Study of the degree of phosphorus saturation in Walloon Region (Southern Belgium)

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Abstract
Phosphorus losses from agricultural land can be a major source of eutrophication of surface waters. To meet the objectives of the Water Framework Directive, measures should be taken in agricultural soils. The degree of phosphorus saturation (DPS) is used in some countries to evaluate levels soil P saturation and subsequent risks of losses. The adequacy of this parameter to the Walloon situations had to be assessed before large-scale surveys. As a prior stage, this study has shown that DPS=P_{ox}/0.66*(Al_{ox}+Fe_{ox}) was relevant to study the P saturation of studied soils. A mean DPS of 32% was observed. Risks of P losses seem high in some areas and should be attributed to 2 factors: soil properties which drive the sorption capacity on the one hand and soil fertility management by farmers. A close relationship was found between DPS and available P and with sorption capacity and P_{av}/P_{ox} ratio, which suggests that phosphorus availability is favoured when sorption sites are saturated, that is on soils with low PSC. However, as P transfers from soil to water may occur through particulate erosion, the total sorbed P should be taken into account too. DPS is thus of interest as environmental indicator but it shouldn't be used alone.

Key Words
Oxalate phosphorus, phosphorus sorption capacity, eutrophication, soil, indicator, fertilization.

Introduction
Just like as nitrogen, phosphorus (P) losses from agricultural soils can lead to eutrophication of surface water. P is essential for plant growth and may be considered as the main limiting resource for algae development in surface water. The surface water contaminations by human activities are a major concern in Europe and appropriate P management becomes crucial to meet the Water Framework Directive objectives. Measures have already been taken for some years to reduce urban P losses and agricultural diffuse inputs have become the major source of P in surface water. High rates of P fertilization result in P accumulation in soils which may lead to saturation of sorption sites and therefore increase risks of P loss to surface or groundwater via runoff or leaching. To evaluate these risks, we need environmental easily determinable and interpretable indicators and thresholds.

The Degree of Phosphorus Saturation (DPS) has already been used as an environmental indicator in some regions/countries all around the world, because DPS was shown to present a strong relationship with P runoff or P leaching. This parameter evaluates the proportion of soil exchange sites that are effectively bound to P.

\[
\text{DPS (\%)} = 100 \times \frac{P_{\text{ox}}}{\text{PSC}} \quad (\text{Van der Zee and Van Riemsdijk 1988}) \tag{1}
\]

Where P_{ox} is oxalate-extractable P (mmol/kg) and PSC is the Phosphorus Sorption Capacity (mmol/kg). The soil PSC is a finite characteristic that depends on clay, organic matter, aluminium, iron, and calcium contents and pH. Factors that affect these properties such as soil type or land use also determine PSC. It can be estimated by (Börling et al. 2001):

\[
\text{PSC} = \alpha (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) \tag{2}
\]

where Al_{ox} and Fe_{ox} are oxalate-extractable Al and Fe, and \( \alpha \) is a scaling factor.

The scaling factor \( \alpha \) depends on soil type and experimental conditions. The \( \alpha \) value of 0.50 has been largely used but its relevance was seldom verified. Some authors found different values that ranged from 0.44 (Van der Zee et al. 1988) to 0.68 (Paulter and Sims 2000) in other situations. Wrong estimates of \( \alpha \) can therefore lead to serious misinterpretations of the soil sorption saturation.
This study aims to verify the dependency of DPS to soil type and agricultural soil fertility management in three important crop production regions of Southern Belgium. In the first step, the α scale factor was assessed for a selected set of soil samples representative of soil diversity in cultivated areas. Then, the relationships between DPS and soil characteristics as well as the influence of cultivation systems on DPS were investigated for selected farms.

Material and methods

Study Area and Soil Sampling

Six reference farms were selected within a network dedicated to the management of agricultural N-resources in Southern Belgium. These farms cover a wide range of soils, reliefs, and agricultural systems. They are located in three important crop production areas which are also the most problematic regarding phosphorus leaching, runoff and eutrophication. Soil samples were taken in 24 arable parcels. One composite (16 cores in a 2 m² area) topsoil sample (0 to 20 cm) was collected for each soil type within each parcel. Thus, one to five soil samples were collected within each of 24 fields for a total amount of 57 samples.

Chemical Characterization

All samples were dried at 40°C and sieved at 2 mm prior to storage and laboratory analyses. Soil pH in water (2:5) and 1N KCl (2:5) were measured and total organic carbon (TOC), total nitrogen (TN), cation exchange capacity (CEC), and clay content were predicted by near-infrared spectroscopy (NIRS). Available phosphorus (P_{av}) was determined following Lakanen-Erviö method (Lakanen and Erviö 1971). Oxalate extractable Fe (Fe_{ox}), Al (Al_{ox}) and P (P_{ox}) were determined after extraction with oxalate solution using a 1:20 (w:v) soil:solution ratio (Ross and Wang 1993). The suspension was equilibrated for 2 hours in the dark with continuous shaking, centrifuged (10'), and filtered. Al and Fe concentrations were measured by atomic absorption spectroscopy (AAS - VARIAN 220) and P by blue-colorimetry (Murphy and Riley 1962). PSC and DPS were calculated according to equations (1) and (2) (Van der Zee and van Riemsdijk 1988). The scale factor, α, was determined beforehand.

α determination

The use of the equation (2) requires the prior assessment of the α scale factor. This factor corresponds to the proportion of poorly crystallized Al- and Fe-oxides that can actually sorb P, known as total phosphorus sorption capacity (PSC_t). PSC_t is divided into P-occupied sites and remaining P sorption capacity (PSC_r) (Equation 3). The amount of P sorbed on the PSC_t is evaluated by oxalate-extractable P (P_{ox}) and PSC_t is calculated by multiplying an experimental P sorption capacity (F_r) by 2.75 (Equation 4). F_r is determined by the standardized one-point short-term isotherm method (Bache and Williams 1971). Three grams of 2 mm soil were shaken with 60 mL of a 75 mg P/L (as KH_2PO_4 equivalent to 1.5 g P/kg soil) 0.01 M CaCl_2 solution during 18 hours with some drops of chloroform. Samples were then centrifuged (10') and filtered (Whatman 602). Finally, the P remaining in solution was measured by colorimetry (Murphy and Riley 1962). The sorbed P (F_r) is calculated as the difference between added P and P remaining in solution. This method allows rapid appraisal of the remaining soil P-sorbing capacity. However short-term experiments usually under-evaluate PSC_r. To correct the estimates of PSC_r, the 18-hours F_r is multiplied by 2.75 (Maguire et al. 2001). Finally, the α scale factor can be estimated (equation 5).

\[
PSC_t = PSC_r + P_{ox} \tag{3}
\]

\[
PSC_r = F_r \times 2.75 \tag{4}
\]

\[
\alpha = \frac{P_{ox} + PSC_r}{Fe_{ox} + Al_{ox}} \tag{5}
\]

The F_r, PSC_r, PSC_t parameters and α scale factor were determined for the 57 soil samples and the mean α was used to calculate PSC and DPS.

Results

Soil characteristics

Dominant soil order in the studied area is Luvisol, but some Fluvisols, Regosols and Leptosols were also observed. Textural classes, as assessed in the field, were mainly silt, sandy loam and clay loam. Soils were also differing by the quality of natural drainage observed by the depth and intensity of redox mottles. The soil characteristics measured in the laboratory are summarized in Table 1. The ranges for clay content...
Influence of P management on DPS presented higher DPS than other farms, which we attribute to intensive pig farming. A 5-years P balance has parameter should be determined for each natural region according to soil map. The mean value of α is close to results of Paulter and Sims (2000) or Maguire et al. (2001), 0.68 and 0.65, respectively. Further DPS calculations (equation 2) in this study were based on the mean α value of 0.66.

Soil sorption saturation
PSC and saturation are summarized in Table 1, with the oxalate-extractable Al, Fe and P. All of them are moderately variable. A close relationship was observed between the P total capacity of sorption and the sum of Al_{ox} and Fe_{ox} which confirms that PSC, of Belgian soils is controlled by amorphous Al and Fe. The remaining phosphorus sorption capacity (F_s) and DPS are logically negatively correlated. The more the soil is saturated with P, the less P-binding sites remain available.

Influence of soil properties on sorption capacity
The PSC depends on soil texture, clay content or CEC. The total sorption capacity ranged from 64 to 144 mmol/kg. It was higher in clayey or silty soils than in sandy soils. On that particular point, these latter soils are therefore more vulnerable to soil losses. In our study, farm 2 implemented a cultivation system with minimal P inputs. However, DPS appears relatively high, due to very low soil capacity. On the other hand, soil from farm 3 presented relatively high P content but the high PSC reduces the risks of P loss.

Influence of P management on DPS
The surface soils in this study presented DPS values ranging from 12.9 to 63.8%, with a mean of 32% (Table 1). In this study, some differences between farms were observed (Figure 1). For instance, farms 1 and 6 presented higher DPS than other farms, which we attribute to intensive pig farming. A 5-years P balance has been calculated for each farm and compared to DPS. No clear relationship could be found. DPS is a ratio which depends both on P management and soil characteristics. It allows a better evaluation of the P availability and the P loss risk, but is not a relevant agronomic indicator of past fertilization. Another ratio can be used to identify farms with P management presenting a risk for the environment. The ratio P_{av} / P_{ox} evaluates the fraction of sorbed P which is more susceptible to desorb and migrate to plants or in the soil.

Table 1. Characterization of studied soils.

<table>
<thead>
<tr>
<th>Clay content (%)</th>
<th>Organic C (%)</th>
<th>Nitrogen (%)</th>
<th>CEC (cmol/kg)</th>
<th>pH_{water}</th>
<th>P_{ox} (mmol/kg)</th>
<th>Al_{ox} (mmol/kg)</th>
<th>Fe_{ox} (mmol/kg)</th>
<th>PSC (mmol/kg)</th>
<th>DPS (%)</th>
<th>Pav (mg/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>0.53</td>
<td>0.57</td>
<td>0.56</td>
<td>0.57</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Mean</td>
<td>15.8</td>
<td>1.4</td>
<td>0.13</td>
<td>13.1</td>
<td>7.6</td>
<td>15.4</td>
<td>29.8</td>
<td>46.4</td>
<td>50.3</td>
<td>32.0</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>3.6</td>
<td>0.2</td>
<td>0.02</td>
<td>2.1</td>
<td>0.4</td>
<td>3.3</td>
<td>7.1</td>
<td>10.6</td>
<td>10.5</td>
<td>9.9</td>
</tr>
<tr>
<td>Coefficient of variation (%)</td>
<td>23.0</td>
<td>17.6</td>
<td>16.19</td>
<td>16.1</td>
<td>4.7</td>
<td>21.5</td>
<td>23.9</td>
<td>22.9</td>
<td>29.9</td>
<td>30.9</td>
</tr>
<tr>
<td>Minimum</td>
<td>6.7</td>
<td>0.9</td>
<td>0.08</td>
<td>7.6</td>
<td>6.5</td>
<td>6.4</td>
<td>18.3</td>
<td>27.5</td>
<td>32.7</td>
<td>12.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>25.3</td>
<td>2.2</td>
<td>0.18</td>
<td>19.2</td>
<td>8.0</td>
<td>25.5</td>
<td>43.8</td>
<td>75.8</td>
<td>77.0</td>
<td>63.8</td>
</tr>
</tbody>
</table>

(6.7 to 23.3%) and CEC (7.6 to 19.2 cmol/kg) and the moderate CV reflect the influence of aeolian silt deposits which lead to relative homogenization of soil parent material in the studied area. Compared to regional values for cultivated soils, the mean P_{av} of studied soils (12.8 mg P/100g) appears high. However, P_{av} presented the largest relative variability (CV = 66.8%) among measured or calculated soil characteristics probably due to the diversity of P management in studied farms.

α parameter assessment
Sorption isotherms were processed on studied samples to calibrate the α value to the regional natural environment. Our results for α values varied from 0.43 to 0.93, with a mean value of 0.66 and a standard deviation of 0.13. Clayey soils showed a higher α (mean of 0.88) than the other soils. This confirms that this parameter should be determined for each natural region according to soil map. The mean value of α is close to results of Pautler and Sims (2000) or Maguire et al. (2001), 0.68 and 0.65, respectively. Further DPS calculations (equation 2) in this study were based on the mean α value of 0.66.

Influence of soil properties on sorption capacity
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Figure 2 illustrates the relationship between this ratio and soil sorption capacity. The higher the PSC, the smallest the proportion of available P to sorbed P for the plant growth but also for the environment. This suggests that the binding strength depends upon the number of sites and that availability of P is improved with soil saturation. Figure 2 also allows one to distinguish intensive pig farming from other cultural systems.

Some thresholds have been proposed to DPS as environmental indicators. In the Netherlands, a threshold of 25% was proposed (Breeuwsma et al. 1995) and 40% in Flanders (Chardon and Schoumans 2007). According to that, 77% of our samples are above the Dutch threshold and 20% should be classified as saturated according to Flemish legislation. Care should then be taken when defining such thresholds. They should rely on effective measurements of P transfers from soil to surface waters.

The good relationship (r=0.818) between P_{av} and DPS shows the potential use of P_{av} which is more easily measurable, for environmental indication. This relationship is even improved when the correlation analysis takes the texture into account.

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Conclusion
DPS is an environmental indicator to estimate the P release to surface waters which can induce eutrophication. To be useful in Southern Belgium, the calculation of this parameter had to be adapted and the relationship with soil properties and P management were investigated. The study of the sorption capacity showed that fixing the α to 0.50, such as is done in many studies, overestimates the saturation status. A value of 0.66 would be more adequate for the Walloon situation. DPS is a double indicator. It allows one to determine the availability of P in the soil because DPS is well correlated with $P_{0.66}$. Moreover, this parameter shows also the capacity of a soil to retain additional P. Indeed, the remaining P sorption diminishes when DPS increases. The evaluation of DPS has shown that differences between regions were due to P management. DPS was higher in pig breeding areas. However DPS is also influenced by soil properties, and mainly by texture. The low PSC in sandy soils results in a high DPS, even if P content is low. That leads to environmental problems in some regions. These high DPS areas correspond to eutrophication areas. In consequence, DPS is a good environmental indicator which takes soil characteristics and P management into account. But to be used efficiently, thresholds should be developed for the Walloon context. Moreover, it shouldn't be used alone because they can't integrate the processes of soil-water transfers by particulate P.

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References