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Ecologically relevant phosphorus pools in soils and their dynamics: The story so far^{\bigstar}

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ARTICLE INFO ABSTRACT Handling Editor: Junhong Bai There has been much soil phosphorus (P) research in the last decades, but few basic publications exist summarizing the current state of knowledge on ecologically relevant P forms and their reactions in soils. The present Keywords. paper aims at giving such a literature overview. The major P forms occurring in soils are presented. Organic P Soil phosphorus results from biogenic processes when organisms take up P from the soil. After their death, this P is returned into Organic phosphorus Inorganic phosphorus the soil and has to be mineralized before the next uptake. Mineralization intensity depends on the concentration Dissolved phosphorus of dissolved inorganic P in the soil solution. Only this soil P fraction can be taken up by plants and microorganisms Sorbed phosphorus and enter the food chain. Thus, it is critical for ecosystem nutrition. Dissolved P is highly affine for binding to the Mineral phosphorus soil matrix and strives for equilibrium with bonded P forms. On the one hand, there is sorbed P, regularly forming quickly and being easily exchanged back into the soil solution. Sorbed P strongly depends on which and how many sorption sites a soil offers. Some of these sites are not easily accessible. Thus, P needs time to be sorbed there and is slightly soluble afterwards. This fraction is termed "occluded P". It is considered fixed and not bioavailable for long times. On the other hand, there is mineral P, resulting from the precipitation of P anions and metal cations when the soil solution is oversaturated with these ions. The stability of mineral P depends on its degree of order, amorphous phases being less stable than highly crystalline minerals. Organic, sorbed and mineral P are tightly interconnected with dissolved P and strive for equilibrium with it. Due to changes in temperature, precipitation and vegetation/edaphic patterns such equilibrium is hardly attained and soil P reactions must dynamically adjust to present conditions.

1. Introduction

The global supplies of raw materials for high-grade phosphorus (P) fertilizers are growing shorter. According to some scenarios, they might run out within the current century (Cordell and White, 2013, 2011). This is supposed to cause widespread famine and hunger-related mortality as well as severe geo-political issues (Cordell and White, 2013; Vaccari, 2011; Blume et al., 2010; Syers et al., 2008). Becoming more and more aware of that so-called "P crisis" (Abelson, 1999), research on P and its dynamics in soils was spurred within the last decades (Lal, 2017; Delgado and Scalenghe, 2008). Soils are the bottleneck of the P cycle where the element is converted into phosphate and can thus enter the food chain (Kruse et al., 2015; Finck, 2007). Hence, understanding P dynamics in soils is indispensable for developing efficient and environmentally friendly P management strategies as well as feasible P conservation measures in agriculture and economy.

There has been much soil P research in the last decades, adding bits and pieces to our understanding of environmentally relevant P forms and their reactions in soils. Loads of scientific papers and articles were published, differing in quantity, conceptual and methodological approach, results and, sometimes, even in quality. Still, up-to-date basic works of soil scientific P research are rare. There are only few books and other longer publications summarizing what happens to P in soils (e.g. Lal and Stewart, 2017; Bünemann et al., 2011; Turner et al., 2004; VanWazer, 1958).

In a literature survey on "Geoderma", 242 soil scientific P research papers were identified between January 1990 and October 2016. Only six of these (equal to 2.5%) are review papers. Hence, on average, review papers were published once every four years, arithmetically. In the same time, by mean 39 regular (i. e. empirical) research papers were published. Thus, entering the field of soil scientific P research is time-consuming and requires more extensive literature enquiry than is needed for many other topics. This is especially true, when literature enquiry is focused on ecologically relevant, not on operationally defined P fractions.

The methods we use in soil science to detect and measure P in soil

* Note: The present paper is a revised English version of Chapter 3 "Phosphor im Boden" from Weihrauch (2018, in press). * Corresponding author.

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Fig. 1. Major P fractions and their interrelations in soils (according to Syers et al., 2008; after Weihrauch 2018, Fig. 16, extended and translated). Inorganic P is conceptually divided into five pools forming a increasing solubility (0 = mobile orthophosphate ions; 1 = labile, easily soluble, 2 = moderately labile and soluble, 3 = stable, slightly soluble, 4 = "fixed", least soluble P compounds). Pools 1-4 comprise sorbed and mineral P forms. Next to organism uptake and translocation (e.g. leaching), a soil's P content can also be diminished by erosion, which could affect all the P fractions likewise, but is not shown in the graphic.

samples "[...] give us some understanding of the chemical nature of the soil P" (Condron and Newman, 2011:838), but they are in fact somewhat arbitrary and artificial. They are e.g. based on the application of certain pretreatments, chemicals in certain concentrations with a special timetable or using special machines and procedural routines. As a consequence, the P forms extracted and detected by these specific methods mostly rather reflect the methodological background, e.g. the chemical solubility of P in certain reagents (Margenot et al., 2017; Galván-Tejada et al., 2014; Negassa and Leinweber, 2009). Yet, they often poorly represent the ecological relevance (e.g. the bioavailability) of the P species in soils and their dynamics in the environment (Condron and Newman, 2011; Turner et al., 2005). Thus, some authors called for a paradigm shift from applying operationally defined P fractions to rather using environmentally functional P fractions (Kruse et al., 2015). Therefore, the present review article aims at giving a summary of the current state of research on the ecologically relevant P fractions in soils and the reactions they undergo. Because of this focus, we do not treat the methodology of P science in the present paper. Nevertheless, methods are the base of our empirical approaches and should thus not be neglected. The interested reader might therefore find extensive and useful information on P detection methods in the review articles by Kruse et al. (2015), Condron and Newman (2011), Negassa and Leinweber (2009), Turner et al. (2005) and Cross and Schlesinger (1995). These could be used as a starting point for further literature enquiry.

2. Ecologically relevant P forms in soils

On average, soils have a C:N:P ratio of 186:13:1 (Cleveland and Liptzin, 2007, after Reed and Wood, 2017). Thus, P is far less abundant than the other macronutrients. In unfertilized soils, P largely stems from bedrock and is set free by weathering (Pecoroni et al., 2014; Scheffer, 2002). Moreover, texture, developmental stage and age strongly influence a soil's P content. Old sandy and strongly weathered soils are generally poor in P (< 100 mg P/kg of soil; e.g. old Podzols in the Temperate Zones, Ferralsols, Plinthosols, Acrisols, Vertisols in the tropics and subtropics). Younger soils developed from basalt or volcanic ashes (e.g. Andosols) are instead often rich in P (> 1000 mg P/kg of soil; Blume et al., 2010). Even greater amounts can be found in organic soils (> 2000-3000 mg P/kg of soil; Prietzel et al., 2016; Amberger,

1996). Very high P contents of > 8000 mg P/kg of soil were recorded in fertilized grassland soils in Northern Germany (Leinweber, 1996), but are mostly site-specific.

In the present text, we use "P" as a simplification. Yet, soils do generally not contain elemental P, but orthophosphate (H₂PO₄⁻, HPO_4^{2-} , PO_4^{3-}) that is dissolved in the soil solution or bound to soil particles and organic substances (Prasad et al. 2017b; Blume et al., 2010; Emsley, 2000). Orthophosphates are the salts of phosphoric acid (H_3PO_4) , where a small central P^{5+} -ion builds a tetraeder with four bigger O^{2-} -ions. The remaining three negative charges are equalized by H⁺-protons (Scheffer, 2002).

There are many different orthophosphates in soils. In the present text, they are first distinguished by their general chemical association into organic and inorganic P. Organic P (Porg) is contained in biogenically produced compounds with C-H-bonds. Inorganic P (Pinorg) compounds do instead not necessarily result from organisms' life processes (e.g. minerals; Nguyen et al., 2017; Prasad et al., 2017a; Pecoroni et al., 2014; Sharpley and Rekolainen, 1997).

In soils, Porg and Pinorg occur in forms of comparable solubility. Still, Pinorg undergoes different processes than Porg (Gerke, 2015). Porg is controlled by biological constraints (e.g. urge for nutrients), P_{inorg} instead by the striving for chemical equilibrium. Thus, both fractions build separate continua at the left- and right-hand side of Fig. 1. Because the dynamics of P_{inorg} dominated the scientific history of soil P research (Condron and Newman, 2011), there is considerably more information on this P fraction in the literature. Thus, ecologically relevant inorganic P forms are treated more extensively in the present paper.

The structure of the text and the organization of Fig. 1 are furthermore shaped according to whether P is found in the soil solution or bound to the soil matrix. The first group of P forms is central for ecosystem nutrition and is prone to be lost from soils due to its high spatial mobility. Thus, P forms in the soil solution form the center of Fig. 1. They are flanked by the ecologically relevant P_{org} and P_{inorg} forms bound to the soil matrix. In the text, these general P fractions are presented according to their position in Fig. 1 from left to right. Thus, Porg forms bound to the soil matrix (Section 2.1) are outlined before the P forms within the soil solution (Section 2.2). Then, matrix-bound Pinorg is presented (Section 2.3). It is further distinguished by the general processes of P_{inorg} formation into sorbed (Section 2.3.1) and Download English Version:

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