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Removal of phosphorus from agricultural subsurface drainage water with woodchip and mixed-media bioreactors

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Abstract: Woodchip bioreactors that stimulate denitrification are proposed to reduce nitrogen (N) loads emanating from subsurface agricultural drainage. However, agricultural drainage water contains both N and phosphorus (P), frequently in concentrations exceeding environmental criteria. A mixed-media bioreactor containing woodchips plus reactive media that binds soluble P could concurrently lower both N and P loads in subsurface agricultural drainage. This study evaluated the P concentration and load reductions achieved with woodchip and mixed-media bioreactors in full-scale field installations in the cold, humid climate of Quebec, Canada, during a three-year period. Bioreactors contained either woodchips-only or woodchips plus an activated alumina/gravel mixture (mixed media). Total P, particulate P, soluble P, soluble reactive P, and soluble organic P concentrations and loads for the bioreactor influents and effluents were assessed weekly and also following >10 mm rainfall events. In the first two months of operation, both woodchips-only and mixed-media bioreactors released P but became either a negligible source or net sink for P retention within the first year of operation. While the mixed-media bioreactor had 9% lower total P concentration and about 19 times greater reduction in total P load than woodchips-only bioreactors during the study period, the total P concentration was not reduced to the critical environmental threshold level of 0.03 mg L^{-1} with either bioreactor type. Both configurations were effective at reducing the soluble P fraction, especially the soluble reactive P species that are bioavailable and thus contribute directly to eutrophication. A woodchips-only bioreactor can adsorb P from subsurface agricultural drainage; however, a woodchips bioreactor containing the activated alumina/gravel mixture has greater P sorption capacity and should be considered as part of an integrated system for concurrent N and P removal from subsurface agricultural drainage.

Key words: activated alumina—agricultural drainage—eutrophication—integrated nutrient control—phosphorus—woodchip bioreactor

Diffuse phosphorus (P) pollution from agricultural land is a major contributor to water quality impairment in streams, rivers, and lakes (Parry 1998; USEPA 2004). Agricultural fields in cold, humid climates are particularly vulnerable to nutrient loss due to high water flows occurring during spring snowmelt, as well as winter freeze/thaw events (Jamieson et al. 2003). Future climate change scenarios predict more frequent and intense rainfall events in agricultural regions of the northern hemisphere, which will result in higher subsurface drainage flow and more surface runoff (Nearing et al. 2004; Wang et al. 2015). The agricultural regions of Ontario and Quebec, Canada, receive more than 1,100 mm of precipitation each year, and about 2 million ha of agricultural land have subsurface drainage systems (Helwig et al. 2002). Subsurface drainage modifies the hydraulic regime of agricultural land because it favors water infiltration (Dolezal et al. 2001; Macrae et al. 2007). Water moving past the root zone carries soluble P, particulate P, and other nutrients through the soil profile. Nutrient-rich water intercepted by subsurface tile lines is then drained into field ditches, which eventually empty into brooks, streams, rivers, and lakes. Systematic drainage of agricultural land (e.g., with subsurface drainage and field ditches) collects and transports more water and nutrients, including P, than is emitted from agricultural landscapes where water outflows are transmitted by surface runoff (Heathwaite and Dils 2000).

Numerous reports cite subsurface agricultural drainage as a major pathway for the transfer of soluble and particulate P to surface waters, at concentrations that often exceed environmental criteria (Eastman et al. 2010; Gächter et al. 1998; King et al. 2014; Kinley et al. 2007; Macrae et al. 2007; Ryden et al. 1974; Smith et al. 2015; Sunohara et al. 2015; Zhang et al. 2015). The environmental criteria for streams and rivers vary according to the jurisdiction but are generally ≤0.03 mg total P L^{-1}, including those of Ontario and Quebec, Canada (Ministry of Sustainable Development, Environment, and the Fight Against Climate Change 2016; Ontario Ministry of Environment 1994). The outflow from subsurface agricultural drainage frequently exceeds the 0.03 mg total P L^{-1} environmental threshold. For instance, King et al. (2014) found that more than 90% of samples from tile drainage exceeded the critical level of 0.03 mg total P L^{-1}, with bioavailable P forms typically predominating. The bioavailable P forms are problematic because they are readily metabolized by cyanobacteria, algae, and other aquatic organisms that contribute to eutrophication. Zhang et al. (2015) found that soluble reactive P, a bioavailable P species, represented more than 72% of the total

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P loss in subsurface agricultural drainage in a cold climate zone. Elevated bioavailable P concentrations in subsurface outflows may be the legacy of long-term P fertilization (MacDonald and Bennett 2009; Sims et al. 2000) that will continue to be a source of diffuse P pollution, even if agricultural P inputs and outputs are eventually balanced through nutrient management programs and other agricultural best management practices (BMPs) (Carpenter 2005; Schulte et al. 2010).

Woodchip bioreactors, combined with controlled drainage structures, have potential to remove nutrients from subsurface agricultural drainage before the outflow reaches field ditches and downstream water bodies. Such bioreactors are a proven cost-effective method of nitrate-nitrogen (NO_3-N) removal from agricultural subsurface drainage systems in field-scale installations, as well as an efficient conservation practice standard (Christianson et al. 2012; USDA NRCS 2013; Schipper et al. 2010). The reducing conditions in woodchip bioreactors accelerate NO_3 removal via microbiological denitrification before drainage water exits the field. Whether woodchip bioreactors could be adapted to achieve simultaneous removal of NO_3 and P from subsurface agricultural drainage under field conditions is uncertain. Since P removal from water is achieved through sorption or precipitation reactions, laboratory-scale studies have tested woodchip bioreactors containing P-sorptive media such as biochar, drinking water treatment residuals containing aluminum (Al), steel turnings, or steel byproducts (Bock et al. 2015; Goodwin et al. 2015; Hua et al. 2016; Zoski et al. 2013). Field-scale testing of woodchip bioreactors reported that soluble reactive P concentrations were initially higher in the effluent than influent water, although the difference was nonsignificant after one month of operation (Bell et al. 2015). In higher latitude regions with cold, humid climates, the low temperatures experienced during winter months cause freezing in the soil profile and interrupt subsurface drainage flows, which are expected to reduce the efficiency of the biological and chemical sorption processes in woodchip bioreactors (Jin et al. 2008). In addition, precipitation events are episodic, and P concentrations fluctuate due to the volume of water flowing through the bioreactor, which affects the contact time between P compounds and the P-sorptive media within the bioreactor. The dynamics and extent of P removal from subsurface agricultural drainage by woodchip bioreactors, with and without P-sorptive media at the field scale, is poorly understood and requires multiyear investigation.

To address this critical knowledge gap, this study aimed to determine (1) if total P concentrations in untreated subsurface drainage water from agricultural fields exceeded environmental thresholds; (2) if the total P concentration in subsurface drainage water from these fields was reduced below the critical environmental threshold of 0.03 mg total P L^{-1} when a controlled drainage structure and woodchip bioreactor, with and without P-sorptive media, were installed; (3) whether total P loads were reduced in the woodchips-only and woodchips plus P-sorptive media bioreactors; (4) the effectiveness of P removal by these bioreactors for various P species; and (5) whether the P removal performance of the bioreactors changes over time, particularly when exposed to wet-dry cycles and freeze-thaw cycles in a multiyear study. The P removal from subsurface drainage water was evaluated in tile lines with controlled drainage structures and four in-field woodchip bioreactors, with and without sorptive media, during a three-year period, for a total of 12 "bioreactor years." Data on the N removal from these bioreactors was reported elsewhere (Husk et al. 2017).

Materials and Methods

Experimental Site. The experimental site is located in south-central Quebec, Canada, on a commercial dairy farm situated within the hypereutrophic Petit-lac-St-François watershed, part of the greater Saint Lawrence River basin. Bioreactors were installed in farm fields that drain into a first-order, intermittent flow stream (figure 1). The stream reach drains an area of 34 ha, of which 20% is forested and 80% is used for intensive agriculture. All agricultural fields draining into this stream reach have subsurface drains located 70 to 100 cm below the surface, which are spaced across the slope at 15.3 m lateral intervals and are constructed of perforated, corrugated, single wall, high density polyethylene (HDPE), 8 to 10 cm in diameter. Soils in the study area are part of the Brompton stony loam series, classified as a poorly drained Podzol (Lamontagne and Nolin 1997) and described by Husk et al. (2017). Briefly, soil test P analysis of these fields averaged 40 mg P kg^{-1} (Mehlich-3 extractable P) with a P saturation ratio of 4.5% (calculated as the Mehlich-3 extractable P divided by Mehlich-3 extractable Al), which is considered to be less than the critical environmental P saturation index of 13.1% for these soils (Parent and Gagné 2010). Weather conditions in this cold, humid climate region indicate a mean annual temperature of 5.6°C, a 120-day frost-free period, and total annual precipitation of 1,147 mm y^{-1}, based on long-term (30-year) average data (Environment Canada 2015). The region of this study is classified as a Plant Hardiness Zone 4 (Natural Resources Canada 2013) and thus is a colder climatic zone than the fields used for other woodchip bioreactor studies, which were located in zones 5 through 7 (Christianson et al. 2012).

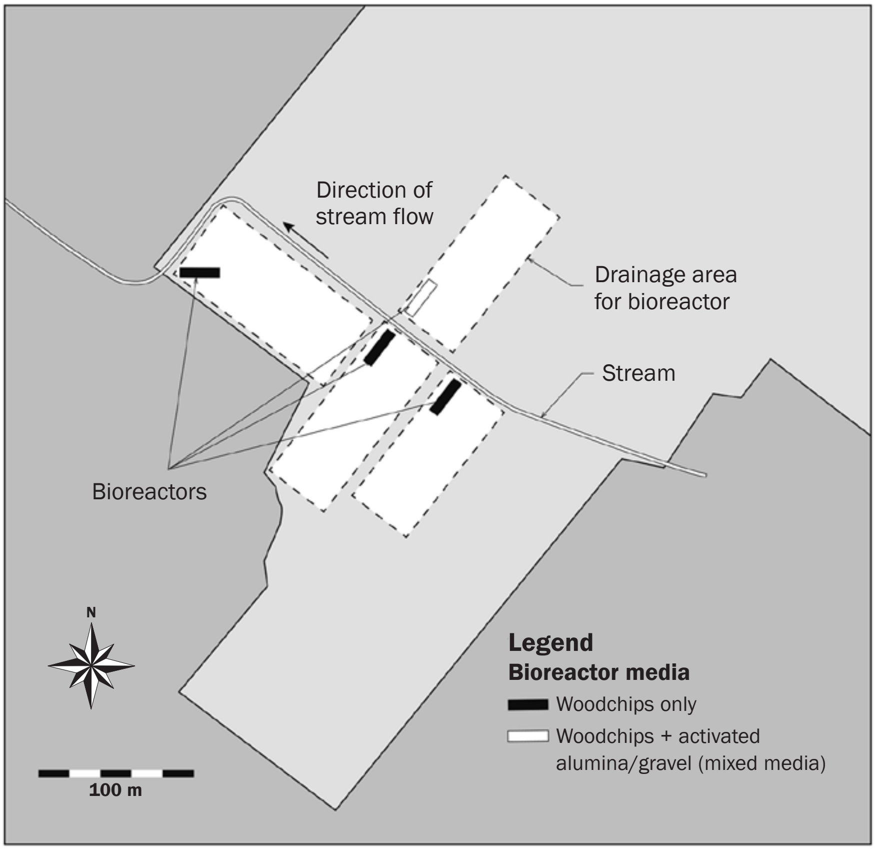
Experimental Design. Four woodchip bioreactors were constructed and installed for this project, using identical materials and methods for each, with one exception. In one of the four woodchip bioreactors, mixed-media material was included, in addition to woodchips, specifically for the reduction of P. Results for the mixed-media bioreactor (n = 1) are presented separately and compared with the woodchips-only bioreactors (n = 3) using nonparametric statistics (see below).

The mixed media contained activated alumina and gravel. Activated alumina (Al_2O_3, hereafter referred to as AA) beads of 5 to 8 mm diameter (Desican Inc., Markham, Ontario) were selected because AA has a P sorption capacity of approximately 30 mg phosphate (PO_4^{3-}) g^{-1} Al_2O_3 (Narkis and Meiri 1981) across a pH range of 6 to 9 (Yan et al. 2014). Gravel was used as the bulking material, employing a locally sourced material (Construction DJL Inc., Canton-de-Hatley, Quebec) that was composed primarily (75% to 95%) of hard metamorphic schist, 1.9 cm diameter. Gravel was selected as a low-cost bulking material that acts as a filler in the mixed material of the bioreactor, allowing sufficient pore space for water flow and permitting water contact with the AA distributed evenly in the mixed material.

Mixed media was prepared by blending AA uniformly with the gravel in a 15% AA/85% gravel mixture, by volume (figure 2). These proportions were based on laboratory tests of the P removal capacity from water flows of AA/gravel mixtures, which showed that AA was responsible for P removal and gravel alone could not lower the P concentration by more than 4% (Gordon Balch, Fleming College, personal commu-

Figure 1

Map of the study site, located within the Petit-lac-St-François watershed, showing farm fields, stream, and location of woodchip bioreactors and mixed-media bioreactor.



nication, 2013). Mixed media was placed in two galvanized wire mesh pallet cages (each 0.975 × 0.610 × 0.762 m with a volume of 453 L), which were lined with finer scale galvanized wire mesh of 6.4 mm openings (figure 3). Together, the two cages held 906 L of mixed media containing 136 L (15%) of AA and 770 L (85%) of gravel and were placed longitudinally in the outlet end of the designated woodchip bioreactor trench.

Woodchip Bioreactor Design and Installation. The woodchip bioreactors in this study were designed and installed according to methods established by Christianson (2011), and operated under the site-specific conditions of this study at the hydraulic retention times described by Husk et al. (2017). A bioreactor and site parameter summary is presented in table 1. These side-stream bioreactors were installed parallel to the main field tile drains (figure 4) to optimize treatment volumes of drainage water for denitrification, while ensuring a sufficient hydraulic retention time in the bioreactor. Briefly, this involved excavating the tile drain near the field ditch and installing drainage control structures, then excavating the bioreactor trenches, lining them with plastic sheet, filling with woodchips, covering them with a geotextile material and backfilling with approximately 30 cm of soil. The woodchips were square with dimensions of approximately 1.5 × 1.5 cm, derived from maple (*Acer* sp. L.) trees and obtained from a local supplier. The bioreactor design is meant to optimize conditions for denitrification and not necessarily for P removal, so the novelty of this work arises from the comparison of the woodchips-only bioreactor and woodchips plus mixed-media bioreactor to reduce P concentration in tile drainage outflows.

Crop and Field Management Practices and Inputs. The commercial dairy farm employs conventional, nonorganic agricultural practices. A variety of field crops are grown, in predetermined annual rotations, as indicated in Husk et al. (2017), and include corn (*Zea mays* L.), soybean (*Glycine max* L.), and wheat (*Triticum* spp.), as well as a mixed forage hay crop blend of 42% bromegrass (*Bromus* sp.), 37% alfalfa (*Medicago sativa*), 13% timothy-grass (*Phelum pratense*), and 8% fescue (*Festuca* sp.). Tillage, cultivation, fertilization, and crop protection decisions were made by the farm operators throughout the study period. The drainage control structure gates were adjusted on four separate occasions during the year to heights indicated as follows: (1) lowered after snow melt, prior to seeding, to 90 cm; (2) raised after seeding, to 120 cm; (3) lowered prior to fall harvest, to 90 cm; and (4) raised after fall harvest, to 150 cm. The purpose of these adjustments was primarily to allow soils to dry prior to any machinery traffic required for planting and harvesting operations. The woodchip bioreactors installed in this study did not affect the farming activities or crop yields in the treated area, nor did they require significant intervention or maintenance by the farm owners (Ferme Ridelo, G.P., personal communication, 2015).

On-Site Measurements, Sampling Procedures, and Laboratory Analysis. Drainage water sampling was performed weekly at the four bioreactors during the spring to fall period each year (mid-March to end-December), as well as within the 24-hour period following rain events exceeding 10 mm, due to the importance of P losses related to storm events (Grant et al. 1996). During the winter period (end-December to mid-March) when the field soils were frozen, drain flows were nonexistent or ephemeral, and sampling was suspended.

The bioreactor and control structure layout, indicating the location of sampling stations, are illustrated in figure 4. Sampling of each bioreactor involved collecting water from three points, working upstream within the bioreactors—first from the main subsurface field drain outlet (point C), followed within 20 minutes in the bioreactor outlet control structure (point B), then within 5 minutes in the bioreactor inlet control structure (point A). The sampling location for bioreactor effluent water collection (point B) was assumed to represent the change in water chemistry occurring in the bioreactor during the hydraulic retention time.

Samples of 500 mL were collected in HDPE bottles. A siphon was used to withdraw water from the control structures, taking the sample from mid-depth of the water column. Samples were placed on ice in the field and transported to the lab overnight, according to standard water sampling methods (Canadian Council of Ministers of the Environment 2011). All individual, discrete samples collected during the 97 field sampling dates (n = 5 in 2013, n = 39 in 2014, and n = 53 in 2015) over the 37-month period underwent P analysis according to standard test methods (Eaton et al. 2005) in an independent laboratory (Centre for Alternative Wastewater Treatment, Fleming College, Lindsay, Ontario, Canada). Laboratory method detection limits (MDL) were the following: total P, 0.010 mg L^{-1}; soluble P, 0.010 mg L^{-1}; and soluble reactive P, 0.003 mg L^{-1}. Particulate P was expressed as the result of total P minus soluble P. Soluble organic P was expressed as soluble P minus soluble reactive P. Flow rates were determined at the same time that water samples were collected. Drain flow rates (L s^{-1}) were determined by collecting outflow from the field drain outlet in a graduated cylinder for a defined period of time.

Data Analysis. Results for the three years of this field trial are separated into two categories according to the materials used in the bioreactors: (1) woodchips only and (2) mixed media. Each bioreactor was treated as an independent experimental unit. Performance was then evaluated for the two categories: woodchips-only bioreactor (n = 3) and mixed-media bioreactor (n = 1), considering the concentration reduction (mg L^{-1}) and load removal (g m^{-3} of bioreactor volume d^{-1}) of various P species. The results are presented for all three years combined, as well as by year, to evaluate any temporal variation related to the aging of woodchips and other materials.

The effectiveness of the woodchips-only and mixed-media bioreactors in removing P species from the drainage water was calculated as P species in the bioreactor influent water minus P species in the bioreactor effluent water. For each bioreactor, we calculated the difference in total P, particulate P, soluble P, soluble reactive P, and soluble organic P concentrations and loads in paired samples of bioreactor influent water and effluent water for discrete temporal sampling events. Results are presented as the mean ± standard error of the mean (sem). P-value significance levels for differences were determined according to the Student's t-test, the null hypothesis being that there was no difference in means in the concentrations or loads of paired influent and effluent water samples. When the measured concentration was less

Figure 2

Activated alumina/gravel (15%/85%) mixed media, as placed in the wire mesh pallet cages.

Figure 3

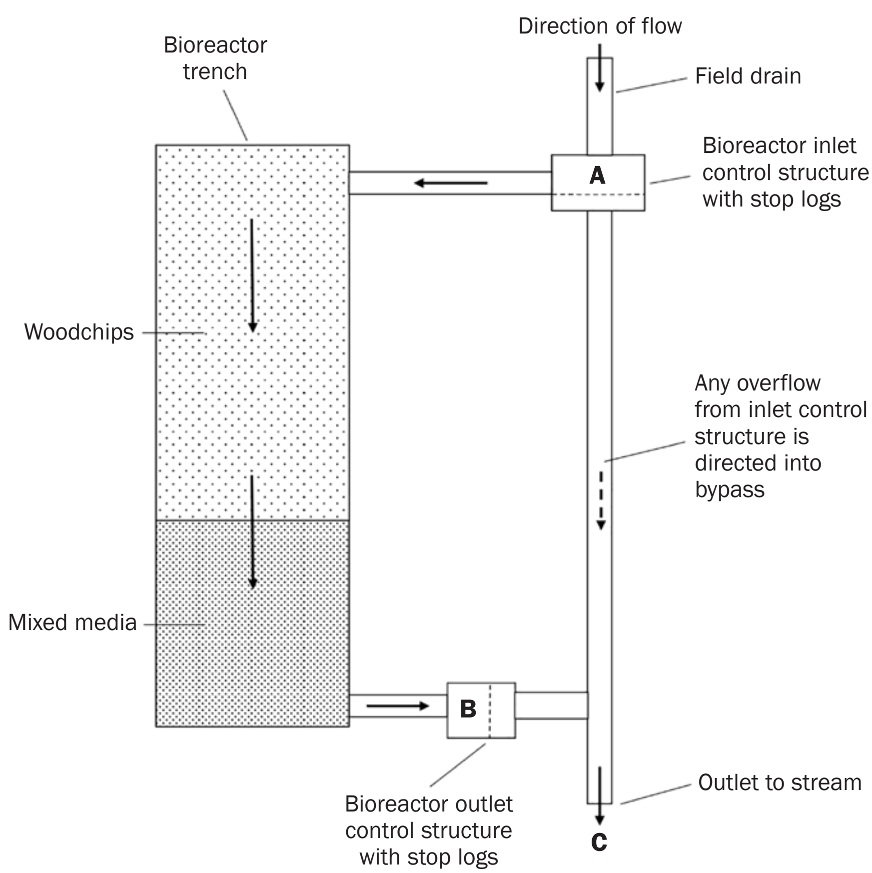
Wire mesh pallet cages filled with activated alumina/gravel (15%/85%) mixed media, prior to placement in the bioreactor.

Table 1
Bioreactor (BR) and study site parameters.

Bioreactor and site parameters	BR-1	BR-2*	BR-3	BR-4
Length (m)	19.83	12.20	27.45	19.83
Width (m)	1.83	0.91	0.91	1.83
Depth (m)	0.91	0.91	0.91	0.91
Surface area (m^2)	36.30	11.10	25.00	36.30
Volume (m^3)	33.00	10.10	22.70	33.00
Drainage area (ha)	0.61	0.69	0.93	1.28
Bioreactor area as percentage of drainage area (%)	0.60	0.20	0.30	0.30
Slope of drainage area (%)	1.38	2.00	1.04	0.50

*Woodchip + mixed-media bioreactor.

Figure 4
Schematic of bioreactor installation, top view, showing drainage water flow directions; bioreactor inlet from the main field drain and bioreactor outlet control structures; sampling points A, B, and C; as well as the placement of woodchips and mixed media within the bioreactor. (Not to scale.)



than the MDL, the results were estimated as follows: (1) when fewer than 10% of all measured results in water samples from a field site were <MDL, they were expressed as one-half MDL, or (2) when more than 10% of the results in water samples from a field site were <MDL, the Kaplan-Meier nonparametric estimator method was used (Helsel 2011). Performance comparisons were also made between the woodchips-only bioreactors versus the mixed-media bioreactor for the three years combined employing a nonparametric, one-tailed Mann-Whitney *U*-test of median values.

Results and Discussion

Untreated Total Phosphorus Concentrations and the Environmental Threshold. We asked whether the total P concentrations in the untreated agricultural subsurface drainage water (i.e., as emitted from the subsurface drains before bioreactor treatment, and discharged directly into the surface stream) at the study site exceeded the environmental threshold. Mean total P bioreactor influent concentration for all four bioreactors during the three-year study period was 0.114 mg L^{-1} (n = 138; sem = 0.013), which is four times greater than the critical environmental criterion of 0.030 mg L^{-1}. Measured mean concentrations of influent total P exceeded the 0.030 mg L^{-1} criterion on 69% of sampling dates. Total P concentration was partitioned into particulate P, which represented 0.054 mg L^{-1} (47.5%), and soluble P, which accounted for 0.060 mg L^{-1} (52.5%). Given the higher eutrophication potential of bioavailable P (equal to soluble reactive P), it was notable that soluble reactive P and soluble organic P made up 0.046 mg L^{-1} (78%) and 0.014 mg L^{-1} (22%), respectively, of the soluble P (figure 5). These results suggest that untreated water outflows from subsurface drainage of this agricultural field were a source of bioavailable P and would contribute to the total P loading of waterways in the region. Clearly, measures must be taken to reduce the total P concentration emanating from the agricultural subsurface drainage systems so that it complies with the environmental criterion of 0.030 mg L^{-1}.

Ability to Reduce Total Phosphorus Concentrations below the Environmental Threshold. The question was whether woodchip bioreactors combined with controlled drainage and sorptive media could reduce total P concentrations below the critical environmental threshold of 0.030 mg L^{-1}. Neither bioreactor media configuration (woodchips-only or mixed media) was capable of achieving this criterion over the three-year period; however, the mixed-media configuration resulted in a net decrease in the mean total P concentration of 0.015 mg L^{-1}, or 9% (figure 6, table 2). During this three-year study, the mean total P concentration in woodchips-only bioreactors increased significantly by 0.042 mg L^{-1} (p = <0.05, n = 97, sem = 0.021), or by 44%, from 0.095 mg L^{-1} influent concentration to 0.136 mg L^{-1} effluent concentration. In the mixed-media bioreactor, the total P concentration declined from 0.159 mg L^{-1} (influent concentration) to 0.144 mg L^{-1} (effluent concentration) after passing through the bioreactor. Although numerically lower (0.015 mg L^{-1}), this was not a significant reduction in total P concentration ($p \geq 0.10$, $n = 41$, sem = 0.043).

Ability to Reduce Total Phosphorus Loads. While total P concentration reduction is a useful parameter and has biological significance to aquatic organisms, it is primarily of importance for evaluating compliance with environmental standards for water quality in streams and varies in space and time, according to the water volume passing through the subsurface drainage system. Load reduction is of greater importance for measuring the effectiveness of agri-environmental practices in reducing the mass of contaminants delivered to aquatic environments, especially lakes, and may be a more accurate assessment of contributions to water quality protection (Stamm et al. 2013). In this study, load removal is expressed as grams of P removed per cubic meter of bioreactor volume per day.

A positive load removal of 0.019 g total P m^{-3} d^{-1} during the three-year study period was realized for the three woodchips-only bioreactors ($p \geq 0.10$, $n = 74$, sem = 0.034) (figure 7, table 3). For the mixed-media bioreactor, 0.363 g m^{-3} d^{-1} of total P was removed ($p \geq 0.10$, $n = 37$, sem = 0.112) (figure 7, table 3), approximately 19 times more P removal than the woodchips-only bioreactors. Thus, both woodchips-only and mixed-media bioreactors can reduce P loads from agricultural drainage water, as measured by removal per unit of bioreactor volume. Flow rates can vary by approximately 4 to 15 times within a particular bioreactor, probably due to the variability in drainage area served by each bioreactor (Husk et al. 2017), but the mean flow rates of 0.021 to 0.036 L s^{-1} suggest that the bioreactors and their functions are comparable (figure 10). Comparing the bioreactor categories (woodchips-only versus mixed media) with a nonparametric one-tailed Mann-Whitney U-test of median values ("Media difference," table 2, concentrations; table 3, loads) confirmed a significant improvement in P reduction with the mixed-media bioreactor as compared to the woodchips-only bioreactors. Improved performance was demonstrated with the mixed-media bioreactor, which emitted lower concentrations and loads for most P fractions, with the exception of particulate P. The relatively better performance of the mixed-media bioreactor is particularly significant for bioavailable P species, and indicates that the design has potential for removing soluble P fractions that are implicated in eutrophication.

Figure 5
Phosphorus (P) concentrations in untreated subsurface drainage water prior to entry into the bioreactors, mean values (mg L^{-1}) and percentage of total P by P species, all bioreactors combined for the three-year study period (n = 138).

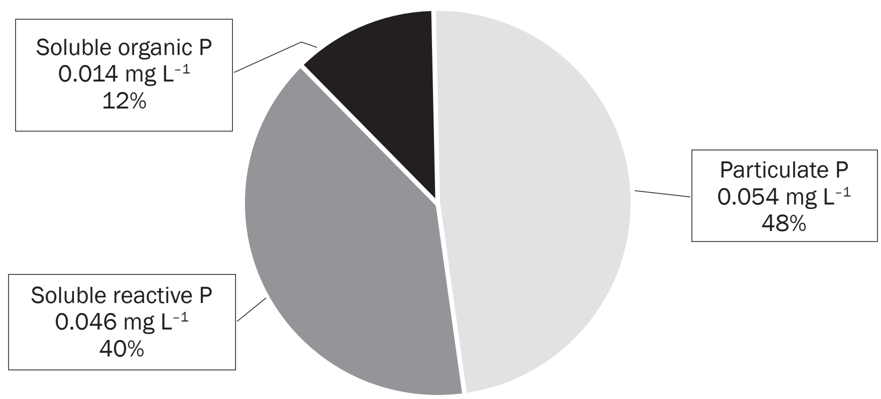


Figure 6
Mean phosphorus (P) concentration reduction (mg L^{-1}) within the bioreactors by P species, three years combined, comparing woodchip and mixed-media bioreactors.

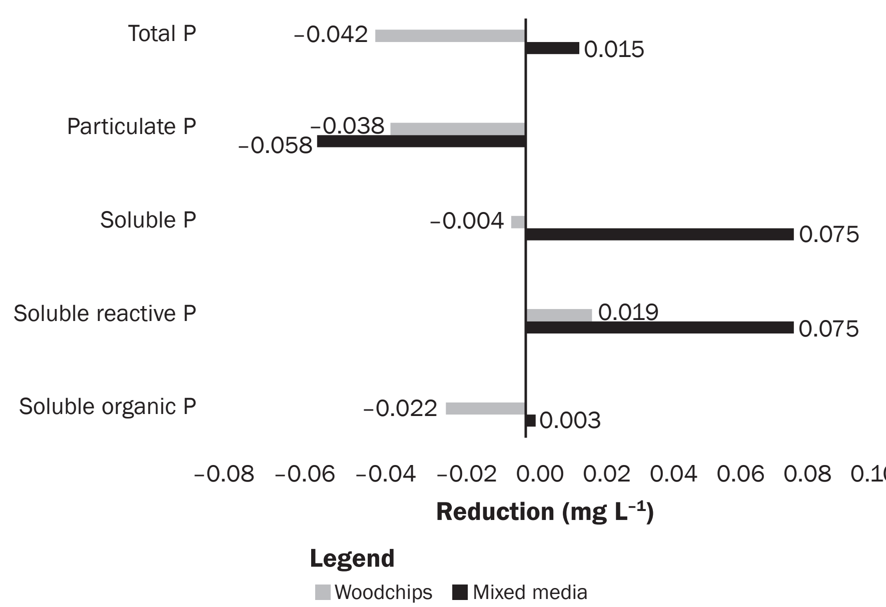


Table 2
Concentration reduction (mg L⁻¹) of phosphorus (P) within the bioreactors, separated according to media type, by P species, by study year and three years combined, indicating the reduction (or increase) between influent and effluent mean values, the standard error of the mean, as well as the significance level of the difference between influent and effluent values. The number of samples by media, by year, and total are indicated.

Phosphorus fraction	Media	Criteria	Year 1	Year 2	Year 3	Three years	Media difference
	Woodchips (*n*)		5	39	53	97	
	Mixed media (*n*)		2	24	15	41	
Total P	Woodchips	Reduction	−0.070	0.002	−0.067	−0.042	*U* < 0.05
		Standard error	0.147	0.024	0.031	0.021	
		Significance level	ns	ns	*p* < 0.05	*p* < 0.05	
	Mixed media	Reduction	−0.478	−0.012	0.124	0.015	
		Standard error	0.459	0.041	0.076	0.043	
		Significance level	ns	ns	*p* < 0.10	ns	
Particulate P	Woodchips	Reduction	−0.127	−0.015	−0.058	−0.038	ns
		Standard error	0.148	0.022	0.021	0.017	
		Significance level	ns	ns	*p* < 0.01	*p* < 0.01	
	Mixed media	Reduction	−0.546	−0.044	−0.015	−0.058	
		Standard error	0.455	0.042	0.011	0.035	
		Significance level	ns	ns	*p* < 0.10	*p* < 0.05	
Soluble P	Woodchips	Reduction	0.057	−0.004	−0.009	−0.004	*U* < 0.001
		Standard error	0.022	0.006	0.014	0.008	
		Significance level	*p* < 0.05	ns	ns	ns	
	Mixed media	Reduction	0.066	0.034	0.142	0.075	
		Standard error	0.046	0.004	0.071	0.027	
		Significance level	ns	*p* < 0.001	*p* < 0.05	*p* < 0.01	
Soluble reactive P	Woodchips	Reduction	0.070	0.011	0.019	0.019	*U* < 0.001
		Standard error	0.020	0.005	0.012	0.007	
		Significance level	*p* < 0.01	*p* < 0.05	*p* < 0.05	*p* < 0.01	
	Mixed media	Reduction	0.060	0.033	0.137	0.072	
		Standard error	0.035	0.004	0.070	0.027	
		Significance level	ns	*p* < 0.001	*p* < 0.05	*p* < 0.01	
Soluble organic P	Woodchips	Reduction	−0.032	−0.048	−0.089	−0.022	*U* < 0.001
		Standard error	0.007	0.002	0.007	0.004	
		Significance level	*p* < 0.05	*p* < 0.001	*p* < 0.001	*p* < 0.001	
	Mixed media	Reduction	0.008	0.002	0.003	0.003	
		Standard error	0.011	0.002	0.004	0.002	
		Significance level	ns	ns	ns	*p* < 0.05	

Notes: ns = not statistically significant, $p > 0.10$. Media difference indicates the Mann-Whitney *U*-value for the statistical difference between media categories for concentration reduction.

Effectiveness of Removal of Individual Phosphorus Species. The effectiveness of removal of the individual P species was examined with respect to concentration reduction (figure 6, table 2) and load reduction (figure 7, table 3). While neither bioreactor was effective at reducing the particulate P concentration, the mixed-media bioreactor was capable of reducing the soluble P fraction concentration by 83%. For the soluble reactive P fraction concentration, the woodchips-only reduced it by 53% and the mixed-media bioreactor reduced it by 97%. Considering the load reduction by P species, both bioreactor configurations were successful at reducing loads of all P species over the three-year period. However, the mixed-media bioreactor was more effective than the woodchips-only bioreactor, reducing total P by 0.363 g m^{-3} d^{-1} versus 0.019 g m^{-3} d^{-1}, and soluble reactive P by 0.232 g m^{-3} d^{-1} versus 0.018 g m^{-3} d^{-1}, respectively.

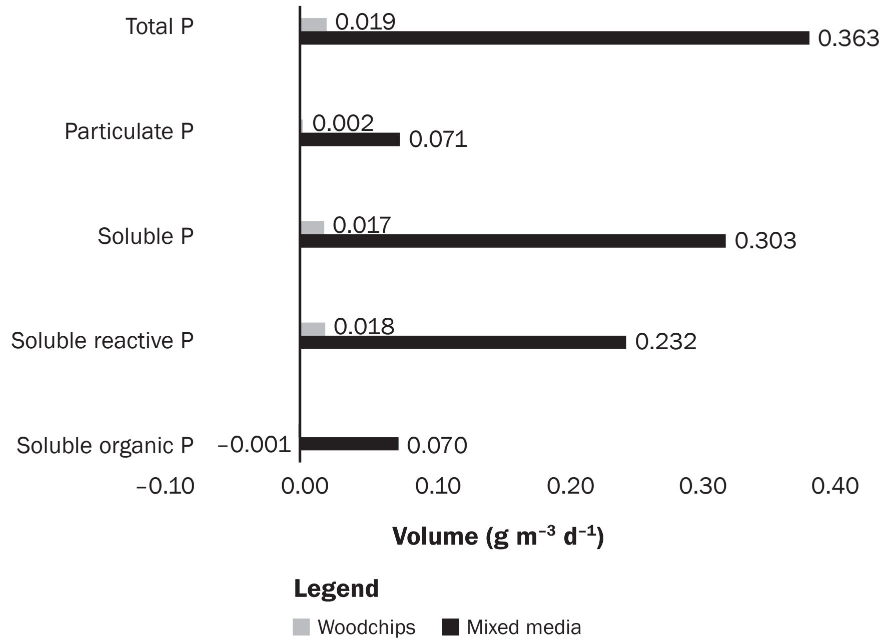
Our findings indicate that total P concentrations increase, while total P loads decline, in the woodchip bioreactors. The increase in total P concentration is due to the fact that higher total P concentrations are recorded when flows are low, and most sampling events occurred during low flows. Consequently, the total P concentration increased during the three-year study period. In contrast, total P loads are reduced during high flow events, and the load reduction during those events resulted in a significant total P load reduction for the three-year study period.

The ability of bioreactors, particularly the mixed-media bioreactor, to reduce soluble P concentration and load in subsurface drainage water, is extremely promising for surface water protection. Most agricultural BMPs aiming to prevent P loss from agricultural land have focused on preventing particulate P losses (e.g., with riparian strips, no-till, grassed waterways, etc.), and the bioavailable, soluble P forms were largely neglected. It is clear from this study, along with others (Dodd and Sharpley 2016), that agri-environmental programs designed to protect surface water quality must prevent soluble P and particulate P losses from agricultural land.

Temporal Variation in Phosphorus Removal Performance of the Bioreactors. Previous lab- and field-scale studies reported P leaching from woodchip bioreactors during the start-up phase, following their installation (Healy et al. 2012, 2015; Sharrer et al. 2016). We examined temporal changes in P concentration reduction (figure 8) and P load removal (figure 9) by separating results into the three annual periods of the study. This included periods when the bioreactors were subjected to variable water regimes due to soil freezing and negligible or no drainage flow during the winter months, variable subsurface flows during spring thaw, and periodic and heavy rainfall events (>10 mm within 24 hours) during the growing season, all of which are expected to have an impact on bioreactor performance over time. Both bioreactor configurations initially released total P at start-up, but reverted to near neutral or positive total P removal or load reduction within the first year of operation (figure 8, concentrations; figure 9, loads). The magnitude of total P release appears to be greater from the mixed-media bioreactor than the woodchip bioreactors in the first year, but this is attributed to the time at which drain flows occurred (mostly during the fall runoff period in the mixed-media bioreactor, which results in higher P flows versus mostly during the summer months with lower P flows in the woodchip bioreactors). In addition, the disparity between reactor types is accentuated by unequal number of observations between mixed-media and woodchip bioreactors. Bioreactors continued to reduce P for the remainder of the three-year study, with the exception of total P concentration for the woodchips-only configuration. This configuration reverted to net concentration loss in the third year of the study, although total P load removal remained positive during this time. The results of this study support previous evidence for an initial rapid P leaching phase, followed by a period of conditioning and gradual decrease in P leaching from woodchip bioreactors.

Figure 7

Mean phosphorus (P) load reduction within the bioreactors by P species (g m^{-3} d^{-1} of bioreactor volume), three years combined, comparing woodchip and mixed-media bioreactors.



Summary and Conclusions

This three-year field-scale study demonstrates that an agricultural subsurface drainage system with a woodchips-only bioreactor had lower P load in its outflow and a significant reduction in the bioavailable, soluble P fractions. Installing a mixed-media bioreactor in the subsurface drainage system was even more effective in lowering the P load and removing the soluble P fractions, of critical importance to efforts to reduce eutrophication of surface waters. Adding mixed media for P removal to a woodchip bioreactor provides a substantial improvement in the overall effectiveness and functionality of this nutrient removal technique, and was consistent for field operations across multiple seasons in a cold, humid climate (zone 4). As the first field evaluation of this technology in Canada, it will be of interest to Canadian-based and other cold-region researchers, as well as to Canadian government and agri-environmental agencies in regard to policy development, similar to that which has already been conducted by US agricultural agencies.

It is recommended that further research be undertaken to evaluate the P removal effectiveness of this mixed media in woodchip bioreactors under additional climate, soil, and cropping conditions, ideally over multiyear periods and at different scales, in order to develop predictive design models. In particular, it may be advantageous to evaluate the placement of the mixed media at alternative or multiple locations within the bioreactors to optimize P removal. Future research would also benefit from the examination of the potential effective P removal lifespan of mixed media within woodchip bioreactors, as well as possibilities for its eventual reuse, regeneration, or recycling. Finally, future research into the functioning of these bioreactors would benefit from an examination of other operational parameters (pH, biochemical oxygen [O] demand, conductivity, etc.), allowing an improved understanding of those which potentially influence P reduction, including microbially mediated processes, as well as their ability to remove agrochemical products and bacterial or viral contaminants commonly found in these waters.

While it is beyond the scope of this study to quantify the broad economic and environmental impacts that could be realized by P removal with woodchip and mixed-media bioreactors, their use in cold, humid agricultural regions where subsurface drainage is common could have a significant positive impact on reducing agricultural P loads to surface waters and the slowing of accelerated eutrophication. Consequently, they merit further investigation and consider-

Table 3
Load reduction (g m^{-3} d^{-1}) of phosphorus (P) within the bioreactors, separated by media type, by P species, by study year and three years combined, indicating the reduction (or increase) between influent and effluent mean values, the standard error of the mean, as well as the significance level of the difference between influent and effluent values. The number of samples by media, by year, and total are indicated.

Phosphorus fraction	Media	Criteria	Year 1	Year 2	Year 3	Three years	Media difference
	Woodchips (*n*)		2	25	47	74	
	Mixed media (*n*)		2	21	14	37	
Total P	Woodchips	Reduction	−0.266	−0.009	0.046	0.019	$U < 0.05$
		Standard error	0.292	0.010	0.052	0.034	
		Significance level	ns	ns	ns	ns	
	Mixed media	Reduction	−0.233	0.091	0.855	0.362	
		Standard error	0.203	0.077	0.564	0.112	
		Significance level	ns	ns	ns	ns	
Particulate P	Woodchips	Reduction	−0.275	−0.001	0.015	0.002	ns
		Standard error	0.260	0.007	0.034	0.023	
		Significance level	ns	ns	ns	ns	
	Mixed media	Reduction	−0.266	0.033	0.173	0.071	
		Standard error	0.228	0.067	0.167	0.076	
		Significance level	ns	ns	ns	ns	
Soluble P	Woodchips	Reduction	0.008	−0.008	0.031	0.017	$U < 0.001$
		Standard error	0.032	0.004	0.033	0.021	
		Significance level	ns	$p < 0.01$	ns	ns	
	Mixed media	Reduction	0.032	0.064	0.682	0.303	
		Standard error	0.025	0.027	0.467	0.185	
		Significance level	ns	$p < 0.05$	ns	$p < 0.10$	
Soluble reactive P	Woodchips	Reduction	0.018	−0.003	0.029	0.018	$U < 0.001$
		Standard error	0.019	0.002	0.028	0.018	
		Significance level	ns	ns	ns	ns	
	Mixed media	Reduction	0.028	0.048	0.525	0.232	
		Standard error	0.020	0.018	0.424	0.166	
		Significance level	ns	$p < 0.01$	ns	ns	
Soluble organic P	Woodchips	Reduction	−0.010	−0.005	0.001	−0.001	$U < 0.001$
		Standard error	0.012	0.002	0.013	0.008	
		Significance level	ns	$p < 0.05$	ns	ns	
	Mixed media	Reduction	0.004	0.016	0.157	0.070	
		Standard error	0.006	0.009	0.140	0.055	
		Significance level	ns	ns	ns	ns	

Notes: ns = not statistically significant, $p > 0.10$. Media difference indicates the Mann-Whitney *U*-value for the statistical difference between media categories for load reduction.

ation as an agri-environmental BMP for water quality improvement.

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References

Bell, N., R.A. Cooke, T. Olsen, M.B. David, and R. Hudson. 2015. Characterizing the performance of denitrifying bioreactors during simulated subsurface drainage events. Journal of Environmental Quality 44(5):1647-1656.

Bock, E.M., B. Coleman, and Z.M. Easton. 2015. Effect of biochar on nitrate removal in a pilot-scale denitrifying bioreactor. Journal of Environmental Quality 45(3):762-71.

Canadian Council of Ministers of the Environment. 2011. Protocols manual for water quality sampling in Canada. No. PN 1461. Ottawa, Canada: Canadian Council of Ministers of the Environment. https://www.ccme.ca/files/Resources/water/water_quality/protocols_document_e_final_101.pdf.

Carpenter, S.R. 2005. Eutrophication of aquatic ecosystems: Bistability and soil phosphorus. Proceedings of the National Academy of Sciences of the United States of America 102(29): 10002-10005, doi:0503959102.

Christianson, L.E. 2011. Design and performance of denitrification bioreactors for agricultural drainage. PhD dissertation, Iowa State University.

Christianson, L.E., A. Bhandari, and M.J. Helmers. 2012. A practice-oriented review of woodchip bioreactors for subsurface agricultural drainage. Applied Engineering in Agriculture 28(6):861.

Dodd, R., and A. Sharpley. 2016. Conservation practice effectiveness and adoption: Unintended consequences and implications for sustainable phosphorus management. Nutrient Cycling in Agroecosystems 104(3):373-392.

Figure 8
Total phosphorus (P) mean concentration reduction (mg L⁻¹) by study year, comparing woodchip and mixed-media bioreactors.

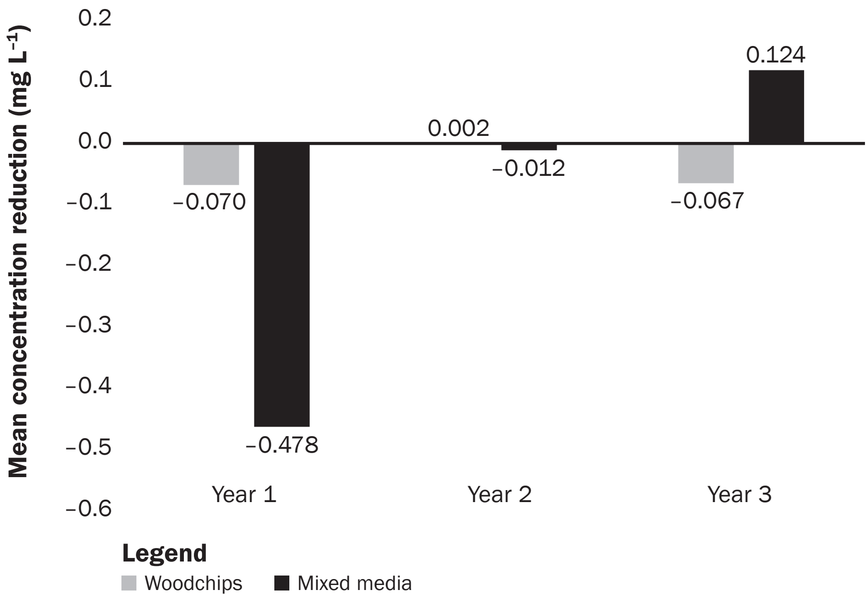
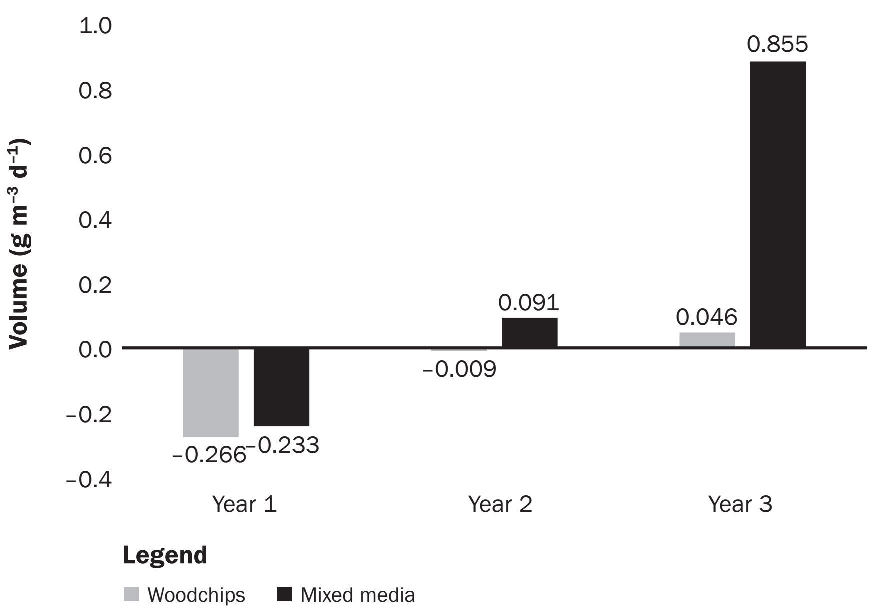


Figure 9
Total phosphorus (P) mean load reduction (g m⁻³ d⁻¹ of bioreactor volume) by study year, comparing woodchip and mixed-media bioreactors.



Dolezal, F., Z. Kulhavy, M. Soukup, and R. Kodesova. 2001. Hydrology of tile drainage runoff. Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere 26(7):623-627.

Eastman, M., A. Gollamudi, N. Stämpfli, C. Madramootoo, and A. Sarangi. 2010. Comparative evaluation of phosphorus losses from subsurface and naturally drained agricultural fields in the Pike River watershed of Quebec, Canada. Agricultural Water Management 97(5):596-604.

Eaton, A.D., L.S. Clesceri, E.W. Rice, A.E. Greenberg, and M.A.H. Franson. 2005. Standard Methods for the Examination of Water and Wastewater, 21st edition. Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation.

Environment Canada. 2015. Canadian Climate Normals, 1981-2010 station data, Bromptonville, QC. Ottawa, ON, Canada: Environment Canada.

Gächter, R., J.M. Ngatiah, and C. Stamm. 1998. Transport of phosphate from soil to surface waters by preferential flow. Environmental Science and Technology 32(13):1865-1869.

Goodwin, G.E., R. Bhattarai, and R. Cooke. 2015. Synergism in nitrate and orthophosphate removal in subsurface bioreactors. Ecological Engineering 84:559-568.

Grant, R., A. Laubel, B. Kronvang, H. Andersen, L. Svendsen, and A. Fuglsang. 1996. Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. Water Research 30(11):2633-2642.

Healy, M.G., M. Barrett, G. Lanigan, A.J. Serrenho, T. Ibrahim, S. Thornton, S.A. Rolfe, W.E. Huang, and O. Fenton. 2015. Optimizing nitrate removal and evaluating pollution swapping trade-offs from laboratory denitrification bioreactors. Ecological Engineering 74:290-301.

Healy, M.G., T.G. Ibrahim, G.J. Lanigan, A.J. Serrenho, and O. Fenton. 2012. Nitrate removal rate, efficiency and pollution swapping potential of different organic carbon media in laboratory denitrification bioreactors. Ecological Engineering 40:198-209.

Heathwaite, A., and R. Dils. 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. Science of the Total Environment 251:523-538.

Helsel, D.R. 2011. Statistics for censored environmental data using Minitab and R, 2nd edition. Hoboken, NJ: John Wiley and Sons.

Helwig, T., R. Jannasch, R. Samson, A. DeMaio, and D. Caumartin. 2002. Agricultural biomass residue inventories and conversion systems for energy production in eastern Canada. Final report. Prepared for Natural Resources-Canada. Quebec, Canada: Resource Efficient Agricultural Production (REAP)–Canada. http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.485.5787&rep=rep1&type=pdf.

Hua, G., M.W. Salo, C.G. Schmit, and C.H. Hay. 2016. Nitrate and phosphate removal from agricultural subsurface drainage using laboratory woodchip bioreactors and recycled steel byproduct filters. Water Research 102(1):180-189.

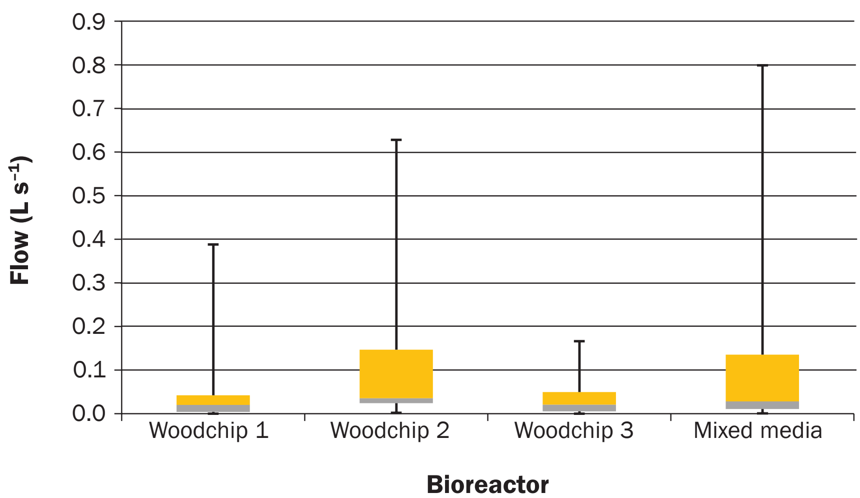
Husk, B., B. Anderson, J. Whalen, and J. Sanchez. 2017. Reducing nitrogen contamination from agricultural subsurface drainage with denitrification bioreactors and controlled drainage. Biosystems Engineering 153:52-62.

Jamieson, A., C.A. Madramootoo, and P. Enright. 2003. Phosphorus losses in surface and subsurface runoff from a snowmelt event on an agricultural field in Quebec. Canadian Biosystems Engineering 45:1.1-1.7.

Jin, C., G. Sands, H. Kandel, J. Wiersma, and B. Hansen. 2008. Influence of subsurface drainage on soil temperature

Figure 10

Flows of each bioreactor (L s⁻¹) for all sampling events, represented as box and whisker plots indicating the median and quartile values, as well as the highest and lowest observations.



in a cold climate. Journal of Irrigation and Drainage Engineering 134(1): 83-88.

King, K.W., M.R. Williams, and N.R. Fausey. 2014. Contributions of systematic tile drainage to watershed-scale phosphorus transport. Journal of Environmental Quality 44(2):486-9.

Kinley, R.D., R.J. Gordon, G.W. Stratton, G.T. Patterson, and J. Hoyle. 2007. Phosphorus losses through agricultural tile drainage in Nova Scotia, Canada. Journal of Environmental Quality 36(2):469-477.

Lamontagne, L., and M.C. Nolin. 1997. Dossier des noms de sols du Québec 1997: SISCan—Système d'information des sols du Canada. Ottawa, Ontario, Canada: Agriculture and Agri-Food Canada.

MacDonald, G.K., and E.M. Bennett. 2009. Phosphorus accumulation in Saint Lawrence River watershed soils: A century-long perspective. Ecosystems 12:621.

Macrae, M., M. English, S. Schiff, and M. Stone. 2007. Intra-annual variability in the contribution of tile drains to basin discharge and phosphorus export in a first-order agricultural catchment. Agricultural Water Management 92(3):171-182.

Ministry of Sustainable Development, Environment, and the Fight Against Climate Change. 2016. Quality criteria for surface water. http://www.mddelcc.gouv.qc.ca/EAU/criteres_eau/details.asp?code=S0393.

Narkis, N., and M. Meiri. 1981. Phosphorus removal by activated alumina. Environmental Pollution Series B, Chemical and Physical 2(5):327-343.

Natural Resources Canada. 2013. Plant hardiness zones 1981-2010. Ottawa, ON, Canada: Natural Resources Canada.

Nearing, M.A., F.F. Pruski, and M.R. O'Neal. 2004. Expected climate change impacts on soil erosion rates: A review. Journal of Soil and Water Conservation 59(1):43-50.

Ontario Ministry of Environment. 1994. Water management: Policies, guidelines, provincial water quality objectives of the Ministry of the Environment. Ontario, Canada: Queen's Printer for Ontario. http://www.ene.gov.on.ca/envision/gp/3303e.pdf.

Parent, L., and G. Gagné. 2010. Guide Référence en Fertilisation, 2nd edition. Québec, Canada: Centre de Référence en Agriculture et Agroalimentaire du Québec.

Parry, R. 1998. Agricultural phosphorus and water quality: A US Environmental Protection Agency perspective. Journal of Environmental Quality 27(2):258-261.

Ryden, J.C., J.K. Syers, and R.F. Harris. 1974. Phosphorus in runoff and streams. Advances in Agronomy 25:1-45.

Schipper, L.A., W.D. Robertson, A.J. Gold, D.B. Jaynes, and S.C. Cameron. 2010. Denitrifying bioreactors—An approach for reducing nitrate loads to receiving waters. Ecological Engineering 36(11):1532-1543.

Schulte, R.P.O., A.R. Melland, O. Fenton, M. Herlihy, K. Richards, and P. Jordan. 2010. Modelling soil phosphorus decline: Expectations of water framework directives policies. Evironmental Science and Policy 13:472.

Sharrer, K.L., L.E. Christianson, C. Lepine, and S.T. Summerfelt. 2016. Modeling and mitigation of denitrification 'woodchip' bioreactor phosphorus releases during treatment of aquaculture wastewater. Ecological Engineering 93:135-143.

Sims, J., A. Edwards, O. Schoumans, and R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. Journal of Environmental Quality 29(1):60-71.

Smith, D.R., K.W. King, L. Johnson, W. Francesconi, P. Richards, D. Baker, and A. Sharpley. 2015. Surface runoff and tile drainage transport of phosphorus in the midwestern United States. Journal of Environmental Quality 44(2):495-502.

Stamm, C., H.P. Jarvie, and T. Scott. 2013. What's more important for managing phosphorus: Loads, concentrations or both? Environmental Science and Technology 48(1):23-24.

Sunohara, M., N. Gottschall, G. Wilkes, E. Craiovan, E. Topp, Z. Que, O. Seidou, S.K. Frey, and D. Lapen. 2015. Long-term observations of nitrogen and phosphorus export in paired-agricultural watersheds under controlled and conventional tile drainage. Journal of Environmental Quality 44(5):1589-1604.

USDA NRCS (Natural Resources Conservation Service). 2013. Natural Resources Conservation Service (Iowa) conservation practice standard denitrifying bioreactor (ac.) interim code 747. Washington, DC: USDA Natural Resources Conservation Service.

USEPA (Environmental Protection Agency). 2004. National water quality inventory: Report to Congress. Washington, DC: US Environmental Protection Agency.

Wang, Z., Z. Qi, L. Xue, M. Bukovsky, and M.J. Helmers. 2015. Modeling the impacts of climate change on nitrogen losses and crop yield in a subsurface drained field. Climatic Change 129(1-2):323-335.

Yan, Y., F. Liu, W. Li, X. Feng, and D. Sparks. 2014. Sorption and desorption characteristics of organic phosphates of different structures on aluminium (oxyhydr) oxides. European Journal of Soil Science 65(2):308-317.

Zhang, T., C. Tan, Z. Zheng, and C. Drury. 2015. Tile drainage phosphorus loss with long-term consistent cropping systems and fertilization. Journal of Environmental Quality 44(2):503-511.

Zoski, E., D. Lapen, N. Gottschall, R. Murrell, and B. Schuba. 2013. Nitrogen, phosphorus, and bacteria removal in laboratory-scale woodchip bioreactors amended with drinking water treatment residuals. Transactions of the American Society of Agricultural and Biological Engineers 56(4):1339-1347.