NUTRIENTS IN MARGINAL LAND SOILS AND THEIR POTENTIAL EFFECT ON THE ENVIRONMENT

NICOLE RODRIGUEZ, TIMOTHY HO, ZHONGWEI SHI & JULIA LU
Department of Chemistry and Biology, Ryerson University, Canada

ABSTRACT
Increasing global population leads to an increase in demand for foods and cleaner energy such as biofuel and bioenergy that are produced from feedstocks. Utilizing marginal land for production of these feedstocks alleviates the competition of fuel versus food that comes with use of prime agricultural land. Canada has a large area of marginal land. Sorghum is an important plant for food, fodder, and forage production. It is regarded as a nature-cared plant with low input requirements and is recommended as a top crop for removing carbon from the atmosphere. As a part of a collaborative project to develop a system for producing biomass (sorghum) on marginal land in Canada, this research focuses on the species and their distribution, mobility and availability (to plants) of nitrogen (N) and phosphorous (P) in marginal land soils from selected locations in Canada. US EPA method 1312 was followed to simulate the leaching process of nutrients from soils in the natural environment. Colorimetry and ICP-OES were used for the determination of the nutrient species. Preliminary results show that the predominant leachable and plant-usable form of nitrogen is nitrate (NO_3^-) while the majority of phosphorus in the soil is not water leachable; depth variation of leachable nitrogen and phosphorus species in the soils is indicated; the concentrations of nitrate in the soils increased shortly after N-fertilizer application but the level decreased to that observed before planting, suggesting that atmospheric precipitate/deposition can move nitrogen from marginal land soils to surface water.
Keywords: soil nutrients, biomass, marginal land, mobility, nitrogen, phosphorus.

1 INTRODUCTION

1.1 Renewable energy

Renewable energies are gaining attention and importance recently with the awareness of limited non-renewable energies and their impact on the environment. Biomass has the potential to be used in a variety of bioenergy applications. There is evidence to predict that global bioenergy could evolve to meet the global energy demand by 2050 [1], [2]. The production of such feedstocks is, however, depending on the land and its cost. The major feedstocks for biofuel consist of agricultural crops such as corn, sugarcane, and soybean and their production compete land for food production. There has been a shift in activity towards growing alternative biofuel feedstocks (e.g., sorghum) and utilizing non-agricultural (e.g., marginal) land [3].

1.2 Marginal land

Marginal land is broadly defined as land that is either not economically suitable for agricultural use, or less productive than agricultural land [4], [5]. The classification of marginal land varies, but common characteristics involve soil quality, climatic conditions and land attributes such as evaluation, irregular terrain. Canada has 9.48 million hectares of land that is classified by the Canada Land Inventory (CLI) as marginal land (Class 4–6) [6]. There is great potential for Canada to produce biomass on its marginal land [3]. Stoof et al. [5] noted concerns of nutrient availability for these marginal soils. Sorghum is regarded as a

WIT Transactions on Ecology and the Environment, Vol 259,
www.witpress.com, ISSN 1743-3541 (on-line)
doi:10.2495/AWP220021

nature-cared plant with low input requirements, and it is recommended as a top crop for removing carbon from the atmosphere [7], [8].

1.3 Nitrogen and phosphorus

Nitrogen and phosphorus are essential elements in plant growth and development. Nitrogen supply in a crop system is predominantly represented by the level of N-species available for plant use. Inorganic nitrate (NO_3^-) and ammonium (NH_4^+) are the main forms of nitrogen that can be taken by plants, thus be removed from the soils [9]. In addition, ammonium (NH_4^+) can move from surface soil to the atmosphere through volatilization; NO_3^- can leave soil through denitrification process and it can be easily removed by leaching or runoff. Phosphorus is never found in high concentrations, making it highly conserved and is stored through sedimentation and rock formation [10], [11]. Phosphorus may be bound to metal oxides such as aluminium or iron oxides, which are much harder to leach out due to the common ion effect governed by small solubility product constants [12], [13]. Organic phosphorus can be categorized into different organic phosphate compounds in soil. Both inorganic and organic phosphorus are non-labile when in a solid-state and they make up most of the soil phosphorus. The most soluble form of inorganic phosphorus is orthophosphate (PO_4^{-3}) and is can easily be removed by leaching and runoff if not taken up by plants or converted into a non-labile form [14].

1.4 Water pollution

Fertilizer is commonly used to promote crop production. Many factors, such as placement, timing, type of fertilizer, and rate of application, have to be considered in utilizing fertilizer. Rate of fertilization is of particular importance, as excess fertilizer to a crop system can be easily lost via various processes [9], [15]. Excessive use of fertilizers has caused negative impacts through runoff which pollutes water and surrounding ecosystems [16].

1.5 Research objectives

This research studies the species of nutrients (N and P) in soil at different depths through the growing period of sorghum on marginal land and assesses the potential effect of these species on water quality.

2 EXPERIMENTAL

Field studies were carried out in 2019. Three sorghum hybrids: CSSH45, 10AX118, and 10AX131, were tested. Half of the plots at each field received one application of N-fertilizer (urea, 46-0-0, rate of 45 kg ha^{-1}) about two weeks after planting.

2.1 Study sites

Three field sites in Ontario, Canada are evaluated in this research and they are located in London (43°01’49.0”N, 81°12’23.6”W), Simcoe (42°51’35.0”N, 80°16’17.0”W), and Ottawa (45°19’30.0”N, 75°52’55.2”W). The field designs are shown in Fig. 1.

2.2 Sample collection and preparation

Soil cores were collected from each site three times during the growing period: before planting, about two weeks after the fertilizer application (after planting) and at harvest. The

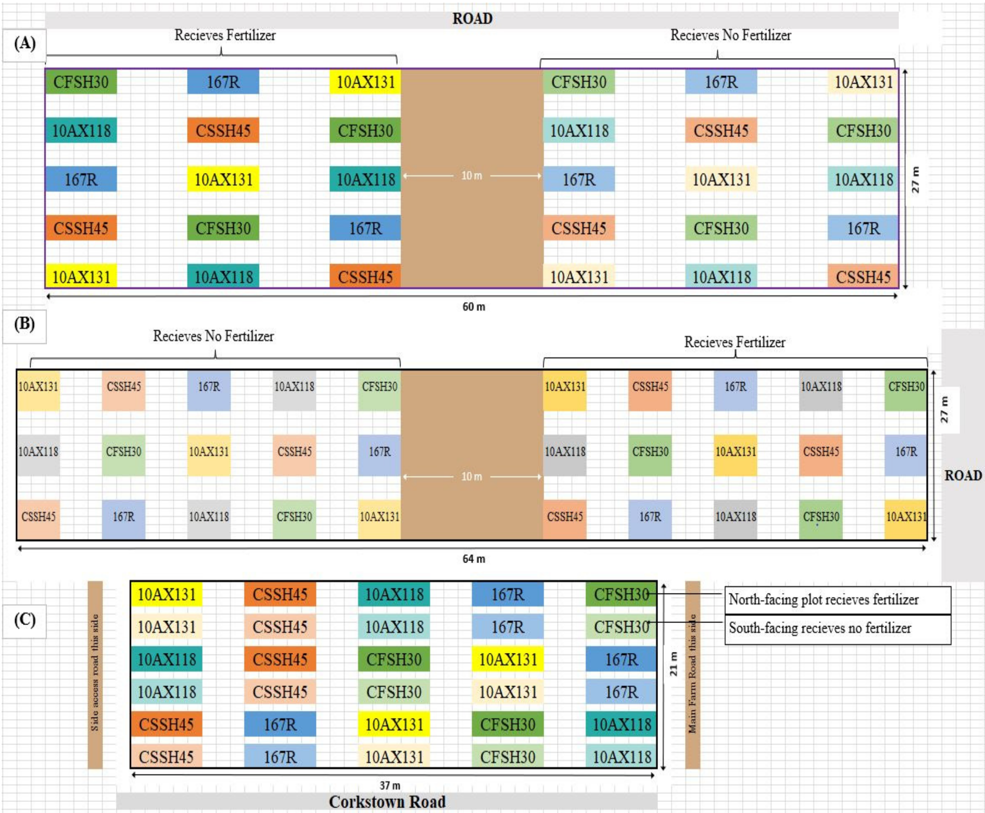

Figure 1: Field plot design for (A) London; (B) Simcoe; and (C) Ottawa, Canada.

soil samples at 0–10 cm and 20–30 cm depths from the soil cores were collected. After the collection, soil samples were stored in sealed Ziploc bags and stored in a freezer until analysis. Field soil samples were thawed for 24 hours, grinded, and passed through a 2 mm sieve using a mortar. The homogenized soil samples were extracted using water of pH 5.0 following EPA method 1312 [17] at a mixing ratio of 1.5 g soil:30 g water (1:20) for 18 ± 2 hours. Centrifugation was used to separate the liquid (soil extract) from the soil residuals.

2.3 Analysis methods

2.3.1 Nitrogen species

Concentration of NO_3^- ($[NO_3^-]$), NO_2^- ($[NO_2^-]$), and NH_4^+ ($[NH_4^+]$) in the soil extracts were determined (2.00 g soil extract for NO_3^- and NO_2^-, 3.00 g soil extract for NH_4). The $[NO_2^-]$ was analyzed using Griess reaction, a scaled-up version outlined by Hood-Nowotny et al [18]. NO_3^- was reduced to NO_2^- with vanadium chloride (VCl_3) then determined using the same Griess reaction as for NO_2^- [19]. After the colour reaction, the $[NO_2^-]$ was determined using UV-Vis (Cary 60, Agilent) at 540 nm and $[NO_3^-]$ was then calculated. The $[NH_4^+]$ is analyzed using a modified Berthelot reaction catalyzed by sodium nitroprusside [20] and is then determined using UV-Vis (Cary 60 Agilent) at 687 nm. The analysis was done in triplicate.

2.3.2 Phosphorus

Orthophosphate concentration ([PO_4^{-3}]) and total phosphorous ([P]$_{total}$) in soil extracts were determined (1.00 g soil extract for PO_4^{-3}, 0.35 g soil for total phosphorous). The analysis of PO_4^{-3} based on molybdenum blue reaction [21] followed by UV-Vis (Cary 60, Agilent) determination at 890 nm. Microwave digestion (EPA 3051A) + ICP-OES were used for the determination of [P]$_{total}$ in the soil samples [22]. The analysis was done in triplicate.

2.4 Data QA/QC

The analysis methods were validated using standard reference materials (nutrients in soil; lot: LRAC0708, and anions in soil; lot: LRAC1295, Sigma Aldrich). One or more blank solutions and a standard solution measurement were carried out each day of analysis to monitor changes or trends in each method. The limit of detection (LOD) for each species is defined as:

$$LOD = \frac{3 * S_{blank}}{b},$$

where S_{blank} is the standard deviation of the blank values, b is the slope of the calibration curve [23]. The LODs were 0.03, 0.01, and 0.04 mg kg^{-1} for NO_3^-, NO_2^-, and NH_4^+. The LODs were 0.40 mg kg^{-1} for PO_4^{-3} and 2.40 mg kg^{-1} for total P.

2.5 Data analysis

One-way ANOVA was used for data analysis to determine whether or not the difference in nitrogen levels between the groups is significant. The groups evaluated were between the top and bottom soil layers within each field, plots with and without fertilizer application within each field, fields between agricultural and marginal lands, temporal effects within each field over the growing season.

3 RESULTS AND DISCUSSION

3.1 Nitrogen species

A total of 453 soil samples were analyzed and the results show [NO_3^-] in 98% of the samples, [NO_2^-] in only 34%, and [NH_4^+] in 8% of the samples above their LODs. NO_2^- is an intermediate species in the nitrification reaction, which rarely accumulates in soil. For NH_4^+, as it is a positive cation, it tends to be more tightly bound to soil particles which are inherently negatively charged. Since acidified water was used as the extracting solution instead of salt solution, it was not expected the [NH_4^+]$_{soil}$ to be high. The following results and data analysis will, therefore, focus on NO_3^- in the soil samples only.

The NO_3^- concentrations in the soil samples collected before planting at 0–10 cm and 20–30 cm depths from all three sites are shown in Fig. 2. At each site, the [NO_3^-] is higher in the top layer soil but the values in each soil layer are not statistically significant (p-values $\geq$ 0.05) at all three sites, regardless soil type (agricultural vs marginal land).

Fig. 3 shows the [NO_3^-] in the soil samples collected about two weeks after fertilizer application and at harvest from the plots with different sorghum hybrids and with and without the application of the N-fertilizer from all the experimental sites. The results show similar trends across all three hybrids in terms of [NO_3^-] within each field. There is a general decrease in [NO_3^-] at deeper soil layer from both the unfertilized and fertilized plots. Statistical

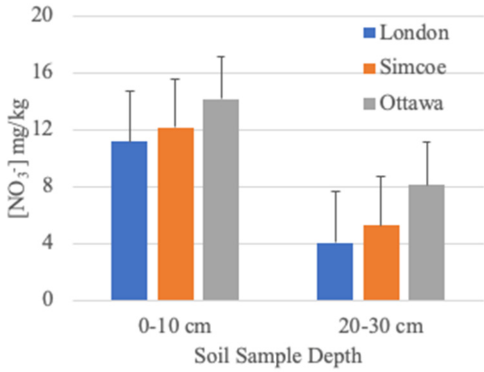

Figure 2: [NO_3^-] in the soil of two layers from the field sites before planting (n = 4). Whiskers represent standard errors.

analysis resulted in p-values < 0.05 thus the difference was significant for the [NO_3^-] values between the two soil layers within each hybrid at all three sites during the growing period. This can be explained that soil was tilled at about 15 cm deep as agricultural practice, whereas the untilled soil located below was more compact. This physical difference could limit NO_3^- downward movement with water as the pore space is limited. After planting [NO_3^-] is higher in the soil from the plots with urea applied, especially at the 0–10 cm as urea was directly applied on the surface. However, the difference is less apparent at harvest. Further data analysis will therefore be focused on 0–10cm soil layer only.

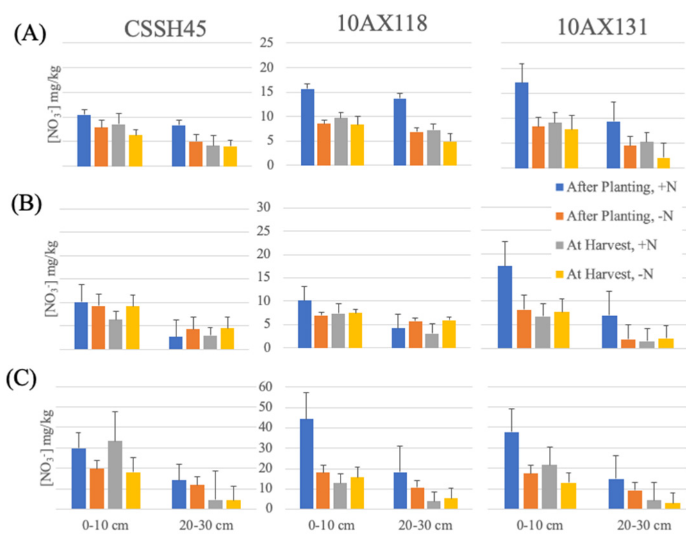

Figure 3: [NO_3^-] levels at two soil depths from the plots with sorghum hybrids (CSSH45, 10AX118, 10AX131) at (A) London; (B) Simcoe; and (C) Ottawa fields. –N = unfertilized plots; +N = fertilized plots (n = 3). Whiskers represent standard errors.

www.witpress.com, ISSN 1743-3541 (on-line)

Statistical analysis (Table 1), shows that N-fertilizer application has significant effect on the $[NO_3^-]_{soil}$ levels after planting at the London and Ottawa sites. This difference was expected as the application of urea two weeks before the sample collection would theoretically increase the amount of N available in soil. The same effect, however, is not indicated for the Simcoe site, possibly due to factors such as lower organic content, compared with that in the agricultural soil at the London site and lower $[NO_3^-]$, compared with that at the Ottawa site, in the soil before planting (Fig. 2), soil texture, etc. At harvest, however, the effect is no longer significant at all three sites as indicated in Table 1. The results in Table 1 also show that sorghum variety does not have a statistically significant impact on the $[NO_3^-]_{soil}$. The same finding was reported by Chen et al. for a marginal site in China [24].

Table 1: Summary of statistical analysis for the effects of N-fertilizer (N) and sorghum hybrid (H) on $[NO_3^-]$ in the top 10 cm soil collected after planting and at harvest from the field sites.

Collection period	Field	N	H
After planting	London	*	ns
	Simcoe	ns	ns
	Ottawa	*	ns
At harvest	London	ns	ns
	Simcoe	ns	ns
	Ottawa	ns	ns

* Denotes a significant effect at p-value < 0.05; ns denotes non-significant effects, p-value ≥ 0.05.

Since sorghum hybrids have no significant effect on the $[NO_3^-]$ in the soils, the data of all hybrids were combined at each collection to assess the temporal effect on the $[NO_3^-]$ in the soil throughout the growing season, noting that three collection periods (i.e., before planting, after planting, at harvest) for unfertilized while only two (i.e., after planting and at harvest) for fertilized condition were used for the assessment. Statistical analysis results summarized in Table 2 show that, throughout the growing season, the difference in the $[NO_3^-]$ in the unfertilized soil is significant at the agricultural site in London but not significant at the marginal sites in Simcoe and Ottawa, but the difference in the $[NO_3^-]$ in the N-fertilized soil is significant at all the sites tested, regardless soil type.

Table 2: Summary of statistical analysis for temporal effect on the $[NO_3^-]_{soil}$ in the top 10 cm soil from the field sites over the growing season.

Field	Soil depth	Temporal effect on unfertilized samples	Temporal effect on fertilized samples
London	0–10 cm	*	*
Simcoe	0–10 cm	ns	*
Ottawa	0–10 cm	ns	*

* Denotes a significant effect at p-value < 0.05; ns denotes non-significant effects, p-value ≥ 0.05.

To further evaluate the changes in the $[NO_3^-]_{soil}$ over the 2019 growing season, NO_3^- in the top 10 cm soil (kg ha^{-1}) during the growing period at each site was calculated and the values are listed in Table 3. An average bulk density of 1.45 g cm^{-3} for sandy loam soils was used for the estimate [25]. The 20–30 cm depth was excluded from this comparison as the soil at this depth pasts the tillage depth.

Table 3: Summary of [NO_3^-] (kg ha^{-1}) in the top 10 cm soil at the collection periods from the field sites.

	Before planting	After fertilizer application (theoretical)	After planting		At harvest	
Fertilizer / Field	–N	+N	–N	+N	–N	+N
London	14.5 ± 3.7	59.5	11.8 ± 2.2	19.5 ± 5.7	9.7 ± 3.0	12.1 ± 2.3
Simcoe	15.5 ± 5.4	60.5	9.8 ± 3.8	15.0 ± 9.8	9.9 ± 3.9	9.9 ± 2.3
Ottawa	19.3 ± 3.1	64.3	21.9 ± 6.5	37.6 ± 21.0	16.0 ± 10.1	21.4 ± 17.0

The values in Table 3 show that, overall, the NO_3^- in the soils with and without N-fertilizer application decreased from before planting to at harvest, but the changes are not statistically significant in the soils from the plots without N-fertilizer application at all sites tested.

Nitrogen in the soils with N-fertilizer application decreased from after fertilizer application to at harvest at each field site, with net change (i.e., N-loss) of 47.4, 50.6, and 42.9 kg ha^{-1} in the soil for London, Simcoe and Ottawa site, respectively. NO_3^- can be removed from soil by various processes such as plant uptake, denitrification process, leaching, runoff. The results obtained by Tian's group (Agriculture and Agri-Food Canada, personal communication) show that N-fertilizer application had no significant effect on the dry sorghum mass produced at each of the sites tested. Data analysis showed that $[NO_3^-]_{soil}$ was anti-correlated to the amount of precipitate during the collection periods after N-fertilizer application and at harvest, suggesting leaching and runoff play a role in removing [NO_3^-] from the soils.

3.2 Phosphorus

The [PO_4^{-3}] in 88% of the soil samples analyzed were above LOD. The [PO_4^{-3}] in the soil samples collected before planting from all the field sites are shown in Fig. 4. It can be seen that the [PO_4^{-3}] levels in the 0–10 cm soil layer are higher than those in the 20–30 cm soil layer. Data analysis resulted in p-values < 0.05, confirming the difference is statistically significant.

The [PO_4^{-3}] in the soil samples collected after planting and at harvest from all the field sites are shown in Fig. 5 and statistical results are summarized in Table 4. The [PO_4^{-3}]s in all the soil samples with N-fertilizer applied between the two soil layers are statistical different for both after planting and at harvest, but the values in the two soil layers without the fertilizer application are not statistically significantly different, except in the soils from plots with 10AX118 sorghum hybrid after planting. The [PO_4^{-3}] in the soils at both depths at Ottawa site is relatively low, but statistical analysis suggests that difference is significant between the depths.

Total P in the soil samples, ranged from 479 to 938 mg kg^{-1} for the London site; 346 to 1106 mg kg^{-1} for the Simcoe site and 386 to 1156 mg kg^{-1} for the Ottawa site. Statistical analysis showed no significant difference on the $[P]_{total}$ for all except the London field site. $[P]_{total}$ profile pattern is observed, more prominently, in the soils at the London site (i.e.,

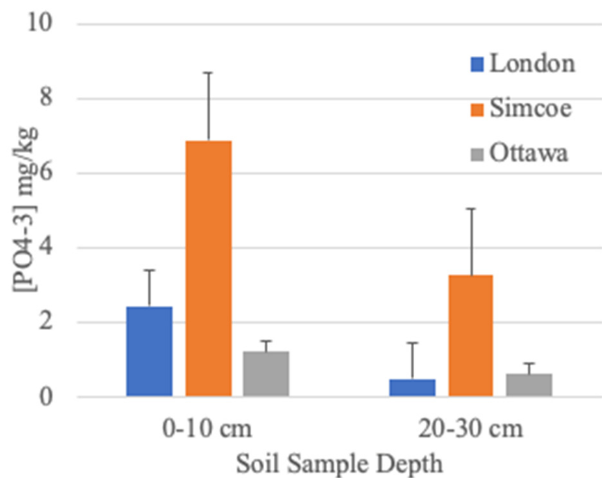

Figure 4: Comparison of [PO_4^{-3}] levels in two soil depths at three fields before planting (n = 4). Whiskers represent standard errors.

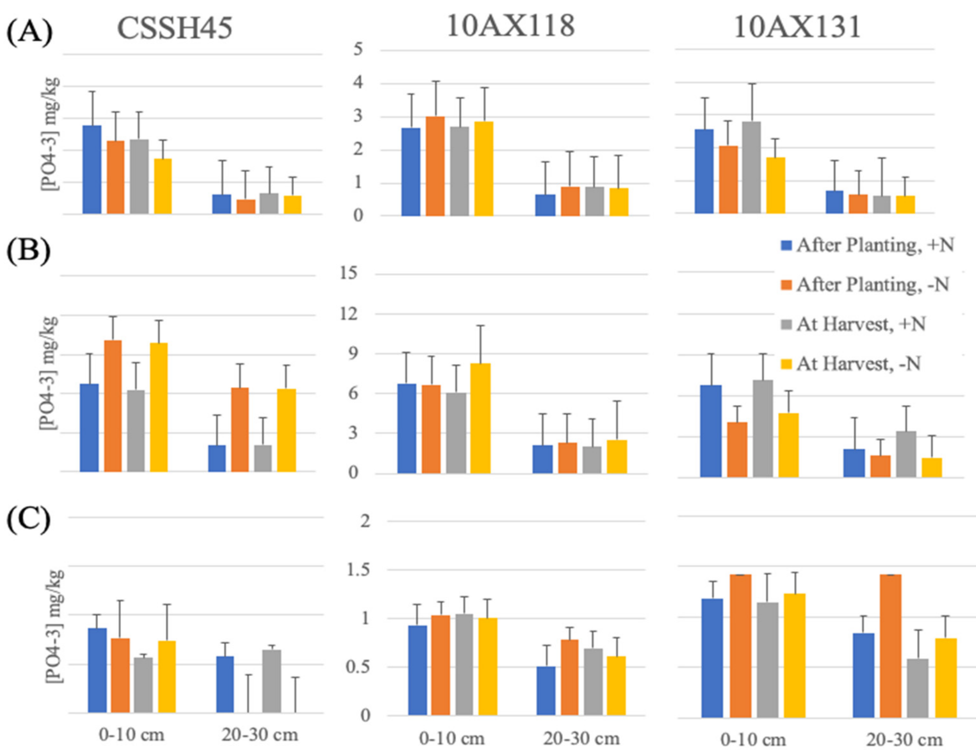

Figure 5: [PO_4^{-3}] levels (n = 3) at two soil depths with three different sorghum hybrids (CSSH45, 10AX118, 10AX131) at (A) London; (B) Simcoe; and (C) Ottawa field sites, 2019. –N = unfertilized plots; +N = fertilized plots. Missing bars are due to values <LOD. Whiskers represent standard errors.

Table 4: Summary of statistical analysis for the effects of nitrogen fertilizer (N) and sorghum hybrid (H) on [PO_4^{-3}] at the corresponding depth and collection periods at the field sites.

		After planting		At harvest	
Field	Soil depth	N	H	N	H
London	0–10 cm	ns	ns	ns	ns
	20–30 cm	ns	ns	ns	ns
Simcoe	0–10 cm	ns	ns	ns	ns
	20–30 cm	ns	ns	ns	ns
Ottawa	0–10 cm	ns	ns	ns	ns
	20–30 cm	ns	ns	ns	ns

ns denotes non-significant effects, p-value ≥ 0.05.

agricultural land), likely due to the past application of P fertilizer. Ottawa did not exhibit the same pattern: $[P]_{total}$ is highly homogenous across the two depths in Ottawa regardless of sorghum hybrids or the N-fertilizer application. The collection periods appeared to have no statistically significant impact on $[P]_{total}$ in the soils. The results show that less than 1% P in the soils is present as PO_4^{-3}.

Table 4 shows the summary of statistical analysis that evaluates the effect of N-fertilizer and sorghum hybrid on $[PO_4^{-3}]_{soil}$, showing that neither N-fertilizer nor sorghum hybrid had statistically significant effect on the [PO_4^{-3}] in the soils.

4 CONCLUSION

Analysis of nitrogen species showed that NO_3^- is the predominant leachable and mobile N-species in the soils. N-fertilizer increased the [NO_3^-] in the soils but the level decreased to that observed in the soils collected before planting. Leach and runoff play roles in removing NO_3^- from the soil regardless the land types and fertilizer acts as a source of pollutants to freshwater. The majority of P in soils is not mobile thus will unlikely have significant effect on water quality under the experimental conditions.

ACKNOWLEDGEMENT

Financial support from Biomass Canada Cluster (BMC) through Agriculture and Agri-Food Canada's AgriScience program and industry partners to Julia Lu.

REFERENCES

[1] Ladanai, S. & Vinterbäck, J., *Global Potential of Sustainable Biomass for Energy*, SLU, Institutionen för Energi Och, p. 29, 2009.
[2] World Bioenergy Association, Global Bioenergy Statistics, 2019.
[3] Liu, T. et al., Bioenergy production on marginal land in Canada: Potential, economic feasibility, and greenhouse gas emissions impacts. *Appl. Energy*, **205**, pp. 477–485, 2017.
[4] James, L.K., Theory and identification of marginal land and factors determining land use change. *Science*, pp. 1–99, 2010.
[5] Stoof, C.R. et al., Untapped potential: Opportunities and challenges for sustainable bioenergy production from marginal lands in the northeast USA. *Bioenergy Res.*, **8**, pp. 482–501, 2015.
[6] Government of Canada, Canada Land Inventory (CLI). https://sis.agr.gc.ca/cansis/nsdb/cli/classdesc.html.

[7] Holou, R.A.Y. & Kindomihou, V.M., The biofuel crops in global warming challenge: Carbon capture by corn, sweet sorghum and switchgrass biomass grown for biofuel production in the USA. *Front. Bioenergy Biofuels*, 2017.

[8] Nenciu, F., Vlăduț, V., Nae, G., Popa, L.-D. & Constantin, O.E., Developing efficient practices for producing bioethanol from sweet sorghum, evaluating several varieties of the plant and growing environments. *E3S Web Conf.*, **286**, 03020, 2021,

[9] Jämtgård, S., Näsholm, T. & Huss-Danell, K., Nitrogen compounds in soil solutions of agricultural land. *Soil Biol. Biochem.*, **42**, pp. 2325–2330, 2010.

[10] Wood, T., Bormann, F.H. & Voigt, G.K., Phosphorus cycling in a northern hardwood forest. *Biological and Chemical. American Association for the Advancement of Science*, **223**(4634), pp. 391–393, 2008.

[11] Perring, M.P., Hedin, L.O., Levin, S.A., McGroddy, M. & De Mazancourt, C., Increased plant growth from nitrogen addition should conserve phosphorus in terrestrial ecosystems. *Proceedings of the National Academy of Sciences of the United States of America*, **105**(6), pp. 1971–1976, 2008.

[12] Lide, D.R., Solubility product constants, *CRC Handbook of Chemistry and Physics*, 2006.

[13] Fink, J.R., Inda, A.V., Tiecher, T. & Barrón, V., Iron oxides and organic matter on soil phosphorus availability. *Ciencia e Agrotecnologia*, pp. 369–379, 2016.

[14] Frossard, E., Condron, L.M., Oberson, A., Sinaj, S. & Fardeau, J.C., Processes governing phosphorus availability in temperate soils. *Journal of Environmental Quality*, **29**(1), pp. 15–23. 2000.

[15] Kim, J. & Rees, D.C., Nitrogenase and biological nitrogen fixation. *Biochemistry*, **33**, pp. 389–397, 1994.

[16] Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., Daniel, T.C. & Reddy, K.R., Managing agricultural phosphorus for protection of surface waters: Issues and options. *Journal of Environmental Quality*, 1994.

[17] United States Environmental Protection Agency (USEPA), Method 1312: Synthetic precipitation leaching procedure, Vol. 1, 1994.

[18] Hood-Nowotny, R., Umana, N.H.-N., Inselbacher, E., Oswald-Lachouani, P. & Wanek, W., Alternative methods for measuring inorganic, organic, and total dissolved nitrogen in soil. *Soil Sci. Soc. Am. J.*, **74**, pp. 1018–1027, 2010.

[19] Miranda, K.M., Espey, M.G. & Wink, D.A., A rapid, simple spectrophotometric method for simultaneous detection of nitrate and nitrite. *Nitric Oxide – Biol. Chem.*, **5**, pp. 62–71, 2001.

[20] Weatherburn, M.W., Phenol-hypochlorite reaction for determination of ammonia. *Anal. Chem.*, **39**, pp. 971–974, 1967.

[21] Harwood J.E., van Steenderen R.A. & Kühn A.L., A rapid method for orthophosphate analysis at high concentrations in water. *Water Research*, **3**(6), pp. 417–423, 1969.

[22] United States Environmental Protection Agency (USEPA), Method 3051A: Microwave assisted acid digestion of sediments, sludges, soils, and oils, 2007.

[23] Skoog D.A., West D.M., Holler F.J. & Crouch S.R., Fundamentals of analytical chemistry. Cengage Learning, p. 214, 2014.

[24] Chen, F. et al., Effects of nitrogen fertilization on soil nitrogen for energy sorghum on marginal land in China. *Agron. J.*, **109**, pp. 636–645, 2017.

[25] Government of Canada, Canadian Soil Information Service (CanSIS). https://sis.agr.gc.ca/cansis/index.html.