







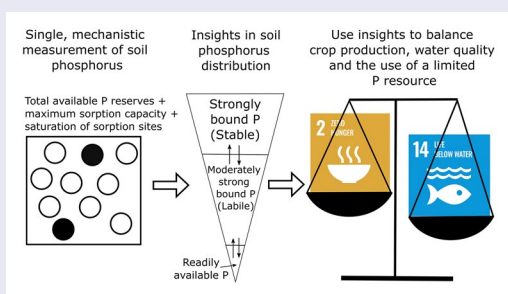
The phosphorus saturation degree as a universal agronomic and environmental soil P test

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ABSTRACT

Phosphorus (P) is an essential nutrient for crops and is applied to agricultural soil to bring or keep the soil at a certain target soil P status in view of an optimal crop yield. Environmental objectives, however, are rarely considered in current P fertilizer recommendations. In this review paper, we argue that current P fertilizer recommendations must be revised in order to balance crop yield, water quality and the use of finite P resources. This revision requires insights into the total pool of reversibly bound P and the capacity of the soil to bind P. Current soil P tests (SPTs) used in routine agronomic soil testing do not provide these insights. We identify the oxalate extraction method as a high-potential agri-environmental SPT as it measures the total pool of reversibly bound P acting as a reserve for plant-available P while it also quantifies the maximum soil P sorption capacity from the simultaneous measurement of amorphous iron- and aluminium-(hydr)oxides. From these results, the Phosphorus Saturation Degree (PSD) can be calculated. We show that those insights are pivotal for the combined assessment of crop response, the risk of P losses to the water system and the judicious use of finite P reserves. In practice, agronomic target P levels should be lowered in soils with a low P sorption capacity to decrease the risk of P leaching. Agronomic target levels should also be lowered in soils with a high P sorption capacity to ensure a judicious use of finite P reserves.




KEYWORDS Phosphorus saturation degree; phosphorus sorption capacity; sustainable phosphorus use; water quality; legacy phosphorus; oxalate

HANDLING EDITORS Amit Bhatnagar and Lena Q. Ma

1. Introduction

Phosphorus (P) is an essential nutrient for crop production and is applied to agricultural soils to overcome crop P deficiency and to maintain the soil P status at an agronomically sufficient level. However, a historical excess of P fertilization - especially in regions with

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intensive animal husbandry - has led to so-called “P-saturated” or “legacy P” soils (Condon et al., 2013; Li et al., 2011; McDowell et al., 2020; Pavinato et al., 2020; Sattari et al., 2012; Sharpley et al., 2013). In those regions, soil P accumulation has led to elevated risks of eutrophication due to substantial P losses from soils to surface waters through subsurface flow and surface runoff of dissolved P forms and erosion of soil-bound P (Garnier et al., 2015; Powers et al., 2016; Qin & Shober, 2018; Sharpley et al., 2013). On a global scale different studies (Carpenter & Bennett, 2011; Springmann et al., 2018; Steffen et al., 2015) show that the planetary boundary for P losses from agricultural soils through surface runoff and erosion has been crossed due to freshwater eutrophication and enhanced P discharge to the oceans. In addition, global rock phosphate reserves are depleting (Alewell et al., 2020; Cordell et al., 2009; Ros et al., 2020; Sattari et al., 2012). Considering the P-induced environmental impacts and limitation of rock phosphate reserves, it is key to use P in agricultural systems more sustainably (Foley et al., 2011).

To boost the sustainability of P use in agriculture, there is a pressing need to re-assess the rationale behind current fertilization recommendations. These recommendations are based on agronomic soil P testing that represent a certain available soil P pool and allow an economic optimization of crop yield versus P inputs as a function of soil P level. To make them more sustainable, a soil P test (SPT) is required which provides insights for both agronomic and environmental objectives (Khiari et al., 2000; Kleinman, 2017; Kristoffersen et al., 2020; Sims et al., 2002).

The objective of this paper is to assess which measurable insights into the soil system are required to combine agronomic and environmental objectives in P fertilizer recommendations. We substantiate why the 0.2M acid oxalate extraction method of Schwertmann (1964) has the highest potential to be used for an agri-environmental SPT. The most notable advantage of this method is that it combines insights into the quantity of the total available pool of reversibly bound P (P_{OX}), the maximum P sorption capacity (PSC, in the form of amorphous Fe- and Al-(hydr)oxides) and hence the extent to which soil sorption sites are saturated with P, i.e., the so-called Phosphorus Saturation Degree (PSD) (van der Zee et al., 1987). We aim to show that these mechanistic insights are pivotal to derive measures boosting a more sustainable P use in agriculture. The outcome is a framework to derive a P plant nutrition optimum for both agronomic and environmental objectives.

In this paper, we first discuss the need to revisit current P fertilizer recommendations and the role of SPTs in routine agronomic soil testing (Chapter 2). We then critically reflect on the usefulness of current SPTs for both agronomic and environmental objectives (Chapter 3). Finally, we identify the theoretical advantages of using the PSD as a combined agri-environmental SPT including a proof of principle by relating PSD to routine agronomic SPTs used in Western Europe and to crop yields (Chapter 4). We conclude that the PSD has a high potential to optimize P fertilization strategies with respect to crop yield, water quality and the use of finite P reserves (Chapter 5).

2. The need to revisit phosphorus fertilizer recommendations

2.1. Phosphorus fertilizer recommendations

A more sustainable P use implies a judicious use of limited P resources for maximizing crop production while preserving ground- and surface water quality. Currently, this is hindered by the rationale behind fertilization recommendations, which strongly focuses on crop production while neglecting environmental objectives (Jordan-Meille et al., 2012).

Fertilizer P recommendations generally follow the Build-Up and Maintenance approach (Jordan-Meille et al., 2012), where SPTs are used to classify the soil P status, which, in turn, is used to derive the recommended P fertilizer strategy for a specific crop. With this approach,

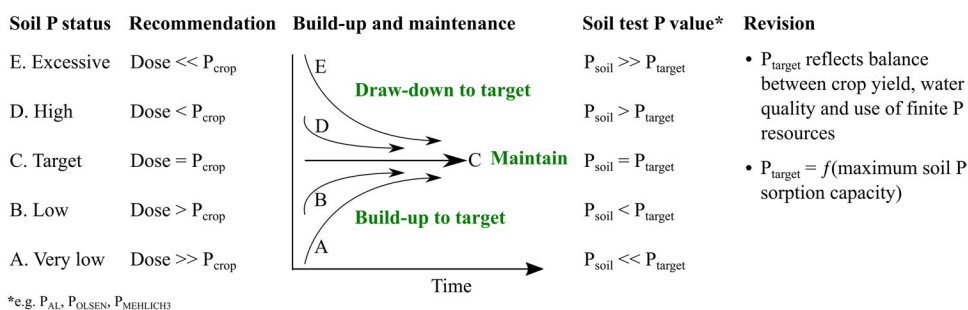


Figure 1. The “Build-Up and Maintenance approach” which is used to derive P fertilizer recommendations to enhance crop yields, based on the soil P status (adapted from Jordan-Meille et al., 2012). In this study, we plea that the target soil P status should be site-specific and balance agronomic and environmental objectives, accounting for the maximum P sorption capacity.

all agricultural soils ultimately reach a “target” soil P status (Figure 1). Currently, this target soil P status is determined by the economic optimization of crop yield at which the P fertilizer inputs equals crop P removal, although some countries recommend adding additional P to correct for “inevitable” P losses caused by a progressive shift of plant-available P to less available soil P forms and environmental P losses (Ehlert et al., 1996). The target soil P status currently corresponds to the P status at which over 90% of relative crop yield is achieved (Jordan-Meille et al., 2012). This target soil P status is derived from long-term P fertilization experiments (e.g. Nawara et al., 2017). The Build-Up and Maintenance approach is thus based on the concept that the soil is fertilized to an optimal level for crop yield.

2.2. Redefining and attaining the target soil P status

To unify agronomic and environmental objectives in fertilizer recommendations, we plea to define the target soil P status as a balance between crop yield, water quality and a judicious use of limited P resources instead of the economic optimization of crop yield only (Figure 1, Kleinman, 2017; Sharpley et al., 2001; Smith et al., 2018). Ignoring these factors besides crop yield may exceed environmental thresholds, for example due to unfavorable P sorption-desorption characteristics or a risk of environmental P losses for situations where the field and water system are strongly connected, e.g. when high groundwater levels or steep slopes occur (Kleinman, 2017; Sharpley et al., 2001). In addition, the amount of P that is required to build-up the soil P status to a certain target level may be so large that the target soil P status should account for judicious use of P by accepting a lower yield. For example, on so-called “P-fixing” soils, decades of high P fertilizer applications are required to bring the soil P status to an agronomic optimal level (Roy et al., 2016, 2017), raising the question if the increase in crop production outweighs the use of finite P resources.

To attain the target soil P status, measures aiming for a more sustainable P use entail: (i) increasing the soil P status in regions where the soil P status is below agri-environmental target levels by fertilizing soils above crop P uptake, and (ii) decreasing the soil P status in regions where the soil P status is higher than the agri-environmental target level by either withholding fertilization or fertilizing soils below the crop P uptake (Condrón et al., 2013; Koopmans, Chardon, Ehlert, et al., 2004; Pavinato et al., 2020).

A shift in the rationale behind fertilizer recommendations based on the revised Build-Up and Maintenance principle implies a shift in how we measure soil P in routine agronomic soil testing. Specifically, a SPT ought to provide insight in (i) the soil P availability to the crop, (ii) potential P losses to the water system and (iii) the required soil P balance to in- or decrease the soil P status to a certain target level.

3. Soil P processes and soil P tests

3.1. Soil P processes

Phosphorus in soil can be present as organic and inorganic P, with inorganic P typically contributing between 35 and 70% to total soil P (Hesterberg, 2010). For soils receiving long-term inputs of P fertilizers and animal manures, the contribution of inorganic P to total soil P usually increases (Koopmans et al., 2007; Lehmann et al., 2005), as inorganic P is abundant in animal manures (Sharpley & Moyer, 2000). Inorganic P includes phosphate sorbed to reactive soil particles (such as amorphous Fe- and Al-(hydr)oxides and oxidic clay mineral edges) and phosphate-bearing minerals (Gérard, 2016; Hesterberg, 2010). In the normal pH range of 5 to 8 of most agricultural soils, P sorption is the major mechanism controlling the P concentration in soil solution (Weng et al., 2011). The extent to which soils can sorb P depends on the maximum P sorption capacity which for non-calcareous soils relates to the amorphous Fe- and Al-(hydr)oxides contents (Schoumans & Chardon, 2015). As for reaction mechanisms, an increase in the P concentration in soil solution induces P adsorption to the oxide surfaces. In turn, this induces diffusion of P from the oxide surfaces into the oxide interior where P binds inside aggregates (Barrow, 1983). This process is reversible, i.e., when the P concentration in soil solution is lowered by plant-uptake or leaching, P desorbs from the reactive oxide surfaces to soil solution, inducing the desorption of P bound inside aggregates followed by diffuse P transport to the outer layer of the aggregates (Barrow, 1983, 2015). The rate of the sorption-desorption reaction on the oxide surfaces is faster than the rate of diffusion (Barrow, 2015). Nonetheless, both P sorbed to oxide surfaces and P diffused within the oxide particles are reversibly bound (Barrow, 1983, 2015; Lookman et al., 1995). For details on kinetics and thermodynamics we refer to a mechanistic P sorption-desorption model (Barrow, 2015).

The P concentration in soil solution determines the actual P uptake in the short term, as plants can only take up soluble phosphate species from solution whereas these dissolved P species usually contribute <0.015% to the total soil P content (Hesterberg, 2010). However, the annual crop P uptake is substantially higher than the size of the soil solution P pool (Morel et al., 2000), showing that most of the P is largely replenished - or buffered - through mineralization of organic P, dissolution of phosphate-bearing minerals and desorption of reversibly bound P. Modeling studies show that the P desorption rate can limit crop P availability (Koopmans, Chardon, de Willigen, 2004; Smolders et al., 2021). Faster growing plants require more available P in soil because they rely on high diffuse P fluxes (Smolders et al., 2021).

The capacity of a soil to replenish soil solution P is defined as the soil P buffer capacity (PBC). The PBC is generally derived from experimentally derived quantity-intensity curves (Q-I curves), where a measure of the soil P pool that is responsible for the buffering of the P concentration in soil solution (Q) is plotted against a measure of the P concentration in soil solution (I). The PBC is derived as the first derivative of Q to I (Ehlert et al., 2003). Such curves can be described with the Langmuir adsorption isotherm that asymptotically approaches a sorption maximum, assuming equilibrium (Eq. 1, van der Zee et al., 1987):

$$Q = \frac{Q_{\max} \cdot K \cdot I}{1 + K \cdot I} \quad (1)$$

where Q represents the P quantity that is sorbed by the soil solid phase (mmol P kg^{-1}), I the P concentration in soil solution ($\mu\text{mol l}^{-1}$), K a conditional soil P sorption affinity constant ($\text{l } \mu\text{mol}^{-1}$) and Q_{\max} the apparent sorption maximum of P (mmol kg^{-1}). For non-calcareous soils, Q_{\max} depends on the soil contents of Fe- and Al-(hydr)oxides, type and specific surface area of these oxides and other soil properties that affect P sorption such as pH and ionic strength (Hesterberg, 2010; Mendez et al., 2020; Rahnemaie et al.,

2007; Wang et al., 2013). Furthermore, the presence of Ca^{2+} and organic matter affect P sorption, as Ca^{2+} can promote P sorption by Fe- and Al-oxides (Weng et al., 2011) whereas organic matter can decrease P sorption through competition (Hiemstra et al., 2010; Weng et al., 2011). The soil P affinity constant K depends on the type of reactive groups that are present at the surface of amorphous oxides and is also affected by solution chemistry (Weng et al., 2012).

3.2. Routine agronomic soil P tests

Re-defining the target soil P status as a balance between crop production, water quality and the use of finite P resources (Figure 1) has implications for the selection of a SPT in routine agronomic soil testing protocols. Currently, P fertilization recommendations follow a three-step procedure: (i) measurement of soil available P via a SPT, (ii) interpretation of the SPT value by relating it to crop response, as derived from P fertilization experiments, and (iii) recommendation of the agronomically desirable P dose to achieve an optimal yield (Jordan-Meille et al., 2012). Consequently, routine agronomic SPTs have been optimized for crop production while environmental impacts are not explicitly considered.

Routine agronomic SPTs have in common that they make use of extraction methods to determine a certain fraction of total soil P that is correlated to crop response (Olsen et al., 1954). The extracted amount of P varies with the nature of the extraction solution and methodological factors such as soil pretreatment, the soil-to-solution ratio and the analytical technique used for P measurement (Fuhrman et al., 2005; Koopmans et al., 2002; Zhang et al., 2004). Soil P can be considered to exist in a continuum of P pools differing in availability, which can be simplified by arbitrarily classifying these pools into distinct pools (Figure 2, Liu et al., 2017). The extent to which the availability of these P pools differ can be explained by differences in the rates by which P is released from these pools to solution where it can be taken up by crops (Lookman et al., 1995; Chapter 3.1).

SPTs can be operationally defined according to the soil P pools distinguished in Figure 2. For measuring readily available P forms that can be taken up by the crop in the short-term, SPTs (referred to as P intensity methods) such as the 0.01 M CaCl_2 extraction method (P_{CaCl_2}) of Houba et al. (2000) and the water extraction method (P_{W}) of Sissinigh (1971) can be used. For the measurement of labile or moderately strong bound P (referred to as P quantity methods),

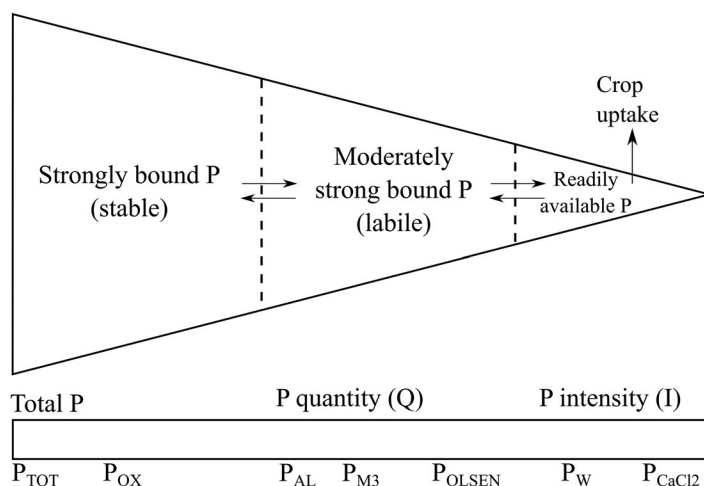


Figure 2. Distribution of phosphorus for a hypothetical soil distinguishing strongly bound, moderately bound and readily available P. Total P is measured as P_{TOT} , total reversibly bound P as P_{OX} , P quantity as P_{AL} , P_{M3} or P_{OLSEN} and P intensity as P_{W} or P_{CaCl_2} . Figure based on van Rotterdam-Los, 2010.

extractions with acid ammonium acetate-lactate (P_{AL} , Egnér et al., 1960), Mehlich3 (P_{M3} , Mehlich, 1984) and sodium bicarbonate (P_{OLSEN} , Olsen et al., 1954) can be used. Plotting P quantity against P intensity leads to the construction of Q-I curves (Chapter 3.1). In agriculturally managed soils, the stable or strongly bound P pool is generally thought to be of little importance because the rate at which P from this pool is released to the readily available P pool is considered irrelevant on the time scale of a single crop growing season (Noordwijk et al., 1990). Consequently, none of the conventional agronomic SPTs quantify the total amount of reversibly bound P in soil (Nawara et al., 2017). To illustrate this, Neyroud and Lischer (2003) compared the amounts of P extracted with 15 soil P tests to P extracted with oxalate - the latter being an estimate of the total reversibly bound P pool (Lookman et al., 1995) - and observed that agronomic soil P tests extracted 2–38% of oxalate-extractable P.

While SPTs in routine agronomic soil testing have shown to be suitable for the optimization of P fertilization rates in view of crop yield, we identify two drawbacks. Firstly, the P pool that is extracted is operationally defined and a clear process-based understanding of how this pool contributes to the uptake of P by crops is lacking. Specifically, the use of SPTs relies heavily on empirical correlations to crop response and insights into the speciation and phyto-availability of the extracted P are missing. This lack of mechanistic understanding also limits the potential to link the measured soil P pool to the risk of P losses to the environment. Secondly, none of the agronomic SPTs provide insight in the total reversibly bound P pool, the maximum P sorption capacity and the extent to which sorption sites are loaded with P. This is in particular relevant since those parameters influence crop P uptake, the risk of P losses to the water system (Ehlert et al., 2003; Kleinman, 2017) and the amount of P that is required to bring a soil to the desired soil P status. Both drawbacks hamper the use of conventional agronomic soil P tests to develop a P fertilizer strategy that combines both agronomic and environmental objectives.

3.3. Routine environmental soil P tests

To assess the risk of P losses from agricultural fields to the environment, we distinguish three soil P testing approaches, namely the use of: (i) agronomic SPTs, (ii) environmental SPTs and (iii) adapted agronomic SPTs mimicking environmental SPTs.

Agronomic SPTs have been used for environmental risk assessment since they are already widely applied. Often, the SPT value (e.g. P_{M3} , P_{OLSEN}) is combined with field-specific source and transport factors into a P risk index. Various P risk indices have been proposed, including factors such as the distance to surface water, the slope of the landscape, site hydrology and the soil P status (Buczko & Kuchenbuch, 2007; Habibiandehkordi et al., 2020; Heckrath et al., 2008; Sharpley et al., 2001). These risk indices assume that the risk of P losses through runoff and erosion increases as the soil P status increases, which is based on empirical relations between the SPT value and dissolved or particulate P concentrations in soil solution or leachates (Sharpley, 1995; Wortmann et al., 2013). However, this assumption ignores that the P concentration in solution and associated P losses are largely controlled by P sorption-desorption characteristics (Kleinman, 2017), thereby limiting the use of these SPTs to assess the leaching or runoff risk of P (Buczko & Kuchenbuch, 2007; Sharpley et al., 2001). To illustrate this, rainfall experiments show that at a given level of P quantity (P_{M3}) the dissolved P concentration in runoff water is higher at a low soil P sorption capacity than at a high soil P sorption capacity (Kleinman, 2017; Sharpley, 1995). In addition, total soil P is not measured in routine agronomic testing whereas this pool substantially contributes to P losses through erosion (Buczko & Kuchenbuch, 2007).

Environmental SPTs are designed to assess the potential of soils for P losses to aquatic environments. The most common one is the Phosphorus Saturation Degree (PSD). The concept of PSD was developed in the 1990s to provide quantitative insight in the risk of downward transport of P in non-calcareous sandy soils with an historical excess of P-fertilization (van der Zee & Riemsdijk, 1986a, 1986b, 1988). It has been successfully applied to assess the implications of

soil P management on ground- and surface water quality (Breeuwsma et al., 1995; Breeuwsma & Silva, 1992; Schoumans & Chardon, 2015). The PSD is based on the 0.2M acid ammonium oxalate extraction method of Schwertmann (1964). Amorphous Fe- and Al-(hydr)oxides and P reversibly bound to those oxides are simultaneously extracted from soil, followed by the measurement of Fe (Fe_{OX}), Al (Al_{OX}) and P (P_{OX}) in the extract. Subsequently, the maximum Phosphorus Sorption Capacity (PSC) is derived as the sum of Fe- and Al-(hydr)oxides multiplied with an empirical maximal saturation factor (α_{max}). Notably, relationships between Fe_{OX} and Al_{OX} and the PSC can be explored more process-based, for example by assessing the effective reactive surface area of the oxides (Mendez et al., 2020). The PSD is derived by dividing P_{OX} - which can be interpreted as the total pool of reversibly bound P in soil (Lookman et al., 1995) - by the PSC (Eq. 2).

$$\text{PSD} = \frac{\text{P}_{\text{OX}}}{\alpha_{\text{max}} \cdot (\text{Fe}_{\text{OX}} + \text{Al}_{\text{OX}})} \cdot 100 \quad (2)$$

where P_{OX} , Fe_{OX} and Al_{OX} are in mmol kg^{-1} and the PSD in %.

The use of PSD as an environmental SPT builds upon four assumptions. Firstly, the PSC of a soil is solely related to the amount of amorphous Fe- and Al-(hydr)oxides. Secondly, all P_{OX} being extracted consists of phosphate that is bound to amorphous Fe- and Al-(hydr)oxides. Thirdly, P_{OX} represents the total reversibly bound soil P pool. Lastly, α_{max} must be known and be rather constant across soils (Schoumans, 2000). Regarding the first assumption, Schoumans and Chardon (2015) applied the PSD concept to non-calcareous sandy, non-calcareous clay, calcareous clay and peat soils showing a broad applicability. However, Gérard (2016) states that oxidic edges of clay minerals also substantially contribute to P sorption in most soils. In contrast, P sorption in a soil series representative of Dutch agricultural soils was dominated by Fe- and Al-(hydr)oxides whereas the contribution of clay minerals was much less important (Mendez et al., 2020). Regarding the second assumption, Mendez et al. (2020) observed that phosphate contributed $74 \pm 9\%$ to the total amount of P that was extracted with acid ammonium oxalate, the difference being interpreted as organic P. This implies that the use of this extraction method can overestimate the amount of P bound to amorphous Fe- and Al-(hydr)oxides if P in the extract is measured as total P instead of inorganic P. Regarding the third assumption, desorption experiments provide strong evidence that all P_{OX} is reversibly bound (e.g. Lookman et al., 1995). Lastly, the empirical maximal saturation factor (α_{max}) usually varies from 0.3 to 0.7 when experimentally derived, depending on soil properties and the reaction time of phosphate with soil in the experiment (de Campos et al., 2018; Freese et al., 1992; Maguire et al., 2001; Pautler & Sims, 2000; van der Zee & van Riemsdijk, 1988). Generally, an α_{max} of 0.5 is used (Lookman et al., 1996; Nair et al., 2004; Schoumans & Chardon, 2015).

Aforementioned assumptions are met for most agricultural soils. Clear exceptions are coarse calcareous sandy soils and soils where the PSC is not only a function of amorphous but also of crystalline Fe- and Al-(hydr)oxides. In calcareous sandy soils, which generally have low Fe_{OX} and Al_{OX} contents (Koopmans et al., 2006), the use of the acid ammonium oxalate extraction is less appropriate. In those soils, dominant P retention processes are P sorption and precipitation at the surface of calcite and time-dependent precipitation of Ca-P minerals (Schoumans, 2014). In addition, in highly weathered tropical soils, crystalline Fe- and Al-(hydr)oxides have been observed to play an important role in P sorption (de Campos et al., 2018). This implies that an additional extraction method is required that allows for the quantification of the soil contents of crystalline Fe- and Al-(hydr)oxides (Mendez et al., 2022).

The PSD has been used as an environmental SPT for both P leaching risks as well as P losses via surface runoff and erosion. In areas where subsurface leaching is the major pathway of P losses, a critical PSD threshold of 25% was originally derived for non-calcareous sandy soils to prevent a phosphate concentration of 0.1 mg P l^{-1} at the depth of the average annual highest groundwater level (Breeuwsma & Silva, 1992; van der Zee et al., 1990a, 1990b). To derive this

critical threshold for the PSD, a mechanistic relationship between the PSD and the equilibrium P concentration in soil solution was used (van der Zee et al., 1990a, 1990b). Over time, this concept has been extrapolated to non-calcareous and calcareous clay soils, peat soils and calcareous sandy soils (Schoumans & Chardon, 2015). In areas where surface runoff and erosion are the most important pathways, the PSD has been related to both dissolved inorganic P and particulate P in surface runoff water (Pote et al., 1996; Sharpley et al., 1996; Uusitalo & Aura, 2008), illustrating its potential to assess the risk of P surface runoff and erosion as well (Sharpley et al., 1996). In addition to the PSD, measures of P_{OX} and the PSC provide additional insight in the risk of P losses through erosion. Soils with a high PSC likely contain higher levels of inorganic P (P_{OX}) compared to soils with a low PSC, which increases the risk of P losses to the water system through runoff and erosion (Weaver & Reed, 1998). For example, when the PSD is 25%, the risk of P losses through runoff and erosion is higher on a soil with a PSC of 80 mmol kg⁻¹ ($P_{OX} = 20$ mmol kg⁻¹) compared to a soil with a PSC of 20 mmol kg⁻¹ ($P_{OX} = 5$ mmol kg⁻¹).

Whereas the PSD has proven to be valuable for environmental risk assessments, it is not a soil test offered by agronomic soil testing laboratories hindering large-scale adoption in the short-term (Maguire & Sims, 2002). For this reason, several studies suggest adapting agronomic SPTs to mimic the PSD. Alternative PSD indices have been proposed where acid ammonium oxalate was replaced with Mehlich-3 for calculating PSD_{M3} using the molar ratio between P_{M3} and $[Al_{M3}+Fe_{M3}]$ (Kleinman & Sharpley, 2002; Maguire & Sims, 2002; Nair et al., 2004). Other studies used acid ammonium acetate-lactate to calculate PSD_{AL} (Blombäck et al., 2021; Kristoffersen et al., 2020), Mehlich-1 yielding PSD_{M1} (Nair et al., 2004) or divided a SPT value (e.g. P_{AL} or P_{OLSEN}) by another estimate of the PSC such as the single point sorption index (Blombäck et al., 2021).

Alternative PSD indices often significantly correlate with both the original PSD and P intensity (Blombäck et al., 2021; Kleinman & Sharpley, 2002; Kristoffersen et al., 2020; Maguire & Sims, 2002; Nair et al., 2004). However, the validity of alternative PSD indices is questionable. The extraction methods that are used for alternative PSDs have not been developed to estimate the PSC and the total reversibly bound P pool. Consequently, correlations between alternative PSD indices and the original PSD or P intensity methods remain empirical. For example, Maguire and Sims (2002) observe that Mehlich-3 poorly extracts amorphous Fe-(hydr)oxides and suggest that PSD_{M3} may not be valid for soils where amorphous Fe-(hydr)oxides are important contributors to the PSC. We identify that the potential of alternative PSD indices for environmental risk assessment purposes need to be mechanistically underpinned. Future research should underpin both the observed relationships between the PSD and alternative PSD indices, and the suitability of the extraction methods to quantify the PSC.

A concise overview of agronomic and environmental SPTs is included in the SI (Table S-1). For detailed comparisons of SPTs we refer to others (Blombäck et al., 2021; Fixen & Grove, 1990; Jordan-Meille et al., 2012; Neyroud & Lischer, 2003; Wuenscher et al., 2015; Zehetner et al., 2018).

4. Substantiating phosphorus saturation degree as a universal agronomic and environmental soil P test

4.1. PSD as an agri-environmental soil P test

We identify the acid ammonium oxalate-derived PSD as a high-potential agri-environmental SPT facilitating a more sustainable P fertilizer management. This is possible because the acid ammonium oxalate-derived PSD provides a combined measure of the total pool of reversibly bound P that acts as a soil reserve for crop P uptake and the maximum P sorption capacity, which taken together allows for calculating the PSD (Chapter 3.3). These three measures enable

to (i) derive a target agri-environmental soil P status and (ii) quantify the amount of P a farmer must apply to attain the desired target P status.

To derive a target for the agri-environmental soil P status, it is required to link the soil P status to both crop response and environmental risk. Regarding crop response, the PSD is a mechanistically-sound measure for plant-available P because it is based on the occupation of the P binding capacity of the soil with P, a property controlling the P concentration in soil solution. Regarding environmental risk, the link between PSD and P in soil solution allows for estimating the risks of dissolved P losses to freshwater ecosystems through subsurface leaching. In addition, the PSD and P_{OX} can aid in estimating the risk of dissolved and particulate P losses through erosion and runoff by using more empirical-oriented relationships (Chapter 3.3) in areas where erosion and runoff are the major pathways of P losses to the water system.

A desired target soil P status is achieved by following a build-up or draw-down strategy (Figure 1). The use of P_{OX} provides insight in how the total pool of reversibly bound P changes in response to a positive or negative P surplus. At the same time, the resulting PSD can be calculated as the oxalate extraction also quantifies the PSC (Eq. 2). Hence, this approach provides insight in the total amount of P that needs to be added through P fertilization or that needs to be removed to reach a certain target PSD.

In this chapter, we substantiate how the PSD can be used for both the derivation of the agri-environmental target soil P status and P fertilization strategies to reach this target. For this purpose we use two datasets. The first dataset contains crop yield responses from 11 long-term European field experiments (Nawara et al., 2017), including barley, maize, wheat, sugar beet, flax and potato. The dataset also includes results on the P_{OX} , Fe_{OX} , Al_{OX} , PSD, routine agronomic soil P tests including P_{CaCl_2} , P_{OLSEN} and P_{AL} (Chapter 3.2) and the soil texture class. The second dataset contains results on the P_{OX} , Fe_{OX} , Al_{OX} , PSD, P_{AL} and general soil properties like pH, clay and soil organic matter (SOM) for a wide range of soil types across the Netherlands (NMI, 2022). In both datasets, an α_{max} of 0.5 was used to derive the PSD (Eq. 2). A detailed description of the data is provided in the supporting information (Table S-2). We focus on the applicability of the PSD for agronomic objectives since its use as an environmental soil P test is widely acknowledged (Chapter 3.3) and that the adoption of the PSD as an agri-environmental soil P test is mainly hampered by a lack of understanding of its agronomic applicability.

4.2. The relationship between the PSD and P quantity

Combined insight in P quantity and P intensity (Chapter 3.1) is needed for the combined assessment of the P availability for crops (Chapter 3.2) and potential P losses to the environment (Chapter 3.3). While the PSD has mainly been used for environmental risk assessment due to its relationship with P intensity, there are limited studies unraveling the mechanisms driving the relationship between the PSD and P quantity. Since crop yield is highly controlled by P quantity in many regions (e.g. European soils, Nawara et al., 2017), strong correlations between PSD and P quantity (e.g. P_{AL} in Blombäck et al. (2021); P_{MI} in Pautler and Sims (2000) and Nair et al. (2004); $P_{AA-EDTA}$ in Renneson et al. (2015)) suggest that the PSD is applicable to assess the crop response to P availability in soils as well.

To improve the understanding of the relationship between PSD and P quantity, we constructed a non-linear machine learning regression model (randomForest, consisting of an ensemble of decision trees), predicting P_{AL} from the PSD, P_{OX} , Al_{OX} , Fe_{OX} , clay, SOM and pH. We used the dataset of NMI (2022), which contains data of Dutch soil types that cover a wide range in soil properties, reflected in the interquartile range ($Q_{0.05}$ - $Q_{0.95}$) for Fe_{OX} (5–484 mmol kg⁻¹), Al_{OX} (4–121 mmol kg⁻¹), clay (1–40%), SOM (1–39%) and pH_{CaCl_2} (4.2–7.2) (Table S-2). Details on the statistical procedures are given in the supporting information.

In the agronomic relevant range (1–60 mg P₂O₅ 100 g⁻¹) P_{AL} is predicted with a high accuracy with a RMSE of 7.75 and MEC of 0.77 (Figure 3A). At P_{AL} values higher than the agronomic

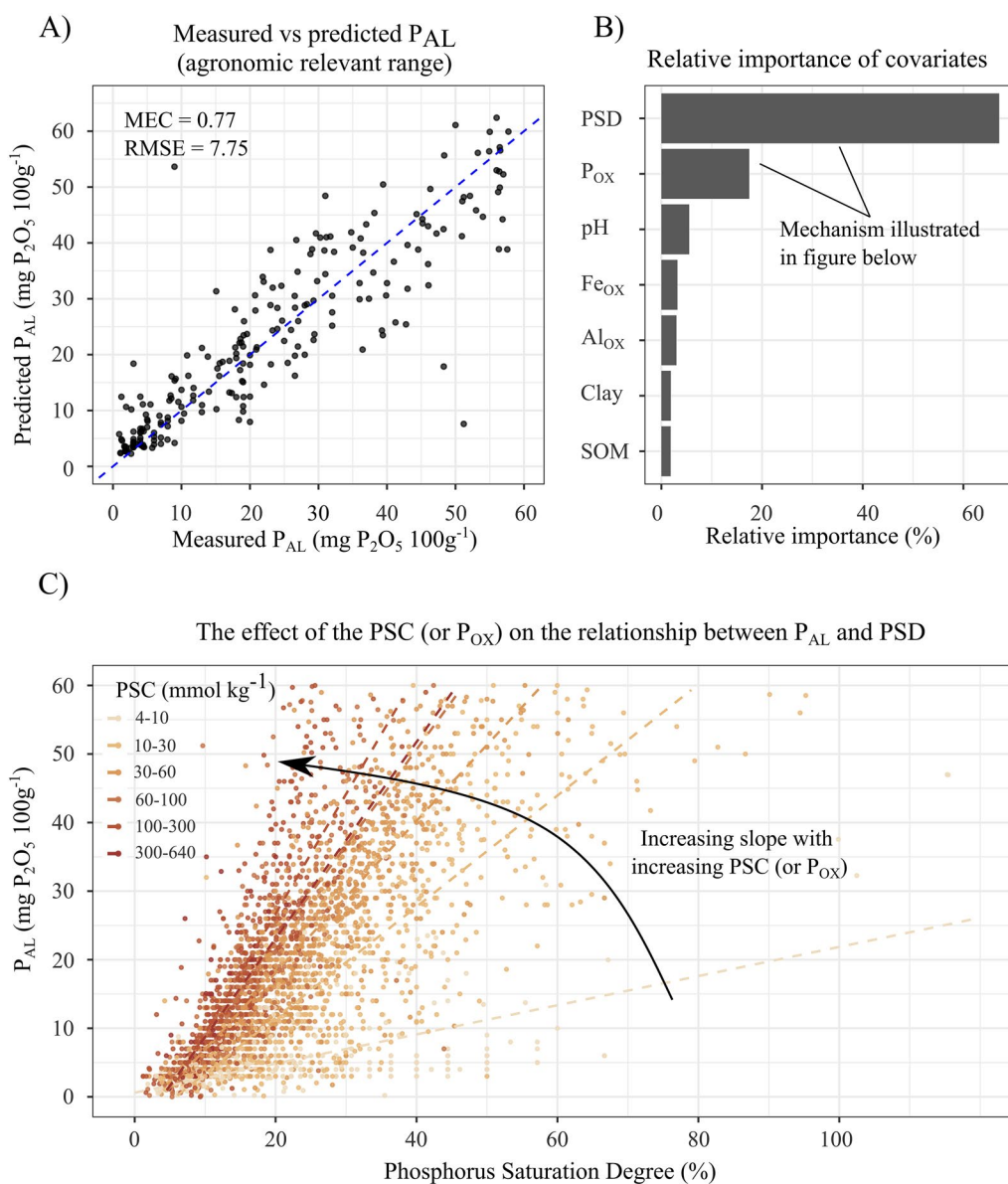


Figure 3. Predicting P_{AL} from the PSD, oxalate-extractable P, Fe and Al, clay, SOM and pH for Dutch soils using the ranger implementation of randomForest. (A) Measured vs predicted P_{AL} on a spatially independent hold-out sample, (B) relative importance of covariates, and (C) the effect of the PSC on the relationship between P_{AL} and PSD.

relevant range (60–157 $mg\ P_2O_5\ 100\ g^{-1}$), the model underpredicts P_{AL} (Figure S-5) likely due to the limited number of soils having P_{AL} values higher than 60 $mg\ P_2O_5\ 100\ g^{-1}$ (Table S-2).

Unraveling the main factors controlling the relationship between P_{AL} and PSD shows that the PSD and P_{OX} (reflecting the PSC) are the most important covariates (Figure 3B). Given a similar PSD value, the level of P_{AL} is higher at a higher PSC because a larger amount of reversibly bound P is required for the soil with a higher PSC to reach the same PSD. This has the effect of increasing P_{AL} , because more P is available at the surface of Fe- and Al-(hydr)oxides which can be extracted by P_{AL} (Figures 3B and C, see Figures S-6 and S-7 for more detail). Clay, SOM and pH were relatively unimportant with a relative importance smaller than 5% (Figure 3B).

Nevertheless, P_{AL} was observed to be higher at higher pH under a similar PSD and P_{OX} or PSC (Figure S-8), likely reflecting (partial) dissolution of Ca-P (Ottobong et al., 2009).

The observed interaction effect of PSD and P_{OX} on P_{AL} implies that fertilizing soils to an agronomic optimal level of P_{AL} will lead to a lower PSD for soils that have a high PSC compared to soils that have a low PSC. To illustrate this, fertilizing a soil with a PSC of 15 mmol kg⁻¹ to a P_{AL} of 30 mg P₂O₅ 100 g⁻¹ likely corresponds to a PSD of roughly 45% compared to a PSD of roughly 25% when the PSC is 80 mmol kg⁻¹ (Figure S-7). This insight can be used for limiting the risk of potential P leaching, since a lower PSD corresponds to a lower P concentration in soil solution and therefore a lower risk of dissolved P losses through subsurface leaching (Chapter 3.3). We elaborate on this aspect in the following sections, amongst others by discussing direct relations between the PSD and crop response.

4.3. Using PSD to balance crop yield and water quality

Since there is a link between PSD and well-established agronomic SPTs such as P_{AL} , this suggests that the PSD is correlated to crop yield as well and that it can be used as a basis to develop P fertilizer recommendations similar to current agronomic SPTs. Indeed, Kristoffersen et al. (2020) found a significant correlation between the PSD and barley yields in pot experiments. To further explore the relationship between the PSD and crop yield, we used the first dataset from long-term field experiments on European sand-clay soils (Nawara et al., 2017). Following the methodology of Nawara et al. (2017), crop yields were standardized by recalculating crop yield to relative yield (Eq. S3) and relative yield was related to PSD, P_{OLSEN} and P_{AL} using asymptotic regression (Eq. S4). Critical agronomic PSD values were derived for relative yields at 90 and 95% of the maximum yield. For comparison, asymptotic regression models were also fit for P_{AL} and P_{OLSEN} since Nawara et al. (2017) observed that these SPTs had the highest goodness-of-fit in their regression models. Notably, potato and flax were omitted since they were cultivated in one trial only having too little datapoints to fit reliable crop-response curves (Figure S-4).

The observations from long-term field experiments confirm that the PSD can be used to assess crop-response curves for barley, maize, sugar beet and wheat as it has a goodness-of-fit that is close to those found for P_{AL} and P_{OLSEN} (Figure 4). Still, the goodness-of-fit of P_{AL} and P_{OLSEN} is higher compared to the PSD showing that the more holistic use of the PSD (retrieving insights for both agronomic and environmental objectives) comes at the cost of a lower (but adequate) accuracy to predict crop response. Apparently, the fraction of the total soil P content that is extracted by agronomic SPTs better reflects the availability of P in soil to crops than the PSD. Likely, P_{AL} and P_{OLSEN} are not only dependent on the PSD but are also affected by soil properties that are important for soil P availability (e.g. pH, SOM, Steinfurth et al., 2021). This is in line with our observation that P_{AL} increases at an increasing pH under a similar PSD and P_{OX} (Figures 3B & S-8). This implies that the relationship between the PSD and crop response can be improved when adding more covariates to the model (Eq. S4), but since paired data on soil properties were lacking this was not further tested here.

An advantage of the oxalate extraction is that the measurement of the PSC provides context to crop-response curves (Figure 4). To illustrate this, the PSC of the fields included in the long-term field experiments of Nawara et al. (2017) is generally low (32 ± 10 mmol kg⁻¹) and it can be expected that the crop-response curve is different at a higher PSC due to the effect of the PSC on the Q-I relationship (Figure 3C). In the case of these relatively low PSC values, critical agronomic PSD levels vary between 17 and 23% to ensure a crop yield at 90–95% of the maximum (Figure 4). For soils having higher PSCs (and thus a higher P_{OX}), the critical PSD level will likely be lower due to a higher PBC.

In temperate soils, crop yield is often controlled by P quantity. In this case, the interaction effect between PSD and PSC when describing the variation in P_{AL} (Figure 3C) implies that the

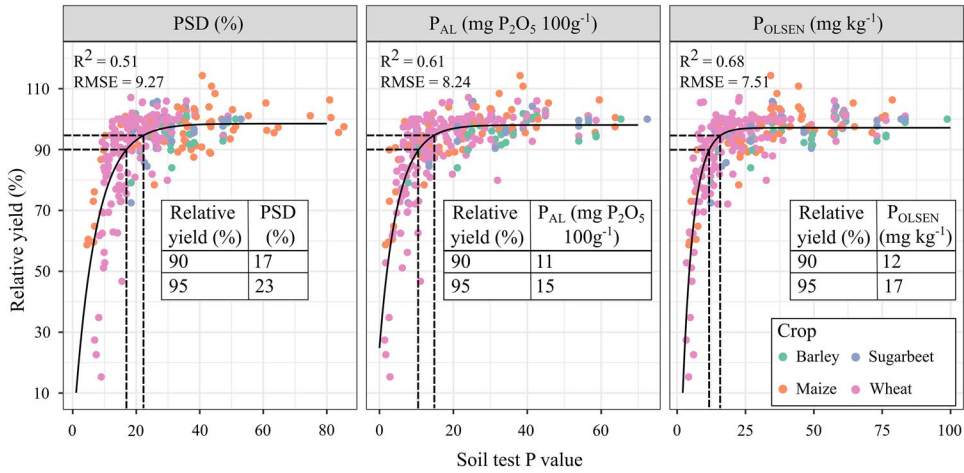


Figure 4. Relationships between soil test P values of PSD, P_{AL} and P_{OLSEN} and relative yield of barley, sugar beet, maize and wheat for European long-term field experiments (Nawara et al., 2017). The black solid line refers to the asymptotic regression curve. The black dashed lines refer to x and y intercepts at relative yields of 90 and 95%.

crop-response curve of P quantity depends on the PSC, i.e., the agronomic target level that corresponds to the optimal yield being higher at a lower PSC. When using the PSD as an index for P losses to the environment this implies that soils with a high PSC have a lower risk of losses to the environment by leaching when fertilizing to an agronomic target level that has been set for P quantity based SPTs. Preferential fertilization of high PSC soils above low PSC soils seems a promising strategy to safeguard water quality objectives. This is not kept into account by current P fertilizer recommendations. An exception is the Netherlands, where the target soil P status is derived from the combined measure of P intensity (P_{CaCl2}) and P quantity (P_{AL}). This indirectly allows for the prevention of high PSD levels on low PSC soils.

4.4. Fertilization strategy to reach the agri-environmental target soil P status

The PSD in combination with P_{OX} and PSC also give insight in the effect of (withholding) fertilization on the changes in soil P quantity and intensity pools and in the timespan at which the target soil P levels are met. These insights are needed to reduce soil P in legacy P soils to avoid excessive P losses to the water system (Figure 1, Schoumans et al., 2014; Tyson et al., 2020) and to increase soil P when P deficiency occurs (Figure 1, Magnone et al., 2019).

To estimate the impact of a net positive or negative P balance on the soil P status, one needs to know both the actual and desired PSD as well as the PSC (Dunne et al., 2021). The influence of PSC on the amount of P that has either to be added or removed to realize a certain change in a SPT value has been proven in multiple short -and long-term experiments (Burkitt et al., 2001; Coad et al., 2014; Dodd et al., 2012; McDowell et al., 2020; Nishigaki et al., 2021). For example, Burkitt et al. (2001) observed that soils with a higher PSC required higher P inputs to increase P quantities measured by P_{OLSEN} and P_{COLWELL} with one unit than soils with a lower PSC.

Theoretically, simple mass balance approaches can be used in combination with the measured values for P_{OX}, Al_{OX} and Fe_{OX} to estimate at which timespan agri-environmental targets are met given a net P balance (surplus or deficit) (Eq. 3). Here, we assume that the net P balance is directly related to the increase or decrease in P_{OX}, without considering vertical P movement and crop P uptake from deeper soil layers.

$$\text{Years} = \frac{(\text{PSD}_{\text{target}} - \text{PSD}_{\text{current}}) \cdot \alpha_{\text{max}} \cdot (\text{Fe}_{\text{OX}} + \text{Al}_{\text{OX}}) \cdot \rho \cdot A \cdot d \cdot 31 \cdot 10^{-8}}{P_{\text{balance}}} \quad (3)$$

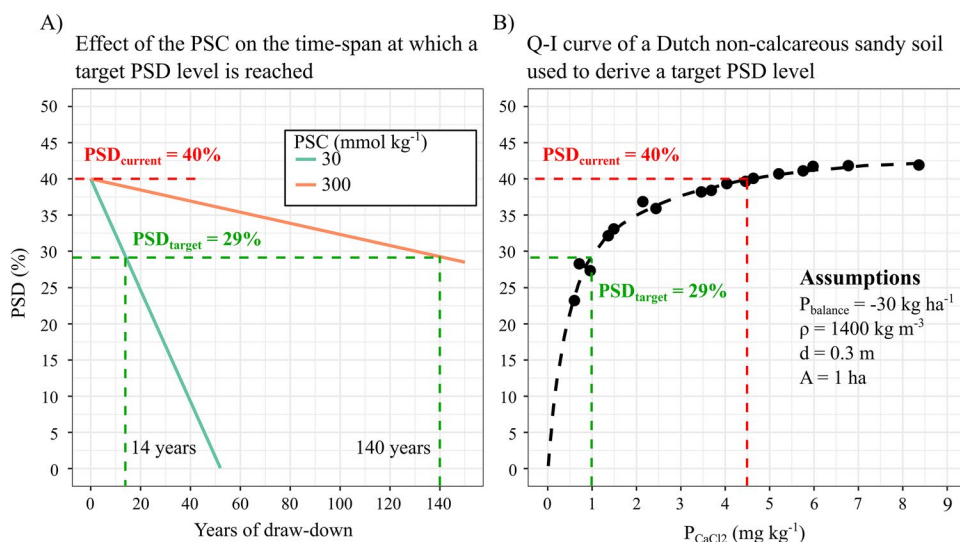


Figure 5. The change in PSD over time (A) for two soils differing in PSC to reach agri-environmental target levels, calculated using a mass balance approach (Eq. 3) under the assumptions of a net P balance of -30 kg ha^{-1} , bulk density of 1400 kg m^{-3} , soil depth of 0.3 m, area of the field of 1 ha and an initial PSD of 40%. For the assessment of a target PSD level, we used a Q-I curve (PSD versus P_{CaCl_2}) derived in a mining experiment for a P-rich non-calcareous sandy soil (Koopmans, Chardon, Ehlert, et al., 2004) (B).

where Years represents the timespan at which the soil P target status is met (years), $\text{PSD}_{\text{target}}$ the target PSD and $\text{PSD}_{\text{current}}$ the current PSD (%), Fe_{OX} and Al_{OX} the Fe- and Al-(hydr)oxides (mmol kg^{-1}), ρ the bulk density (kg m^{-3}), A the area of the field (m^2), d the relevant soil depth (m), 31 the molar P mass (mg mmol^{-1}), 10^{-8} a conversion factor and P_{balance} the average P balance ($\text{kg P m}^{-2}\text{year}^{-1}$) being equal to the net annual P accumulation, derived from the difference between annual P inputs (P fertilization) and outputs (P uptake and P losses).

To illustrate the effect of the PSC on the timespan at which an agri-environmental target value of the PSD is reached through a draw-down scenario for grassland, we applied Eq. 3 on two hypothetical soils differing in PSC, assuming a net negative P_{balance} of -30 kg ha^{-1} (van der Salm et al., 2009), a depth of 30 cm, a bulk density of 1400 kg m^{-3} and a current PSD of 40%. To assess the target PSD level, we assumed a Q-I curve derived from a pot experiment in which a P-rich non-calcareous soil was mined for 978 days with 31 grass harvests (Figure 5B, Koopmans, Chardon, Ehlert, et al., 2004). We set the target PSD level to 29% which corresponds to a P_{CaCl_2} level of 1 mg kg^{-1} in that soil. As the soil-to-solution ratio that is employed during the 0.01 M CaCl_2 extraction method is 0.1 kg l^{-1} (Houba et al., 2000), this P_{CaCl_2} level corresponds to a phosphate concentration of 0.1 mg P l^{-1} that has been used as an environmental threshold for non-calcareous sandy soils in the Netherlands (Chapter 3.3). The result of the balance calculation shows that the rate of change in PSD is lower for the high PSC soil than for the low PSC soil (Figure 5A), which is due to the fact that the total pool of reversibly bound P (P_{OX}) is 10-fold larger for the soil with the higher PSC. For the high PSC soil, decreasing the PSD from 40% to the target of 29% will likely require over a century of draw-down whereas this will only take roughly 14 years for the low PSC soil (Figure 5A).

4.5 A judicious use of a limited P resource

So far, we illustrated the use of the PSD and PSC to derive the target agri-environmental soil P status (Figure 1), balance crop production and water quality (Chapter 4.3), and derive fertilization strategies to reach this target (Chapter 4.4). A more sustainable P use, however, also includes a judicious use of a limited P resource (Ros et al., 2020; Roy et al., 2016). To balance

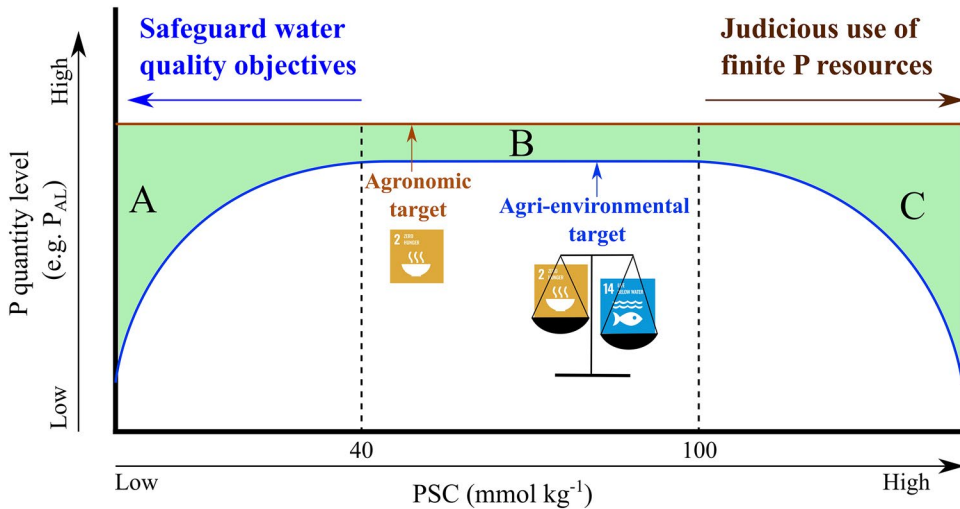


Figure 6. The target agri-environmental level of P quantity, determined as a balance between crop production, water quality and the use of finite P reserves, as a function of the maximum P sorption capacity (PSC). We distinguish low, medium to high and very high PSC soils (groups A, B and C respectively), with their own tradeoffs. PSC cutoffs of 40 and 100 mmol kg^{-1} are added as rough guidelines.

crop yield, water quality and the use of finite P reserves, we argue that an agri-environmental P target level is largely dependent on the PSC (Figure 6). We distinguish three groups with different tradeoffs.

Firstly, there are soils with a low PSC (group A in Figure 6). At a certain soil P level (e.g. P_{AL}), a low PSC leads to a higher PSD compared to soils with a high PSC (Figure 3C). This higher PSD increases the P concentration in the soil solution and therewith the risk of P leaching to the water system. For this reason, there is a relatively large tradeoff between crop production and safeguarding water quality objectives for soils with a low PSC. Secondly, there are soils where the PSC is medium to high (group B in Figure 6). Those soils require a lower PSD to reach an agronomic optimum than the low PSC soils in group A (Figure 3C). For this reason, there is a relatively small tradeoff between crop production and safeguarding water quality objectives. Thirdly, there are soils where the PSC is very high (group C in Figure 6). On those soils, decades of high fertilization rates are required to increase soil P availability to an agronomic sufficient level (Figure 5). It might not be worth it to fertilize those soils to an agronomic optimum given the amount of (finite) P it requires (Roy et al., 2016). In addition to the high requirements of finite P inputs to raise P availability, high P_{OX} levels also increase the risk of P losses through erosion (Chapter 3.3). Especially in areas where the erosion risk is high, fertilizing very high PSC soils to an agronomic optimal P level is therefore not recommended. Instead, the soil can be brought to a lower soil P target level and alternative fertilization strategies should be implemented to increase crop yields, such as the “feed the crop, not the soil” rationale where fertilization is targeted to the crop instead of the soil (Withers et al., 2014). Furthermore, new practices in these high PSC soils can be used to reduce the crop P demand, e.g. by promoting the growth of extensive rooting systems, multi-cropping and promotion of biological interactions and soil biological activity (Caron et al., 2014; Rowe et al., 2016; Vos et al., 2022; Withers et al., 2014).

5. Conclusion

This research addresses the need to combine agronomic and environmental objectives in P fertilizer recommendations. We plea that the target soil P status should be defined as a balance

between crop yield, water quality and the use of finite P resources instead of the economic optimization of crop yield. We show that SPTs used in routine agronomic soil testing do not provide the insights required for this revision. Instead, we identify the phosphorus saturation degree (PSD) - based on the oxalate extraction - as a high-potential universal agri-environmental SPT in farming systems on non-calcareous soils and calcareous clay soils. We show that the simultaneous measurement of amorphous Fe- and Al-(hydr)oxides and the total pool of reversibly bound P with the oxalate extraction, and the associated PSD, allows for the combined assessment of crop-response, risk of P losses to the water system and the amount of P required to build-up or draw-down the soil P status to a target level. We illustrate that this combined assessment is pivotal to derive agri-environmental target P levels and the amount of P required to reach those levels, contributing to a more sustainable P use in agriculture.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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