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Phosphorus sorption and availability in an andosol after a decade of organic or mineral fertilizer applications: Importance of pH and organic carbon modifications in soil as compared to phosphorus accumulation

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Credit author statement

All authors designed the experiments and methods. C.M.N conducted the experiments and analyzed the data. C.M.N and M.N.B wrote the manuscript. All authors reviewed and validated the manuscript.

Journal Proposi

1 Phosphorus sorption and availability in an andosol after a decade of organic or mineral

2 fertilizer applications: importance of pH and organic carbon modifications in soil as compared

- 3 to phosphorus accumulation
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11 Abstract

12 The effect of organic fertilizers on soil phosphorus (P) availability is usually mainly associated with the 13 rate and forms of P applied, while they also alter the soil physical-chemical properties, able to change P 14 availability. We aimed to highlight the impact of pH and organic C modifications in soil on the inorganic P 15 (Pi) sorption capacity and availability as compared to the effect of P accumulation after mineral or 16 organic fertilizers. We conducted a 10-years-old field experiment on an andosol and compared fields that 17 had been amended with mineral or organic (dairy slurry and manure compost) fertilizers against a non-18 fertilized control. Water and Olsen extractions and Pi sorption experiments were realized on soils 19 sampled after 6 and 10 years of trial. We also realized an artificial and ex situ alkalization of the control 20 soil to isolate the effect of pH on Pi sorption capacity. Organic fertilizer application increased total P, pH, and organic C in soil. Pi-Olsen increased mainly with soil total P (r^2 adj = 0.79), while Pi-water increased jointly with soil total P and pH (r^2 adj = 0.85). The Pi sorption capacity decreased with organic fertilizer application. Artificial and *ex situ* alkalization of the control soil showed that Pi sorption capacity decreased with increasing pH. Our study demonstrated that, beyond the P fertilization rate, the increase in organic C content and even more so in pH induced by a decade of organic fertilizer applications in soil decreased the Pi sorption capacity and consequently increased Pi-water in soil.

27 Keywords

28 Adsorption, Field trial, Organic residues, Phosphate, Residual P, Solid-solution partitioning coefficient

1. Introduction

30 The major phosphorus (P) fertilizer used in the world is derived from nonrenewable mineral 31 resources. The forecasts are highly disputed, but mineral fertilizer production could start decreasing 32 around 2035 (Cordell et al., 2011; Ulrich and Frossard, 2014). In addition, only three countries, i.e. 33 Morocco, China and the USA, produce 85% of mineral fertilizer, which could create dependencies and 34 tensions between countries (Elser and Bennet, 2011). These two concomitant P issues strongly suggest 35 the need for P recycling in agriculture, with greater use of P-containing organic fertilizers such as 36 agricultural and urban wastes. Nevertheless, P-containing organic fertilizer applications must be efficient 37 enough to meet crop P nutrition needs, while also limiting P loss into the environment and the 38 consequent risk of eutrophication (Shoumans et al., 2014).

The application rate of organic and mineral fertilizers only partially drives soil P availability in the long-term (Nobile et al., 2018). In laboratory experiments, fertilizers are applied at a same P rate, but soil P availability is measured only several weeks after a single fertilizer application, thus only highlighting the short-term effects of fertilization. Studies based on laboratory experiments usually show that P

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43 availability in organic fertilized soil is lower than P availability in mineral fertilized soil (Frossard et al., 44 1996; Shafqat and Pierzynski, 2013). Medium (5-10 years) or long-term (\geq 10 years) field experiments 45 with repeated fertilizer applications, which are designed to highlight direct and indirect effects of 46 fertilizers, are however less conclusive than short-term laboratory experiments. Firstly, substantial 47 differences in P fertilization rate have been noted between soils amended with organic and mineral 48 fertilizers as N inputs rather P inputs are usually balanced in field experiments (Oehl et al., 2002; Morel 49 et al., 2014). Hence, fertilizers applied at different P application rates are compared by relating available 50 P to the cumulative P budget, i.e. P applied with fertilization minus P output via crop harvests, or to the 51 soil total P content which tends to increase with P fertilization rate. In field experiments, some studies 52 showed an equivalent P availability in soils fertilized with two types of sewage sludge or with mineral 53 fertilizer (e.g. Morel et al. 2013), while some other studies showed a higher P availability in soil fertilized 54 with farmyard manure than with mineral fertilizer (e.g. Vanden Nest et al. 2016). These contrasted 55 results suggest that some other processes in addition to the P application rate drive P availability in soils 56 amended with mineral and organic fertilizers in the long-term.

57 Phosphorus speciation in organic fertilizers is often mentioned as a potential factor determining 58 the effect of organic fertilization on soil P availability. Although mineral fertilizers contain only inorganic 59 P (Pi), organic fertilizers such as animal waste typically contain about 60 to 75% of Pi (Toor et al., 2006; 60 Darch et al., 2014) and consequently also a variety of organic P (Po) species. Nevertheless, Annaheim et 61 al. (2015) showed that P speciation in organic fertilizers did not impact P speciation in soil after 62 years 62 of application. More generally, the amount of Po in soil is little affected by long-term organic or mineral 63 fertilization (Huang et al., 2017). Consequently, P speciation in organic fertilizers is usually not the 64 principal factor explaining their long-term effects on P availability.

65 Stimulation of soil microbial activity induced by organic fertilizer application is another potential 66 factor explaining the effect of organic fertilizer application on soil P availability. It is thought that higher

67 activity of microorganisms that mineralize Po into Pi could increase P availability in organic fertilized 68 soils. Microbial P and phosphatase activity in soil can increase after organic fertilizer application (Mäder 69 et al., 2000), but this does not necessarily lead to an increase in P availability. Firstly, because 70 microorganisms take up both Po and Pi from the soil solution, so the net amount of Pi released in the 71 solution can be low. Secondly, because Pi released in the soil solution by microorganisms could be 72 rapidly sorbed on the soil solid phase. Oehl et al. (2004) showed in 20 years field experiments with 73 organic or mineral fertilizer applications that the contribution of Po mineralization to the release of 74 available Pi was much lower (< 10%) than the contribution of physical-chemical mechanisms. In 75 agreement, Stutter et al. (2015) concluded that Pi sorption, directly added with fertilizers or released via 76 Po mineralization, seems to be the main factor that limits P availability in organic or mineral fertilized 77 soils in the long-term. Consequently, the effects of organic or mineral fertilizer application on the soil P sorption capacity could thus be a key factor, along with P application rate, explaining their effects on soil 78 79 P availability.

80 Long-term organic fertilization is known to drastically impact soil physical-chemical properties. 81 Organic fertilizer application can increase the soil pH and organic carbon content (Haynes & Mokolobate, 82 2001). Previous studies based on short-term laboratory investigations revealed the separate effects of 83 these two factors on the soil Pi sorption capacity. In soils containing minerals with variable charges, such 84 as allophanes, imogolites, Fe or Al oxides, increasing the soil pH can decrease Pi sorption due to a 85 decrease in electrical potential on sorption surfaces (Antelo, 2005; Barrow et al., 2017). Increasing the 86 organic carbon content can decrease Pi sorption due to a competition between negatively-charged 87 organic molecules and Pi for the same sorption sites (Regelink et al., 2015). Nevertheless, to our 88 knowledge, no studies based on field experiments have demonstrated that the effect of organic fertilizer 89 application on Pi sorption capacity and availability was due to pH and organic carbon modifications 90 (Haynes and Mokolobate, 2001). For instance, Vanden Nest et al. (2016) showed a decrease in Pi

91 sorption in soil fertilized with dairy manure, but the relationships with pH and organic carbon 92 modifications in soil were only hypothesized.

Our study was aimed at highlighting the importance of pH and organic carbon modifications on the Pi sorption capacity and availability as compared to the effects of P accumulation in soil after a decade of mineral or organic fertilizers application. We conducted a 10 years field experiment on an andosol with a high sorption capacity and compared fields that had been amended with mineral or organic (dairy slurry and manure compost) fertilizers against a non-fertilized control.

98

2. Materials and methods

99 2.1. Field experiment and soil sampling

100 The field experiment was located in Réunion, a French volcanic island (2 500 km²) in the Indian 101 Ocean (55°30'E, 21°05'S). The field experiment initially aimed at evaluating the potential productivity of 102 fodder crops based on N input with organic fertilizers issued from local livestock farms in comparison 103 with the usual imported mineral fertilizers. For 10 years, four types of organic and mineral fertilizers 104 were applied on fodder crops, with plots respectively: unfertilized (hereafter referred to as control), 105 fertilized with N in the form of ammonium nitrate and P in the form of soft rock phosphate (75% soluble in 2% formic acid) at 52 kg ha⁻¹ yr⁻¹ (hereafter referred to as mineral), fertilized with a liquid dairy slurry 106 107 at two doses equivalent to 170 or 290 kg P ha⁻¹ yr⁻¹ (hereafter referred to as slurry), or fertilized with a 108 dairy manure (i.e. dairy slurry mixed with sugarcane straw used as cow bedding) compost at two doses equivalent to 70 or 120 kg P ha⁻¹ yr⁻¹ (hereafter referred to as compost). The fodder was cut five to eight 109 110 times per year. The slurry and the compost were respectively applied after every cut or every two cuts. 111 At each application, compost and slurry were lyophilized, ground, sieved at 2 mm, and analyzed for C 112 organic and total N, P, and K by a soil routine testing laboratory (CIRAD, Recycling and Risk research unit, 113 Réunion, France). Table 1 shows the average properties of the slurries and the composts applied

throughout the 10 year field experiment. Water-extracted Pi and pH were measured in the compost and slurry applied during the last year of the field experiment. The average amounts of nutrients applied yearly for each treatment are summarized in Table S1.

117 Plots were arranged in a randomized block design with three replicates. The soil is classified as 118 an andosol (IUSS Working Group WRB, 2014) and exhibits a high Pi sorption capacity and a low Pi 119 availability (Nobile et al., 2018). The high content of imogolite and/or proto-imogolite, allophane, 120 ferrihydrite, and poorly crystallized gibbsite and goethite (Raunet et al., 1991; Levard et al., 2012) can 121 explain the high Pi sorption capacity of the andosol studied here (Gérard et al., 2016). The soil was 122 sampled after 6 and 10 years of fertilization at 0-15 cm depth in each plot, corresponding to the three 123 replicates of the six fertilization treatments investigated: i.e. control, mineral, slurry Ld (low dose) and Hd 124 (high dose), and compost Ld and Hd (n = 24). Soil samples (hereafter referred to as soils) were air dried, 125 sieved at 2 mm, and analyzed by a routine soil testing laboratory (CIRAD, US Analyses, France). Table 2 126 shows the soil properties at the beginning of the field experiment.

127 2.2. Measurement of total phosphorus in soil

According to NF ISO 14869-1 (Afnor, 2001), soil was dried at 105 °C, sieved at 2 mm, crushed (< 200 μm), and heated in a muffle furnace at 500 °C to ensure the oxidation of organic P (Po) into inorganic P (Pi). The ashes were then digested with hydrofluoric, perchloric and nitric acids. The P concentration was then determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).</p>

132 2.3. Measurement of inorganic phosphorus availability in soil

Water and Olsen extractions were used to assess soil Pi availability. Water extraction, considered as a proxy of the soil solution targeting Pi readily available for plants, was performed by shaking the 1:10 soil:liquid mixtures for 24 h in an end-over-end shaker (Morel et al. 2014). Olsen extraction (NaHCO₃ 0.5 M at pH 8.5), based on the exchange between carbonate and Pi sorbed on the soil surface, was

137 performed by shaking the 1:20 soil:liquid mixtures for 30 min in an end-over-end shaker (Olsen et al. 138 1954). After centrifugation at 3 500 \times q for 5 min and filtration of the supernatant at 0.22 μ m (Minisart, 139 Sartorius), the P concentration was measured in Olsen and water extracts by colorimetry using the 140 malachite green method (Rao et al. 1997). According to Van Moorleghem et al. (2011), we considered 141 colorimetrically-measured P as Pi (i.e. ionic and colloidal Pi). In water extracts, we also measured P by 142 inductively coupled plasma mass spectrometry (ICP-MS, Q-ICP-MS X Series II+CCTTM, Thermo Fischer), 143 which corresponds to total P. We then calculated Po in the water extract according to the difference 144 between ICP-MS and colorimetrically-measured P. Each extraction was replicated twice on each soil.

145 2.4. Inorganic phosphorus sorption experiments

146 Sorption experiments were carried out on eight soils collected after 10 years in the field 147 experiment. These eight soils corresponded to five soils from one replicate of control, mineral, slurry Ld, 148 compost Ld, and compost Hd plots and three additional soils from the control plot whose pH was 149 artificially increased in the laboratory. These three latter soils were prepared by mixing 11 g of soil (dry 150 mass equivalent) with 0, 1.4 and 2.4 mL of NaOH 300 mM, respectively. Ultra-pure water was added to 151 reach 75% of the maximum water holding capacity (i.e. pF 2.5) and the mixture was then incubated at 28 152 °C in the darkness for 48 h. The sorption experiments were started immediately following the incubation 153 step.

154 The sorption experiments involved shaking 1 g of each soil (dry mass equivalent) with 10 mL of KH₂PO₄ at either 0, 25, 50, 75, 100, 125, 150, 200, and 250 mg P L⁻¹ for 64 h at 23 °C in an end-over-end 155 156 shaker (protocol adapted from Barrow and Debnath, 2014). After centrifugation at $3500 \times q$ for 5 min 157 and filtration of the supernatant at 0.22 µm, the Pi remaining in solution was measured colorimetrically 158 as described in section 2.3. Each sorption experiment was replicated twice on each soil. Because using 159 CaCl₂ 0.01 M as background electrolyte was showed to strongly altered soil Pi sorption and more

160 particularly to remove the pH effect on Pi sorption by fixing Ca at a pretty similar concentration in all 161 fertilization treatments (Devau et al. 2009; Weng et al., 2011; Barrow 2017), we chose to perform 162 sorption experiments with water rather than with CaCl₂ 0.01 M as usually done. Preliminary 163 investigations showed that Ca concentration in water extracts of the andosol studied herein is 5 to 25-164 fold lower than in CaCl₂ 0.01 M and also varies as a function of the type and number of fertilizer applications (results not showed). Measurements of pH in water extracts at the end of sorption 165 166 experiments showed that pH increased by ca. 0.3 pH unit with increasing KH₂PO₄ addition for the three 167 soils exhibiting an initial pH below 6.5 (Fig. S1). Such pH modifications therefore led to an 168 underestimation of Pi sorption with increasing KH₂PO₄ addition in these three soils. As these three soils 169 exhibited the highest Pi sorption, this means that pH modifications did not lead to reconsider the 170 comparison of sorption curves between soils. Accordingly, pH was not corrected.

171 According to Barrow (2008), Pi sorption in the soil solid-phase was described with a Freundlich-172 like equation as follows:

173 Pi–sorbed

Pi-sorbed = $a C_f^b - q$

where *Pi-sorbed* is the amount of Pi sorbed in mg kg⁻¹, C_f is the final Pi concentration in solution (i.e. presumably in equilibrium with Pi-sorbed) in mg L⁻¹, *a* and *b* are shape parameters whose product, and *q* is the amount of Pi in mg kg⁻¹ that could be desorbed when the concentration in solution is maintained at zero. Sorption curves were represented in a log scale.

178 2.5. Data processing and analysis

The whole data set is accessible via Dataverse (Nobile et al., 2019). Data were statistically analyzed with the R package (R Core team, 2013). The effect of fertilization on soil properties was assessed using ANOVA, and pairwise Tukey HSD (honest significant difference) tests were used to rank fertilization treatments. The effect of the P fertilization rate was studied with linear regressions between soil total P

and Olsen-extracted Pi (Pi-Olsen), water-extracted Pi (Pi-water), and the proportion of Pi versus Po in
water extracts (%Pi-water). The ratio between soil total P and Pi-Olsen (Pi-Olsen/Total P), Pi-water (Piwater/Total P), or %Pi-water (%Pi-water/Total P) was used to eliminate the influence of the P fertilization
rate on Pi availability and %Pi. Linear regressions between pH or organic carbon in soil and Pi-Olsen/Total
P, Pi-water/Total P, %Pi-water/Total P were used to study the effect of soil properties.

188

3. Results and discussion

189 3.1. Decadal organic or mineral fertilizer applications alter physical-chemical properties and
 190 phosphorus availability in soil

191 The application of organic and mineral fertilizers for 10 years progressively changed the soil pH 192 (Fig. 1a, Table S2). After 10 years of fertilization, the soil pH decreased by 0.6 units with mineral 193 fertilization compared to the control soil (pH 5.7). By contrast, the soil pH increased with organic 194 fertilization compared to the control soil by up to 0.7 and 1.2 units on average with compost and slurry 195 at high dose, respectively. The soil pH also changed after only 6 years of mineral or organic fertilization, 196 but to a lower extent than after 10 years (Table S2). A decrease in soil pH after long-term application of 197 NH₄NO₃ was previously reported (Stroia et al., 2011). It could have resulted from the production of 198 protons produced by the nitrification of NH_4^+ that was not balanced by the uncomplete consumption of 199 protons associated to NO₃ uptake in plants because of NO₃ leaching in soil. An increase in soil pH with 200 long-term organic fertilization was also found in several studies (Noble et al., 1996; Haynes and 201 Mokolobate, 2001), and could mainly have been due to the decarboxylation of carboxylic groups borne 202 by the organic matter contained in the organic fertilizers applied (de Vries and Breeuwsma, 1987; Yan et 203 al., 1996).

Ten years of organic fertilizer application progressively increased the soil organic C content compared to control and mineral fertilization (Fig. 1b, Table S2). After 10 years without fertilization,

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organic C was equal on average to 122 g kg⁻¹ in the control soil. Slurry induced lower C accumulation than 206 compost (+ 15 vs. + 32 g C kg⁻¹ at high dose, respectively). The soil organic C content also increased after 207 208 only 6 years of organic fertilization, but to a lower extent than after 10 years (Table S2). The C dose yearly applied was much higher with slurry than with compost (16800 vs. 3900 kg C ha⁻¹ y⁻¹ at high dose). 209 210 Considering the soil apparent density (0.5 g cm⁻³) and 10 cm incorporation depth (no tillage was performed), slurry and compost added 33.6 and 7.8 g C kg⁻¹ soil y⁻¹, respectively. During the 10 year field 211 212 trial, the proportion of C accumulated in soil compared to the amount of C added was thus equal to 4% 213 with slurry and 41% with compost. These results agreed with previously reported findings, showing that 214 the proportion of C accumulated in soil with long-term organic fertilization increased with the 215 abundance of stabilized compounds in organic fertilizer, which usually increases during composting 216 (Peltre et al., 2012).

Ten years of organic fertilizer application progressively increased the soil total P compared to the 217 218 control and mineral treatments (Fig. 1c, Table S2). After 10 years without (control) or with mineral 219 fertilization, soil total P was on average equal to 3.0 g kg⁻¹. After 10 years of organic fertilization, soil total 220 P increased up to 4.3 g kg⁻¹ in soil receiving compost at high dose. Slurry induced P accumulation similar 221 to the rate noted with compost (4.2 g kg⁻¹ vs. 4.3 g kg⁻¹ at high dose, respectively). Differences in soil 222 total P between fertilization treatments firstly resulted from different rates of P application, which were 223 much higher with organic than with mineral fertilizers (Table 2), secondly resulted from different extents 224 of P uptake by plants and presumably from additional P loss by leaching, especially with slurry (Fig. S2). 225 As in numerous long-term field experiments where P application rate was not balanced between 226 fertilization treatments (Morel et al., 2014; Vanden Nest et al., 2016), high rates of P applied with organic 227 fertilizer application lead thus to high level of P accumulated in soil.

Ten years of organic fertilizer application progressively increased Pi-Olsen, Pi-water, and %Piwater compared to the control and mineral treatments (Fig. 1d, 1e and 1f, Table S2). After 10 years of

10

230 fertilization, Pi-Olsen, Pi-water and %Pi-water were the lowest in control and mineral soils (down to 231 17.1 mg kg⁻¹, 0.15 mg kg⁻¹, and 22%, respectively), and the highest in the soil fertilized with compost or slurry at high dose (71.1 mg kg⁻¹, 2.55 mg kg⁻¹, and 66%, respectively). Pi-Olsen and Pi-water also 232 233 increased after only 6 years of organic fertilization, but to a lower extent than after 10 years (Table S2). 234 By contrast, %Pi-water did not differ between fertilization treatments after 6 years of fertilization. We 235 previously observed a similar increase of Pi compared to Po in other soil types from Réunion amended 236 with a variety of organic fertilizers (Nobile et al., 2018). This agreed with previous findings showing that 237 long-term (> 20 years) organic fertilization increased available Pi but had little effect on available Po in 238 soils (Huang et al., 2017).

239 3.2. Fertilization-induced phosphorus accumulation in soil increases phosphorus availability

Pi-Olsen increased with soil total P according to a strong log-log relationship after 6 and 10 years without fertilization or with the application of mineral or organic fertilizers (r² adj = 0.79) (Fig. 2a). Previous studies also showed an increase in Pi-Olsen with soil total P (Bai et al. 2013; Nobile et al. 2018) or with a cumulative P budget (Morel et al. 2013), regardless of whether P was applied as mineral or organic fertilizers. In agreement with previous reports, our results showed that soil Pi-Olsen changed mainly with the rate of P applied.

Pi-water also increased with soil total P according to a log-log relationship after 6 and 10 years of fertilizer application, but with a weaker regression coefficient than observed for Pi-Olsen (r^2 adj = 0.60) (Fig. 2b). Considering the type of fertilizer applied didn't not improve the relationship between Pi-water and soil total P. The regression coefficients were even much weaker when considering only the compost (r^2 adj = 0.41) or the slurry (r^2 adj = 0.28) treatments rather than considering all fertilization treatments together. Correlations between Pi-CaCl₂ and soil total P calculated from Vanden Nest et al. (2016) were also moderate in two field trials receiving mineral or organic fertilizers for either 13 years (r^2 adj = 0.53) 253 or 6 years (r^2 adj = 0.38). In this study, fertilization treatments also modified the soil pH and organic 254 carbon, which could impact Pi-CalCl₂ and thus explain the week correlation between Pi-CaCl₂ and total P. 255 By contrast, Shepherd & Withers (1999) found a strong linear relationship between Pi-water and the 256 cumulative P budget in a sandy soil after 8 years of mineral or poultry manure fertilization (r^2 adj = 0.86). 257 As Pi sorption capacity is expected to be very low in this low clay content (4-6%) soil, we can thus 258 suppose that Pi-water depended mainly on the rate of P applied, but little on the changes of pH or 259 organic C. Our results suggest that the P fertilization rate was not the sole factor determining the content 260 of Pi-water in the andosol we studied, even when we distinguish the type of fertilizers. We presumed 261 that the observed modifications in pH and organic carbon content in soil may also have partly 262 determined the content of Pi-water.

263 The proportion of Pi in water extract (%Pi-water) increased with soil total P after 10 years of 264 fertilizer application (r^2 adj = 0.86), while after 6 years %Pi-water did not change at all with soil total P 265 (Fig. 2c). The fertilization treatments had little effect on the amount of Po- and Pi-water after 6 years of 266 fertilization (Fig. S1), while it had a strong effect on Po-water and even more so on Pi-water after 10 267 years (Fig. 1e and Table S2). This suggests that 6 years was too short a period to observe any significant 268 differences between treatments in the andosol we studied. This agreed with previous findings, showing 269 that a decade of organic fertilization led to an increase in available Pi, while the effect on available Po 270 was low (Nobile et al., 2018), and that available Pi increased with fertilization from the short-term (< 10 271 y) to the medium- (10-25 y) and long-terms (> 25 y) (Negassa and Leinweber, 2009). These results 272 showed that a decade of organic fertilization favored Pi relative to Po in soil solution.

3.3. Fertilization-induced changes in pH and organic carbon in soil also contribute to phosphorus
availability

275 The Pi-water to soil total P ratio increased with soil pH according to a strong relationship (r^2 adj = 276 0.78), while the Pi-Olsen (r^2 adj = 0.54) or %Pi-water (r^2 adj = 0.43) to soil total P ratios were much less 277 correlated with the soil pH (Fig. 3). The positive relationship between Pi-water and soil pH at a given soil 278 total P content could be explained by a decrease in Pi sorption with increasing pH. The increase of pH can 279 decrease the electric potential of surfaces, which increases the electrostatic repulsion between the 280 charged surface and Pi and thus decrease Pi sorption (Antelo, 2005). This process may be particularly 281 important in andosols that contain high amount of minerals with pH-dependent charge surfaces, such as 282 allophane, proto-imogolite, ferrihydrite, and poorly crystallized gibbsite and goethite (Raunet, 1991; 283 Levard et al., 2012). The effect of pH was lower on Pi-Olsen. The solution used for Olsen extraction 284 (NaHCO₃ at pH 8.5) reduced the modifications of ionic strength and pH of the soil solution between 285 fertilization treatments, and thus reduced the effect of the soil pH on Pi sorption. The low effect of soil 286 pH on %Pi-water could be explained by a different pH effect on Pi and Po sorption to soil. Soil pH can 287 affect the sorption of both Pi and Po, but the sorption rate is specific to each Po molecule (Celi and 288 Barberis, 2005). Our findings suggested (i) that pH had a stronger negative effect on the Pi sorption 289 capacity than on Po and (ii) that, when normalizing the data by the P fertilization rate, soil pH had a 290 major effect on Pi-water. These results suggest that the P efficiency of organic and mineral fertilizers is 291 also tightly related to their effect on soil pH.

The Pi-Olsen, Pi-water, or % Pi-water to soil total P ratios increased with the soil organic carbon content according to moderate and linear relationships (r^2 adj = 0.59, 049, and 0.63, respectively) (Fig. 4). The positive log-log relationships between organic C and available Pi at a given soil total P content could be explained by competition between negatively-charged organic matter and Pi for the same sorption sites (Regelink et al. 2015; Weng et al., 2011). Shen et al. (2014) previously showed that the Pi-Olsen to soil total P ratio increased with organic C to a result in a strong linear relationship (r^2 = 0.96) in soils fertilized with poultry manure. In this previous study, changes in organic C with fertilization thus had a

major effect on available Pi, but no data on pH changes with fertilization were provided to compare their relative effects. Our results showed that, when normalizing the data according to the P fertilization rate, soil organic carbon had an effect on available Pi and %Pi-water in soil, but for Pi-water this effect was much lower than the effect of soil pH.

303 The joint variations in total P, pH, and/or organic carbon in soil strongly explained the variations 304 in Pi-Olsen, Pi-water, and %Pi-water (Table S3). Total P, pH and organic C in soil jointly explained 88% of 305 the Pi-Olsen variations. Total P and pH in soil jointly explained 85% of the Pi-water variations, while soil 306 organic C did not contribute. Organic C and pH in soil jointly explained 76% of the %Pi-water variations, 307 while soil total P did not contribute significantly, unless we considered only soils sampled after 10 years 308 of fertilization. These results confirmed the suggestion that fertilization and particularly organic 309 fertilization in our study influenced the soil Pi availability by concomitantly increasing total P, pH, and 310 organic matter in soil (Haynes and Mokolobate, 2001). Our results showed that the rate of P applied was not the sole factor driving P availability in soil and that the modifications of pH and organic carbon 311 312 content in soil due to organic and mineral fertilization also determined available Pi and %Pi-water.

313 3.4. Soil pH modification induced by organic or mineral fertilizer application is the main driver of 314 inorganic phosphorus sorption capacity

At each Pi concentration in solution, less Pi was sorbed in soils amended with organic fertilizers than in the control soil (Fig. 5a). Sorption of Pi was equivalent in soils with slurry or compost at low dose, and the lowest in soil with compost at high dose. By contrast, at each Pi concentration in solution, more Pi was sorbed in the soil amended with mineral fertilizer than in the control soil. These results agreed with the findings of previous studies showing that long-term organic fertilizer application can decrease soil *Kd*, i.e. the solid-liquid partitioning of Pi (Nobile et al., 2018; Vanden Nest et al., 2016). Our results

showed that a decade of organic or mineral fertilization is able to strongly change soil Pi sorptioncapacity, even in soil with high sorption capacity such as the andosol studied herein.

323 While it is considered that an increase in total P, organic C, or pH in soil is likely to induce a 324 decrease in Pi sorption (Barrow 2015; Regelink et al. 2015; Barrow 2017), the relative patterns of the 325 sorption curves for the five fertilization treatments can be consistently explained only with the pH 326 difference between the five soils (Fig. 5a and Table S4). While soil total P was higher in the mineral 327 treatment than in the unfertilized control and soil organic carbon was equal, only the lower soil pH in the 328 mineral treatment can support its higher Pi sorption than in the control. Also, the similar Pi sorption 329 observed in the slurry and compost at low dose is only supported by the similar soil pH in these two 330 treatments, while both total P and organic C in soil were higher in the compost at low dose than in the 331 slurry at low dose. Finally, the decrease in Pi sorption following the order control > slurry and compost at 332 low dose > compost at high dose can be inseparably explained by the increase in total P, organic C, and 333 pH in soil following the order control < slurry and compost at low dose < compost at high dose. Soil pH is 334 therefore the unique soil parameters able to support the variation of Pi sorption between the 335 fertilization treatments.

336 An artificial and ex situ alkalization of one control soil was realized while maintaining total P and 337 organic C in soil at the same level to demonstrate how an increase in soil pH alone is able to decrease Pi 338 sorption in the andosol studied herein (Fig. 5b and Table S4). The alkalization of the control soil from pH 6.0 to 6.5 led to decrease Pi sorption for Pi concentrations lower than ca. 2 mg L⁻¹, while at higher Pi 339 340 concentrations the increase in pH of the non-alkalinized control soil led to similar pH and thus similar Pi 341 sorption than in the control soil alkalinized at pH 6.5 in which the pH remained stable. The alkalization of 342 the control soil from pH 6.5 to 6.9 led to an additional decrease in Pi sorption up to Pi concentrations 343 lower than ca. 10 mg L^{-1} . Previous studies showed that the anion sorption capacity decreased with 344 increasing pH in soils exhibiting a high sorption capacity, such as andosols or ferralsols, that contain

345 minerals with variable surface charges (i.e. allophanes, imogolites, and Fe and Al oxides) (Okamura et al., 346 1983; Becquer et al., 2001). Our results confirmed that increasing soil pH, while maintaining total P and 347 organic C in soil at the same level, is able by itself to decrease Pi sorption with an equivalent magnitude 348 as observed between the five fertilization treatments and over most of the investigated Pi 349 concentrations in solution.

4. Conclusion

351 We aimed at distinguishing the relative importance of modifications of pH and organic carbon in soil 352 after mineral or organic fertilization compared to the rate of P applied on soil Pi sorption and soil P 353 availability. After 10 years, organic and mineral fertilization drastically changed the pH, organic C, and 354 total P in the andosol studied. Our study shows that Pi-water and Pi-Olsen in the andosol changed firstly 355 with the rate of P applied with organic or mineral fertilizers, secondly with the soil pH modifications 356 induced by fertilizer applications, and thirdly with the organic carbon modifications induced by fertilizer 357 applications. Long-term organic fertilizer application decreased the soil Pi sorption capacity, principally 358 by increasing the soil pH. Our study therefore suggests that the increase in soil P availability after long-359 term organic or mineral fertilization greatly depends on their effect on the soil physical-chemical 360 properties, especially on pH, in addition to the primary effect of P application rate.

361 Nevertheless, the overall P efficiency of organic or mineral fertilization does not only depend on soil 362 P availability, but above all on the amount of P readily taken up in crops. Barrow (2017) recently argued 363 that soil pH may have an opposite effect on soil Pi availability and plant P uptake. Accordingly, it appears 364 necessary to check if plant P uptake is driven by the same mechanisms as P availability when pH, organic 365 C, and total P is concomitantly changing in soil under long-term organic and mineral fertilization.

16

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Table 1 Properties of organic fertilizers used in the field experiment. Fertilizers were analyzed at each application during the 10 year experiment. Average values are given with their standard error in brackets (n = 28 for compost, n = 48 for slurry), except for water-extracted inorganic phosphorus (Piwater) and pH-water, which were measured in the organic fertilizers applied in the last year of the experiment.

	Unit, dry mass	Slurry	Compost
Dry matter 105°C	%	9.1 (1.3)	46.3 (9.3)
Organic C ^a	g kg ⁻¹	439 (12)	232 (44)
N total ^a	g kg⁻¹	24.8 (1.9)	22.4 (5.4)
K total	g kg⁻¹	49.5 (8.2)	12.5 (4.6)
P total ^b	g kg⁻¹	8.0 (1.1)	7.0 (2.4)
Ca total	g kg⁻¹	16.7	55.5
Pi-water ^c	g kg⁻¹	0.6	0.9
pH-water ^d		7.5	7.5

^aNF ISO 10694 (Afnor, 1995)

^b NF ISO 14869-1 (Afnor, 2001)

^c Inorganic phosphorus extracted with water (see section 2.3 for rationale)

^d Soil:liquid ratio 1:5

	Unit, dry mass	
Clay (< 2 μm)	g kg ⁻¹	139
Silt (2 - 50 μm)	g kg⁻¹	680
Sand (50 – 2 000 μm)	g kg⁻¹	181
Bulk density	g cm ⁻³	0.55
Organic C ^a	g kg⁻¹	123
N total ^b	g kg⁻¹	10.9
P total ^c	mg kg ⁻¹	3030
Pi-Olsen ^d	mg kg ⁻¹	23.7
Pi-water ^e	mg kg ⁻¹	0.36
pH-water ^f		5.8
Mineralogy ^g	noi Pri	Imogolite and/or proto-imogolite, allophane, poorly crystallized gibbsite, ferrihydrite, poorly crystallized goethite, maghemite, magnetite, halloysite

Table 2 Properties of the andosol sampled at 0-15 cm under grassland cover at the beginning of the field experiment.

^a NF ISO 10694 (Afnor, 1995)

^b NF ISO 13878 (Afnor, 1998)

^c NF ISO 14869-1 (Afnor, 2001) ^d Inorganic phosphorus extracted with the Olsen method

^e Inorganic phosphorus extracted with water

^fSoil:liquid ratio of 1:5

^g Minerals are given in order of abundance; data from Raunet (1991) and Levard et al. (2012)

Figure 1 Changes in the properties and phosphorus (P) availability in the andosol after 10 years without fertilization (control) or with the application of mineral or organic P fertilizers. Organic fertilizers were either dairy slurry or compost at low (Ld) or high (Hd) dose. Inorganic P (Pi) availability was measured in water (Pi-water) and Olsen (Pi-Olsen) extracts and %Pi-water is the proportion of Pi relative to total P in the water extract. Error bars stand for standard error (n = 3). Different letters indicate a significant difference at p < 0.05.





Pi-water (mg kg⁻¹)







%Pi-water

e

f



Figure 2 Log-log relationships between indicators of phosphorus (P) availability and soil total P in the andosol after 6 or 10 years without fertilization (control) or with the application of mineral or organic P fertilizers. Organic fertilizers were either dairy slurry or compost at low or high dose. Inorganic P (Pi) availability was measured in water (Pi-water) and Olsen (Pi-Olsen) extracts and %Pi-water was the proportion of Pi relatively to total P in water extract. Error bars stand for standard error (n = 2). Different letters indicate a significant difference at p < 0.05. Circled data points in chart b identify soils used for the sorption experiments.



Figure 3 Relationships between indicators of phosphorus (P) availability (log transformed) and soil pH in the andosol after 6 or 10 years without fertilization (control) or with the application of mineral or organic P fertilizers. Organic fertilizers were either dairy slurry or compost at low or high dose. Inorganic P (Pi) availability was measured in water (Pi-water) and Olsen (Pi-Olsen) extracts and %Pi-water was the proportion of Pi relative to total P in the water extract. Indicators were corrected by soil total P (P total) to eliminate the influence of the P fertilization rate. Error bars stand for standard error (n = 2). Different letters indicate a significant difference at p < 0.05. Circled data points in chart b identify soils used for the sorption experiments.



Figure 4 Log-log relationships between indicators of phosphorus availability and soil organic carbon in the andosol after 6 or 10 years without fertilization (control) or with the application of mineral or organic P fertilizers. Organic fertilizers were either dairy slurry or compost at low or high dose. Inorganic P (Pi) availability was measured in water (Pi-water) and Olsen (Pi-Olsen) extracts and %Piwater was the proportion of Pi relative to total P in the water extract. Indicators were corrected by soil total P (P total) to eliminate the influence of the P fertilization rate. Error bars stand for standard error (n = 2). Different letters indicate a significant difference at p < 0.05.



Figure 5 Inorganic phosphorus (Pi) sorption curves in the andosol after 10 years without fertilization (control) or with the application of mineral or organic P fertilizers. Organic fertilizers were either dairy slurry or compost at low (Ld) dose and compost at high (Hd) dose (a). The pH of the control soils was also set in the laboratory at 6.0, 6.5, and 6.9 (b). Data points are the mean of two replicates, but the error bars are too small to be visible.



Highlights

A decade of organic fertilizers application increased pH and organic C in soil Increase in organic C and pH induced by organic fertilizers decreased soil P sorption A decade of mineral fertilizer application reduced soil pH which increased P sorption Fertilizers application changed soil P availability by altering soil pH

Journal Proposition