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

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ABSTRACT

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

1. Introduction

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

In some other studies, the variation of P forms with depth was examined. Qualls and Richardson [4] reported that the concentration of most forms of P decreased with distance along the gradient. It was further reported that for most P forms, the trends are weaker or absent at lower soil depths. The insoluble organic P, the humic P, and the Ca-bound P which are all P forms that are not easily decomposed were reported to show the highest decrease in concentration with distance. This observation is also corroborated by the results of Reddy et al. [5] in which it was reported that the concentration of most P forms were higher in the surface layers and decreased with depth and with distance from the inflow structure. Such examination of P adsorbed in a CW substrate can also be used in evaluating the availability and potential recovery of P accumulated onto the CW substrate. The P examination is usually determined by sequential extraction with acid and alkaline reagents as modified for wetland soils by Qualls and Richardson [4] and Reddy et al. [5]. The P forms in various groups are usually identified and the form of P will influence its availability and recycling capacity. It should be noted that based on the sequential extraction, the term availability refers to both extractable and non-extractable P forms. The non-extractable P implies a form of P that is also available but in a form that cannot be extracted. Table 1 shows the different P forms including those that are grouped based on their availability for plant uptake. The classification is adopted from Qualls and Richardson [4].

However, it is also important to note that different CW substrates may have specific properties that may be related to the P

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Table 1
Forms of extracted phosphorus.

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

dynamics. Hence, it is necessary to carry out individual examination of P forms for different substrates. In this study, alum sludge was used as substrate in laboratory-scale CW systems. Alum sludge, an aluminium-containing drinking water treatment residual in dewatered cake form, has been revealed as a new potential CW substrate due to its high P adsorption capacity [6], and physico-chemical characteristics which conform to the recommended standards for CW substrates [7]. The alum sludge (in dewatered cake form) was used as main substrate in laboratory-scale CW systems and it was shown to significantly enhance P removal [8]. The study of beneficially reusing alum sludge as raw material is part of a larger project aimed at the eventual development of a novel alum sludge based CW system for wastewater treatment. The project has been carried out for the past 5 years at the University College Dublin (UCD), Ireland and it has entailed series of sub-projects of different scales. The sub-projects have included: (a) extensive studies on identifying the P adsorption ability of the dewatered alum sludge and the removal efficiencies of other pollutants (COD, BOD$_5$) using alum sludge as main substrate in the novel CW system [6–9]; (b) investigating the lifespan of the system [9]; (c) examining the mechanism and characteristics of P adsorption onto the alum sludge [10]; and (d) examining the release of other materials/elements from the alum sludge. As such, the current study is aimed at further gaining a holistic view of the development of the novel alum sludge based CW system by examining the fate of the P adsorbed by the alum sludge, alongside other sub-projects as highlighted above.

Examination of the fate of P adsorbed in the alum sludge is crucial in determining the recycling potential of the alum sludge when it is saturated and also in evaluating the 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 (1.0 m long, Ø = 0.095 m) and they were unplanted. The dewatered alum sludge was taken from the Ballymore Water Treatment Plant in Southwest Dublin, Ireland and its characteristics have been detailed in Yang et al. [10]. The sludge depth in the two systems was 0.6 m. 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 ± 2.1 to 309 ± 27.9 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$_2$PO$_4$) 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 preset digital electronic timers ensured that the pumping operation was done in batches according to the intermittent feeding strategy design.

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 20 cm and then topped with 30 cm 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 10 cm 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 30–40 and 40–50 cm.

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.

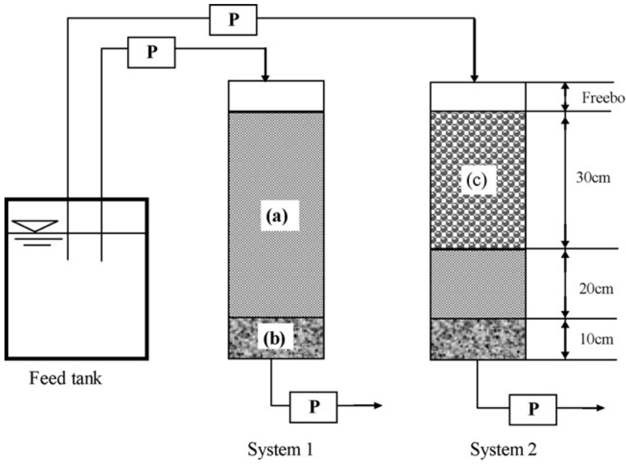

Fig. 1. Schematic diagram of the unplanted laboratory-scale alum sludge based CW systems. P = timer controlled peristaltic pumps, a = dewatered alum sludge cakes, b = gravel layer for support, c = pea gravel.

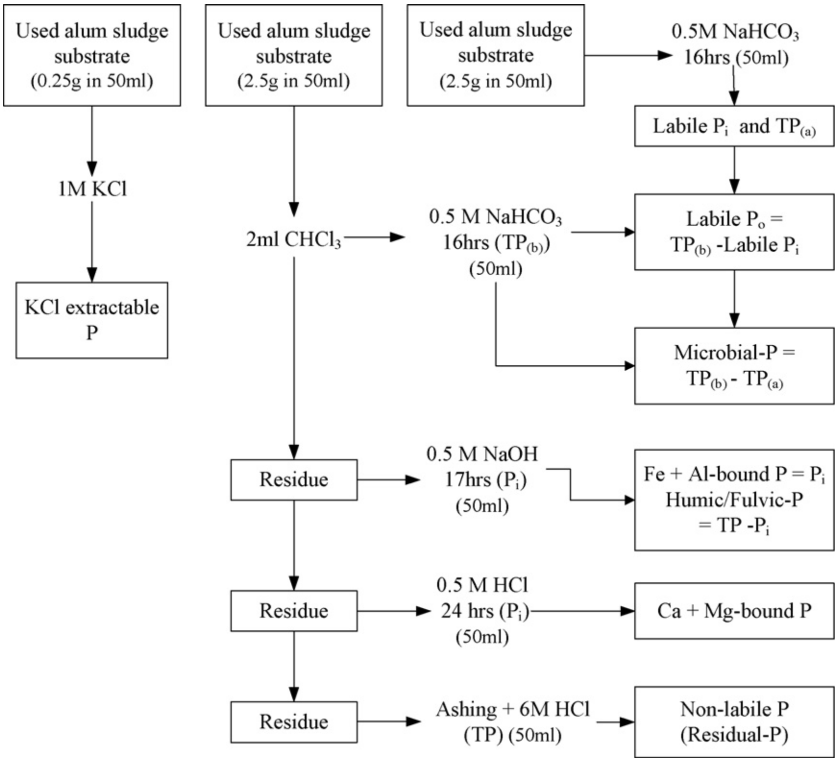

Fig. 2. Scheme of sequential phosphorus extraction procedure for used alum sludge substrate.

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. 0.25 g of the alum sludge was equilibrated with 50 ml of 1 M KCl for 2 h using a rotary shaker. Thereafter, the mixture was centrifuged and then filtered through a 0.45 μm 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 2–5 ml of chloroform to lyse the microbial cells, and then extracted with 0.5 M $NaHCO_3$. The mixture was then mechanically shaken using a mechanical shaker for 16 h. After this, the samples were analysed for Total P (TP) by ashing samples at 550 °C for 4 h followed by extraction with 6 M 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 0.5 M $NaHCO_3$, but these samples were not fumigated with chloroform. The samples were shaken for 16 h, 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 2.2.3–2.2.5.

The rationale for bicarbonate extraction of the P_i is that soil/samples that contain some 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 2.2.2 was treated with 0.5 M NaOH and allowed to equilibrate for 17 h 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 0.5 M HCl and equilibrated for 24 h 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 h. The ash was then dissolved in 6 M HCl and then analysed for TP. The result was referred to as non-labile P (i.e. residual P).

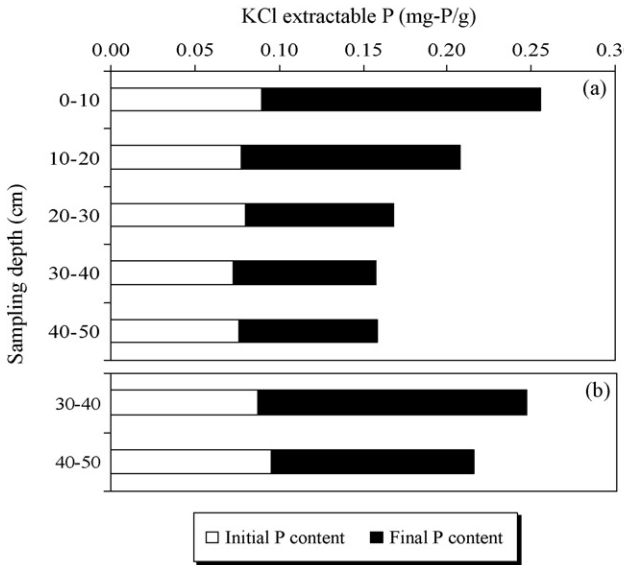

Fig. 3. (a and b) Initial and final KCl extractable P in the used alum sludge from systems 1 and 2, respectively.

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 and 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. 0–10 cm in system 1 and 30–40 cm 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.

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 to 1.6 mg-P/g for depths ranges of 0–10 and 40–50 cm, respectively.

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

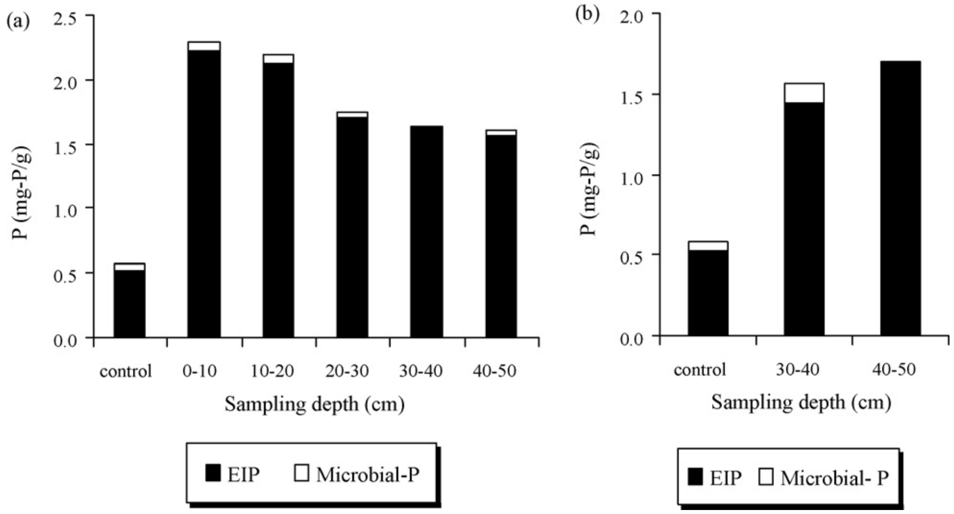

Fig. 4. Profiles of readily cycled/plant-available P in the used alum sludge samples (note: a and b refer to systems 1 and 2, respectively; control refers to the unused alum sludge).

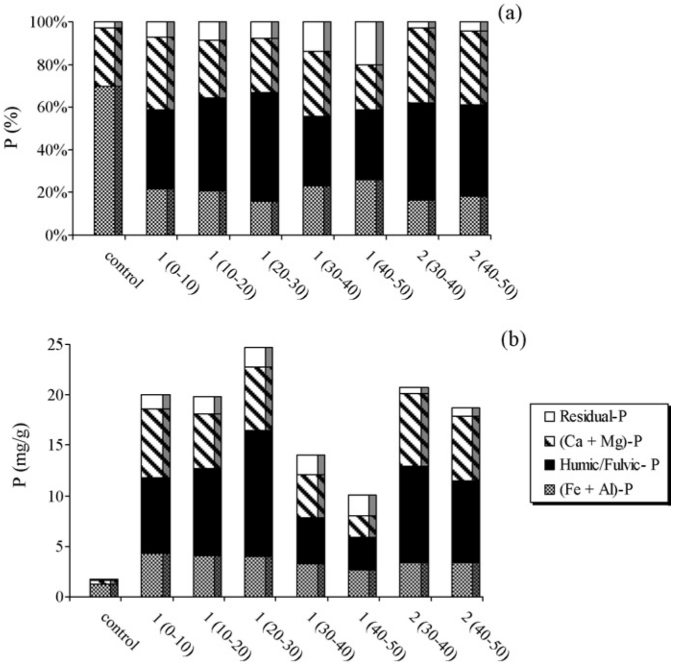

Fig. 5. Profiles of P forms that are not easily decomposed in the used alum sludge samples: (a) relative proportion in %; and (b) relative quantity in mg-P/g of the different proportions (note: 1 and 2 refers to systems 1 and 2, respectively, while values enclosed in bracket indicate the sampling depth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

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. 5a and 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 (for 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 [7]. 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. 5b), humic/fulvic acid bound P increased with increase in depth 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.

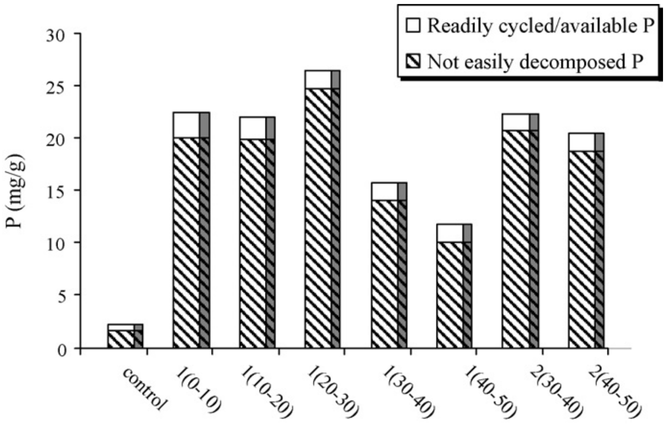

Fig. 6. Comparative profiles of P forms that are not easily decomposed and readily cycled/plant-available P in the used alum sludge samples (note: 1 and 2 refer to models systems 1 and 2, respectively, while values enclosed in bracket indicate the sampling depth range in cm. Control refers to the unused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

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. 5a). 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 to 24.7 mg-P/g and 18.7 to 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 to 2.3 mg-P/g and 1.6 to 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 [17], 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 depth from the inlet. This is particularly due to the fact that the amount of residual P increased with depth 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. 5a.

4. Conclusions

The forms, patterns and extractability of phosphorus (P) retained in 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 to 24.7 mg-P/g while the total amount of P held in forms that are readily cycled/plant-available ranged from 1.6 to 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 (for 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 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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