



Long-term effects of crop rotation and nitrogen fertilization on phosphorus cycling and balances in loess-derived Mollisols

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ABSTRACT

Developing meaningful agroecosystem soil P inventories necessitates moving beyond single measures of readily extractable inorganic P (P_i) limited to surface depths. We drew on a long-term (36 year) experimental field trial in the US Maize Belt (northwestern Illinois) to evaluate how crop rotation [maize-maize (*Zea mays* L.) vs maize-soybean (*Glycine max* L. Merr.)] and N fertilization (0 vs 269 kg N ha⁻¹) impact P dynamics throughout the soil profile by using sequential fractionation and phosphatase activity assays, contextualized by soil P stocks and agronomic P balances. Distribution of P fractions by depth (0–15, 15–30, 30–60, 60–90 cm) indicate that management effects were limited to the surface soil layers (0–30 cm). Soil P fractions differed more by depth than by experimental treatments. Long-term N fertilization significantly decreased pH concurrently with labile organic P (P_o) and phosphodiesterase activity. Soil labile inorganic P (P_i) was two-fold lower under N fertilization compared to zero N fertilization, reflecting greater yield and thus P export via grain harvest. Under N fertilization, integration of soybean elevated soil phosphodiesterase activity and decreased water-extractable P_o . Higher stocks of soil P_o than labile P_i at surface depths (0–30 cm) corroborated a hypothesized appreciable pool size of soil P_o relative to the labile P_i pool to which most agronomic assessments are limited. Large negative agronomic balances over the 36-year period (–426 to –945 kg P ha⁻¹) are suggestive of legacy P from pre-experiment manure application and high native P stocks, with net P export equivalent to 11–35% of soil P stocks at 0–90 cm depth at the initiation of the experiment. These results contribute to a better understanding how N fertilization and rotation practices influence soil P cycling and stocks, thereby informing P budgets for comprehensive agroecosystem P management.

1. Introduction

Agricultural intensification of the major grain belts of the world has driven profound anthropogenic alteration of the global P cycle in less than one century (Bennett et al., 2001; Chen and Graedel, 2016), with consequences for crop productivity and environmental quality (Sharpley et al., 2016). Grain yield increases driven by N inputs have entailed requisite increases in P inputs. For example, from 1940 to 1980, P fertilizer inputs to agroecosystems globally increased by nearly seven-fold (Yuan et al., 2018). Regions such as the US Midwest, which accounts for one-third of global maize (*Zea mays* L.) grain production and the majority of US P fertilizer inputs (Metson et al., 2016; Margenot et al., 2019), are global hotspots of accelerated P fluxes with inputs of fertilizer

P and outputs of grain P that are orders of magnitude (up to 60 kg P ha⁻¹ y⁻¹) greater than pre-agricultural fluxes (David and Gentry, 2000; Metson et al., 2016). Intensification of US Maize Belt agroecosystems has been accompanied by a simplification of crop rotations, largely to maize-soybean (*Glycine max* L. Merr.) or continuous maize production (Liebman et al., 2013; Aguilar et al., 2015). Accompanying the increased flux of P inputs and outputs in these grain cropping systems are unintentional P losses via erosion and runoff from agricultural fields to surface waters that compromise water quality from local to continental watershed scales (Smith et al., 2018), most notably the Mississippi River watershed (Robertson and Saad, 2013; Robertson et al., 2014). In maize-based systems, much work has evaluated the effects of P management, largely P application rates, on the distribution of P across pools of

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varying availability (e.g., Liu et al., 2008; Luo et al., 2017; Arruda Coelho et al., 2019), revealing strong effects of P input rates on P fractions characterized by enrichment of inorganic P (P_i) pools in surface soils (generally < 30 cm depth). While the majority of management practices are likely to impact soil P in surface soils, information is lacking on the effects of management practices on soil P speciation, including organic P (P_o) that constitutes 20–80% of total soil P (Richardson and Simpson, 2011), and to depths relevant to maize and soybean rooting (e.g., >50 cm) (Fehrenbacher et al. 1954; Douglas et al. 1967).

However, non-P management practices such as high N rates and crop rotation could indirectly influence soil P availability via abiotic and biotic mechanisms. Though the indirect effects of N fertilization on P cycling are likely to be subtle, even relatively small changes may accrue over the long-term to have an appreciable impact on P cycling and use efficiency, and can strongly influence on off-farm P losses (MacDonald et al., 2011a,b). Though changes in soil P pools such as mineralization of P_o to P_i by phosphatases are generally thought to be less than crop P needs in high-yielding agroecosystems such as the US Maize Belt (Bünemann, 2015; Bender et al., 2013), off-farm P losses at even agronomically minor magnitudes (e.g., <2 kg P ha⁻¹) are sufficient to severely compromise water quality (McDowell and Monaghan, 2015; Rowe et al., 2016) as is the case for the Mississippi watershed co-located in much of the US Maize Belt (Robertson et al., 2014). Characterizing the speciation of soil P under crop rotation and N fertilization practices can help inform understanding of how such practices influence P availability to the crop and the risk of loss to the environment.

Nitrogen fertilization in agroecosystems could affect P dynamics via crop uptake and subsequent redeposition of P in organic (residue) forms and by altering biochemical drivers of soil P processes (Brown et al., 2014; Cassman, 1999; Russell et al., 2009). Nitrogen inputs influence crop residue quantity and quality, as well as the rate of decomposition, thus indirectly influencing soil P cycling via soil P uptake and redeposition as organic (P_o) and inorganic (P_i) forms in crop residues returned to the soil. For example, N fertilization increased maize residue production by 40 to 50% in a maize-soybean rotation (Gregorich et al., 2001) and by 93% to 176% in continuous maize (Brown et al., 2014). The maize-soybean rotation can produce up to 4.5 t ha⁻¹ of residues per maize phase (Poffenbarger et al., 2017), containing an estimated 9 kg P ha⁻¹ assuming a maize residue P content of 0.19% (Margenot et al., 2017a). Concurrently, the high input rates of N needed to support maize yield in intensive systems (Dick, 1983; Liebig et al., 2002; Chen et al., 2020) but can induce soil acidification that may influence P cycling via abiotic and biotic mechanisms. Soil acidification induced by H⁺ generation from nitrification of ammonium from fertilizers (Barak et al., 1997; Tian and Niu, 2015), can increase exchangeable Al³⁺ and Fe³⁺ (Huang et al., 2019) and in turn influence crop-available orthophosphate sorption (Hou et al., 2018; Vitousek et al., 2010). This is consistent with observations that N fertilization in the long-term can decrease labile P_i while increasing Fe- and Al-associated P_i (i.e., NaOH-extractable P_i) (Yang et al., 2015). Changes in soil pH may also alter microbial communities and thus the activities of enzymes that mineralize OM, including mineralization of P_o into crop-available P_i (Dick et al., 2000; Nannipieri et al., 2011; Margenot et al., 2018b). Mineralization of P_o by phosphatases is a potential contributor to crop P uptake (Acquaye, 1963; Oberson et al., 1999; Oberson et al., 2006), and N inputs are known to impact the production of these enzymes (Marklein and Houlton, 2012; Tian et al., 2016). Whereas in unmanaged (and often forested) ecosystems, N fertilization tends to increase soil phosphatase activities (Marklein and Houlton, 2012). In agroecosystems, long-term N fertilization can either increase (Geisseler and Scow, 2014) or decrease (Jian et al., 2016) phosphatase activities. This suggests that N management may influence, albeit less predictably, soil P_o mineralization in agroecosystems.

Independently of N fertilization, crop rotation may directly influence soil P dynamics by residue P contribution and, it can also impact P pools

via legume-specific soil–plant interactions. Residue amount and quality (e.g., C:P and C:N) affect soil phosphatases that drive the mineralization of P_o (Arenberg and Arai, 2019). For example, the addition of crop residues generally stimulates phosphodiesterase activity (Perucci and Scarponi, 1985), with more rapid decomposition of lower C:N soybean residues relative to maize residues (Green and Blackmer, 1995), which suggests greater cycling of soybean residue P into soil P_i . Crop rotation can alter pools of P identifiable by sequential P fractionation (Maltais-Landry et al., 2015; Yang et al., 2015), consistent with rotation-induced shifts in OM decomposition that influence P_o that is stoichiometrically a component of SOM (McDaniel et al., 2014; McDaniel et al., 2016). Greater rhizosphere acidification (Li et al., 2007) and secretion of phosphatases (Li et al., 2004) of many crop legumes compared to maize, as well as differences in root architecture and rooting depth (Masaoka et al., 1993; Turner, 2008), may explain increased soil P availability and maize P uptake following the integration of legumes in low-input (Jemo et al., 2006; Li et al., 2007) as well as in intensified Midwest agroecosystems. For example, phosphatase activities in Canadian maize agroecosystems enhanced by crop rotation were estimated to contribute up to 29 kg ha⁻¹ to crop P uptake (Tiecher et al., 2012). Across diverse soils in Nebraska, 50% lower critical soil test P values for maize following soybean compared to continuous maize (Wortmann et al., 2009) implied that additional P pools beyond agronomic tests of labile P_i contributed to maize P uptake as a result of soybean rotation.

We investigated the effect of non-P management practices (N fertilization and crop rotation) on soil P dynamics after 36 years of treatments in northwestern Illinois, a major maize-producing region in the intensively managed US Maize Belt (USDA ERS, 2017). Sequential fractionation of soil P, a valuable tool for characterizing changes in P_i and P_o pools (Hedley et al., 1982; Negassa and Leinweber, 2009), was used in conjunction with assays of soil phosphatase activities to quantify the effects of N fertilization and crop rotation on soil P cycling. The aims of this study were to (1) evaluate the potential effects of long-term crop rotation and N fertilization practices on soil P fractions and phosphatase activities; (2) identify soil variables that may explain observed impacts on non-P management practices on soil P cycling; (3) determine the depth distribution of P fractions and relative importance of non-labile P_i stocks (e.g., total P_o), contextualized by an agronomic P balance. Evaluating soil P response across the profile to two non-P management practices dominant in the US Maize Belt will enable accurate P budgets for improving comprehensive agroecosystem P management.

2. Materials and methods

2.1. Site description

A long-term agronomic trial at the Northwestern Illinois Agricultural Research and Demonstration Center (40°55'50"N, 90°43'38"W) was used to evaluate crop rotation and N fertilization impacts on soil P cycling. The soil is the Muscatine series (fine-silty, mixed, superactive, mesic Aquic Argiudolls; FAO/WRB Chernozem) with an extent of over 207,000 ha in Illinois (Soil Survey Staff, 2014). This series is representative of the loess-derived soils of the recently glaciated region of Illinois, developed on 2.0 – 7.6 m of loess (Smith, 1942), and the most productive states of the US Maize Belt (ERS, 2017). Loess, an accumulated aeolian sediment, was deposited in this region following the Wisconsinian glaciation ≈12,000 years before present. The resulting soils, specifically the Muscatine series, are characterized by a relatively deep A horizon (0–40 cm) with high organic matter content (30–40 g kg⁻¹), silty clay loam texture, and acidic pH of 6.0–6.3 (measured 1:1 soil: water). At 40–90 cm depth, a series of B_{tg} horizons express acidic pH (pH 5.2–5.7) with silty clay loam texture (Soil Survey Staff, 2021). Historical mean annual precipitation is approximately 978 mm, and mean annual temperature is 10.5 °C (ISWS, 2016). Additional details of the experimental field trial are provided by Huang et al. (2019).

2.2. Crop rotation and N treatments

To study the crop rotation and N fertilization impacts on soil P cycling, we tested two of the three crop rotation levels and two of the three N rates, from the long-term experimental site established in 1981 as described in Huang et al. (2019). Treatments were arranged in a split-plot design of crop rotation as main plots (18×30 m) with N fertilization treatments as subplots (18×6 m) in a randomized complete block design ($n = 3$ replicates per plot). The research plots evaluate two crop rotations of continuous maize (M–M) and maize-soybean (M–S), which collectively represent 11.2 million ha in Illinois alone (USDA ERS, 2017). To bound N fertilization effects on soil P cycling, application rates of 269 and 0 kg N ha⁻¹ were selected. By evaluating these extremes, our study enables a comprehensive assessment of the potential range of impacts of N management on soil P cycling. The range of N rates recommended for maize in Illinois are typically 160–180 kg N ha⁻¹ for M–S and up to 250 kg N ha⁻¹ for M–M (Aller et al., 2018), though farmers self-report higher rates of 169 to 202 kg N ha⁻¹ for M–S rotations (Smiciklas et al., 2008) and economically optimum N rates (EONR) range from 0 to 315 kg N ha⁻¹ (Ransom et al., 2020). Lower N rates are used for maize following soybean compared to maize following maize across the U.S. Maize Belt (Seifert et al., 2017; Ransom et al., 2020) due to greater immobilization of N by maize residue with high C:N (Green and Blackmer, 1995) which can also retard soil N mineralization rates (Gentry et al., 2013). Nitrogen fertilization of maize was performed in the spring at or before planting by incorporating urea-ammonium-nitrate 28% N (UAN-28) (Huang et al. 2019), and without the use of an inhibitor given the spring application time. As per farmer and recommended practices, N fertilizer was not applied to the soybean phase of the M–S rotation (Fernández and Hoef, 2009). Tillage consisted of primary tillage with a chisel plow to 25 cm depth in the fall (Oct–Nov) after harvest, with secondary tillage by cultivator immediately prior to spring planting (Huang et al., 2019). Maize and soybean were planted in April–May each year using 76 cm and 38 cm rows, respectively. Maize was planted at 75,000–85,000 seeds ha⁻¹ and soybean at 340,000–350,000 seeds ha⁻¹. Weeds were controlled using recommended rates and timing of appropriate herbicides according to the Illinois Agronomy Handbook (Nafziger, 2009).

To calculate the agronomic P balances for the four treatments, inputs of P applied as fertilizer and outputs of P removed by grain harvest were determined over the 36 year period (i.e., P applied – P removed). Historical yield data for maize from both M–M (from 1981 to 2017) and M–S systems (in alternate years from 1981 to 2017), and for soybean from M–S system (in alternate years from 1984 to 2017) were obtained from records at the Northwestern Illinois Agricultural Research and Demonstration Center (Kim et al., 2021; Villamil, 2021). A single application of fertilizer P as 45.4 kg P ha⁻¹ as diammonium phosphate (DAP) was made in 2011 as per soil test P recommendations in the Illinois Agronomy Handbook (Fernández and Hoef, 2009) for all treatments, enabling the attribution of potential changes in soil P variables to non-P management practices. The former use of the area as a swine manure stockpiling site before the experiment establishment (pre-1981) means that high soil test P concentrations were sufficiently high for 35 of the 36 years to not mandate P application, consistent with relatively high historical (1945–1998) P net loading in Illinois estimated at +230 kg P ha⁻¹ (David and Gentry, 2000). Pre-experimental (i.e., pre-1981) levels of manure are unknown, which is not atypical of historical manure application rates that entail legacy P accumulation (Andino et al., 2020). Mean grain P concentrations in Illinois agroecosystems of 0.267% for maize and 0.521% for soybean (Villamil et al., 2019) were used to estimate P export with grain harvest. As an agronomic balance, this estimated balance does not account for P inputs via atmospheric deposition, nor outputs via soil erosion, surface run-off and tile drain leachate (Hao et al., 2019). However, the magnitudes of these potential inputs and outputs are minimal in the study region of northwestern Illinois: atmosphere deposition is estimated to be 0.1 – 1.0 kg P ha⁻¹ y⁻¹

(IEPA, 1986), and the low slope (<0.5%) at the study entails minimal erosional, run-off and/or tile-drainage losses, consistent with a regional off-farm loss average of 0.7 – 1.1 kg P ha⁻¹ y⁻¹ (David and Gentry, 2000; IEPA, 1986). The relatively minor magnitude of these potential non-agronomic inputs and outputs enable interpretation of 36-year agronomic P balance based on the difference between cumulative fertilizer inputs and cumulative grain outputs.

2.3. Soil sampling and characterization

In spring of 2017, 36 years from the initiation of the experiment, soils were sampled to 90 cm in depth to resolve the long-term impacts of crop rotation and N rates on P cycling across the soil profile. For each treatment plot (i.e. field replicate), three individual soil cores (4.3 cm diameter) to a depth of 90 cm were taken with a tractor-mounted hydraulic probe sampler with sleeve inserts (Amity Tech, Fargo, ND). Soils cores were split into 0–15, 15–30, 30–60, and 60–90 cm intervals, and each core \times depth sample were combined into one composite sample per depth per treatment plot. These soil samples were analyzed for pH using 1:1 soil/water paste (McLean, 1982), for soil organic matter (SOM) by loss on ignition at 360 °C (Nelson and Sommers, 1996), and for bulk density (BD, g cm⁻³) by the core method (Blake and Hartge, 1986). The complete data set is publicly available (Villamil, 2021).

2.4. Soil P fractions

Soil P distribution was assessed by sequential extraction of P according to the fractionation scheme developed by Hedley et al. (1982). Triplicate soil samples were sequentially extracted by the Hedley fractionation (Hedley et al., 1982; Tiessen and Moir, 2008) using an anion-exchange membrane (AEM) in distilled water, 0.5 mol L⁻¹ NaHCO₃ (pH 8.5), 0.1 mol L⁻¹ NaOH, and 1 mol L⁻¹ HCl. A negative control (no soil) and soil standard were also included in triplicate. All extractions were performed by 16 h of horizontal shaking (120 rpm). AEM (1 \times 4 cm, VWR International, West Chester, PA) was loaded with carbonate as the counterion and used to extract soils in 18.2 MΩ-cm water. Inorganic P (P_i) was desorbed from the membranes by shaking for 1 h in 0.25 mol L⁻¹ H₂SO₄. All other extracts were centrifuged (8000 RCF, 15 min) and an aliquot decanted for analysis. Organic P (P_o) in the distilled water used to extract AEM-P_i was quantified as P_i following acid–persulfate digestion (80 °C, 16 h) (Rowland and Haygarth, 1997) by molybdate colorimetry (Murphy and Riley, 1962). For NaOH aliquots, OM was precipitated with 1.2 mol L⁻¹ H₂SO₄ to avoid interference with colorimetry. For NaHCO₃ and NaOH extractions, aliquots were neutralized and analyzed for P_i and total P (P_t) determined as P_i following acid–persulfate digestion. P_o was estimated as the difference between total and inorganic P (P_o = P_t – P_i). Total soil P_o was calculated as the sum of H₂O-P_o, NaHCO₃-P_o and NaOH-P_o. Fractions were calculated on a soil mass basis as mg P kg⁻¹ soil. We calculated organic C to organic P (C:P_o) ratio by converting total SOM to organic C using a conversion factor of 1.72 and total P_o.

2.5. Soil phosphatase activities

Activities were assayed for two major phosphatases that catalyze mineralization of soil P_o: phosphomonoesterase (Enzyme Commission 3.1.3.2; PME) and phosphodiesterase (EC 3.1.4.1; PDE). Activities of enzymes represent a potential maximum activity (Nannipieri et al., 2018), which may fluctuate during the growing season but are still sensitive to relative differences long-term effects of management practices (e.g., Acosta-Martínez et al., 2010). Enzymes were assayed in duplicate for each soil based on Schneider et al. (2000) as modified by Margenot et al. (2018a) using 1.0 g of oven-dried soil equivalent incubated for 1 h at 37 °C in 4 mL of 18.2 MΩ-cm water. Assays employed a final substrate concentration of 25 mmol L⁻¹ *para*-nitrophenyl phosphate (PME) or 10 mmol L⁻¹ *bis-para*-nitrophenyl phosphate (PDE). This

concentration of substrate was used to ensure measurement of potential activities as a maximum activity under conditions of substrate saturation (German, et al., 2011, Malcolm, 1983, Margenot, et al., 2018a). To further ensure the accuracy and sensitivity of enzyme assays, termination conditions were performed according to Margenot et al. (2018a) to minimize interference from dissolved organic matter in high SOM samples. Reactions were halted by the addition of 4 mL of 0.1 mol L⁻¹ Tris base (pH 12.0) and 1 mL of 2 mol L⁻¹ CaCl₂. This termination method was found to maximize recovery of a *para*-nitrophenol (pNP) standard and minimize interference from co-extracted dissolved organic matter compared to other termination methods (Margenot et al., 2018a). Assays were centrifuged (3000×g, 90 sec) to remove sediment, and pNP in the clear supernatant was quantified colorimetrically using absorbance at 410 nm. Mean absorbance of triplicate negative controls were subtracted from absorbance of soil assays to account for non-enzymatic hydrolysis of substrate during the incubation (Neal, et al., 1981, Turner, et al., 2002). Enzyme activities were corrected for incomplete recovery of pNP using single-point sorption in the same assay conditions using a relevant concentration of pNP (Margenot et al., 2018a). Similar corrections of the enzyme-released product are performed in fluorometric assays of phosphatase activities (e.g., Cooper and Morgan, 1981). Phosphatase activities were expressed as μmol pNP g⁻¹ h⁻¹.

2.6. Statistical analyses

Statistical analyses were performed using GLIMMIX procedure of SAS software version 9.4 (SAS Institute, Cary, NC). Normality of residuals for response variables were confirmed using the Shapiro-Wilk test. Crop rotation, N fertilizer application rate, and sampling depth were considered fixed effects in the ANOVA model, whereas replicates (blocks) were considered random effects. These linear mixed models included a repeated measures approach for depth using a heterogeneous autoregressive [ARH(1)] model for the variance-covariance matrix of the residuals (Littell et al., 2002). The results were reported as treatment mean values with their corresponding standard error (S.E.). Least square means were separated using the pdiff option of LSMEANS in PROC GLIMMIX setting the Type I error at $\alpha = 0.05$.

3. Results

3.1. Soil properties and P fractions

Soil pH was lower at 0–15 cm depth for M–M with 269 kg N ha⁻¹ (pH 4.9) relative to other crop rotations and N fertilization combinations, which ranged pH 6.5–6.8 (Table 1). This effect was maintained up to 30 cm depth. While pH was similar at 30–60 cm across treatments, the fertilized rotations (M–M 269 and M–S 269) had higher pH (6.85) than their unfertilized counterparts (6.70) at 60–90 cm depth (Table 1, Table S1). Nitrogen fertilization but not crop rotation decreased BD by 12% (1.45 vs 1.35 g cm⁻³) at 0–15 cm depth only (Table 1). Impacts of N fertilization and crop rotation on soil P were largely limited to labile P_i and P_o fractions at 0–15 cm depth, and independent of treatments, all soil P fractions differed significantly by depth (Table 2). Across treatments, labile P_i fractions (AEM-P_i and NaHCO₃-P_i) at 0–15 cm depth were significantly higher than at other depths, but there were no significant differences in labile and non-labile P_o fractions of H₂O-P_o and NaOH-P_o at depths of 0–15 and 15–30 cm (Fig. 1; Table 3). Across treatments, NaHCO₃-P_o was greatest at 0–15 cm depth (34.8 mg kg⁻¹), decreased by 25% at 15–30 cm depth (26.2 mg kg⁻¹), and further decreased sharply at 30–60 cm and 60–90 cm depths (13.6 mg kg⁻¹). The C:P_o was generally lower under continuous maize compared to maize-soybean rotation, in particular for continuous maize without N fertilizer relative to maize-soybean with N fertilizer (Table 2). With depth, C:P_o increased in magnitude and varied more across treatments, from C:P_o of 81–94 at 0–15 cm to 136–181 at 60–90 cm.

Table 1

Mean values and standard errors (se) for soil pH, soil organic matter (SOM), and bulk density (BD), at successive depths as affected by N fertilization rate (0 vs 269 kg N ha⁻¹) under maize-maize (M–M) or maize-soybean (M–S) rotation. Within each depth and for a given soil property, different letters denote statistically significant differences at $p < 0.05$.

Rotation	N rate kg ha ⁻¹	pH		SOM g kg ⁻¹		BD g cm ⁻³	
			mean		mean		mean
0–15 cm							
M–M	0	6.6 ± 0.29	a	40 ± 4.2	a	1.4 ± 0.1	a
M–M	269	4.9 ± 0.30	b	41 ± 1.9	a	1.2 ± 0.04	b
M–S	0	6.8 ± 0.15	a	37 ± 0.6	a	1.5 ± 0.08	a
M–S	269	6.5 ± 0.27	a	37 ± 0.9	a	1.3 ± 0.02	b
15–30 cm							
M–M	0	6.5 ± 0.09	ab	37 ± 5.2	a	1.4 ± 0.04	a
M–M	269	6.0 ± 0.26	b	38 ± 2.9	a	1.4 ± 0.01	a
M–S	0	6.7 ± 0.06	a	33 ± 1.9	a	1.5 ± 0.03	a
M–S	269	6.7 ± 0.09	a	34 ± 1.0	a	1.4 ± 0.04	a
30–60 cm							
M–M	0	6.6 ± 0.15	a	27 ± 4.0	a	1.3 ± 0.03	a
M–M	269	6.4 ± 0.23	a	26 ± 2.0	a	1.2 ± 0.06	a
M–S	0	6.8 ± 0.03	a	21 ± 2.1	a	1.4 ± 0.06	a
M–S	269	6.8 ± 0.19	a	24 ± 1.0	a	1.3 ± 0.02	a
60–90 cm							
M–M	0	6.7 ± 0.21	a	14 ± 1.5	a	1.4 ± 0.02	a
M–M	269	6.9 ± 0.27	a	14 ± 0.4	a	1.3 ± 0.03	a
M–S	0	6.7 ± 0.03	a	13 ± 0.9	a	1.4 ± 0.01	a
M–S	269	6.8 ± 0.00	a	14 ± 0.4	a	1.4 ± 0.04	a

Nitrogen fertilization (0 vs 269 kg ha⁻¹) impacts on P_i fractions were limited to 0–15 cm depth (i.e., N rate × depth, $p < 0.05$) (Table 3). At 0–15 cm depth, N fertilization decreased Fe- and Al-associated P by a mean of 37% (NaOH-P_i, $p < 0.05$) and Ca-associated P by a mean of 17 % (HCl-P_i, $p < 0.05$) (Fig. 2, Table S2). Labile P_i fractions (AEM-P_i and NaHCO₃-P_i) were also lower with N application. Organic P fractions exhibited a more limited response to crop rotation and N application than labile P_i fractions. At 0–15 cm depth, the water-soluble fraction of P_o (H₂O-P_o) was elevated under M–M compared with M–S (Fig. 2, Table S2). Although there were no differences in NaOH-P_o between N fertilization at 0–15 cm depth, the proportion of NaOH-P_o as a percentage of total extractable P fractions increased from 49% to 56% with N application (Table 2). At 60–90 cm depth, the concentration of NaOH-P_o was elevated under M–M with no N fertilization relative to M–S without N fertilization and M–M with fertilization, and was similar compared to M–S with N fertilization.

As with soil P fractions, stocks of P fractions differed more by depth and than by N fertilization and crop rotation (Table 4). Stocks of NaHCO₃-P_o, NaOH-P_o, and total P_o were greater at 0–30 cm depth than at 30–60 cm and 60–90 cm depth (Fig. 3). At 0–30 cm depth, P_o fraction stocks as a proportion of total extractable P were 5–9 %, 21–26 %, and 65–73 % for soil H₂O-P_o, NaHCO₃-P_o, NaOH-P_o, respectively. At this

Table 2

Mean values of soil phosphorus (P) fractions and the organic carbon (C) to total organic P (P_o) ratio at successive depths as affected by N fertilization rate (0 vs 269 kg N ha^{-1}) under maize-maize (M–M) or maize-soybean (M–S) rotation. Within each depth and for a given P fraction, different letters indicate statistically significant differences $p < 0.05$.

Rotation	N rate kg ha ⁻¹	Inorganic P								Organic P						C:P _o	
		AEM-P _i		NaHCO ₃ -P _i		NaOH-P _i		HCl-P _i		H ₂ O-P _o		NaHCO ₃ -P _o		NaOH-P _o			
		mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹		mg kg ⁻¹			
0–15 cm																	
M–M	0	29 ± 5.2	a	25 ± 2.3	a	82 ± 7.0	a	77 ± 6.3	a	9 ± 0.6	a	45 ± 10.2	a	233 ± 56.7	a	81 ± 8.5	b
M–M	269	8 ± 1.4	b	3 ± 0.2	c	45 ± 0.8	b	54 ± 1.3	b	8 ± 0.9	ab	34 ± 1.9	a	213 ± 16.5	a	93 ± 4.3	ab
M–S	0	14 ± 3.3	ab	15 ± 1.0	b	63 ± 3.9	ab	64 ± 4.3	a	7 ± 0.6	b	31 ± 0.3	a	202 ± 8.6	a	90 ± 1.5	ab
M–S	269	10 ± 1.9	b	11 ± 1.2	b	46 ± 6.4	b	63 ± 5.9	a	7 ± 0.2	b	30 ± 2.6	a	191 ± 6.5	a	94 ± 2.3	a
15–30 cm																	
M–M	0	11 ± 5.7	a	9 ± 2.8	a	51 ± 10.3	a	51 ± 5.2	a	10 ± 1.0	a	34 ± 9.3	a	234 ± 59.3	a	77 ± 10.9	b
M–M	269	4 ± 0.7	a	3 ± 0.3	a	27 ± 1.0	a	36 ± 2.9	a	8 ± 0.2	a	25 ± 3.0	a	199 ± 19.6	a	95 ± 7.3	ab
M–S	0	7 ± 0.2	a	5 ± 0.5	a	36 ± 0.6	a	42 ± 1.3	a	8 ± 0.5	a	24 ± 1.8	a	161 ± 19.2	a	99 ± 5.7	a
M–S	269	4 ± 1.7	a	4 ± 1.1	a	28 ± 4.6	a	41 ± 2.5	a	8 ± 0.2	a	22 ± 2.2	a	170 ± 16.9	a	99 ± 2.9	a
30–60 cm																	
M–M	0	2 ± 1.0	a	4 ± 1.8	a	27 ± 2.4	a	38 ± 4.0	a	7 ± 0.4	a	15 ± 2.6	a	69 ± 12.4	a	173 ± 25.6	a
M–M	269	1 ± 0.8	a	4 ± 0.3	a	30 ± 6.0	a	42 ± 0.2	a	7 ± 0.6	a	18 ± 2.5	a	66 ± 2.6	a	166 ± 12.8	a
M–S	0	2 ± 0.9	a	4 ± 0.6	a	31 ± 3.5	a	42 ± 8.6	a	6 ± 0.6	a	15 ± 2.1	a	57 ± 8.4	a	157 ± 15.6	a
M–S	269	2 ± 1.0	a	3 ± 0.4	a	27 ± 0.8	a	38 ± 5.0	a	7 ± 1.2	a	15 ± 1.4	a	56 ± 5.7	a	179 ± 7.5	a
60–90 cm																	
M–M	0	3 ± 1.5	a	5 ± 1.3	a	39 ± 3.3	a	78 ± 11.0	b	4 ± 1.2	a	12 ± 2.2	a	44 ± 1.0	a	136 ± 14.5	b
M–M	269	4 ± 0.6	a	6 ± 1.0	a	48 ± 3.7	a	54 ± 5.1	c	3 ± 1.5	a	12 ± 0.9	a	31 ± 2.9	b	177 ± 5.1	a
M–S	0	4 ± 0.7	a	6 ± 0.8	a	53 ± 7.4	a	100 ± 8.7	a	4 ± 1.7	a	12 ± 0.9	a	30 ± 2.9	b	164 ± 11.4	ab
M–S	269	4 ± 0.4	a	5 ± 0.5	a	51 ± 3.7	a	66 ± 6.8	bc	2 ± 1.5	a	10 ± 0.6	a	33 ± 2.5	ab	181 ± 5.2	a

depth, stocks of P_i fractions were significantly affected by N fertilization but not by crop rotation (Table S3). At 30–60 cm depth, crop rotation and N fertilization only influenced the stocks of the most labile P_i fraction of AEM- P_i (Fig. 3). Soil pH was negatively correlated with labile P (H_2O-P_o), $NaHCO_3-P_o$, $NaOH-P_o$ and total P_o , but unrelated to P_i fractions (Table S4).

3.2. Phosphatase activities

Crop rotation and N fertilization impacted soil phosphatase activities at surface depths only, and these effects were less strong than the attenuation of activities with increasing depth (Fig. 4). The activity of PDE was greater under M–S compared to M–M (Table S5), and within M–M was higher without N fertilization at 0–15 cm depth (Fig. 4). At 15–30 cm depth, PDE was uniquely lower for M–S without N fertilization compared to other crop rotation and N fertilization combinations. Across treatments, the activity of PDE significantly differed among the four depths, in the order of 0–15 cm ($1.96 \mu\text{mol pNP g}^{-1}\text{h}^{-1}$) > 15–30 cm ($1.48 \mu\text{mol pNP g}^{-1}\text{h}^{-1}$) > 30–60 cm ($0.61 \mu\text{mol pNP g}^{-1}\text{h}^{-1}$) > 60–90 cm ($0.18 \mu\text{mol pNP g}^{-1}\text{h}^{-1}$) ($p < 0.001$). In contrast, PME was not influenced by crop rotation and N fertilization managements, and decreased less strongly with depth. Phosphatase activities and soil P fractions across depths were generally unrelated, with correlations only between $NaHCO_3-P_o$, total P_o and PME, H_2O-P_o and PDE at 0–15 cm depth, $NaHCO_3-P_o$, and total P_o , and PME at 60–90 cm depth ($p < 0.05$)

(Table S6). PME and PDE activity were unrelated to C: P_o within depths across treatments. However, PDE was strongly negatively correlated to C: P_o within each treatment across depths, as was PME activity but only under continuous maize with N fertilization.

3.3. Agronomic P balances

Annual grain harvest over 36 years with a one-time application of P fertilizer entailed large negative agronomic P balances, driven mainly by maize yields across crop rotation and N fertilization treatments (Fig. 5). Agronomic P balances over the 36-year period were least negative for M–M without N fertilization (-426 kg ha^{-1}) and greatest for M–M with N fertilization (-945 kg ha^{-1}). Net P export was greater for M–S treatments with N fertilizer (-541 kg ha^{-1}) due to greater maize yield than for M–S without N fertilizer (-328 kg ha^{-1}). Soil P export over this 36-year period corresponded to 12–35% of soil P stocks (0–90 cm depth) originally present at the initiation of the experiment in 1981 (Fig. S1).

4. Discussion

4.1. Distribution of P with depth

As expected, soil P fractions differed more by depth than by N fertilization and crop rotation. Total P_o and P_o fractions were greatest in surface soils (0–30 cm), reflecting SOM distribution (Condron et al.,

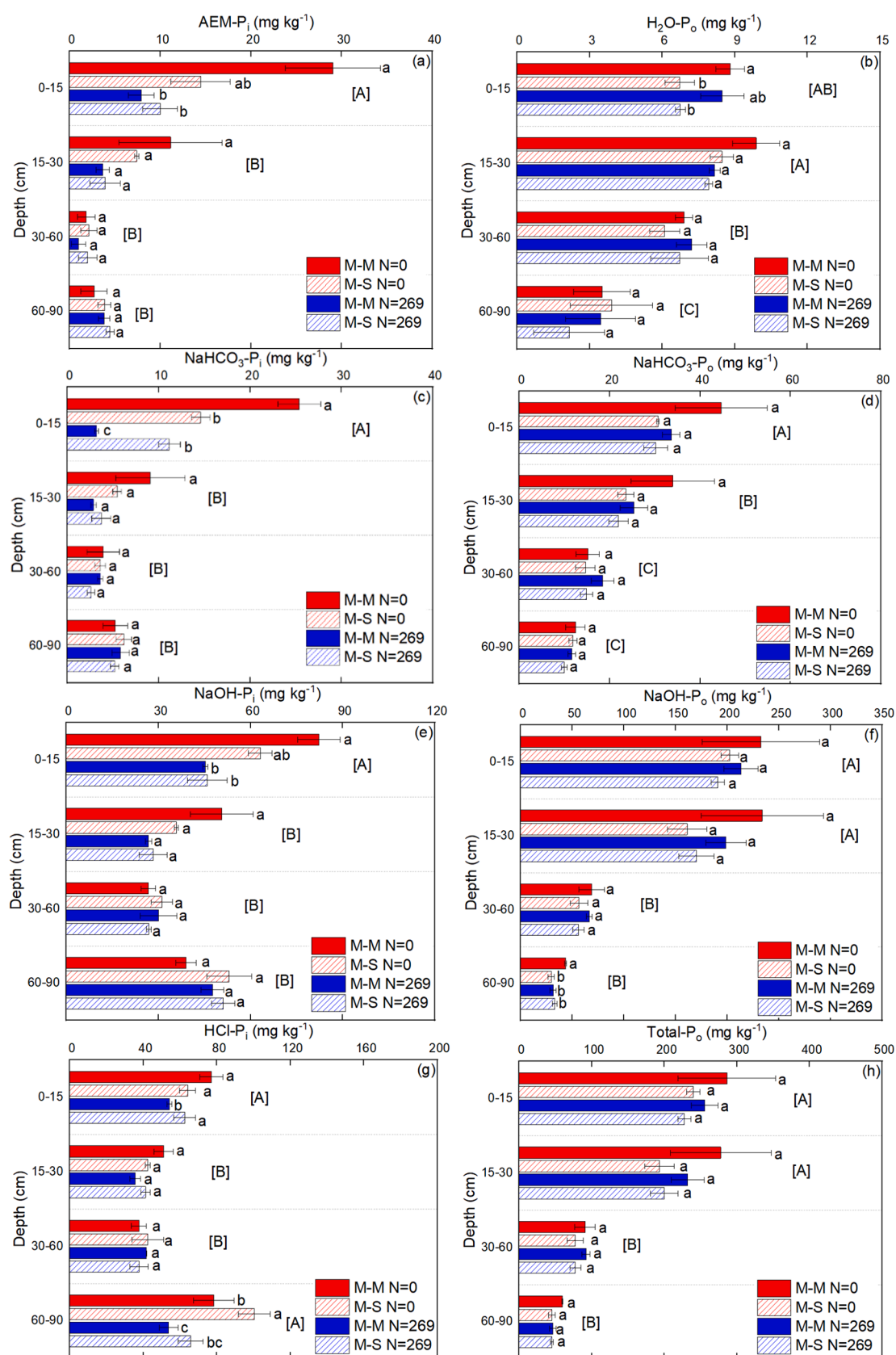


Fig. 1. Soil phosphorus (P) fractions at successive soil sampling depths under rotation practices (continuous maize, M–M and maize-soybean, M–S) affected by contrasting N fertilization rates (0 vs 269 kg ha⁻¹). Error bars represent standard error of the means. Statistically significant differences by treatments within each depth are represented by lowercase letters while the comparison of P fractions among depths are denoted by uppercase letters ($p < 0.05$).

Table 3

F-values of the analysis of variance (ANOVA) of the effects of N fertilization rate (0 vs 269 kg N ha⁻¹) and crop rotation as maize-maize (M–M) or maize-soybean (M–S) on concentrations of soil phosphorus (P) fractions at successive depths (0–15, 15–30, 30–60, 60–90 cm).

Source of variation	df	Inorganic P				Organic P			Total P _o
		AEM-P _i	NaHCO ₃ -P _i	NaOH-P _i	HCl-P _i	H ₂ O-P _o	NaHCO ₃ -P _o	NaOH-P _o	
Rotation	1	2.14 ns	0.6 ns	0.2 ns	1.0 ns	3.8 ns	5.1 ns	1.8 ns	1.7 ns
N rate	1	18.7***	16.3***	7.5*	16.4***	0.8 ns	1.6 ns	0.3 ns	0.4 ns
Depth	3	24.1***	123.3***	78.4***	47.4***	17.4***	41.2***	59.6***	55.7***
Rotation × N rate	1	6.4*	5.8*	0.4 ns	0.5 ns	0.0 ns	0.6 ns	0.3 ns	0.3 ns
Rotation × Depth	3	1.8 ns	0.5 ns	3.3*	1.8 ns	0.8 ns	1.3 ns	0.7 ns	0.7 ns
N rate × Depth	3	7.2**	41.3***	10.7***	4.2*	1.2 ns	2.9 ns	0.2 ns	0.7 ns
Rotation × N rate × Depth	3	2.3 ns	26.7***	3.2*	2.2*	0.3 ns	1.3 ns	0.8 ns	0.8 ns

df: Degrees of freedom. Codes: ***p < 0.001, **p < 0.01, *p < 0.05, ns: not significant.

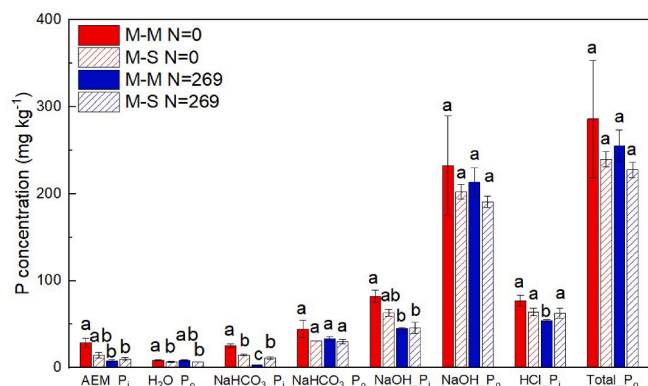


Fig. 2. Changes in surface soil (0–15 cm) phosphorus (P) fractions under contrasting rotation and N fertilization rates. Lowercase represents differences between treatments for a given soil P fraction. Different letters indicate significant differences at $p < 0.05$. Error bars represent standard error of the means.

2005; Jobbágy and Jackson, 2001; Turner et al., 2003), whereas, non-labile P_i pools (NaOH-P_i and HCl-P_i) were enriched in deeper soil layers (60–90 cm). The abrupt doubling of C:P_o ratios below 30 cm depth likely reflects the transition to the B horizon and is a proportionally greater decrease in P_o than in SOM. These findings are consistent with surface-limited effects of P fertilization (Weihrach and Opp 2017) and the influence of soil-forming factors on soil P speciation with depth (Walker and Syers 1976). In the landscapes of the US Maize Belt developed on loess deposited following glaciation events as recently as ≈12,000 years before present, subsurface soil P can be relatively high (500–790 mg kg⁻¹) and has been found to be constant across land use (Schilling et al. 2009; Fenton 1999; Pearson et al., 1940; Godfrey and Riecken, 1954). Loess parent material is dominated by (hydroxy)apatites (Fenton 1999) extractable by HCl (Mehmood et al. 2018), consistent with our findings of an increasing proportion of extractable P as HCl-P_i with depth. While total P concentrations varied little by depth in loess parent material (e.g., up to 370 cm) (Schilling et al., 2009), future

work should identify mobile forms of soil P to test for differences in subsurface sediments responsible for P losses via tile drainage.

Additionally, that maize rooting depth can extend up to 93–233 cm depth, well beyond the classical boundary of the solum of soils developed on loess in the US Midwest (Fehrenbacher et al. 1954; Douglas et al. 1967), raises the possibility of subsurface P to contribute to maize uptake. However, NaOH-P_i and HCl-P_i fractions are generally regarded as the least crop-available P forms, and represent secondary and primary P forms, respectively (Buckingham et al., 2010; Cross and Schlesinger, 1995). Relatively lower weathering of primary P (i.e., Ca-P) in loess relative to other parent materials (e.g., sandstone, shale) (Mehmood et al. 2018) may explain the dominance of the HCl-P_i fraction at our study site, which is representative of the upper US Midwest. Co-weathering of Fe and Al from loess (Akhtar et al., 2014; Margenot et al., 2017b; Wilson et al., 2017) likely explains the secondary dominance of NaOH-P_i at depth.

Though organic P and SOM exhibited broadly similar depth-wise trends in these high organic matter soils (Mollisols), greater sensitivity of C:P_o to treatments and variation by depth could be indicative of P_o dynamics being influenced by organic matter mineralization indirectly driven by N demand. That continuous maize without N fertilizer had lowest C:P_o at all but one depth is consistent with greater SOM mineralization under severe N limitation of this treatment. In contrast to C-N bonds of organic matter, organic P (i.e. esters) is not directly bound to and thus biochemically decoupled from C (Condron and Tiessen, 2005). Thus, N-driven mineralization of organic matter may impact C but not necessarily P. Notably, the C:P_o values at our site are 3.6- to 1.5-fold lower than the median C:P_o of 282 reported across diverse agroecosystems and unmanaged systems (Nakayama et al., 2021). Similar to our study site, where phosphomonoesterase activity was unexpectedly largely unrelated to C:P_o given its putative influence on mineralization-immobilization thresholds of P_o (Arenberg and Arai, 2019), the systematic literature review by Nakayama et al. (2021) did not identify significant relationships of phosphomonoesterase with C:P_o. However, we did identify significant and inverse relationships of PDE – generally underreported compared to PME (Nakayama et al., 2021) – with C:P_o across all treatments, suggesting that immobilization-mineralization

Table 4

F-values of the analysis of variance (ANOVA) of the effects of N fertilization rate (0 vs 269 kg N ha⁻¹) and crop rotation as maize-maize (M–M) or maize-soybean (M–S) on stocks of soil phosphorus (P) fractions at successive depths (0–15, 15–30, 30–60 cm).

Source of variation	df	Inorganic P				Organic P			Total P _o
		AEM-P _i	NaHCO ₃ -P _i	NaOH-P _i	HCl-P _i	H ₂ O-P _o	NaHCO ₃ -P _o	NaOH-P _o	
Rotation	1	0.0 ns	0.1 ns	0.6 ns	3.0 ns	0.5 ns	1.2 ns	3.0 ns	2.9 ns
N rate	1	6.7*	9.2**	2.2 ns	11.4**	0.9 ns	4.8*	2.3 ns	2.5 ns
Depth	2	14***	21.6***	12.8***	74.8***	11.5***	10.1***	65.0***	59.0***
Rotation × N rate	1	1.9 ns	0.9 ns	0.3 ns	0.2 ns	0.1 ns	0 ns	0.9 ns	0.6 ns
Rotation × Depth	2	4.8*	0.5 ns	6.5**	2.9*	0.04 ns	1.0 ns	0.3 ns	0.3 ns
N rate × Depth	2	22.5***	18.2***	10.2***	6.7**	0.5	4.4*	0.3 ns	0.6 ns
Rotation × N rate × Depth	2	4.5*	12.5***	4.5*	1.5 ns	0.2 ns	2.3 ns	0.5 ns	0.4 ns

df: Degrees of freedom. ***p < 0.001, **p < 0.01, *p < 0.05, ns: not significant.

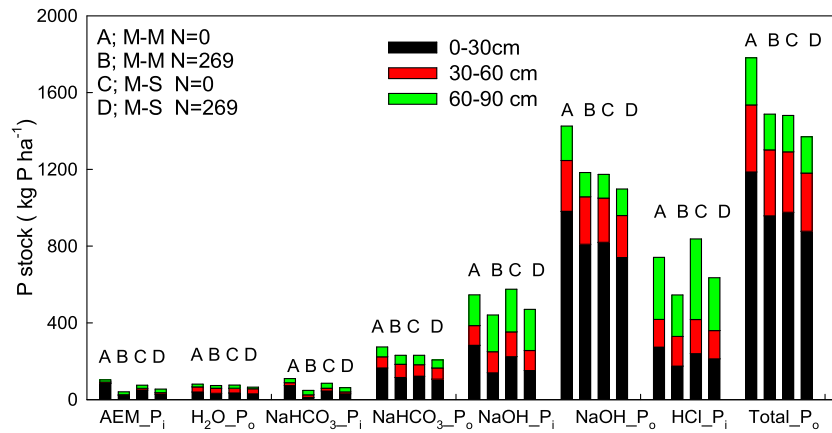


Fig. 3. Stocks of soil phosphorus (P) fractions under contrasting rotations of maize (M) and soybean (S) and N fertilization rates (0 vs 269 kg ha⁻¹) treatments.

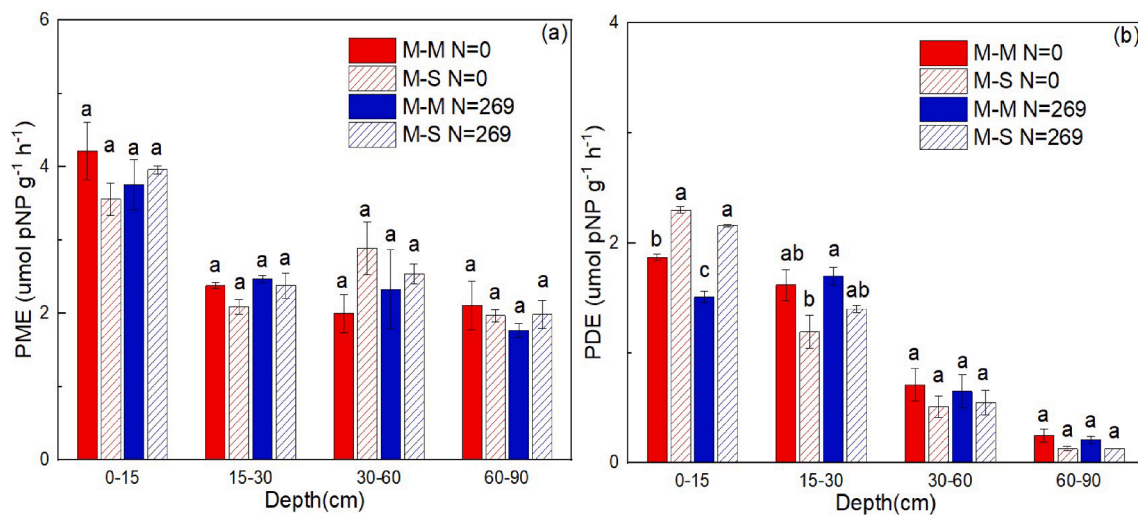


Fig. 4. Soil phosphomonoesterase (PME) and phosphodiesterase (PDE) activities as affected by N fertilization (0 vs 269 kg N ha⁻¹) under two rotation practices of maize-maize (M-M) or maize-soybean (M-S). Different lowercase letters denote statistically significant differences among N fertilization rates and crop rotation treatments for a given depth at $p < 0.05$. Error bars represent standard error of the means.

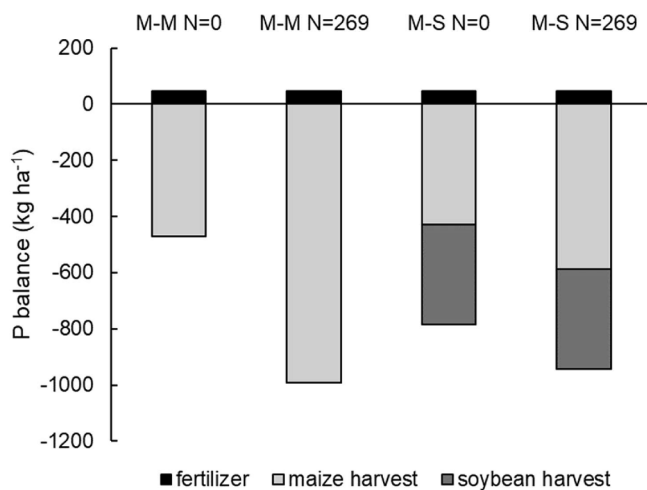


Fig. 5. Agronomic phosphorus (P) balances (output via grain harvest minus inputs via fertilizer) over 36-years of four treatments resulting from the combination of crop rotation, consisting of continuous maize (M-M) or maize-soybean (M-S), and N fertilization at 0 and 269 kg ha⁻¹ in the maize phase.

dynamics proxied by this ratio may be more closely related to the first and putatively rate-limiting step (Turner and Haygarth, 2005) of organic P mineralization catalyzed by this phosphatase.

4.2. Soil P_i fractions

Greater maize yield under N application indirectly led to lower labile P_i stocks (AEM-P_i and NaHCO₃-P_i) due to increased crop P uptake and thus export. At soil depths beyond 0–15 cm, labile P_i and P_o fractions were not significantly affected by crop rotation or N fertilization. This reflects vertical stratification of labile P_i from surface-applied P and residues, which corroborates the utility of surface-focused sampling in assessments of soil P response to management practices. Beyond the marked changes in P_i fractions with soil depth that reflect parent material and weathering (see Section 4.1), N fertilization largely impacted surface soil P fractions indirectly via crop uptake of P, and recalcitrant fractions at the greatest depth. This finding is consistent with previous studies that N fertilization significantly decreases the concentration of crop-available P in surface soils compared to no N fertilization due to greater plant demand for P with lifting of N constraints (Yang et al., 2015). At our study site, maize grain yields were 120% greater with 269 vs 0 kg ha⁻¹N, and as a result, drove differences in soil P_i contents via crop P uptake. That soybean rotation rotated with N-fertilized maize did not significantly affect either soil P_i fractions or yield-based P export

likely reflects similar P uptake by maize and soybean (kg P ha^{-1}); the lower grain yield of soybean compared to maize (t ha^{-1}) is partially offset by its higher grain P concentration (Johnson et al., 1992; Malvarino et al., 1999).

Our study revealed that soil acidification in surface soil (0–15 cm depth) with N fertilization did not necessarily co-occur with expected changes in soil P fraction. A decrease in Ca-associated P (HCl-P_i) would be expected at lower pH (4.9 vs 6.6) given dissolution of apatite and other Ca-P minerals under acidic pH (Kanabo and Gilkes, 1987). On the other hand, HCl-P_i was lower with N fertilization at 60–90 cm depth despite pH being similar among treatments and highest of any depth (pH 6.7–6.9). This scenario could be interpreted as greater crop demand for P being met by subsurface P acquisition, though it is not clear why intermediate depths (15–30, 30–60 cm) did not exhibit lower HCl-P_i under N fertilization. In contrast to HCl-P_i , lower NaOH-P_i is inconsistent with the observed soil pH decrease if this fraction is interpreted as Fe- and Al-associated P because acidification to pH 4.9 favors sorption of P to Fe and Al (hydroxy)oxides (Bolan et al., 2003; Sparks, 2003; Margenot et al., 2017a). One possible explanation is that greater P maize uptake driven by N fertilization may have led to depletion of HCl-P_i in addition to labile P_i fractions. In contrast to HCl-P_i , which decreased only for the treatment with lowest pH of 4.9 (M–M with 269 kg N ha^{-1}) at 0–15 cm depth, NaOH-P_i fractions decreased under M–M and M–S with N fertilization despite the latter having a pH 6.5.

4.3. Organic P cycling: Phosphatases

Nitrogen fertilization and crop rotation altered the activity of PDE that catalyzes the first and rate-limiting step of soil P_o mineralization (Turner and Haygarth, 2005). Depressed PDE activity under N fertilization conflicts with the lower concentrations of labile P_i relative to no N application because high levels of bioavailable P are thought to inhibit phosphatase activity, i.e. feedback inhibition (Nannipieri et al., 2011). This suggests a non-P mediated impact of N fertilization on PDE, notably the observed acidification that would attenuate activity of generally circumneutral to alkaline pH optima of this enzyme (e.g., pH 6.0–8.0) (Herbien and Neal, 2008). This finding broadly supports the hypothesized indirect effects of N fertilization and crop rotation on P cycling via these hydrolytic enzymes. Mineralization of P_o by phosphatases is a potential contributor to P for crop uptake (Acquaye, 1963; Oberson et al., 1999; Oberson et al., 2006), and N inputs are known to impact the production of these enzymes (Marklein and Houlton, 2012; Tian et al., 2016). That PME activity was unresponsive to treatment-driven changes in soil pH does not agree with previous findings of decreases in the activity of this phosphatase due to N fertilizer-induced acidification (Weand et al., 2010; Yang et al., 2015). However, since concerted activities of PME and PDE activities are necessary to release crop-available orthophosphate from (diester) P_o (Turner and Haygarth, 2005), the observed change in the PME/PDE ratio could signify alteration of P cycling via P_o mineralization (Dick et al., 2000). Lower phosphatase activities with depth in this study broadly tracked changes in soil P_o fractions and are consistent with previous observations (e.g., Gelsomino and Azzellino, 2011; Steinweg et al., 2013). That PME activity was maintained more with soil depth than PDE could indicate more processed monoester P_o pool derived from surface inputs of diester-enriched P_o via crop residues (Turner and Haygarth, 2005).

4.4. Soil P_o under crop rotation and N fertilization

Though intensively managed agricultural systems tend to decouple soil C–N–P dynamics via high inputs of inorganic forms of individual elements (Recous et al., 2019), this study identifies a weak but significant effect of N inputs on soil P cycling via labile P_o . Changes in $\text{H}_2\text{O-P}_o$ with crop rotation under the same P input rate support the hypothesized influence of crop residue quality and quantity on soil P cycling via residue P_o inputs. Decreases in $\text{H}_2\text{O-P}_o$ under N fertilization may be

attributed to greater P uptake by non-N limited maize and export via maize grain, which in addition to consuming labile P_i pools may have stimulated mineralization of labile P_o (Oehl et al., 2004; Yu et al., 2006).

Our results demonstrate that soil P_o fractions ($\text{H}_2\text{O-P}_o$, $\text{NaHCO}_3\text{-P}_o$, NaOH-P_o) and stocks constituted 58–69% (concentrations) and 62–73% (stocks) of total extractable P. This is in agreement with the widely cited figure of P_o representing 20–80% of total P in soils globally (Condon et al., 2005; Richardson and Simpson, 2011), though there is generally limited data on P_o , and to depth, compared to agronomic measures of labile P_i (i.e., soil test P) (Metson et al., 2017). Given the large magnitude of P_o stocks in these soils, mineralization of even a small proportion of this total would make it an important contributor to crop uptake. Mineralization of P_o depends on the forms and concentrations of soil P_o (Bünemann, 2008), though estimates of P_o mineralization are limited and vary widely. Using radiolabeled, ex situ lab studies, maximum potential P mineralization rates in arable soils are coarsely estimated to be as high $0.5 - 0.9 \text{ mg P kg}^{-1} \text{ soil day}^{-1}$ (Bünemann et al., 2007; Lopez-Hernandez et al., 1998). Assuming a 120-day growing season and a BD of 1.4 g cm^{-3} , this would correspond to 227 kg ha^{-1} of P mineralized at 0–15 cm depth. Clearly, these values suggest that P mineralization estimates based on ex situ approaches carry a high degree of uncertainty, which points to P mineralization as a largely understudied potential source of crop-available P in temperate agroecosystems.

Significant effects of crop rotation and N fertilization on the water-soluble fraction of P_o ($\text{H}_2\text{O-P}_o$) reveal potential long-term management impacts on soluble P losses. Water-soluble P_o can be lost from agroecosystems via surface runoff or tile drainage (Beauchemin et al., 1998; Ron Vaz et al., 1993) and is more mobile than dissolved orthophosphate P (Dodd et al., 2018; Dodd and Sharpley, 2016). Hydrolysis of dissolved P_o can significantly contribute to orthophosphate loading of surface waters, meaning that losses of labile P_i alone may underestimate P risk (Dodd et al., 2018; McDowell and Koopmans, 2005). For example, in the eastern US Maize Belt (Ohio), up to 70% of P losses from the soil as leachate and water-soluble P occurred as P_o (Reddy et al., 1978). As the majority of P inputs to soils in the US Maize Belt and intensive maize agroecosystems globally are in the form of P_i as ammonium phosphate and superphosphate fertilizers, immobilization of P_i into microbial biomass or crop tissues can play an important role in P use efficiency at the agroecosystem and long-term (decadal) scales (Rowe et al., 2016). The return of P_i inputs in P_o forms (e.g., phytate, nucleic acids, phospholipids) could help explain why P fertilization rates, unrelated to P_o , may not fully predict P losses via this pathway (King et al., 2017; Sharpley et al., 2013).

4.5. Soil P stocks and budgets

Relatively few studies have investigated P stocks beyond surface depths despite the hypothesized large magnitude of subsurface P stocks, which must be accounted for to develop accurate P budgets from field to regional watershed scales (Metson et al., 2017). Labile P_i (AEM-P_i and $\text{NaHCO}_3\text{-P}_i$) is generally regarded as the most crop-available form but only accounts for a small proportion of total soil P stocks, as supported by our findings. A global dataset of total soil P stock at 0–50 cm depth indicated that labile P_i across US soils accounted for approximately 7% of total P (Yang et al., 2013). In a more recent assessment of P balances across US agroecosystems, Swaney and Howarth (2019) estimated that labile P_i comprised 3% of total soil P. These modeled estimates are consistent with our measurements at the field-scale, for which labile P_i constituted 5.1 % of total P stocks at the pedon scale (0–90 cm). The proportion of total P stocks as labile P at our site is lower than that of Yang et al. (2013), likely because deeper sampling in our study (80% deeper) entailed a lower proportion of total P as labile P, which is more concentrated at the soil surface.

Our assessment of deep soil P fractions has key implications for soil P supplying capacity and soil P balances that form the basis of many US Maize Belt state recommendations on P management. For example, the

Illinois Agronomy Handbook categorizes soils and thus P application rates by “P supplying power” based on loess type and thickness. Soils developed on thicker loess deposits are interpreted as having a higher P supplying power (Fernández and Hoefft, 2009). However, to our knowledge, there is only one non-peer-reviewed evaluation of P supplying power in the form of P stocks or fractions to substantial (100 cm) depth in the US Midwest: Fenton (1999) found that the ratio of Ca-P to the Fe- and Al-P increased with soil depth, and the largest amount of Bray-1P (Bray and Kurtz, 1945) occurred in the C horizon.

In general, there is a lack of data on total soil P stocks and none on soil stocks of P species despite their value in informing models to predict P dynamics from field to continental scales (Metson et al., 2017; Swaney and Howarth, 2019; Schilling et al., 2009). Resolving full-profile soil P stocks and beyond total P to include P fractions thought to approximate biogeochemical pools (Cross and Schlesinger, 1995; Negassa and Leinweber, 2009; Turner and Blackwell, 2013) would enable moving beyond balances (P input versus P output) to develop agroecosystem P inventories. This stands to resolve regional P estimates since soil available P measures at surface depths are insufficient to calculate meaningful soil P budgets (Swaney and Howarth, 2019). For example, under N fertilization, net agronomic P export for our 36-year experimental field trial was equivalent in magnitude to approximately one-third of soil P stock (to 90 cm depth), more than half of which was present in organic form.

Maize in the US Maize Belt is the greatest single agricultural sink for fertilizer P in the US at exactly half of the national usage (724 Gg P) (Liebman et al., 2013; Aguilar et al., 2015; Metson et al., 2016). Resolving soil P stocks in these agroecosystems can reveal the extent of legacy P and enable its integration into agronomic strategies to mitigate P loss reductions (e.g., draw-down) (Haygarth et al., 2014). At our 36-year experimental site, adequate soil test P values despite large negative agronomic P balances (-426 to -945 kg ha⁻¹) suggest a magnitude of legacy soil P that is 2- to 4-fold higher than the estimated statewide average of 230 kg P ha⁻¹ (David and Gentry, 2000). As expected, grain yields resulting from N fertilization and crop rotation practices drove net P export over the 36-year period. That the negative soil P balance was driven by harvest export is consistent with soil P drawdown being more rapid with phytoextraction than by cessation of P fertilization (von Arb et al., 2021). In contrast to less productive agroecosystems, the high yielding conditions of the US Maize Belt may enable more rapid draw-down of legacy P entailing both short-term fertilizer cost savings to producers and long-term mitigation of non-point source P to surface waters (Jarvie et al., 2013; Rowe et al., 2016).

4.6. Implications for P management

Soil labile P_i and P_o fractions were unaffected by crop rotation and N fertilization at depths beyond 30 cm, corroborating the assumption of surface-limited soil sampling to assess soil P dynamics in intensively managed maize-based agroecosystems. Within this surface depth, continuous maize production and N fertilization significantly decreased soil H₂O-P_o in surface soils. Since water-soluble P_o has high loss risk potential and can contribute to crop P uptake via mineralization (Oehl et al., 2004; Yu et al., 2006), our study reveals that the non-P managements (i.e., N application, crop rotation) may accelerate P external fluxes via loss and internal fluxes via mineralization (Jarosch et al., 2019).

5. Conclusion

A 36-year crop rotation and N fertilization experiment offered insight on the degree to which N fertilization and crop rotations can impact soil P cycling in intensively managed maize agroecosystems in the US Midwest. Greater changes in soil P fractions occurred by depths (0–90 cm) than by management treatments, with higher water-soluble P_o (H₂O-P_o) under M–M compared with M–S. Nitrogen fertilization most strongly decreased both water-soluble P_o and labile P_i at 0–15 cm

depth, attributable to greater maize yield-driven P uptake and export with grain harvest. Acidification of surface soils under high N fertilization was inconsistent with differences among soil P_i fractions. Only under N fertilization did the inclusion of soybean in the maize rotation elevate phosphodiesterase activity, and at surface depths. Intensive N application and crop rotation practices thus appear to indirectly but significantly influence soil P cycling in the long-term, and these subtle changes may scale to be appreciable across the US Maize Belt at decadal timescales. The magnitude of total P_o and HCl-P_i (interpreted as apatite) stocks supports that these P pools constitute a major proportion of P in loess-derived soils in the US Maize Belt, and are therefore important for modeling agroecosystem P dynamics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2022.115829>.

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