



Phosphorus stocks and speciation in soil profiles of a long-term fertilizer experiment: Evidence from sequential fractionation, P K-edge XANES, and ^{31}P NMR spectroscopy

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ABSTRACT

Agricultural productivity depends on the use of phosphorus (P) of which not only the topsoil, but also the subsoil, can hold immense stocks. To assess their importance for plant nutrition, we compared the P status of Stagnic Cambisol profiles in experimental plots that received different P fertilizer applications for 16 years. Sequential fractionation was combined with P K-edge X-ray absorption near edge structure (XANES) spectroscopy and liquid ^{31}P nuclear magnetic resonance (NMR) spectroscopy to identify the chemical P speciation. Fertilized topsoils showed P stocks larger by a factor of 1.2 to 1.4, and subsoil stocks larger by a factor of 1.3 to 1.5 than the control. P-XANES revealed the predominance of mainly inorganic P species, such as moderately labile Fe- (46 to 92%), Al- (0 to 40%) and Ca- (0 to 21%) P compounds besides organic P (0 to 12%). This was supported by ^{31}P NMR with decreasing proportions of orthophosphate monoesters from topsoil (20 to 28%) towards the second subsoil layer (7 to 13%). In summary, fertilizer application maintained or increased P stocks but only slightly altered the P speciation throughout the profiles. The kind of fertilizers had no significant effect on soil P, only affecting the inorganic P pools. Our findings proved that subsoil P stocks are potentially important contributors to plant nutrition, but their accessibility must be assessed for improved soil P tests and reduced fertilizer recommendations.

1. Introduction

Phosphorus (P) plays a key role in agricultural productivity (Cordell et al., 2009), and seems to be a future constraint in agricultural systems (Gilbert, 2009). The arising uncertainties and ongoing discussions about unevenly distributed, and above all finite, P rock reserves are summarized by Baveye (2015). For future agriculture, a more sufficient (not more than required) and efficient (higher yields per P applied) use of P is necessary, whereas also alternative ways of P supply must be developed (Kruse et al., 2015). In this respect, the unexploited subsoil P reserves deserve special attention. Actual P stocks in soil profiles vary between 1200 and 30,000 kg P ha⁻¹ (Stevenson and Cole, 1999), and in particular European agricultural important soils seem to have an

high P supply due to high and excessive P fertilizer applications in the past (Smil, 2002; Tunney et al., 2003; Sattari et al., 2012; Tóth et al., 2014). So far the fate of surplus fertilizer P in soil is not known for all important agricultural soils in central and northern Europe. It is well established that some of the surplus P ends up in aquatic systems (Smith and Schindler, 2009) but processes of intermediate binding and remobilization in soil profiles, depending on different fertilization strategies, are far from being understood. Fertilizer P is mainly associated to silicate clay minerals, Al- and Fe-(hydro)oxides, Ca-carbonates, humic substances, or in the soil biomass shortly after application (e.g. Sattari et al., 2012; Tóth et al., 2014; Kruse et al., 2015; Eriksson et al., 2016). Various studies investigated and compared the effects of organic and inorganic P fertilization on the P status and P availability in soils

Abbreviations: DPS, Degree of phosphorus saturation; IHP, Inositol hexakisphosphate; NMR, Nuclear magnetic resonance spectroscopy; PSC, Phosphorus sorption capacity; TSP, Triple superphosphate; XANES, X-ray absorption near edge structure spectroscopy

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(Fuentes et al., 2008). A few studies indicated that fertilizer application had no effect on P speciation (e.g., Friesen and Blair, 1988; Wang et al., 2007; Requejo and Eichler-Löbermann, 2014) whereas others found that the application of organic P (P_o) fertilizers (such as compost or manure), compared to mineral P fertilizers, improved the P utilization in soils (e.g., Hue et al., 1994; Bah et al., 2006; Pizzeghello et al., 2011; Yan et al., 2013). Although many studies delivered valuable insights to P fertilizer effects in the topsoils, they totally omitted the subsoil below the plough horizon. Beside the P rich agricultural topsoils, also the subsoils hold immense P reserves, which account for 25% up to 70% of total P (P_{tot}) in the soil profile (Godlinski et al., 2004; Kautz et al., 2012; Barej et al., 2014). Current estimates indicated that the plants acquire 10 to 50% (Kautz et al., 2012), in extreme cases even up to 80% of their P_{tot} supply from the subsoil when the topsoil P supply is decreased (Kuhlmann and Baumgartel, 1991). However, Kautz et al. (2012) summarized that only rare and divisive information about plant-accessible and plant-available subsoil P exist because its distribution and speciation were not yet assessed widely. Disclosing the role of subsoil as P reservoir for crop plants requires a detailed chemical speciation of abundant soil P components by state-of-the-art methods (Liu, J. et al., 2013; Kruse et al., 2015). The commonly applied sequential P fractionation approach developed by Hedley et al. (1982) is used to differentiate labile, increasingly stable, and stable organic and inorganic P fractions in soils (e.g., Bühler et al., 2002; Kruse et al., 2010; Alamgir and Marschner, 2013; Siebers et al., 2013). Limitations arise from inconsistencies about carryover or neutralization reactions between the successive P fractionation steps as well as the nature and quality of the Residual-P, which massively depends on the previous extraction steps as critically discussed by Condon and Newman (2011). Therefore, complementary spectroscopic techniques are applied to obtain an overview about the P speciation in environmental samples. Phosphorus K-edge X-ray absorption near edge structure (XANES) spectroscopy is an element-specific and non-invasive direct P speciation method for identifying P species in complex soil matrices (e.g., Ajiboye et al., 2008; Eriksson et al., 2015; Kruse et al., 2015). Solution ^{31}P liquid nuclear magnetic resonance (^{31}P NMR) spectroscopy, first applied to soil research by Newman and Tate (1980), enables the identification and speciation of P_o classes such as orthophosphate monoesters and diesters (Turner et al., 2005; Doolette and Smernik, 2011; Ahlgren et al., 2013). However, this method is unsuitable for identification of inorganic P (P_i) species associated with the soil particles and requires an extraction step before analysis altering the sample probe (Cade-Menun and Liu, 2013). Complementary studies with the above mentioned techniques facilitate a substantiated characterization of P speciation and precise quantification of predominant P species in agriculturally used soils on the molecular scale (e.g., Kizewski et al., 2011; Kruse et al., 2015; Liu et al., 2015). Such an approach has been firstly applied in a study by Liu, J. et al. (2013), but have not yet been applied for the investigation of fertilizer effects on the P status in whole soil profiles in long-term fertilizer experiments. Therefore we would like to answer the following research questions in the present study: What is the difference between the P stocks and the P speciation of the topsoil (0 to 30 cm) and the underlying subsoil (30 to 60 cm, and 60 to 90 cm)? Which impact has long-term application of different fertilizer on the P stocks and P speciation in the topsoil compared to the subsoil? Is there a P reservoir in the subsoil, which can be utilized by the plants? Therefore, our objectives were to (i) estimate if different long term P fertilizer applications altered the soil P stocks within the soil profile, (ii) evaluate the P dynamics and differences in P speciation under different P fertilizer treatments, and (iii) evaluate whether subsoil P stocks accumulated from long-term fertilizer applications can contribute to a more efficient and sufficient P plant supply. Consequently, the availability of predominant inorganic and organic P species in top- and subsoils up to 90 cm depths from a long-term fertilizer treatment were studied and related to the potential use efficiency of plants. We hypothesize that fertilizer P inputs sustained or increased P distributions in the whole

soil profile and with that also the speciation of soil P affecting P bioavailability.

2. Material and methods

2.1. Soil sampling and basic characteristics

Soil samples were collected from an agricultural long-term experimental site (54° 3′ 41.47″ N; 12° 5′ 5.59″ E) at the University of Rostock, Germany, which was established in 1998. The soil is classified as a non-calcareous soil, predominantly a Stagnic Cambisol according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015). A full description of the experimental design and soil characteristics were published by Requejo and Eichler-Löbermann (2014). For the present study soil samples were taken at the end of April 2015 from four different fertilization treatments: control with no P fertilization, compost (in total 378 kg P ha⁻¹ within 16 years; mainly green waste from a composting plant near Rostock), triple superphosphate (TSP) (in total 393 kg P ha⁻¹ within 16 years), and a combination of compost and TSP (compost + TSP) (in total 771 kg P ha⁻¹ within 16 years). Fertilization with compost was triennial at a level of 69 kg P ha⁻¹, while TSP was applied annually. The N:P ratio in the compost was between 3 and 5.6 from the start of the experiment in 1998 till the last triennial fertilizer application in 2016. To avoid soil nutrient imbalances, soil N was monitored by mineral N measurements and if needed an additional mineral fertilizer application was performed. Application concentrations were according to the plant need under consideration of the mineral N concentration in soil in spring (before the vegetation period). However, the differences between mineral N concentrations in soil between the treatment were low (Table 1). Maize was grown at the various plots before and after soil sampling. For each treatment three replicate plots were sampled. At each replicate plot, soil samples were taken at three randomly selected spots and three depths, namely 0 to 30 cm (topsoil), 30 to 60 cm (subsoil1), and 60 to 90 cm (subsoil2) using an auger with 4 cm diameter. Afterwards, samples from the same depth interval of each plot were compiled into a homogenous composite sample. The bulk densities of the samples were calculated for each depth by multiplying soil dry weights (g) after drying at 105 °C and the auger volumes (cm³) at certain sampling depths with a factor of 0.01.

The soil samples were air-dried and ground to pass through a 2 mm sieve. Soil texture was determined after chemical disaggregation (H_2O_2 , $\text{Na}_4\text{P}_2\text{O}_7$) by wet-sieving (2 to 0.063 mm) and automated sedimentation analysis (Sedimat 4–12, UGT GmbH, Müncheberg, Germany) according to Köhn (DIN ISO 11277) (< 63 μm to 2 μm silt, < 2 μm clay). Soil pH (0.01 M CaCl_2) was measured according to Godlinski et al. (2004). Soil C and N analyses were done using dry combustion followed by heat conductivity detection of the released trace gases (vario MICRO cube, Elementar, Hanau, Germany). Total elemental concentrations of P from bulk soil (P_{tot}), iron (Fe_{tot}), aluminum (Al_{tot}), manganese (Mn_{tot}), magnesium (Mg_{tot}), potassium (K_{tot}), calcium (Ca_{tot}), and sodium (Na_{tot}) were determined after microwave-assisted digestion of 150 mg with 0.7 mL HNO_3 and 2 mL HCl using an inductively coupled plasma-optical emission spectroscopy (ICP-OES; Thermo Fisher iCAP™ 7600). Total elemental stocks were calculated for every sampling depth with the certain bulk density. Ammonium oxalate extractable phosphorus (P_{ox}), aluminum (Al_{ox}), iron (Fe_{ox}), and manganese (Mn_{ox}) were determined by extraction with 0.2 M ammonium oxalate and 0.2 M oxalic acid (pH 3.1) for 2 h in the dark (Schwertmann, 1964) and elemental analyses by ICP-OES. The P sorption capacity (PSC) and the degree of P saturation (DPS) were calculated according to Eckhardt and Leinweber (1997). The total concentration of organic P ($P_{o,tot}$) was estimated by subtraction of the total concentration of inorganic P ($P_{i,tot}$) from P_{tot} .

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