Indicators of phosphorus status in soils: significance and relevance for crop soils in southern Belgium. A review

Malorie Renneson, Sophie Barbieux, Gilles Colinet

University of Liège - Gembloux Agro-Bio Tech. TERRA. AgricultureIsLife. Passage des Déportés, 2. BE-5030 Gembloux (Belgium).
University of Liège - Gembloux Agro-Bio Tech. Biosystems Engineering. Water-Soil-Plant Exchanges. Passage des Déportés, 2. BE-5030 Gembloux (Belgium). E-mail: malorie.renneson@ulg.ac.be

Received on April 3, 2015; accepted on February 19, 2016.

Introduction. Phosphorus (P) is an essential element for plant growth. Therefore, it is essential to accurately evaluate its content in the soil. This requires reliable indicators of soil P status.

Literature. This paper reviews literature regarding the indicators of P status in soils. Many indicators can be found, including single extractions (soluble, available, or total P), which are the most common indicators used worldwide. Over time, increasingly complex P indicators have been developed as sequential extractions which characterize the various forms of P, degree of P saturation, diffusive gradients in thin films, biological extractions, isotopic methods, or more complex models. To make a choice among them, different criteria should be applied, including relevance, cost and time, ease of interpretation, and, most importantly, the objective of the analysis. It is also necessary to analyze the appropriateness to soil and climate. Firstly, this paper describes the various types of indicators present in the literature, and proposes a classification system. Secondly, all cited indicators are evaluated and compared. Finally, the P indicators met in Wallonia, southern Belgium are discussed.

Conclusions. Each P indicator presents advantages and disadvantages. This review highlights the importance of careful consideration of indicator choice, and the establishment of interpretation thresholds.

Keywords. Soil, phosphorus, indicators, fertility, soil analysis, Belgium.

Indicateurs de l’état du phosphore : signification et pertinence dans les sols agricoles en Wallonie (synthèse bibliographique)

Introduction. Le phosphore (P) est un élément essentiel pour la croissance des plantes dont il est nécessaire de connaître précisément la teneur dans le sol. Cela passe inévitablement par l’utilisation d’indicateurs adéquats.


Conclusions. Tous les indicateurs du P présentent des avantages mais également des inconvénients. Cette revue bibliographique souligne l’importance de bien réfléchir au choix des indicateurs et de disposer de seuils d’interprétation correspondant.

Mots-clés. Sol, phosphore, indicateurs, fertilité, analyse de sol, Belgique.

1. INTRODUCTION

Phosphorus (P) is an essential nutrient for plant growth, and is therefore a critical part of the fertilization requirements for crop production. However, excessive bioavailable P inputs can lead to the eutrophication of surface waters, which represents a major concern in the world. Increasing environmental issues and rise in fertilizer prices have led to the reconsideration of certain agricultural practices. According to the National Union
of French Fertilizer Industries (UNIFA; www.unifa.fr), the consumption of phosphate mineral fertilizer has decreased by nearly 80% over the past 30 years. This decline threatens the availability of P in soils over the long term, and increases the risk of P deficiency in the most sensitive soils. Thus, the identification of soil deficiency risk, concomitant with the minimization of environmental losses by erosion and run-off, requires the development of relevant indicators of P status in soils.

In soil, total P can be separated into different pools of organic and inorganic fractions. Inorganic P includes primary P minerals (apatite, strengite, variscite); secondary P minerals (Ca, Mg, Fe or Al phosphates); P adsorbed onto the edges of clay minerals; P bound to organic matter through metallic cations; and dissolved P (\(\text{H}_3\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-}\)). Dissolved P represents more than 96% of the P taken up by plants according to Beck et al. (1994) and can be considered as the P form directly available to plants, the quantity depending on the time of ions exchange (Fardeau, 1993). The mobility and bioavailability are controlled by the low levels of dissolved P in soil solution, which is mainly governed by high rates of adsorption and/or precipitation of dissolved P with positively charged soil compounds, including metal cations (Ca, Mg, Fe, Al) and Fe-, Al-oxyhydroxide (Hinsinger, 2001). So, P ions concentration in soil solution is therefore largely controlled by cationic activity in soil solution, which is influenced by soil pH and environmental factors as redox potential and mineral solubility (Pierzynski et al., 2005). However, P estimated available for plants can highly differ from P really taken off by crops because it depends on plant species and soil conditions.

Organic fraction is defined as P bound with C (organic matter and biological compounds such as DNA and phospholipids) (Condron et al., 2005). The proportion of this fraction depends on factors such as land use and pedo-climatic conditions, and can vary from 25-30% to 75-80% of total P (Fardeau et al., 1994). Soil P flows occur between organic and inorganic pools via immobilization and mineralization processes mediated largely by soil microorganism activity (Oberson et al., 1996). Soil conditions, including soil moisture, temperature, pH, and surface chemical properties are integral factors promoting these reactions.

Due to the profusion of existing indicators, it can be difficult to identify the most appropriate indicator for a given set of conditions. The management of a given environment requires indicators which are adapted to local conditions, indicators which are easy to measure, and indicators with known thresholds and limitations. It is not the purpose of this article to provide an exhaustive list of existing methods that currently serve to indicate P status in soil. Rather, the goal of this study is to evaluate the most common types of methods in order to highlight the advantages and limitations of each. This evaluation was also applied more specifically in Wallonia, a region situated in southern Belgium, though results can be extrapolated to facilitate both agronomic and environmental management of P in other regions, provided that the specific edaphic properties of a given region are considered.

2. MAIN METHOD CLASSES FOR P CHARACTERIZATION IN SOIL

Many diagnostic tools have been developed to evaluate soil fertility. According to the literature, the available tools are based on the following variables:

- the objective (agronomic, environmental, or both);
- the scale of the study (e.g., a cultivated field or watershed), or
- the measurement principle.

These classifications are described in the following sections and in figure 1.

2.1. Chemical extractions

Various chemical methods have been developed to estimate the capacity of a soil to provide the levels of P necessary for plant growth. Currently, several dozen methods exist, with varying degrees of complexity. Most of these methods were developed under specific conditions (soil or cultivation system), and were fixed with respect to interpretation references. Consequently, it is difficult to apply a uniform method worldwide, despite regulatory efforts within Europe for the establishment of a standardized set of methods (Proix, 2013). Therefore, defining specific thresholds becomes important.

Single extractions of P content. Main existing indicators estimate the levels of available (or exchangeable) P based on “the sum of P immediately available to plants and of P that can be converted into an available form through physical (desorption), chemical (dissolution), or biological (enzymatic degradation) processes in nature during a growing season” (Boström et al., 1988). Some analytical methods utilize extractants to mimic the action of roots through dissolution, desorption, or chelation reactions. Of the several dozen chemical extraction methods reported in literature, these differ depending on the extractant used, the extraction time, and the ratio of soil to extractant. Some extraction methods are also specific to a country or region, while other methods are more universal (e.g., the methods of Olsen, Mehlich 3, or Bray; see table 1). Within the same country, several methods
Indicators of phosphorus in soils

...can also coexist. This is particularly evident in France, where levels of available P are commonly evaluated according to the methods of Olsen, Joret-Hébert, and Dyer (Table 1), explained partly by diversity of soils.

Rather than providing an exhaustive survey of the existing methods, the following discussion will be limited to the most commonly cited methods in the literature (Table 1). Proix (2013) proposed that extraction methods can be classified into four types (I–IV), depending on which soil binding mode is affected by the extraction performed (Table 2).

Type I analysis methods that detect soluble P are not commonly used as agronomical indicators. Instead, these are routinely used as environmental indicators in some countries. To formulate the risk of P loss, P is extracted with distilled water (Sissingh, 1971). This method is used in The Netherlands, Austria, and Switzerland, among others; it estimates the

Table 2. Classification of the chemical extractions proposed by Proix (2013) — Classification des méthodes d’extraction chimique proposée par Proix (2013).

<table>
<thead>
<tr>
<th>State of P in the soil</th>
<th>How it works</th>
<th>Extraction methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I Soluble</td>
<td>Dissolution of soluble elements is performed and this is used as the soil solution</td>
<td>Water, CaCl₂</td>
</tr>
<tr>
<td>Type II Linked to clay-humic complexes</td>
<td>P is mainly released from clay and organic matter</td>
<td>Neutral salts, buffering effect (Olsen, etc.)</td>
</tr>
<tr>
<td>Type III Adsorbed or precipitated on oxyhydroxides</td>
<td>P is released from iron and aluminium oxyhydroxides</td>
<td>Neutral salts, buffering effects, chelating molecules (AA-EDTA, acetate-lactate, etc.)</td>
</tr>
<tr>
<td>Type IV Total or pseudo-total stock</td>
<td>Total P concentration is determined in order to perform a pedological characterization of a given soil</td>
<td>Triacid, Aqua regia</td>
</tr>
</tbody>
</table>

Figure 1. Classification of the different indicators of phosphorus status in soils — Classification des différents indicateurs du phosphore dans les sols.
<table>
<thead>
<tr>
<th>Method</th>
<th>Chemical extractants</th>
<th>Extraction time and ratio of soil to extractant *</th>
<th>Countries</th>
<th>Soil types</th>
<th>Indicator types</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium acetate and EDTA</td>
<td>0.5 M ammonium acetate + 0.5 M acetic acid + 0.025 M EDTA, pH 4.65</td>
<td>1:10 (w:v), 30 min shaking</td>
<td>Belgium (Wallonia), Switzerland</td>
<td>Acidic to neutral soils</td>
<td>A</td>
<td>Lakanen et al., 1971</td>
</tr>
<tr>
<td>Acetate lactate</td>
<td>0.1 M ammonium lactate + 0.4 M acetic acid, pH 3.75</td>
<td>1:20 (w:v), 2 h shaking</td>
<td>Belgium (Flanders), Sweden, Norway</td>
<td>All soils</td>
<td>A</td>
<td>Egner et al., 1960</td>
</tr>
<tr>
<td>Bray 1</td>
<td>0.03 M NH₄F + 0.025 M HCl, pH 3.75</td>
<td>1:10 (w:v), 5 min shaking</td>
<td>USA, Spain, Italy, Greece, India</td>
<td>Acidic soils rich in iron, not in neutral to calcareous soils, not in clayey soils with high degree of exchangeable bases</td>
<td>A</td>
<td>Bray et al., 1945</td>
</tr>
<tr>
<td>CaCl₂ Soluble</td>
<td>0.01M CaCl₂</td>
<td>1:10 (w:v), 2 h shaking</td>
<td>The Netherlands</td>
<td>Acidic to neutral soils</td>
<td>A, E</td>
<td>Houba et al., 2000</td>
</tr>
<tr>
<td>CAL</td>
<td>0.05 M lactate de Ca + 0.05 M calcium acetate + 0.3 M acetic acid, pH 4.1</td>
<td>1:20 (w:v), 2 h shaking</td>
<td>Germany</td>
<td>All soils</td>
<td>A</td>
<td>Schüller, 1969</td>
</tr>
<tr>
<td>Dyer</td>
<td>Citric acid 2%, pH 2</td>
<td>1:5 (w:v), 2 h shaking</td>
<td>France, Belgium (forest soils)</td>
<td>Acidic to neutral soils</td>
<td>A</td>
<td>Dyer, 1894</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF 31-160, 1999</td>
</tr>
<tr>
<td>Joret-Hébert</td>
<td>0.2 M oxalate d’NH₄, pH 7</td>
<td>1:20 (w:v), 2 h shaking</td>
<td>France</td>
<td>Neutral to calcareous soils</td>
<td>A</td>
<td>Joret et al., 1955</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NF X31-161, 1999</td>
</tr>
<tr>
<td>Mehlich 1</td>
<td>0.0125 M H₂SO₄ + 0.05 M HCl</td>
<td>1:4 (w:v), 5 min shaking</td>
<td>USA</td>
<td>Acidic to neutral soils</td>
<td>A</td>
<td>Mehlich, 1953</td>
</tr>
<tr>
<td>Mehlich 3</td>
<td>0.015 M NH₄F + 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.013 M HNO₃ + 0.001 M EDTA</td>
<td>1:10 (w:v), 5 min shaking</td>
<td>Canada, USA</td>
<td>All soils</td>
<td>A</td>
<td>Mehlich, 1984</td>
</tr>
<tr>
<td>Morgan</td>
<td>0.72 M sodium acetate + 0.52 M acetic acid, pH 4.8</td>
<td>1:5 (v:v), 15 min shaking</td>
<td>USA</td>
<td></td>
<td>A</td>
<td>Morgan, 1941</td>
</tr>
<tr>
<td>Morgan modified</td>
<td>0.62 M NH₄OH + 1.25 M CH₃COOH</td>
<td>1:5 (v:v), 15 min shaking</td>
<td>Ireland, USA</td>
<td>Acidic soils with a CEC below 20 cmol·kg⁻¹</td>
<td>A</td>
<td>McIntosh, 1969</td>
</tr>
<tr>
<td>Olsen</td>
<td>0.5 M NaHCO₃, pH 8.5</td>
<td>1:20 (w:v), 30 min shaking at 20 °C</td>
<td>France, England, USA, Spain, Tunisia, South Africa, Greece, India, Iran, etc.</td>
<td>Calcareous soils extended to all soils excepted highly acidic soils</td>
<td>A</td>
<td>Olsen et al., 1954</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ISO 11263:1994</td>
</tr>
</tbody>
</table>
Indicators of phosphorus in soils

Table 1 (continued). Characteristics of single extractions of phosphorus content most commonly cited in the literature (completed from Jordan-Meille et al., 2012) — Caractéristiques des principales méthodes chimiques d’extraction du phosphore rencontrées dans la littérature (complété de Jordan-Meille et al., 2012).

<table>
<thead>
<tr>
<th>Method</th>
<th>Chemical extractants</th>
<th>Extraction time and ratio of soil to extractant *</th>
<th>Countries</th>
<th>Soil types</th>
<th>Indicator types</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triacid</td>
<td>HCl + HF + HClO₄</td>
<td>Hot extraction</td>
<td>All soils</td>
<td>T</td>
<td>NF X 31-147, 1996</td>
<td></td>
</tr>
<tr>
<td>Truog</td>
<td>0.002 M H₂SO₄ + (NH₄)₂SO₄, pH 3.0</td>
<td>1:200 (w:v), 30 min shaking</td>
<td>Neutral to calcareous soils</td>
<td>A</td>
<td>Truog, 1930</td>
<td></td>
</tr>
<tr>
<td>Water Soluble</td>
<td>H₂O</td>
<td>1:60 (w:v), 22 h incubation and 1 h shaking</td>
<td>The Netherlands, Germany</td>
<td>All soils</td>
<td>A, E</td>
<td>Sissingh, 1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:10 (w:v), 5 min shaking</td>
<td></td>
<td></td>
<td></td>
<td>Pansu et al., 2003</td>
</tr>
</tbody>
</table>


Although it is difficult to compare the various methods of extraction, many authors have attempted to do so (Hemsy et al., 1992; Pace et al., 2002; Neyroud et al., 2006). Consequently, some authors have proposed a classification of extractants based on the amount of P that is extracted (Hemsy et al., 1990; Neyroud et al., 2006). However, this classification is not universal for all types of soil. Thus, it is essential to account for the specifics of an analytical method prior to selecting the method to choose one unique method due to differences in the edaphic properties of a country or region. A more robust methodology is also satisfactory in acidic soils of the Triacid extraction method can potentially be applied to a wide range of soils, such as Mellitch 3 in Quebec (Beaudin, 2006). However, the cost of this methodology is also satisfactory in acidic soils of the Olsen method. Interestingly, the latter method was developed in calcareous soils, while the results of this methodology are also satisfactory in acidic soils (More et al., 2000).
Finally, total P content (type IV) is occasionally used as an indicator of the P reserve present in soil. Various acid methods exist and consist of using acids such as HF, HClO₄, HNO₃, HCl, or H₂SO₄ separately or in combination, with variable efficiency. This indicator may be useful in evaluating the P content of sediment lost by erosion, or in assessing the pedological characterization of a given soil. Recently, total P content was used to estimate P reserves bound to parent materials in Wallonia (Renneson et al., 2013).

**Sequential extractions.** Complementary to the approach of estimating available P, some authors have developed sequential extraction methods to identify P pools of varying solubility in soil. Different extraction methods are combined sequentially in order to deplete a soil of its content from decreasingly available fractions. Residual P is determined by the difference of P forms compared to total P.

Many protocols for sequential extraction have been proposed (Table 3), and two major types have been distinguished. One major type involves classification on the basis of the type of bonding, while the other involves classifications on the basis of the degree of availability to plants. The most commonly used protocols were originally developed by Chang et al. (1957) and Hedley et al. (1982). The original purpose of the former work was to distinguish different forms of P depending on the type of bonding to soil minerals (e.g., P bound to iron vs aluminium vs calcium, etc.). However, the selectivity of the extractant in this protocol was often questioned. Fractionation schemes are unable to isolate discrete mineral, as they solubilize groups of minerals usually defined as P associated with Al, Fe, Ca, or residual forms (Pierzynski et al., 2005). Nevertheless, this protocol led to the development of a second type of protocols. In particular, Hedley et al. (1982) incorporated the consideration of P availability for plants, without specifying the forms of bonding within each fraction, thereby assuming the same chemical form is present in different fractions.

Many studies have attempted to compare a variety of extraction methods using the same set of soil samples (Levy et al., 1999; Taoufik et al., 2004). However, the results are difficult to generalize due to the influence of soil types. Williams et al. (1967) demonstrated that the method outlined by Chang et al. (1957) was not applicable for calcareous soils or sediments. According to Tiessen et al. (1993), the fractionation of Hedley et al. (1982) is the only method that can be used with moderate success for the evaluation of available organic P. In acid soils, some pools are not completely separated (bicarbonate and hydroxide-extractable Pi) and represent a continuum of Fe- and Al-associated P extractable (Tiessen et al., 1993). The Hedley fractionation is also used in tropical soils, following protocol modifications (use of resin P fraction and generally less P fractions) (Negassa et al., 2009).

Overall, while these methods provide an extensive characterization of the different forms of P present in a soil, they are expensive and time consuming to implement, thereby preventing their routine use.

**Degree of P saturation.** Given the importance of the environmental issues related to P, and the influence of edaphic properties on the results of chemical extractions, an environmental indicator which accounts for the distinguishing characteristics of a particular soil was developed. This indicator evaluates the degree of soil P saturation by measuring the proportion of potential binding sites in soil which are actually occupied by P, with main binding sites involving the oxide and hydroxide groups of iron and aluminium (van der Zee et al., 1988). Thus, the indicator accounts for both the binding capacity and the fixed P content of the soil. Leinweber et al. (1999) have demonstrated

<table>
<thead>
<tr>
<th>Method</th>
<th>Chemical extractants</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chang &amp; Jackson</td>
<td>NH₄Cl, NH₄F, NaOH, H₂SO₄, Na₂S₂O₇-citrate</td>
<td>Chang et al., 1957</td>
</tr>
<tr>
<td>Williams et al.</td>
<td>NH₄Cl, NH₄F, NaOH, Na₂S₂O₇-citrate, NaOH, HCl</td>
<td>Williams et al., 1967</td>
</tr>
<tr>
<td>Hieltjes &amp; Lijklema</td>
<td>NH₄Cl, NaOH, HCl</td>
<td>Hieltjes et al., 1980</td>
</tr>
<tr>
<td>Hedley</td>
<td>Anion exchange resins, NaHCO₃, NaOH, dissolved HCl, concentrated HCl, H₂SO₄</td>
<td>Hedley et al., 1982</td>
</tr>
<tr>
<td>Ruttenberg</td>
<td>MgCl₂, CDB, acetate, HCl, hot HCl</td>
<td>Ruttenberg, 1992</td>
</tr>
<tr>
<td>Paludan &amp; Jensen</td>
<td>H₂O, bicarbonate-dithionite, NaOH, HCl</td>
<td>Paludan et al., 1995</td>
</tr>
<tr>
<td>Golterman</td>
<td>Distilled water, Ca-EDTA/dithionite, Na-EDTA, H₂SO₄, H₂SO₄ in autoclave</td>
<td>Golterman, 1995</td>
</tr>
<tr>
<td>Rydin &amp; Welch</td>
<td>NH₄Cl, Na₂S₂O₇/NaHCO₃, NaOH, HCl</td>
<td>Rydin et al., 1998</td>
</tr>
</tbody>
</table>

Table 3. Sequential P extractions most commonly cited in the literature — Principales méthodes de fractionnement du phosphore retrouvées dans la littérature.
that this parameter can be calculated according to the following equation:

\[
\text{Degree of P saturation} = \frac{P_{\text{ox}}}{\alpha(Al_{\text{ox}} + Fe_{\text{ox}})} \times 100 \quad (Eq. 1)
\]

where the degree of P saturation is expressed as a percentage, and \( P_{\text{ox}}, Al_{\text{ox}}, \) and \( Fe_{\text{ox}} \) represent the amounts of P, aluminium (Al), and iron (Fe) that are extracted with ammonium oxalate (mmol·kg\(^{-1}\)), respectively, while \( \alpha \) represents a scaling factor (generally 0.5).

This method was originally developed in the acidic sandy soils of The Netherlands, and since has been applied to other regions and countries (e.g., Flanders [northern Belgium], Quebec, etc.). In Quebec, this indicator has been defined as the ratio between P and Al, as determined by the Mehlich 3 extraction (Khiari et al., 2000). In 1999, Beauchemin et al. identified the various formulas that had been used to calculate the degree of P saturation in the literature. In a study conducted in Wallonia (Renneson et al., 2015), it was demonstrated that the equation has first to be adapted to the pedological and geological context of the soil under investigation.

Moreover, it was shown that the degree of P saturation is correlated with the concentrations of P present in run-off (Pote et al., 1999) and in drainage water (Leinweber et al., 1999), thereby indicating that it represents a relevant environmental indicator. In The Netherlands and in Flanders, this index has been incorporated into legislation, whereby a degree of P saturation that exceeds 25% is defined as unacceptable due to the risk of P transfer to the soil solution and water (Breeuwsma et al., 1995).

**Agronomic and environmental thresholds.** To be relevant as an agronomic indicator, the amount of extractable P must be closely related to crop response, such as plant growth or uptake of P (Figure 2). The correlation between soil and plants can be conducted in greenhouse, a growth chamber, or on the field. Test calibrations must be conducted over a broad range of soils in order to define fertility classes according to soil properties, such as texture or pH values (Genot et al., 2011; Jordan-Meille et al., 2012).

Similarly, environmental threshold can be defined if extractable P is correlated with P lost by run-off and leaching. The threshold typically corresponds to:

- the content of P which is tolerated in water upon legislation, or
- the “change point” of the curve relating soil loss to soil P content, which is the point of the curve where the slope increases (Pote et al., 1999) (Figure 2).

![Figure 2. Representation of agronomic and environmental thresholds determination](image)

Generally, environmental threshold is higher than agronomic threshold, providing a control lever for the management of P.

### 2.2. Anion exchange resins and diffusive gradients in thin films (DGT)

Anion exchange resins were developed for water and sediment samples in the 1930s to assess the presence of labile P in soil samples or the presence of P in soil solutions. Upon contact with water and soil, the anion exchange resins act as a sink for P. Since then, analytical protocols designed to mimic the effects of roots have evolved (Qian et al., 2002).

In the 1990s, the use of DGT was preferred over anion exchange resins for estimates of P availability in soils to obviate the disadvantages of the latter (Chardon et al., 1996). These disadvantages included:

- modification of the physicochemical balance of the soil examined;
- the absence of an infinite binding capacity, thereby resulting in the potential for non-maximal desorption;
- difficulty in separating the resin from the soil;
- lack of specificity in the adsorption and desorption of certain anions;
- the influence of sulphate or nitrate concentrations on the quantities of P extracted.

Diffusive gradients in thin films (DGT) are a passive sampling technique which has been successfully applied to aquatic systems for measuring P (Zhang et al., 1998), and more recently, for predicting crop response to applied P in soil (Mason et al., 2010). Based on the same principle as anion exchange resin, DGT is composed of a layer of ferrihydrite binding gel with a strong affinity for P behind a diffusive hydrogel layer and an overlying protective filter membrane (Six et al., 2012). Diffusive gradients in thin films
can be placed directly onto a saturated soil paste, allowing for field measurements. Diffusive gradients in thin films provide a better estimate of P uptake by plants compared to certain chemical extraction methods (Zhang et al., 2014), and are less vulnerable to potential chemical constraints, such as anionic interferences or pH (Mason et al., 2008). Moreover, a low coefficient of determination for the regression fit between DGT and resin measurement was observed by Mason et al. (2008). Despite the results appearing hopeful for tropical soils, additional studies are necessary to expand the types of plants, soil, and climatic conditions that can be tested (especially in European soils), and to correctly interpret DGT-derived results (Zhang et al., 2014).

### 2.3. Biological extractions

To overcome the disadvantages of chemical extractants, it has been proposed that plants could be used to evaluate the bioavailability of P.

In bioassays, algae are grown in water in which P is a limiting factor, for which the only source is the soil sample. Unicellular algae are generally used in these tests, including *Selenastrum capricornutum* or *Scenedesmus quadricauda*. The experiments are generally performed aerobically for 2 to 4 weeks, and the algae are renewed weekly (Ekholm et al., 2003). Phosphorus availability is calculated on the basis of the algae biomass present, and results can be extrapolated for longer periods of time to determine the long-term availability of P. Several studies, including that of Boström et al. (1988), have shown that the results obtained using such bioassays are consistent with results obtained using chemical extractions. However, bioassay results are only relevant for the experimental conditions tested, and cannot be extrapolated to the natural environment. Furthermore, numerous species of algae exist in natural environments, and they can adapt to various forms of P.

Other biological methods have been used to estimate the capacity of a soil to supply P to a plant, including the use of micro-cultures (Stanford et al., 1957). In these cultures, plant growth is used to analyze the amount of absorbed P. Unlike chemical methods, this technique more accurately accounts for all of the factors affecting plant food.

However, bioassays are difficult to establish, more time-consuming to perform, and the experiments must be repeated to achieve the repeatability and accuracy of results. Therefore, these bioassays do not represent a substitute for chemical extraction methods, but should rather be a method performed to complement chemical extraction methods.

### 2.4. Isotopic methods

Time plays a significant role in determining P availability (Fardeau, 1993). Methods involving radioactive isotopes of P were developed in France by Fardeau (1993), and more recently by Morel et al. (2000) and Morel et al. (2014). Isotopes, unlike chemical reactions, enable the observation of soil behavior with regard to P without affecting the balance between the forms of P present in soil. The main isotopes used, $^{32}$P and $^{33}$P, have a half-life of 14.3 days and 23 days, respectively.

In general, isotopic methods consist of an injection with a defined amount of radioactivity into a solution, followed by subsequent measurements of the radioactivity remaining in the solution after a defined period of time. The ability to detect P is based on three principles:

- the concentration of phosphate ions in solution is constant over time;
- the isotopic tracer is instantly and uniformly distributed in the soil solution;
- the flow of labelled P ions is equal to the flow of unlabelled P ions (Némery, 2003).

The kinetics of the isotopic exchange method also enables the development of a compartmental representation of soil P reserves, as shown in figure 3 (Fardeau, 1993). This diagram illustrates the heterogeneity of phosphate ions that have the potential to reach the soil solution over variable periods of time. Moreover, this representation can also be linked to chemical methods used to determine the available and total reserves of P (Figure 3). The shapes of the extracted P vary depending on the extractant used (Figure 3).

Additional studies have demonstrated a range of potential applications for P isotopes. For example, in 2000, Morel used isotopic methods to model the dynamics of P ion transfer between soil and the soil solution as a function of the duration of P transfer and the concentration of P in solution. More recently, Morel et al. (2014) determined the relationship between the phosphate balance sheet and P exchanges using long-term test parcel data. Finally, P isotopes have been used in the study of plant growth and to measure the efficiency of plant growth following the addition of isotope-labelled fertilizers (Frossard et al., 1996).

However, there are disadvantages associated with the use of isotopes. In addition to the lack of information regarding the organic fraction of P, this method cannot be routinely used, and the manipulation of radionuclides is extremely delicate. Furthermore, it is difficult to generalize the results obtained under experimental conditions to events occurring naturally in soils. To address the latter point, scientists have attempted to relate the parameters of kinetic equations...
to the physicochemical characteristics of soil (Morel et al., 2014).

2.5. Complex models

**P indices for risk of P loss.** Knowledge of a soil’s status is not sufficient for estimating the risk of P export to surface or subsurface water since the losses that occur are influenced by both source and transport factors. Indices for risk of P loss represent management tools at the scale of a parcel which are used to identify critical source areas of P loss and farming practices that increase the risk. Critical source areas of P loss can be defined by their coinciding source (soil, crop, and management inducing high P loss) and transport (runoff, erosion, and proximity to water course or body) factors (Sharpley et al., 2014). This indice was developed to solve problems of localized excess of P.

Source factors represent the amount of P that can potentially be mobilized, as well as the conditions predisposing it to accumulation (e.g., soil test P, rate, method, timing of application of biological or mineral fertilizers, and leaching of P from plant residues), while transport factors are essentially hydrological in nature and affect the transport of P to rivers (e.g., erosion, surface run-off, subsurface drainage, connectivity). Phosphorus indices (PI) are simple models derived from the results of more complex experiments or models (Buczko et al., 2007).

A number of P indices, all of which are based on the original PI of Lemunyon et al. (1993) (Equation 2), have been developed according to the regional characteristics of a given state and/or country. Several P indices use the Pennsylvania PI. Currently, the PI approach is routinely used in 47 U.S. states, some Canadian provinces, and was adopted by several European countries, including Finland (2001), Ireland (2003), Sweden (2005), Norway (2005), Denmark (2006), and Germany (currently in progress).

Site vulnerability = 1.5*soil erosion + 1.5*irrigation erosion + 0.5*runoff class + 1*soil p test + 0.75*P fertilizer application rate + 0.5*P fertilizer application method + 1*organic P source application rate + 1*organic P source application method (Eq. 2) where the values for each characteristic are specified in Lemunyon et al. (1993), according to level.

The primary advantage of using a PI is in its speed and ease of use. However, some parameters, such as mode of farm management, are difficult to map. In addition, a PI can accommodate corrective measures. Therefore, a PI is not only an indicator that can provide an integrative approach, but it can also be easily adapted to local conditions (Buczko et al., 2007). Correspondingly, P indices have become highly popular tools from both scientific and political standpoints. Phosphorus indices require readily available data, and they can be automated using computer software which links them to a database of interest.

**Modelling of P loss.** Hydrological models of increasing complexity have been generated to quantify volumes of run-off water, as well as sediment loss and P loss, while also accounting for local specificities (e.g., connectivity of parcels with a river and topography, among others). With different models available, it may become difficult to select the most appropriate model. It is important to consider the scale of study for each of the models being considered, as well as their disadvantages. Hydrological models are very time-consuming and difficult to implement. In particular, they require extensive calibration, and are therefore not typically suitable for routine use. Moreover, these models can often prove to be
inadequate due to ground conditions which are difficult to foresee and transfer processes which are not always complete. These models are based on the hypothesis that P transfer is a result of runoff and erosion. However, in practice, the situation is more complex.

Nevertheless, some regions have developed these models and use them to evaluate the export of P from agricultural parcels. In particular, Quebec employs a Phosphorus Export Diagnostic Tool (ODEP) that is based on the SWAT model, and is able to integrate data regarding the topography, soil type, drainage, and agronomic management of a parcel. Consequently, this software tool can be used to quantify P losses, to identify the factors responsible for the losses, and to simulate different scenarios of P management. In Wallonia, Dautrebande et al. (2006) used the EPICgrid model to estimate P export from parcels.

3. EVALUATION OF DIFFERENT INDICATORS

Many indicators of P levels exist worldwide, and it is often difficult to select the most appropriate indicator. Moreover, many criteria exist to evaluate indicators, and each of the existing methods present advantages and disadvantages (Table 4). For this study, indicators were evaluated according to the framework of the “Sustainability Assessments of Farming and the Environment” (SAFE) hierarchical framework developed by Van Cauwenbergh et al. (2007). This framework has defined the following six criteria for environmental indicators:

- ability to discriminate in time and space,
- analytical accuracy,
- cost and time of analysis,
- ease of interpretation,
- relevance to regulations,
- the ability to extrapolate the results obtained using a given indicator.

The main indicators were evaluated according to these criteria (Table 5).

One of the most important considerations is the objective of the analysis to be performed, and therefore, the ability to discriminate in time and space. Three types of indicators exist: agronomic, environmental, and agro-environmental (Table 1). An indicator can be considered as having an agronomic interest if the relationship with plant uptake or yields has been proven. Similarly, a parameter can be considered as an environmental indicator when it presents a good relationship with P transferred to aquatic systems. Environmental indicators generally require mild extractants such as water or calcium chloride, which simulate desorption or solubilisation of P from soil to solution. Naturally, there is a link between these two objectives. When P in soil solution increases, P yield can increase, though P loss is also susceptible to increase. That is why some indicators as the degree of P saturation present both an agronomic and environmental interest.

Secondly, according to SAFE criteria, indicators must be easy to analyze within a reasonable cost, and analysis should be accurate. Some analyses are time-consuming and expensive to implement, or require specific conditions (Table 5). For example, isotopic methods, while being extremely accurate can only be performed by specialized laboratories. Moreover, although main extraction methods consist of a soil-extract suspension using a ratio which is seldom representative of soil conditions, ratios are often more representative of the aquatic environment. Each method extracts different forms of P and the chemical extractants often mobilize significant amounts of unavailable forms along with plant-available P (Frossard et al., 2004). Additionally, the determination of P can become unreliable in some soils if P concentrations in the extract are close to detection limits, as observed in water or CaCl₂ extractions.

Thirdly, Tiessen et al. (1993) stated that available P measures “a pool of soil P that is somehow related to that portion of soil P which is plant available”. Therefore, results should not be interpreted independently, but according to regional standards, which are defined according to experimentation with plants. To this end, Jordan-Meille et al. (2012) compared current methods used for recommending P fertilizers in Europe, despite the large number of analytical methods employed. Two different soils were tested, and the recommended P dosage varied between 0 and 89 kg P·ha⁻¹ for both soils, depending on the country and method used.

Lastly, extrapolating methods and results to other soils is not a simple task. Indeed, no one indicator is suitable for all soils. For example, levels of available P can be determined using the method of Joret et al. (1955). However, this method is more suitable for calcareous soils, whereas the Dyer method provides satisfactory results in soils ranging from acidic to neutral (Table 1).

An ideal indicator should be scientifically validated, be relevant in relation to the stakeholders and objectives, discriminate against expected changes, have an interest/cost ratio greater than 1, be based on readily available data, and be consistent with existing regulations. However, in practice, indicators rarely fulfill all of these criteria. Therefore, the selection of an indicator is based on a compromise between fixed objectives and cost in order to characterize a complex and often problematic phenomenon. Based on the criteria established by Van Cauwenbergh et al. (2007), it is evident that water extraction of P was one of the most advantageous indicators available (Table 5).
In contrast, other methods, such as sequential fractionation, are of little to no interest.

In practice, indicators are often correlated to each other. Phosphorus availability is determined by total P content and buffering capacity. Currently, the selection of indicators for a given country or region is a result of historical origin. It is very difficult to introduce changes into these methodologies, primarily due to the necessity of ensuring the standardization and continuity of databases, and the use of specific thresholds.

### Table 4. Advantages and disadvantages of various types of methods of phosphorus characterization in soil — *Avantages et inconvénients des différents types de méthodes de caractérisation du phosphore du sol.*

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Methods</th>
<th>Countries using these indicators</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical extractions</td>
<td>Available P (Olsen, AA-EDTA, Dyer, etc.)</td>
<td>All countries</td>
<td>Quick, inexpensive, easy to use</td>
<td>Specific to certain types of soil; specific thresholds for each country; modifies the physicochemical conditions of the medium</td>
</tr>
<tr>
<td>Water soluble P</td>
<td>The Netherlands</td>
<td>Quick, inexpensive, easy to use</td>
<td>May underestimate the available phosphorus</td>
<td></td>
</tr>
<tr>
<td>Degree of P saturation</td>
<td>The Netherlands, Belgium (Flanders), Quebec</td>
<td>Indicator is both agronomic and environmental; presence of thresholds</td>
<td>Sometimes difficult to interpret; the analysis is more time-consuming than others</td>
<td></td>
</tr>
<tr>
<td>Biological extractions</td>
<td>Bioassays</td>
<td>None</td>
<td>Reproduces the behaviour of plants</td>
<td>Time-consuming and impossible to use routinely</td>
</tr>
<tr>
<td>Anion exchange resins</td>
<td>Brazil</td>
<td>Mimics the effect of roots; suitable for all soils</td>
<td>Affects the physico-chemical equilibria; does not provide an infinite binding capacity</td>
<td></td>
</tr>
<tr>
<td>Isotopes</td>
<td>None</td>
<td>Provides a model of P ion transfer kinetics; suitable for a wide range of soils; its results can be extrapolated to longer periods of time; it permits observation without changing equilibria</td>
<td>Cannot be used routinely; manipulation of radioelements is extremely delicate; a lack of information about the organic fraction; experimental dilution conditions do not represent natural conditions</td>
<td></td>
</tr>
<tr>
<td>More complex models</td>
<td>PI, ODEP, etc.</td>
<td>Quebec, USA, Norway, Finland, Denmark</td>
<td>Comprehensive; takes into account both source and transport factors; predicts the amounts and forms of P</td>
<td>Great complexity; significant amount of required data; often imperfect; moderately operational</td>
</tr>
</tbody>
</table>

4. **Which indicators can be used in Wallonia?**

In Wallonia (Belgium), there are no measures currently scheduled to assess the management status of P. Incidentally, according to the Organisation for Economic Co-operation and Development (OECD), Belgium is considered as the first European country to possess a surplus of P delivered to agricultural parcels. This surplus, amounting to 21 kg P ha⁻¹ yr⁻¹, is...
Table 5. An evaluation of different indicators according to SAFE requirements that a good indicator should meet — Évaluation des différents indicateurs sur base des exigences SAFE que doit remplir un bon indicateur (Van Cauwenbergh et al., 2007)

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Ability to discriminate in time and space</th>
<th>Analytical accuracy</th>
<th>Cost and time of analysis</th>
<th>Transparency and ease of interpretation</th>
<th>Relevance to regulations</th>
<th>Transfer and extrapolation of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicators of P bioavailability</td>
<td>++ Available P according to Lakanen-Erviö</td>
<td>+ Available P by other methods</td>
<td>++ Soluble P in water</td>
<td>++ May vary depending on the season</td>
<td>++ Fast</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>++ Available P according to Lakanen-Erviö</td>
<td>+ In general</td>
<td>++ Average</td>
<td>++ Very fast, low cost</td>
<td>++ Fast</td>
<td>- Depends on P and soil binding capacity</td>
</tr>
<tr>
<td>Degree of P saturation</td>
<td>++ Takes into account soil properties</td>
<td>+</td>
<td>+ Fast</td>
<td>- Depends on P and soil binding capacity</td>
<td>+ Environmental threshold of 25%</td>
<td>+ Environmental threshold of 25%</td>
</tr>
<tr>
<td>Sequential extractions</td>
<td>+ Depends on agricultural practices</td>
<td>- Can be difficult to achieve repeatability</td>
<td>- Time-consuming and not used routinely</td>
<td>- Difficult due to the many forms of P</td>
<td>~ None</td>
<td>~</td>
</tr>
<tr>
<td>Anion exchange resins</td>
<td>+</td>
<td>~ Depends on the presence of NO₃ and SO₄</td>
<td>+ Simple</td>
<td>+</td>
<td>~</td>
<td>+ Suitable for all soils</td>
</tr>
<tr>
<td>Biological extractions</td>
<td>~</td>
<td>- Poor repeatability</td>
<td>~</td>
<td>~</td>
<td>None</td>
<td>+ Suitable for all soils</td>
</tr>
<tr>
<td>Isotopes</td>
<td>+ Depends on P inputs</td>
<td>+ Cannot be used anywhere</td>
<td>- Delicate manipulations need to be performed by an accredited lab</td>
<td>+ Kinetic modelling</td>
<td>~ None</td>
<td>+ Not bound to soil</td>
</tr>
<tr>
<td>Indices of risk of P loss</td>
<td>++ Takes into account soil properties</td>
<td>- Calibration required</td>
<td>~ Rapid once calibrated, but time-consuming and costly</td>
<td>++ Provides losses and risks, possible simulations</td>
<td>+ In Nordic countries</td>
<td>- Calibrated for each soil</td>
</tr>
</tbody>
</table>

++: very good — très bon; +: good — bon; ~: mixed — moyen; :- bad — mauvais.
largely the result of pig farms being primarily located in Flanders. However, Wallonia contains lower surplus, despite significant regional disparities (Genot et al., 2009; Renneson et al., 2015).

In Wallonia, the soils predominantly range from neutral to acidic, and P extraction has been routinely performed by soil analysis laboratories since 1990 using ammonium acetate and EDTA (pH 4.65) (Lakanen et al., 1971). Ammonium acetate is used to dissolve any aluminium phosphate present, while the acidity leads to a reversible release of P from iron, aluminium, and partly calcium (Hons et al., 1990; Woodard et al., 1994). The chelating agent, EDTA, aids in the prevention of newly released P from binding to iron (Dao, 2004). Thus, ammonium acetate facilitates the dissolution of a subset of P associated with iron oxide molecules that are either not crystallized or slightly crystallized, corresponding with the different forms of P that are available to plants. However, ammonium acetate is largely unable to dissolve calcium phosphates, thus rendering it unsuited to carbonated soils. In Wallonia, carbonated soils represent less than one per cent of the territory.

According to table 5, available P from Lakanen-Erviö (P\textsubscript{AA-EDTA}) presents different advantages. However, to be an adequate agronomic indicator, it should be related to P uptake or yields. Hons et al. (1990), Homsy (1992) and Woodard et al. (1994) studied the relationship between P exported by plants and yields. P\textsubscript{AA-EDTA} was correlated with P fertilizer level P (R\textsuperscript{2} = 0.89), primarily in slightly acidic soils (Hons et al., 1990). In a study by Woodard et al. (1994), P\textsubscript{AA-EDTA} predicted yields and P concentration responses in plants more accurately than Olsen P. Thresholds have been defined for Wallonia according to P plant levels and soil property results (Genot et al., 2011).

Significant correlations between P\textsubscript{AA-EDTA} and other P extraction methods have been observed, most strongly with the methods of Bray, Olsen, and Sissingh (Ryser et al., 2001). Hons et al. (1990) and Homsy (1992) found R\textsuperscript{2} values (between ammonium acetate and EDTA extraction and others) varying between 0.66 and 0.91 and between 0.64 and 0.90, respectively, depending on the soil. Therefore, the Lakanen-Erviö method is well correlated with other predominant methods used worldwide. Neyroud et al. (2003) classified the amount of extractable P according to 16 methods. The Lakanen-Erviö method extracts less P than Mehlich 3 or Bray methods, but more than the Olsen method.

The northern region of Belgium consists of soils (loamy and sandy texture) which exhibit a relatively limited P binding capacity and relatively high levels of available P. Extraction of P by the method of Lakanen et al. (1971) has been performed in Wallonia in an agricultural context without consideration for its impact on the environment. Celardin (2003) discovered a significant relationship between Lakanen-Erviö P content and water-extractable P, which is representative of P loss risk (R\textsuperscript{2} of 0.625 and 0.47 for pH 4.6-6.5 and pH 6.6-8.6, respectively). Houben et al. (2011) and Renneson et al. (2015) have evaluated the potential for using the degree of P saturation as an environmental indicator in the Walloon region. The latter may represent a promising indicator of P status in Wallonia, provided that the existing equations are adapted to the soil characteristics beforehand (Renneson et al., 2015). Moreover, Renneson et al. (2015) showed that extraction of P using the method of Lakanen et al. (1971) correlated (R = 0.78) with the extraction of P performed with ammonium oxalate, which is used for calculating the degree of P saturation.

Other indicators such as P index for risk of P loss could be developed. However, relatively few data are currently available regarding the amount of P loss occurring in the agricultural parcels of Wallonia.

5. CONCLUSIONS

A profusion of P indicators types can be found in the literature. The majority of indicators currently used are designed to characterize the status of the soil based on their P content, whereas other, more complex indicators are designed to model P flow to the environment and estimate the risk of P loss. The latter assesses P loss while simulating contributions to, or management of, P content. This approach has a certain advantage, yet these methods can be time-consuming difficult to implement. Consequently, most countries use simpler measurement indicators of soil P, involving various types of analyses ranging from single extraction methods to the use of P isotopes. Several methods also use ion exchange resins or biological extractions. Moreover, some authors have combined single extractions to measure P forms into the soil (sequential extraction).

Correlations can often be found between the different indicators reported in the literature. However, these results can rarely be applied generally and depend from one soil to another. Some authors have proposed a classification system based on the amount of P that is extracted. However, this is not universal for all types of soil.

Each of the methods available has certain advantages and disadvantages, and no indicator is suitable for every soil. The appropriateness of all indicator types has been evaluated according to various criteria. The selection of an indicator is generally a compromise between fixed objective and other criteria, such as the cost and time of analysis. However, to make a choice in existing indicators, a global analysis must be made.
Some indicators, such as isotopic methods have great potential as P indicators, though their routine use is difficult (necessity of specialized laboratories). Current indicators are generally explained by their historical use. Some authors suggest that extraction methods should be harmonized throughout Europe. However, it is difficult to change a method due to the inadequacy in some soils, lack of threshold in each country, and the necessity to maintain soil quality monitoring.

At present, in Wallonia (southern Belgium), P extraction has been performed using ammonium acetate and EDTA (pH 4.65). This extraction method is well correlated with other extraction methods and crop yields. A reflection is made to study the interest of other indicators as the degree of P saturation which is an environmental indicator.

This review highlights the importance of careful consideration of indicator choice, and the establishment of interpretation thresholds. This review creates a comparison of appropriate and regionalized reference values.

Bibliography


Genot et al., 2011. Un conseil de fumure raisonné. Le cas du phosphore. Gembloux, Belgique : REQUASUD.

Indicators of phosphorus in soils


Mehlich A., 1953. *Determination of P, Ca, Mg, K, Na, NH\textsubscript{4}*. Raleigh, NC, USA: Department of Agriculture.


Morgan M.F., 1941. *Chemical soil diagnosis by the universal test system*. New Haven, CT, USA: Connecticut Agricultural Experiment Station.


NF X 31-160, 1999. *Qualité des sols – Désorption du phosphore soluble dans une solution à 20 g·l\textsuperscript{-1} d’acide citrique monohydraté – Méthode Dyer*. La Plaine Saint-Denis, France : AFNOR.

NF X 31-161, 1999. *Qualité des sols – Désorption du phosphore soluble dans une solution d’oxalate d’ammonium à 0,1 mol·l\textsuperscript{-1} – Méthode Joret-Hébert*. La Plaine Saint-Denis, France : AFNOR.

Soil

L’analyse du sol

versus

Actes des

In

In

272


Schüller H., 1969. Die CAL-Methode, eine neue Methode


