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1 **Forms, patterns and extractability of phosphorus retained in**
2 **alum sludge used as substrate in laboratory-scale constructed**
3 **wetland systems**

4

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25 **Abstract**

26 This study examined the form, pattern and extractability of phosphorus (P) retained
27 in alum sludge (an aluminium-containing drinking water treatment residual in
28 dewatered cake form), which was used as substrate in laboratory scale constructed
29 wetland systems for P-rich wastewater treatment. Used alum sludge samples from
30 successive depth ranges in the laboratory scale vertical flow constructed wetland
31 systems were examined for KCl extractable P. The samples were also sequentially
32 fractionated into two main categories consisting of readily available P and P forms that
33 are not easily decomposed. The extracted fractions included labile P, microbial P, (Fe +
34 Al) P, humic P, (Ca + Mg) P and residual P. A major proportion of P retained in the
35 used alum sludge was in forms that are not easily decomposed. Of the P forms that are
36 not easily decomposed, the P associated with Ca and Mg accounted for a higher
37 proportion of the inorganic fraction as compared to the P associated with the Fe and Al.
38 The results also show that in most cases, the concentration of the P forms decreased
39 with increasing depth from the topmost surface of the alum sludge in the systems.

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43 **Key words:** alum sludge, constructed wetlands, labile phosphorus, phosphorus,
44 sequential fractionation, phosphorus extraction

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48 **1 Introduction**

49 The primary phosphorus (P) removal mechanisms in constructed wetland (CW)
50 systems are microbial anabolism, wetland plant uptake and substrate adsorption.
51 However, substrate P adsorption represents the main P removal pathway. Hence,
52 emphasis is being placed on the use of specialized P removal substrates with high P
53 removal capacity. Upon the saturation of such substrates with P, the investigation of the
54 form, pattern and extractability of P retained in them becomes very crucial. This will
55 help in determining the reuse potential of the saturated substrates, plant availability and
56 possible recovery of the adsorbed P. Several studies have examined the form of P-
57 association with elements contained in used CW substrates, but few have identified the
58 form and fate of the retained P. In two separate studies, Sakadevan and Bavor [1] and
59 Johansson [2] showed that large amount of P sorbed onto the surface of blast furnace
60 slag is predominantly associated with light elements, such as calcium, aluminium,
61 magnesium and silicon, with calcium hydroxide found to adsorb the largest amount of
62 P. In other studies, it was reported that P sorbed to blast furnace slag, which had been
63 previously used for wastewater treatment, was readily available for barley growth in a
64 pot experiment [3].

65 In other studies, the variation of P forms with depth was examined. Qualls and
66 Richardson [4] reported that the concentration of most forms of P decreased with
67 distance along the gradient. It was further reported that for most P forms, the trends are
68 weaker or absent at lower soil depths. The insoluble organic P, the humic P, and the
69 Ca-bound P which are all P forms that are not easily decomposed were reported to
70 show the highest decrease in concentration with distance. This observation is also
71 corroborated by the results of Reddy et al. [5] in which it was reported that the
72 concentration of most P forms were higher in the surface layers and decreased with

73 depth and with distance from the inflow structure. Such examination of P adsorbed in a
 74 CW substrate can also be used in evaluating the availability and potential recovery of P
 75 accumulated onto the CW substrate. The P examination is usually determined by
 76 sequential extraction with acid and alkaline reagents as modified for wetland soils by
 77 Qualls and Richardson [4] and Reddy et al. [5]. The P forms in various groups are
 78 usually identified and the form of P will influence its availability and recycling capacity.
 79 It should be noted that based on the sequential extraction, the term availability refers to
 80 both extractable and non-extractable P forms. The non-extractable P implies a form of
 81 P that is also available but in a form that cannot be extracted. Table 1 shows the
 82 different P forms including those that are grouped based on their availability for plant
 83 uptake. The classification is adopted from Qualls and Richardson [4]
 84

Table 1 Forms of extracted phosphorus

1. Forms readily cycled or available to plants (labile)	
Inorganic	Organic
➤ Exchangeable inorganic P (bicarbonate extractable)	➤ Microbial tissue P (chloroform-released P)
	➤ Bicarbonate extractable organic P
2. Forms not easily decomposed (refractory)	
Inorganic	Organic
➤ Calcium bound P (soluble in 1M HCl)	➤ Humic organic P (organic P bound to humic and fulvic acids extractable in 0.1M NaOH)
➤ Iron and aluminium bound inorganic P (0.1M NaOH-extractable inorganic P)	➤ Residual (insoluble P)
➤ Iron and aluminium bound inorganic P occluded in particle matrix (0.1M NaOH-extractable inorganic P after sonication)	

85 However, it is also important to note that different CW substrates may have
86 specific properties that may be related to the P dynamics. Hence, it is necessary to carry
87 out individual examination of P forms for different substrates. In this study, alum
88 sludge was used as substrate in laboratory scale constructed wetland systems. Alum
89 sludge, an aluminium-containing drinking water treatment residual in dewatered cake
90 form, has been revealed as a new potential CW substrate due to its high P adsorption
91 capacity [6], and physico-chemical characteristics which conform to the recommended
92 standards for CW substrates [7]. The alum sludge (in dewatered cake form) was used as
93 main substrate in laboratory scale CW systems and it was shown to significantly
94 enhance P removal [8]. The study of beneficially reusing alum sludge as raw material is
95 part of a larger project aimed at the eventual development of a novel alum sludge based
96 CW system for wastewater treatment. The project has been carried out for the past five
97 years at the University College Dublin (UCD), Ireland and it has entailed series of sub-
98 projects of different scales. The sub-projects have included: (a) extensive studies on
99 identifying the P adsorption ability of the dewatered alum sludge and the removal
100 efficiencies of other pollutants (COD, BOD₅) using alum sludge as main substrate in
101 the novel CW system [6,8,9]; (b) investigating the lifespan of the system [9]; (c)
102 examining the mechanism and characteristics of P adsorption onto the alum sludge [10]
103 and (d) examining the release of other materials/elements from the alum sludge. As
104 such, the current study is aimed at further gaining a holistic view of the development of
105 the novel alum sludge based constructed wetland system by examining the fate of the P
106 adsorbed by the alum sludge, alongside other sub-projects as highlighted above.

107 Examination of the fate of P adsorbed in the alum sludge is crucial in determining
108 the recycling potential of the alum sludge when it is saturated and also in evaluating the
109 potential for recovery of the adsorbed P. Therefore, the objectives of this paper are to

address the following concerns: (i) in what forms is the adsorbed P stored in the used alum sludge substrate (ii) is the P adsorbed stored in rapidly recycled forms or in forms that are resistant to decomposition and plant uptake; (iii) does the concentration of P forms increase or decrease with increasing depth from the topmost surface of the alum sludge in the lab-scale CW systems.

2 Materials and methods

2.1 Constructed wetland systems and used alum sludge samples

The simulated CW systems from which the used alum sludge samples were collected are shown in Fig. 1. The systems were made from Pyrex columns (1.0m long, $\varnothing = 0.095\text{m}$) and they were unplanted. The dewatered alum sludge was taken from the Ballymore Water Treatment Plant in Southeast Dublin, Ireland and its characteristics have been detailed in Yang et al., [10]. The sludge depth in the two systems was 0.6m. Similar configuration utilizing columns to depict laboratory scale CW systems are used in such laboratory scale studies [11]. The two systems were fed with wastewater from the same feed tank. The wastewater used was collected periodically from an animal farm, located in Lyons Estate, Newcastle, Dublin. Influent P into the systems ranged from $9.8 \pm 2.1 \text{ mg-P/l}$ to $309 \pm 27.9 \text{ mg-P/l}$. It should be noted that the wastewater collected in the feed tank was sometimes diluted with tap water or spiked with artificial P-rich solution (prepared using potassium dihydrogen phosphate (KH_2PO_4) salt) to obtain desired operational P concentration before it is pumped into the systems. The wastewater pumping operation into the two systems was carried out intermittently, i.e. in batch strategy, and this was realised using peristaltic pumps connected to each individual systems. The pre-set digital electronic timers ensured that the pumping operation was done in batches according to the intermittent feeding strategy design.

Fig. 1 Schematic diagram of the unplanted laboratory-scale alum sludge based CW systems. P = timer controlled peristaltic pumps, a = dewatered alum sludge cakes, b = gravel layer for support, c = pea gravel

A typical intermittent feeding consists of a ‘fill’ and ‘drain’ period. The fill period refers to the time of contact of the wastewater with the alum sludge in the system, while the drain period refers to the pumping out of the wastewater from the system. System 1 was filled entirely with the dewatered alum sludge whereas system 2 had a different substrate configuration. System 2 was firstly filled with the dewatered alum sludge up to a depth of 20cm and then topped with 30cm of pea gravel. The experiment was conducted over a total period of 25 weeks. At the end of the experimental period, the systems were gently dismantled and the used alum sludge samples were collected at every 10cm depth increment from the top of the alum sludge in the systems and sequential P extraction was carried out. Note that in system 2, the used alum sludge samples were collected from depth range of 30-40cm and 40-50cm.

Sequential P extractions were then carried out. The sequential P extraction procedures used in this study were modified from those developed for subsurface flow CW substrates by Forbes et al. [12]. In each step of the fractionation scheme, both organic and inorganic P forms were extracted. The extraction scheme used are discussed below and also depicted sequentially in the extraction scheme shown in Fig. 2.

Fig 2. Scheme of sequential phosphorus extraction procedure for used alum sludge substrate

2.2 Sequential P extraction

2.2.1 KCl extractable P

KCl extractable P was determined by modifying the method proposed by Makris and O'Connor [13] and used for the alum sludge. 0.25g of the alum sludge was equilibrated with 50ml of 1M KCl for 2 hours using a rotary shaker. Thereafter, the mixture was centrifuged and then filtered through a 0.45µm membrane filter. The filtrate was acidified to pH < 2 and then analysed colorimetrically for soluble reactive P using a HACH DR-2400 spectrophotometer according to standard methods [14].

2.2.2 Labile inorganic (P_i) and organic (P_o) phosphorus forms

In order to determine the different fractions of the labile P_i and P_o, duplicate samples (2.5 g each) were used. The first sample was fumigated with about 2-5ml of chloroform to lyse the microbial cells, and then extracted with 0.5M NaHCO₃. The mixture was then mechanically shaken using a mechanical shaker for 16 hours. After this, the samples were analysed for Total P (TP) by ashing samples at 550°C for 4 h followed by extraction with 6M HCl [12]. The extract was then analysed for TP following sulfuric acid-potassium persulfate digestion, using an autoclave. All P forms were determined analytically using a HACH DR-2400 spectrophotometer. The second set of the samples was extracted with 0.5M NaHCO₃, but these samples were not fumigated with chloroform. The samples were shaken for 16 hours, filtered using the whatman no. 41 filter and analysed for both SRP (soluble reactive phosphorus) and TP. The SRP determined is referred to as labile P_i. It should be noted that this step is the first stage in the entire sequential extraction scheme. The residue obtained from this particular set of extraction was used in subsequent extraction as explained in sections 2.2.3 to 2.2.5.

The rationale for bicarbonate extraction of the P_i is that soil/samples that contain levels of calcium have been shown to have decreased level of calcium activity in solution by precipitation as CaCO_3 , and therefore, P extracted using this method is found to be effective in determining plant-available P [5]. The derivation of labile P_o (living and dead microbial biomass) and the labile P_i can be seen diagrammatically in Fig. 2. Specifically, microbial mass is calculated as the difference between TP in the extracts from chloroform treated and untreated samples [15], while total labile organic P is calculated as the difference between TP in solution extracted with NaHCO_3 from samples subjected to chloroform fumigation and P_i extracted from soils without chloroform [5].

2.2.3 NaOH extractable P

The residue of the samples extracted as described in section 2.1.2 was treated with 0.5M NaOH and allowed to equilibrate for 17 hours on a mechanical shaker. This was followed by centrifugation and filtration and the filtered solution was analysed for SRP and TP. These fractions are referred to as NaOH- P_i and NaOH-TP respectively. The NaOH- P_i is considered to represent iron and aluminium bound P (Fe- and Al-bound P). The difference between NaOH-TP and NaOH- P_i is taken as organic P (NaOH- P_o), which is associated with fulvic and humic acids [5].

2.2.4 HCl extractable P

The residue from the above extraction step was further treated with 0.5M HCl and equilibrated for 24 hours on a mechanical shaker. This was also followed by centrifugation and filtration and the filtered solution was analysed for SRP, while the residue was kept for the next extraction step. The HCl- P_i fraction is taken as calcium and magnesium bound P (Ca- and Mg- bound P).

2.2.5 Residual phosphorus and total phosphorus

The residue from the above extraction step was combusted at 550°C for 4 hours. The ash was then dissolved in 6M HCl and then analysed for TP. The result was referred to as non-labile P (i.e. residual P).

3 Results and discussion

3.1 KCl extractable P

The result of the KCl extractable P is shown in Fig. 3. It can be seen that the alum sludge had an initial KCl extractable P content ranging from 0.08 to 0.10 mg-P/g and this increased to between 0.08 to 0.17 mg-P/g in the used alum sludge substrate. From Fig 3, it can also be seen that the greatest increase was in the topmost surface of the alum sludge in both systems (i.e. 0-10cm in system 1 and 30-40cm in system 2). Even though the used alum sludge was considerably loaded with P during the operating period, the general increase in the KCl extractable P content of the used alum sludge can be considered marginal in comparison to the P loading. This suggests the strong P binding ability of the alum sludge and also shows that the adsorbed P in the alum sludge may not be easily available. KCl extractable P is the most available (labile) pool of P [13, 16], which can be easily released (most loosely bound pool of P). However, it does not differentiate among the different forms of P.

Fig 3 (a & b) Initial and final KCl extractable P in the used alum sludge from systems 1 and 2, respectively.

3.2 Sequential phosphorus fractionation

3.2.1 P forms that are readily cycled or available to plants

Fig. 4 shows the concentration of P forms that are readily cycled or available to plants at various depths in the two systems. This group consists of the exchangeable inorganic P (EIP) and organic P (microbial and bicarbonate extractable P). From the figure, it can be seen that the concentration of EIP was mostly highest at the topmost surface of the alum sludge in the systems. In particular, the result for system 1 shows that the concentration of EIP decreased with increasing depth from the topmost surface of the alum sludge. For system 1, the concentration of EIP decreased from 2.2 mg-P/g to 1.6 mg-P/g for depths ranges of 0-10cm and 40-50cm, respectively.

Fig. 4 Profiles of readily cycled/plant- available P in the used alum sludge samples (note: a and b refer to systems 1 and 2, respectively; control refers to the unused alum sludge).

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235 The high concentration of EIP close to the top surface of alum sludge in the systems
 236 suggests that the inorganic P may be loosely bound to organic matter, bound to solid
 237 phases such as CaCO_3 , or present as recently precipitated, amorphous, monocalcium
 238 phosphate [5]. However, of the readily cycled/plant-available forms of P, the EIP
 239 accounted for the largest proportion stored in the used alum sludge samples. The
 240 readily cycled or plant available forms of P are classified into exchangeable inorganic P
 241 (extracted with NaHCO_3) herein referred to as EIP; the organic microbial tissue-P
 242 (chloroform released and extracted with NaHCO_3) and the exchangeable organic P
 243 (extracted with NaHCO_3), herein referred to as EOP [4]. The EIP represents free SRP
 244 in soil water, plus the weakly adsorbed inorganic P on surfaces. This pool also
 245 represents an immediately available pool of P, and a buffer regulating solution

concentration. In comparison, the microbial P accounted for only a very little proportion of the readily cycled/ plant-available P as can be seen in Fig. 4. Furthermore, has been noted that the microbial biomass P is not deposited in the same sense as other forms of organic P, but it may represent a larger pool in enriched areas [4]. In the two laboratory scale constructed wetland systems studied, the only contribution to microbial-P would have come from the biomass, but this amount is very small, compared to the EIP, and it does not represent a substantial pool for P storage under the current conditions.

Also from Fig. 4, it can be observed that the concentration of EIP and the microbial-P forms decreased with increasing depth from the surface in most cases. The results also indicate that the high concentration of soluble P used in the influent wastewater into the systems promoted the diffusion of initially adsorbed P into the pores/interior in the alum sludge. Therefore, any labile inorganic P would likely be converted from short-term to long-term storage by either precipitation or incorporation into the interior structure of the alum sludge. Thus, most P would be in the forms that are not easily decomposed compared to the readily cycled/plant-available form. However, it should be noted that negative values were obtained for the exchangeable organic P (EOP). This is because, analytically, EOP is calculated as the difference between TP in solution extracted with NaHCO_3 from samples subjected to chloroform fumigation, and P_i extracted from soils without chloroform [5, 12]. However, the spiking of the influent wastewater with synthetic inorganic P greatly increased the P_i , such that its value was higher than the TP obtained by extraction with NaHCO_3 and chloroform fumigation. This consequently led to the negative values.

3.2.2 P forms that are not easily decomposed

Fig. 5 (a & b) shows the relative percentage of each of the P forms that are not easily decomposed across the sampling depth and also the total amount of these P forms stored in each system and across the depths. The figure shows that across depth, most of the P forms are stored in the inorganic form. In system 1, the range of concentration of the inorganic P form across depth was 2.6-4.3 mg-P/g (for Fe- and Al-bound P) and 2.2-6.9 mg-P/g (Ca- and Mg-bound P) while for inorganic P, the range was 3.3-12.6 mg-P/g (for humic and fulvic acids bound P) and 1.4-2.0 mg-P/g (for residual P). For system 2, the range across depth was 3.4 mg-P/g (relatively unchanged for Fe- and Al-bound P) and 6.5-7.3 mg-P/g (for Ca- and Mg-bound P) while for inorganic P, the range was 8.0-9.5 mg-P/g (for humic and fulvic acids bound P) and 0.6-0.8 mg-P/g (for residual P). Being that the alum sludge is chiefly composed of aluminium, one may presumably expect a significant fraction of the inorganic P forms that are not easily decomposed to be associated with the Fe and Al fraction.

According to Qualls and Richardson [4], four major processes can cause the deposition of calcium bound-P: (a) chemical precipitation of calcium phosphates, (b) coprecipitation with calcium carbonate, (c) adsorption and precipitation of phosphate on the surfaces of calcium carbonate, or (d) precipitation by calcareous algae. It should be noted that the influent wastewater used in these systems contains a significant amount of calcium, which has been shown to be removed onto the alum sludge [17]. Consequently, the relative concentration of calcium in the sludge increased significantly, while that of aluminium decreased. Although it is noted that acidic conditions may favour formation of P bound to Fe and Al secondary minerals, while more alkaline conditions favour the formation of Ca bound P [4], this is not likely to be case in this study, as the pH values were circumneutral. In the case of the humic/fulvic acid bound-P, there was no definitive trend observed. For instance, in system 1 (See Fig

5, b), humic/fulvic acid bound-P increased with increase in depth and distance from the topmost alum sludge surface up to the 20-30 cm depth, and then decreased and increased again between the 30-40 and 40-50 cm depth respectively.

Fig. 5 Profiles of P forms that are not easily decomposed in the used alum sludge samples: (a) relative proportion in %; and (b) relative quantity in mg-P/g of the different proportions (note: 1 and 2 refers to systems 1 and 2, respectively, while values enclosed in bracket indicate the sampling depth range in cm. Control refers to the unused alum sludge).

However, for system 2, there were only two sampled points, and the humic/fulvic acid bound-P decreased with increasing depth from the topmost alum sludge surface. Notwithstanding, the relatively high amount of P associated with the humic/fulvic acid

can be explained by the high organic content in the alum sludge. The percentage of the residual P increased with depth away from the topmost surface (See Fig. 5, a). Again, the fact that some amount of P is extracted as residual P shows that the systems relatively functioned as a long-term P-sink.

Fig. 6 shows a comparative plot of the P forms that are not easily decomposed and the readily cycled/plant-available P in the used alum sludge samples. It can be seen that more P is held in forms that are not easily decomposed which can be viewed as a long-term storage. On the other hand, P stored in the readily cycled/ plant-available form is comparatively smaller in all cases. The total amount of P held in forms that are not easily decomposed in systems 1 and 2 ranged from 10.1–24.7 mg-P/g and 18.7-20.7 mg-P/g respectively, while the total amount of P held in forms that are readily cycled/plant-available ranged from 1.6-2.3 mg-P/g and 1.6-1.7 mg-P/g for systems 1 and 2 respectively. The P held in readily cycled/plant-available form is exchangeable and according to Craft and Richardson [18], this pool should only be viewed as a temporary storage or an intermediate pool and not as a long-term storage mechanism. In most cases, the total amount of P stored in forms that are not easily decomposed increased with distance from the inlet. This is particularly due to the fact that the amount of residual P increased with distance from the topmost surface, and this contributed to the total P retained in forms that are not easily decomposed. The residual P, which is organic, is highly refractory and it may not be bioavailable [5]. The relative proportion of this residual P generally increased with depth in the systems as can be seen in Fig 5 (a).

Fig. 6 Comparative profiles of P forms that are not easily decomposed and readily cycled/plant-available P in the used alum sludge samples (note: 1 and 2 refer to models systems 1 and 2, respectively, while values enclosed in bracket indicate the sampling depth range in cm. Control refers to the unused alum sludge)

4 Conclusions

The forms, patterns and extractability of dewatered alum sludge used as substrate in laboratory-scale constructed wetland system were examined in this study. Results obtained indicate that a major proportion of P retained in the used alum sludge samples were in forms that are not easily decomposed. The total amount of P held in forms that are not easily decomposed in the systems ranged from 10.1–24.7 mg-P/g while the total amount of P held in forms that are readily cycled/plant-available ranged from 1.6-2.3 mg-P/g. Analysis of the P forms that are not easily decomposed across the two simulated constructed wetland systems indicate the following: In system 1, the range of concentration of the inorganic P form across depth was 2.6-4.3 mg-P/g (for Fe- and Al-bound P) and 2.2-6.9 mg-P/g (Ca- and Mg-bound P) while for inorganic P, the range

was 3.3-12.6 mg-P/g (for humic and fulvic acids bound P) and 1.4-2.0 mg-P/g (for residual P). In system 2, the range across depth was 3.4 mg-P/g (relatively unchanged for Fe- and Al-bound P) and 6.5-7.3 mg-P/g (for Ca- and Mg-bound P) while for inorganic P, the range was 8.0-9.5 mg-P/g (for humic and fulvic acids bound P) and 0.6-0.8 mg-P/g (for residual P). Therefore, the results imply that P fractions associated with Ca and Mg, and Fe and Al are the dominant forms of the P forms that are not easily decomposed. The concentration of most of the P forms was also found to decrease with increasing depth from the topmost surface of the alum sludge in the lab-scale constructed wetland systems. The alum sludge showed an overall increase in its P content and this could increase its agronomic value and potential for P recovery.

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