SOIL PHOSPHORUS FORMS AND CYCLING ARE ALTERED BY ACIDIFICATION FROM NITROGEN IN LONG-TERM WHEAT PLOTS IN SWIFT CURRENT, SASKATCHEWAN

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ABSTRACT

Nitrogen (N) fertilization is widely recognized as a contributor to soil acidification. This in turn can alter soil phosphorus (P) cycling, because P is optimally soluble in soils within a limited pH range. This study used continuous wheat plots in Saskatchewan Canada to determine the effects of N and P fertilization or cessation on soil P cycling. The +N+P and -N+P plots were established in 1967, while subplots of +N-P and -N-P were established in 1995 by stopping P fertilization. Long-term NH_4-N addition produced a pH change equivalent to 0.5 pH units per 1000 kg NH_4-N ha^{-1}; in 2016, pH in water ranged from 5.6 (+N+P) to 6.7 (-N-P). This pH change altered aspects of both the biology and chemistry in these soils, and both N and P addition or withdrawal altered soil P cycling. Acidification affected exchangeable cations, and shifted P pools from P associated with calcium (-N-P) to P associated with aluminium and iron (+N+P, +N-P). Phosphorus addition or withdrawal significantly affected soil test P (Olsen, Mehlich, $CaCl_2$-extractable) and soil total P, while soil pH and P addition/withdrawal affected soil organic P concentrations and phosphatase activities.

INTRODUCTION

It has long been recognized that nitrogen (N) fertilization can decrease soil pH (acidification), particularly products containing ammonia (NH_3) or ammonium (NH_4), such as ammonium nitrate, urea, monoammonium phosphate (MAP) or ammonium sulphate (Darusman et al. 1991; Bouman et al. 1995; Barak et al. 1997; Guo et al. 2010). Soil acidification can affect many aspects of soil and plant health. Acidification reduces soil cation exchange capacity and decreases the concentrations of calcium (Ca), magnesium (Mg) and potassium (K). Acidification will also increase other cations, such as aluminum (Al), iron (Fe) and manganese (Mn), some of which (e.g. Al) can be toxic to crops such as wheat. Soil phosphorus (P) cycling is particularly vulnerable to acidification, because P is optimally soluble in soils within a limited pH range (Barrow 2017; Penn et al. 2019).

In SK, Canada, concerns about pH changes from N fertilization have existed for decades. Campbell and Zentner (1984) reported acidification in continuous wheat in long-term plots established in 1967 at the Agriculture & Agri-Food Canada (AAFC) Swift Current Research and Development Centre (SCRDC). These plots were fertilized with P, and with or without N. In 1995, P fertilization ceased in sub-plots established on these main plots. The objective of this study was to study changes in P pools in these long-term plots, with and without N and P fertilization.

MATERIALS AND METHODS

Samples were collected from an experiment established in 1967 on Orthic Brown Chernozem (Aridic Haploboroll, USDA; Haplic Kastanozem, FAO) soils at the AAFC SCRDC in Saskatchewan, Canada (latitude 50º170′N, longitude 107º480′W). This study used two treatments, each with three replicate plots: continuous wheat receiving 10 kg P ha^{-1} yr^{-1} (monoammonium phosphate, MAP) and either a) no N fertilizer (the -N+P treatment); or b) 32-50 kg N ha^{-1} yr^{-1} (ammonium nitrate, NH_4NO_3 from 1967-2007, urea from 2008; the +N+P treatment). In 1995, subplots without P fertilization were established on all plots for both treatments, hereby designated as the +N-P and -N-P treatments. More details are available in Selles et al. (1995, 2011), Liu et al. (2015), and Li et al. (2020). For this study, crops were seeded on June 13, 2016, and soil samples were collected at anthesis (August 15, 2016) and after crop harvest (November 14, 2016) at 0-7.5 cm depth. At each sampling date, three separate samples were collected from each plot. These were kept separate for analysis, giving nine samples per plot per collection date. A subset of soils was refrigerated for enzyme assays; the remainder was dried and ground (< 2 mm).

Using dried soils, pH was measured in water saturation paste, total P (TP) was determined by digestion and total organic P (TP_o) was determined by the ignition method (O'Halloran and Cade-Menun, 2008), with colorimetric analysis (Murphy and Riley, 1962). Samples were extracted with 0.5 M bicarbonate (Olsen-P; Olsen et al., 1954), and 0.01 M $CaCl_2$-P (Self-Davis et al., 2009), followed by colorimetric analysis. Mehlich 3 extraction (Mehlich 1984), followed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific ICAP 6300 Duo) was used to determine the concentrations of Mehlich-P and Mehlich-Fe, -Al, and -Ca.

Using refrigerated surface soils within five days of sampling for both sampling dates, the potential activities of acid and alkaline phosphomonoesterase were assayed with *p*-nitrophenyl phosphate at pH 5.5 and 11, respectively (Tabatabai, 1994).

Dried soils from the anthesis samples were sequentially extracted (Zhang & Kovar 2009) into the fractions NH_4Cl-P (soluble and loosely bound P), NH_4F-P ("Al-P"), NaOH-P ("Fe-P"), citrate-bicarbonate dithionite P ("CBD-P"; reductant-soluble P), and H_2SO_4-P ("Ca-P"). Extracts were analyzed colorimetrically without digestion for molybdate-reactive P (MRP) concentration or following persulfate digestion in an autoclave for TP concentration. Molybdate-unreactive P (MUP) was calculated as the difference between TP and MRP for each extract. Residual P and P recovery were calculated from the sum of TP in each fraction compared to soil TP concentrations. For this study, MRP is P_i and MUP is P_o, although MUP could also contain complex P_i forms such as polyphosphates. The fraction identifications ("Al-P", etc.) are from the fractionation protocol (Zhang & Kovar, 2009); however, sequential fractionation is not precise, and each fraction likely contains a range of P compounds.

Two-factor analysis of variance (ANOVA) was conducted (treatment, date and the treatment*date interaction) with a standard least squares model, followed by Tukey's highest significant differences (HSD) tests.

RESULTS AND DISCUSSION

There were no significant treatment*date interactions for any of the parameters shown here. As such, data from both sampling dates was averaged together to give a single mean for each treatment.

Soil pH was significantly affected by N fertilization (Table 1), with a pH change equivalent to 0.5 pH units per 1000 kg NH_4-N ha^{-1}. Stopping P fertilization also significantly affected pH, which was highest in the -N-P plots compared to other treatments. This is due to the reduction in NH_4-N from not applying MAP fertilizer. Soil exchangeable cations were also significantly affected by N fertilization. Mehlich-Ca was significantly reduced in the +N plots compared to the -N-P plots, while Mehlich-Al and –Fe were significantly increased.

Stopping P fertilization significantly affected all analyzed P pools. Concentrations of total P, Olsen P, Mehlich P and $CaCl_2$-P were greater in -N+P soils, and were significantly greater than in treatments not receiving P (+N-P and -N-P). Olsen P and $CaCl_2$-P concentrations were also significantly higher in the –N+P treatment compared to the +N+P treatment. Yields in these plots were significantly lower in treatments without N in these plots, which decreased plant uptake of these labile P pools and thus increased their soil concentrations. Organic P, both concentration and as a percentage of total P, was significantly higher in the treatments with N than without N, regardless of P fertilization, with no significant differences with and without P within each N treatment. This suggests that organic P inputs are related to crop yields and to soil pH, rather than organic P mineralization with P fertilizer cessation. This is supported by the increase in organic P as percentage of total P for the +N-P treatment, which indicates a drawdown of inorganic P.

Table 1. Soil pH, Mehlich-extractable aluminum (Al), calcium (Ca), iron (Fe) and phosphorus (P), soil total P, total organic P, Olsen (bicarbonate-extractable P) and $CaCl_2$-extractable P in samples collected in 2016 from long-term plots (0-7.5 cm depth). Values are means ± standard error (n=18), in mg P kg^{-1} soil unless otherwise indicated.

	+N+P	+N-P	-N+P	-N-P
Soil pH (in water)	5.58 c ±0.04	5.74 c ± 0.08	6.26 b ± 0.07	6.72 a ± 0.11
Mehlich Al	1026 a ± 54.7	899 a ± 64.8	718 ab ± 52.9	477 b ± 53.3
Mehlich Ca	1215 b ± 56.4	1299 b ± 54.9	1533 ab ± 61.7	1849 a ± 141
Mehlich Fe	277 a ± 13.4	232 a ± 17.9	193 a ± 13.9	127 b ± 14.2
Total P	656 ab ± 7.1	556 c ± 12.0	667 a ± 9.3	607 bc ± 11.8
Organic P	323 a ± 4.3	312 ab ± 10.0	292 bc ± 11.0	262 c ± 16.5
Organic P/TP (%)	49.3 ab ± 0.82	56.1 a ± 1.34	43.6 b ± 1.21	43.1 b ± 2.30
Olsen P	44.6 b ± 1.24	15.8 d ± 1.26	64.7 a ± 2.00	33.1 c ± 3.02
Mehlich P	98.7 a ± 4.57	44.4 b ± 5.32	114.1 a ± 7.24	58.9 b ± 6.50
$CaCl_2$-P	44.6 b ± 1.24	15.8 d ± 1.26	64.7 a ± 2.00	33.1 c ± 3.02

Sequential fractionation (Table 2) shows an increase in fractions with Al- and Fe associated P (NH_4F-P and NaOH-P) in the treatments with lower soil pH, and an higher

Table 2. Data from sequential phosphorus (P) fractionation and enzyme (phosphomonoesterase) assays for soils samples collected in 2016 from long-term plots (0-7.5 cm depth) from 0-7.5 cm depth. Values are means ± standard error (α = 0.05)

			+N+P	+N-P	-N+P	-N-P
NH_4Cl-P	MRP	mg kg^{-1}	2.8 b ± 0.1	1.6 c ± 0.2	5.1 a ± 0.6	4.0 ab ± 1.5
(loosely bound)	MUP	mg kg^{-1}	0.2 ± 0.0	0.4 ± 0.1	0.4 ± 0.3	0.1 ± 0.1
NH_4F-P	MRP	mg kg^{-1}	62.5 a ± 2.1	25.0 b ± 7.4	78.1 a ± 7.3	41.5 b ± 9.0
(Al-P)	MUP	mg kg^{-1}	72.6 a ± 5.6	55.0 ab ± 14.5	43.2 ab ± 19.5	40.7 b ± 13.1
NaOH-P	MRP	mg kg^{-1}	95.1 a ± 1.5	64.3 b ± 9.0	101.2 a ± 10.5	63.7 b ± 22.0
(Fe-P)	MUP	mg kg^{-1}	154.9 a ± 4.9	143.7 ab ± 8.3	87.8 b ± 36.2	94.5 b ± 20.9
CBD-P	MRP	mg kg^{-1}	35.7 a ± 1.8	27.8 b ± 8.2	36.4 a ± 1.4	38.3 a ± 0.3
(reductant soluble)	MUP	mg kg^{-1}	61.6 ab ± 18.8	37.6 b ± 13.0	113.3 a ± 29.3	112.9 a ± 18.9
H_2SO_4-P	MRP	mg kg^{-1}	146.9 ± 8.2	146.5 ± 15.9	163.6 ± 20.8	193.4 ± 42.0
(Ca-P)	MUP	mg kg^{-1}	2.0 b ± 0.3	1.8 b ± 1.1	8.5 a ± 3.6	8.0 ab ± 3.0
Total MRP		mg kg^{-1}	342.6 b ± 9.2	265.2 c ± 9.1	384.4 a ± 3.6	340.9 b ± 14.6
		%	54.2 ± 1.8	52.8 ± 2.2	58.6 ± 0.9	59.5 ± 5.7
Total MUP		mg kg^{-1}	291.3 ± 17.5	238.5 ± 15.4	253.0 ± 25.6	256.2 ± 45.6
		%	45.8 ± 1.8	47.2 ± 2.2	38.7 ± 3.5	41.7 ± 5.4
Total P recovery, % of TP		%	96.8 ± 3.9	89.1 ± 2.0	98.1 ± 5.1	97.7 ± 3.4
Residual P		mg kg^{-1}	29.4 ± 11.6	61.5 ± 12.0	33.0 ± 11.5	47.3 ± 17.9
Acid Phosphomonoesterase		µg mL^{-1} g^{-1} h^{-1}	20.5 a ± 1.13	21.2 a ± 1.17	16.7 ab ± 0.27	11.7 b ± 2.43
Alkaline Phosphomonoesterase			3.76 b ± 0.21	4.25 b ± 0.58	2.98 ab ± 1.08	10.1 a ± 1.98

concentrations of H_2SO_4-extractable P, representing relatively insoluble P associated with Ca. This is consistent with the Mehlich-extractable cation results, and suggests that acidification is influencing soil chemical P pools. Activities of acid phosphomonoesterase were highest in treatments with the lowest pH (+N+P, +N-P) and while the reverse was true for activities of alkaline phosphomonoesterase. This suggests that pH changes will influence organic P mineralization, and is consistent with changes in the microbial community reported for these soils (Li et al. 2020).

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