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ORIGINAL ARTICLE

Phosphorus release kinetics in a soil amended with biosolids and vermicompost

M. Islas-Espinoza · L. Solís-Mejía · M. V. Esteller

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Abstract Wastewater biosolids are large potential sources of macronutrients for agriculture, conservation and restoration of soils; there are, however, few studies on phosphorus (P) release in soils amended with biosolids. Biosolids and vermicomposted biosolids were tested in concentrations (5–30 g amendment kg^{-1} soil) equivalent to 18–100 Mg ha^{-1}. Desorption of P was determined by successive extractions for 65 days. Soil P was low, and biosolid and vermicompost addition released 8 and 6 times more P, respectively, than soil alone. To describe the release of P, zero-, first- and second-order equations, simple Elovich and power functions and the parabolic diffusion law were compared based on their coefficient of determination (r^2) and standard error (SE). In all treatments, the power function and especially the parabolic diffusion law were the best fit, with 0.898–0.996 r^2 and 0.022–0.732 SE. The general behavior of the kinetic parameters mostly depended on the amendment doses. Eutrophication posited to start beyond 16 mg P kg^{-1} soil was more likely allayed by a maximum vermicompost dose of 50 Mg ha^{-1}, higher than the 36 Mg ha^{-1} maximum biosolid dose. The higher vermicompost P addition and lower P release could favor gradual and longer-term P absorption by plants and may reduce leaching or runoff P losses.

Keywords Phosphorus · Biosolids · Vermicompost · Release kinetics · Soil

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M. Islas-Espinoza (✉) · L. Solís-Mejía · M. V. Esteller
Centro Interamericano de Recursos del Agua (CIRA),
Universidad Autónoma del Estado de México,
Cerro Coatepec, s/n, C.U., 50130 Toluca, Mexico
e-mail: marinaislas@ymail.com

Introduction

Wastewater treatments produce biosolids (microbially digested sludge) which, under certain conditions, can add organic matter to soils (Franco-Hernández et al. 2003; Rostagno and Sosebee 2001), as well as P and other macro and micronutrients (Maguire et al. 2001; Solís-Mejía et al. 2012). Bioavailability of these nutrients to plants usually occurs through mineralization of organic matter present in biosolids, a process facilitated and accelerated by earthworms (Cardoso-Vigueros and Ramírez-Camperos 2002). The earthworms' metabolism and interaction with microorganisms convert organic waste into humus and other nutrients that induce plant growth (Capistrán et al. 2004).

As the application rate of biosolids on agricultural land is often based on nitrogen content, the significant amounts of P in biosolids (Korboulewsky et al. 2002; Penn and Sims 2002) can exceed the needs of plants and soil microorganisms; water runoff or infiltration can cause eutrophication of surface water and groundwater pollution (Esteller et al. 2009; Penn and Sims 2002; Shober and Sims 2003).

In soil amended with animal manure and sewage sludge, P release can be described by a power function (Siddique and Robinson 2004). P release kinetics in calcareous soils, amended and unamended with sewage sludge, fit first-order, Elovich, power and parabolic diffusion equations adequately (Hosseinpur and Pashamokhtari 2008). In other calcareous soils, amended with composted manure and pistachio, P release kinetics is best described by Elovich and power functions (Fekri et al. 2011).

However, no reports have yet described P release in waste-amended sandy clay loam soils. Tropical soils subject to heavy seasonal rains have seldom been studied

(Quesada et al. 2011; Schad et al. 2001). Mexican sandy clay loam soils (Améndola et al. 2005) are often in intensive agriculture and P-deficient. This type of soil has high porosity and favors water infiltration, which facilitates penetration by plant roots (FAO 2006) but also could promote P lixiviation if excess nutrients are supplied. Accordingly, the objectives of this research were firstly to measure P release in a sandy clay loam soil at different doses of organic waste amendment (biosolid and vermicomposted biosolid); and secondly, to compare different P release kinetics models in the treatments and soil control.

Methods

Soil sampling and analysis

Eight samples were collected randomly from the Ap horizon (0–30 cm) of agricultural land in Xonacatlán (19°24′N, 99°32′W, State of Mexico, Mexico). Samples of 1.5 kg each, were mixed in a composite sample subsequently air dried and sieved (<2 mm). Particle size was determined (Bouyoucos 1962), as well as bulk density (Jaramillo 2002), electrical conductivity in a 1:2 soil: water suspension with a conductivity meter (Rhoades 1996) and pH in the same suspension with a potentiometer (Thomas 1996). Also analyzed were available phosphorus (Olsen and Sommers 1982), organic matter content by the wet oxidation method (Primo and Carrasco 1987), total organic carbon, total Kjeldahl nitrogen (Cardoso-Vigueros and Ramírez-Camperos 2002). Available nitrogen was extracted with KCl (Mariani et al. 2007; Siddique and Robinson 2004) and cation exchange capacity with $BaCl_2$-triethanolamine (Primo and Carrasco 1987). The same techniques to determine cation exchange capacity, C, P, and N were used in soil, biosolids and vermicompost.

Biosolids sampling and analysis

Biosolids were obtained from the North Toluca domestic wastewater treatment plant (Mexico State). The sludge is produced during wastewater treatment consisting of thickening, aerobic digestion and drying on filters (Gobierno del Estado de México 1996). Three 20-kg samples of biosolids were collected in 1 day, from which two 1-kg subsamples were mixed in a composite sample which was air dried, sieved (<2 mm) and analyzed for physicochemical characteristics. The pH was measured in a 1:5 water: biosolid solution, as was electrical conductivity (NMX-FF-109-SCFI-2007). The organic matter was estimated by ignition and total organic carbon was obtained assuming that the organic C corresponds to 58 % of the total organic matter (Primo and Carrasco 1987).

Vermicompost processing, sampling and analysis

The biosolid previously described was also used as vermicompost substrate. However, fresh biosolid as the sole substrate for the earthworm *Eisenia fetida* led to high earthworm mortality, possibly due to the presence of heavy metals in the domestic wastewater, as well as possible excess moisture (Dayananda et al. 2008; Mahimairaja 2000). Metal concentrations in biosolids from the wastewater treatment plant under study were 1,656 and 247 mg kg^{-1} (Zn and Cu, respectively, Gomez-Beltran 2009) which were 62 and 110 % of earthworm median lethal concentration (LC_{50}); furthermore, these concentrations did not take into account synergistic lethal effects among these and other, less concentrated metals (Song et al. 2002). A 90:10 biosolid: composted manure mixture in three containers allowing for leachate evacuation ensured earthworm survival (Solís-Mejía et al. 2012). The amount of substrate in each container was approximately 0.8 kg dry matter. During vermicomposting, moisture was monitored with a soil hydrometer and kept between 70 and 80 % (Cardoso-Vigueros and Ramírez-Camperos 2002) by adding distilled water. Temperature was kept at 15 ± 2 °C.

Vermicomposting consisted in adding 50 adult earthworms in each container (Contreras-Ramos et al. 2005; Natchimuthu and Thilagavathy 2009), equivalent to 40 g of earthworm biomass. Vermicomposting went on for 2 months. A sample of approximately 200 g from each container was mixed to form a composite sample, which was air dried, ground and sieved (<2 mm). Additional details on the vermicompost are provided elsewhere (Solís-Mejía et al. 2012).

P release kinetics

The fresh biosolid was mixed with 100 g of soil in proportions equivalent to 0 (control), 18, 36, 50, 80 and 100 Mg ha^{-1} biosolid, considering 30-cm-thick topsoil and 1.1 g cm^{-3} soil bulk density. The same procedure was carried out with vermicompost. The mixtures were incubated at 29 ± 2 °C for 10 days and moisture content was maintained at 100 % of the field capacity (Siddique and Robinson 2004). At the end of incubation, the mixtures were dried at room temperature (Vaca-Paulín et al. 2006). The samples were subjected to a successive extraction process using 0.01 M KCl solution (Lair et al. 2009) for which three 5-g replicates were added 25 mL of KCl solution and agitated for 1 h on an orbital shaker at 180 rpm and then placed in an incubator at 25 ± 1 °C.

After 23 h, the samples were removed from the incubator, stirred for 1 h and centrifuged for 15 min at 3,000 rpm (Shariatmadari et al. 2006) to precipitate the solid part of the sample and so avoid particles in the subsequent colorimetry analysis. The supernatants were decanted and filtered using Whatman filter paper No. 42, and P was analyzed by colorimetry (Murphy and Riley 1962). The centrifuged and filtered samples were again added 25 mL of 0.01 M KCl solution and placed in the incubator for the following extractions after 2, 4, 7, 11, 15, 20, 25, 30, 37, 44, 51, 58 and 65 days (Hosseinpur and Pashamokhtari 2008).

Data analysis

The concentration of P (mean of triplicates) was plotted against time. The P release kinetics were fitted using zero-, first- and second-order equations, the simple Elovich function, the power function and the parabolic diffusion law (Table 1). Curve fitting used Microsoft Excel 2007 and linear regressions used SPSS version 19. The resulting equations were compared based on r^2 and standard errors of the estimates $\mathrm{SE} = \left[\left(\Sigma(P_t - P_0)^2\right)/(n-2)\right]^{1/2}$, where P_t and P_0 are the measured and calculated quantities of P released at time t, respectively, and n is the number of measurements (Wayne 1989).

The interpretation of the kinetic parameters is as follows. In the simple Elovich model an increasing α and decreasing β indicate an increase in desorption rate. The same applies to an increasing and decreasing b in the power function whereby higher doses lead to faster P desorption (Fekri et al. 2011); a stands for extracted P and b for the rate of extraction (Siddique and Robinson 2004). Others have similarly interpreted P release as a function of P concentration and availability (McDowell and Sharpley 2003). It must be noticed that no systematic attempt has been made in the P release kinetics literature to interpret the parameters or their simultaneous behavior.

Results

Physicochemical characteristics of soil, biosolids and vermicompost

The soil was classified as sandy clay loam (ESM Table S1) and bulk density was 1.1 g cm^{-3}, a value used to calculate the amendment doses. Soil pH was acidic. The values of organic matter, total organic carbon, total P, available P, electrical conductivity, and cation exchange capacity were vermicompost > biosolids > soil, whereas soil had higher acidity and available N (ESM Table S1).

P addition and release

The soil amendments had 27 and 31 times more available P than the soil (vermicompost and biosolids, respectively, ESM Table S1). Once mixed with soil, available P augmented from 74.8 mg P kg^{-1} soil to up to 144 mg P kg^{-1} amended soil (ESM Table S1 and 2). In turn, the addition of biosolid and vermicompost increased P release between 8 and 6 times, respectively. Release presented different empirical patterns: low doses and vermicompost were more linear, denoting a gradual release while concentrations increased dramatically for high doses of biosolids and tended to plateau after 1,000 h and up until day 65 (Fig. 1). These patterns indicated that P release responded to the amount of P added and to amendment type.

In this fast desorbing period (within 360 h or 15 days) P release ranged between 44 and 62 % responding to biosolid dose (Fig. 1a). In a quite different fashion, release oscillated without a clear trend between 46 and 45 % without clear influence of vermicompost doses (Fig. 1b); this was a lower release than both biosolid and soil alone (49 % in the latter).

The amount of P released after 1,560 h (65 days) in the soil control was 5.17 mg kg^{-1}, as compared to 10.47–39.66 mg kg^{-1} at doses of 18–100 Mg ha^{-1} in biosolid-amended soil (Fig. 2). In vermicompost-amended

Table 1 Equations used to describe the P release kinetics (Fekri et al. 2011; Hosseinpur and Pashamokhtari 2008; Shariatmadari et al. 2006)

Model	Kinetic equation	Parameters
Zero order	$P_o - P_t = a - k_o t$	a: initial desorption rate constant (mg P kg^{-1} h^{-1}) k_o: zero-order rate constant (h^{-1})
First order	$\ln P_t = \ln P_o - k_1 t$	k_1: first-order rate constant (h^{-1})
Second order	$1/P_t = 1/P_o + k_2$	k_2: second-order rate constant [(mg P kg^{-1})$^{-1}$]
Simple Elovich	$P_t = 1/\beta \ln(\alpha\beta) + (1/\beta) \ln t$	α: initial desorption rate (mg P kg^{-1} h^{-1}) β: desorption constant [(mg P kg^{-1})$^{-1}$]
Power function	$\ln P_t = \ln a + b \ln t$	a: initial desorption rate constant (mg P kg^{-1} h^{-1}) b: desorption rate coefficient [(mg P kg^{-1})$^{-1}$]
Parabolic diffusion	$P_t/P_o = c + r t^{0.5}$	r: diffusion rate constant [(mg P kg^{-1})$^{-0.5}$] c: P_t/P_0 when $r = 0$ or $t = 0$ (dimensionless)

P_o: P amount (mg P kg^{-1}) which can be released at equilibrium

P_t: P amount (mg P kg^{-1}) released over time t (h)

Table 2 Available P added to the sandy clay loam soil depending on the amendment doses

Amendment dose (Mg ha^{-1} equivalent)	Amendment concentration (mg amendment kg^{-1} soil)	P added by biosolid (mg P kg^{-1} soil)	P added by vermicompost (mg P kg^{-1} soil)
0*	0	0	0
18	5454.5	10.88	12.75
36	10909.0	21.76	25.09
50	15151.5	30.21	34.84
80	24242.4	48.36	55.75
100	30303.0	60.45	69.69

* Soil control

Table 3 Goodness-of-fit and parameter estimates for P release kinetics fitted to the desorption data, depending on amendment doses and soil improvers, simple Elovich model

Dose (Mg ha^{-1})	Amendment	Goodness-of-fit		Equation parameter estimates	
		Simple Elovich		Simple Elovich	
		r^2	SE	α	$1/\beta$
0	Soil control	0.933	0.086	0.0081	0.237
18	Biosolid	0.903	0.096	0.0101	0.344
	Vermicompost	0.914	0.145	0.0101	0.344
36	Biosolid	0.897	0.195	0.0113	0.366
	Vermicompost	0.911	0.156	0.0113	0.366
50	Biosolid	0.944	0.246	0.0123	0.537
	Vermicompost	0.929	0.203	0.0123	0.537
80	Biosolid	0.937	0.415	0.0241	1.047
	Vermicompost	0.930	0.393	0.0246	1.047
100	Biosolid	0.953*	0.512	0.0295	1.387
	Vermicompost	0.899	0.635	0.0295	0.387

* $r^2 > 0.95$

P_o: P amount (mg P kg^{-1}) which can be released at equilibrium

P_t: P amount (mg P kg^{-1}) released over a time t (h)

soil, final P release was 7.55–30.79 mg kg^{-1}, 15–43 % lower than in biosolids (Fig. 2) even though P added by biosolids was 15 % lower (Table 2).

P dose should be lower than 16 mg kg^{-1} to prevent eutrophication and so the maximum P amendment dose should be 36 Mg biosolid-amendment ha^{-1}, or 50 Mg vermicompost-amendment ha^{-1} in which case the 14.27 mg kg^{-1} P release would still be lower than the limit.

Kinetic models

P release could not be fitted by zero-, first- or second-order models: their lack of goodness-of-fit was due to non-linearity at short contact times. Conversely, the simple Elovich model adequately showed a linear relationship between P_t (P concentration at a given time t) and ln t at 100 Mg ha^{-1} biosolid amendment (Table 3). In the power function ln P and ln t were linearly related in all treatments except 100 Mg biosolids ha^{-1} (this treatment had the second lowest r^2 and highest SE, and its $1/\beta$ parameter is an outlier in the upward trend of this parameter as doses augment). Finally, the parabolic diffusion law was the best fit considering all treatments (all $r^2 > 0.95$). The parameter r (diffusion rate constant) was higher as amendment dose increased. This is consistent with Fig. 2, which shows that higher amendment doses lead to higher final concentration of desorbed P.

From the three most adequate models, β, b and r from the simple Elovich, power and parabolic models, respectively, depend on the P concentration only. α and a, from the simple Elovich and power models depend on both P concentration and time (Table 1). The general behavior of the kinetic parameters mostly responded to amendment: release parameters were higher at higher doses, and soil practically always had the lowest parameters. The simple Elovich and power models behaved as expected: a larger initial desorption rate and lower desorption constant

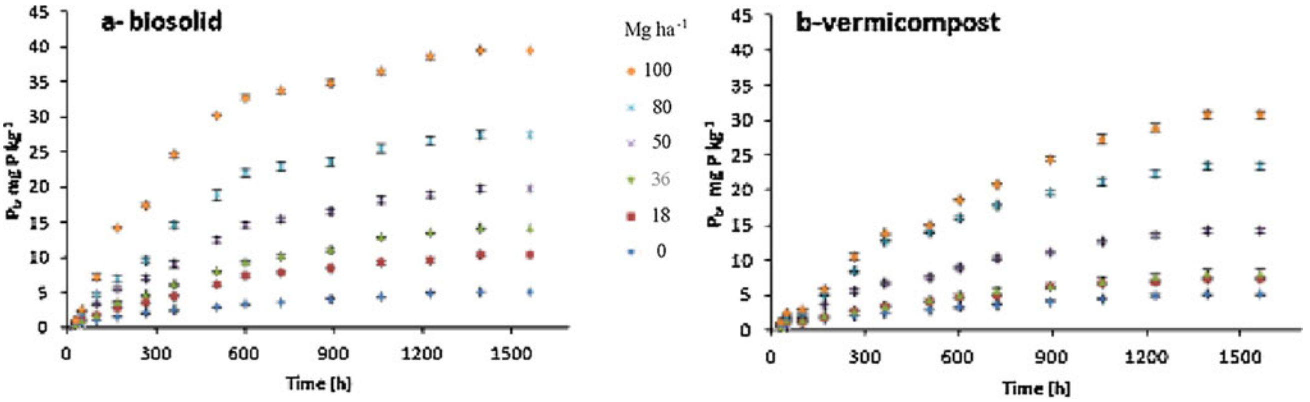


Fig. 1 Cumulative desorbed P over time in soil amended with biosolid (**a**) and soil amended with vermicompost (**b**). Confidence intervals are ± 1 standard error around the mean

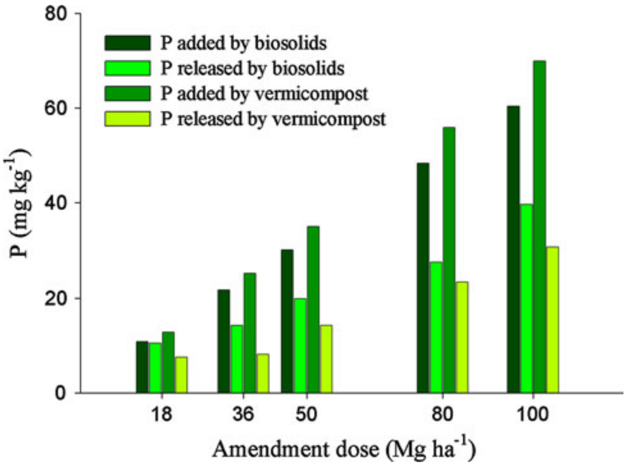


Fig. 2 Added P and final P release (after 65 days), in soils amended with biosolids and vermicompost. Eutrophication is likely above 16 mg P kg^{-1} (Hosseinpur and Pashamokhtari 2008) and would affect surface water and groundwater (Brenton et al. 2007; Korboulewsky et al. 2002)

augmented release; release also augmented with a higher amendment dose. However, even the parameters expressed in the same units did not yield similar values from one model to the other.

In the simple Elovich, α and β could be predicted from one another and responded directly to higher doses in biosolids; neither patterns were observed in vermicompost, though. At all doses but the highest, both amendments showed virtually the same α and β, highlighting the importance of dose over amendment in this case (Table 3).

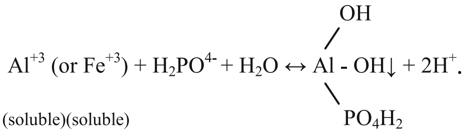
In the power function (Table 4; Fig. 3), the parameters were not predictable from either doses or amendment: release augmented at higher doses, but not as predictably as in the simple Elovich model; also, the parameters of the amendments did not resemble each other (suggesting a model sensitive to amendments and doses). Again, biosolids a and b were somewhat predictable from one another (except at the lowest dose), and in this model, a and b could predict each other well in vermicompost.

In the parabolic diffusion model, the release parameters were predictable from each other in vermicompost, not in biosolids. Parameter c is the value of the ratio comparing P release concentration by time t and final (equilibrium) P release concentration, when the diffusion rate $r = 0$ or $t = 0$; c clearly depended on dose in vermicompost and biosolid (except at the latter's highest dose); r directly responded to dose in both amendments, and vermicompost higher doses augmented P release.

Discussion

Physicochemical characteristics of soil, biosolids and vermicompost

The P system is conditioned by pH and the presence of Ca, Al and Fe, according to the following equation (Navarro and Navarro 2003):



$$\underset{\text{(soluble)}}{\mathrm{Al^{+3}}\ (\text{or } \mathrm{Fe^{+3}})} + \underset{\text{(soluble)}}{\mathrm{H_2PO^{4-}}} + \mathrm{H_2O} \leftrightarrow \underset{\qquad \mathrm{PO_4H_2}}{\overset{\qquad \mathrm{OH}}{\mathrm{Al}}}\text{ - }\mathrm{OH}{\downarrow} + 2\mathrm{H^{+}}.$$

Calcium content was 0.43 % (low as per Navarro and Navarro 2003) and would not interact with P at the acid soil pH (4.62) found here (Fekri et al. 2011). P bound to Al and

Table 4 Goodness-of-fit and parameter estimates for P release kinetics fitted to the desorption data, depending on amendment doses, amendment and fitted function

Dose (Mg ha^{-1})	Amendment	Goodness-of-fit				Equation parameter estimates			
		Power function		Parabolic diffusion		Power function		Parabolic diffusion	
		r^2	SE	r^2	SE	a	B	c	r
0	Soil control	0.996*	0.052	0.996*	0.022	0.0160	0.5790	0.0414	0.0288
18	Biosolid	0.981*	0.157	0.985*	0.092	0.0022	0.8360	0.1961	0.0622
	Vermicompost	0.985*	0.077	0.991*	0.048	0.0171	0.6208	0.1263	0.0435
36	Biosolid	0.968*	0.258	0.990*	0.103	0.0010	1.0480	0.3824	0.0873
	Vermicompost	0.983*	0.154	0.993*	0.046	0.0209	0.5995	0.1267	0.0460
50	Biosolid	0.942	0.316	0.979*	0.207	0.0039	0.9429	0.4078	0.1212
	Vermicompost	0.980*	0.147	0.990*	0.102	0.0099	0.7535	0.2951	0.0825
80	Biosolid	0.954*	0.258	0.959*	0.414	0.0106	0.8647	0.5112	0.1704
	Vermicompost	0.963*	0.261	0.977*	0.264	0.0076	0.8946	0.5725	0.1458
100	Biosolid	0.898	0.450	0.995*	0.732	0.0182	0.8561	0.3474	0.2384
	Vermicompost	0.980*	0.185	0.986*	0.265	0.0103	0.8831	0.9776	0.1918

* $r^2 > 0.95$

P_o: P amount (mg P kg^{-1}) which can be released at equilibrium

P_t: P amount (mg P kg^{-1}) released over a time t (h)

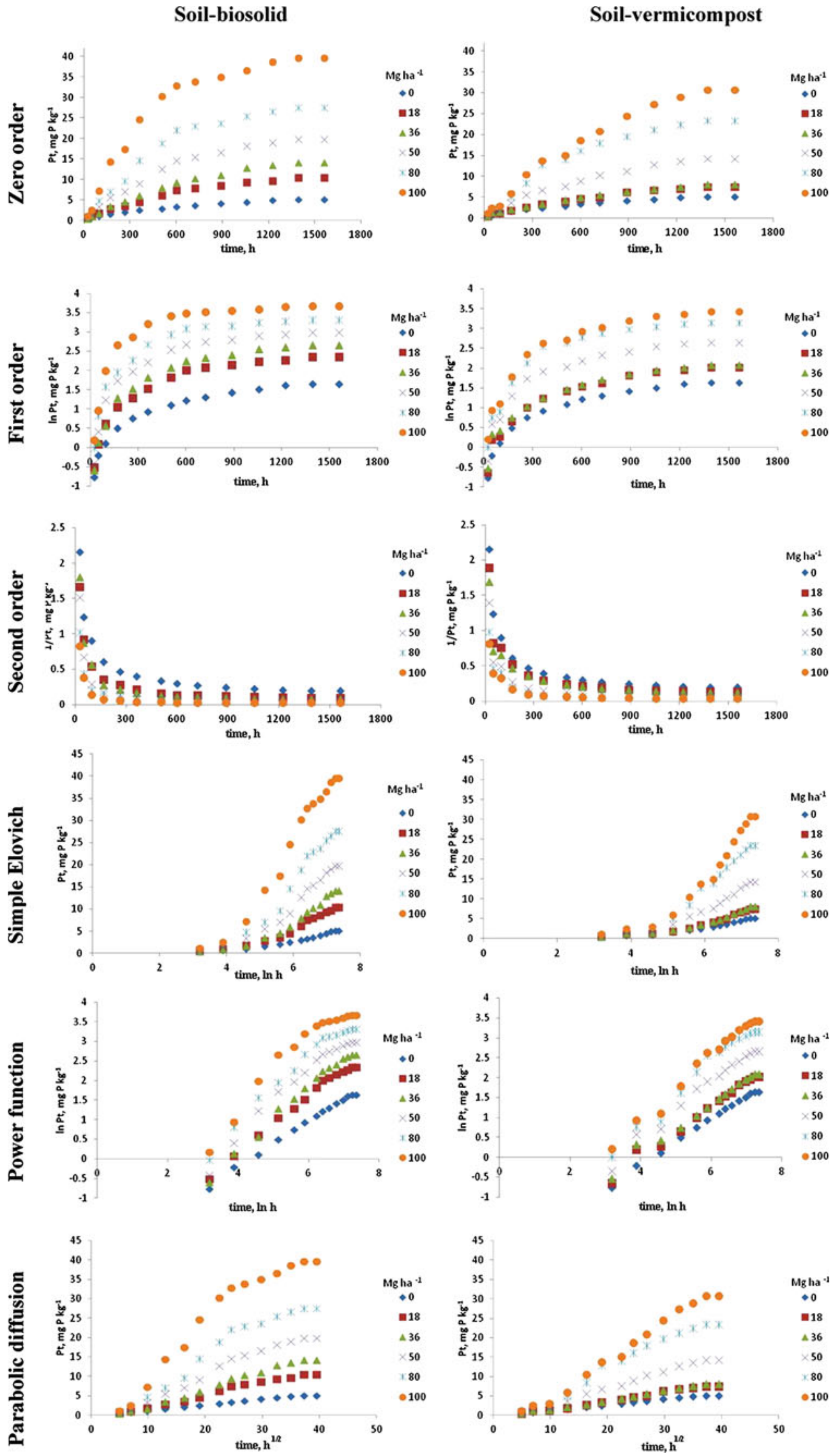


Fig. 3 P release data fitted to the different kinetic models

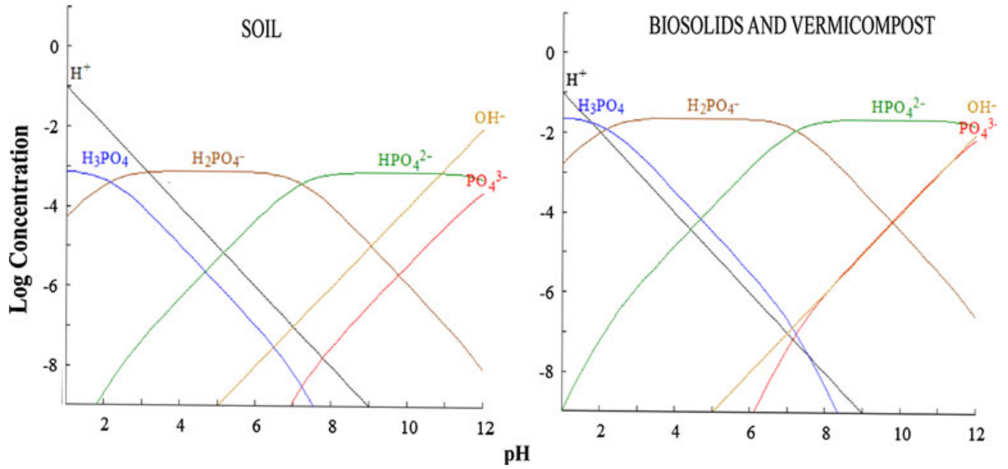


Fig. 4 MEDUSA existence-predominance diagram for P species (ionic strength 0.01 M KCl, 25 °C). In soil, a pH of 4.6 pointed to a $H_2PO_4^-$ predominance and presence of HPO_4^{2-}. In slightly acidic soils, the predominant solubilized species is H_2PO^{4-} (Soinne 2009). In biosolids and vermicompost, $H_2PO_4^-$ still predominated but HPO_4^{2-} increased noticeably

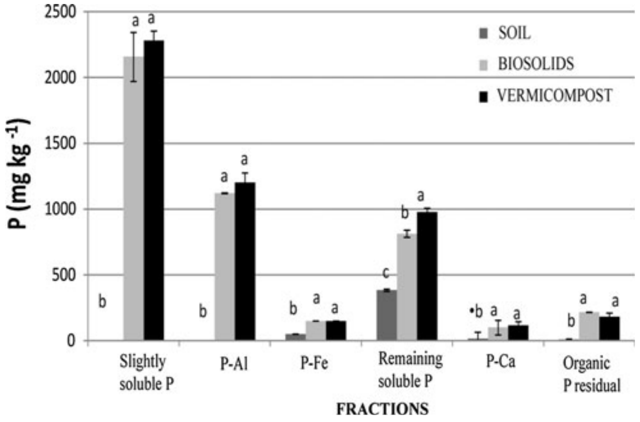


Fig. 5 Fractionation of P inorganic (mg kg^{-1}) in soil, biosolid and vermicompost. *Different letters* indicate significant statistical differences ($p < 0.05$). *Error bars* refer to one standard deviation of the mean

Fe were significantly higher in amendments than soil; these fractions augment P retention (Lu and O'Connor 2001; Maguire et al. 2001).

Phosphate precipitates in soil were expected from low pH and Fe and Al ions (Fig. 4). Inorganic phosphates are suggested to respond to meteorization and soil maturation: in mature soils–such as the sandy clay loam soil studied here–the occluded phosphates (i.e. the Remaining soluble P fraction) predominate (Fassbender and Bornemisza 1987). Occluded soils have a very limited solubility and P is seldom available to plants. As to the slightly soluble P fraction, it was absent in the soil but dominant in biosolids and vermicompost (47.35 and 46.46 %, respectively, (Fig. 5). The slightly soluble fraction was a likely factor in P release.

P is a scarce resource in the lithosphere but a pollutant in the hydrosphere (Elser and Bennett 2011). The treatments proposed here are geared toward reaching a balance by recirculating hydrosphere P into the soils, especially where available P is a plant growth limiting factor. Available P: available N ratios in biosolid and vermicompost were, respectively, 12,000 and 1,000. The accepted explanation is that in Mexico as in other developing countries discharges of phosphates from detergents ending up in sewage sludge are very high (de Haan 1981; Vaca-Paulín et al. 2011). Additionally, Fe and Al salts are used as coagulants in wastewater treatments which cause P to end up in biosolids (Coker and Carlton-Smith 1986; Lee and Lin 2007); this was in particular the case in the wastewater treatment plant under study.

Available P: total P ratios were on average 0.44 and 0.47 in biosolid and vermicompost, respectively. These were values almost thrice that of soil available P because detergents are a source of inorganic P in biosolids and vermicomposted biosolids (Fassbender and Bornemisza 1987). Despite this mineral form of P, the vermicompost managed to increase slightly the available P content, possibly derived from earthworm intestinal transit which helps desorb P from the solid phase material (Jimenez et al. 2003) and bacterial phosphatase activity in vermicompost which largely enhances P mineralization (Garg et al. 2006). However, available P was not significantly different in biosolid and vermicompost, due to very variable domestic detergent discharges as shown in the high standard error of available P in biosolid.

The higher available P content in vermicompost was consistent with other reports (Buchanan et al. 1988; Garg et al. 2006). It can be attributed to mineralization by earthworm digestion and its accompanying microorganisms (Capistrán et al. 2004; Liu et al. 2005).

P addition and release

This P release assessment used a sandy clay loam soil with Al and Fe interactions (Islas-Espinoza et al. 2013). The biosolid under study also included Fe or Al salts added during wastewater treatment to remove soluble P. This could have lowered P solubility in the treatments, given the formation of sparingly soluble Al–P and Fe–P forms, particularly when applied to acidic soils in tropical or highly weathered soils (Sims and Pierzynski 2005).

Even so, P release with amendments was 6–8 times that of soil alone, similar to a 7.5 times amendment with biosolids with relatively high P (Hosseinpur and Pashamokhtari 2008) which can be found in organic molecules such as nucleic acids, lipids and inositol polyphosphates (Siddique and Robinson 2003). P release reached 62 % on day 15 (biosolid amendment) similar to 73 % on day 15 with 100 Mg ha^{-1} biosolid amendment (Hosseinpur and Pashamokhtari 2008 in calcareous soil).

However, the soil amended with biosolids released more P at a higher rate than vermicompost amendment, even though biosolids added less P than vermicompost (Figs. 1, 3). This is consistent with biosolid P released more readily (Capistrán et al. 2004), which could impair water quality (Penn and Sims 2002), particularly beyond 16 mg P kg^{-1} soil (Hosseinpur and Pashamokhtari 2008). The slow P release with vermicompost amendment may help prevent erosion washing or leaching losses of this nutrient.

The probable reasons for slower P release in vermicompost amendment were threefold. Firstly, it might be attributable to earthworm casts that retain their porosity and structure and contain more water-stable aggregates than surrounding soil, probably due to polysaccharide gums produced by earthworm intestinal bacteria and proliferation of fungal hyphae on the surface of casts. Secondly, phosphatases are produced in the gut of earthworms in response to a need for P by microorganisms suggesting a P release partly regulated by enzymatic processes (Capistrán et al. 2004; Edwards and Arancon 2005; Tate 1985). Thirdly, vermicompost-amended soils contain more organic matter which enhance nutrient retention, as well as humic acids, fulvic acids and humans which regulate the release of nutrients (Heal et al. 1997; Arancon et al. 2006).

To the best of our knowledge there are no similar studies on P release in soils amended with vermicomposted biosolids. However, by way of comparison, P release in temperate soils (UK and New Zealand, McDowell and Sharpley 2003) was 9–55 times faster after 33 days (despite similar available P) than in the soil amended with biosolid and vermicomposted biosolid studied here. However, P release in (semi)arid soils and biosolid-amended soils at 100 Mg ha^{-1} doses (Iran, Hosseinpur and Pashamokhtari 2008) were of the same order of magnitude as that resulting from the 36–50 Mg ha^{-1} maximum doses recommended here (despite lower available P). As to the maximum recommended 36 Mg biosolid amendment ha^{-1} (d/w) dose, it fell within the 30–60 Mg ha^{-1} range applied in an uncharacterized temperate soil (Spain, Carbonell et al. 2009). The recommendation was low enough to comply with for instance, the French biosolid authorized limit of 30 Mg ha^{-1} (10 year)$^{-1}$ (d/w) (Maisonnave et al. 2002). As to the maximum recommended 50 Mg vermicomposted biosolid ha^{-1} (d/w) dose, it was higher than applications which achieved similar P releases with lower amendment doses: 5 Mg sugar mill vermicompost ha^{-1} clay loam and sandy loam soil (India, Manivannan et al. 2009) and 15 Mg sheep manure vermicompost ha^{-1} loamy soil (Iran, Azarmi et al. 2008). Similar P releases with 3–10 times lower doses could again be attributable to lower P solubility in the biosolid and soil under study due to reactions with Al and Fe.

A cautionary note is warranted with regard to the laboratory P extraction procedures used here and their difference with leachability on the field. The latter is likely to be controlled by soil: water ratio, rate of infiltration, in situ pH, and generally invoked factors influencing P desorption in soils, including mineralogy, crystallinity, particle size of the mineral, as well as clay, Al, Fe, carbonate and organic matter contents, and soil solution chemistry (pH, ionic strength, competing anions, oxidation–reduction status, P species) (Hosseinpur and Pashamokhtari 2008; Sims and Pierzynski 2005).

Kinetic models

The zero-, first- and second-order models were not adapted to the P release kinetics in the amended soil. Some such models are suggested to follow at least two first-order kinetics (Shariatmadari et al. 2006 in calcareous soils). In turn, the Elovich simple model (Steffens 1994, in Alfisols with organic fertilizers) and the power equation (McDowell and Sharpley 2003) have been reported as best describing P release. The results here coincided with the simple Elovich, power function and parabolic diffusion as best P release models (Shariatmadari et al. 2006) and especially with the parabolic diffusion law as the best fit (Hosseinpur and Pashamokhtari 2008; Shariatmadari et al. 2006).

The simple Elovich and power models behaved as expected: a larger initial desorption rate and lower desorption constant augmented release (Fekri et al. 2011) as amendment dose increased (McDowell and Sharpley 2003). The parabolic diffusion was not expressed in the same manner by all authors cited in Table 1 and this study followed Hosseinpur and Pashamokhtari (2008).

Often the initial fast desorption phase involves labile P, P bound to reactive surfaces in the aqueous phase, soluble P from recent amendment, physically adsorbed orthophosphate, and P complexed by organic matter. Initially rapid reactions correspond to dissolution of poorly

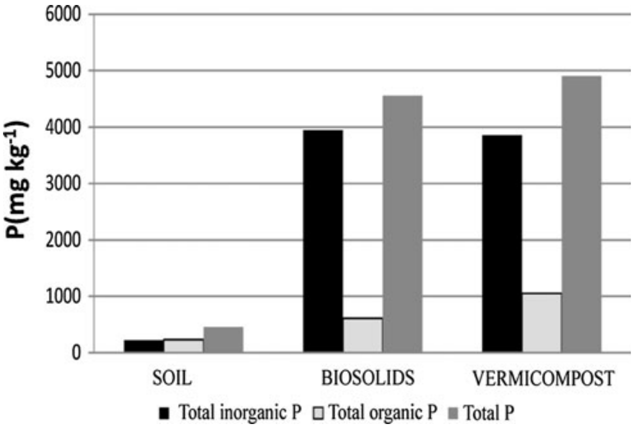


Fig. 6 Organic, inorganic and total P (mg kg^{-1}) in soil, biosolid and vermicompost

crystalline or amorphous phosphates. Less mobile fractions are proportional to the number of sites occupied by phosphate. Later on, slow P release most likely originates from diffusion from interior sites inside soil solid phases, aggregates or slow dissolution of amorphous or crystalline solid phases of P. The gradual reduction in P release rate over time may result from decreasing surface charge and decreasingly interacting adsorbed phosphorus ions (Fekri et al. 2011; Siddique and Robinson 2004; Sims and Pierzynski 2005).

Kinetics are relevant for plant nutrition. Inorganic orthophosphates $H_2PO_4^-$ and HPO_4^{2-} probably dominated P forms as a result of low soil pH (Fig. 4); these inorganic orthophosphates are almost exclusively the P form absorbed by plants, however, they have to be replenished and easily released (Mozaffari and Sims 1994). More generally, inorganic (more available) P largely dominated the amendments (Fig. 6). In other biosolid-amended soils, inorganic forms also predominate (Su et al. 2007). The slightly soluble P, P–Al and P–Fe fractions of inorganic P were considerably increased in the amendments (Fig. 5). While slightly soluble P is the most available to plants (Boschetti et al. 2003; Chang et al. 1983), P–Al and P–Fe could be responsible for P retention in amended soil, similar to other conclusions that Al and Fe compounds slow down P release (Lu and O'Connor 2001; Maguire et al. 2001). $H_2PO_4^-$ might also have reacted with hydrous oxides of Al and Fe under acidic conditions (Navarro and Navarro 2003).

Innocuity of the amendments seemed fairly reachable: water eutrophication is preventable provided maximum doses, such as those recommended here, are complied with. Unacceptable accumulation of P in soils amended with manure is common (Nair and Graetz 2002), which is why only 10 % manure was used here and it was composted prior to addition to biosolid for vermicomposting. Finally, earthworms acted as toxicity bioindicators in biosolids (see Sanchez-Hernandez 2006): their survival and reproduction could ensure that plants receive pollutant concentrations below toxic effect threshold.

Conclusions

Maximum amendment doses were identified for wastewater and solid waste reuse. P release in soil with biosolid and vermicompost was initially rapid and subsequently slowed down, which corresponded to a fast initial and then prolonged fertilizing effect. Low soil pH facilitated P bound to aluminum and iron (hence P retention) and inorganic orthophosphates dominance was probably crucial for plant growth. Similarities were found with kinetics in other soils and amendments in the liberation of P with respect to time: the parabolic diffusion law seems to be the best fit, suggesting diffusion as a probable limiting step in the liberation of P. Vermicompost added more available P, and released less than biosolids; in addition, earthworms bioindicated that the vermicomposted biosolids were fairly innocuous. The amendments studied here could play a salient role in both P replenishing and easy release and, within dose limits, avoid contamination to surface and groundwater. The foregoing would assist in the conservation of intensively used sandy clay loam soils.

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