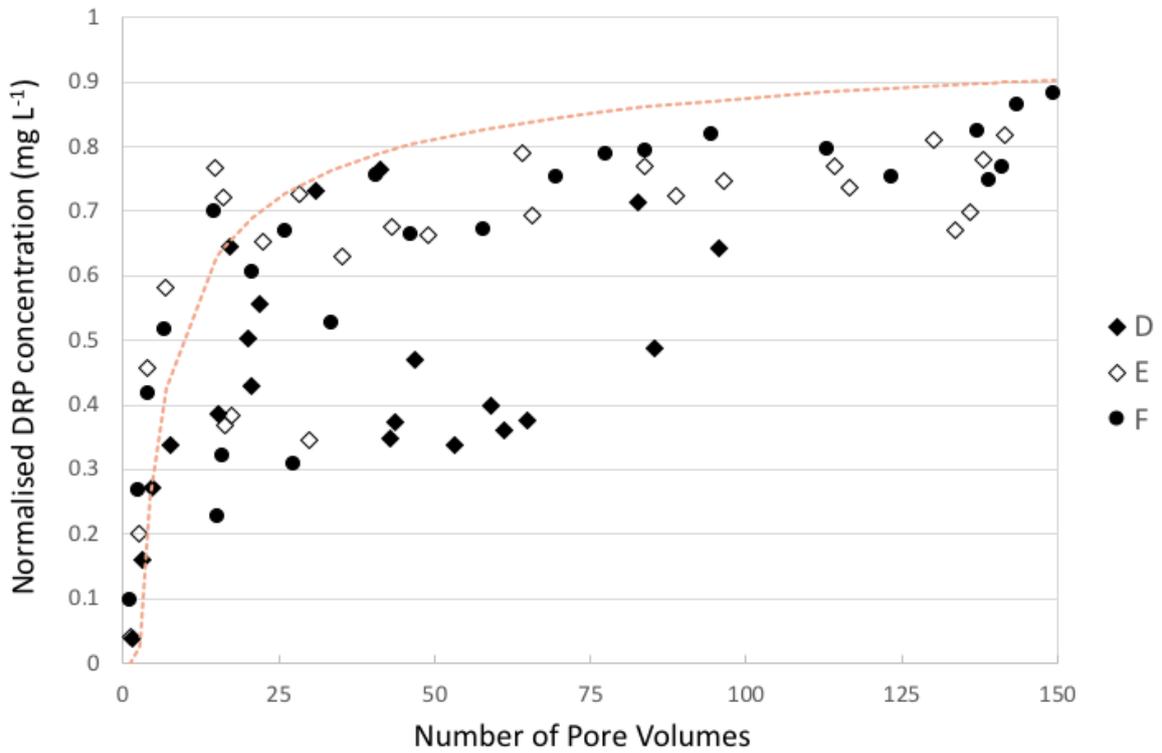
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683 **Figure 2**



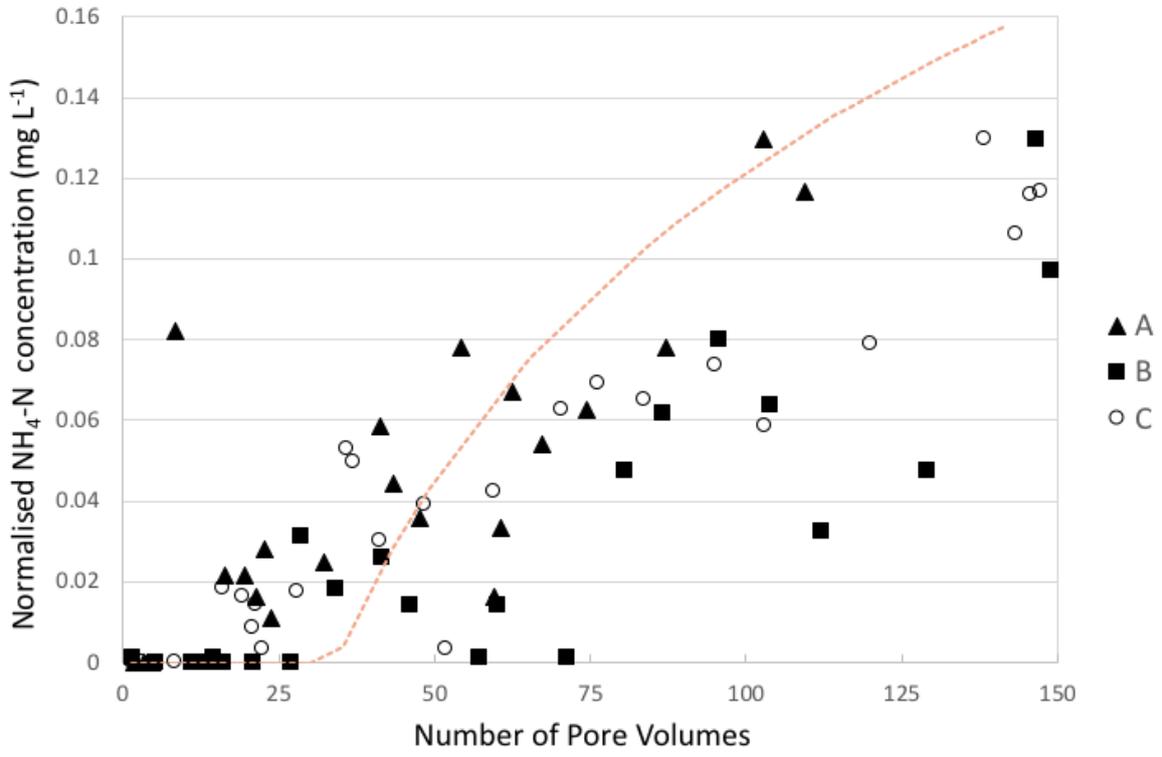
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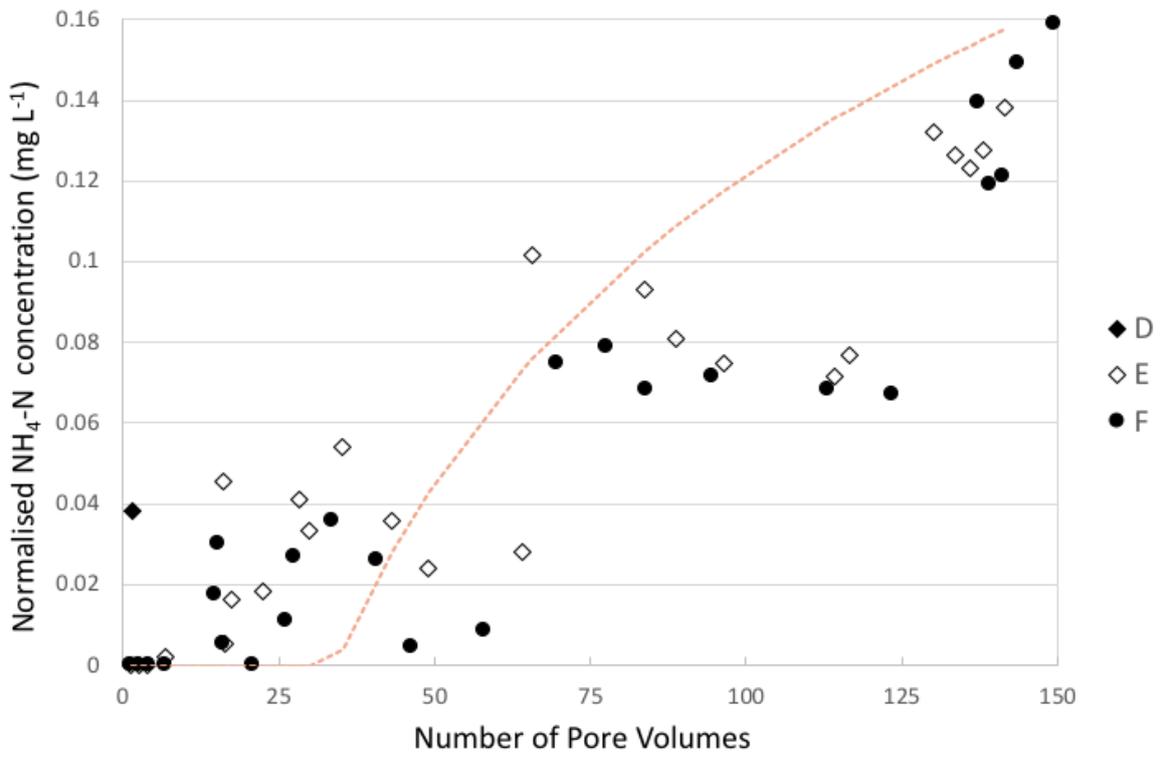
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687 **Figure 3**



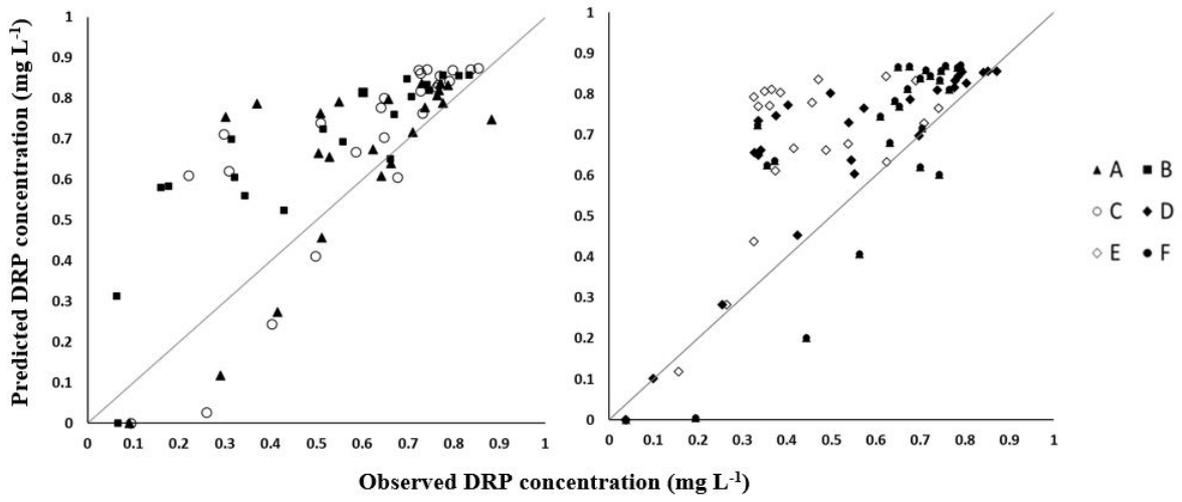
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691 **Figure 4**



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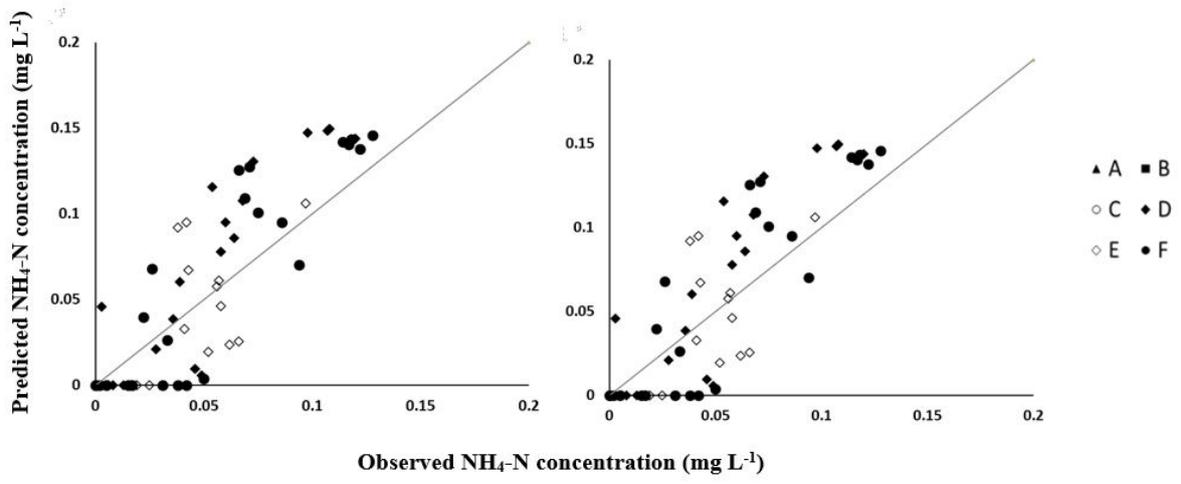
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705 **Figure 5**



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