Short communication

Use of a fractionation procedure to assess the potential for P movement in a soil profile after 14 years of liquid pig manure fertilization

J.A. Hountin\textsuperscript{a}, A. Karam\textsuperscript{b,*}, D. Couillard\textsuperscript{c}, M.P. Cescas\textsuperscript{b}

\textsuperscript{a} Agriculture and Agri-Food Canada, Pacific Agri-Food Research Centre, P.O. Box 1000, Agassiz, B.C., Canada V0M IA0
\textsuperscript{b} Équipe de Recherche en Sols Agricoles et Miniers (ERSAM), Département des sols et de génie agroalimentaire, Université Laval, Sainte-Foy, Qc., Canada G1K 7P4
\textsuperscript{c} INRS-Eau, Université du Québec, Sainte-Foy, Qc., Canada G1V 4C7

Received 2 October 1998; received in revised form 5 July 1999; accepted 23 July 1999

Abstract

The accumulation of P originating from animal wastes in the soil profile is of agronomic and environmental concern. Sequential extraction procedure provides relevant information to mobility, bioavailability and distribution of P in animal manure-amended soils. Such information is needed to assess the potential for biological P leaching, under organic amendments, in some Quebec agriculture ecosystems. This study was conducted using soil samples from the long-term experimental plots of the Soil Research Station of the Quebec Ministry of Agriculture, Fisheries and Food at St-Lambert de Lévis, Quebec, Canada. The objective of this work was to examine the distribution of P fractions in the profile of a Le Bras silt loam soil (Gleysol) growing corn (Zea mays L.) which had received liquid pig manure (LPM) for 14 years. The surface soil was fertilized annually with various rates of LPM (0, 30, 60, 90 and 120 cm$^3$ ha$^{-1}$) in a randomized complete block design with four replicates since 1979. In the fall of 1992, soil samples were collected after the corn harvest from 20 soil plots at 20-cm intervals to a depth of 100 cm. Soil samples were air-dried, crushed, sieved through a 2-mm sieve, and analyzed for soil P fractions using a sequential extraction technique. All treatments resulted in an increase in the labile P pool contents of surface or profile soil compared with the control. Without exception, the amounts of P pools decreased with soil depth and were highly correlated with the LPM rates. The proportion of total P as labile (resin-P$_i$ + NaHCO$_3$-P + NaOH-P) in the soil profile increased from 61 (control) to 79% (highest LPM rate). The amounts of P generally increased in the following order: moderately labile NaOH-P$_i$ and -P$_o$ (254 mg kg$^{-1}$) > labile P extracted by resin and NaHCO$_3$ (209 mg kg$^{-1}$) > stable P (172 mg kg$^{-1}$). On average, the amount of labile P$_i$ forms (304 mg kg$^{-1}$) was larger than the amount of labile P$_o$ forms (159 mg kg$^{-1}$) and represented an important fraction of the total labile P pools. Compared to the control treatment, the mean concentration of geochemical P (resin-P$_i$ + NaHCO$_3$-P$_i$ + NaOH-P$_i$ + HCl-P$_i$ + residual P) increased in the soil profile by 16, 26, 33 and 50% for 30, 60, 90 and 120 m$^3$ ha$^{-1}$ LPM, respectively. On a profile basis, the soil receiving the highest rate of LPM contained 1.8-fold the biological P (NaHCO$_3$-P$_o$ + NaOH-P$_o$) of the unamended soil. Amounts of labile P$_o$ pools in the soil profile were highly correlated with the organic carbon content. Results from this study suggest that heavy application of LPM over the 14-year period has likely increased the bioavailability of P in the soil profile.

\textsuperscript{*} Corresponding author. Tel.: +418-656-2131, ext.: 7420; fax: +418-656-3223. E-mail address: antoine.karam@sga.ulaval.ca (A. Karam).
period promotes P movement to lower portions of the soil profile. The leaching or translocation of P compounds would be responsible for the distribution of P in the various soil layers. Management of LPM rates is necessary after a long-term fertilization of corn. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Pig manure; Inorganic labile P; Organic labile P; Soil-P fractionation

1. Introduction

Phosphorus (P) management is of agronomic and environmental importance (Sharpley et al., 1994). In sustainable agroecosystems, livestock manures should be managed so that they maintain an environment favorable to adequate production and minimize surface and groundwater pollution, especially in agricultural systems in which soils are fertilized at high manure P rates. Although P is considered immobile in agricultural soils, a decrease in the P adsorption capacity of soil following manure addition at rates greater than nutritional P requirements of plants may increase the potential for leaching of soluble P (Sutton et al., 1982). Beauchemin et al. (1996) suggested that agricultural soils in Quebec associated with high animal density would be more at risk to leach P into drainage waters than low animal density or forest soils. The potential environmental P hazard of swine manure depends on many factors among which are the application rate and the mobility of bioavailable P. The bioavailability of P is controlled by its chemical pools indicating that it is desirable to determine the amount of P pools in a soil profile rather than in a surface layer. Sharpely et al. (1984) stated that the increases in the amounts of surface soil inorganic P and organic P with cattle feedlot waste (FLW) application over an 8-year period were due mainly to incorporation of FLW-P into labile soil P fractions. However, the authors observed little movement of inorganic, organic, or available P through the soil profile and concluded that FLW presented little threat to the contamination of groundwater with P. In another study, Simard et al. (1995), observed an enrichment in the amount of soil total P of the C horizons from hog (Porcus sp.) farms with a known surplus of on-farm manure N. They concluded that a significant portion of P moving downward in Quebec agricultural soils from the Beaurnage River Watershed accumulated in very labile P forms.

Little information, particularly in the eastern Quebec agroecosystem region, is available on the pattern of P pools distribution in soils receiving high rates of LPM for many years. Data on soil P fractions distribution may be helpful in guiding long-term applications of LPM to control labile P pool losses in the intensive monocultural cropping system and to protect the environment. The aim of this work was, therefore, to obtain information on the distribution of P fractions in the profile of a soil growing corn (Zea mays L.) which had received LPM for 14 years.

2. Material and methods

2.1. Experimental design and soil samples

Soil samples for this study were collected in the fall of 1992 from long-term liquid pig manure (LPM) application on experimental plots located at the St-Lambert de Lévis Soil Research Station of the Quebec Ministry of Agriculture, Fisheries and Food. The soil is classified as a Le Bras silt loam (Canadian: Humic Gleyso; FAO: Gleyso). The un-amended top soil (0–20 cm) contained 24.5 g organic C kg⁻¹, 1118 mg N kg⁻¹, 664 mg total P kg⁻¹, 32 mg Mehlich-3 extractable-P kg⁻¹, and had a pH (H₂O) of 6.2. The materials and experimental treatments of this study were reported in a previously published paper (Hountin et al., 1997); consequently, only a brief outline will be presented here together with the analytical methods. Experimental treatments consisted of five application rates of LPM (0, 30, 60, 90 and 120 m³ ha⁻¹) applied to the soil surface at a growth stage of 15–25 cm each year beginning in 1979 (Côté and Tran, 1996). The average chemical composition (kg m⁻³) of the manure was as follows: total N, 3.37; N-NH₄, 2.32; P₂O₅, 1.66; K₂O, 1.64 (Côté and Tran, 1996); and total C, 29 (Ndyegeamiye and Côté, 1989). The experimental design was a randomized complete block with four replications. Inorganic fertilizer was not applied. In the fall of 1992, three 7-cm diameter soil cores per plot were taken at 20 cm
increments to a depth of 100 cm to assess the movement and distribution of C, N and P in the soil profiles (Hountin, 1996). The three cores were composited, air-dried, crushed, and sieved to pass a 2-mm sieve prior to sequential P extraction.

2.2. Hedley soil P pools

The amounts of soil inorganic and organic P (Pi and Po, respectively) in labile (resin-Pi, NaHCO3-Pi and NaHCO3-Po), moderately labile (NaOH-Pi, NaOH-Po), relatively insoluble apatite-P (HCl-Pi) and resistant (in primary minerals) pools was determined in each soil layer samples by the procedure of Hedley et al. (1982) as outlined in O’Halloran et al. (1987). This fractionation technique uses a series of extractants to identify labile inorganic (Pi) and organic (Po) fractions followed by the more stable forms. In brief, soil samples were sequentially extracted by each of the following extractants: HCO3-exchange resin (Dowex-50w-x8), 0.5 M NaHCO3 (pH 8.5), 0.1 M NaOH, 1 M HCl, after 16 h shaking with each extractant. The residue containing fairly insoluble Pi and Po forms (residual P) was then digested using 30% H2O2/concentrated H2SO4. Total P (Pi + Po) in the NaHCO3 and NaOH extracts was determined according to the method of Rowland and Grimshaw (1985). The Po content of a given fraction was calculated by subtracting Pi content from total P content of the extract. For all extracts the concentration of Pi was determined colorimetrically by the method of Murphy and Riley (1962) using ascorbic acid as reducing agent. Acid or alkali filtered extracts were neutralized prior to P determination.

3. Results

3.1. Labile and moderately labile inorganic P pools

The distribution of resin-Pi in the soil profiles is illustrated in Fig. 1. The resin-Pi represented on average 21% of the total labile forms (resin-Pi + NaHCO3-Pi + NaOH-Pi) in the top surface layer. Essentially, resin-Pi represents the labile pool of native adsorbed P (Fitter and Sutton, 1975), even though some of the more soluble precipitated P forms may be extracted by the resin (Tiessen and Moir, 1993). The increase in resin-Pi over the control in the 0–20 cm layer varied from 25 mg kg−1 for the lowest rate of LPM (30 m³ ha−1) to 125 mg kg−1 for the highest rate of LPM (120 m³ ha−1). The resin-Pi content of the surface layer was largely in excess for silage corn P requirement (52 mg kg−1 as resin-Pi) when rates of LPM >60 m³ ha−1 were applied. On a profile basis, the soil receiving the lower rates (30–60 m³ ha−1) and the higher rates (90–120 m³ ha−1) of LPM contained, respectively, 1.3- and 2.0-fold the resin-Pi of the unamended soil. This finding suggests that continued surface application of LPM has a significant effect on resin-Pi accumulation and movement. A similar trend was also observed for a surface loamy soil (Canadian: Dark Brown Chernozemic; FAO: Kastanozem) brought about by 20 years of feedlot manure loadings (0, 30, and 90 t/ha) under non-irrigated condition (Dormaar and Chang, 1995). The resin-extractable Pi constituted from 8 in the control soil to 32% of total P in the amended soil (90 t ha−1).
As was observed for resin-P$_i$, the amounts of NaHCO$_3$-P$_i$ and NaOH-P$_i$ (Fig. 2) were significantly ($p < 0.01$) affected by the LPM application rates (Table 1) and decreased with soil depth. These results are in agreement with those of Meek et al. (1979), where it was observed that manure application at high rates to a calcareous soil caused P movement and a resulting increase in NaHCO$_3$-extractable P$_i$ at the 30–60 cm depth. O’Halloran (1993), in a study with dairy liquid manure (DLM) applied on a continuous corn production under reduced tillage, found that DLM application affected the levels of labile P$_i$ fractions. The NaHCO$_3$-P$_i$ levels (Fig. 2) were higher than those for resin-P$_i$ (Fig. 1). On average, the values for NaHCO$_3$-P$_i$/resin-P$_i$ varied from 1.7 to 2.7 in the soil profiles. The average values for NaHCO$_3$-P$_i$ and NaOH-P$_i$ in the various soil depths (Fig. 2) showed that although most of the P$_i$ was located in the first 0–40 cm of the soil, there were still substantial amounts in the lower depths. The average level of NaHCO$_3$-P$_i$ + NaOH-P$_i$ located in the 60–100 cm soil layer was ca. 222 mg kg$^{-1}$ where P had been applied (Fig. 2), and 182 mg kg$^{-1}$ where no P had been applied (control soil profile) indicating that a constant input of P from LPM to surface soil resulted in an increase in P$_i$ extracted by NaHCO$_3$ and NaOH in deeper horizons.

### 3.2. Readily labile and moderately labile organic P pools (biological P)

As was observed for easily and moderately labile P$_i$ forms, biological P (NaHCO$_3$-P$_o$ and NaOH-P$_o$) also increased with LPM application rate and decreased with soil depth (Fig. 3). According to Cross and Schlesinger (1995) organically bound P could be a source of labile, plant-available P. Compared to the control, NaHCO$_3$-P$_o$ and NaOH-P$_o$ contents in

### Table 1

Summary of analysis of variance (significance of $F$ values) to determine the effect of LPM rate, soil layer depth and their interactions on the concentrations of inorganic and organic soil P fractions in a Le Bras silt loam soil growing corn which had received LPM for 14 years$^a$

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Degrees of freedom</th>
<th>Resin-P$_i$</th>
<th>NaHCO$_3$</th>
<th>NaOH</th>
<th>HCl-P$_i$</th>
<th>Residual P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P$_i$</td>
<td>P$_o$</td>
<td>P$_i$</td>
<td>P$_o$</td>
<td></td>
</tr>
<tr>
<td>LPM rate (R)</td>
<td>4</td>
<td>254</td>
<td>106</td>
<td>55</td>
<td>43</td>
<td>95</td>
</tr>
<tr>
<td>Soil depth (D)</td>
<td>4</td>
<td>876</td>
<td>224</td>
<td>40</td>
<td>1180</td>
<td>338</td>
</tr>
<tr>
<td>Interaction (R × D)</td>
<td>16</td>
<td>45</td>
<td>20</td>
<td>8</td>
<td>17</td>
<td>34</td>
</tr>
<tr>
<td>Model</td>
<td>24</td>
<td>218</td>
<td>69</td>
<td>21</td>
<td>214</td>
<td>95</td>
</tr>
</tbody>
</table>

$^a$F values significant at $p < 0.01$. 

Fig. 2. Distribution of (a) NaHCO$_3$-P$_i$ and (b) NaOH-P$_i$ with depth in Le Bras silt loam soil amended with liquid pig manure over 14 years. Horizontal bars indicate standard deviation.
the 0–20 cm layer increased, respectively, by 4–47 and 12–31 mg kg\(^{-1}\) for 30 to 120 m\(^3\) ha\(^{-1}\) LPM application rates. Similar to resin-\(P_i\), NaHCO\(_3\)-\(P_o\) and NaOH-\(P_o\), frequent LPM applications had significant \((p < 0.01)\) effect on NaHCO\(_3\)-\(P_o\) and NaOH-\(P_o\) content (Table 1). Although the amounts of NaHCO\(_3\)-\(P_o\) were smaller than those of NaOH-\(P_o\), these two fractions followed the same pattern of distribution in the soil profiles.

3.3. Stable P forms (HCl-\(P_i\) and residual \(P\))

In general, the HCl-\(P_i\) contents were very low in all the soil layers (Fig. 4), indicating that only a small proportion of manure \(P\) was added to this fraction. The HCl-\(P_i\) pool would correspond to the \(P\) bound to Ca at the surface of apatite and other minerals (Simard et al., 1995). Sharpley et al. (1991), studying the impact of long-term swine manure application on soil and water resources in Eastern Oklahoma reported that only small amounts of HCl-\(P_i\) accumulated in the soil profile. The content of HCl-\(P_i\) was shown to be not affected by repeated applications of barnyard manure (Campbell et al., 1986). As seen from Fig. 5, the application rates had little influence on the distribution of HCl-\(P_i\) form in the soil profile when compared with each other. Large amounts of residual \(P\) were found in the soil profiles (Fig. 5). As the amount of residual \(P\) in the first 0–40 cm layer ranged from 83.6% of the total stable \(P\) fraction for the control treatment to 93.0% for the highest rate of LPM. In all treatments,
the residual P distribution pattern followed the same trend as the labile and moderately labile P pools. Without exception, concentrations of residual P decreased with depth.

4. Discussion

After 14 years of organic fertilization of corn, the amounts of soil P pools were significantly affected (p < 0.01) by LPM treatments compared to the check (Table 1). The average soil P pool contents in the various depths showed that both P_i and P_o concentrations were highest in the manured soil (Figs. 1–5). This is in agreement with the result of Tran and N’dayegamiye (1995), who found that long-term application of dairy cattle manure to the same Le Bras soil increased both surface soil P_i and P_o forms in each pool measured by the Hedley et al. (1982) fractionation procedure. Similar findings were also reported by Dormaar and Chang (1995), where after 20 years of cattle feedlot manure (CFM) loading, the amounts of all labile P_i and P_o forms in the Ap horizon of a Lethbridge loam soil generally increased with all CFM applications compared with the check. On a profile basis, the soil receiving the highest rate of LPM (120 m^3/ha) over 14 years contained 1.8-fold the total labile P_o of the unamended soil, suggesting that long-term application of LPM and returning plant residues to the soil significantly correlated with each other (data not shown). These relationships are in agreement with the known fact that available soil P pools are constantly replenished through reactions of dissolution or desorption of more stable inorganic P and through the mineralization of organic P (Tiessen and Moir, 1993). Similar relationships were reported by McKenzie et al. (McKenzie et al., 1992a, b) in a long-term crop rotation and fertilizer effects study on P transformations in a Chernozemic and a Luvisolic soil. On a profile basis, increasingly higher average amounts of P pools were obtained in the following order (Figs. 1–5): P extracted by NaOH (254 mg kg^{-1}) > P extracted by resin and NaHCO_3 (209 mg kg^{-1}) > stable P (172 mg kg^{-1}).

Compared to the NaHCO_3-P_i content, greater amounts of NaOH-P_i were found in the soil profiles. Tiessen and Moir (1993) reported that NaOH-extractable P_i is thought to be associated with amorphous and some crystalline Al and Fe phosphates while NaHCO_3-extractable P_i is thought to consist of P_i adsorbed on surfaces of more crystalline P compounds, sesquioxides or carbonates. The high proportion of NaOH-P_i in the soil profile could probably be due to amorphous Al and Fe retention. In many Quebec soils, P sorption capacity has been related to Fe and Al amorphous sesquioxides (Laverdière and Karam, 1984). For the manure P_i system, moderately labile P_i would constitute the major soil P sink derived directly from added inorganic P and indirectly from amorphous Fe and Al-bound P_i.

On average, the amount of total labile P_i forms (304 mg kg^{-1}) was larger than the amount of labile P_o forms (159 mg kg^{-1}) and represented an important fraction of the total labile P (P_i + P_o) pools. The proportion of total P as labile (resin-P_i + NaHCO_3-P_i + NaOH-P_i) in the soil profile increased from 61% (control treatment) to 79% (highest LPM rate). Compared to the control treatment, average geochemical P (resin-P_i + NaHCO_3-P_i + NaOH-P_i + HCl-P_i + residual P) concentration increased in the soil profile by 16, 26, 33 and 50% for 30, 60, 90 and 120 m^3 ha^{-1} LPM, respectively. Moreover, average geochemical P con-
tent in the lower depths of the soil was higher under LPM conditions. Such results would indicate that high inputs of LPM would favour the movement and build up of P in lower depths.

When compared to the control treatment, the lower (30–60 m³ ha⁻¹) and higher (90–120 m³ ha⁻¹) application rates over 14 years produced, respectively, a 1.1- and 1.3-fold increase in HCl-Pᵢ. A similar trend could be observed with the data of Tran and N’dayegamiye (1995) where manured soil contained 1.2-fold the HCl-Pᵢ of the unamended soil. This was probably due to the low P input from mineralization of manure P₀ under the prevalent acidic conditions in the soil profiles. The pH(H₂O) values of the soil samples ranged from 5.2 to 6.4, depending on treatment and soil depth. On a profile basis, the soil receiving the highest rate of P (1.70 Mg P ha⁻¹) over 14 years produced a 1.5-fold increase in residual P, suggesting that primary minerals present in the Le Bras soil could be important sinks for the soluble P originating from LPM. The results are consistent with the findings of Sharpley et al. (1991) which established a relationship between levels of added P (from manure) and soil residual P. From an agronomic point of view, this increase would appear to have little practical significance considering the fact that this fraction would contribute little to actual P uptake by plants.

5. Conclusion

The results showed that 14-years of LPM application has increased soil P pools in the soil profile of Le Bras silt loam. There was a moderate accumulation of labile P pools in subsurface soil horizons compared with untreated soil. On average, 1.7-, 1.4-, 1.2- and 1.3-fold increases were found in resin-Pᵢ, NaHCO₃-P, NaOH-P and total labile P pools contents, respectively, of treated compared with untreated 0–100 cm profiles. Soil profiles which had received up to 60 m³ ha⁻¹ LPM for 14 years have a lower proportion of labile P pools than plots treated with 90–120 m³ ha⁻¹ LPM. Although the downward movement of P in the soil profile has been demonstrated in this study by using the P fractionation procedure, further studies are needed to assess the impact of soil labile P pools accumulated through years of application of LPM on groundwater quality.

Acknowledgements

The financial support of this study by a grant from the National Science and Engineering Research Council of Canada and by a dedicated financial assistance provided to the senior author by the Institut National de la Recherche Scientifique, Université du Québec, are greatly appreciated. The authors acknowledge the Soil Research Service Staff of the Ministry of Agriculture, Fisheries and Food of Quebec for allowing the use of one of their long term experimental trials to conduct the present study. Special thanks are extented to Mr. Denis Côté for his assistance in selecting the site for collection of soil samples. Mr. D. Côté kindly permitted access to his research plots and provided the chemical composition of liquid pig manure.

References


