

Phosphorus Use Efficiency of Bio-Based Fertilizers: Bioavailability and Fractionation



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ABSTRACT

Although to date some technologies producing bio-based phosphorus (P) fertilizers have been proposed and implemented, the efficient use of the recovered products is still limited due to legislative constraints and lack of insights in the P release with time and in the corresponding mechanisms. The aim of this work was to evaluate the fertilizer performance in terms of P release and use efficiency of recovered struvite, FePO₄-sludge, digestate, and animal manure as compared to fossil reserve-based mineral triple superphosphate (TSP). First, product physicochemical characteristics and P fractions in the context of European fertilizer legislation were assessed. Next, a controlled greenhouse experiment was set up to evaluate plant reactions as well as changes of P availability in a sandy soil with high P status and a Rheinsand soil with low P status. Soil P fractions were determined in the extracts with water, ammonium lactate and CaCl₂, and in soil solution sampled with Rhizon soil moisture samplers. Based on all results, it is worth conducting long-term field trials to evaluate the P release effect of struvite and digestate as compared to animal manure and TSP on different soil types with varying P status. These products showed promise as sustainable substitutes for conventional P fertilizers and could contribute to a more efficient use of P in agriculture. A refined classification of P application standards/recommendations in terms of soil P status, soil texture, and fertilizer characteristics, next to the crop P demand, is recommended. Moreover, the additional use of Rhizon samplers for determination of direct available P, including dissolved organic P, is proposed for better understanding and categorization of different P fertilizers in environmental and fertilizer legislations.

Key Words: chemical soil analysis, digestate, nutrient recovery, Rhizon samplers, struvite

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The rapid and increasing phosphorus (P) consumption in modern agriculture has raised concerns on both its supply security (Godfray *et al.*, 2010; Elser and Bennett, 2011; Neset and Cordell, 2012; Scholz and Wellmer, 2013) and its impact on the environment (soil P accumulation, leaching, and/or eutrophication) (Syers *et al.*, 2008; Kang *et al.*, 2011; Ranatunga *et al.*, 2013). Consequently, the effective use of soil P and P-containing mineral and organic fertilizers, as well as the cradle-to-cradle recycling of P from municipal, agricultural, and other biodegradable waste sources as green renewable fertilizers with high P use efficiency (*e.g.*, slow-release granules), has become highly important (Syers *et al.*, 2008; Ma *et al.*, 2011; Schröder *et al.*, 2011; Huang *et al.*, 2012; Zhang *et al.*, 2013).

Traditional P removal processes from waste(water) streams often involve the addition of Fe or Al salts, resulting in the production of substantial quantities

of Fe/AlPO₄-sludge (Sano *et al.*, 2012). Alternatively, in the past decades, the controlled precipitation of struvite (MgNH₄PO₄·6H₂O) through addition of Mg to waste flow has gained interest as a route for P recovery (Latifian *et al.*, 2012; Ryu *et al.*, 2012). Moreover, the anaerobic (co-)digestion of animal manure, sludges, organic biological food waste, and/or energy crops has proven to be an effective technology for bio-energy production and release/mineralization of nutrients, which are concentrated in the remaining digestate (Fehrenbach *et al.*, 2008). During a preceding field-scale assessment, it has been observed that the use of a formulated mixture of digestate with its liquid fraction in agriculture as a substitute for animal manure may stimulate P mobilization in the soil, thereby increasing the use efficiency of soil minerals (to be confirmed) (Vaneeckhaute *et al.*, 2013, 2014). Especially in P saturated regions (*e.g.*, Flanders, Quebec, eastern China, Italy,

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northern Spain, *etc.*; MacDonald *et al.*, 2011), the extraction of P from agricultural fields is relevant for local reuse (*e.g.*, in the horticultural sector or for plants with high P demand) and/or for industrial purposes. On the other hand, although the use of liquid digestate, with high effective N:P ratio, is interesting in terms of current legislative fertilization standards, its supply of plant-available P may be insufficient, depending on crop P demand and soil P status. Hence, additional fertilization with a source of bioavailable P may be required.

It must be understood that only a small proportion (15%–20%) of the total amount of P uptake in the plant ($\pm 2.5 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1} \text{ d}^{-1}$; EFMA, 2000) is directly provided by the fertilizer applied to that crop. The remainder comes from soil reserves. Hence, there must be adequate reserves of readily available P in the soil (Syers *et al.*, 2008). The P status of European soils has been estimated by EFMA (2000). For many countries, about 25% (5%–55%) of soils test as very low and low in readily available P. Such soils require significantly more P application to increase soil reserves and thus soil fertility. On the other hand, in many countries, some 40% (15%–70%) of soils test as high and very high in readily available P. On such soils, when growing the crops that have small, inefficient root systems, but a large daily uptake of P at critical growth stages, it may be necessary to apply more P. On soils with a medium P analysis value, applications need to sustain the P status. This may require a small extra amount of P on top of that removed with the harvested crop (EFMA, 2000).

All the above clearly indicates the relevance of fundamental comparative research on the P release pattern over time of potential sustainable alternatives for chemical P fertilizers produced from natural and exhaustive phosphate rock and/or for animal manure (products with improved P use efficiency). Such an evaluation is essential to determine the agricultural potential of new fertilizers and their responsible application (Erro *et al.*, 2011). Yet, such studies are currently lacking in literature for the above-mentioned bio-based products (struvite, digestate, Fe/AlPO₄-sludge), although their production and availability is on the rise (Vaneckhaute, 2015).

The performance of a fertilizer can be evaluated *via* product fractionation, plant reaction analysis, and/or chemical soil analysis (Sissingh, 1971; Prummel and Sissingh, 1983; Singh *et al.*, 2005; Dekker and Postma, 2008; van Dam and Ehlert, 2008; Millier and Hooda, 2011; Wang *et al.*, 2013). P fractionation of fertilizers is, in general, based on the P solubility in sol-

vents with different strength and selectivity (Frossard *et al.*, 2002; He *et al.*, 2004, 2007). With respect to European legislation, the most important solvents are, ranked from strong to weak: i) mineral acid, ii) neutral ammonium citrate (NAC) solution, and iii) water (EU, 2003). Next to the P solubility, the fertilizer performance is usually expressed as bioavailability indices, such as P use efficiency (PUE). It can be based on the fresh weight (FW) and dry weight (DW) biomass yield, the growth rate, the P uptake (rate), and the degree and rate in which the P status of the soil changes, as determined by chemical methods (van Dam and Ehlert, 2008). Previous studies have shown that the crop response to P fertilization gives insufficient guidance to determine the fertilizer performance (no correlation), while chemical soil analyses can be conclusive (Prummel and Sissingh, 1983; Árendás and Csathó, 2002; van Dam and Ehlert, 2008). Therefore, most studies evaluating P fertilizers to date are based on soil bioavailability indices. Soil measurements can be divided into P capacity and P intensity of the soil, based on the strength of the extraction method. The P intensity gives an indication of the total amount of inorganic P which is directly available for the plant during a short period of time, while the P capacity gives an indication of the amount of P that may be released in the long term (Dekker and Postma, 2008).

In some countries, *e.g.*, the Netherlands, Switzerland, and Norway, fertilizer recommendations are based on the P status of the soil, measured as the ammonium lactate- and water-extractable P (P_{AL} and P_{water} , respectively). The P_{AL} value is a measure of soil P capacity, whereas the P_{water} value reflects a combination of soil P capacity and intensity. In the latest decade, the method of plant-available elements (PAE) has also received increased attention. It concerns a multi-element extraction with $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$, and hence provides a simple alternative for many extraction procedures that are currently used for single nutrient (van Erp *et al.*, 1998; Houba *et al.*, 2000; Ehlert *et al.*, 2006). With respect to CaCl_2 -extractable P (P_{CaCl_2}), this measurement gives an indication of soil P intensity (Houba *et al.*, 2000). An important limitation of all these standard methods is that root formation, soil compaction, and mineralization of organic matter are not or not sufficiently accounted for (Ehlert *et al.*, 2006; Soine, 2009; Amoakwah *et al.*, 2013). Underestimations have been observed in literature, especially for the determination of direct available P (Amoakwah *et al.*, 2013; Sánchez-Alcalá *et al.*, 2014). Alternatively, the use of Rhizon soil moisture samplers (SMS) allows assessing the total amount of P

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