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Using soil phosphorus sorption saturation with Mehlich 3 extractant as a predictor for estimating risk of phosphorus losses by leaching from arable land

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Abstract. Phosphorus (P) is essential for plant growth and yield. Balanced fertilization can produce a yield-sustaining effect, but excessive P applied to agricultural soils poses a risk by losing excess of phosphorus to the aquatic environment. This is undesirable from both an economic and environmental perspective as it wastes a finite phosphorus rock and represents a serious environmental hazard in the form of pollution and eutrophication of the aquatic resources. For this reason, proven methods of estimating the risk of P losses from agricultural land are needed. The aim of this study was to assess the content of soil available phosphorus (SP) and soil phosphorus sorption saturation (Psat) in arable soils and assess if they can be used to predict P in waters from drainage outlets from adjacent arable land. The determination of phosphorus content in the soil and determination of Psat was carried out using Mehlich 3 extractant. Psat was calculated as the molar ratio of P to the extractable Fe and Al in one solution. The average phosphorus content determined in the soil by the Mehlich 3 method was 101.8 mg kg^{-1}. Psat was on average 11.8%. The average content of phosphorus in water samples from drain outlets was 0.1 mgP dm^{-3}.

Key words: soil phosphorus sorption saturation, phosphorus losses, soil phosphorus, Mehlich 3, drainage water

INTRODUCTION

Agricultural sector in Poland is expected to provide food for approximately 38 million of its citizens and, apart from that, to generate export profit. Despite the naturally occurring pool of soil available phosphorus (SP), a fertilization in the conditions of Polish soils is an inseparable element of modern intensive agriculture. In order to achieve that, farmers need to use phosphorus fertilizers, both from mineral (as shown on Figure 1) and organic sources.

As balanced fertilization can produce sustainable effect maintaining yields, P applied to agricultural soils in excessive doses creates a hazard through P losses to the water environment (Fischer et al., 2018). From the environmental perspective this is undesirable for many reasons as it poses an important threat of eutrophication and toxicity for aquatic environment (Fischer et al., 2018; Gérard, 2016; Jalali, Jalali, 2017; Maguire, Sims, 2002; Nair, 2014; Pastuszak et al., 2018; Wang et al., 2012), metallic pollution of soils and uneffective use of natural finite resources (Gérard, 2016). Counteracting this phenomenon is a task to which all Baltic countries of the EU, including Poland, have committed themselves (HELCOM, 2018). In order for phosphorus fertilization to be effective and safe for the environment, it is necessary to properly manage it. The first step to the sustainable use of fertilizers is an accurate diagnosis of the soil condition, for which soil tests are used. Classification of soil phosphorus abundance is one of the basic, most common indicators used in soil phosphorus management. However, it is oriented towards the yield response of crops, and not at the estimation of P losses to waters (Jadczyszyn et al., 2010). For this purpose, other indicators are used.

There are many approaches to estimate the risk of phosphorus losses from the agricultural soil to water (Kleinman, Sharpley, 2002). One of them, studied in many parts of the world, is the soil phosphorus sorption saturation (Psat) (Fischer et al., 2018, 2017; Nair, 2014; Sharpley, 1995, 2020). It is based on a concept that in acidic soil's P sorption capacity is defined mainly by the amount of free amorphous Fe and Al compounds that are able to bind phosphorus (Kleinman, Sharpley, 2002). There are different formulas for calculating Psat, but for acidic soils and for the cost- and time- effectiveness the molar ratio of P to the extractable Fe and Al is probably the most common approach (Beauchemin, Simard, 1999; Nair, 2014; Sharpley, 1995, 2020).

Different extracting solutions are used to obtain Psat, among which, the most used are: ammonium oxalate ex-

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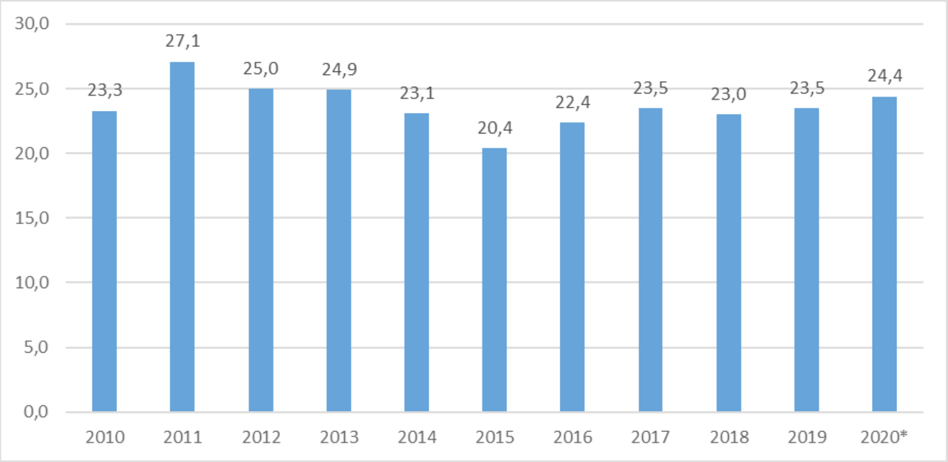

*preliminary data of the Agricultural Census

Figure 1. Consumption of mineral phosphorus fertilizers in terms of pure ingredient (kg) per 1 ha of agricultural land 2010-2020 (Statistics Poland, 2021).

tractant, Mehlich-1, and Mehlich 3 (Beauchemin, Simard, 1999; Ige et al., 2005; Jalali, Jalali, 2017; Nair, 2014). Mehlich 3 extraction procedure was used in this research as it enables for simultaneous determination of the content of available forms of many macro- and microelements in single soil extract, namely: phosphorus, potassium, calcium, sodium, magnesium, iron, aluminum, manganese, copper, zinc, boron and sulfur (Kęsik, 2016). Additionally, this universal extraction solution (pH 2.5 ±0.01) is intended for the determination of acidic and neutral soil samples (Mehlich, 1984), which constitute the majority of agricultural soils in Poland (Ochal, 2014). It should be also mentioned that one of the arguments in favor of testing this method in Poland was the fact that in neighbouring countries with similar agrochemical conditions, i.e. Estonia, the Czech Republic and Slovakia, the Mehlich 3 method has already been tested and implemented in the fertilizer advisory system.

As already proven in the literature (McDowell et al., 2002; Maguire, Sims, 2002; Wang et al., 2012) Psat, originally developed mainly for agronomic consultancy, might as well be used to assess the potential risk of P loss from agricultural soils (Sims et al., 2000; Hooda et al., 2000; Beauchemin, Simard, 1999; Kęsik, 2016; Fischer et al., 2017; Jalali, Jalali, 2017; Kleinman, Sharpley, 2002; Maguire, Sims, 2002; Sharpley, 1995; Sharpley et al., 2020; Wang et al., 2012). In Poland, there is not much research on this topic (Kęsik, 2016; Szara, Sosulski, 2018; Szara et al., 2019).

The aim of this study is to assess the possibility of using the Psat for estimating/evaluating the risk of phosphorus losses from arable land and to forecast pollution of drainage water with phosphorus.

MATERIAL AND METHODS

Both soil and water samples had been collected by professional samplers as a part of Soil Nitrogen Monitoring Programme run by National Agrochemical Station (KSChR). The monitoring points are presented in Figure 2.

Leachate samples (n=216) originated from drainage outlets discharging soil filtrate. Phosphorus ($P\text{-}PO_4^-$) in water was determined spectrometrically in laboratories of relevant local district agrochemical stations using PN-EN ISO 15681-2:2006 standard (Polski Komitet Normalizacyjny, 2006). In this method phosphates react with ammonium molybdate in the presence of reducing agents (an ascorbic acid) to form a blue coloured complex, the intensity of which is directly proportional to the concentration of phosphates in the solution. Water samples were determined by a continuous flow analysis method (CFA) using San^{SERIES} analyzer (by Skalar Analytical B.V.) with spectrometric detection. Number of water samples does not match number of soil samples as at 5 monitoring points it was not possible to collect water samples (too little water in the drainage outlet).

Soil samples (n=221) were collected according to PN-R-04031:1997 standard (Polski Komitet Normalizacyjny, 1997) from the plough layer (0 to 30 cm) using a standard soil-sampling auger from arable land adjacent to drainage outlets, air dried and sieved to < 2 mm. The determination of soil particle size composition was done using the laser diffraction method standard (Polski Komitet Normalizacyjny, 1998). The pH was measured potentiometrically in 1:2.5 (m/V) suspension of soil in 1 mol L^{-1} KCl solution (ISO 10390 2005).

The P, Al and Fe were extracted following the Mehlich 3 method (Mehlich, 1984). 10 g of soil samples (±0.01 g) were extracted using 100 mL (± 0.5 mL) of solution that is composed of of 0.2 M glacial acetic acid, 0.25 M ammonium nitrate, 0.015 M ammonium fluoride, 0.013 M nitric acid, and 0.001 M ethylene diamine tetraacetic acid (EDTA). After the P extraction (that took place as a result of the action of fluorine compounds and acetic acid) the extractant was analyzed by emission spectrometry with inductively coupled plasma (ICP) (Kęsik et al., 2015).

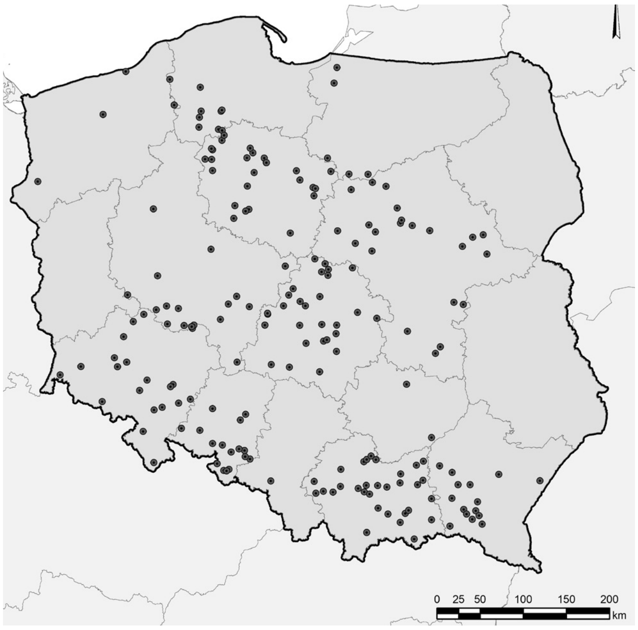

Figure 2 The monitoring points for soil and water samples.

Psat

To determine the soil phosphorus sorption saturation the contents of P, Al, Fe (mg kg^{-1} of soil) were divided by their molar mass (Table 1) and calculated according to the following formula:

$$Psat = \frac{P}{(Al + Fe)} \times 100\%$$

where:
Psat – soil phosphorus sorption saturation,
P, Al, Fe – P, Al and Fe content determined by the Mehlich method 3, expressed in mmol kg^{-1}

Table 1. Molar mass values of aluminum, iron and phosphorus expressed in mg mmol^{-1}.

	Fe	Al	P
Molar mass	55.85	26.98	30.97

The obtained results were statistically evaluated with the use of the Statistica 10.1 program, with the method of analysis of variance, using the Tukey confidence interval, with the significance level of $\alpha = 0.05$. The relationship between SP and Psat and phosphorus in drainage outlets was determined through Spearman rank correlations coefficient at 5% probability.

In this paper a soil classification is presented according to a simplified division of soils into four agronomic categories, depending on fine (<0.02 mm) particle content (Jadczyszyn et al., 2010). This approach includes the following categories of soil: very light, including soil units with 10 % content of fine particles, 2) light, including soil units between 10–20% of fine particles content, 3) medium, including soil units between 20–35% of fine particles content, 4) heavy, including soil units with more than 35% of fine particles.

RESULTS

Soil distribution across tested samples was dominated by heavy soil (34%) while almost half of tested samples presented light or very light agronomic category (Figure 3).

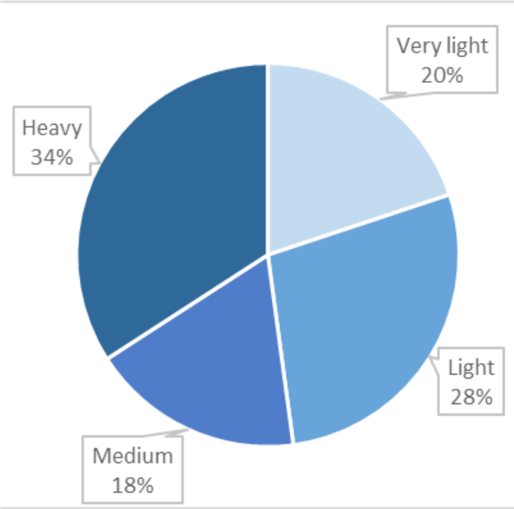

Figure 3. Agronomic categories of tested soil samples according to soil texture.

Presented water parameters and soil indiced, apart from pH, was characterized by great variability (expressed by coefficient of variation) as shown in Table 2. It proves that the distribution of soil phosphorus indices and the P content in water significantly differs from the normal distribution, because the standardized skewness and kurtosis lie outside the <-2, + 2> range. Therefore, the medians were adopted in this paper as the appropriate measure of the features (the average value).

Median value for SP in the top 30 cm was 101.8 mg kg^{-1} with 75% of tested points represent SP $\leq$ 176.3 mg kg^{-1}. Psat was on average 11.8% (with a coefficient of variation of 105.85%), the average content of phosphorus from drainage outlets samples was 0.09 mg dm^{-3}. In the tested sample population only 25% of water samples exceeded 0.22 mg P dm^{-3}. Among the examined soils, soils with a neutral or acid pH were predominant as upper quartile of observed results was pH=6.7 with median value of 6.1. The detailed characterisation of the tested soil and water samples is presented in Table 2.

Table 2. Distribution and main statistical characteristics of tested phosphorus indices.

Characteristic	pH	Soil P content (SP) [mg kg^{-1}]	Soil phosphorus sorption saturation (Psat) [%]	Water P-PO$_4^-$ [mg P dm^{-3}]
Count	130	221	221	216
Mean	5.8	124.4	16.7	0.24
Median	**6.1**	**101.8**	**11.8**	**0.09**
Stnd. deviation	1.1	91.4	17.6	0.42
Coeff. of variation [%]	19	71	105	170
Minimum	3.6	10.1	0.7	0.00
Maximum	7.9	536.4	133.2	3.82
Lower quartile	5.0	55.2	5.8	0.03
Upper quartile	6.7	176.3	23.6	0.22
Stnd. skewness	-0.28	8.4	20.5	25.31
Stnd. kurtosis	-1.0	7.8	48.2	81.22

Table 3. Average values of soil P content [mg kg^{-1}], soil phosphorus sorption saturation [%] and water P-PO$_4^-$ [mgP dm^{-3}] depending on agronomic categories (the values with different letters in a column are significantly different for $p<0.05$).

Agronomic categories	Soil P content [mg kg^{-1}]	Soil P saturation [%]	Water P-PO$_4^-$ [mg P dm^{-3}]
Very light	146.7 a	19.13 a	0.12 a
Light	162.8 a	18.70 a	0.28 a
Medium	132.3 a	21.35 a	0.29 a
Heavy	85.9 b	12.28 a	0.26 a

Table 4. Spearman rank correlations.

	pH	Soil P content [mg kg^{-1}]	Soil P saturation [%]	Water P-PO$_4^-$ [mgP dm^{-3}]
pH		**0.28496**	-0.02378	**-0.23745**
		0.0000	0.70278	0.00011
Soil P content [mg kg^{-1}]	**0.28496**		**0.8960**	**0.1766**
	0.0000		0.0000	0.0096
Soil P saturation [%]	-0.02378	**0.8960**		**0.2094**
	0.70278	0.0000		0.0021
Water P-PO$_4^-$ [mg P dm^{-3}]	**-0.23745**	**0.1766**	**0.2094**	
	0.00011	0.0096	0.0021	

The values in bold are statistically significant.

Heavy soils presented the lowest values of SP and Psat, but only for SP this was statistically significant. Highest SP content was observed in light soil while highest values of Psat in medium soils (Table 3). There was no statistical differences in phosphorus from drainage outlets among agronomic categories but lowest values were observed in sample taken from very light soils.

Due to the significant skewness of the observations, the correlation between the ranks was taken into account (Table 4). pH values of soil samples does not correlate with Psat, but significantly correlates with SP and phosphorus from drainage outlets. There is a strong correlation between SP and Psat as expected since SP is a function of Psat. Phosphorus from drainage outlets significantly correlates with every tested parameter, it has negative correlation wit pH and weak positive correlation with SP and Psat.

DISCUSSION

An average soil phosphorus content determined with Mehlich 3 solution was 101.8 mg kg^{-1} and less than a 25% of samples showed SP of 55.2 mg kg^{-1} . An average soil P saturation was 11.8% and 75% of the tested samples did not exceed the value of 23.6%. This means that only 11.8% of the free Al and Fe sites were occupied by phosphorus and the soil can still bind significant amounts of phosphorus. In acidic mineral soils containing significant amounts of iron and aluminium ions poorly soluble combinations are formed with orthophosphates known as hydroxyphosphates and the end products of these reactions are insoluble phosphates. Phosphorus availability decreased with increase in pH thus it was important to incorporate pH analysis in this research. According to criteria used in assessment of soils in Poland soils classified as very acid and acid pH≤ 4.5 and pH≤ 5.5 respectively) covers over 50% of the country (Latawiec et al., 2017). In our study, majority of samples fall into acid soil classification as upper quartile pH=6.7 thus estimation of phosphorus sorption based on the content of aluminium and iron proved its validity. This is also important information as Mehlich 3 solution has been successfully used in acidic soils previously (Sharpley 1995). In our study pH was significantly correlated with SP and (negatively) with phosphorus in water from drainage outlets but not with Psat.

For practical purposes the key issue is to establish a threshold value for Psat, which, if exceeded, would mean an increased risk of phosphorus losses. The literature provides some research results in this area.

According to Pautler and Sims (2000), Psat values of 25 to 40% are correlated with a higher risk of P loss during soil leaching or runoff. Breeuswma et al. (1995) found in their study that Psat (obtained through ammonium-oxalate solution) values of 25% in the soil profile, under medium and high water table conditions, would contribute to shallow groundwater contamination in the Netherlands. In the light of the above research, the obtained own results are not too alarming as less than 25% of tested samples exceeds Psat=23.6% (upper quadrile), but it is important to underline that authors of this study has used Mehlich 3 solution not the ammonium-oxalate solution.

To investigate the degree of soil phosphorus sorption saturation using ammonium-oxalate solution, 296 soil samples were analyzed in Belgium (and average Psat values of 57, 22 and 11% were obtained for soil horizons 0–30, 30–60 and 60–90 cm, respectively (De Smet et al., 1996). Authors had proposed the threshold values of Psat=30% (measured for depths between 0 and 90 cm) to protect shallow groundwater. The following considerations should be interpreted with the greatest caution, because the ammonium-oxalate solution is a much stronger extractant than the Mehlich 3 solution used in this research, however, for speculative purposes, a discussion with the results of our own study will be presented. It is worth noting that the values obtained by these authors for the soil layer 0–30 cm were more than five times higher than the values obtained in our study. Moreover, the level Psat oscillating around 11% was observed only at a much deeper soil layer, i.e. 60–90 cm, which suggests that Belgian soils may be less capable of maintaining P and be much more susceptible to release P into the soil solution. Considering Belgian Psat threshold of 30%, less than 25% of tested samples from this study could exceed this proposed "safe value". The proposed limit of 30% is also reflected in the results obtained by Pote and others (1999). They showed that the observed values of dissolved reactive phosphorus in runoff from three Ultisols in Arkansas increased at Psat values between 20 and 30%.

After examining 8539 soil samples, Kęsik (2016) found that the average Psat value for soil in the country is 18.1%. These results corroborate unpublished research by Jurga, who examined a set of over 1000 soil samples from all voivodeships in the country (n=1023) and obtained an average Psat value = 19%. The study by Kęsik (2016) also shows that an excess of Psat = 25% (irrespective of agronomic category and soil pH range) should be considered unjustified from the point of view of plant fertilization needs and environmental risk. Taking into account all studies mentioned above, the results from our study (average Psat=11.8%) allow to consider the recorded average values as safe for the aquatic environment. Thus, it indicates that the risk of phosphorus leaching into the soil profile and the associated risk of water contamination can be considered as rather low.

Although some researchers believe that P loss through leaching is related strictly to soil properties (Jalali, Jalali, 2017), both the reports of Zhang et al. (2005) and the results presented in this paper contradict this. The differences in average values of soil P content depending on agronomic categories was statistically significant only for two categories, namely light and heavy soil (162.8 and 85.9 mg kg^{-1} respectively) (Table 3). For Psat no statistically significant difference was found between categories, the lowest values was found in heavy soils and the highest in medium soils (12.28 and 21.35%).

The average content of phosphorus in water was 0.09 mg P dm^{-3} with maximum values of 3.82 mg P dm^{-3}. Over 75% of the obtained results did not exceed 0.22 mg P dm^{-3}. "The Ordinance of Minister of Infrastructure of 25 June 2021 on the classification of ecological status, ecological potential and chemical status and the method of classifying the status of surface water bodies, and the environmental quality standards for priority substances" will be used to interpret the obtained results (Rozporządzenie, 2021). According to the above legal act, the average phosphorus content in drainage waters is in the first class of water quality, considering both: a stream or lowland stream and a stream or sandy lowland stream. Almost 80% of tested water samples comply with requirements for second class of water quality (threshold value ≤ 0.33 mg P dm^{-3}) in terms of P content in water.

The phosphorus in water significantly correlates with the SP and Psat, confirming results obtained by Sharpley (1995). The rank correlation coefficients for P in water turned out to be rather weak for both SP and Psat, but Psat slightly better describes risk of P losses to drains. The performed statistical analysis allows us to draw three assumptions: Firstly, soil available phosphorus extracted with Mehlich 3 solution and resulting Psat parameter could be used for estimating risk of P leaching to water, however the minimal relationship between the variables indicates that more studies are needed to determine if greater population size will create a better model or not. Secondly, local threshold values (including thresholds for deeper soil layers) and validation of them on a larger population of samples is required. Thirdly, P leakage from soil to water could be largely determined by factors other than SP and Psat as they do not account for processes controlling the transport of P such as water erosion, runoff potential, subsurface drainage, modified connectivity or contributing distance (Maguire 2002) .

CONCLUSIONS

1. Results from our study (average Psat=11.8%, average water P-PO$_4^-$=0.1 mgP dm^{-3}) allow to consider the recorded average values as safe for the aquatic environment.
2. According to presented results, soil texture has a lower than expected impact on soil phosphorus sorption saturation.

3. Soil phosphorus sorption saturation might be used for identifying soils or zones vulnerable to phosphorus leaching in Poland, however more studies are needed on developing thresholds unique for specific soil condition as well as on including this parameter in a more comprehensive index.

4. Considerable fluctuations in soil phosphorus sorption saturation values within single agronomic category suggest that improvement in agricultural advisory system might be reached through extending the monitoring of soil phosphorus to include the phosphorus sorption saturation parameters.

5. Phosphorus leakage from agricultural soil into drainage water could be largely determined by factors other than soil phosphorus sorption saturation but more research on this, including integration with other site properties and P management practices is needed.

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