Agriculture, Ecosystems and Environment 141 (2011) 58–66

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Phosphorus forms and P-sorption properties in three alkaline soils after long-term mineral and manure applications in north-eastern Italy

Diego Pizzeghello[a], Antonio Berti[a], Serenella Nardi[b], Francesco Morari[a,*]

[a] Dipartimento di Agronomia Ambientale e Produzioni Vegetali, Università di Padova, Agripolis, Viale dell'Università 16, 35020 Legnaro (Padova), Italy
[b] Dipartimento di Biotecnologie Agrarie, Università di Padova, Agripolis, Viale dell'Università 16, 35020 Legnaro (Padova), Italy

ARTICLE INFO

Article history:
Received 14 November 2010
Received in revised form 4 February 2011
Accepted 7 February 2011
Available online 5 March 2011

Keywords:
Phosphorus
Long-term fertilization
Manure
Mehlich-3-P
Carbonate
Degree of saturation

ABSTRACT

In areas of intensive agriculture continuous applications of mineral and organic fertilizers can lead to an accumulation of phosphorus (P) in the soils and progressive saturation of their sorption capacities, increasing the risk of P losses to aquatic ecosystems. The long-term evolution (44 years) of soil P forms has been studied in a factorial experiment combining three soils (sandy, clay and a peaty) with three types of fertilization (no fertilizer, farmyard manure and mineral fertilizer). The P distribution in the calcium P (P_{Ca}), iron P (P_{Fe}), iron + aluminium P (P_{Fe+Al}) forms, and the effect of treatments on P availability (oxalate extractable-P, Mehlich-3-P, Olsen-P, water extractable-P) were determined. Two sorption P indices and the degree of soil saturation were also calculated.

Soil P forms were affected by both quantity and quality of P inputs. Farmyard manure caused a more consistent increase in soil P content, affecting the water soluble and labile P forms (Mehlich-3-P and Olsen-P) in particular. Readily assimilable and potentially mobile P forms were positively correlated with the amount of high molecular weight humic fractions, thus stressing the importance of the type of incorporated materials and their evolution in determining soil P behaviour. Soils treated with farmyard manure, and to a lesser extent with mineral fertilizer, exceeded the threshold values of 20 mg kg^{-1} for Olsen-P and 150 mg kg^{-1} for Mehlich-3-P, thus evidencing a potential risk of P loss to water bodies. While in absolute terms the more consistent accumulations were observed in clay and peaty soils, the P content of sandy soils is of particular concern, given their lower P sorption capacity and higher degree of saturation. Among the soil P tests, Mehlich-3-P proved to be the best indicator to assess Italian soil conditions for both agronomic and environmental purposes.

1. Introduction

In Northern Italy long-term applications of animal manures have resulted in a dramatic accumulation of phosphorus (P) in the soils and progressive saturation of their sorption capacities (Castaldi et al., 2009; Delgado and Scalenghe, 2008), increasing the risk of P losses to aquatic ecosystems (e.g. Djodjic et al., 2004; Vadas et al., 2005; Heredia and Cirilli, 2007).

Indeed, most animal manures contain N:P ratios that are much lower than needed for optimal crop growth. Because N is the limiting nutrient in manures, they have been applied at rates designed to meet crop N requirements resulting conversely in a dramatic P over-fertilization (Morari et al., 2011). As a consequence highly manured soils have less capacity to retain phosphate (Sharpley et al., 2001), posing a higher risk for the environment than soils that received manure rarely or not at all (Brock et al., 2007).

For these reasons, considerable emphasis has recently been placed on quantifying aspects of the soil P cycle to establish a threshold in the P content for environmental rather than agronomic purposes (e.g., Torrent et al., 2007; Hao et al., 2008).

Mobility of P is strongly affected by its reactions with soil constituents. Many attempts have been made to describe the sequence of reactions that leads to phosphate retention in acid soils (Börling et al., 2004a,b; Allen and Mallarino, 2006). In acid soils, P is fixed into slightly soluble forms by precipitation and sorption reactions with Fe and Al compounds as well as crystalline and amorphous colloids. Phosphorus sorption is highly correlated with the clay content and with amorphous Fe and Al oxides content (Börling et al., 2001). Nevertheless, there is limited information on the behaviour and availability of P in alkaline soils, especially those of the calcareous type (von Wandruszka, 2006; Jalali, 2007; Ige et al., 2008). In calcareous soils, surface adsorption and precipitation are major P retention processes depressing the P availability and mobility. For soils rich in carbonates ($CaCO_3$) the P solubility may be controlled by solid phase dicalcium phosphate or by chemisorption of P on calcite, with the formation of a surface complex of calcium

---

* Corresponding author. Tel.: +39 0498272857; fax: +39 0498272839.
E-mail address: francesco.morari@unipd.it (F. Morari).

0167-8809/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.agee.2011.02.011

carbonate-P with a well-defined chemical composition (Samadi and Gilkes, 1999). The dynamics of organic P compounds, their relationships with carbonate minerals and their interactions with soil organic matter dynamics have not received much attention in the past (Cross and Schlesinger, 2001). Significant changes in labile inorganic and organic P associated with the long-term use of organic and mineral fertilizers in calcareous soils have been reported (Colomb et al., 2007; Romanyà and Rovira, 2007; Hao et al., 2008; Vu et al., 2008). However, it was not clear whether changes in P availability led to significant variations in the total pool or were associated with the alteration in P sorption mechanisms resulting from changes in soil chemistry and biological processes (Sharpley, 2003; Zhang et al., 2006; Romanyà and Rovira, 2009).

There have been no studies on the long-term effects of P application on total P and soil P saturation in the Po Valley (Northern Italy). This area is the most extensive plain in Mediterranean Europe, covering an area of 46,000 km^2 and has developed on a calcareous matrix (*i.e.*, more than 50% of the soils have a content of total carbonate >10%) derived from dolomitic parent material. The area includes the majority of Italian livestock rearing activities. Understanding the transformations and distributions of various P forms in calcareous soils receiving continuous manure is essential in order to develop appropriate P management strategies for sustainable agricultural production and environmental protection.

The main starting hypotheses of this paper are that (a) the N-based fertilization regimes used in Northern Italy have led to P saturation conditions in the soils, (b) the type of fertilizer plays a pivotal role in influencing the mobility, availability and saturation of P in alkaline soils, and (c) the Olsen method (Olsen and Sommers, 1982), which has been extensively used in Italy to test the available soil P content, gives only a partial evaluation of the associated environmental risks.

The objectives of our study were to determine in a long-term experiment (44 years) how P distributes across the different chemical forms in three alkaline soils of the Po Valley and the long-term effects of mineral and manure applications on P availability and saturation. A secondary objective was to test different soil P test methods for environmental purposes.

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 °C) to July (maximum average: 27.2 °C). The reference evapotranspiration (ET$_o$) is 945 mm with a peak in July (5 mm/day). ET$_o$ 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

The experiment began in 1964 in 4 m^2 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 (Table 1), with six types of mineral, organic or mixed fertilization, organized in two randomized blocks (36 lysimeters) (Giardini, 2004).

Table 1
Main physical and chemical characteristics of the top layer (0–20 cm) at the beginning of the experiment (1964).

Parameters	Clay	Sand	Peaty
Sand (2 mm to 50 μm) (g kg^{-1})	250	934	380
Silt (50–2 μm) (g kg^{-1})	230	60	136
Clay (<2 μm) (g kg^{-1})	520	6	484
pH	7.9	8.1	4.9
$CaCO_3$ (g kg^{-1})	26	139	0
OC (%)	1.45	0.17	10.5
N (%)	0.15	0.01	0.67
C/N	10	12	16

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 – US classification (SSS, 1998; 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 montmorrilonite content (16%) than the other soils and considerable amounts of mica (19%) and dolomite (15%). PTY (typic sulfisaprists euic, mesic–ARPAV, 2005) has a higher mica content (25%) and 12% of montmorrilonite.

Fertilization treatments considered for this study were as follows: control (UNT); farmyard manure – FYM (40 t ha^{-1} y^{-1}); mineral fertilizer – MIN (200 kg ha^{-1} y^{-1} N – 100 P_2O_5 – 240 K_2O). The FYM applied about the same amount of macroelements as MIN and around 3.5–4 t C ha^{-1} y^{-1}. 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 dug each autumn and crop residues were removed.

2.3. Soil sampling and analysis

In April 2008, samples from the 0 to 20 cm depth were taken from five points and bulked to obtain a sample of about 3 kg per plot. The samples were crushed by rolling pin to break up clods and pass a 2 mm sieve, air dried and stored at low humidity.

Soil pH was measured potentiometrically on 1:2.5 soil/water extracts. Organic C 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 and by gravimetric loss of CO_2. Total aluminium (Al_T), calcium (Ca_T), magnesium (Mg_T) and iron (Fe_T) concentrations were determined after digestion with concentrated sulphuric and perchloric acids. Extractable aluminium (Al), calcium (Ca), magnesium (Mg) and iron (Fe) were determined by Mehlich-3 (M3) solutions (Mallarino and Sawyer, 1999; Setter et al., 2009) and limited to Al and Fe plus ammonium oxalate (Ox) (Schwertmann, 1964). The metals in the extracts were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a SPECTRO CIROS (Spectro Analytical Instruments, Kleve, Germany). Total P (TP) was determined by two methods: perchloric acid digestion (TPp) (Sparks et al., 1996), and ignition and HCl extraction (TPi) (Chaya, 1996). For perchloric acid digestion, 0.5 g of soil were treated with concentrated H_2SO_4 (6.25 mL) and $HClO_4$ (1.25 mL), and digested at 150 °C. After cooling, the mixture was diluted with