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Research Article

Seasonal Dynamics of N, P, and K in an Organic and Inorganic Fertilized Willow Biomass System

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The seasonal variations in soil nutrient supply and bioavailability were assessed in a willow biomass crop (*Salix miyabeana*, SX64) treated with 150 and 200 kg available N ha^{-1} of commercial fertilizer (CF), biosolid compost (BC), dairy manure (DM), and control (CT0) at Delhi, NY. Plant root simulator probes were used to measure nutrient supply (inside) and bioavailability (outside) of root exclusion cylinders. Measurements were made in September 2008 and May, August, and October of 2009. Soil moisture content (θd) and foliar nutrient concentrations were also determined. The BC treatments increased soil P supply more than CF and CT0. The supply of NH_4^+ and K in the soil increased in August but their bioavailability increased in May and October. Soil NO_3^- and P supply and bioavailability were both high in May. Foliar N and K concentrations were significantly high in May and low in August which could be due to dilution effect caused by increased soil moisture foliar dry weight. Foliar P concentrations increased in September and October. The observed higher soil NO_3^- mineralization and plant uptake in May suggest that in high soil NO_3^- conditions willow biomass crops can level and minimize leaching out of the root zone into groundwater.

1. Introduction

An adequate supply of nutrients is essential to support the high yields that are necessary to make short rotation woody crops (SRWC) like shrub willow viable both economically and biologically. Soil nutrient supply and bioavailability in short rotation woody crops (SRWC) systems may vary depending on the type and form of nutrient input added, conditions at the site, and how the system is managed. Systems that receive high organic inputs would be expected to have greater soil nutrient supplying ability than those that receive only mineral fertilizers [1]. The use of mineral N fertilizers (100 kg N per rotation cycle) in willow biomass production systems has been estimated to represent 10% of the production cost [2] and account for as much as 37% of the nonrenewable fossil energy inputs [3]. The use of commercial fertilizers for willow biomass production therefore reduces the environmental and economic benefits of the feedstock production system [4].

Land application of organic residues represents an economically and environmentally safe way to recover value from these materials. The organic matter and nutrient contents of the waste materials can supply crops' needs and maintain soil fertility. However, due to increased public concerns about environmental issues, farmers are reluctant to use sewage sludge on lands used for food crop production. Since SRWC are nonfood crops, they are an attractive system for utilizing organic waste streams. The ability of willow to retain high amounts of nutrients in combination with its high biomass production makes it a preferred candidate for utilizing organic wastes [5].

The traditional method of measuring soil nutrient supply and availability represents only a "snapshot" of available nutrients and may not adequately reflect nutrient supply

throughout the growing season [6]. *In situ* burial of ion-exchange membranes (IEM), such as the plant root simulator (PRS) probe, on the other hand, allows the measurement of nutrient supplies according to the actual field conditions with minimal soil disturbance. The use of PRS probe provides insight into the dynamics of ion flux in the soil. When buried in the soil, it can serve as a measure of nutrient supply rate by continuously adsorbing charged ionic species over the burial period. This measured flux of soil nutrients over time can provide a reliable index of nutrient bioavailability [7].

In contrast to soil tests, foliar nutrient analysis can be used to provide insight into a plant's response to fertilization. It is a measure of plant's nutritional status and therefore reflects nutrient pools that are available for plant growth [8]. Leaves constitute the dominant sink for N in plants during the active growth period. At the end of the growing season, a significant part of the leaf N is withdrawn and stored in perennial tissues. The stored N is remobilized in the following spring and used for growth of new shoots [9, 10]. Phosphorus behaves in a manner similar to that of N, as a significant part of the leaf P is withdrawn before leaf abscission [11], as is potassium [12].

The seasonal dynamics of N and other macronutrients has been studied in willow biomass crops [9, 13, 14]. However, most of these studies were carried out in a controlled environment, either in the laboratory or as pot experiments in a green house. There is only limited information on the seasonal dynamics of foliar nutrient concentrations in short rotation willow biomass production systems under field conditions [15, 16]. No studies integrate the seasonal variations in soil nutrient supply and availability with foliar nutrient dynamics of SRWC systems under field conditions in organic and inorganic amended soils.

A better understanding of nutrient supply, bioavailability, and uptake over the entire growing season in SRWC systems fertilized with organic waste and commercial fertilizer is important since the timings of nutrient release and crop uptake are not always synchronized. The aim of this study is to investigate the seasonal dynamics of soil supply and bioavailability, as well as foliar concentrations of N, P, and K in a willow biomass production system that has received varying rates of organic amendments and commercial fertilizer. The specific objectives of this study are to

(1) compare the effects of varying rates of organic and inorganic fertilizers on soil N, P, and K supply and bioavailability,

(2) determine the effects of varying rates of organic and inorganic fertilizers on foliar N, P, and K concentrations as an indication of foliar nutrient response to fertilization,

(3) assess the seasonal dynamics in the supply and bioavailability of soil N, P, and K and foliar concentrations in a shrub willow *Salix miyabeana* (SX64).

2. Materials and Methods

2.1. Site Description and Preparation. This study was conducted in Delhi, NY (42° 15′ 8.65″ N, 74° 56′ 22.03″ W), on a field that had previously been used for agricultural purposes but had been left fallow for about five years prior to the establishment of the research plots. The soil at the site is a Basher silt loam (mesic Fluvaquentic Dystrudepts) with a loamy alluvium parent material derived from acid, reddish sandstone, siltstone, and shale. The soil is moderately well drained with a slope of 0–3%.

Site preparation was done using a combination of mechanical and chemical treatments in the autumn of 2006. A contact herbicide, glyphosate, was sprayed at the rate of 2.3 kg a.i. ha^{-1} followed by plowing and disking. Unrooted cuttings, about 20 cm in length, of the shrub willow cultivar *Salix miyabeana* (SX64) were planted flush with the ground in the spring of 2007 using a step planter. About 15,000 cuttings ha^{-1} were planted in double rows (1.5 m and 0.75 m distance between and within rows, respectively, and 0.6 m between cuttings in a row) to accommodate future weeding, fertilization, and harvesting operations. Preemergent herbicide, simazine, was applied at the rate of 4.5 kg a.i. ha^{-1} immediately after planting.

2.2. Characterization of Organic Materials Used and Soil at the Study Site. Prior to treatment application, soil samples were collected to characterize the initial soil properties and to determine if there were differences in the blocks that might bias posttreatment results. Samples were collected from the 0–15 and 15–30 cm layer at three locations across the diagonal of each block and composited. Soil samples were air dried and crushed to pass through a 2 mm sieve after stones, and visible roots and plant parts were removed. Soil chemical analyses were done at the Ag Analytical Lab of Penn State University. Total N was determined by combustion method [17]. Available P, K, Ca, and Mg were determined via inductively coupled plasma (ICP) following Mehlich 3 extraction. Cation exchange capacity (CEC) was determined by summation and organic matter content by loss on ignition [18] and soil pH was determined in water (1 : 2).

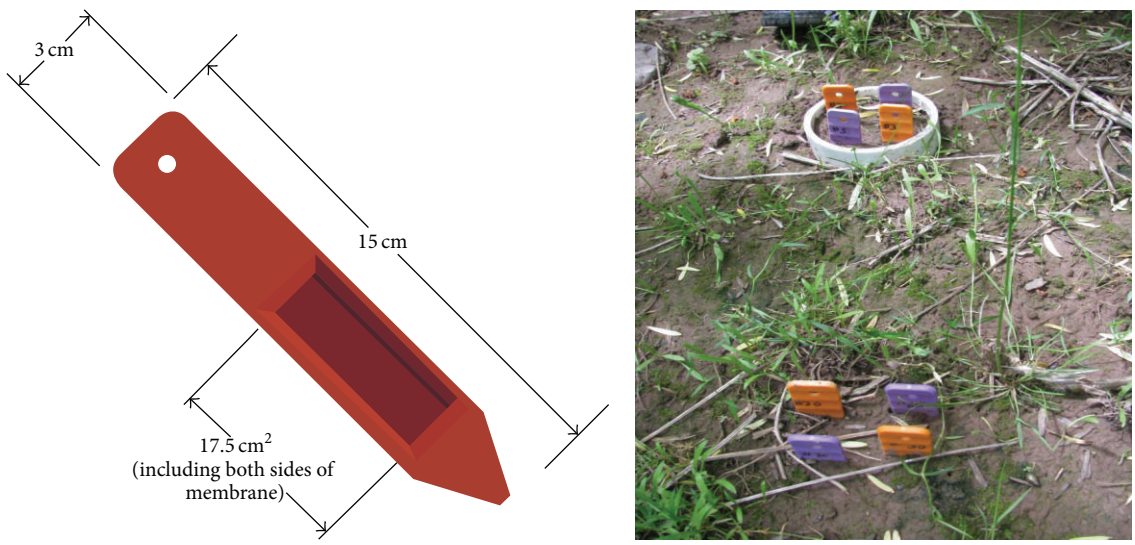
Samples of biosolid compost (BC) and digested dairy manure (DM) were stored at 4°C until analysis could be completed. Subsamples of BC and DM were oven dried at 105°C until mass loss ceased. The dried samples were ground in a Wiley mill to pass through a 1 mm mesh sieve and used for chemical analysis at the Ag Analytical Lab services of Penn State University using the same methods as above.

2.3. Treatments and Experimental Design. Experimental plots were set up to accommodate six fertilization treatments and a control in a randomized complete block design with three replications. Each treatment plot was comprised of three double rows and measured 7.92 m × 6.86 m. The middle double row within each treatment plot, measuring 4.27 m × 2.29 m, was used as measurement plot for data collection. The fertilization treatments comprising two rates (150 kg N ha^{-1} and 200 kg N ha^{-1}) of each of the three fertilizing materials were applied in June 2008. Urea (46-0-0) was used as commercial fertilizer (CF). The biosolid compost (BC) was sourced from the Delaware County Waste Treatment Plant (DCWTP) at Delhi, NY, and the digested dairy manure (DM)

Table 1: Precipitation temperature and gravimetric soil moisture content in the sampling periods when PRS probes were installed in shrub willow plots treated with organic wastes and commercial fertilizers.

Code	Burial period	Season	Total rainfall/month (mm)	Average temp./month (°C)	Gravimetric soil moisture content (θd)
Sept.	Sept. 24–Oct. 7, 2008	Fall	189.74	14.61	0.32
May	May 20–June 2, 2009	Spring	89.92	11.97	0.18
Aug.	August 10–23, 2009	Summer	198.4	19.6	0.39
Oct.	October 11–24, 2009	Fall	112.78	7.54	0.29

Temperature and precipitation data for the burial periods was downloaded from a nearby weather station: http://www4.ncdc.noaa.gov/cgi-win/wwcgi.dll?wwDI~StnSrch~StnID~20019716.



(a) (b)

Figure 1: Dimensions of the PRS probe (a) and installation in the field (b). Two sets each of cation and anion probes were buried inside and outside RECs to measure soil nutrient supply and bioavailability, respectively, and in the double row and between the double rows in shrub willow biomass crops that had been amended with organic wastes and commercial fertilizer.

was sourced from AA Dairy Farms located in Candor, NY. The fertilizing materials were manually spread evenly over the treatment plots at the respective rates of application, using wheelbarrows and shovels.

2.4. Nutrient Supply and Bioavailability Measurement. Plant root simulator (PRS) probes manufactured by Western Ag Innovations Inc., Saskatoon, SK, Canada, were used to measure soil nutrient supply and bioavailability in the measurement plots. The PRS probes consist of a cation- or an anion-exchange resin membrane encased in a plastic holding device ($15 \times 3 \times 0.5$ cm, $L \times W \times H$). The probes were inserted vertically into the top 15 cm of the soil to expose the ion-exchange membrane surface (which measures 17.5 cm^2, including both sides of the membrane) to the soil zone with the largest concentration of roots, microbial activity, and active biogeochemical processes. To measure the bioavailability of nutrients, four pairs each of cation and anion probes were installed outside of root exclusion cylinders (RECs). The same sets of probes were installed inside RECs to measure nutrient supply rate (Figure 1).

The probes were buried *in situ* for a period of two weeks in each of four sampling periods/seasons (Table 1). At the end of each burial period, the probes were removed from the soil, cleaned, and sent to Western Ag Innovations for extraction and analysis. The set of probes within each treatment plot at each burial spot were combined, much like a composite soil sample. This helped to account for any microscale variability. Nutrient accumulation rates are expressed as microgram (μg) of nutrient absorbed per 10 cm^2 per 2 weeks (i.e., μg 10 cm^2 2 wk^{-1}) and are used as a measure of nutrient supply and bioavailability. At probe retrieval, soil samples were collected in triplicate at spots near the points where the probes were installed and then composited and used to determine gravimetric soil water content by drying subsamples at 105°C. Temperature and precipitation data for the burial periods (Table 1) were downloaded from a nearby NOAA weather station [19].

2.5. Foliage Sampling and Analysis. Foliar analysis was used to determine if nutrient supply rate and uptake reflect the foliage nutrient concentrations and also to assess the nutrient

Table 2: Initial soil characteristics (mean and standard error) before organic wastes and commercial fertilizer were applied to shrub willow biomass crops.

Depth	N	P	K	Mg	Ca
	$g\,kg^{-1}$	$mg\,kg^{-1}$			
0–15	1.8 (0.1)	17.9 (3.8)	62.3 (21.9)	92.3 (2.9)	728.9 (29.2)
15–30	1.3 (0.2)	13.9 (3.3)	24.0 (7.8)	90.7 (15.0)	852.0 (138.3)
Depth	S	OM	pH	CEC	EC
	$mg\,kg^{-1}$	%		meq/100 g	mS/cm
0–15	22.2 (1.1)	9.1 (3.0)	5.4 (0.1)	14.1 (1.1)	3.9 (1.6)
15–30	26.0 (7.8)	4.4 (1.3)	5.7 (0.1)	12.4 (1.7)	3.6 (1.8)

status of the plants. At the time of probe retrieval exactly 100 fully expanded leaves in the third quarter from the bottom of the plant canopy were sampled per plot. The foliage samples were oven dried at 60°C to constant mass and then ground in a Wiley mill to pass through a 1 mm mesh sieve and used for chemical analysis using the same methods as indicated above.

2.6. Statistical Analysis. Effects of the fertilization and sampling time (seasons) on soil nutrient supply and bioavailability as well as foliar nutrient concentrations measured in the various burial periods (seasons) were analyzed using analysis of variance with repeated measures (ANOVAR). The PROC MIX procedure in SAS was used. Pearson correlation coefficients were used to examine the relationship between soil moisture and the supply and bioavailability of soil N, P, and K and the correlation between soil availability and foliar concentrations of N, P, and K and amongst the nutrient elements in soil and foliage. Statistically significant differences are reported at $\alpha = 0.05$. All statistical analyses were done using SAS [20].

3. Results

3.1. Characteristics of Soil and Organic Materials. Analysis of the soil properties between blocks prior to treatment application did not show any significant differences that could bias the posttreatment results. This pretreatment analysis indicates that the nutrient levels were typical for the type of soil in the region (Table 2). Between the organic materials, biosolid compost showed significantly higher concentrations of most nutrient elements than the manure with the exception of K. Manure K concentration was significantly higher than that of biosolid compost (Table 3).

3.2. Temperature, Rainfall, and Soil Moisture Content. The August sampling period had the highest soil moisture level (0.39 θd) as a result of the high total amount of rainfall received in that month (198.40 mm). Average air temperature was also higher in August (19.6°C) than in other sampling periods. Rainfall was lowest in May (89.92 mm) and thus the lowest soil moisture content (0.18 θd). The similarity in the patterns of monthly rainfall and soil moisture content indicates that the total amount of rainfall received per month influenced soil moisture content (Table 1).

3.3. Seasonal Patterns in Soil Supply and Bioavailability of N, P, and K. Nitrogen (NO_3^- and NH_4^+) ions released into the soil solution exhibited significant seasonal patterns. Supply and bioavailability of NO_3^- were both higher in May than in August and October (Figure 2(a)). The index of NO_3^- uptake (supply rate-bioavailability) followed the same seasonal patterns as its supply rate; it was highest in May and declined in August. Supply and bioavailability of NH_4^+ followed a different seasonal pattern. While supply rate was higher in August than in October, bioavailability was higher in October than in May (Figure 2(b)). The uptake index of NH_4^+ was greatest in May, followed by August. In October, NH_4^+ ion accumulation on the probes outside the REC (bioavailability) exceeded accumulation on the probes inside the REC (supply rate). Consequently, the NH_4^+ uptake index was negative (Figure 2(b)). In general, NO_3^- was the dominant form of N in the soil, with ratio of $NO_3^- : NH_4^+$ ranging from 7 : 1 to 22 : 1 measured inside the RECs and 3 : 1 to 15 : 1 measured outside the RECs.

The supply rate, bioavailability, and uptake index of P and K also exhibited significant seasonal variability. Both supply and bioavailability of P increased significantly in May and August and then decreased in September and October (Figure 2(c)). The P uptake index was negative in all seasons because bioavailability exceeded supply rate.

The uptake index for K was positive only in May because its supply was significantly higher than bioavailability but the supply decreased below bioavailability levels in August and October. Though K bioavailability was also high in the spring and decreased in the summer and autumn, the decrease in supply rate in the summer and autumn was greater than the decrease in bioavailability. As a result, K uptake index was negative in the summer and autumn (Figure 2(d)).

3.4. Effect of Fertilization on Soil Supply and Bioavailability of N, P, and K. The fertilization treatments had no statistical significant effect on soil N and K supply and bioavailability (Figures 3 and 4). There was also no significant treatment by season interaction effect on soil N and K supply and bioavailability. The patterns for P were different from N and K. The bioavailability of P was also not affected by fertilization but the BC1 treatment raised P supply rate significantly compared to CF1 across all seasons (Figure 4(b)). There was significant interaction effect on soil P supply rate and bioavailability. Supply and bioavailability of P in DM2 treatment were significantly higher in May than in October (Figure 4(a)). The application of DM2 treatment also increased P supply rate compared to CF1 in May (Figure 4(b)). With the exception of CF2 in August and October, the P uptake index was negative for all treatments in all seasons.

3.5. Seasonal Patterns in Foliar N, P, and K Concentrations. Foliar dry weight and concentrations of N and P exhibited significant seasonal patterns but foliar K concentration did not show any significant seasonal variability. Foliar dry weight was low at the beginning of the growing season. It increased as the season progressed and reached a maximum

Table 3: Nutrient content (mean and standard errors) of the biosolid compost and manure used as organic amendments for shrub willow biomass crops.

Organic material	Total N	Org N	NH_4^+	P	K	Ca	Mg	S
				$g\,kg^{-1}$				
Biosolid	18.1† (0.24)	17.8† (0.24)	0.3 (0.01)	14.0‡ (0.48)	6.2 (0.07)	36.3‡ (1.12)	3.5 (0.15)	6.3‡ (0.13)
Manure	15.4 (1.39)	15.2 (1.45)	0.2 (0.12)	6.0 (0.39)	8.2‡ (0.69)	10.1 (0.59)	3.5 (0.18)	3.3 (0.17)

†Significant difference between biosolids and manure at alpha level ($P < 0.05$); ‡significant at alpha level ($P < 0.01$).

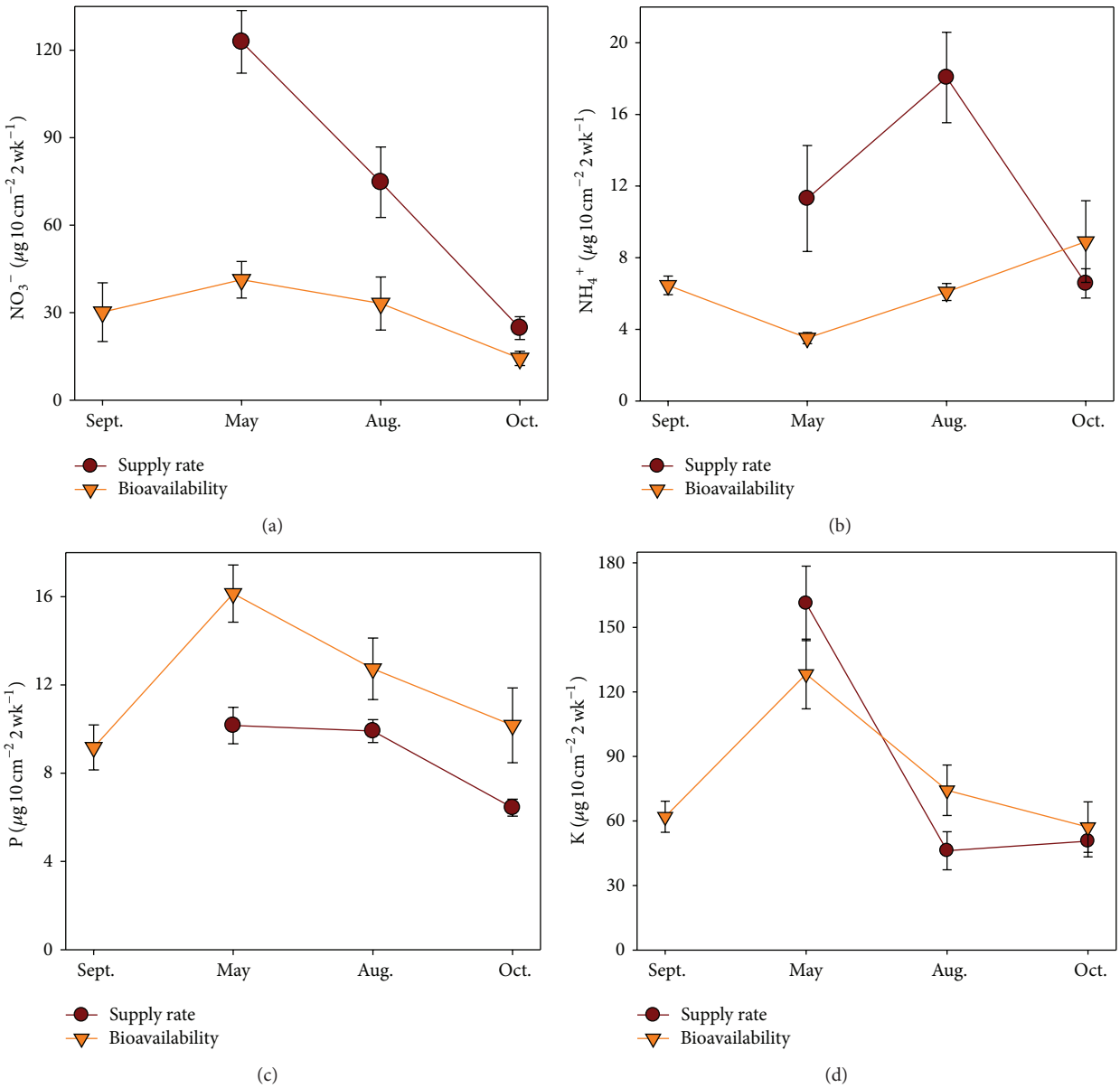


Figure 2: Seasonal dynamics in soil nutrient supply rate and bioavailability (mean and standard error) of four different compounds ((a) NO_3^-, (b) NH_4^+, (c) P, and (d) K) in a shrub willow (*S. miyabeana* SX64) biomass crops that had been amended with organic wastes and commercial fertilizer.

in August before decreasing again towards the end of the growing season (Figure 5). Foliar N concentration was also significantly higher in May but decreased as leaf development progressed into the summer and rose again in the fall (Figure 5). Foliar P concentration was high in May, when soil moisture content was low and leaf development had just begun. It then decreased to a minimum in August as leaf development progressed. However, towards the end of the growing season in October, foliar P concentration increased again (Figure 5).

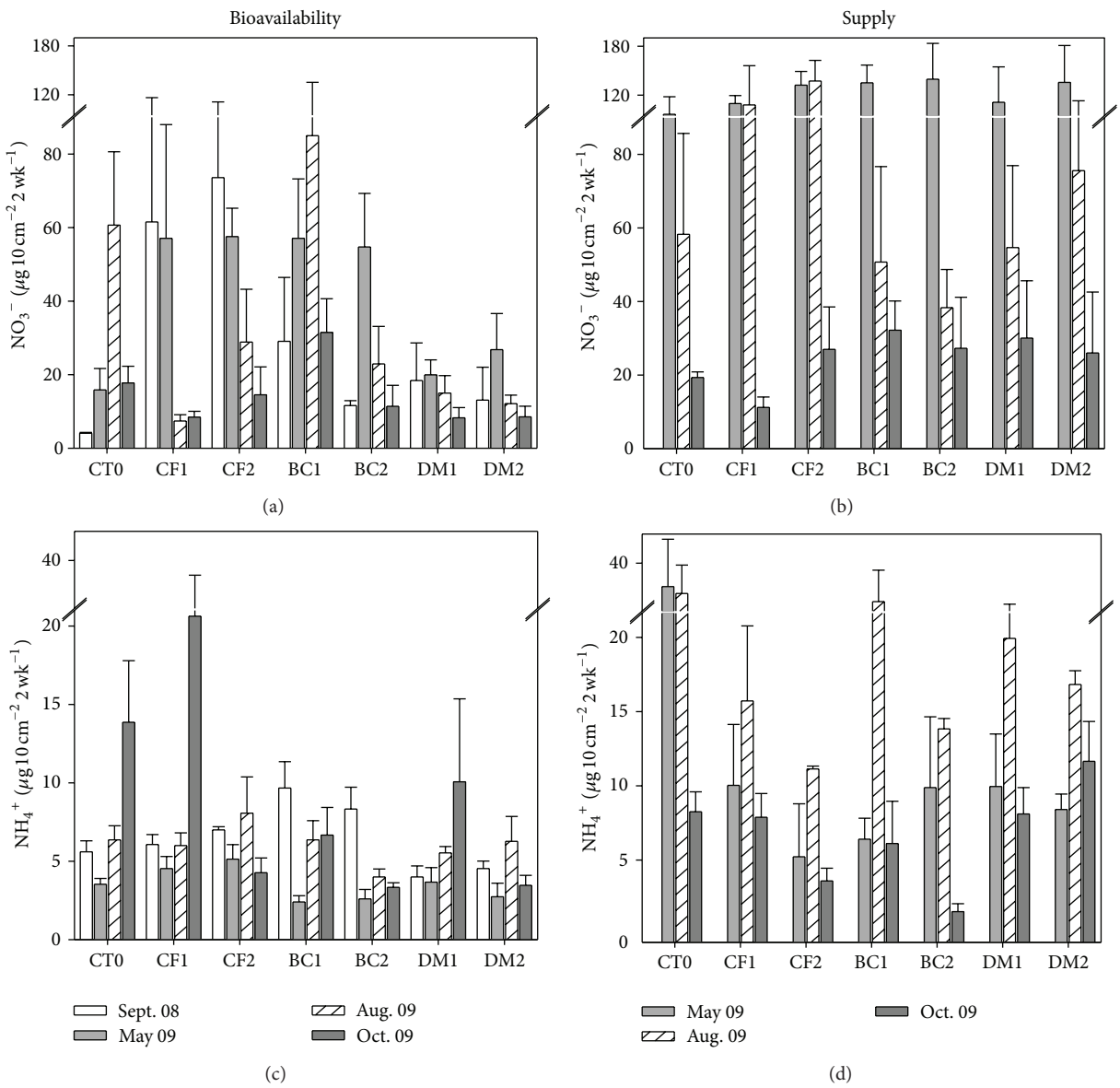


Figure 3: Soil N (NO_3^- and NH_4^+) bioavailability and supply rate (mean and standard error) in four sampling periods (seasons) of a shrub willow (*S. miyabeana* SX64) field that has been treated with two rates each of commercial fertilizer (CF), biosolid compost (BC), and dairy manure (DM). CT0 is unfertilized control.

3.6. Effect of Fertilization on Foliar N, P, and K Concentrations. There was no significant fertilization effect on foliar dry weight and N, P, and K concentrations ($P > 0.70$). There was only an interaction (treatment × season) effect on foliar N concentration ($P = 0.05$). Generally, this effect resembled more of a seasonal effect than a combination of treatment and seasonal effect. For example, foliar N concentration of the unfertilized plants was significantly higher in May than in September (Figure 6). It was also higher in all the fertilized plots in October than in August with the exception of DM1. Generally, foliar N concentration was significantly higher in May than in August for all treatments including CT0 (Figure 6).

4. Discussion

The seasonal variability in soil moisture appeared to be an important determinant in the seasonal dynamics of soil nutrient supply and bioavailability as well as foliar nutrient concentrations. The effect of soil moisture on plant nutrient supply and availability has been reported elsewhere [21]. Nitrate is soluble in the soil solution and is therefore drawn to the root through mass flow of water. Conversely, NH_4^+, P, and K are primarily moved in the soil by diffusion [22, 23].

The characteristics of organic materials, particularly C : N ratio, determine its behavior in the soil, as well as the amount of N that becomes available through mineralization [1].

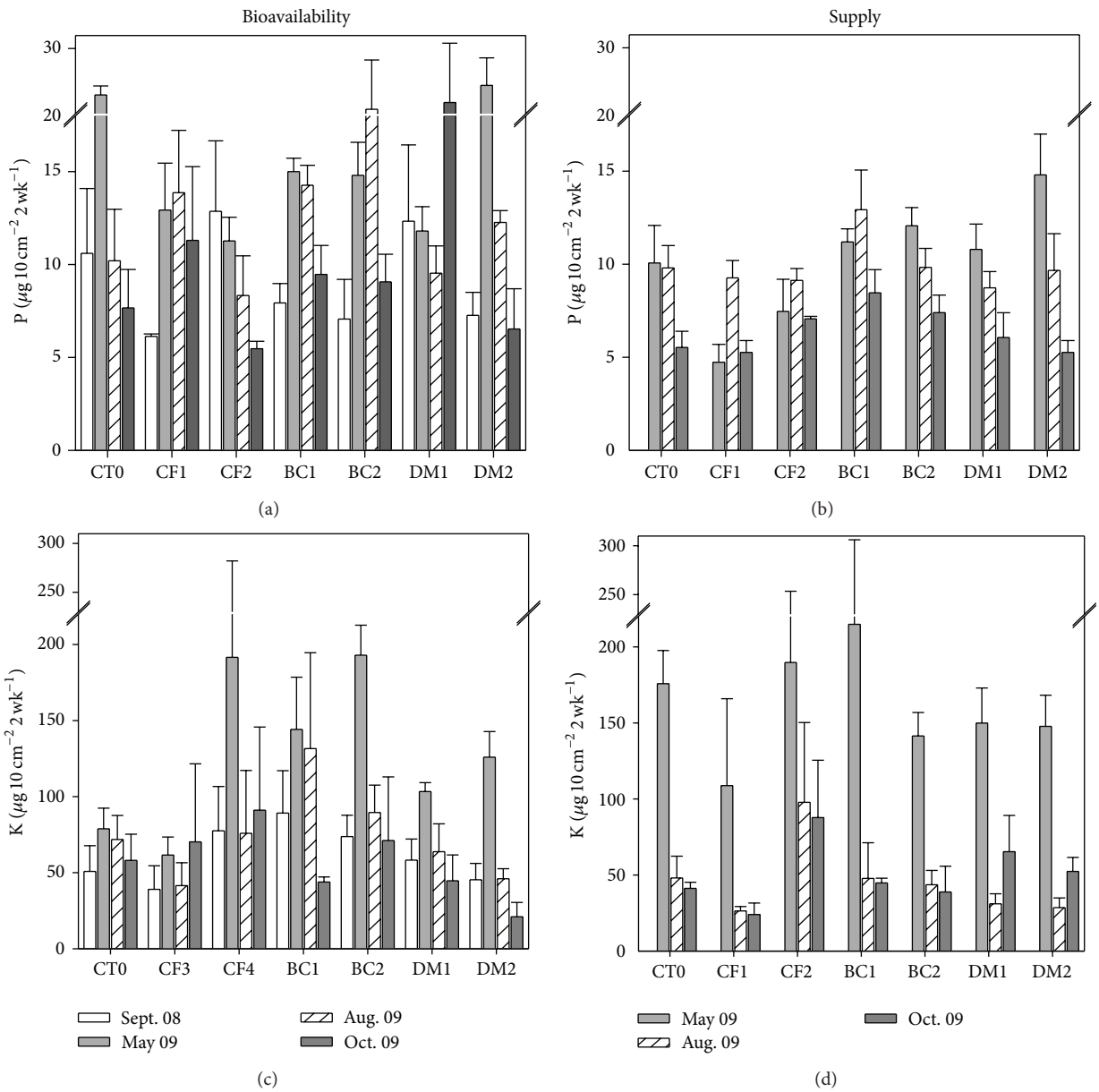


Figure 4: Soil P and K bioavailability and supply (mean and standard error) in four sampling periods (seasons) of a shrub willow (*S. miyabeana* SX64) field that has been treated with two rates each of commercial fertilizer (CF), biosolid compost (BC), and dairy manure (DM). CT0 is unfertilized control.

The organic materials used in this study contained an appreciable amount of macronutrients. The biosolid compost had significantly higher levels of N and P compared to the manure (Table 3) and was therefore expected to enrich the soil with these nutrients. The soil pH and CEC values indicate that the soil is moderately acidic and has good availability of basic cations. The characteristics of the fertilizing materials and the inherent soil properties are important factors to be considered when interpreting the results observed in this study. With a bulk density of 1.25 g cm^{-3} and soil N content of 1.8 g kg^{-1}, the total N content of the top 15 cm soil is about 3,375 kg N ha^{-1}. The addition of 200 kg N ha^{-1} is only an increase of 6%. When this is added in organic amendments with most of the N being tied up initially, it can mask the response to fertilization. Even with the commercial fertilizer, where more of the N is available over a shorter time frame, the amount of N available in the soil may overwhelm the input.

4.1. Seasonal Dynamics in Soil Supply and Bioavailability of N, P, and K. In this study, maximum NO_3^- supply rate and bioavailability occurred in May while minimum NO_3^- supply rate and bioavailability occurred in October. The NO_3^- uptake index was also high in May, indicating that even the one-year-old, above-ground willow biomass crops

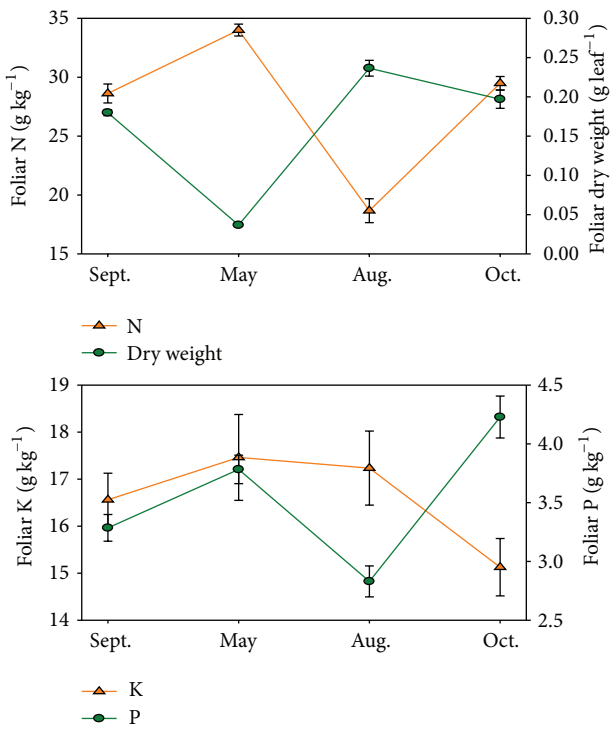


Figure 5: Seasonal dynamics in foliar dry weight and N, P, and K concentrations (mean and standard error) of a shrub willow (*S. miyabeana* SX64) crop that has been fertilized with organic and inorganic N sources.

are able to modulate the high supply of NO_3^- in the field in spring. This observation agrees with the findings of Mitchell et al. [21] who observed high NO_3^- concentration and flux in spring and low NO_3^- flux in summer and autumn. On the contrary, Huang and Schoenau [24] reported minimal soil NO_3^- supply in May and maximum supply later in the growing season in an aspen forest in Saskatchewan, Canada. Unlike the findings of Mitchell et al. [21], the decline in NO_3^- supply rate in August in this study cannot be attributed to vegetation uptake alone because the index of NO_3^- uptake was also higher in May than in August and October. Soil NH_4^+ supply rate was highest in August and lowest in October, while bioavailability was highest in October and lowest in May. The relatively higher NH_4^+ observed in August than in May could perhaps be due to inhibition of nitrification and high ammonification rates in the presence of favorable soil moisture and temperature in the summer. The negative correlations between NO_3^- and NH_4^+ supply and bioavailability support the existence of this condition in the soil. Similar observation was made by Casals et al. [17] who reported that mineral N uptake followed a seasonal pattern that matched N supply rate.

The supply rate and bioavailability of P in this study were high in May. On the contrary, Zhao et al. [25] found greater mineral P in the summer and attributed it to the combined effect of the high temperature and moisture which promote the biological transformations of soil P and lead to increased availability of inorganic P in the soil. However, other researchers have observed greater P accumulation during autumn than in spring and summer [24, 26] and ascribed it to the greater plant uptake and increased biological activity in the soil.

In this study, phosphate ion supply rate was lower than bioavailability. Consequently, the P uptake index was negative across all seasons and treatments. Though P uptake could be low at this site, biologically, it cannot be negative. The low P supply rate could therefore be attributed to microbial immobilization due to disturbance caused by the installation of the cylinders. Inserting the PVC into the soil could have caused some root damage and lead to root exudation and elevated microbial activities [26]. A second possible factor that could contribute to this observation is soil moisture. The soil inside the REC could be drier relative to that outside and could thus affect P mineralization resulting in a lower P supply rate inside the REC than outside. P mineralization is also known to be higher in the presence of plant roots, because organic P from root exudates may be mineralized to an inorganic form [27]. As an anion, phosphate participates in outer sphere reactions and its release can be a function of root chemistry [23]. In fact, the two ways by which inorganic P is released into soil solution—ligand exchange and congruent dissolution—both require the chemical action of plant roots [23]. Soil P availability is controlled by the biogeochemical transformation of the different forms of organic and inorganic P in the soil [26]. Particularly, the mineralization-immobilization of organic P is strongly influenced by seasonal variations in temperature, moisture, plant growth, and root activity and by organic matter [10, 25]. Soil P availability is particularly sensitive to soil moisture regimes, not only because of the indirect impacts through microbial activity, but also because of the movement of phosphate ions in soils by diffusion through pores filled with water.

Soil K supply rate was higher in May than in other sampling periods and showed no particular pattern with soil moisture content. The negative uptake index for K in August and October could be attributed to microbial uptake, low soil water in the RECs, and the effects of roots exudates which could result in lower K supply than bioavailability [27].

4.2. Fertilization Effects on Soil Supply and Bioavailability of N, P, and K. Neither the fertilization treatments nor their interactions with the seasons had any significant effects on soil NO_3^- and NH_4^+ supply rate compared to unfertilized plots. This lack of treatment effect may be related to internal nutrient cycling, especially when high nutrient containing leaves remain on site [28]. Internal cycling of nutrients from litter and fine roots decomposition can reduce the demand for the addition of external nutrients [29]. For example, Adegbidi [30] reported that three-year-old unfertilized *S. dasyclados* (SV1) added 80.3 kg N ha^{-1} yr^{-1} to the soil via litter fall. Rytter [31] found that 34–69 kg N ha^{-1} yr^{-1} was recycled back into the soil from three-year-old willows due to rapid turnover rates of fine roots. In addition, this site is in a flood plain and it flooded during this trial which brought additional nutrients to this site, which may have masked some of the nutrient addition in the organic amendments.

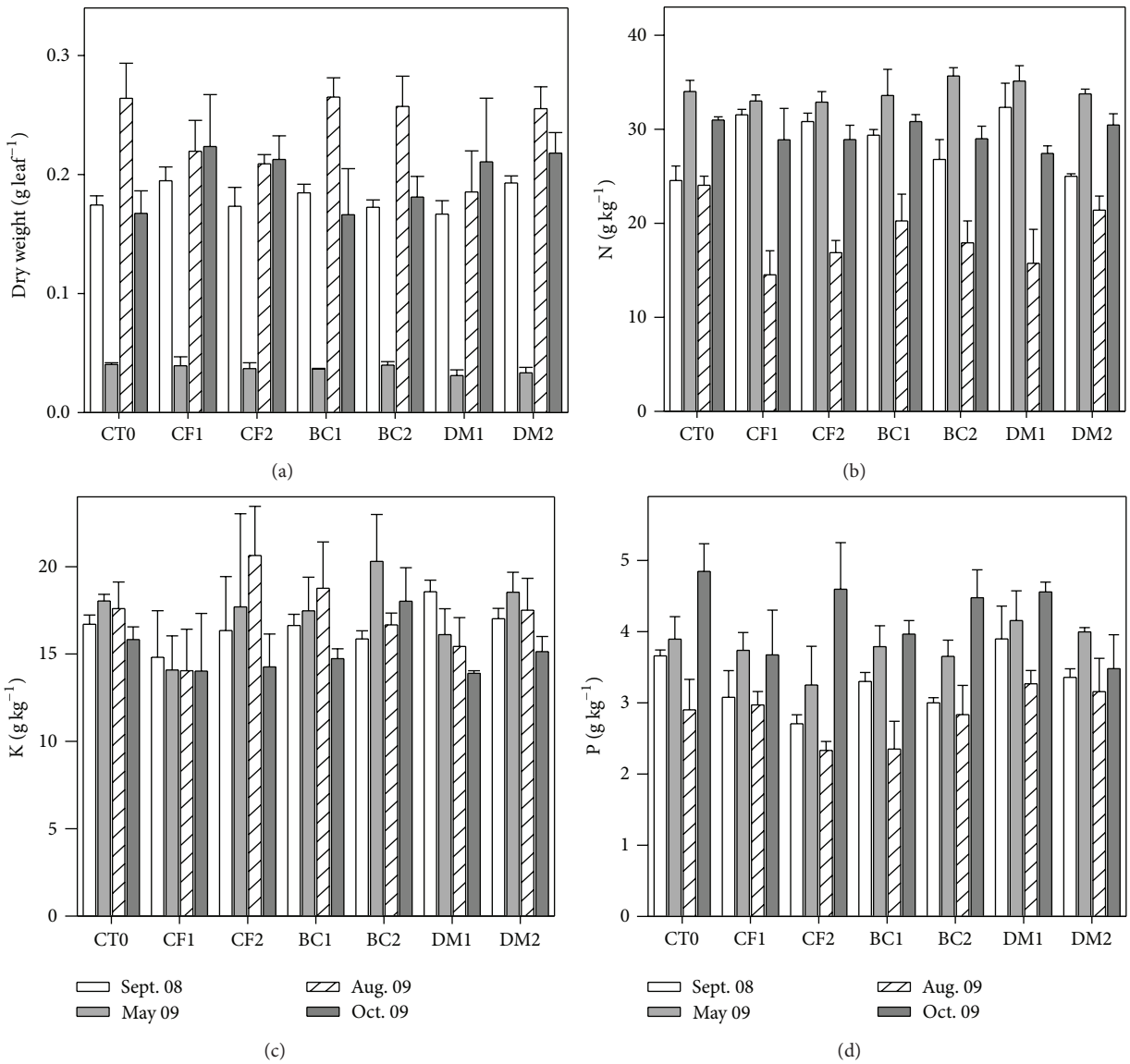


Figure 6: Foliar dry weight and N, P, and K concentrations (mean and standard error) in four sampling periods (seasons) of a shrub willow (*S. miyabeana* SX64) field that has been treated with two rates each of commercial fertilizer (CF), biosolid compost (BC), and dairy manure (DM). CT0 is unfertilized control.

The biosolid compost used in this study had twice the P concentration present in the manure. Urea contains only N and no other nutrient element. The significantly increased soil P supply rate in the organic amended plots compared to the urea treated plots was therefore expected. The contribution to mineralizable organic P content by the organic materials may have led to an increase in the P supply power in the organic amended plots. Organic matter and litter decomposition play an important role in soil P availability [22, 26]. Zhao et al. [25] also reported that P release from litter decomposition is generally higher than from the mineral soil. The increased P supply by the application of the organic wastes in this study could therefore be attributed to the decomposition of the organic matter added to the soil through the application of these materials.

Unlike N, P release showed a more variable pattern. The low values observed in September and May in the fertilized plots could be due to an initial P immobilization. Greater P mineralization occurred at later sampling periods after treatment application (August and October) as exhibited by high P levels in the organic amended plots relative to the urea treated plots. This initial immobilization followed by mineralization could be attributed to the influence of other nutrient elements such as N on P mineralization. The CF2 treatment increased soil K supply. Similarly, Hangs et al. [32] also reported an increase in soil K supply after fertilizer N addition. This may be explained by ammonium ions derived from the urea fertilizer which could displace potassium ions from exchange sites on the surface and interlayer of clay minerals into soil solution.

4.3. Seasonal Dynamics of Foliar Nutrients. The decrease in foliar N concentration between May and August was associated with increased foliar dry weight as the season progressed. This rapid increase in foliar dry weight caused dilution of N in the leaves. High foliar N concentration has been observed in deciduous trees in the spring followed by a decrease in foliar N as leaf development progressed [33]. The increase in foliar N concentration from August to October in this study is contrary to the observation made by von Fircks et al. [14]. They reported a rapid decrease in foliar N concentration of willow leaves from August to October. The higher foliar N concentration in May corresponded with the increased soil NO_3^- ion supply rate during the same period. This is consistent with NO_3^- being the predominant form of inorganic N in the soil and readily available N form for plant uptake. Secondly, it reveals that the release of plant available N from the soil N pool via mineralization in this study can be considered sufficient for normal plant growth. Thirdly, this common seasonality in soil NO_3^- supply and foliar N concentration indicates that the biogeochemical processes that influence soil N mineralization and supply rate are also determining factors in willow N uptake. Last and most importantly, it reveals the willows' ability to utilize the high soil NO_3^- in the spring, which could otherwise be leached and lost into groundwater.

Like N, foliar P concentration was also lowest in August when soil moisture and foliar dry weight were both high. Both N and P are mobile nutrient elements in plants [33] and are generally regarded as being in limited supply in most ecosystems. In other studies, P and N concentrations in leaves have been found to exhibit somewhat similar trends during the growing season [14, 33]. During the period of rapid leaf expansion in spring, both N and P exhibit increased concentrations. Though foliar P concentration in this study was relatively high in May and agrees with the above literature [14, 33], maximum foliar P concentration was observed in October, which is contrary to observation made in the literature. Foliar P concentrations in willow plants have been reported to decrease in autumn as a result of P withdrawal from the leaf prior to leaf abscission [11, 14]. The high foliar P concentration observed in this study towards the end of the growing season could be attributed to the early immobilization and late mineralization of P in the soil. The minimum foliar P concentration observed in August could also be attributed to leaching of foliar P due to the high rainfall amount received in that month. Foliar P leaching has been found to range between 5 and 15% and thus can be regarded as a major factor influencing foliage P concentration [33].

Foliar K concentrations in this study were fairly stable from September through August but decreased in October. This observation was expected because K is a mobile element in plants and thus it withdraws from the leaf before abscission [12, 14]. Like foliar N, maximum K concentration occurred in May (spring) when there was rapid accumulation in the newly formed leaves. Contrary to the results of this study, low foliar K concentrations of deciduous trees in the spring were reported by Grizzard et al. [33]. The readily available K in the soil and its high degree of mobility within the plants probably influenced its seasonal trend more than the biogeochemical processes.

4.4. Response of Foliar Nutrient Concentrations to Fertilization. Foliar nutrient concentrations have been used as an indicator of tree response to fertilization, because it is a function of available nutrients as well as the factors that influence nutrient uptake by plants [34]. In this study, foliar nutrient concentrations did not show any significant response to the fertilization. In September, plants in the fertilization treatments had high foliar N concentration relative to the unfertilized plants. However, in the May–October sampling periods, the fertilization treatments depressed foliar N relative to CT0 with the exception of BC2 and DM1 in August. This pattern of foliar N concentration with respect to fertilization is the same as observed for soil NO_3^- and therefore portrays the synchrony between soil N supply and plant N uptake.

With the exception of the DM treatments in September, the fertilization regime depressed foliar P and K concentrations relative to CT0. Similarly, Jug et al. [35] observed reduction in foliar P concentration relative to control plots after applying N fertilizer to *S. viminalis* and attributed their observation to dilution effect due to larger leaves. This does not appear to be true in this study. It is however important to note that the reduction in foliar P by the fertilization treatments did not cause any increase in the foliar N : P ratio.

This lack of response of foliar nutrient concentrations to fertilization has been observed in an earlier study where *S. dasyclados* (SV1) was fertilized with paper sludge, manure, and urea [36]. Similar results have also been reported in other willow varieties that were fertilized with waste water in Quebec [37]. The nonresponsiveness of willow foliar nutrients to the applied fertilization materials in these different studies has been attributed to the relatively high internal nutrient cycling at the sites [36–38], which is also true for the site used for this study. Significant increases in willow foliar nutrient concentrations due to the application of fertilizer and organic amendments have been reported elsewhere [15, 37, 38], but it is evident from the literature that where plants can readily access internally supplied nutrients, they do not show growth response to applied fertilizer [39].

The foliar nutrient levels measured in this study reached or even exceeded values reported for optimal growth of field grown *Salix* species [13, 35, 39, 40]. Foliar N concentrations in this study fall within the 23–30 $g\,kg^{-1}$ reported by van den Burg [40] as required for normal willow growth. In August, however, the fertilization treatments showed mean foliar N concentrations of less than 23 $g\,kg^{-1}$ which could be considered suboptimal for normal growth. However, since the decline in foliar N in August may be attributable to the dilution effect, the actual N content of the plant was not affected. Previous studies have shown that this particular shrub willow cultivar (SX64) has high biomass production but falls in a group with significantly lower foliar N concentration than other varieties of willow with high biomass production [41] suggesting that this cultivar is more

effective at N use than other cultivars. Foliar P concentrations are above the range recommended for normal growth [40] and can be considered sufficient for optimal growth. The P levels are also higher than values reported by Labrecque and Teodorescu [39] and are comparable to values reported by Jug et al. [35] and Rytter and Ericsson [13] for various field grown willow clones. Values of foliar K concentrations are sufficient for normal growth and compared well with values reported by van den Burg [40], Labrecque and Teodorescu [39], and Rytter and Ericsson [13].

5. Conclusions

Both the supply rate and uptake index of NO_3^- were high in the spring indicating a synchrony of NO_3^- supply and plant uptake. This reveals the ability of the willow biomass crop to retain the high soil NO_3^- in the spring to minimize leaching out of the root zone into groundwater. The lack of a fertilization effect on soil N supply is related to the inherently high internal nutrient cycling of soil at the site. The P-rich biosolid compost increased soil P supply rate, but the digested manure which had a lower P loading rate did not have any impact on P supply rate. Although foliar nutrient concentrations in this study did not show any significant response to the fertilization treatments, they reached or even exceeded values reported for optimal growth of field grown *Salix* species. This nonresponsiveness of willow foliar nutrient to fertilization could be attributed to high internal nutrient cycling at the site. The significant effect of the organic amendments on soil P supply rate and their comparable effects on foliar nutrient concentrations make them a better fertilization option for SRWC systems considering the cost of commercial fertilizers and the added environmental benefits of land application of organic wastes. The common seasonal patterns and the significant correlations observed between soil moisture content and soil and foliar nutrient elements show the importance of the biogeochemical processes on soil supply and plant uptake of nutrients.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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