Ecological Engineering 84 (2015) 559–568

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Synergism in nitrate and orthophosphate removal in subsurface bioreactors

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ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form 9 August 2015
Accepted 7 September 2015

Keywords:
Environment
Nutrient removal
Subsurface drainage
Water quality
Woodchips

ABSTRACT

Fertilizers replenish soil nutrients removed by crops and help in producing high yielding crops, but the overuse of these fertilizers can have a detrimental effect on the receiving waters. There is a need for better management practices and remediation techniques to reduce and potentially eliminate the transport of nutrients from agricultural lands. The objective of this study was to evaluate the removal of orthophosphate using an industrial waste (iron turnings) as well as examine the synergistic effects of using it in conjunction with a woodchip bioreactor known to have a high affinity for nitrate-N removal. A laboratory-scale column reactor was constructed using the iron-based material and woodchips as reactor media. Synergism was displayed as a result of alternating media arrangement with the observation of 25% higher reduction in nitrate-N concentrations, on average, as a result of interaction with woodchips when woodchips were downstream of steel turnings as opposed to upstream. This was also demonstrated in the orthophosphate results, where woodchips reduced orthophosphate concentrations by 8.54% on average when upstream of steel turnings, but yielded a net increase in orthophosphate concentration (23.8% of initial concentration on average) by converting bound phosphate back to orthophosphate when downstream of steel turnings. This led to a final experiment where the steel turnings were placed both upstream and downstream of woodchips. This confirmed earlier findings of enhanced nitrate-N removal by woodchips downstream of iron, while showing that the second iron section downstream of woodchips could once again remove orthophosphate from solution down to non-detectable concentrations.

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1. Introduction

The use of fertilizers to replace soil nutrients has helped to increase crop yields over the years but they are often applied in quantities in excess of crop uptake. This practice has led to a net increase in certain nutrient concentrations such as Nitrogen (N) and Phosphorus (P) in soils in many crop production areas throughout the world (Carpenter et al., 1998). Past studies have identified excess nutrients as being primarily responsible for the eutrophication of surface waters as well as the large hypoxic zone present in the Gulf of Mexico (Burkart and James, 1999; Alexander et al., 2008). Agricultural watersheds accounts for 70% of the total N and P delivered to receiving waters, with corn and soybean acres alone accounting for 52% of the total N delivered and 25% of the total P delivered in the Mississippi River Basin (Alexander et al., 2008). In the case of nitrogen, some derived compounds have also been shown to have adverse health effects on humans above certain concentrations (Manassaram et al., 2006).

Nitrate is the most common contaminant of groundwater in the United States and the world (Mueller and Helsel, 1996; Gurdak and Qi, 2012). The gently sloping, poorly drained soils throughout much of the intensely cultivated Midwestern United States has led to leaching and subsurface drainage being the predominate pathways for nitrate transport (Zhao et al., 2001). In the meantime, positively charged ammonium ions can become bound to soil particles and can be transported surface runoff to receiving waters as well (Dodds and Oakes, 2008). A wide range of results have been reported in case of P transport pathways, the dominant pathways being both surface and subsurface depending on site characteristics. The common consensus in the literature published over the past few decades was that P is predominately transported in surface runoff due to its low mobility in soils (Sharpley et al., 1993; Sims et al., 1998; Heathwaite and Dils, 2000; Hansen et al., 2002). Based on this belief, studies during this period were largely focused on quantifying P transport in surface runoff and neglected to investigate the subsurface

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http://dx.doi.org/10.1016/j.ecoleng.2015.09.051
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fraction of P transport (Sims et al., 1998; Hansen et al., 2002; Algoazany et al., 2007). However, Algoazany et al. (2007) reported that subsurface flow was the dominant transport pathway for soluble P in a flat tile-drained agricultural watershed in East Central Illinois.

The implementation of subsurface (tile) drainage has resulted in the increase in land productivity of poorly drained soils throughout the Midwestern United States and other parts of the world. However, the same practice has an adverse environmental effect on the receiving waters of tile drained agricultural lands (Skaggs et al., 1994; Shirmohammadi et al., 1995; Kladivko et al., 2001; Algoazany et al., 2007; Bhattarai et al., 2009). In case of the presence of subsurface drainage, wetlands and end of the pipe treatment approaches are most common best management practices (BMPs) in order to reduce nutrient transport from agricultural fields. Wetlands have been identified as an effective means of reducing nutrient concentrations and improving water quality from agricultural lands. A study by Kovacic et al. (2006) demonstrated that volume-weighted concentrations of nitrate-N in runoff were reduced by 42% and 31% in two wetlands and combined P mass retention was 53%. However, they also reported that 450 ha wetland needed to reduce N loading by 46% would cost about $3.5 million. Another study indicated that soil amendments must often be added to increase the sorption capacity of the soil in order to extend the wetlands effectiveness to remove soluble P (Ann et al., 2000). Although the implementation of a wetland is far less expensive compared to current water treatment plant nutrient removal methods, less expensive alternatives which do not remove land from agricultural production are desirable.

An outlet treatment approach is increasing in popularity for use as a subsurface drainage nutrient removal BMP. This method typically consists of a diversion structure which intercepts the subsurface drainage tile outlet and diverts flows through a filter media before the water enters the receiving water body. In contrast to wetlands, current designs of these systems are installed parallel to receiving streams and take little to no agricultural land out of production. Woodchips and other carbon containing substrates are used as filter media, which promote denitrification and have greatly reduced NO_3-N loads in several studies (Cooke et al., 2001; Greenan et al., 2006; Chun, 2007; Jaynes et al., 2008; Robertson and Merkley, 2009; Robertson, 2010; Woli et al., 2010; Christianson et al., 2012, 2013). However, the achievement of highly reduced NO_3-N loads has increased interest to investigate this method using other types of media to remove other nutrients and contaminants such as soluble P and pesticides. Few studies have explored industrial waste products as sorbents, generally containing large percentages of natural minerals such as calcium (Ca), aluminum (Al), and iron (Fe) in various forms for the removal of soluble P (McDowell et al., 2008; King et al., 2010; Penn et al., 2014). McDowell et al. (2008) observed 70% of reactive P removal by placing a mix of 90% melter slag and 10% basic slag (steel and energy industry by-products) in a porous mesh and locating it at the end of the tile drain. King et al. (2010) found that using a blend of clinoptilolite (a type of zeolite), alumina (aluminum oxide), and activated carbon reduced dissolved reactive P loads by an average of 51.6%. While such research has begun to address efficient and cost effective approaches for controlling contaminant release from tiled drained agricultural lands, the methods and materials are far from refined. For example, King et al. (2010) were able to cut dissolved reactive phosphorus loads in half but NO_3-N removal rates were negligible at 4.7% on average. Based on the results of earlier studies, the main objective of this study was to test the efficacy of combining an easily available industrial waste (steel by-product) with woodchips as subsurface bioreactor media for their ability to remove both nitrate and soluble P from the nutrient laden waters. The impact of media arrangement on nutrient removal was also investigated.

2. Materials and methods

2.1. Construction of column reactor

A laboratory-scale column reactor was constructed at the Agricultural Engineering Sciences Building located on the University of Illinois campus in Urbana, IL. The reactor was designed to test a steel turnings material for its capacity to remove soluble phosphorus from tile drainage water, while simultaneously examining the effect of the steel media on woodchip media used for nitrate removal. To allow for simultaneous experimental repetitions, the reactor consisted of four identically constructed horizontal PVC columns 0.15 m in diameter. Each column consisted of two sections, one a 1.33 m long section filled with steel turnings, and one a 5.69 m long section filled with woodchips. Material was secured in the columns by PVC plates with evenly distributed 28 holes with 1.91 cm diameter, covered by a non-reactive mesh at each end. Flow through the columns was regulated using a controlled drainage structure connected to a manifold, which diverted the flow equally and served as the inlet for each of the four columns. The outlet of each column consisted of a 5.08 cm diameter PVC pipe. The outlet pipe could be rotated to any angle to achieve any head difference from 0 to 1.52 m below the inlet water level to induce flow.

In order to test the effect of the steel turnings on the nitrate removal efficiency of the woodchips, two columns were positioned with the steel turnings section upstream of the woodchips section and two were placed with the steel turnings section downstream of the woodchips section. Sampling ports for collecting water samples were installed at the intersection of the steel turnings section and the woodchips section in each column. The ports were installed to allow for samples to be collected from the center of the flow profile by extending in to the center of the 0.10 m diameter PVC pipe that was used to adjoin the steel turnings and woodchips sections of each column. Fig. 1 shows a plan view of the reactor at its location at the Agricultural Engineering Sciences Building on the University of Illinois campus in Urbana, IL.

2.2. Collection and preparation of materials

Woodchips, steel turnings, and creek water were collected from local sources for use in the laboratory-scale column reactor study. The woodchips used in the study were collected from an existing field-scale bioreactor near Decatur, IL which had been in operation for three years. The woodchips in the bioreactor consisted of a random mixture from a municipal source in the Decatur, IL area. The woodchips were collected from the surface down to a depth of approximately 0.61 m. This depth was assumed to be deep enough to contain woodchips which had been previously inundated allowing for the establishment of denitrifying microorganisms. The woodchips were collected in plastic bins and transported back to the Agricultural Engineering Sciences Building on the University of Illinois campus where they were packed in to the PVC columns. The columns sections were vertically packed, to achieve an approximately uniform density throughout all of the columns.

The steel turnings material was collected from Clifford-Jacobs Forging Co. in Champaign, IL. The turnings were lightly coated with lubricating oil from the manufacturing process, so the turnings were washed in order to remove the oil. The process consisted of washing the savings in a solution of degreasing dish detergent and hot water, a rinse with hot water, and a final rinse with deionized (DI) water. The washed turnings were vertically packed into each of the columns at approximately the same density as woodchips.

Creek water used during the column reactor experiments was collected from a location near the University of Illinois campus in Urbana, IL on Embarras River. This location for creek water collection was the same one used for similar laboratory scale

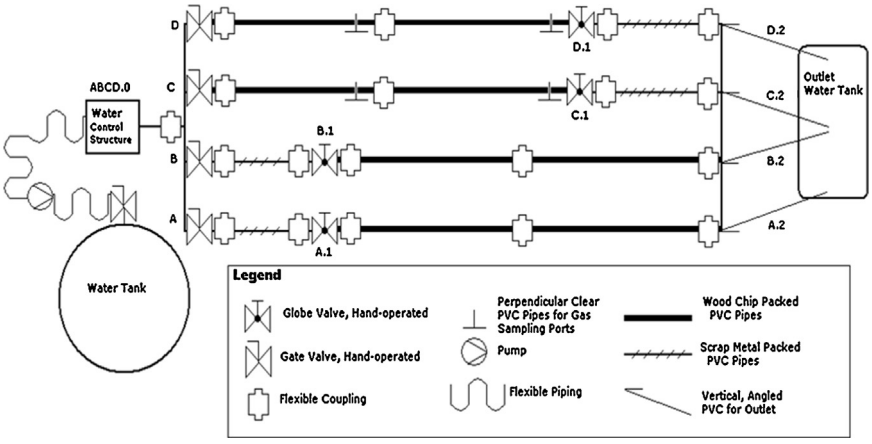

Fig. 1. Plan view of column reactor (locations A, B, C, and D: before bioreactor; A.1 and B.1: after steel turnings; A.2 and B.2: after steel turnings + woodchips; C.1 and D.1: after woodchips; C.2 and D.2: after woodchips + steel turnings).

column experiments conducted by Chun (2007). The drainage area at this location is about 40 square mile and nitrate concentration of the collected creek water varied from below the detection limit 0.07 mg/L to 2 mg/L. This lower nitrate concentration may be explained by considering that the creek receives urban runoff which then passes through a stilling pond just upstream of the abstraction point (Chun, 2007). The use of stream water instead of tile water has been recommended by Blowes et al. (1994) where they found that the chemical components of stream water very closely resembled those of tile water in their study.

2.3. Characterization of materials

Effective porosity and bulk density (dry basis) of filter media (woodchips and steel turnings) were measured in order to better characterize the material used in these experiments. The effective porosity was determined on a mass basis while the materials were compacted to densities representative of the media during the experiments. It was measured by placing the two different materials in containers of known volume and measuring the net increase in mass after enough water was added to the container to fully inundate the material. The volume of water added was then calculated using a density of 1.0 g/cm^3 and ratio of this volume to the total volume of the material and water was used to calculate the effective porosity.

Bulk density (dry basis) was also measured for both materials. This was done by packing the materials (to densities approximating those used during the experiments) into containers of known mass and volume, drying the materials in an oven at 140 °C for 24 h, and then weighing the materials. The results of these measurements can be seen in Table 1.

Size distribution of the materials was not physically measured, but can be observed in Fig. 2. The general distribution based on observation ranged from approximately 0.25–10 cm for the woodchips and 0.5–3 cm for the steel turnings. The woodchips were of varying thickness and length, while the steel turnings tended to be more uniform and generally shaped like a ribbon.

Table 1
Bulk density and effective porosity of steel turnings and woodchips.

Parameters	Steel turnings	Woodchips
Material characteristics		
Bulk density (g/cm^3)	0.988	0.200
Effective porosity (%)	89.3	54.5

2.4. Calibration of columns

The columns were calibrated before conducting the actual experiment. The calibration procedure consisted of collecting volumetric flow measurements from the outlet of each column and surveying the established inlet and outlet height corresponding to each flow rate measurement taken. Three different flow rates were used. The effective hydraulic conductivity (K_e) values for each column were solved for according to Darcy's equation:

$$K_e = \frac{Q}{A} \cdot \frac{L}{\Delta H}$$

where: K_e, effective hydraulic conductivity (L/T); Q, flow (L^3/T); A, area (L^2); L, column length (L); ΔH, head difference (L).

The effective hydraulic conductivity (K_e) values found during the calibration are listed in Table 2. With the exception of Column B, conductivity values were consistent across columns, with average values of 3.101 cm/s, 3.014 cm/s, and 2.573 cm/s for columns A, C, and D, respectively. Column B had the lowest average conductivity, 1.149 cm/s, which indicated that the woodchips were packed tighter in this column. However, due to the ability to vary outlet elevation for each column, flow rate for the columns could be independently adjusted to achieve similar retention times between columns.

2.5. Column reactor experiments

Before the beginning of the experiment, approximately 400 L of stream water was used to flush and initialize the columns. At the start of each experiment, approximately 1600 L of stream water was spiked with the appropriate amount of KH_2PO_4 and $KHNO_3$ to produce an approximate 5 mg-P/L and 12 mg-N/L solution. This solution was then pumped by an electric pump into the controlled drainage structure that served as a constant head device and the inlet for the manifold connected each of the four column reactors. The overflow from the constant head device was allowed to spill back into the holding tank, continuously mixing the solution.

At the beginning of the experiment, an initial water sample and water quality parameters were collected from the holding tank. During each experimental run, two consecutive 30 mL water samples were collected from the inlet, the sampling port at the intersection, and the outlet of each column. One sample was vacuum filtered by a 0.45 μm filter and stored at 4 °C and analyzed for ortho-phosphorus according to EPA Method 365.1 (USEPA, 1993a) and another one was treated with concentrated sulfuric acid (0.25 mL) and stored at 4 °C and analyzed for nitrate-N according to EPA Method 353.2 (USEPA, 1993b). In addition to the collection of

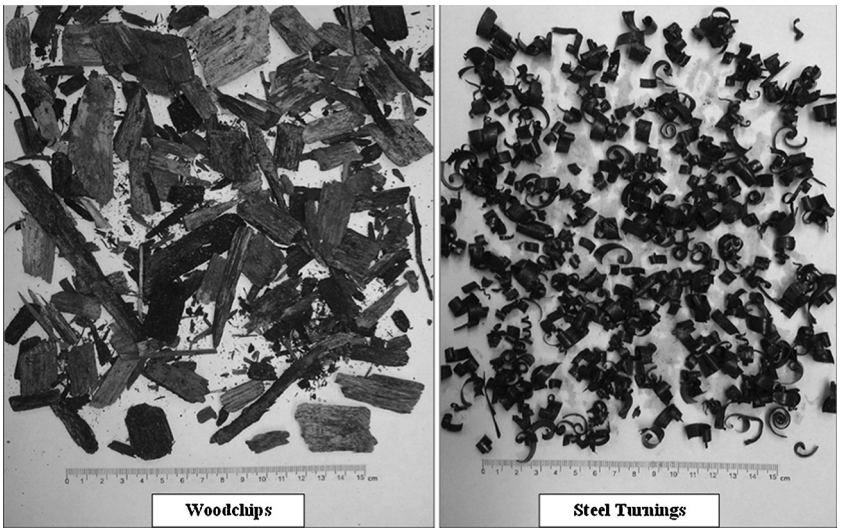

Fig. 2. Size distribution of woodchips and steel turnings.

Table 2
Effective hydraulic conductivity values listed per column for three different flows.

	K_e 1 (cm/s)	K_e 2 (cm/s)	K_e 3 (cm/s)	Average K_e (cm/s)
Column A	3.023	3.309	2.972	3.101 ± 0.182
Column B	1.505	1.120	0.823	1.149 ± 0.342
Column C	2.628	3.159	3.255	3.014 ± 0.338
Column D	2.318	2.643	2.757	2.573 ± 0.228

water samples for soluble phosphorus and nitrate nitrogen analysis, water quality parameters including dissolved oxygen (DO), hydrogen ion concentration (pH), and temperature were measured using a Hach Quanta multi-parameter water quality probe. The probe was calibrated according to manufacturer procedures prior to every experiment (Hydrolab, 2002). Volumetric flow measurements were also taken on every 4 h interval using a graduated bucket and stop watch. The outlet elevations for each column were adjusted, if needed, to maintain an approximately constant flow throughout the experiment.

During the experiment, samples were collected every 4 h for a span of 28 h. For the first set of experiments (experiment 1), columns A and B were replicates of each other and had the same media configuration (steel turnings upstream and woodchips downstream) and columns C and D were also replicates of each other and had the same media configuration (woodchips upstream and steel turnings downstream). Second set of experiments (experiment 2) were also conducted which had the similar media setup as experiment 1 but with a slightly higher flow rate and smaller retention time. During third set of experiment (experiment 3), a different experimental setup and procedure was implemented. The steel turnings sections from columns A and B were moved to the upstream ends of columns C and D to provide steel turnings on both the upstream and downstream ends of the woodchip column. For this experimental trial, only columns C and D were tested. Due to the extra steel turnings material placed at the outlets of columns C and D, the flow rates were increased by approximately 30% more than the flow rates observed in experiments 1 and 2. During this trial, water samples were collected at the inlet, intersections where media changed, and at the outlet.

3. Results and discussion

3.1. Column experiments 1 and 2

The setup for column experiments 1 and 2 were similar but slightly higher flow rate was used in experiment 2 compared to experiment 1. For experiment 1, the 4-h and 8-h time samples were not included in the calculation due to insufficient time for the nutrients to reach the outlet based on the calculated retention times. For the same reason, the 4-h time samples were not included in the calculation in experiment 2. While computing nutrient reduction, the results from columns A and B and the results from columns C and D were averaged as those columns had the same media configuration. Table 3 represents the average changes in orthophosphate and nitrate concentration leaving each treatment section for two different media arrangements.

3.1.1. Orthophosphate results

Significant changes in the orthophosphate concentrations were observed as a result of passing the nutrient spiked influent through the woodchip and steel turnings sections of the column reactors in experiment 1. It was observed that there was an average reduction of 95.6% (from 4.36 to 0.19 mg/L PO_4) in orthophosphate concentration after water was passed through the steel turnings section of the column reactor throughout the duration of the experiment. However, subsequent passage of the water through the woodchip section of the reactor resulted in a significant increase (to over 50% of the initial influent concentration in some cases) in orthophosphate concentration, giving a mean concentration at the outlet of the two sections of 2.30 mg/L PO_4. The results from the alternate media arrangement (woodchips upstream and steel turnings downstream) were somewhat different than those occurring from media arrangement in columns A and B. The woodchips sections in these columns seemed to have little effect on the orthophosphate concentration with an average reduction of 4.6% (from 4.36 to 4.16 mg/L PO_4), while the steel turnings section again greatly reduced orthophosphate remaining in solution by an average of 98.6% (average reduction from 4.16 to 0.06 mg/L PO_4).

The orthophosphate results from experiment 2 were very similar to those observed in experiment 1 among both media arrangements. For the media arrangement where steel turnings were upstream of woodchips, the average reduction in

Table 3
Measured orthophosphate and nitrate concentrations for experiments 1 and 2.

Setup		Steel turnings upstream of woodchips (A and B)			Woodchips upstream of steel turnings (C and D)		
Location		Initial	After steel turnings	After steel turnings + woodchips	Initial	After wood chips	After woodchips + steel turnings
PO_4 (mg/L)	Exp 1	4.36 ± 0.15	0.19 ± 0.11	2.30 ± 1.18	4.36 ± 0.15	4.16 ± 0.16	0.06 ± 0.03
	Exp 2	4.70 ± 0.38	0.02 ± 0.04	0.57 ± 0.33	4.70 ± 0.38	4.09 ± 0.6	0.00 ± 0.00
NO_3 (mg/L)	Exp 1	12.59 ± 0.53	12.16 ± 0.43	1.36 ± 0.97	12.59 ± 0.53	6.97 ± 1.11	3.70 ± 1.30
	Exp 2	12.23 ± 0.51	11.99 ± 0.72	2.29 ± 1.73	12.23 ± 0.51	5.58 ± 1.57	4.61 ± 2.54

orthophosphate concentration after passage through steel turnings was 99.6% (from 4.70 to 0.02 mg/L PO_4). However, orthophosphate removal rate decreased to 87.9% (from 4.70 to 0.57 mg/L PO_4) of original values after subsequent passage through the woodchips. This result was very similar to the result for this media arrangement on orthophosphate concentration in solution from experiment 1. The results from the alternate media arrangement of woodchips upstream of steel turnings on orthophosphate concentration very closely mimicked the results of experiment 1. In this experiment, orthophosphate reduction was just 13.0% (from 4.70 to 4.09 mg/L PO_4) after passage through woodchips. However, orthophosphate reduction efficiency increased to 100% after subsequent passage through steel turnings. These results indicated that steel turnings were the primary media responsible for orthophosphate removal as high reduction in orthophosphate levels were observed as the nutrient solution passed through the media during the experiments 1 and 2.

3.1.2. Nitrate results

Significant changes in nitrate concentration were also observed in the influent water as a result of passage through the woodchip and steel turnings sections of the column reactor for both media arrangements in experiment 1. It was observed that the steel turnings section upstream of woodchips had essentially no effect on the concentration of nitrate remaining in solution (average reduction of 3.4%), but nitrate concentration leaving the woodchip section was reduced by an average of 88.8% (from 12.16 to 1.36 mg/L NO_3) over the course of the experiment. Nitrate concentrations in water leaving the woodchip sections of columns with woodchips upstream of steels turnings, however, only resulted in an average reduction of 44.6% (from 12.59 to 6.97 mg/L NO_3). Also, nitrate concentrations leaving steel turnings sections following woodchip sections showed further reduction for a total overall reduction of 70.6% (from 12.59 to 3.70 mg/L NO_3) for this media arrangement.

The nitrate results for experiment 2 were similar to those observed during experiment 1. For the media arrangement where steel turnings were upstream of woodchips, the nitrate concentration after passage through steel turnings was essentially unchanged. However, after subsequent passage through woodchips, the nitrate concentration was reduced by 80.9% (from 11.99 to 2.29 mg/L NO_3). The alternate media arrangement also yielded nearly the same results as experiment 1, with the exception of the reduction in nitrate from steel turnings. Woodchips upstream of steel turnings resulted in a reduction in nitrate concentration of 54.4% (from 12.23 to 5.58 mg/L NO_3) of original concentration after passage through the woodchips, yet only an additional reduction of 17.4% (from 5.58 to 4.61 mg/L NO_3) after passage through steel turnings. Based on these observations, it can be inferred that woodchips were the primary media responsible for nitrate removal as high reduction in nitrate levels were observed as the nutrient solution passed through the media during the experiments 1 and 2.

3.1.3. Flow and retention times

Table 4 represents the measured flow rate and retention time for each treatment section for two different media arrangements for experiments 1 and 2. Flow rates and associated retention times for experiment 1 were comparable for columns that had the same media arrangement (A comparable to B and C comparable to D), but some variation was observed in columns with different media arrangements (A compared to C or D, or B compared to C or D). The average flow rates for columns A and B (steel turnings upstream of woodchips) throughout the experiment 1 were 2.52 mL/s and 1.85 mL/s with associated average retention times of 6.69 h and 8.82 h for woodchip sections and 2.54 h and 3.35 h for steel turning sections, respectively. Flow rates were higher but the retention times were smaller for columns C and D compared to columns A and B. Columns C and D had average flow rates of 3.56 mL/s and 2.99 mL/s and associated average retention times of 4.45 h and 5.25 h for woodchip sections and 1.69 h and 2.00 h for steel turning sections, respectively. From examining the measured flow rate data, it can be determined that there were differences in parameters in both columns for each media arrangement and placing the steel turnings section upstream of the woodchip section significantly slowed flow rate, therefore increasing associated retention times. Although these differences in flow rate between columns with different media arrangements did not have a noticeable effect on the orthophosphate data, it can be interpreted that the retardations in flow rate likely reflect some of the variations observed in

Table 4
Flow rate and retention time for woodchips and steel turnings media during experiments 1 and 2.

Experiment No.	Column	Flow rate (mL/s)	Retention time (h)	
			Woodchips	Steel turnings
1	A	2.52 ± 1.23	6.69 ± 2.18	2.54 ± 0.83
	B	1.85 ± 0.61	8.82 ± 2.13	3.35 ± 0.81
	C	3.56 ± 0.49	4.45 ± 0.59	1.69 ± 0.23
	D	2.99 ± 0.19	5.25 ± 0.33	2.00 ± 0.13
2	A	3.12 ± 0.81	5.15 ± 0.89	1.96 ± 0.34
	B	2.43 ± 0.31	5.91 ± 1.08	2.24 ± 0.41
	C	3.79 ± 0.58	4.30 ± 036	1.63 ± 0.14
	D	3.75 ± 0.66	4.32 ± 0.54	1.64 ± 0.20

Table 5
Measured temperature, dissolved oxygen (DO) and pH concentrations for experiments 1 and 2.

Setup		Steel turnings upstream of woodchips (A and B)			Woodchips upstream of steel turnings (C and D)		
Location		Initial	After steel turnings	After steel turnings + woodchips	Initial	After wood chips	After woodchips + steel turnings
Temp. (°C)	Exp 1	24.3 ± 0.53	20.7 ± 2.1	20.3 ± 4.1	24.3 ± 0.53	20.5 ± 3.5	20.3 ± 4.2
	Exp 2	22.5 ± 2.4	19.9 ± 2.6	19.9 ± 4.7	22.5 ± 2.4	19.6 ± 4.2	19.9 ± 4.7
DO	Exp 1	11.75 ± 1.76	2.38 ± 0.72	4.28 ± 0.66	11.75 ± 1.76	2.12 ± 0.45	3.50 ± 0.91
	Exp 2	12.39 ± 1.27	3.29 ± 0.58	5.22 ± 1.28	12.39 ± 1.27	2.41 ± 0.47	3.95 ± 1.45
pH	Exp 1	8.24 ± 0.17	8.34 ± 0.20	7.14 ± 0.31	8.24 ± 0.17	7.31 ± 0.30	7.35 ± 0.15
	Exp 2	7.92 ± 0.28	8.04 ± 0.22	7.00 ± 0.20	7.92 ± 0.28	6.91 ± 0.21	7.08 ± 0.20

the nitrate data due to longer associated retention times in columns A and B.

For experiment 2, flow and associated retention times were slightly higher compared to experiment 1. In general, the flow rates and associated retention times for each media showed the same trends as observed in experiment 1. The average flow rates for columns A and B (steel turnings upstream of woodchips) throughout the experiment were 3.12 mL/s and 2.43 mL/s with associated average retention times of 5.15 h and 5.91 h for woodchip sections and 1.96 h and 2.24 h for steel turning sections, respectively. Flow rates were higher but the retention times were smaller for columns C and D compared to columns A and B. Columns C and D had average flow rates of 3.79 mL/s and 3.75 mL/s and associated average retention times of 4.30 h and 4.32 h for woodchip sections and 1.63 h and 1.64 h for steel turning sections, respectively. Columns with media arrangements where steel turnings were placed upstream of woodchips (columns A and B) tended to have retarded flow rates, which in turn caused longer associated retention times for the media. However, this was less pronounced during experiment 2 than experiment 1 due to the more consistent adjustment of outlet elevation to produce similar flow rates among columns during experiment 2.

3.1.4. Temperature, dissolved oxygen, and pH variations

Measured temperature, dissolved oxygen and pH for each treatment section for two different media arrangements for experiments 1 and 2 is presented in Table 5. No change in water temperature was observed between woodchips sections and steel turnings sections across either media arrangement during experiment 1. Inlet temperatures tended to be higher throughout the experiment, but this is likely do to heat exchange with the supply pump as water was circulated before entering the columns. The DO values displayed the general trend of decreasing significantly (from 11.75% to 2.25% DO on average) after passage through the first treatment section, regardless of media type (woodchips or steel turnings), and then slightly increasing (from 2.25% to 3.89% DO on average) after passage through the second treatment section, again irrespective of media type. The pH results generally showed that pH is only affected by the woodchips sections. For both media arrangements, the water became more acidic (from pH 8.29 to 7.22 on average) after passage through the woodchip section and essentially remained unchanged by the steel turnings. A slight increase in pH was also observed throughout the course of the experiment (approximately 0.5) and was observed at all locations sampled, irrespective of treatment or media arrangement.

Similar to experiment 1, the temperature data collected throughout experiment 2 did not illustrate any significant changes in varying media sections. The only significant observation was that the inlet temperature remained warmer throughout most of the experiment, which can be attributed to the heat exchange between the water and pump at the inlet prior to the water entering the treatment sections. The dissolved oxygen data collected during experiment 2 again displayed the same trends observed during experiment 1. There was a significant decrease in DO (from 12.39% to 2.85% DO on average) after water was passed through the first treatment section (regardless of material) and a subsequent increase (from 2.85% to 4.58% DO on average) after passage through the second treatment section (also regardless of treatment material). The pH data collected during this experiment also displayed the same trends observed during earlier one. In general, pH values were lowered by nearly one (from pH of 7.98 to 7.04 on average) by woodchip sections and slightly increased by steel turnings sections (by 0.14 on average). Just as in experiment 1, an overall increase (of approximately 0.5) was observed in pH at all locations sampled over the course of the experiment.

3.2. Column experiment 3

Results for the samples collected for first 4 h were not included due to insufficient time for the nutrients to reach the outlet based on the calculated retention times.

3.2.1. Orthophosphate results

The orthophosphate results from this experiment displayed the same trends observed in both experiments 1 and 2. Flow through the steel turnings treatment section upstream of woodchips again yielded about 96.9% reduction (from 4.68 to 0.14 mg/L PO_4) in the orthophosphate concentration. However, the orthophosphate concentration increased to a 0.59 mg/L PO_4 after water passed through the woodchip treatment section. The second steel turnings treatment section, downstream of the woodchip treatment section, was able to remove the orthophosphate from solution producing an average outlet concentration of 0.02 mg/L PO_4. In overall, this system was able to remove 99.5% orthophosphate concentration.

3.2.2. Nitrate results

The nitrate data collected during experiment three again displayed the same overall trends observed during the first two experiments. The nitrate concentration changed by only 2.6% (from 11.56 to 11.26 mg/L NO_3) as the water passed through the upstream steel turnings. However, samples collected at the end of woodchips treatment section displayed a reduction of nearly 62% (from 11.56 to 4.39 mg/L NO_3) in nitrate concentration. The nitrate concentration leaving the final steel turnings section downstream of the woodchip section was reduced by an additional 22.8% (from 4.39 to 3.39 mg/L NO_3). In overall, this system was able to remove 70.7% nitrate concentration.

3.2.3. Flow and retention times

In general, the flow rates were maintained slightly higher than in earlier experiments, implying shorter retention times for the treatment sections. However, since a second steel turnings section was added during these experiments, the retention times for steel turnings were doubled. For the two columns used in this experiment,

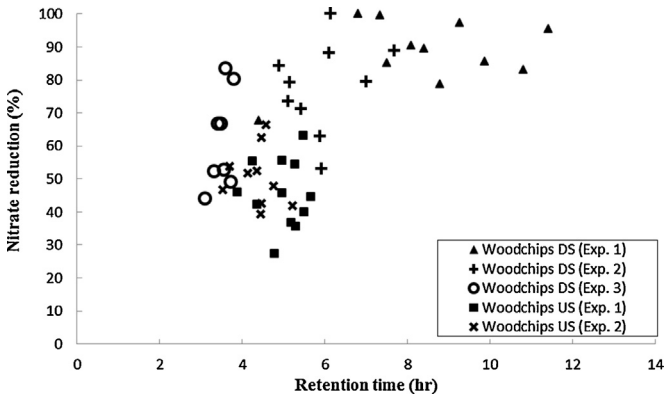

Fig. 3. Relationship between nitrate reduction and retention time at the outlet of woodchip sections for both media arrangements tested (upstream and downstream denoted US and DS, respectively, in the figure legend).

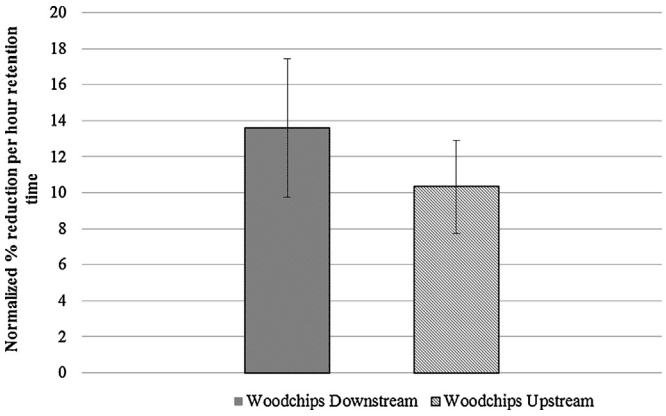

Fig. 4. Mean normalized percent reduction of nitrate for both woodchips upstream and downstream of steel turnings (error bars representing standard deviations, $n = 30$ with $p = 0.008$).

the average flow rates of 4.03 mL/s and 4.38 mL/s and associated average retention times of 3.62 h and 3.47 h for woodchip sections and 2.82 h and 2.98 h for steel turning sections, respectively. Throughout the course of the experiment flow rates were also adjusted more consistently to achieve approximately steady state conditions.

3.2.4. Temperature, dissolved oxygen, and pH variations

In general, the inlet temperature was higher, again likely due to heat exchange between the water and pump, and there was little difference observed between the other locations throughout time. An overall decrease in temperature occurred, but was likely a result of the ambient air temperature.

The dissolved oxygen values throughout this experiment displayed trends that closely followed the results from first two experiments. After water was passed through the first treatment section, the dissolved oxygen concentration was lowered significantly from 12.32% to 2.62% DO on average. The DO level remained almost constant (2.30% DO) as the water passed through the second and third section. A slight increase in DO was observed in some samples collected at the outlet, but this trend was not consistent throughout time.

The measured pH level at the inlet, end of upstream steel turnings section, woodchips section and downstream steel turnings section were 7.86, 7.54, 6.98, and 7.02, respectively, on average. The trend observed for pH closely resembled the results from the previous two experiments. However, in this experiment, pH was not increased but slightly reduced by upstream most steel turnings section as it was observed in previous experiments. Conversely, woodchips did have the same effect on the pH as it consistently lowered pH by approximately 0.9 compared to inlet level. The downstream steel turnings displayed no effect on pH, as in previous experiments.

3.3. Synergistic effects

3.3.1. Difference in nitrate reduction

The plot of nitrate reduction as a function of retention time is presented in Fig. 3. Although there is high variability in the data, it can be observed that longer retention times tend to be associated with greater reduction. This observation is consistent with results presented by Chun (2007) from a similar woodchip column experiment where he used similar initial concentrations. Chun (2007) reported that a retention time of approximately 12 h was needed to completely reduce nitrate at these initial starting concentrations. It can also be observed in Fig. 3 that the removal efficiencies for the media arrangement of woodchips downstream of iron (approximately 45–85% removal) were generally greater than woodchips upstream of iron (approximately 25–65% removal) for the retention time ranging from 3 to 6 h.

While the plot depicts all samples taken from the outlet of woodchip sections across all experiments, there is a distinct difference in the distributions of samples collected from woodchip sections downstream of steel turnings as compared to upstream. When examining samples collected from woodchip sections upstream of steel turnings sections, the range of retention times and amount of reduction was much less variable. Although this is not true in all cases, these samples also tended to result in lower reductions when compared with samples having similar retention times collected from woodchip sections downstream of steel turnings sections. From this evidence, it can be speculated that iron may play an important role in the denitrification process within the woodchip sections. However, it remains unclear as to the dynamics behind the observation of this effect.

Although the specific processes at work behind this observation could not be determined, differences in the data populations were compared. Although woodchips upstream of steel turnings were not subjected to higher retention time (>6 h) compared to downstream of steel turnings, normalizing the percent reduction results of the two experimental conditions by the retention time allowed for the comparison of the means of these two conditions without consideration of the factor of retention time using a student's *t*-test (Fig. 4). This resulted in the rejection of the null hypothesis of the two sample means being equal at the 99% confidence interval ($p = 0.008$) indicating a significant difference among sample means.

3.3.2. Orthophosphate reduction by iron

The plot of orthophosphorus reduction as a function of retention time is presented in Fig. 5. It was observed there was high variability in the data and longer retention times did not result in greater reduction. The orthophosphate reduction rate in steel turnings was higher and the variation in retention time was smaller compared to nitrate reduction in woodchips. This was due to very low concentrations of orthophosphate remaining in solution after passing through the steel turnings. Similarly, pre-rusting of the turnings in the column experiments from the wash process and calibration runs likely initiated the oxidation of the steel turnings prior to the start of the experiments, allowing iron-oxide to react with the orthophosphate. This is supported by the findings of Boujelben et al. (2008) with iron oxide coated sorbents, where they observed equilibrium to be reached after time periods of just 15–60 min of contact time. While the plot depicts all samples taken from the outlet of steel turnings sections across all experiments, there is a

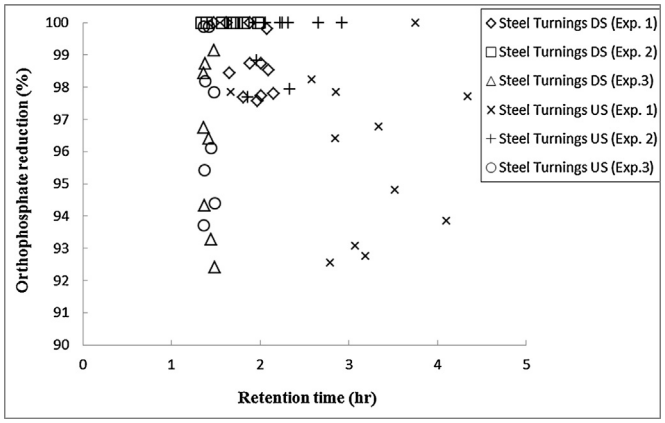

Fig. 5. Relationship between orthophosphate reduction and retention time at the outlet of steel turning sections for both media arrangements tested (upstream and downstream denoted US and DS, respectively, in the figure legend).

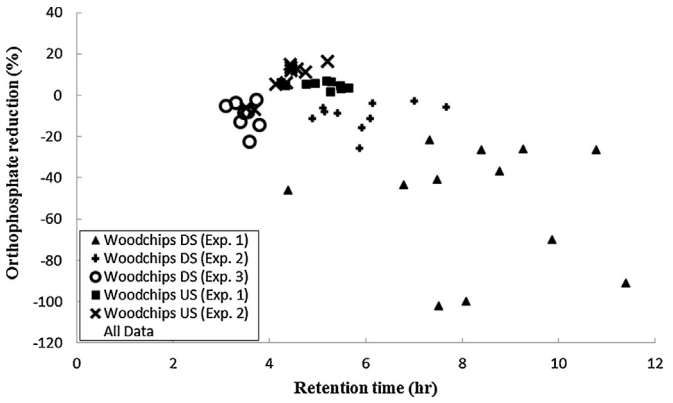

Fig. 7. Relationship between orthophosphate reduction and retention time at the outlet of woodchip sections for both media arrangements tested (upstream and downstream denoted US and DS, respectively, in the figure legend and negative percent reductions indicate a net increase in orthophosphate concentration).

distinct difference in the distributions of samples collected from steel turning sections downstream of woodchips as compared to upstream. When examining samples collected from steel turnings sections upstream of woodchips sections, the range of retention times was much more variable compared to downstream of woodchips section.

Normalizing the percent reduction results of the two experimental conditions (steel turnings upstream or downstream of woodchips) by the retention time allowed for the comparison of the means of these two conditions without consideration of the factor of retention time using a student's *t*-test (Fig. 6). This resulted in the rejection of the null hypothesis of the two sample means being equal at the 99% confidence interval ($p = 0.00023$) indicating a significant difference among sample means.

3.3.3. Release of orthophosphate

Although the reductions in orthophosphate concentrations leaving steel turnings sections were very high for all experimental runs, the subsequent passage of water through woodchip sections resulted in elevated orthophosphate concentrations. This effect was observed to a varying degree among experiments resulting in 10–52% increase in orthophosphate concentrations. It was noticed that greater retention times also tended to result in a greater release of orthophosphate (Fig. 7). While the specific reason behind the release cannot be determined from these experiments, a possible explanation is offered by the observation of orthophosphate release from iron oxides under prolonged anaerobic conditions in inundated paddy rice fields. Under these conditions, it was found that iron in these complexes can be reduced from Fe^{3+} to Fe^{2+}, making the iron–phosphate complex more soluble, causing the release of phosphorus into solution (Brady and Weil, 2002). This is said to happen as a result of siderophores, whose purpose is to solubilize Fe^{3+}, making it available for uptake by the organism (Sylvia et al., 2005). Sylvia et al. (2005) also notes that the chelation of Fe^{3+} by siderophores from iron phosphate minerals can result in the liberation of orthophosphate. Although there are obvious differences in the experimental conditions in this research as compared to that presented in the literature, the two most critical elements being the state of prolonged anaerobic conditions and mechanisms by which the orthophosphate was previously bound are similar.

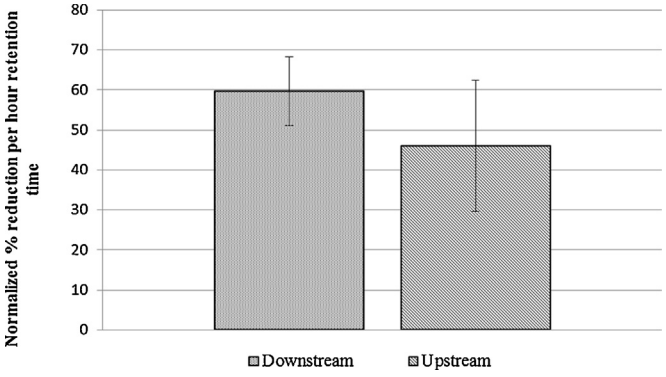

Fig. 6. Mean normalized percent reduction of orthophosphate for both steel turnings upstream and downstream of woodchips (error bars representing standard deviations, $n = 30$ with $p = 0.00023$).

The release of orthophosphate leaving woodchip sections also gives insight into the dynamics of how orthophosphate reacts with iron-oxide. Since elevated orthophosphate concentrations were observed downstream of woodchip sections, orthophosphate ions bonded with iron-oxide particles and remained in solution rather than being bound to iron-oxides residing on the surface of the elemental iron or forming iron–phosphate precipitates that settle out of solution. Based on these observations, it can be proposed that the iron–phosphates formed under these experimental conditions (i.e., subsequent reactor sections tested at these flow rates) remained in solution and were transported into woodchip sections where the orthophosphate was unbound from the iron oxide, releasing orthophosphate back into solution.

The arrangement of woodchips upstream of steel turnings yielded a reduction in the orthophosphate concentration in most cases (Fig. 7). This reduction was in the range of 5–15%. It was speculated that this reduction was likely the result of immobilization of the inorganic orthophosphate to the organic form due to the high carbon to phosphorus (C:P) ratio in the woodchip sections of the columns. Brady and Weil (2002) suggested that immobilization of orthophosphate can occur in soils when C:P ratios become greater than 300:1. The C:P ratio in these experiments was found to be much greater, due to the vastly greater C:P ratio within wood as opposed to most soils (Romero et al., 2005). Even considering that this ratio is dampened because of the relatively low surface area to mass ratio of the woodchips as compared to soils, an availability of only 2% of carbon content in the woodchips surpasses this ratio given these experimental conditions. It should be noted, however, that Romero et al. (2005) observed a release of total phosphorus in the first few months of wood decay, but this was followed by a gross uptake of total phosphorus between years 1 and 2 of their study. This further support the findings of this research, given that the source of wood for this experiment was an existing bio-reactor, established for a period greater than 1 year.

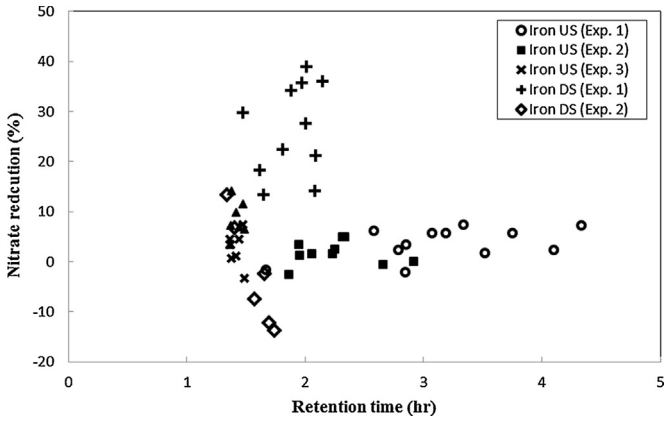

Fig. 8. Relationship between nitrate reduction and retention time at the outlet of steel turnings sections for both media arrangements tested (upstream and downstream denoted US and DS, respectively, in the figure legend and negative percent reductions indicate a net increase in nitrate-N concentration).

3.3.4. *Reduction of nitrate by steel turnings*

Although the primary focus of using iron media in this research was to identify its potential to bind orthophosphate, the design of these experiments simultaneously allowed the testing of the effect on nitrate concentration. When examining this effect, the steel turnings were found to reduce nitrate concentrations from approximately −14% (negative percentages representing higher nitrate concentrations leaving than entering that section) to nearly 39% (Fig. 8). Greater reductions were more prevalent in iron sections that were downstream of woodchip sections, with the exception of some negative values observed during experiment two. The observed reductions were also somewhat variable and reduction did not appear to be directly linked to retention time.

Although the use of iron media to remove nitrate in bioreactor is not a common practice, it has been utilized to remove nitrate from wastewater. Hao et al. (2005) examined the ability of the scrap iron filings (SIF) to remove nitrate from solution in a batch study. They found that up to 80% nitrate removal could be achieved under conditions of low initial pH (2.5) and SIF dosage of 100 g/L in a period of 4 h. They observed that initial pH was inversely proportional to nitrate reduction and less than 10% reduction to occur at an initial pH of 4.0 but pH drastically increased shortly after the start of the experiment (up to 6.2 at initial pH of 2.5). Cheng et al. (1997) found that this reaction nearly stopped at a pH of 8.8. Although the conditions in these experiments are not considered optimal for this reaction to occur, the ranges of pH (approximately 6.75–8.5) and relatively low DO (approximately 2–6%) fall within the ranges known to promote this reaction and iron dosage was nearly 10 times greater (988 g/L) in this experiment. These non-optimal conditions can also account for the wide variability in ranges of nitrate reduction observed.

4. Conclusion

Three laboratory-scale column experiments were conducted to examine changes in orthophosphate and nitrate concentrations as a result of interaction with woodchip and iron media. The synergistic effects on nutrient removal ability of each media were also tested by alternating media arrangements among columns during each experiment. This allowed for the observation of previously untested interaction scenarios using this type of remediation media. Water quality parameters including temperature, pH, and dissolved oxygen were also collected and used as indicators of the biological and chemical processes responsible for observed changes in soluble nutrient concentrations.

It was observed that woodchips media was primarily responsible for nitrate reduction while iron turnings media was responsible for orthophosphate removal from nutrient solution. The high levels of reductions of orthophosphate (more than 90% in all the cases) achieved as a result of interaction with the chosen iron media validated the choice of this iron material for use in these column trials. It was also observed that there was a slight difference in orthophosphate reductions from interaction with iron as a result of alternating media configuration. Iron section downstream of woodchips seemed to have slightly higher orthophosphate removal efficiency compared to the upstream. Data from experiments 1 and 2 reflected that this media configuration (the woodchip then steel turnings) provided 28–65% N removal at relatively short retention time and near complete P removal. Similarly, higher levels of nitrate reduction were found in woodchip sections downstream of iron sections as opposed to upstream.

Although the synergistic effects of media arrangement suggested opposite arrangements were preferred for the reduction of either orthophosphate or nitrate concentrations but not both. These effects were overcome by placing iron both upstream and downstream of woodchips as tested in experiment three. This arrangement confirmed the findings from experiments one and two, of enhanced nitrate removal in woodchips downstream of iron, as well as demonstrating that orthophosphate released by woodchip sections downstream of iron could be removed by the downstream iron section a second time. From these findings it can be concluded that the media arrangement of iron sections both upstream and downstream of woodchips is favorable for the enhanced removal of both orthophosphate and nitrate. The media arrangement may also depend upon targeted water quality efforts (e.g., N vs. P TMDL in a watershed).

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