



# Phosphorus-related properties in the profiles of three Italian soils after long-term mineral and manure applications



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## ABSTRACT

The long-term evolution (44 years) of phosphorus (P) in 1-m profile of three reconstructed soils (0–80 cm = sandy, SDY; clay, CLY; and peaty, PTY; 80–100 cm = native layers) typical of the Po Valley (northern Italy) has been studied in a factorial experiment with farmyard manure and mineral fertilizer. Calcium, magnesium, aluminium, and iron concentrations were determined as total ( $Ca_T$ ,  $Mg_T$ ) and pseudo-total ( $Al_{PT}$  and  $Fe_{PT}$ ) amounts and as extractable forms by Mehlich-3 (M3) and ammonium oxalate (Ox) extracting solutions. The P distributions in total P (TP), organic P ( $P_{org}$ ),  $H_2SO_4$  P ( $P_{H_2SO_4}$ ), and the more mobile  $NH_4F$  P ( $P_{NH_4F}$ ) and NaOH P ( $P_{NaOH}$ ) were also measured.

As expected soil type always influenced P sorption related soil properties.  $Ca_{M3}/Ca_T$  ratios indicated the presence of easily dissolved/released Ca in PTY while Al and Fe dominated in CLY and PTY soils as crystalline and poorly crystalline oxides forms. Treatments affected the pseudo-total Al and Fe with higher contents in manure than mineral, whereas mineral induced higher oxalate/total ratios of both Fe and Al than manure and untreated. Treatment affected the P content with a pattern strongly influenced by soil type and depth. Despite the comparable P balance between mineral and manure, P forms were generally higher in amended plots than mineral fertilized. Manure increased  $P_{H_2SO_4}$  down to 50 cm in CLY and down to 80 cm in SDY and PTY. High values of  $P_{NaOH}$  were also induced by manure throughout the 0–80 cm of SDY.

The occurrence of leaching process has been indicated by the general change in some P sorption related properties and P forms found in the native layers. In particular, both stable (i.e. TP) and labile forms (i.e.  $P_{NaOH}$ ) increased following 44 yr of fertilization. The phenomenon occurred not only in the overfertilized SDY but also in CLY and PTY where the P balance was negative. Long-term factors influencing the mobility of P within the soil profile are due not only to excessive P inputs, but also the forms of P fertilizer applied.

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## 1. Introduction

Runoff and erosion have long been recognized as the main phosphorus (P) loss pathways. By contrast some studies showed that P leaching and subsurface transport can also be relevant especially in soil with preferential flow pathways or limited sorption capacity (Withers and Hodgkinson, 2009; Borda et al., 2011; Yan et al., 2013). Turner and Haygarth (2000), for example, observed that subsurface P transport, primarily in the dissolved form, can occur at concentrations that could cause eutrophication.

In Northern-Italy, continued long-term fertilizations have led to available P concentrations in topsoils that exceed those required

for optimal plant growth, thus increasing the potential for P loss to surface and ground water (Pizzeghello et al., 2011). Manure rates, in particular, being designed to meet crop nitrogen requirements resulted conversely in P over-fertilization (McDowell and Sharpley, 2004; Morari et al., 2011). Manure also affects P availability (a) reducing P adsorption through the competition for fixation sites by organic acids, (b) favouring the formation of metal–humates–phosphates complexes (e.g. von Wandruszka, 2006), and (c) decreasing the rate of precipitation of non-soluble calcium (Ca) phosphates (Vu et al., 2010).

Knowledge of the factors affecting transformation of P added to the soil has become essential for long-term planning of fertilization strategies to sustain crop production and minimize the impact on water quality (Valkama et al., 2009). The fate of surplus P fertilizer depends on the transport mechanisms, soil properties (e.g. P sorption sites) and type of fertilizer (Eghball et al., 1996). The movement

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and redistribution of P in the soil profile is important both for plant uptake and the risk of P losses. If P concentrates in the root zone, it can be taken up by plants, but if it is transported to deeper layers the risk increases of P losses through leaching (Börling et al., 2004). Previous studies have shown that P can accumulate in the subsoil up to a depth of 180 cm following long-term fertilization with organic and inorganic P fertilizers (Sharpley et al., 1993; Kingery et al., 1994). Although the movement of P through the soil profile has been shown to be possible, it is not yet known how the source and rate of P will affect the P sorption properties and forms of P that move through the profile. Several authors, studying the P sorption capacity in soil profiles, have obtained contradictory results with both higher and lower P sorption capacity in the subsoil compared to the topsoil as soil properties and amount of sorbent surfaces can change with depth. For example, Mozaffari and Sims (1994) found that soil P capacity, measured either with P sorption isotherms or through a single-point P sorption index, increased with depth, whereas Peltovuori et al. (2002) found a decrease with depth of the P sorption capacity estimated by the extraction of Al and Fe with acid ammonium oxalate solution. Leaching of P to groundwater was considered less of an issue for calcareous soils due to their considerable capacity to adsorb P. James et al. (1996), for example, found that the risk of groundwater P contamination due to manure application was negligible for irrigated calcareous soils in Utah because subsoils were not enriched in total P and had a large capacity to retain P. However, environmentally significant P loss can occur before soils are saturated (Olson et al., 2010).

When P fertilizers are added to soils, they increase soluble P concentration and alter the equilibrium between solid and soluble P. In calcareous soils the transformation of P from soluble to solid phase is controlled by precipitation and sorption reactions (von Wandruszka, 2006). Precipitation of Ca phosphates in calcareous soils is complex (Mackay et al., 1986) and high Ca activity and pH promote the precipitation of non-soluble Ca phosphates (Tunesi et al., 1999). In a previous paper (Pizzeghello et al., 2011) we investigated the phosphorus forms in three soils (sandy, clay and peat) of the Po Valley (northern Italy) evidencing that P forms were affected by both quantity and quality of P input. Nevertheless our analysis considered only the top layer neglecting the effects of P fertilization with depth. The general objective of the present study was to advance our previous work evaluating how some major factors which influence P retention and leaching change within the soil profile according to long-term fertilization practices. In particular, we studied how (a) P chemical forms (P total, organic and associated with Fe and Al, Ca and soil organic surfaces) and some P sorption related soil properties (Ca, Mg, Al and Fe total and extracted with different strength reagents) vary within the 80-cm depth profile of the three reconstructed soils, (b) long-term (44 years) mineral and manure applications affect such parameters, and (c) the properties of the native soil layer (80–100 cm) were influenced by the P leaching processes.

## 2. Materials and methods

### 2.1. Climate

The long-term experiment is located at the Experimental Farm of the University of Padova (Veneto Region, NE Italy 45°21'N; 11°58'E; 6 m a.s.l.). The local climate is sub-humid, with annual rainfall of about 850 mm. In the median year, rainfall is highest in June (100 mm) and October (90 mm) and lowest in the winter months (50–60 mm). Temperatures increase from January (minimum average:  $-1.5^{\circ}\text{C}$ ) to July (maximum average:  $27.2^{\circ}\text{C}$ ). The reference evapotranspiration ( $\text{ET}_0$ ) is 945 mm with a peak in July ( $5\text{ mm day}^{-1}$ ).  $\text{ET}_0$  exceeds rainfall from April to September. The

site has a shallow water table ranging from about 0.5–1.5 m in late winter-early spring to 1–2 m in summer.

### 2.2. Long-term trial

This experiment began in 1964 in 4 m<sup>2</sup> open lysimeters, 80 cm deep. The experimental treatments derive from the factorial combination of three types of soil, hereinafter called sandy (SDY), clay (CLY) and peaty (PTY) in relation to their dominant property, with six types of mineral, organic or mixed fertilization, organized in two randomized blocks with two replicates (36 lysimeters) (Giardini, 2004).

The soils were brought from three locations in the Veneto region: SDY from the central coastal area, CLY from the south-western plain and PTY from the southern plain. The original soil profiles were reconstructed in the lysimeters. SDY (aquic ustipsamment sandy, mixed, mesic—USDA classification, (Soil Survey Staff, 2010; ARPAV, 2005) contains predominantly quartz and feldspar and a significant amount of dolomite (16%). CLY (cumulic, vertic, endoaquoll fine, mixed, calcareous, mesic—ARPAV, 2005) has a higher amount of montmorillonite (16%) than the other soils and a considerable presence of mica (19%) and dolomite (15%). PTY (typic sulfisaprists euc, mesic—ARPAV, 2005) has a higher mica content (25%) and 12% of montmorillonite.

Fertilization treatments considered for this study were as follows: control (UNT); farmyard manure—FYM (40 t ha<sup>-1</sup> y<sup>-1</sup>; N 0.5%, P<sub>2</sub>O<sub>5</sub> 0.25%, K<sub>2</sub>O 0.7% wet wt); mineral fertilizer—MIN (200 kg ha<sup>-1</sup> y<sup>-1</sup> N–100 P<sub>2</sub>O<sub>5</sub>–240 K<sub>2</sub>O). The FYM applied about the same amount of macroelements as MIN and around 3.5–4 t Cha<sup>-1</sup> y<sup>-1</sup>. Until 1984 there was a two-year maize (*Zea mays* L.)–wheat (*Triticum aestivum* L.) rotation. Thereafter, a variable rotation was adopted between 1985 and 1992, with various horticultural crops. From 1993 to 2002 there was a three-year rotation of tomato (*Lycopersicon esculentum* Mill.)–sugarbeet (*Beta vulgaris* L.)–maize, followed by various horticultural crops, maize and sunflower (*Helianthus annuus* L.) from 2003 to 2007. Apart from fertilization, all plots were treated in the same way in terms of rotation and management (tillage, sowing, harvest, etc.). The top 15–20 cm was tilled each autumn and crop residues were removed.

The apparent P balance (difference between P input and P crop removal) in the past 40-yr was negative in CLY (UNT =  $-33.4\text{ kg ha}^{-1}\text{ y}^{-1}$ ; FYM =  $-8.7\text{ kg ha}^{-1}\text{ y}^{-1}$ ;  $-9.8\text{ kg ha}^{-1}\text{ y}^{-1}$  MIN) and PTY (UNT =  $-38.2\text{ kg ha}^{-1}\text{ y}^{-1}$ , FYM =  $-8.4\text{ kg ha}^{-1}\text{ y}^{-1}$ ; MIN =  $-10.2\text{ kg ha}^{-1}\text{ y}^{-1}$ ). Only in SDY organic and mineral input resulted in a P surplus of  $12.1\text{ kg ha}^{-1}\text{ y}^{-1}$  in FYM and  $11.3\text{ kg ha}^{-1}\text{ y}^{-1}$  in MIN while UNT was  $-6.6\text{ kg ha}^{-1}\text{ y}^{-1}$ .

### 2.3. Soil sampling and analysis

Soil samples were collected in April 2008. In each lysimeter, samples were taken with an auger every 10 cm to 1 m depth. Sub-samples were then bulked to obtain a sample of about 0.5 kg per 10-cm layer for each lysimeter. Samples were crushed by rolling pin to break up aggregates, air dried and passed through a 2 mm sieve. The deeper 20-cm layers corresponded to the native soil of the experimental site (for details see Morari et al., 2008).

Soil pH was measured potentiometrically on 1:2.5 soil/water extracts. Organic C (OC) was determined by dry combustion in a CNS Vario Macro elemental analyzer (Elementar, Hanau, Germany) and correcting for the inorganic C. Carbonate content was determined by the calcimeter method. Total (T) content of calcium (Ca<sub>T</sub>) and magnesium (Mg<sub>T</sub>), and pseudo-total (PT) content of aluminium (Al<sub>PT</sub>) and iron (Fe<sub>PT</sub>) in soils were determined by digestion with sulphuric and perchloric acids. A similar approach was used by Beone et al. (2011) who performed an acid hydrolysis without the use of fluoridric acid.

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