Environ Earth Sci (2016) 75:568
DOI 10.1007/s12665-016-5284-3

THEMATIC ISSUE

Phosphorus downward movement in soil highly charged with cattle manure

Ileana Cecilia Ciapparelli[1] · **Alicia Fabrizio de Iorio**[1] · **Ana Rosa García**[1]

Received: 1 June 2015 / Accepted: 16 November 2015 / Published online: 26 March 2016

Abstract In the rolling pampa region, the intensification of beef cattle feeding operations generates large volumes of solid organic manure which has high concentrations of phosphorus (P). This residue can be reused like organic fertilizer in agricultural practices, increasing crop production and closing the nutrients cycle. However, this practice can cause water pollution if not well managed. The aim was to study the vertical and temporal migration of P and its relations with edaphic properties in agricultural soil that has received a single heavy application of cattle manure. Three treatments were analyzed: (1) Zone 4 (Z4)—plot manured with 1600 tn ha^{-1} in 2004; (2) Zone 10 (Z10)—plot manured with 500 tn ha^{-1} in 2010 and (3) Zone control (ZC)—plot free of cattle manure. Water extractable phosphorus—WEP, soil test Bray and Kurtz P—Bray P, total phosphorus—TP, organic carbon—OC, pH and electrical conductivity were quantified. Results indicate high concentration of TP, Bray P and WEP in deeper horizons of impacted plots, showing the mobility of this nutrient. Correlation between TP and OC% were established for Z4 y Z10 in 88 and 84 %, demonstrating that the organic matter that moved in the profile presented high P content. An increase of salinity of 257 and 345 % for Z4 and Z10, respectively, was found in the deepest samples. The quantification of an empirical rate (EARP) showed the downward movement of P reaching 150 cm in Z4 and 90 cm in Z10. The results have shown that application of large volumes of solid manure saturated P retention capacity favoring its movement towards underlying water.

Keywords P movement · Feedlot · Agricultural soils · Environmental impact

Introduction

The intensification of beef cattle feeding operations generates large volumes of solid organic manure which has high concentrations of phosphorus, nitrogen, potash, heavy metals, organic matter, pathogens, hormones, antibiotics, among others (Miller et al. 2004; García et al. 2012). This residue can be reused like organic fertilizer in agricultural practices, increasing crop production and closing the nutrients cycle (EPA 2003). In the rolling pampa region, this practice is not generally planned since the beginning of the livestock activity (feedlot facilities), which may lead to accumulation of P in soil. Consequently, runoff and infiltrations may reach water bodies through diverse mechanisms and affect their quality (García and Iorio 2003; Eghball et al. 2004; García et al. 2013). Phosphorus (P) is a key element in the regulation of the trophic state of water bodies (EPA 2000). The P export by surface runoff from agricultural fields with manure added has been widely studied (Sharpley and Sisak 1997; Elrashidi et al. 2005; Borda et al. 2011), while the loss of this nutrient through the profile has received less attention, especially in the pampa region.

The P from manure inside the edaphic system can follow different paths. It can be either retained by superficial

---

This article is part of a Topical Collection in Environmental Earth Sciences on “3RAGSU”, guest edited by Daniel Emilio Martinez.

✉ Ileana Cecilia Ciapparelli
ciappare@agro.uba.ar

[1] Cátedra de Química Analítica, Departamento de Recursos Naturales y Ambiente, Facultad de Agronomía, Universidad de Buenos Aires (UBA), Av. San Martín 4453, C1417DSE Buenos Aires, Argentina

adsorption to organic, clayed and/or humic-clayed particles or precipitated like forms of P-Ca, P-Fe or P-Al under different pH and redox conditions (Djodjic 2001; Sekhon 2002). In addition, organic acids provided by manure compete with P by adsorption sites (Chardon and Schoumans 2002) and by the formation of interchangeable Fe and Al complexes (Bolster and Sistani 2009). Thus, if the sites are blocked, this nutrient can continue its movement towards lower horizons, being able to reach the phreatic layer. P can also be mobilized by preferential paths such as cracks and galleries (Beven and Germann 1982 quoted by Djodjic 2001; Álvarez Benedí et al. 2001). Researchers who have studied the loss of P in soils affected by manure found that due to the saturation of its sorptive capacity, P was mobilized in depth, even after several years of inactivity (Campbell and Racz 1975; Eghball 2003; Glæsner et al. 2012).

The potential risk of superficial and/or underlying watercourse contamination can be evaluated considering the vulnerability of the environment and contaminant load (INTA 2010). While wastes generated by feedlot operation are characterized by a high load of P, the vulnerability of each ambient is site specific. In this case study, losses of P in the soil profile may present an environmental threat taking into account the vulnerability of the environment, because of climate (tempered and humid), topography, distance to surface water bodies (located in the drainage dividing line between too rivers), proximity of the phreatic water, and dynamics of this nutrient. In this context, the aim was to study the vertical and temporal migration of P and its relations with edaphic properties in agricultural soil that has received a single heavy application of cattle manure.

Materials and methods

Study site

The study was carried out in a crop-livestock farming system in the district of Marcos Paz, in the rolling pampa region (Fig. 1) of the province of Buenos Aires, Argentina. The feedlot facilities are placed in the drainage dividing line between the Reconquista and Matanza rivers. The weather is sub-humid to humid, with annual rainfall of 990 mm and an average annual temperature of 17 °C during the period under study (2004–2013). The soil was classified as typical Argialbol according to USDA soil taxonomy, and is characterized by having more than 180 cm deep with a mollic horizon (A Hz) followed the an eluvial horizon (E Hz) and a strongly textural horizon (Bt Hz), formed by 2Bt1 horizon (40 % of clay) and 2Bt2 horizon (29 % of clay and 27 % of loam). This presents poor drainage and slope less than 1 %, and the phreatic water can reach 2 m below the surface.

The soil under study was characterized by following standard procedures described in Page (1982). The particle size distribution was determined by Boyocous hydrometer method (Gee and Bauder 1986); extractable P (Bray-P), using Bray-2 extract, and water extractable P (WEP) were measured colorimetrically with ammonium molybdate (Kuo 1996). Total recoverable Fe and Al were determined using inductively coupled plasma optimal-emission spectrometry, following digestion according to EPA Method 3050B (EPA 1996). Additionally, the following variables were quantified: bulk density, determined by the core method (Blake and Hartge 1986), and volumetric water content, calculated from bulk density and gravimetric moisture content (determined after oven drying at 105°C for 24 h). Table 1 shows the properties the same. The horizons are highlighted for being non-saline, non-sodic, with calcareous material, according to FAO (2009). The acidity ranged from moderate to neutral (6.7 ± 0.5), the cation exchange capacity from moderate to high (26 ± 5.6 meq 100 g^{-1}), with high content of exchangeable calcium (Ca), potassium and magnesium according to the classification established by Hazelton and Murphy (2007). It presented 2.1–4.7 g 100 g^{-1} of total recoverable iron (Fe) and 4–9.7 g 100 g^{-1} of total recoverable aluminum (Al). Bulk density values were similar to the representative values for the soils of the region, ranging 1–1.3 g cm^{-3}, being E horizon the most dense because its laminar structure. Moisture content in A and E horizons is higher than the field capacity (27.5 and 19.5 %, respectively) (INTA 1980). Average amounts of organic carbon as well as total N and P were found (Table 1), and on the other hand, extractable P was deficient, in correspondence with expected soil values of the pampa region (Conti 2000).

Practice under study

The environmental situation analyzed is a consequence of an unusual practice in the area: the application of very high doses of cattle manure on agricultural soil: 1600 tn ha^{-1} in 2004 in one zone (Z4) and 500 tn ha^{-1} in 2010 in another zone (Z10). Manure applied in each plot was removed from the feedlot pen surface, stacked on the soil of plot for 2 years, in order to partially mineralize organic matter, and finally spread on its surface. Then, in the plots, the production of corn, oats and barley was kept under different rotations. The plots did not receive further organic amendments. Thus, the Z4 and Z10 plots had not been fertilized with manure for 9 and 3 years at the time of sampling (2013).

Fig. 1 Location of study site

Sample collection

Sampling was conducted during 2013 in different plots (Z4, Z10), and control plot (ZC) free of cattle manure. To do this, five soil pits were opened randomly in each plot and composite soil samples at various horizons were taken up to 1.5 m deep in Z4 and ZC, and up to 1.0 m deep in Z10.

Soil analysis

The manure applied presented high amount of P (2.3 %), moderate amount of salts (K: 1.6 %; Mg: 1.5 %; Ca: 0.86 %) and organic matter (19 %) according to Eghball and Power (1994), Ciapparelli and García (2015), Uyanöz et al. (2006) and Eichler-Löbermann et al. (2007). These parameters will be analyzed on soil further below in this study.

P accumulation and movement in the soil profile was evaluated by determining total phosphorus (TP), extractable P (Bray P) and water extractable P (WEP). TP was determined after digesting 1 g of the soil with HNO_3 and H_2SO_4 concentrated. Bray P was determined by Kurtz and Bray No. 2 method and was used to determine P release from Al, Fe and Ca-bound forms in this moderate acidic to neutral soil (SERA-IEG 17 2000). WEP was used to indicate the quantity of labile P that would be readily subject to leaching (Graetz et al. 1999) and it was extracted by using a 1:10 soil to water ratio and shaking it for 5 min. All P determinations were measured colorimetrically with ammonium molybdate and ascorbic acid (Murphy and Riley 1962). Soil pH was determined using potentiometric method on a 1:2.5 soil to water ratio, electrical conductivity—EC by conductimetric method performed in saturated paste, and organic carbon—OC, by loss-on-ignition (Page 1982).

Data analysis

- Empirical advance rate of P (EARP):
  To estimate the P mobility in the soil profile, one empirical advance rate of P (EARP) was defined as the P advance per each centimeter of soil and was calculated as follows: $\mathrm{EARP}_{ij} = \frac{\Delta \mathrm{BrayP}_{ij}}{\mathrm{ThickHz}_{ij}}$ i treatments (Z4, Z10 and ZC). j horizons (A, E, 2Bt1 and 2Bt2). Where, Δ Bray P_{ij} is the variation of Bray P (ppm) at each horizon, for each treatment. Thick Hz is the thickness of each horizon (cm) for each treatment.

- Statistical analysis:
  The effect of the practice on the soil was analyzed by descriptive statistic, using the statistical software InfoStat (Di Rienzo et al. 2008). Comparison of means was performed using Tukey's test ($\alpha = 0.05$). Regression analyses were used to describe relations between P components and organic carbon. Mathematical models were adjusted to the experimental values. Correlation analyses were used to explain P migration between TP and organic carbon. The correlations were significant at $p < 0.05$.

Results and discussion

P distribution in soil profile

Figure 2a shows the increase of mean concentration of total phosphorus (TP) at each plot under study in relation to control plot, at different depths. The results indicate that the soil TP concentration after 9 years of receiving a dose of 1600 tn ha^{-1} of manure (Z4) increased by 8.6 times in the first 10 cm and 0.5 times at 150 cm depth (2BCt Hz), reaching a maximum increase of 11.6 times at 20 cm (A Hz). Similarly, after 3 years of receiving 500 tn ha^{-1} of manure (Z10), the average concentration of TP increased 9.7 times in the first centimeters of soil and 0.1 times at 60 cm depth (2Bt1 Hz). This shows that the older application (Z4) generated a greater migration of P within the profile than the latest one (Z10). The P migration towards deeper layers is maybe due to the longer residence time in soil, affected by farming activities, weather conditions, and the competence with organic matter and other anions provided for manure (Sekhon 2002). Deep roots, heavy equipment, and drying wetting cycles on fine textured soils generate cracks and preferential paths that facilitate P migration (Wyngaard et al. 2011). In addition, through its horizons: loamy (A, E), clayey (2Bt1) and clayey loam (2Bt2), the soil has the buffering capacity of P progress, reducing its concentration in deeper layers. Graetz et al. (1999) and Nair and Graetz (2002) also found high concentrations of WEP, Bray P and TP in deep horizons in highly impacted areas, indicating the mobility of this nutrient and its gradual decrease in the profile.

The extractable P (Bray P) achieved significant increases of 1.1 times for the 150 cm and 2.6 times at 100 cm depth in Z4 and Z10, respectively (Fig. 2b). Also, the WEP showed a maximum increase of 470 times at 50 cm in Z4 and 130 times at 10 cm depth in Z10; whereas for the 150 cm of Z4 treatment, WEP reached background

Table 1 Physical, chemical and biological properties of soil under study

Measured parameters	Units	A	E	2Bt1	2Bt2	3BCt
Depth	cm	0–30	30–40	40–90	90–150	150–180
Gravimetric moisture content	%	30.3	27.2	27.8	26.3	28.1
Bulk density	g cm^{-3}	1.08	1.30	1.24	1.14	n/d
Clay	%	9.9	22.8	41.7	33.1	26.5
Silt	%	50.1	47.5	29.7	38.9	41.3
Sand	%	40.0	29.7	28.6	28.0	32.2
Total N	%	0.18	0.05	0.05	0.04	0.01
Organic carbon	%	1.96	0.80	0.64	0.51	0.28
Total P	mg kg^{-1}	519.3	253.2	321.6	348.6	303.1
Extractable P (Kurtz and Bray 1)	mg kg^{-1}	5.76	2.83	4.31	6.49	3.19
Water extractable P	mg kg^{-1}	1.41	0.88	0.55	0.80	0.49
Electrical conductivity	dS m^{-1}	0.26	0.21	0.44	0.46	0.43
Total recoverable Fe	g 100 g^{-1}	2.1	2.3	4.7	4.0	4.3
Total recoverable Al	g 100 g^{-1}	4.0	4.1	9.7	8.4	7.5
pH in water (1:2.5)		5.9	6.5	6.6	7.1	7.2
$CaCO_3$ Eq	%	11.7	11.3	12.5	12.5	12.8
Exchangeable Na	meq 100 g^{-1}	0.3	0.3	1.1	1.0	0.8
Exchangeable K	meq 100 g^{-1}	1.6	1.1	3.3	2.5	1.5
Exchangeable Ca	meq 100 g^{-1}	14.8	12.0	19.2	18.1	16.8
Exchangeable Mg	meq 100 g^{-1}	2.9	2.4	5.1	2.9	2.4
Cation exchange capacity	meq 100 g^{-1}	26.3	18.2	33.4	28.4	23.8

A horizon includes Ap horizon (0–10 cm)

n/d without data

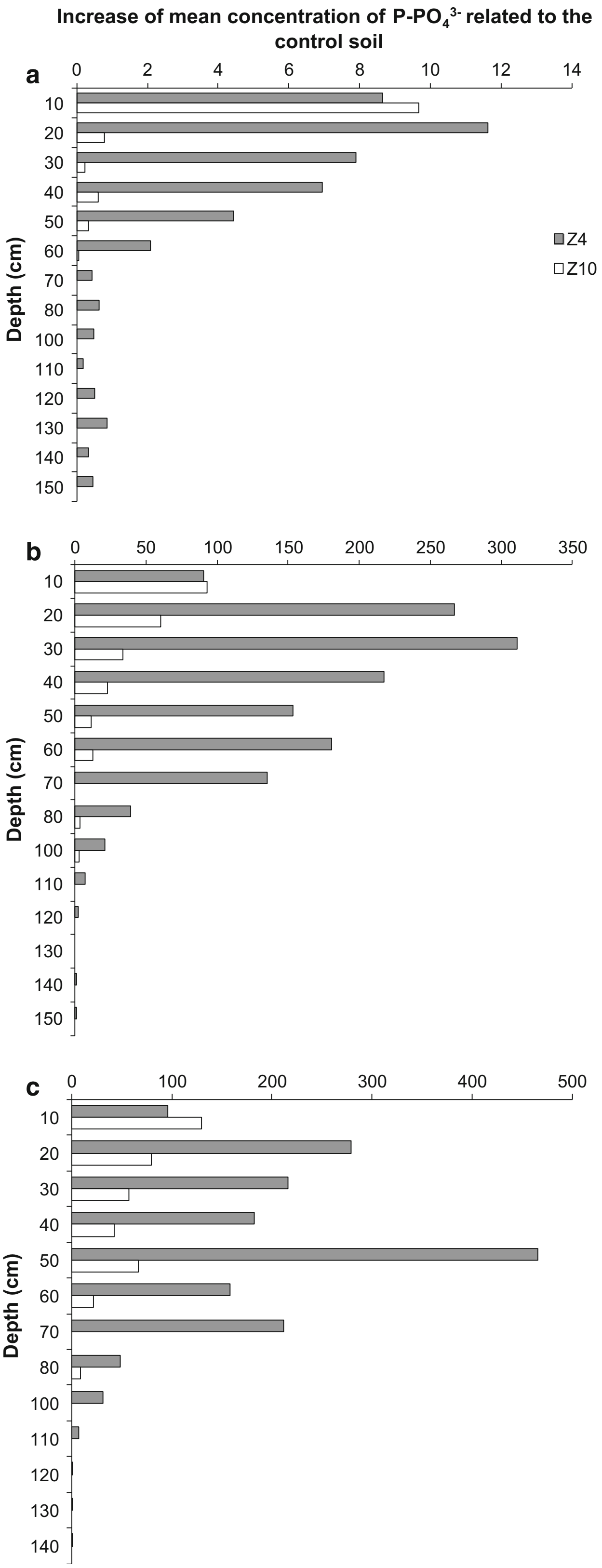

Fig. 2 Increase of mean concentration of TP (**a**), Bray P (**b**) and WEP (**c**) related to the control soil (ZC) in the soil profile for two impacted plots under study (Z4 y Z10)

concentration (ZC) and for 100 cm of Z10 treatment, P increased 910 % (Fig. 2c). From this data it can be said that in Z4, TP and Bray P presented higher concentration than in ZC while WEP did reach background level (for the 150 cm). In Z10, although Bray P and WEP were mobilized below the 1 m depth, TP reached background values (ZC) at 70 cm depth.

WEP was retained by the solid soil matrix on the 2Bt2 horizon (adsorption, complexation, precipitation), with very good content of total recoverable Fe and Al, clays and $CaCO_3$ (Table 1). Bray P could be represented by Fe-P, Al-P and, especially soluble Ca-P compounds, formed by the input of P and Ca from manure after the intense application of this residue. The vertical movement of labile P could have taken place when soil sorptive capacity was saturated with input of P and organic acids from manure (Øgaard 1996). It is worth mentioning that the latter competes with P for sorption sites or by the formation of complexes with Fe and Al (Chardon and Schoumans 2002; Bolster and Sistani 2009). Sharpley et al. (2004) found that intensive annual applications of cattle manure for more than 10 years generated the precipitation of labile forms of Ca-P, not extractable with water, which can be mobilized through the horizons (Nair and Graetz 2002). These findings highlight the high mobility that this nutrient has under conditions of high organic load, and potential to reach the underlying water flow.

Bray P/TP and WEP/TP relationships

Table 2 presents the regression functions of the Bray P/TP and WEP/TP relationships for each plot under study. All data obtained from each sampled horizon was considered in these relationships. ZC data fitted to a polynomial function and data from plots receiving manure fitted to a logarithmic function. Graetz et al. (1999) found different relationships between the variables analyzed, which fitted to linear models, possibly because they considered different land use systems including pasture and forage crops. Regarding Bray P/TP relationship, the fitting of data had a coefficient (R^2) of 0.56 for ZC and 0.97 for Z4 and Z10; while for the WEP/TP relationship these coefficients were 0.89, 0.95 and 0.47 corresponding to Z4, Z10 and ZC. These results agree with those obtained by Graetz et al. (1999), although the correlations established by these researchers were significant, they did not exceed a coefficient of 0.6.

The behavior of the different functions was evaluated by studying its derivatives as instantaneous rates. Also, the instantaneous rates may be related to the sampled depth, because the highest concentrations of P were found in the upper horizons. Almost 5700 ppm of mean TP was

Table 2 Bray P/TP and WEP/TP relations for the three plots under study: Z4, Z10 and ZC

Treatment	Bray P/TP	R^2	WEP/TP	R^2
Z4	Bray P = 378.32 × ln (TP) − 2273.1	0.97	WEP = 91.327 × ln (TP) − 539.39	0.89
Z10	Bray P = 303.34 × ln (TP) − 1753.2	0.97	WEP = 94.498 × ln (TP) − 537.41	0.95
ZC	Bray P = 0.00007 TP^2 − 0.0441 TP + 9.2716	0.56	WEP = 0.00001 TP^2 − 0.0092 TP + 2.2109	0.47

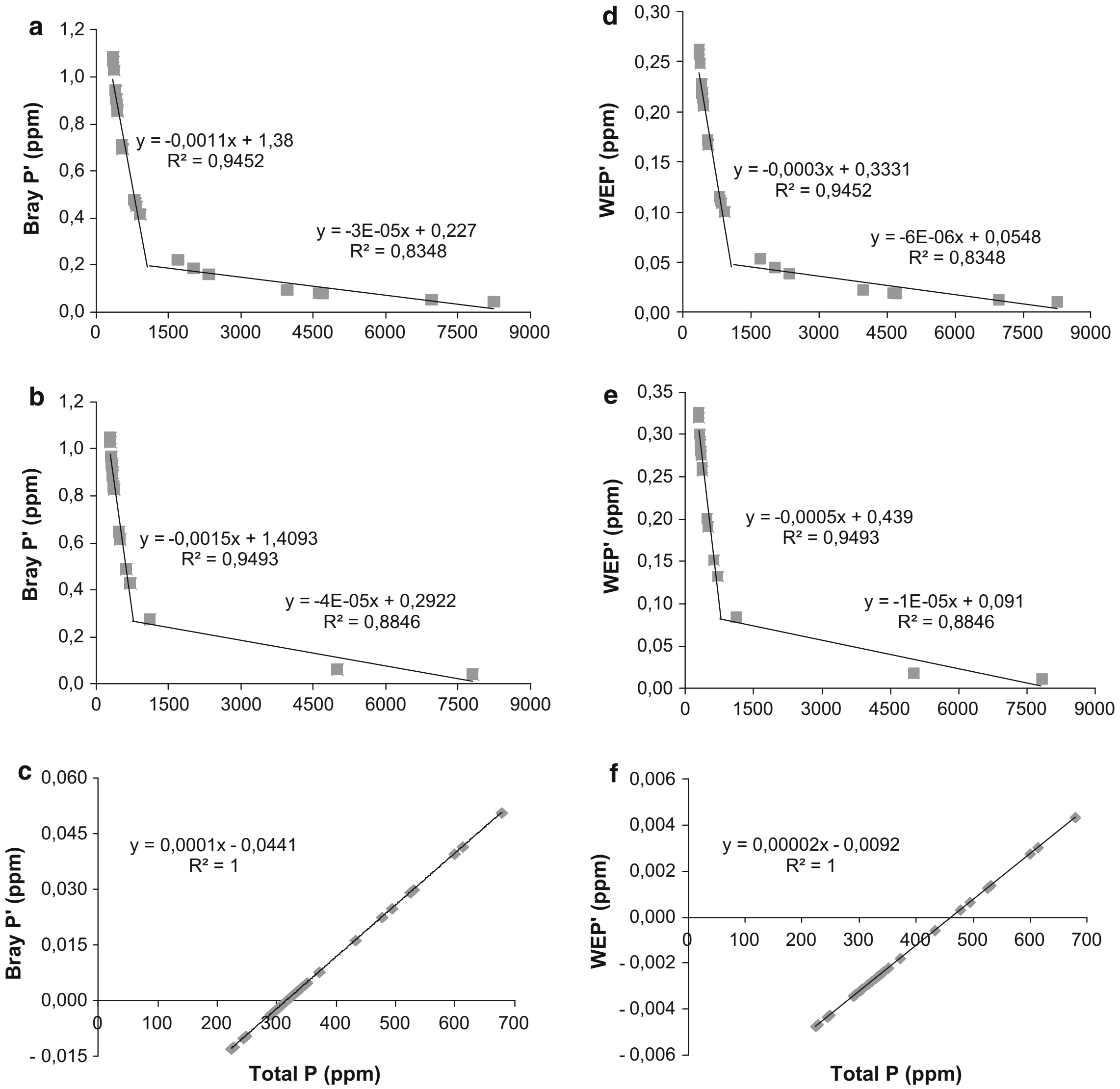

Fig. 3 Bray P/TP (**a–c**) and WEP/TP (**d–f**) linear regression functions derived for the three plots under study. **a**, **d** Z4, **b**, **e** Z10, **c**, **f** ZC

found at 0–30 deep in Z4 meanwhile in Z10, more than 2600 ppm was found at the same depth, in relation to ZC, where that value was 520 ppm. Similar situations were found in Bray P: 1007, 432 and 6 ppm; and for WEP: 235, 144 and 1.4 ppm for Z4, Z10 and ZC, respectively at same depth.

Figure 3 shows the slopes of the tangent lines to each point of the functions relating Bray P and WEP with TP for plots under study. It can be seen that data calculated from the derived functions adjusted very well ($R^2 > 0.83$) to linear functions, showing one set of data in the control plot (ZC) and two sets of data in plots with added manure (Z4 and Z10). In ZC it could be seen that the higher the concentration of TP in the soil profile, the greater the concentration of extractable P and soluble P, resulting in a constant variation of the instantaneous rates throughout the profile (Fig. 3c, f).

However, plots with manure showed a different behavior from ZC. The Z4 soil presented a negative variation of the instantaneous rates of Bray P/TP, where in the first 50 cm depth (equivalent to A and E Hz), the rate was of 0.03 μg kg^{-1}, while in deeper horizons it was 1.1 μg kg^{-1} (Fig. 3a). Performing the same analysis on Fig. 3b, the most recent application of manure (Z10) generated a variation of 0.04 μg kg^{-1} in 0–20 cm depth and of 1.5 μg kg^{-1}, in deeper horizons. The lower variation of instantaneous rates in the upper horizons indicated the soil P saturation. In addition, these results indicated that clayey horizons accumulated 37 times more Bray P than upper layers for both impacted plots, due to their sorptive capacity.

The fraction of WEP presented a similar behavior (Fig. 3d). The plot manured in 2004 (Z4) showed in the first 50 cm depth a variation of 0.006 μg kg^{-1}, while in deeper horizons the slope was 0.3 μg kg^{-1}. In Z10, the variation was 0.01 μg kg^{-1} in the 0–20 cm depth and 0.5 μg kg^{-1} at deeper layers (Fig. 3e). This demonstrates that the WEP was accumulated 50 times more in clayey horizons (Bt) than in the upper horizons (A, E) in both fields. These results confirm the higher P retention in clay particles. Clay has a bigger specific surface than other soil particles, as well as numerous sorption sites. PO_4^{3-} anions can been fixed over positive charges of clay or through cations previously sorbed (Buol et al. 2011).

In Fig. 3a, b, d, e, a threshold between linear relationships of data groups describing the instantaneous rates for Bray P/TP and WEP/TP is observed. The corresponding threshold values for Z4 and Z10 were: Bray P/TP: 1078 and 765 ppm of TP; WEP/TP 947 and 710 ppm of TP. This suggests that at TP concentrations exceeding those thresholds, the extractable content of Bray and WEP remained practically unchanged, much greater in Z4 than in Z10, unlike what occurs below these thresholds. These results reinforce the idea of mobility of inorganic P in depth, and lead to think about an accumulation of organic P from manure in surface horizons. Several authors have studied the composition of cattle wastes and established that between 50 and 80 % of the TP is inorganic P (Barnett 1994; Eghball 2003; Sharpley et al. 2004; Galvão and Salcedo 2009) and this proportion is practically all available P (Whalen and Chang 2001), including water extractable P fraction. The remaining 20–50 % of TP from manure can be considered organic P (OP). Wyngaard et al. (2011) explained that mineralization of organic matter from manure could generate ions PO_4^{3-} that contributed to soluble forms of P in soil. These P forms could be mobilized to deeper layers, supporting the findings of this study.

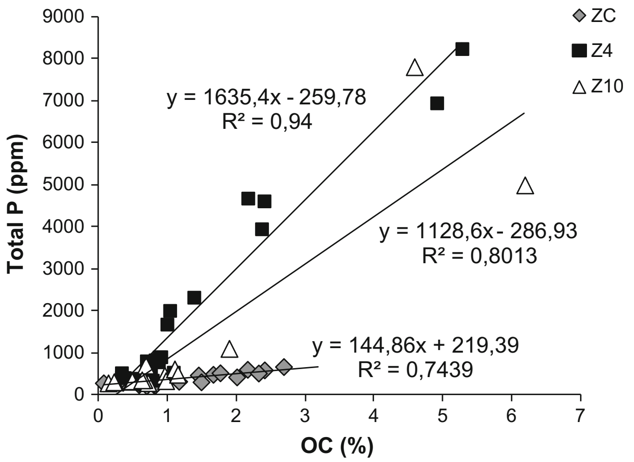

Fig. 4 TP/OC linear regression functions for the three plots under study: ZC (*gray diamonds*), Z4 (*black squares*), Z10 (*white triangles*)

Organic carbon and its relation to P transport

In Fig. 4, the relationship between soil organic carbon (OC%) and TP concentration (ppm P-PO_4^{3-}) was established for the three plots (ZC, Z4 and Z10). It was found that in manured plots, the maximum organic carbon content in soil surface was 5.3 and 6.2 % in Z4 and Z10, unlike ZC which was 2.7 %. Also, a homogeneous and continuous distribution of points in the ZC profile was presented, in contrast to the impacted plots, where continuity occurred in Z4 but not in Z10. This showed a strong impact of waste on soil, due to the increase in OC% content and the advance of organic matter in the profile in Z4 with respect to Z10. The latter accumulated OC in the first horizons (0–20 cm depth, data not shown), confirming the idea outlined in the previous point (OP accumulation in surface horizons of soil impacted).

The correlation coefficients between TP and OC% presented values of 0.88 for Z4 and 0.84 for Z10, in contrast to ZC, which was 0.59. This indicated that the organic matter which moved in the profile is rich in P, matching with manure composition (Damodar Reddy et al. 2000; Galvão and Salcedo 2009). Linear regression functions showed the quantity of input of TP for each unit of OC% provided with manure. The increase was 1635 and 1130 ppm per unit of OC% for Z4 and Z10 respectively, with an adjustment of 94 and 80 % in each case, meanwhile the slope for ZC was of 145 ppm ($R^2 > 0.74$).

Table 3 Means of pH and EC measured in field plots under study, and their correlations with P forms

Horizons	Depth (cm)	pH			EC (µS/cm)		
		Z4	Z10	ZC	Z4	Z10	ZC
A	0–30	6.5 ab	7.1 b	5.9 a	749 b	1032 b	262 a
E	30–40	6.8 a	7.6 a	6.5 a	548 b	991 b	209 a
2Bt1	40–90	7.6 ab	8.2 b	6.6 a	837 b	1407 b	430 a
2Bt2	90–150	7.9 ab	8.5 b	7.1 a	1173 b	1575 b	456 a

Different letters into each horizon indicates significant differences ($\alpha = 0.05$). Because the sampling depth at Z10 was 1 m, data shown in the table for the 2Bt2 horizon correspond to 90–100 cm thickness

PH and electrical conductivity and its relation to P transport

The mean values of pH can be seen in Table 3, together with the results of electrical conductivity (EC). In this table it shows that, except in the E Hz, the pH of Z10 differs significantly from ZC ($p < 0.05$), but not from Z4, indicating that recent application of manure generated an increase in soil pH. This behavior also was established by Nair and Graetz (2002) and Sharpley et al. (2004). Eghball (1999) and Graetz et al. (1999) informed that the increase was mainly due to salts of Ca and Mg provided in animals diets. At 0–90 cm deep, pH values did not affect the availability of nutrients for crops, but in Z10, at deeper horizon, P could precipitate like P-Ca forms, showing less availability. According to Hazelton and Murphy (2007), pH <5.5 and pH >8.5 are indicative of the decreasing availability of P, therefore, in this plots manured, the soil pH supports the idea of vertical migration to deeper horizons.

It is evident from Table 3 that the addition of large volumes of cattle manure increased salt content in whole profile in both plots studied, following the migration of P. Similar results were found by Eghball (2002) and Morari et al. (2008). An average increase of salinity of 257 and 345 % in Z4 and Z10 was found at the maximum depth sampled, in relation to ZC ($p < 0.05$). It may also notice that the salts have been washing over the years due to infiltration of rainwater, accumulating in the deeper layers (2Bt2 in Z4, and 2Bt1 and 2Bt2 in Z10). With reference to Z10 treatment, whose average salt content exceeds 1200 µS/cm throughout the soil profile, it can be seen that in the 0–90 cm deep of Z4 plot the average electrical conductivity (EC) fell below 800 µS cm^{-1} possibly due to salt leaching.

The results suggest that in Z10 plot there was a temporary change of category in the classification of agricultural land of “no saline” (<750 µS cm^{-1}) to “little saline” (750–2000 µS cm^{-1}) (FAO 2006), at the third year of manured. Is likely that if manure incorporated had an EC, e.g. 6500 µS cm^{-1} (Ciapparelli and García 2015), has been generated a higher salinization of soil in the first and second year (>2000 µS cm^{-1}), affecting the productivity of pastures and forage crops (FAO 2006). The same analysis can be made on Z4.

Salts which began to migrate on soil from the moment when the manure was applied on the surface of Z10, have reached the maximum sampled depth 3 years later, mobilizing therefore to a greater rate than total P, which only reached 60 cm depth. However, it may be necessary to deepen the soil sampling to find the saline front advance. It is also possible that the soil under study, poorly drained by clay content and E horizon of laminar structure, but generally well structured, with an average annual rainfall of nearly 1000 mm, and a water table fluctuating between 2 and 4 m, the salts have already reached subsurface water body.

While soil is considered as a buffer of water pollution (INTA 2010), the application of large volumes of solid manure saturated its capacity, may result in entry of various salts to the water system, including chlorides, potash, and especially nitrates, by the rate of mobilization that have as monovalent ions (García et al. 2013). P species mobilized below the sampled depth, together to the latter, could affect surface water courses, considering the zonal

Table 4 Empirical advance rate of Bray P (EARP) for the three plots under study: Z4, Z10 and ZC

Horizons (Hz)	Parameters	Treatment		
		Z4	Z10	ZC
A	Mean Bray P (ppm P-PO_4^{3-})	341.1	980.5	13.2
	Hz thickness (cm)	30	30	30
	EARP (ppm P-PO_4^{3-} cm^{-1})	11.37	32.68	0.44
E	Mean Bray P (ppm P-PO_4^{3-})	57.1	23.1	3.5
	Hz thickness (cm)	10	10	10
	EARP (ppm P-PO_4^{3-} cm^{-1})	5.71	2.31	0.35
2Bt1	Mean Bray P (ppm P-PO_4^{3-})	517.3	18.2	7.7
	Hz thickness (cm)	50	50	50
	EARP (ppm P-PO_4^{3-} cm^{-1})	10.35	0.36	0.15
2Bt2	Mean Bray P (ppm P-PO_4^{3-})	128.4	1.6	3.8
	Hz thickness (cm)	60	10	60
	EARP (ppm P-PO_4^{3-} cm^{-1})	2.14	0.16	0.06

hydrological network. In this way, it can be generated the acceleration and the imbalance of eutrophication process, which occurs and regulates naturally in aquatic systems.

Empirical advance rate of Bray P (EARP) in soil

The empirical advance rate of P (EARP) was calculated to assess how the nutrient has mobilized on the soil profile, considering the extractable P (Bray P) like one of the most indicative P fractions of the reactions that this nutrient suffer on soils. Table 4 shows that for A Hz, $EARP_{Z4}$ was 25.8 times and $EARP_{Z10}$ was 76 times higher than $EARP_{ZC}$ (0.44 ppm $P\text{-}PO_4^{3-}$ cm^{-1}). The latest application of manure (Z10) had higher potential contaminant in surface than Z4, because its advance rate was greater, although the same behavior could have been observed in Z4 soon after being manured. At the E Hz, $EARP_{Z4}$ and $EARP_{Z10}$ were 5.7 and 2.3 ppm $P\text{-}PO_4^{3-}$ cm^{-1}, respectively, while $EARP_{ZC}$ was 0.35 ppm $P\text{-}PO_4^{3-}$ cm^{-1}, showing the eluvial characteristics of this layer. At the followings layers, it can be seen that EARP for Z10 was reduced in 84 % in 2Bt1 horizon, and for Z4 in 80 % in 2Bt2 horizon. Phosphate adsorption to the surface of clays, amorphous Fe and Al oxides and carbonates (Pal 2011; Wyngaard et al. 2011) may have been contributing to reduce the empirical advance rate of Bray P in the soil profile. However, in deeper layers, $EARP_{Z4}$ and $EARP_{Z10}$ were upper than $EARP_{ZC}$, thus some P forms from the cattle manure may becoming a potential contaminant of underlying water bodies.

The traditional phosphorus conception that indicates the slow mobility of this nutrient on soils (Conti 2000) can be seen through EARP of control plot, in surface and subsurface layers. Although it was taken into account that not all the P provided by the manure entered the system, because of different types of losses as runoff, percolation, surface lateral movement and plant absorption, the quantification of this empirical rate enables to estimate the dimension that the downward movement of P can take, due to the application of high doses of beef cattle manure.

Conclusion

In this study, it was possible to observe an increase of TP, WEP and Bray P concentration in the soil profile with manure. This increase was higher in Z4 than Z10, in relation to ZC. Z4 generated a greater migration of P within the soil than Z10 despite the fact that the soil has the buffering capacity to reduce its concentration in deeper layers. For Bray P, the maximum depth sampled was not enough to find a value similar to ZC, for both plots manured. The vertical movement of labile P could have taken place when soil sorptive capacity was saturated with input of P and organic acids from manure.

Clayey horizons accumulated 37 times more Bray P and 50 times more WEP than upper layers for both Z4 and Z10. Also, it was found that in manured plots, the maximum organic carbon content in soil surface was 5.3 and 6.2 % in Z4 and Z10, different from ZC (2.7 %), and the organic matter moved in the profile is rich in P, matching with manure composition.

The pH of Z10 differed significantly from ZC, but not from Z4, indicating that recent application of manure generated an increase in soil pH. There was an increase of salt content in the whole profile in both plots studied (Z4 and Z10), following the migration of P. An average increase of salinity of 257 and 345 % in Z4 and Z10 was found at the maximum depth sampled, in relation to ZC.

The EARP was reduced in nearly 80 % at Bt Hz, because of phosphate adsorption to the surface of clays, amorphous Fe and Al oxides and carbonates. However, in deeper horizons, some P forms from cattle manure may become a potential contaminant of underlying water bodies.

References

Álvarez Benedí J, García Sinovas D, Muñoz Carpena R, Bolado S (2001) Aplicación de la técnica de interrupción de flujo al estudio del transporte de solutos en columnas de suelo. In: López Rodríguez JJ y Quemada Sáez Badillos M (eds) Temas de Investigación en Zona no Saturada (Vol. 5). Actas de las V Jornadas sobre Investigación de la Zona no Saturada del Suelo—ZNS'01.Universidad de Navarra. Pamplona, p 177

Barnett GM (1994) Phosphorus forms in animal manure. Bioresour Technol 49:139–147. doi:10.1016/0960-8524(94)90077-9

Beven K, Germann P (1982) Macropores and water flow in soils. Water Resour Res 18:1311–1325. doi:10.1029/WR018i005p01311

Blake GR, Hartge KH (1986) Bulk density. In: Klute A (ed) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI, pp 363–375

Bolster CH, Sistani KR (2009) Sorption of phosphorus from swine, dairy, and poultry manures. Commun Soil Sci Plant Anal 40:1106–1123. doi:10.1080/00103620902753822

Borda T, Celi L, Zavattaro L, Sacco D, Barberis E (2011) Effect of agronomic management on risk of suspended solids and phosphorus losses from soil to waters. J Soils Sediments 11:440–451. doi:10.1007/s11368-010-0327-y

Buol SW, Southard RJ, Graham RC, McDaniel PA (2011) Front matter, in soil genesis and classification, 6th edn. Wiley, Oxford. doi:10.1002/9780470960622.fmatter

Campbell LB, Racz GJ (1975) Organic and inorganic P content, movement and mineralization of P in soil beneath a feedlot. Can J Soil Sci 55:457–466. doi:10.4141/cjss75-052

Chardon WJ, Schoumans OF (2002) Solubilization of phosphorus: concepts and process description of chemical mechanisms. In: Chardon WJ, Schoumans OF (eds) Phosphorus losses from agricultural soils: processes at the field scale. COST Action 832. Alterra Wageningen, The Netherlands, pp 42–52

Ciapparelli IC, García AR (2015) Use of manure to wheat production in an Argentinean Hapludoll soil. J Pollut Eff Cont. doi:10.4172/2375-4397.1000131

Conti M (2000) Principios de edafología con énfasis en suelos argentinos. 2da ed. Editorial Facultad de Agronomía—Universidad de Buenos Aires. Buenos Aires, p 430

Damodar Reddy D, Subba Rao S, Rupa TR (2000) Effects of continuous use of cattle manure and fertilizer phosphorus on crop yields and soil organic phosphorus in a Vertisol. Bioresour Technol 75:113–118. doi:10.1016/S0960-8524(00)00050-X

Di Rienzo JA, Casanoves F, Balzarini MG, Gonzalez L, Tablada M, Robledo CW (2008) InfoStat, versión 2008. Grupo InfoStat, FCA, Universidad Nacional de Córdoba, Argentina

Djodjic F (2001) Displacement of phosphorus in structured soils. Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala. Acta Universitatis agriculturae Sueciae, Agraria 283. ISSN 1401-6249. ISBN 91-576-5826-9, p 30

Eghball B (1999) Liming effects of beef cattle feedlot manure or compost. Commun Soil Sci Plant Anal 30(19, 20):2563–2570. doi:10.1080/00103629909370396

Eghball B (2002) Waste management—soil properties as influenced by phosphorus- and nitrogen-based manure and compost applications. Agron J 94:128–135. doi:10.2134/agronj2002.0128

Eghball B (2003) Leaching of phosphorus fractions following manure or compost application. Commun Soil Sci Plant Anal 34(19, 20):2803–2815. doi:10.1081/CSS-120025207

Eghball B, Power JF (1994) Beef cattle feedlot manure management. J Soil Water Conserv 49:113–122

Eghball B, Ginting D, Gilleyet JE (2004) Residual effects of manure and compost applications on corn production and soil properties. Agron J 96:442–447. doi:10.2134/agronj2004.4420

Eichler-Löbermann B, Köhne S, Köppen D (2007) Effect of organic, inorganic, and combined organic and inorganic P fertilization on plant P uptake and soil P pools. J Plant Nutr Soil Sci 170:623–628. doi:10.1002/jpln.200620645

Elrashidi MA, Mays MD, Zimmer (2005) Changes in release characteristics and runoff phosphorus for soils amended with manure. Commun Soil Sci Plant Anal 36:1851–1873. doi:10.1081/CSS-200062472

EPA (Environmental Protection Agency) (1996) Acid digestion of sediments, sludges, and soils. Revision 2 [Online]. Available at https://www.epa.gov/sites/production/files/2015-06/documents/epa-3050b.pdf. Accessed 22 Mar 2016, USEPA, Cincinnati, OH

EPA (Environmental Protection Agency) (2000) Profile of the Agricultural Livestock Production Industry. EPA 310-R-00-002. USEPA, Washington DC, p 166

EPA (Environmental Protection Agency) (2003) National Pollutant discharge elimination system permit regulation and effluent limitation guidelines and standards for concentrated animal feeding operations (CAFOs). EPA HQ-OW-2002-0025-0058. USEPA, Washington DC, p 100

FAO (Food and Agriculture Organization) (2006) Evapotranspiración del cultivo. Guías para la determinación de los requerimientos de agua de los cultivos. Estudio FAO, Riego Y Drenaje. No. 56. Food and Agriculture Organization of the United Nations, Rome, p 299

FAO (Food and Agriculture Organization) (2009) Guía para la descripción de suelos, 4ta edn. Food and Agriculture Organization of the United Nations, Rome, p 110

Galvão SRDS, Salcedo IH (2009) Soil phosphorus fractions in sandy soils amended with cattle manure for long periods. R Bras Ci Solo 33:613–622. doi:10.1590/S0100-06832009000300014

García AR, Iorio AF (2003) Phosphorus distribution in sediments of Morales Stream (tributary of the Matanza-Riachuelo River, Argentina). The influence of organic point source contamination. Kluwer Hydrobiol 492:129–138. doi:10.1023/A:1024874030418

García AR, Maisonnave R, Massobrio M, de Iorio AF (2012) Field-scale evaluation of water fluxes and manure solution leaching in feedlot pen soils. J Environ Qual 41:1591–1599. doi:10.2134/jeq2011.0320

García AR, Fleite SN, Vázquez Pugliese D, de Iorio AF (2013) Feedlots and pollution—a growing threat to water resources of agro-production zone in Argentina. Environ Sci Technol 47:11932–11933. doi:10.1021/es4040683

Gee GW, Bauder JW (1986) Particle-size analysis. In: Klute A (ed) Methods of soil analysis: Part 1. 2nd edn. Agron Monogr 9. SSSA and ASA, Madison, WI, pp 383–411

Glæsner N, Donner E, Magid J, Rubæk GH, Zhang H, Lombi E (2012) Characterization of leached phosphorus from soil, manure, and manure-amended soil by physical and chemical fractionation and diffusive gradients in thin films (DGT). Environ Sci Technol 46:10564–10571. doi:10.1021/es301861a

Graetz DA, Nair VD, Portier KM, Voss RL (1999) Phosphorus accumulation in manure—impacted Spodosols of Florida. Agric Ecosyst Environ 75:31–40. doi:10.1016/S0167-8809(99)00070-5

Hazelton P, Murphy B (2007) Interpreting soil test results. What do all the numbers mean?, 2nd edn. CSIRO Publishing, Collinwood, p 160

INTA (Instituto Nacional de Tecnología Agropecuaria) (1980) Instituto de Suelo. Carta de suelo de la República Argentina. Hoja 3560-18-1 Marcos Paz. INTA-CIRN. Buenos Aires, Argentina

INTA (Instituto Nacional de Tecnología Agropecuaria) (2010) Guía de buenas prácticas para el manejo de nutrientes (N y P) en la Pampa Ondulada. Desarrollo de Índices de Riesgo de contaminación por N y P. Grupo Medio Ambiente. EEA INTA Pergamino, p 65

Kuo S (1996) Phosphorus. In: Sparks DL, Page AL, Helmke PA, Loeppert RH (eds) Methods of soil analysis: Part 3. Chemical methods, SSSA Book Ser. 5. SSSA, Madison, WI, pp 869–920

Miller JJ, Handerek BP, Beasley BW, Olson EC, Yanke LJ, Larney FJ, McAllister TA, Olson BM, Selinger LB, Chanasyk DS, Hasselback P (2004) Quantity and quality of runoff from a beef cattle feedlot in southern Alberta. J Environ Qual 33(3):1088–1097. doi:10.2134/jeq2004.1088

Morari F, Lugato E, Giardini L (2008) Olsen phosphorus, exchangeable cations and salinity in two long-term experiments of north-eastern Italy and assessment of soil quality evolution. Agric Ecosyst Environ 124:85–96. doi:10.1016/j.agee.2007.08.001

Murphy LJ, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27(3):31–36. doi:10.1016/S0003-2670(00)88444-5

Nair VD, Graetz DA (2002) Phosphorus saturation in spodosols impacted by manure. J Environ Qual 31:1279–1285. doi:10.2134/jeq2002.1279

Øgaard AF (1996) Effect of fresh and composted cattle manure on phosphate retention in soil. Acta Agric Scand Sect B Soil Plant Sci 46:98–105. doi:10.1080/09064719609413121

Page AL (1982) Method of soil analysis. Part 2: Agronomy Series Monograph No. 9. ASA, Soil Sci. Soc. Am., Inc. Madison, Wisconsin, USA

Pal SK (2011) Phosphorus sorption-desorption characteristics of soils under different land use patterns of eastern India. Arch Agron Soil Sci 57(4):365–376. doi:10.1080/03650341003605743

Sekhon BS (2002) Modeling of soil phosphorus sorption and control of phosphorus pollution with acid mine drainage floc. Dissertation submitted to the Davis College of Agriculture, Forestry, and Consumer Sciences at West Virginia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Plant and Soil Sciences, p 224

SERA-IEG 17 (Southern Extension/Research Activity—Information Exchange Group) (2000) Methods of phosphorus analysis for soils, sediments, residuals and waters. Southern Cooperative Series Bulletin No. 396, p 102

Sharpley AN, Sisak I (1997) Differential availability of manure and inorganic sources of phosphorus in soil. Soil Sci Soc Am J 61:1503–1508. doi:10.2136/sssaj1997.03615995006100050030x

Sharpley AN, McDowell RW, Kleinman PJA (2004) Amounts, forms and solubility of phosphorus in soils receiving manure. Soil Sci Soc Am J 68:2048–2057. doi:10.2136/sssaj2004.2048

Uyanöz R, Çetin Ü, Karaarslan E (2006) Effect of organic materials on yield and nutrient accumulation of wheat. J Plant Nutr 29:959–974. doi:10.1080/01904160600651787

Whalen JK, Chang C (2001) Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. J Environ Qual 30:229–237. doi:10.2134/jeq2001.301229x

Wyngaard N, Picone L, Videla C, Zamuner E, Maceira N (2011) Impact of feedlot on soil phosphorus concentration. J Environ Prot 2:280–286. doi:10.4236/jep.2011.23031