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Phosphorus adsorption onto an enriched biochar substrate in constructed wetlands treating wastewater [☆]



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ABSTRACT

Phosphorus (P) is an essential nutrient, which in excessive concentrations from sewage treatment systems can cause eutrophication of waterways. The use of adsorption substrates is becoming a common method for P-removal from wastewater. To achieve sustained P-removal from passive wastewater treatment systems, such as constructed wetlands, it is essential to select substrates with a high capacity to retain P which can be replaced when saturated. An enriched hemp biochar substrate was added to experimental constructed wetland cells to treat domestic wastewater. Hemp feedstock was treated with hematite, melanterite and dolomite prior to pyrolysis at 400 °C. The amount of P which was present in the wastewater from the biochar wetlands cells after treatment was compared to gravel control wetland cells. During the 7-month study period, the wetlands containing the enriched biochar consistently reduced PO₄-P concentrations in primary treated sewage to lower levels than in the control wetlands, with an average inlet P concentration of 15.5 mg/L, to below 2 mg/L. Various analytical methods were used to characterise the changes in the biochar substrate. Concentration of P in the substrate increased by 77% over the test period. X-ray photoelectron spectroscopy (XPS) analysis revealed iron phosphate formation. Scanning electron microscopy together with energy dispersive X-ray spectroscopy (SEM-EDX) showed P captured on the biochar surface was associated with aluminium, silica, iron, magnesium and calcium-rich mineral phases. This study showed that an enriched biochar can be used as a substrate to capture phosphorus in passive wastewater treatment.

1. Introduction

Horizontal subsurface flow (HSSF) constructed wetlands utilise a gravel or soil substrate along with plants to provide enhanced wastewater treatment with lower costs, maintenance and energy requirements than conventional treatment systems (Xuan et al., 2009; Vymazal, 2010). The HSSF constructed wetland systems are known for their ability to reduce Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Nitrogen (N) and pathogens, through physical and biological processes (Bolton and Bolton, 2013; Kadlec, 2009; Kadlec and Wallace, 2008). These wetlands are commonly used for secondary treatment before release into the environment and typically reduce BOD and TSS to less than 30 mg/L (Kadlec and Wallace, 2008; Bolton and Bolton, 2013). Biochar used as a substrate in these systems

provide the same or higher levels of BOD, TSS and N treatment as a conventional gravel wetland treating domestic wastewater (Gupta et al., 2015; Bolton, 2014).

HSSF wetlands containing a gravel substrate are efficient wastewater treatment devices, however long term P-removal is generally poor (Kadlec, 1999; Vymazal, 2004). The addition of specific types substrates and associated adsorption and precipitation processes are regarded as the primary long-term P-retention mechanisms in constructed wetlands. The effectiveness of these processes is highly dependent on the properties of the added substrates, and P-removal can be maximised if the substrates can be replaced when saturated (Kadlec and Wallace, 2008; Lucas and Greenway, 2011). The use of a cation-enhanced sorption substrate (e.g Fe, Al, and Ca) such as enriched biochar offers a practical method for removing P from wastewater due to

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its high level of P retention and subsequent ability to be removed and replaced when saturated (Rittmann et al., 2011; Streubel, 2011; Chen et al., 2011, Leader et al., 2008; Arias et al., 2003).

Biochar is made by thermal heating of organic material in partial or total absence of O₂ to produce a C-based residue (Yuan et al., 2011). An enriched biochar which has value as both a fertiliser or an adsorbent can be produced by pre- or post-pyrolysis treatment using various minerals (Joseph et al., 2013; Chen et al., 2011; Yao et al., 2014). This promotes bonding between the minerals and organic phases resulting in a high concentration of exchangeable cations (Chia et al., 2014).

When Fe, Al or Ca are present, the enriched biochar can be used as a very efficient adsorbent for P, making it an effective way to remove and reuse P from wastewater and runoff thereby improving water quality (Ghezzehei et al., 2014). Once removed from the wetland the enriched biochar substrate may be used in soil improvement with the added benefits of bioavailable nutrients (Streubel, 2011; Taghizadeh-toosi et al., 2012; Major et al., 2009; Steinbeiss et al., 2009). Other ancillary benefits from biochar production include waste management by using waste material as a feedstock, and climate change mitigation through long term carbon (C) sequestration (Lehmann and Joseph, 2009).

The chemical processes, including adsorption onto the biochar surface of nutrients from the surrounding environment are strongly related to surface chemistry, so evaluating the changes on the biochar surface provides information about its long-term effectiveness as a P-sorption substrate (Brewer, 2012).

2. Materials and methods

2.1. Mineral enriched biochar production

200 kg of chipped hemp fibre were used as the feedstock to produce the enriched biochar. Hemp was chosen as a biochar feedstock due to its porous structure enhancing its ability to adsorb. 20 kg of hematite (Fe₂O₃), 20 kg of melanterite (FeSO₄·7H₂O) and 20 kg of dolomite [CaMg(CO₃)₂] were mixed into a slurry using 60–70 L of water and combined with the feedstock prior to pyrolysis.

This treated feedstock was pyrolysed in an Applied Gia continuous screw reactor, which contained a pre-drying chamber and a pyrolysis chamber. Syngas from the process was reused to heat the reactor. The temperature in the pyrolysis chamber was kept within the range 400–425 °C.

2.2. Experimental design of wetlands

Six small pilot-scale experimental HSSF constructed wetlands were used in the study. Each of the six wetlands, measuring 1.2 m × 0.76 m × 0.4 m were planted with *Melaleuca quinquenervia* trees, and consisted of two cells in series, making 12 cells in total (Fig. 1). Each wetland was made from Aquatec PondMAX 400 L free-standing poly ponds. The two cells in each wetland were separated by a polyethylene baffle, plastic-welded into the wetlands. Three wetlands contained two gravel cells in series (control wetlands), the other three contained a gravel cell followed by an enriched biochar cell (biochar wetlands). The first cell in each of the six wetlands was filled with gravel to trap sediments, thus avoiding blockages in the downstream cell.

The wetlands received primary-treated domestic wastewater from a septic tank for a period of 7 months. Water flowed from the septic tank into a settling sump. A pump and irrigation system with a timer allowed controlled doses of wastewater to be evenly allocated to each of the wetlands from the sump. Each wetland cell had a hydraulic loading rate of 0.023 m per day, giving a nominal retention time of 5.1 days. Hydraulic loading rate (q_i) was calculated using equation 1

and nominal detention time (T_n) was calculated using the equations 2–4. Biochar porosity (ϵ) was calculated to be 0.45.

Inlet flow Hydraulic Loading Rate (md^{-1})

$$q_i = \frac{Q}{A}$$

Porosity

$$\epsilon = \frac{V_L}{V_R}$$

Nominal Volume (m^3)

$$V_n = V\epsilon$$

Nominal Detention Time (days)

$$\tau_n = \frac{V_n}{Q}$$

where

Q = Daily flow rate (m^3d^{-1})

V_L = Total volume of liquid filled void volume (L)

V_R = Volume of the reactor (L)

V = Actual Volume (m^3)

A = wetted land area (m^2)

2.3. Collection and analysis of water samples

Water samples were collected monthly from each of the six wetlands for a 7-month period. The samples were taken mid-column from the last outlet sump of each wetland. Influent water samples were collected from the primary settling sump 30 cm from the surface, in the middle of the sump. Samples were stored on ice and immediately transported to the Environmental Analysis Laboratory in Lismore, NSW, Australia where they were analysed for PO₄-P using the standard methods for the examination of water and wastewater (APHA, 2005).

Analysis of statistical difference was applied using three replicates of both the biochar and control wetlands over a 7-month period. A paired student *t*-test was used to compare the significant difference in PO₄-P with the outlet concentrations from the biochar and control wetlands.

2.4. Surface characteristics of enriched biochar

Analysis of biochar elements before wetland filtration, and after 2 and 7 months of filtration, was conducted at the Environmental Analysis Laboratory in Lismore, NSW Australia, after samples were dried at 60 °C for 48 h. All elements except for C and N were determined by nitric acid/HCl digestion, followed by inductively coupled plasma atomic emission spectroscopy (ICP OES; APHA 3125). C and N were determined using a LECO TruMAC CNS Analyser.

Surface analysis was performed on the biochar substrates before wetland filtration, and after 2 and 7 months of filtration, using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) as described in Joseph et al. (2013). Samples were mounted on conductive tape and then plasma coated with chromium prior to examination.

XPS was performed at the Surface Analysis Laboratory at the University of NSW, Australia using a Thermo Scientific ESCALAB250Xi with a monochromatic Al K α X-ray source ($h\nu = 1486.68 \text{ eV}$) collected at the take-off angle of 90°. The detailed method of analysis is given in Joseph et al. (2013).

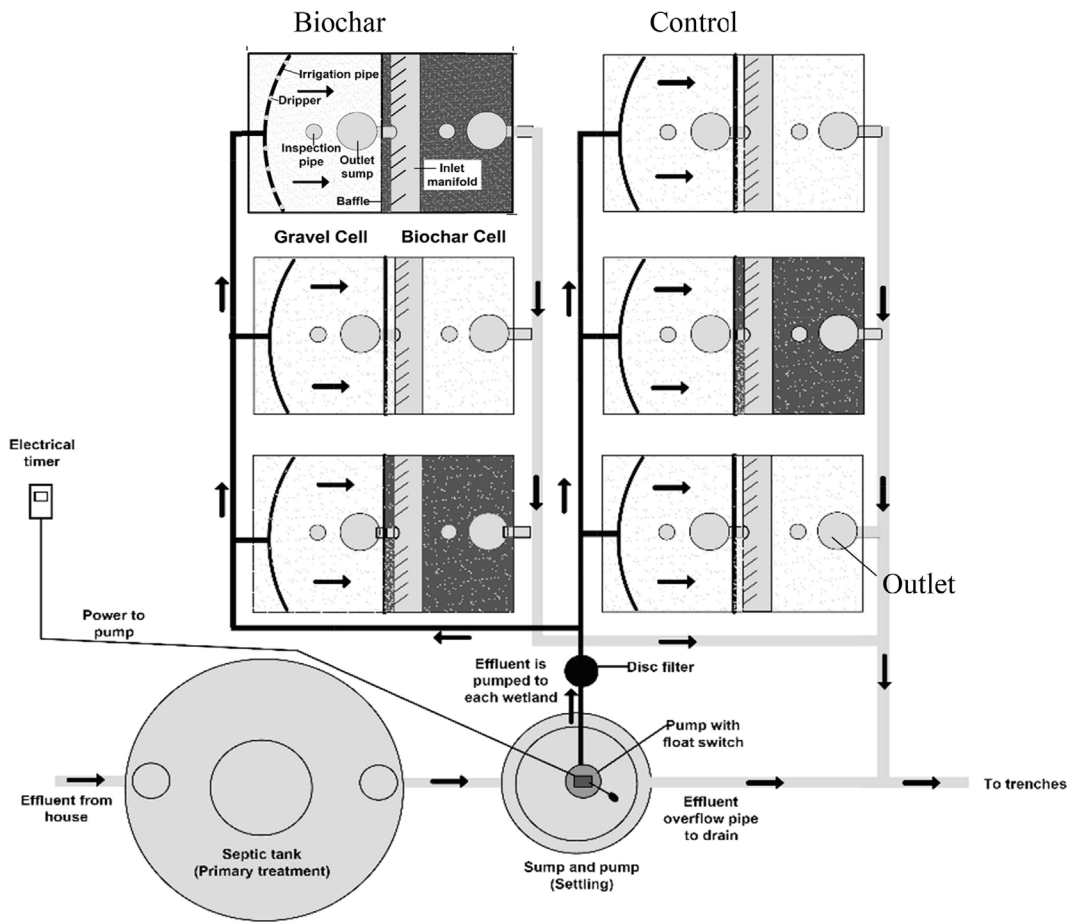


Fig. 1. Diagram showing the six wetlands consisting of three biochar wetlands (gravel cell followed by biochar cell) and three control wetlands (two consecutive gravel cells).

3. Results and discussion

3.1. Phosphorus removal from wastewater

Over the 7-month test period, the biochar wetland consistently reduced $PO_4\text{-P}$ concentrations in wastewater to less than 2 mgL^{-1} regardless of influent concentrations, while the control wetland

reached 4 mgL^{-1} following high inlet concentrations. During the 7-month period, inlet $PO_4\text{-P}$ concentrations ranged from 7.07 mgL^{-1} to 29.87 mgL^{-1} (Fig 2). Higher inlet concentrations of $PO_4\text{-P}$ resulted in lower outlet concentrations within the biochar wetland, most likely due to adsorption equilibrium reactions.

A one-tailed paired samples *t*-test revealed a statistically significant difference in outlet P concentrations between the biochar and control

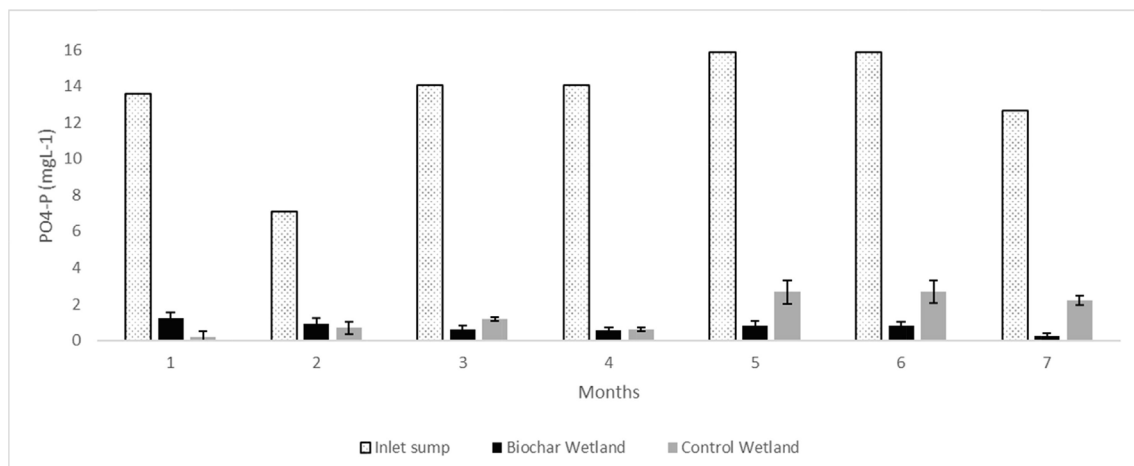


Fig. 2. Average (\pm standard deviation, $n = 3$) $PO_4\text{-P}$ concentrations and standard deviations in biochar and control wetlands over the 7-month sampling period.

Table 1

Characteristics of selected elements of mineral enriched biochar before addition to the wetlands, (raw) and 2 and 7 months after wetland treatment.

Biochar elemental Characteristics gkg ⁻¹						
	C	N	S	C:N	C:S	P
Raw	313.5	7.2	20.8	43.7	15	4
2 months	344.4	11.4	3	30.2	11.4	6.2
7 months	290.6	9.8	3.4	29.8	85	7.1

Table 2

Elemental composition of mineral enriched biochar before addition to the wetlands, (raw) 2 and 7 months after wetland treatment.

Biochar elemental Composition gkg ⁻¹										
	Ca	Mg	Fe	Al	K	Na	Zn	Cu	Mn	Si
Raw	55	18.5	123	3.2	8.1	1.1	0.3	0.1	1.1	0.8
2 months	57.8	19.3	135	1.5	1.8	0.4	0.6	0.1	1.2	1.5
7 months	52.1	18.7	134.3	6.2	1.4	1.4	0.4	0.1	1.2	0.9

wetlands ($P < 0.05$). The PO_4 -P concentrations were consistently lower in the biochar wetland outlet ($m = 0.72$, $s = 0.47$) than in the control wetland ($m = 1.34$, $s = 1.00$).

On average, over the test period, the biochar wetlands had a higher PO_4 -P removal efficiency and lower PO_4 -P outlet concentrations than the controls. The biochar wetlands had an average P mass removal rate of 208.4 mgL^{-1} while the control was 133.2 mgL^{-1} .

Overall the biochar and control wetlands achieved average PO_4 -P removal efficiencies of 94.3%, and 91%, respectively, but in the last 3 months of sampling, the average PO_4 -P removal efficiency of the biochar wetland was 97%, while the control was 87%, indicating that the gravel substrate in the control wetland may have reached P saturation. Removal rates for the biochar wetland were influenced by the concentration of inlet PO_4 -P.

Typically, gravel HSSF wetlands will remove between 25 and 60% of P, with outlet concentrations above 2 mgL^{-1} (Vymazal, 2004; Davison et al., 2001). Both the biochar and the control wetlands reduced considerable amounts of PO_4 -P over the study period. Initial high rates of P retention within constructed wetlands are due to uptake by microbes and algae (Richardson and Craft, 1991). P will be high in wetlands which have not received nutrient inputs and will eventually become saturated. In addition, adsorption processes may be initially higher in previously unused substrates (Vymazal, 2004, 2007; Greenway et al., 2010), however over the lifetime of the substrate this will reduce.

3.2. Composition of biochar elements

Elemental analysis of the enriched biochar substrate (Tables 1 and 2) identified that nutrients such as P and nitrogen (N) increased in the biochar substrate during the 7-month wetland filtration period. P increased overall by 77% and N increased by 36%.

C decreased by 7% over the 7-month period. A small portion of C present in biochar will decompose within the first few years in the environment, the decomposition rate being highly dependent on the pyrolysis conditions and biochar feedstock (Wang et al., 2016). Enriched biochars produced at low temperatures will have lower aromaticity (McBeath et al., 2014) and a higher portion of dissolved organic carbon (Lin et al., 2012) making it more susceptible to microbial decomposition. Additionally, the nutrient rich environment of constructed wetlands increases microbial decomposition of organic matter (Bodker et al., 2015). Low temperature biochar will also increase methane (CH_4) production under anaerobic conditions (Shanmugam et al., 2018).

Table 3

XPS scan comparing the C, O, K and N surface functional groups (at. %) of enriched biochar before (raw) and after 2 months and 7 months' treatment in the wetland.

Element	Functional Group		Results		
	Binding Energy (eV)	Structure	Raw	2 months	7 months
C1s	285.0 ± 0.2	C—C/C—H	48.9	44.99	47.3
	286.5 ± 0.2	C—O	11.7	12.1	11.7
	288.1 ± 0.2	C=O (carbonyl groups)	2.6	3.3	5
	289.2 ± 0.3	COOH (carboxyl groups)	1.9	2.8	1.9
	291.3 ± 0.6	C—C/C—N	1.5	1.9	—
Fe2p _{3/2}	708.82	FeO	—	—	0.1
	711.25	Fe ₂ O ₃ or FeOP	—	—	0.8
	713.21	Fe ₂ (SO ₄) ₃	—	—	0.2
K2p ₃	293.7 ± 0.1	K groups	0.4	—	—
N1s	400.5 ± 0.3	N—C—COOH (pyridone)	1.4	2.2	1.8
	399.0 ± 0.4	NH ₄ /NH ₂ groups	0.5	0.5	0.2
O1s	532 ± 0.2	C—O	31.1	32.3	29.1
S2p ₃	168.99	SO ₄ ²⁻	—	—	0.3
	163.92	S ²⁻	—	—	0.2
P2p	133.64	—	—	—	1.4

— Indicates non-detectable levels.

Fe represented a high proportion of the biochar composition, being the second most abundant element present in the biochar after C. The high Fe content in the biochar was due to the addition of Fe_2O_3 and $FeSO_4 \cdot H_2O$ prior to pyrolysis. Fe, Zn and Mn increased during the 7-month period. High quantities of Mg and Ca in the biochar were a result of the $CaMg(CO_3)_2$ treatment.

Potassium (K) decreased significantly in the biochar during the test period. Fresh biochar will generally contain a high percentage of soluble alkaline cations, such as K (Wan et al., 2014) which will be rapidly released as the biochar weathers (Yao et al., 2010). At pyrolysis temperatures of 400 °C, 90% of K in biochar is in a soluble form (Chan and Xu, 2009) which will be removed with the wastewater out of the wetland.

3.3. X-ray photoelectron spectroscopy (XPS)

Quantitative XPS provided an analysis of the top ~ 5 nm of the surface of the enriched biochar substrate (Tables 3 and S1) and revealed comparable results to the elemental analysis. The concentration of P increased on the surface over the 7-month period. High quantities of metal cations, including Fe, Ca and Mg were present allowing for P retention through precipitation and chemical adsorption processes (Shepherd et al., 2017; Streubel, 2011). Chemical adsorption involves displacement of water or hydroxyl groups from the surface of Fe and Ca oxides (ligand exchange reactions) by phosphate ions, which forms insoluble metal phosphates (Vymazal, 2010; Vymazal and Kröpfelová, 2008). Phosphate (PO_4 -P) bound to Fe will be relatively stable with a slow rate of release (Reddy et al., 1995).

Fe-based functional groups (Table 3) were detected on the biochar surface after it had been in the wetland for 7 months. XPS analysis at 7 months revealed the formation of Fe compounds, with a Fe 2p_{3/2} peak at 711.25 eV that could be assigned to either Fe(II) or Fe(III) species on the surface (Yamashita and Hayes 2008; Descostes et al., 2000; Daou et al., 2007). A peak at 711.4 eV has been used to identify the presence of $FePO_4$, while an oxygen 1 s peak at 532.6 eV can also be assigned to a phosphate oxygen bound to iron (Bouwman et al., 2004; Daou et al., 2007). A P 2p_{3/2} peak at 133.6 eV supports the presence of PO_4^{3-} . A similar P 2p_{3/2} peak (133.8 eV) was observed by Liu et al. (2015) during phosphorus adsorption onto iron-modified biochar. Smaller amounts

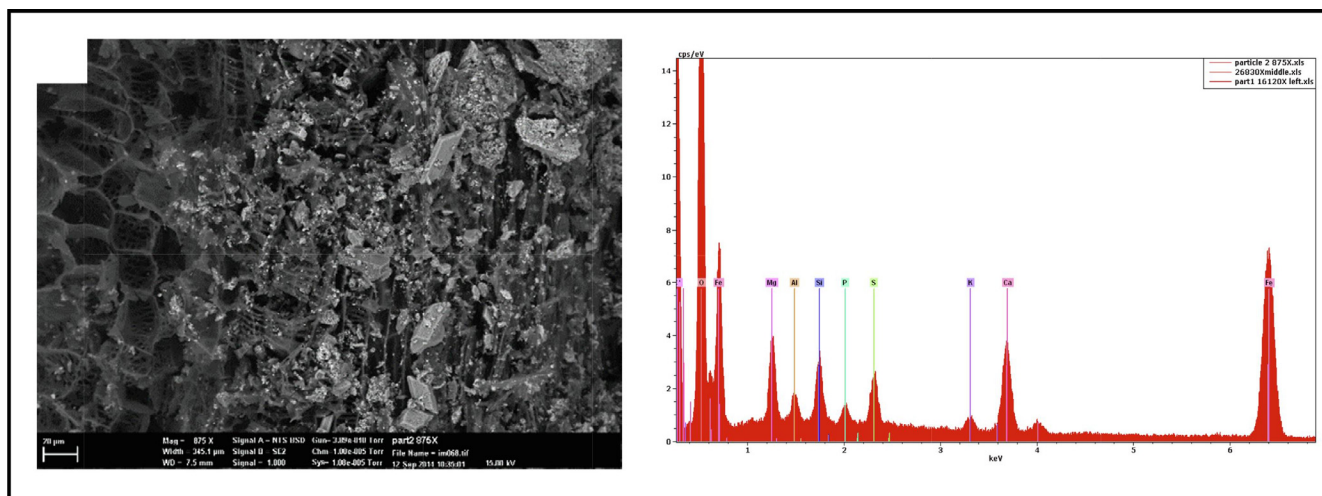


Fig. 3. (a) Secondary electron image and EDS spectrum from the biochar substrate before application in the wetland.

of sulfur, most likely present as iron sulfate ($\text{FeSO}_4 \cdot n\text{H}_2\text{O}$) were detected within the biochar sample with a $\text{S}2p_{3/2}$ binding energy of 713.21 eV (Baltrusaitis, 2007; Descostes et al., 2000).

An increase in surface C composition of the biochar between 2 and 7 months in the wetland was most likely due to the sorption of organic matter (Hammes and Schmidt, 2009). Organic matter may be adsorbed simultaneously with P on Fe-treated biochar (Zach-Maor et al., 2011). An analysis of C surface functional groups revealed increases in C=O (carbonyl) associated with quinones, ketones and aldehydes over the 7-month period as a result of microbiological fermentation (Richardson and Veoraskas 2000).

An initial increase in COOH and C—C/C—N after 2 months was followed by a decrease of COOH and the absence of C—C/C—N on the surface after 7 months wetland treatment. Other N-containing functional groups also increase initially but then decrease after 7 months. Under prolonged submergence wetlands will develop anaerobic conditions in which microorganism will reduce carboxylic acids such as SO_4^{2-} to S^{2-} and NO_3^- to N_2 (Kirk, 2004). In established wetlands, N removal is facilitated by microbial pathways including nitrification and denitrification (Reddy and DeLaune, 2008).

Analysis confirmed that over the test period Ca and Mg ions on the surface of the biochar decreased perhaps due to dissolution (Table S1).

In wetlands however, P may form precipitates with metallic cations such as Ca or Mg to produce poorly crystalline or amorphous solids (Reddy et al., 1995; Leader et al., 2008; Prochaska and Zoubouis, 2006), which can be carried out of the wetland with the wastewater or retained within the wetland. Precipitated P may undergo hydrolysis in the environment and revert to the soluble $\text{PO}_4\text{-P}$ form, which could trigger eutrophication, however this process is usually quite slow and dependent on environmental conditions such as pH and redox potential.

pH is known to affect the removal of phosphorus via precipitation or adsorption. pH in the biochar wetland was 7.3 compared to the control at 6.9. Carbonates and organic anions are responsible for biochar alkalinity. The solubility of P will be higher at higher pH under reduced conditions (Vymazal and Kröpfelová, 2008) which may promote precipitation reactions with Ca, and Fe (Reddy et al., 1995; Leader et al., 2008; Mohammed & Shanshool, 2009). The pH of biochar decreases slightly as it ages partly due to the loss of cations and anions and partly due to the build-up or the organo mineral layer (Mukherjee et al., 2014).

3.4. Scanning electron microscopy (SEM)

SEM was used to examine the enriched biochar structure to identify elements comprising mineral phases on the surface. The structure of

the biochar substrates was compared before addition to the wetlands and 2 and 7 months after wetland treatment.

Fig. 3a shows an image of the biochar structure before introduction into the wetland. It reveals a porous structure that has a non-uniform coverage of minerals. Fig. S1A and C are SEM images of this specimen at higher resolution that reveal the complex phase structure of these chars as well as the distribution of mineral phases. P was associated with the presence of Fe oxides, as well as compounds rich in Mg, Al, Si, P, S and Ca. After immersion in the wetland for 2 months (Fig. 4A and B) there is higher density of coverage of minerals on the surface of the biochar. Fig. S2 shows that a layer of organic material has been adsorbed onto the biochar's surface and a range of minerals have either adsorbed or precipitated out onto this layer. After 7 months, the surfaces of the biochar have a thicker layer of organic compounds and, again, a more complex mineral structure. Fig. 4(C, F) indicates a larger concentration of N-bearing compounds and indicates that P is associated with compounds rich in Fe, S, Ca, Si, Al, and Mg.

3.5. Environmental implications

Results from the field study, suggests that enriched biochar can effectively bind nutrients from wastewater, and considerable amounts of both P and N were captured in this way. The retention of these elements is important for wastewater treatment and furthermore the capture of nutrients onto the enriched biochar substrate makes it of potential value as a fertiliser for soil enhancement. Nutrients captured from effluent using biochar have been found to be in a bioavailable form (Taghizadeh-Toosi et al., 2012; Streubel, 2011), however more research is required to establish its usefulness in this role. While some C was lost from the enriched biochar substrate during the study period the remaining C could promote long term C storage in the soil (Sarkhot et al., 2012).

After the capture of P and N by the enriched biochar substrate, it could potentially be removed and replaced with fresh substrate. It can also be regenerated by applying resting or drying periods. Drying oxidises Fe(II) to amorphous Fe(III) oxides, increasing P-sorption capacity (Drizo et al., 2002; Reddy et al., 1995). Drizo et al. (2002) found that after four weeks' resting period of a steel slag P-sorption substrate, 74% of its capacity was regained.

Biochar also has the potential to remediate contamination by immobilising inorganic pollutants (Beesley and Marmiroli, 2011; Beesley et al., 2011; Rineau and Ladygina, 2013). It can adsorb a range of heavy metals (Tong et al., 2011; Regmi et al., 2012; Lu et al., 2012; Liu et al., 2012) and has been used to immobilise cadmium in the soil

N-reduction in the wastewater because wetlands are generally efficient in removal of N through microbial activity. The efficiency for removal of $\text{PO}_4\text{-P}$ was considerably greater than for the control wetland, the latter exhibiting a diminishing removal rate towards the end of the monitoring period. By contrast, the enriched biochar substrate continued to remove and retain P, verified by elemental and surface analyses. The spent biochar could also be used as a fertiliser for soil enhancement and could have the potential to be regenerated and reused, but more research is required. More investigation is also required into bioavailability of nutrients on enriched biochar.

Conflict of interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecoena.2019.100005>.

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