


Provided by the author(s) and University College Dublin Library in accordance with publisher policies. Please cite the published version when available.

Title	On the fit of statistical and k-C* models to projecting treatment performance in a constructed wetland system
Author(s)	Babatunde, A.O.; Zhao, Y.Q.; Doyle, R.J.; Rackard, S.M.; Kumar, J.L.G.; Hu, Y.S.
Publication date	2011-04
Publication information	Journal of Environmental Science and Health, Part A, 46 (5): 490-499
Publisher	Taylor & Francis
Link to online version	http://dx.doi.org/10.1080/10934529.2011.551729
Item record/more information	http://hdl.handle.net/10197/3111
Publisher's statement	This is an electronic version of an article published in Journal of Environmental Science and Health, Part A, 46 (5): 490-499, available online at: http://dx.doi.org/10.1080/10934529.2011.551729 .
Publisher's version (DOI)	http://dx.doi.org/10.1080/10934529.2011.551729

Downloaded 2017-12-11T09:58:07Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa) 

Some rights reserved. For more information, please see the item record link above.



1 **On the fit of statistical and the $k-C^*$ models to projecting treatment performance in a**
2 **constructed wetland system**

3
4
5 A.O. BABATUNDE, Y.Q. ZHAO*, R.J. DOYLE, S.M. RACKARD, J.L.G. KUMAR
6 and Y.S. HU

7
8 Centre for Water Resources Research, School of Architecture, Landscape and Civil
9 Engineering, University College Dublin, Belfield, Dublin 4, Ireland

10
11
12 **ABSTRACT**

13
14 The objective of this study was to assess the suitability of statistical and the $k-C^*$ models
15 to projecting treatment performance of constructed wetlands by applying the models to
16 predict the final effluent concentrations of a pilot field-scale constructed wetlands system
17 (CWs) treating animal farm wastewater. The CWs achieved removal rates (in $\text{g}/\text{m}^2\cdot\text{d}$) ranging
18 from 7.1-149.8 for BOD_5 , 49.8-253.8 for COD and 7.1-47.0 for $\text{NH}_4\text{-N}$. Generally, it was
19 found that the statistical models developed from multiple regression analyses (MRA) were
20 stronger in predicting final effluent concentrations than the $k-C^*$ model. However, both
21 models were inadequate in predicting the final effluent concentrations of $\text{NO}_3\text{-N}$. The first-
22 order area-based removal rate constants (k , m/yr) determined from the experimental data
23 were 200.5 for BOD_5 , 80.1 for TP and 173.8 for $\text{NH}_4\text{-N}$ and these indicate a high rate of
24 pollutant removal within the CWs.

25 _____
26 *Address correspondence to Yaqian Zhao, Centre for Water Resources Research, School of
27 Architecture, Landscape and Civil Engineering, University College Dublin, Belfield, Dublin
28 4, Ireland; Tel. +353-1-7163215; Fax. +353-1-7163297;
29 e-mail: yaqian.zhao@ucd.ie

31 **Keywords** Alum sludge; constructed wetlands; first-order, k -C* model, regression analysis

32

33 INTRODUCTION

34 Constructed wetlands systems (CWs) are treatment modules systems designed to mimic
35 natural processes involving wetland vegetation, soils, and their associated microbial
36 assemblages in treating wastewater. In recent times, the need to enhance or achieve specific
37 treatment objectives which are often more stringent has led to the emergence of engineered
38 wetland systems. These systems are essentially CWs, but with a more controlled
39 environment.^[1] Constructed and engineered wetland systems have gained widespread
40 popularity as a wastewater treatment technology due to the fact that they are low-cost, easy-
41 to-operate, efficient and robust.^[2] They have been utilized globally for the treatment of
42 various types of wastewaters including municipal wastewater from small communities,
43 industrial and high-strength wastewater from agricultural activities. Contaminants in these
44 systems are removed through a combination of physical, chemical, and biological processes
45 including sedimentation, precipitation, adsorption to soil particles or specialized substrates,
46 assimilation by plant tissue and microbial transformations and interactions.

47 The basis of design for these systems is usually first-order reaction model integrated with
48 a plug-flow (PF) assumption. Although the flow in CWs is generally intermediate between
49 PF and completely mixed, it is acknowledged that the first-order model with PF assumptions
50 provides a conservative design estimate.^[3] However, while this model is simple and widely
51 used, it fails to adequately characterize the complex processes that occur in CWs.^[4] For
52 instance, the findings of numerous tracer studies in literature indicate that CWs typically do
53 not possess ideal PF hydraulics. Furthermore, it is noted that current design procedures fail to
54 incorporate atmospheric interactions such as precipitation, evaporation, and transpiration and
55 these variables produce a secondary hydraulic regime that may influence retention times and
56 invalidate steady state theoretical models.^[5, 6, 7]

57 Several researchers have proposed more sophisticated CWs performance models, which
58 simulate non-ideal hydraulics, either using a tanks in series (TIS) or plug flow with
59 dispersion (PFD) approach.^[6] These models, however, have not been adopted by
60 practitioners due to their complexity and amount of data required to properly use them. In
61 addition, the proposed models still do not incorporate unsteady external hydraulic loading,
62 which can have large effects on CWs performance. Recently, Rousseau et al.^[8] reviewed
63 current CWs design approaches and concluded that the first-order PF model remains the best
64 available method, despite its obvious deficiencies. This agrees with the submissions of Stein
65 et al.^[9] who noted that first-order models are the most widely used for CWs design.
66 Furthermore, Son et al.^[7] remarked that data availability and applicability have meant that
67 simple regression and kinetic models have continued to be used to demonstrate CWs
68 performance. In recent times, a modified first-order kinetic model often called the k - C^*
69 model was proposed by Kadlec and Knight^[10] and the model has been widely applied in
70 CWs design. The k - C^* model allows for a background or residual concentration (C^*), a non-
71 zero lower limit that is approached asymptotically in lieu of the first-order model approach to
72 zero^[9].

73 On the other hand, statistical models including those derived from multiple regression
74 analyses (MRA) have also been found useful for simplified description and analysis of CWs
75 performance, and their accuracy in predicting such performances has been demonstrated.^{[11,}
76 ^{12, 13]} They are widely used in assessing CWs performance as they provide a means of
77 understanding their treatment process/mechanism although this is limited. In this study, we
78 evaluated the fit of statistical models developed from multiple regression analyses and the k -
79 C^* models in projecting the treatment performance of a pilot field-scale CWs treating animal
80 farm wastewater by comparing the predicted final effluent concentrations using these models
81 with those observed from the field trial. The CWs reported here, which has been developed in
82 our research group, is unique in that it employs a by-product, alum sludge (the most widely

83 generated aluminium-coagulated drinking water treatment residual worldwide), as the main
84 substrate primarily to enhance phosphorus (P) removal and also for biofilm
85 attachment.^[14,15,16] Although MRA and $k-C^*$ models have their limitations, the availability
86 and applicability of data from this unique pilot field-scale CWs were tested and discussed.

87

88 **MATERIALS AND METHODS**

89

90 **Pilot field-scale constructed wetland system**

91 The pilot field-scale CWs is located on an animal farm in Newcastle, Co Dublin, Ireland.
92 The set-up and operation of the CWs has been described in Zhao et al.^[16] In brief, the CWs is
93 a four-stage equal sized cell system (each 108cm×94cm×105cm) operated in vertical down-
94 flow mode with a hydraulic loading rate of 0.29 m³/m².d. The four cells are all interlinked by
95 submersible pumps. The pumps are connected to a digital electronic timer which regulates the
96 flow in the CWs according to a programme schedule. Dewatered alum sludge cake was
97 collected fresh from the industrial filter press of the sludge dewatering unit of a drinking
98 water treatment plant in South-West Dublin, Ireland where aluminium sulphate is used as
99 coagulant. The characteristics of the dewatered alum sludge cake and its suitability for use as
100 a substrate in a CWs has been well studied and reported.^[14] The dewatered alum sludge cake
101 was then used as the main substrate in the CWs. The configuration of the CWs is as follows:
102 10cm of 10mm gravel at the bottom to serve as base support, 65cm of the dewatered alum
103 sludge cakes to serve as the main substrate layer and 10cm of 20mm gravel to serve as the
104 distribution layer. Each cell of the CWs was planted with common reeds, *phragmites*
105 *australis*. The CWs was fed with wastewater collected from the secondary holding tank on
106 the farm. However, in order to allow the system and the reeds time to establish, the
107 wastewater from the farm was sometimes diluted with tap water to lower the concentration.

108 The four-stage CWs was operated in series. Influent and final effluent samples were
109 collected from the CWs weekly and analysed for COD (both total and soluble COD,

110 (sCOD)), BOD₅ (Lovibond OxiDirect apparatus, Lennox, UK), TP (Ascorbic method,
111 Clesceri et al.^[17]), PO₄-P, TN (Persulfate method, Clesceri et al.^[17]), NH₄-N, NO₃-N, NO₂-N,
112 SS and Turbidity (Hach turbidity meter 2100N IS). Except where indicated, all the water
113 quality parameters were analysed using a Hach DR/2400 spectrophotometer according to its
114 standard operating procedures. Furthermore, real time measurements of oxidation-reduction
115 potential (ORP), temperature and pH were obtained from a YSI multi-parameter probe
116 inserted in the influent tank and in each stage of the CWs

117

118 **Correlation and regression analysis**

119 Prior to the multiple regression analysis, correlation analysis was conducted between the
120 water quality parameters to investigate any relationships present. This was done to give a
121 greater understanding of suitable parameters to be used in the MRA. MRA was then
122 performed to test the relationship between each of BOD₅, COD, TP, NH₄-N and NO₃-N and
123 other parameters. These parameters were selected based on their relative importance in
124 assessing water quality and the possibility of being able to predict their concentration in the
125 final effluent from data obtained in real time, or from other parameters that are cheaper,
126 easier and/or quicker to analyse. The MRA analysis was performed for each of the dependant
127 variables using a combination of one to five predictor variables. The aim was to determine
128 the optimum model for each combination of input variables by estimating BOD₅, COD, TP,
129 NH₄-N and NO₃-N with as few inputs variables as possible in order to reduce associated
130 errors and costs. A 95% confidence interval was specified for the regressions. The models
131 were tested by examining the adjusted R², the significant F value, the p values and the mean
132 absolute scaled error (MASE), as shown in Eq. (1) & (2).

133

$$q_t = \frac{e_t}{\frac{1}{n-1} \sum_{i=2}^n [Y_i - Y_{i-1}]} \quad (1)$$

134 where q_t is the scaled error of sample point t , e_t is the residual of sample point t , n is the
135 sample size and Y_i is the observed value at step i .

$$136 \quad MASE = \text{mean}(|q_t|) \quad (2)$$

137 **Fitting k - C^* model to experimental data**

138 Further to the MRA, the k - C^* model, as shown in Eq. (3) ^[10], was fitted to the
139 experimental data. First-order area-based removal rate constants (k), assuming removal to
140 non-zero background concentrations (C^*), were estimated for BOD₅, COD, TP, NH₄-N, NO₃-
141 N, TN and SS.

$$142 \quad -\frac{ky}{q} = \ln \frac{C_o - C^*}{C_i - C^*} \quad (3)$$

143 where k is the first order area-based removal rate constant (m/yr), C_o is the outlet
144 concentration (mg/l), C_i is the inlet concentration (mg/l), C^* is the irreducible background
145 concentration (mg/l), q is the hydraulic loading rate (m³/m².day), and y is the fractional
146 distance from inlet to outlet. The equation was rearranged for the fitting procedure, Eq. (4).

$$147 \quad C_o = C^* + (C_i - C^*) \exp^{-ky/q} \quad (4)$$

148 The values of the irreducible background concentrations, C^* , were adopted from the lowest
149 effluent concentration observed for each pollutant in the CWs similar to the approach used by
150 Trang et al.^[18] It is noted that very little information exists on suitable values for C^* and the
151 values adopted in this study (shown later on in Table 5) are intermediate. In the literature, a
152 range of $1.7 \leq C^* \leq 18.2$ mg/l BOD₅ with a mean of 9.9 was reported by Stein et al. ^[9] and
153 Kadlec and Knight^[10], respectively, while Shepherd et al.^[19] reported a range of $23 \leq C^* \leq 450$
154 mg/l COD in a CWs treating winery wastewater.

155

156

157 **RESULTS**

158 **Performance evaluation**

159 The composition of the wastewater varied over time and the range of pollutant
160 concentration in the influent wastewater to the CWs were BOD₅ (31-968 mg/l), COD (124-
161 1634 mg/l), PO₄-P (2.8-60 mg-P/l), TN (16-273 mg-N/l) and SS (25-633 mg/l). It is noted
162 that the characteristics of the source wastewater varied greatly over time in concert with
163 seasonal changes and farming operations. The mean monthly removal efficiencies achieved
164 in the CWs was determined to range from 56.6%-83.5%, 35.6%-84.2%, 11.2%-77.5%,
165 48.5%-92.5%, 75.4%-93.8%, 73.0%-96.5% and 46.3%-83.3% for BOD₅, COD, TN, NH₄-N,
166 TP, P and SS respectively. In most cases, the removal efficiencies were generally lowest at
167 the start-up of the CWs. However, removal efficiencies for TP and PO₄-P were high from the
168 beginning in this study. Table 1 shows the loading and removal rates obtained from the CWs
169 during the monitoring period. It is particularly noted that the CWs was able to efficiently
170 remove PO₄-P both at low loading rates of 2.8 g-P/m².d when 2.6 g-P/m².d (93%) was
171 removed, and high loading rates of 9.5 g-P/m².d when 9.2 g-P/m².d (97%) was removed. The
172 system also performed well at removing BOD₅ both at low loading rates of 12 g-BOD₅/m².d
173 when 7.5 g-BOD₅/m².d was removed and at high loading rates of 201 g-BOD₅/m².d when
174 149.8 g-BOD₅/m².d was removed. However, the removal of COD seemed to be more suited
175 to higher loading rates. This may suggest that at lower COD loadings, internal release within
176 the CWs has a more profound effect on COD removal. For instance, at a loading rate of 376.3
177 g-COD/m².d, 253.8 g-COD/m².d (68%) was removed compared to 49.8 g-COD/m².d (49%)
178 removed at a lower loading rate of 102 g-COD/m².d. A possible reason could be that the
179 loading rate is not high enough to treat. A similar observation was made in the case of a CWs
180 treating piggery wastewater effluent where it was found that the concentration of residual-P
181 increased along the path of the CWs.^[20] However, the exact causes of this observed
182 phenomenon are still unclear. The same trend was observed for the removal of sCOD where

183 at higher loading rates of 304.1 g-sCOD/m².d, 234.8 g-sCOD/m².d was removed compared to
184 14.1 g-sCOD/m².d removed at a lower loading rates of 57 g-sCOD/m².d. The removal of TN
185 fluctuated greatly but it appeared to perform better as the CWs became more established. The
186 system was able to efficiently remove NH₄-N both at low loading rates of 11 g-NH₄-N/m².d
187 when 7.1 g-NH₄-N/m².d was removed, and high loading rates of 51.1 g-NH₄-N/m².d when 47
188 g-NH₄-N/m².d was removed.

189

190

[INSERT TABLE 1 HERE]

191

192 **Correlation analysis**

193 The results of the correlation analysis are presented in Table 2. It shows that the effluent
194 concentrations of BOD₅ are strongly related to the influent concentrations of BOD₅ with a
195 correlation coefficient, R, of 0.794. This suggests that although the CWs was efficient in
196 BOD₅ removal, the influent BOD₅ loading impacts on the final effluent BOD₅ concentration
197 that is obtained. The influent concentrations of COD and sCOD also correlate well with the
198 effluent concentrations of BOD₅ with R values of 0.715 and 0.634, respectively. The effluent
199 concentrations of COD are closely related to both the influent sCOD and SS with R values of
200 0.636 and 0.667, respectively. This also shows that both the influent concentrations of sCOD
201 and SS impacts on the final effluent concentration of COD that is obtained. The concentration
202 of TP in the effluent correlates very well with other water quality parameters such as influent
203 concentrations of BOD₅, COD and sCOD which produced R values of 0.795, 0.802 and
204 0.791, respectively. The effluent concentrations of NH₄-N did not correlate well with other
205 water quality parameters, but did exhibit negative correlation with both influent temperature
206 and pH with R values of -0.624 and -0.561, respectively. It is known that both pH and
207 temperature affect NH₄-N removal processes, and this is also the case in CWs.^[21]

208 The correlation between influent BOD₅ and effluent PO₄-P and effluent BOD₅ and
209 influent PO₄-P is 0.420 and 0.594 respectively, while the correlation between influent COD

210 and effluent TP and effluent COD and influent TP is 0.802 and 0.511 respectively. Except for
211 the correlation between influent COD and effluent TP, all the correlations are of medium
212 strength. Although in the system, different processes account for the removal of organics
213 (BOD₅ and COD- through microbial degradation) and P and TP (mainly through adsorption
214 but not exclusively), the significance of the correlations found is that it can indirectly indicate
215 the loading on the system. For instance, the strength of the wastewater used was characterized
216 from its BOD₅ values based on which appropriate dilution was carried out to generate the
217 influent into the system. Consequently, a medium correlation between influent BOD₅ and
218 effluent PO₄-P would suggest that at high influent BOD₅ values (which would imply
219 comparatively higher organic loading rate on the system since the hydraulic loading rate is
220 fairly constant), a high value of effluent PO₄-P value can be expected as the system is
221 considerably loaded. Similar explanation can be given for the correlation between COD and
222 TP.

223 Nitrification, which is usually defined as the biological oxidation of ammonium-nitrogen
224 to nitrate-nitrogen with nitrite-nitrogen as an intermediate in the reaction sequence, is
225 favoured at high values of both temperature and pH and this could explain the negative
226 relationship observed. Effluent concentrations of NO₃-N displayed strong correlations with
227 TN and NH₄-N concentrations in the influent with R values of 0.621 and 0.632, respectively.
228 The effluent PO₄-P concentrations did not show any strong associations with any other
229 parameters. In the CWs under study, P is primarily removed by adsorption onto the alum
230 sludge substrate through the ligand exchange mechanism and this has been shown in our
231 previous study.^[22]

232
233 **[INSERT TABLE 2 HERE]**
234
235
236
237

238 **MRA for predicting final effluent concentration of selected pollutants**

239 The results of the optimization of input variables for predicting final effluent
240 concentrations for the selected pollutants are presented in Table 3 while regression models
241 adjudged to be the best in predicting the final effluent concentrations for the selected
242 pollutants are presented in Table 4. The results are presented below as they relate to each
243 specific pollutant.

244

245 ***BOD₅***

246 From the regression analysis (see Table 3), it was found that the combination of predictor
247 variables that returned the best adjusted R^2 of 0.86 and the lowest MASE of 0.783 was that of
248 influent BOD_5 , NH_4-N , PO_4-P and COD. From the significant F value of 3.1×10^{-8} it can be
249 seen that the null hypothesis can be rejected as the value is less than the 0.05 confidence
250 interval set during regression. All the p values for the predictor variables are also below the
251 threshold value of 0.05. The model is shown in Table 4. Except for the model constructed
252 using an input combination of three independent variables (i.e. influent concentration of
253 BOD_5 , NH_4-N and PO_4-P) which gave an adjusted R^2 value of 0.837 and a MASE value of
254 0.994, all the other models had MASE values above 1 even though their adjusted R^2 values
255 ranged from 0.760-0.857. It is worth noting that the model constructed for predicting final
256 effluent BOD_5 effluent concentrations using just one predictor variable, which was the BOD_5
257 of the influent, gave the least adjusted R^2 of 0.76 and the worst MASE value of 1.628. This
258 suggests that although there may be reasonable correlation between the influent and effluent
259 BOD_5 concentrations, the latter cannot be solely used to predict the former and they may be
260 sources of organic matter release within the CWs.

261

262 ***COD***

263 The most efficient model developed for predicting final effluent concentrations of COD
264 consists of four input variables (see Table 3). The model gave an adjusted R^2 value of 0.711.
265 This model also has a significant statistical relationship as the F test provides a significant F
266 value of 1.5×10^{-08} which rejects the null hypothesis. The p values for the model shown in
267 Table 3 can be seen to be satisfactory. However, although the MASE value for the model is
268 1.825 which is greater than 1, it was the lowest compared to the MASE values obtained for
269 the other models. The model is presented in Table 4.

270

271 *TP*

272 The most efficient model for predicting influent TP concentrations consisted of two input
273 variables as shown in Table 3. Of all the models constructed for predicting the final effluent
274 concentration of TP, it gave the highest adjusted R^2 value of 0.801 and the lowest MASE
275 value of 1.620. The model is presented in Table 4.

276

277 **[INSERT TABLE 3 HERE]**

278 **[INSERT TABLE 4 HERE]**

279 *NH₄-N*

280 The model developed using a combination of three input variables was adjudged to be the
281 best in predicting final effluent concentrations of NH_4-N (see Table 3). The model gave an
282 adjusted R^2 value of 0.696 and had the lowest MASE of 1.111 compared to the other models.
283 The significant F value for the model was found to be 5.4×10^{-6} , which is lower than the
284 threshold value of 0.05. Both the predictor variables of influent temperature and SS recorded
285 p values that were low enough to be considered significant. The model is presented in Table
286 4.

287

288 *NO₃-N*

289 The models developed for the prediction of final effluent concentrations of NO₃-N were
290 not as strong as models developed using other parameters as dependant variables such as
291 BOD₅ as can be seen from the adjusted R² values in Table 3. Although the models gave
292 adjusted R² values ranging from 0.613-0.669, the MASE values were quite high. The best
293 adjudged model based on the adjusted R² and MASE value is presented in Table 4.

294

295 ***k*-C* model**

296 Using Eq. 3, the *k* values (in m/yr) for each pollutant were calculated to be 200.5, 271.8,
297 80.1, 173.8, 618.5, 271.4 and 223.2 for BOD₅, COD, TP, NH₄-N, NO₃-N, TN and SS
298 respectively (see Table 5). The data was then fitted to Eq. 4, which yielded estimates with R²
299 values of 0.574, 0.350, 0.368, 0.005, 1.6x10⁻⁴, 0.390 and 0.682 for BOD₅, COD, TP, NH₄-N,
300 NO₃-N, TN and SS respectively. The MASE values for these models can also be seen in
301 Table 5. The results show that the *k*-C* model fitted well for predicting final effluent
302 concentration of BOD₅, COD, TN TP and SS but performed poorly for NH₄-N and NO₃-N.

303

304 **[INSERT TABLE 5 HERE]**

305 Table 4 – First-order area-based removal rate constants

306
307

308 **Residual analysis**

309 Fig. 1(a & b) shows the residual analysis from predicting final effluent BOD₅
310 concentrations using the MRA and the *k*-C* model, respectively. For Fig. 1(a), it can be seen
311 that the data points are randomly dispersed about zero for all concentrations, therefore, no
312 pattern is discernable and so the model is reliable. However, in the case of Fig. 1(b), there is a
313 definite positive skew observed and so the model assumptions are not correct. It can therefore
314 be said that the model for predicting the final effluent BOD₅ concentrations using MRA is
315 more reliable than that of the *k*-C* model. Fig. 1(c & d) shows the residual analysis for
316 estimating final effluent COD concentrations using the MRA and *k*-C* model, respectively.

317 From Fig. 1(c), it can be seen that the MRA model has uniform dispersion about the line
318 $R=0$. This indicates that the model is acceptable.

319 However, similar to the performance of the $k-C^*$ model in predicting final effluent BOD_5
320 concentrations, the performance of $k-C^*$ model in predicting final effluent COD
321 concentrations displayed a definite positive skew as can be seen in Fig. 1(d). This arises when
322 the model assumptions are not met, indicating that the model is not as suitable for predicting
323 the final effluent concentrations of COD as the MRA model. The residual analysis for the
324 prediction of final effluent TP concentrations using the MRA and the $k-C^*$ model is
325 presented, respectively, in Fig. 1(e & f). Fig. 1(e) shows that the MRA model again displays a
326 random scattering of points above and below the line $R=0$ signifying that the model is
327 adequate for predicting final effluent TP concentrations. However, the residual plot for $k-C^*$
328 model (Fig. 1(f)) displays a negative skew, again indicating that it is not as appropriate as the
329 MRA model. Fig. 1(g) shows the residual analysis for the prediction of final effluent NH_4-N
330 concentrations using MRA. This plot shows a random scattering of residuals about the line
331 $R=0$ and so indicates that model is adequate in predicting the final effluent NH_4-N
332 concentrations. However, for the kinetic model (Fig. 1(h)), it shows a definite positive to
333 negative skew.

334 **[INSERT FIG 1 HERE]**
335

336 This pattern indicates that the model is not as accurate in predicting final effluent NH_4-N
337 concentrations as the MRA model. In the case of NO_3-N , the residual plots for the MRA and
338 $k-C^*$ models as shown in Fig. 1 (i & j) respectively, indicate that both models cannot be
339 considered accurate enough to predict final effluent concentrations of NO_3-N . However, the
340 reason why both models failed in predicting NO_3-N is still unclear. The MRA model shows a
341 definite pattern in that as the predicted value increases, the residuals increase in magnitude in
342 both the positive and negative directions, creating the cone shape. On the other hand, the $k-$

343 C* model displays an obvious positive skew which is unacceptable as it implies that the
344 model assumptions are false.

345

346 **DISCUSSION**

347

348 Generally, the performance of the CWs in removing key pollutants in the wastewater can
349 be considered as excellent. In all cases, the treatment efficiency obtained was comparable to,
350 or higher than, the performances obtained in conventional and other CWs. The system under
351 trial was able to efficiently remove PO₄-P at both high and low loading rates. The removals
352 of SS, BOD₅ and COD were also generally efficient with a trend of gradual improvement in
353 removal rates as the system matures. This would indicate that the system was emerging from
354 the start-up stage and that the biomass was maturing. However, the reason that the system is
355 so efficient in P removal is due to the abundance of aluminium ions in the dewatered alum
356 sludge which enhances P adsorption from the wastewater through the ligand exchange
357 mechanism.^[22] In relative terms, these removal efficiencies can be considered as excellent
358 and showing good promise. Vymazal^[21] reported that average removal efficiencies in vertical
359 subsurface flow CWs were 44.6% for TN and 59.5% for TP. Therefore, it can be seen that the
360 respective performance efficiencies obtained in this study are considerably higher than the
361 reported averages and this indicates the potential of the CWs described in this study for
362 providing enhanced wastewater treatment by CWs. Furthermore, an interesting feature of the
363 performance worth noting is the ability of the CWs to achieve, concurrently, high-rate
364 removal of organics (BOD₅, COD) and nutrients (emphasis on P). It is well known that it is
365 often a challenge to achieve concurrent high removal efficiencies for P and organic matter in
366 CWs. CWs are usually efficient in organics (BOD₅, COD) reduction, but the corresponding
367 removal efficiencies for nitrogen (N) and P are often low.^[2] The four-stage pilot field-scale

368 CWs described in this study has demonstrated that by using alum sludge as substrate, high P
369 removal efficiency can be achieved alongside high removal efficiency for organics.

370 The statistical models developed for predicting final effluent concentrations of selected
371 key water quality parameters using MRA were found to be promising. The MRA model for
372 predicting final effluent BOD₅ concentrations was exceptionally good and this is reiterated by
373 the p values of each predictor variable and their asterisks as can be seen in Table 4 coupled
374 with the fact that the MASE < 1. This indicates that the model is quite good for predicting the
375 final effluent BOD₅ concentrations and also, the predictions are reliable. However, in the case
376 of COD, although the best MRA model for predicting final effluent COD concentrations gave
377 an adjusted R² of 0.711, the MASE >1 and this suggests that while the model is strong at
378 predicting final effluent COD concentrations, it may contain some errors. This is also the case
379 for the MRA model for predicting final effluent TP concentration which gave an adjusted R²
380 of 0.801, indicating that over 80% of all possible outcomes are covered by the model.
381 However, the MASE >1 also indicates that the prediction may contain some errors. Similar
382 performance was also observed in the MRA model for predicting final effluent concentration
383 of NH₄-N in the CWs. An adjusted R² of 0.696 was obtained but the MASE >1 (1.111) which
384 indicates that the model is strong at predicting the final effluent concentration, but it may
385 contain some errors. In the case of NO₃-N, the model seems unreliable with a MASE of 5.419

386 The values of the first order area-based removal rate constant, *k* (in m/yr), obtained in the
387 study are high and they compare very well with the range of values found in the scientific
388 literature. In vertical flow CWs treating high-strength synthetic wastewater in Thailand,
389 Kantawanichkul et al.^[23] found *k* values of 49.8, 30.1 and 13.5 m/yr for COD, TKN and TP,
390 respectively. Other *k* values (in m/yr) reported in literature range from 8–95 (BOD₅), 22–30
391 (COD), 3.6–24 (TN and TKN) and 4.9–84 (TP).^[3, 24, 25, 26] However, it is the opinion of the
392 authors that these values have limited use for comparison and caution is urged in drawing
393 firm conclusions from them. The estimated removal rate constants and apparent background

394 concentrations have been shown to depend strongly on input water quality as well as
395 hydraulic loading rates (HLR)^[4, 27] For instance, the k values reported by Kantawanichkul et
396 al.^[23] were obtained at an HLR of 80 mm/d which is two orders of magnitude lower than the
397 HLR used in this study. Also, Stein et al.^[9] stated that C^* is relatively more important than k
398 when using the $k-C^*$ model and it was suggested that the rate parameter k may be less
399 important than the residual concentration, particularly when predicting effluent organic
400 matter values. However, as previously noted, very little information exists in literature
401 regarding suitable values for C^* particularly for different types of wastewater. Nonetheless,
402 the k values obtained in this study imply the high rate of pollutant removal in the CWs.
403 However, the k value obtained for nitrate-nitrogen is quite high and cannot be relied upon.
404 Similar observation has been made by Kadlec and Wallace.^[1]

405 From Table 5, it can be seen that the $k-C^*$ model was best fitted to BOD₅ and SS removal
406 in the CWs with R^2 values of 0.574 and 0.682 and MASE values of 0.644 and 0.680
407 respectively, indicating that the values obtained are quite reliable. The MASE values for
408 COD and TN were also <1. Overall, the MRA models were found to be more apt in
409 predicting the final effluent concentrations of pollutants in CWs than the $k-C^*$ model. It
410 should however be noted that the CWs in this study applied alum sludge as substrate, which
411 could give different treatment characteristics when compared to other CWs particularly in
412 terms of P removal. Therefore caution is urged in generalising the results.

413

414

415 **CONCLUSIONS**

416 1. Statistical models developed from multiple regression analyses were found to be
417 strong in predicting final effluent concentrations for the constructed wetland system in
418 this study. In particular, the selected model for predicting final effluent concentration

419 of BOD₅ gave an adjusted R² value of 0.860 between predicted and observed data and
420 a mean absolute scaled error <1 (0.783).

421 2. The k -C* model was also fitted to the experimental data and the first order area-based
422 removal rate constant, k (m/yr), for BOD₅, COD, TP, TN and SS was calculated to be
423 200.5, 271.8, 80.1, 271.4 and 223.2 respectively.

424 3. Comparison of the regression and k -C* models shows that the regression models were
425 much stronger in predicting final effluent concentrations in the constructed wetland
426 system.

427

428 **Acknowledgements**

429

430 Authors gratefully acknowledge financial support received for this field study from: (1)
431 Enterprise Ireland under the *Proof of Concept Scheme* (project No. PC/2007/0308); (2) the
432 Irish state Department of Agriculture, Fisheries and Food under the Research Stimulus Fund
433 (project No. RSF 07-528). The UCD farms, Lyons Estate, Newcastle, Co. Dublin, Dr Edward
434 Jordan and Mr Michael Hegarthy are all sincerely thanked for their support for the field work.

435

436

437 **REFERENCES**

438

439 [1] Kadlec, R.H.; Wallace, S. *Treatment Wetlands*, 2nd edition. CRC Press, Raton, FL, 2009

440 [2] Park, W.H. Integrated constructed wetland systems employing alum sludge and oyster
441 shells as filter media for P removal. *Ecol. Eng.* **2009**, *35*, 1275-1282.

442 [3] Knight, R.L.; Payne Jr. V.W.E.; Borer, R.E.; Clarke Jr, R.A.; Pries, J.H. Constructed
443 wetlands for livestock wastewater management. *Ecol. Eng.* **2000**, *15*, 41-55

444 [4] Kadlec, R.H. The inadequacy of first-order treatment wetland models. *Ecol. Eng.* **2000**,
445 *15*, 105–119.

446 [5] Kincanon, R.; McAnally, A.S. Enhancing commonly used model predictions for
447 constructed wetland performance: as-built design considerations. *Ecol. Model.* **2004**,
448 *174*, 309-322

- 449 [6] Jamieson, R.; Gordon, R.; Wheeler, N.; Smith, E.; Stratton, G.; Madani, A. Determination
450 of first order rate constants for wetlands treating livestock wastewater in cold climates.
451 Environ. Eng. Sci. **2007**, 6, 65-72
- 452 [7] Son, Y.K.; Yoon, C.G.; Kim, H.C.; Jang, J.H.; Lee, S.B. Determination of regression
453 model parameter for constructed wetland using operating data. Paddy Water Environ.
454 **2010**, DOI 10.1007/s10333-010-0211-9
- 455 [8] Rousseau, D.; Vanrolleghem, P.; De Pauw, N. Model-based design of horizontal
456 subsurface flow constructed treatment wetlands: a review. Water Res. **2004**, 38, 1484-
457 1493
- 458 [9] Stein, O.R.; Biederman, J.A.; Hook, P.B.; Allen, W.C. Plant species and temperature
459 effects on the $k-C^*$ first order model for COD removal in batch-loaded SSF wetlands.
460 Ecol. Eng. **2006**, 26, 100-112
- 461 [10] Kadlec, R.H.; Knight, R.L. Treatment Wetlands. Lewis Publishers, CRC Press Inc.,
462 Boca Raton, FL, 1996
- 463 [11] Tomenko, V.; Sirajuddin, A.; Viktor, P. Modelling constructed wetland treatment system
464 performance. Ecol. Model. **2007**, 205, 355-364.
- 465 [12] Murray-Gulde, C.L.; Bridges, W.C.; Rodgers, J.H. Evaluating performance of a
466 constructed wetland treatment system designed to decrease bioavailable copper in a
467 waste stream. Environ. Geosci. **2008**, 15, 21-38
- 468 [13] Tang, X.; Eke, P.E.; Scholz, M.; Huang, S. Processes impacting on benzene removal in
469 vertical-flow constructed wetlands. Bioresour. Technol. **2009**, 100, 227-234
- 470 [14] Babatunde, A.O.; Zhao, Y.Q.; Burke, A.M.; Morris, M.A.; Hanrahan, J.P.
471 Characterization of aluminium-based water treatment residual for potential phosphorus
472 removal in engineered wetlands. Environ. Pollut. **2009**, 157, 2830-2836

- 473 [15] Babatunde, A.O.; Zhao, Y.Q.; Zhao, X-H. Alum sludge-based constructed wetland
474 system for enhanced removal of P and OM from wastewater: Concept, design and
475 performance analysis. *Bioresour. Technol.* **2010**, 101, 6576-6579
- 476 [16] Zhao, Y.Q.; Babatunde, A.O.; Hu, Y.S.; Kumar, J.L.G.; Zhao, X-H. A two-prong
477 approach of beneficial reuse of alum sludge in engineered wetland: First experience from
478 Ireland. *Waste and Biomass Valorization*, **2010**, 1, 227-234
- 479 [17] Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D. *Standard Methods for the Examination of*
480 *Water and Wastewater*, 20th Ed., American Public Works Association, Washington, DC,
481 1998
- 482 [18] Trang, N.D.T.; Konnerup, D.; Schierup, H-H.; Chiem, N.H.; Tuan, L.A.; Brix, A.
483 Kinetics of pollutant removal from domestic wastewater in a tropical horizontal
484 subsurface flow constructed wetland system: Effects of hydraulic loading rate. *Ecol.*
485 *Eng.* **2010**, 36, 527-535
- 486 [19] Shepherd, H.L.; Tchobanoglous, G.; Grisner, M.E. Time-dependent retardation model
487 for chemical oxygen demand removal in a subsurface-flow constructed wetland for
488 winery wastewater treatment. *Water Environ. Res.* **2001**, 73, 597-606
- 489 [20] Lee, S.; Maniquiz, M. C.; Kim, L-H. Characteristics of contaminants in water and
490 sediment of a constructed wetland treating piggery wastewater effluent. *J. Environ. Sci.*
491 **2010**, 22, 940-945
- 492 [21] Vymazal, J. Removal of nutrients in various types of constructed wetlands. *Sci. Total*
493 *Environ.* **2007**, 380, 48-65
- 494 [22] Yang, Y.; Zhao, Y.Q.; Babatunde, A.Q.; Wang, L.; Ren, Y.X.; Han, Y. Characteristics
495 and mechanisms of phosphate adsorption on dewatered alum sludge. *Separ. Purif.*
496 *Technol.* **2006**, 51, 193-200

- 497 [23] Kantawanichkul, S.; Kladprasert, S.; Brix, H. Treatment of high-strength wastewater in
498 tropical vertical flow constructed wetlands planted with *Typha angustifolia* and *Cyperus*
499 *involucratus*. *Ecol. Eng.* **2009**, 35, 238–247.
- 500 [24] Noorvee, A. ; Repp, K.; Põldvere, E., . Mander, Ü. The effects of aeration and the
501 application of the $k-C^*$ model in a subsurface flow constructed wetland. *J. Environ. Sci.*
502 *Health Pt. A.* **2005**, 40, 1445–1456.
- 503 [25] Öövel, M.; Tooming, A.; Muring, T.; Mander, Ü. Schoolhouse wastewater purification
504 in a LWA-filled hybrid constructed wetland in Estonia. *Ecol. Eng.* **2007**, 29, 17-26
- 505 [26] Konnerup, D.; Koottatep, T.; Brix, H. Treatment of domestic wastewater in tropical,
506 subsurface flow constructed wetlands planted with *Canna* and *Heliconia*. *Ecol. Eng.*
507 **2009**, 35, 248–257
- 508 [27] Kadlec, R.H. Effects of pollutant speciation in treatment wetlands design. *Ecol. Eng.*
509 **2003**, 20 1–16.

510

511

512

513

514

515

516

517

518

519

520

521

522

523 **FIGURE CAPTIONS**

524

525 **Figure 1.** Residual analysis from estimation of final effluent concentrations for selected
526 water quality parameters using statistical and the $k-C^*$ models

527

528

529

530

531

532

533

534

535

536

537

538

539

540

541

542

543

544

545

546

547

548

Table 1. Performance summary of the constructed wetland system from Feb.-Dec. 2009

Parameter	g/m ² .d	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
BOD ₅	loading	nd	12.0	13.1	31.9	89.2	69.5	89.1	68.8	119.1	201.4	119.3
	removal	nd	7.5	7.1	21.8	70.6	48.2	64.9	37.9	87.6	149.8	89.0
COD	loading	nd	207.6	140.1	102.0	141.1	109.8	189.3	200.4	285.0	376.3	202.3
	removal	nd	53.7	58.0	49.8	93.0	67.9	151.1	139.3	168.2	253.8	147.3
sCOD	loading	nd	166.8	67.3	57.0	82.9	65.7	109.4	119.9	183.1	304.1	108.6
	removal	nd	36.5	15.3	14.1	46.7	35.9	83.2	78.0	129.9	234.8	82.7
SS	loading	92.1	72.3	41.7	33.6	29.3	29.8	42.1	49.6	66.7	100.5	78.3
	removal	55.2	37.4	23.7	24.3	22.9	21.4	33.9	40.0	44.0	58.9	38.7
TP	loading	nd	4.8	3.1	nd	nd	nd	nd	nd	9.6	8.6	6.4
	removal	3.8	4.2	3.0	2.5	nd	2.6	4.7	6.8	8.9	7.2	4.9
PO ₄ -P	loading	7.4	3.9	2.8	5.2	4.5	3.8	6.9	7.8	9.5	7.9	5.3
	removal	6.1	3.5	2.6	4.8	4.3	3.5	6.5	7.5	9.2	6.9	3.8
TN	loading	24.4	nd	25.4	nd	27.7	24.7	58.3	60.9	63.1	38.2	31.4
	removal	2.9	0.9	11.6	4.4	17.4	15.1	38.3	22.8	24.5	27.9	17.0
NH ₄ -N	loading	23.7	21.0	11.0	13.4	18.6	17.6	37.2	47.1	51.1	31.6	26.5
	removal	16.5	7.5	7.1	11.7	16.6	15.4	33.6	43.5	47.0	24.8	12.9

nd not determined

Table 2. Correlation matrix of influent and effluent concentrations for the water quality variables

		R value											
		Influent											
		BOD ₅	COD	sCOD	PO ₄ -P	TP	NH ₄ -N	TN	SS	NO ₃ -N	Temp	pH	ORP
Effluent	BOD ₅	0.794	0.715	0.634	0.594	0.556	0.452	0.369	0.534	0.156	-0.114	-0.254	-0.369
	COD	0.341	0.581	0.636	0.373	0.511	0.159	0.041	0.667	-0.183	-0.591	-0.541	0.279
	sCOD	-0.071	0.266	0.510	0.115	0.229	-0.084	-0.181	0.471	-0.098	-0.552	-0.442	0.236
	PO ₄ -P	0.420	0.365	0.422	0.296	0.114	0.040	-0.045	0.268	0.104	-0.250	-0.379	-0.039
	TP	0.795	0.802	0.791	0.492	0.556	0.277	0.182	0.650	-0.186	-0.399	-0.469	0.031
	NH ₄ -N	0.104	0.259	0.303	0.039	0.033	0.188	-0.118	0.430	-0.001	-0.624	-0.561	0.354
	TN	-0.206	0.029	-0.081	0.169	0.084	0.558	0.588	-0.031	0.079	-0.011	-0.122	0.432
	SS	0.499	0.729	0.716	0.538	0.666	0.284	0.032	0.855	-0.208	-0.624	-0.583	0.194
	NO ₃ -N	0.012	0.183	0.023	0.214	0.141	0.632	0.621	0.020	0.010	0.076	-0.046	0.102

Table 3. Optimal input variables combination for predicting final effluent concentrations

	Input Variables	Adj R ²	Sig F	P Values					MASE
BOD ₅	1	0.760	2.1x10 ⁻¹⁰	2.2x10 ⁻¹⁰					1.628
	1+2	0.857	7.6x10 ⁻¹¹	8.9x10 ⁻¹⁰	0.004				1.09
	1+2+3	0.837	1.9x10 ⁻⁰⁹	3.8x10 ⁻⁰⁸	0.003	0.209			0.994
	1+2+3+4	0.860	3.1x10 ⁻⁰⁸	0.001	0.013	0.039	0.046		<u>0.783</u>
	1+2+3+4+5	0.849	1.9x10 ⁻⁰⁹	0.006	0.021	0.053	0.149	0.993	1.352
COD	6	0.574	7.5x10 ⁻¹¹	7.5x10 ⁻¹¹					5.043
	5+8	0.707	2.4x10 ⁻⁰⁸	0.002	0.001				2.172
	1+7+8	0.679	6.6x10 ⁻⁰⁸	2.9x10 ⁻⁰⁶	8.9x10 ⁻⁰⁷	0.223			1.934
	1+7+9+11	0.711	1.5x10 ⁻⁰⁸	2.6x10 ⁻⁰⁵	3.7x10 ⁻⁰⁹	4.7x10 ⁻⁰⁴	0.168		<u>1.825</u>
	1+6+7+9+11	0.702	1.3x10 ⁻⁰⁷	2.9x10 ⁻⁰⁴	0.210	3x10 ⁻⁰⁵	0.600	0.297	1.899
TP	7	0.615	3.5x10 ⁻⁰⁹	3.5x10 ⁻⁰⁹					3.350
	6+7	0.801	6.4x10 ⁻¹⁰	0.107	1.7x10 ⁻¹⁰				<u>1.620</u>
	1+7+9	0.718	1.2x10 ⁻⁰⁷	0.069	0.052	0.102			2.545
	1+4+6+7	0.668	2.2x10 ⁻⁰⁵	0.491	0.205	0.104	0.845		2.436
	1+4+6+7+8	0.682	3.6x10 ⁻⁰⁵	0.917	0.147	0.096	0.338	0.181	2.310
NH ₄ -N	6	0.604	3.9x10 ⁻⁰⁸	3.9x10 ⁻⁰⁸					3.038
	6+7	0.649	1.5x10 ⁻⁰⁹	7.0x10 ⁻⁰⁹	0.136				3.308
	6+7+8	0.696	5.4x10 ⁻⁶	0.001	0.512	0.006			<u>1.111</u>
	6+7+8+9	0.739	1.4x10 ⁻⁰⁵	0.057	0.202	0.005	0.805		1.331
	6+7+8+9+4	0.682	4.9x10 ⁻⁰⁴	0.078	0.704	0.028	0.760	0.965	1.446
NO ₃ -N	2	0.613	2.9x10 ⁻¹¹	2.9x10 ⁻¹¹					8.625
	2+10	0.650	3.2x10 ⁻⁰⁸	6.4x10 ⁻⁰⁴	0.053				5.861
	2+3+10	0.670	6.5x10 ⁻⁰⁷	0.002	0.222	0.045			<u>5.419</u>
	2+3+6+10	0.652	1.7x10 ⁻⁰⁶	0.001	0.759	0.241	0.053		6.550
	2+3+6+10+11	0.669	8.6x10 ⁻⁰⁵	0.011	0.593	0.221	0.312	0.372	8.950

1-BOD₅ inf; 2-NH₄-N inf; 3-PO₄-P inf; 4-COD inf; 5-TP eff; 6-Temp inf; 7-sCOD inf; 8-SS inf; 9-pH inf; 10-TN inf; 11-TP inf. Underline indicates best mean absolute scaled error (MASE). inf = influent; eff = effluent

Table 4. Optimum models for predicting final effluent concentrations from multiple regression analysis

BOD ₅	$0.153(\text{BOD}_5 \text{ Inf})^{***} + 0.252(\text{NH}_4\text{-N Inf})^* - 1.872(\text{PO}_4\text{-P Inf})^* + 0.058(\text{COD Inf})^*$	+ 2.940
COD	$-0.326(\text{BOD}_5 \text{ Inf})^{***} + 0.529(\text{sCOD Inf})^{***} - 119.198(\text{pH Inf})^{***} + 0.842(\text{TP Inf})$	+ 1019.043
TP	$-0.078(\text{TEMP Inf}) + 0.005(\text{sCOD Inf})^{***}$	+ 0.147
NH ₄ -N	$-1.866(\text{TEMP Inf})^{***} - 0.004(\text{sCOD Inf}) + 0.065(\text{SS Inf})^{**}$	+ 29.533
NO ₃ -N	$1.020(\text{NH}_4\text{-N Inf})^{**} + 0.980(\text{PO}_4\text{-P Inf}) - 0.513(\text{TN Inf})^*$	- 7.256

* = p≤0.05, ** = p≤0.01 and *** = p≤0.001

Table 5. First-order area-based removal rate constants (k), background concentration (C^*) and coefficients of determination (R^2) for BOD₅, COD, TP, NH₄-N, NO₃-N, TN and SS removal in the constructed wetland system based on the k - C^* model

Parameter	C^* (mg/L)	k (m/yr)	R^2	MASE
BOD ₅	15	200.504	0.574	0.644
COD	60	271.753	0.350	0.929
TP	0.3	80.134	0.368	6.216
NH ₄ -N	1.5	173.758	0.005	2.324
NO ₃ -N	0.5	618.504	1.6×10^{-4}	2.090
TN	10	271.440	0.390	0.693
SS	5	223.184	0.682	0.680

Figure 1

