agronomy

MDPI

Article

Evaluation of the Egner–Riehm DL and Mehlich 3 Tests for the Determination of Phosphorus: The Influence of Soil Properties on Extraction Efficiency and Test Conversion

Jolanta Korzeniowska * and Ewa Stanislawska-Glubiak

Institute of Soil Science and Plant Cultivation-State Research Institute in Pulawy, Department of Weed Science in Wroclaw, Orzechowa 61, 50-540 Wroclaw, Poland; e.glubiak@iung.wroclaw.pl
* Correspondence: j.korzeniowska@iung.wroclaw.pl

Abstract: The leaching of phosphorus (P), together with nitrogen (N), into deep water and runoff from fields into surface water has caused the dangerous phenomenon of eutrophication, which threatens the Baltic Sea. This process has led to a revision of fertilizer recommendations for farmers in most European countries. The basis for proper recommendations is the determination of soil P using a soil test. There are many different soil tests used in Europe for the determination of plant-available P in soil, which is primarily the result of the different soil conditions in the individual countries. In Poland, two soil P tests are currently used: the Egner–Riehm DL (DL) test and the Mehlich 3 (M3) test. The aim of our study was to determine the extraction efficiency of the DL and M3 tests, to explore the possibility of converting the results of one test to another, and to compare the diagnostic value of the tests. For this purpose, a collection of 237 soil–plant sample pairs was taken from maize fields in Poland. The phosphorus content was determined in all the soil and plant samples, with two methods used in the soil samples: DL and M3. The results of our study show that it is not possible to state unequivocally which test extracts more P from the soil. The extraction efficiency of the tests depends on the specific soil properties, particularly pH and texture. The most reliable conversion of DL test results to M3 is possible for soils that contain a 21–35% fraction characterized by particles less than 0.02 mm in diameter, regardless of soil pH. Furthermore, the DL test has better diagnostic value than M3, especially for alkaline soils.

Keywords: plant-available P; extraction; soil tests; conversion model; diagnostic value; plant factor

check for updates

Citation: Korzeniowska, J.; Stanislawska-Glubiak, E. Evaluation of the Egner–Riehm DL and Mehlich 3 Tests for the Determination of Phosphorus: The Influence of Soil Properties on Extraction Efficiency and Test Conversion. *Agronomy* **2024**, *14*, 2921. https://doi.org/10.3390/agronomy14122921

Academic Editor: Bing Li

Received: 22 October 2024
Revised: 22 November 2024
Accepted: 4 December 2024
Published: 6 December 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Soil phosphorus (P) is an essential element for plant growth and development; however, it is often present in insufficient quantities in natural soils. This deficiency can be primarily explained by the fact that P is strongly fixed by clay, aluminum and iron oxides, carbonates, and organic matter [1,2]. In the past, crop production relied on the natural P content of the soil and organic manure, which was often insufficient to achieve high yields. With population growth and increased demand for food came the need to increase crop production. This was achieved through the development of mineral fertilizers, including phosphate fertilizers, which contain forms of the element that are readily available to plants. In the 20th and 21st centuries, the use of mineral fertilizers by farmers became the main source of P in soils [3]. The introduction of high doses of P fertilizers into agricultural production has had a remarkably beneficial effect on crop yields; however, it has also had an incredibly negative impact on the environment. The leaching of P, in addition to N, into deep waters and runoff from fields into surface waters has become a cause of the dangerous phenomenon of eutrophication, and the European continent has faced pollution of its lakes, rivers, and, additionally, the Baltic Sea [4,5]. Given this increasingly dangerous situation, a proper assessment of fertilization needs and the selection of appropriate phosphate fertilizer doses have become particularly important. In general, such doses should be

applied which provide the desired yield level without having a detrimental impact on the environment. The level of phosphorus fertilization should be high enough to ensure that plants can grow and develop optimally but not so high as to exceed the plants' ability to absorb it and the soil's ability to fix it. This requirement is due to the fact that any surplus not taken up by plants and not absorbed by the soil poses a potential threat to water. To meet these challenges, verification of fertilizer recommendations for farmers has become common practice in most countries in recent years [6–9].

The basis for appropriate fertilizer recommendations is the correct identification of plant-available P in soil. This recognition process is performed in two steps. In step 1, referred to as the soil test, P is extracted from the soil with an extraction solution and the amount of P in the solution is measured. In step 2, the results of the soil test are assessed using the corresponding threshold values [8,10].

In Europe, a variety of soil tests are used to determine plant-available P in soil (Table 1). Among the most commonly used tests are the Egner AL, Olsen, and Mehlich 3 tests. This wide variety of tests is primarily the result of the different soil conditions but also differences in economic conditions and the historical background of each country [7,10].

Table 1. Soil P tests used in European laboratories.

Test	Solution Components	Literature Source	Country
Egner AL	0.1 M $NH_4(C_3H_5O_3)$ + 0.4 M CH_3COOH, pH 3.75	Egner 1954 [11]	Belgium, Hungary, Lithuania, Norway, Slovenia, and Sweden
Egner–Riehm DL	0.02 M $Ca(C_3H_5O_3)_2$ + 0.02 M HCl, pH 3.7	Egner et al., 1938 [12], Riehm 1943 [13]	Latvia and Poland
CAL	0.05 M $Ca(C_3H_5O_3)_2$ + 0.05 M $Ca(CH_3COO)_2$ + 0.3 M CH_3COOH, pH 4.1	Schüller 1969 [14]	Austria and Germany
Mehlich 3	0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA, pH 2.5	Mehlich 1984 [15]	The Czech Republic, Estonia, and Poland
Olsen	0.5 M NaHCO3, pH 8.5	Olsen et al., 1954 [16]	Denmark, England, France, Italy, and Spain
Bray 1	0.03 M NH_4F + 0.025 M HCl, pH 6.8	Bray and Kurtz 1945 [17]	Italy
Dyer	citric acid 2%, pH 2.0	Dyer 1984 [18]	France
AAAc	0.5 M CH_3COONH_4 + 0.5 M CH_3COOH, pH 4.65	Vuorinen and Makitie 1955 [19]	Finland
H_2O	H_2O (20 °C), unbuffered	Shick et al., 2013 [20]	The Netherlands

In Poland, two soil P tests are currently used: Egner–Riehm DL (DL) and Mehlich 3 (M3). The first test has been used in Poland for several decades, whereas the second test was introduced in 2015 to reduce costs and simplify analytical procedures [21,22].

The Egner test was initiated in the 1930s and involved the use of calcium lactate as an extractant [12]. It was originally designed for acidic soils of northern Europe. This method was modified by Riehm [13], who doubled the lactate concentration (hence the name "double lactate" DL) to better predict phosphorus availability in calcareous soils. The DL test and similar extraction methods developed based on Egner's original extractant are widely used in the Baltic countries (Table 1).

The M3 test was developed as a multi-element extractant, intentionally adapted to a wide range of soils [15]. The multi-agent test uses different extraction mechanisms: cationic macro-elements (Ca, Mg, K, Na) are mainly extracted by ammonium nitrate, and nitric

acid, iron and other micro-elements (Cu, Mn, Zn, etc.) are solubilized and complexed by ammonium nitrate and EDTA. Phosphorus is released from calcium phosphates by acetic acid. In addition, ammonium fluoride releases P from aluminum phosphates by forming Al–F complexes in solution. The universal applicability of M3 is an advantage that has led to its wide application in the USA, Canada, and many other countries (Table 1).

Currently, agrochemical laboratories in Poland use the DL test if they only need to determine only P or P and K in the soil. However, when it is necessary to determine all macro- and micro-elements in the soil, the M3 test is used, which is a simpler and less costly solution. The reduction in the costs of soil analysis due to the introduction of the M3 test has made farmers more willing, and more frequently, to test the content of nutrients in their fields. We expect that this will improve the precision of fertilization in our country. Cases of under- or over-application of fertilizers will be less frequent, which will both increase yields and improve the environment.

The soil P tests used worldwide have been compared in many studies. For example, Steinfurth et al. [8] derived equations to convert the results of eight different soil tests to those of the Olsen test in order to convert and compare P threshold values used in European countries. Wuenscher et al. [23] compared 14 soil phosphorus extraction methods in terms of their extraction efficiency and their relationship with soil properties. In their study, Jordan-Meille et al. [10] presented 10 tests used in European countries, with emphasis on the calibration and fertilizer recommendations for these tests. Vona et al. [24] and Dari et al. [25] studied the extraction efficiency and relationship between four tests, in addition to the influence of soil properties on these tests. Some authors have conducted comparisons between only two tests but not those used in Poland [26–28].

Despite the plethora of studies on the comparability of soil P tests, only a few authors have addressed the DL and M3 tests in their work. Kabala et al. [29], who examined both tests, did not address the suitability of the tests for fertilizer purposes. Moreover, Vucans et al. [30] did not investigate the possibility of converting the results of two tests into one another. Conversely, Zbiral and Nemec [31], who tested the possibility of converting DL test results into M3 test results, did not consider the effect of soil texture on the comparability of these tests. Similarly, the conversion equation derived by Eriksson et al. [32] did not include any soil features that affect the availability of P. Furthermore, evidence suggests that the test conversion model established for other countries should not be used in Poland due to the different soil conditions. Therefore, a model adapted specifically for the soil of our country should be developed. The current threat of pollution of surface waters and the Baltic Sea by phosphorus creates a need to verify soil P tests and P fertilizer requirements in Baltic countries [33]. In response to this challenge, we wanted to ascertain which of the two tests used in Poland better defines the phosphorus needs of plants and determine the possibility of converting these test results into one another. Precise determination of plant-available P in soil is necessary to determine the correct doses of phosphate fertilizers. By converting the test results, it will be possible to standardize soil P results for determination of the state of soil P in Poland, and it will be possible to compare the results obtained in the past and more recently.

As soil P solubility is strongly related to pH, clay, organic matter, and Fe oxides, the comparability of soil P tests should be studied by taking these soil properties into account [26,29,34]. Furthermore, a good soil test should only extract forms of P from the soil that can be absorbed by the plant. Therefore, the evaluation of soil P tests for fertilizer purposes should take into account its correlation with plant features, e.g., plant P content [27].

The aim of this study was to test the extraction efficiency of the Egner–Riehm DL and Mehlich 3 tests, the examine the possibility of converting the results of one test to the other depending on soil properties, and to compare the suitability of the two tests for fertilizer purposes using plant features. The research hypothesis was that the ability to convert Egner–Riehm DL test results to Mehlich 3 test results depends on soil specificity.

2. Materials and Methods

2.1. Sample Collection

A collection of 237 soil–plant sample pairs was obtained in the spring from maize fields when the plants reached a height of 25–30 cm (BCH 14–15). Sampling points were located in moderately intensive farms in two Polish voivodeships, Kuyavian–Pomeranian Voivodeship in the north (119 samples) and Lublin Voivodeship in the east (118 samples) (Figure 1). Each soil–plant sample pair was taken from an area of 16 m^2. A soil sample was created by mixing 10 subsamples taken using a soil stick to a depth of 20 cm. Soil and corresponding plant samples were taken simultaneously. The plant sample consisted of 20 maize plants cut 5 cm above ground. All of the samples were collected by trained samplers, usually one soil–plant pair from each "gmina", the smallest administration unit in Poland.

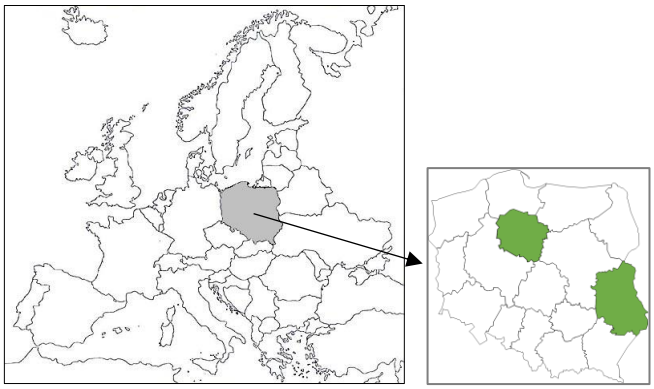


Figure 1. Sampling location.

After collection, the soil samples were dried and sieved through a sieve with a mesh of less than 2 mm. The plant samples were washed, dried at 60 °C, and ground to a fine dust. The phosphorus content in the soil samples was determined using two methods: the Egner–Riehm DL test (P_{DL}) and the Mehlich 3 test (P_{M3}). The phosphorus content in the plant samples was also determined. In addition, pH, fraction with particles < 0.02 mm in diameter (Fr < 0.02), total organic carbon (TOC), and Fe content were measured in the soil samples (Table 2).

Table 2. General characteristics of the sample collection (n = 237).

Feature	Mean ± Standard Error	Range
Soil P_{DL} (mg kg)$^{-1}$	190.3 ± 8.32	32.0–980.0
Soil P_{M3} (mg kg)$^{-1}$	201.2 ± 6.46	31.0–660.0
Plant P (%)	0.46 ± 0.01	0.21–1.04
pH (KCl)	6.13 ± 0.06	4.06–7.67
Fraction < 0.02 mm (%)	19.2 ± 0.57	3.6–39.3
Total organic carbon (%)	1.09 ± 0.03	0.27–4.29
Soil Fe (mg kg)$^{-1}$	381.6 ± 6.58	36.6–661.0

n—number of samples; P_{DL} and P_{M3}—P in the soil determined using the Egner–Riehm or Mehlich 3 test.

2.2. Analytical Procedures

The P content in the soil was determined according to the procedures outlined in Table 3. The P content in the extracts was measured using phosphoro-molybdenum blue spectrophotometry [35]. The P content in the plant material was determined using continuous flow analysis (CFA) with spectrophotometric detection. The TOC in the soil was determined with the Thiurin method using potassium dichromate [36], pH was determined using the potentiometric method in 1 mol KCl dm^{-3} [37], and the texture of the soil was determined with the aerometric method [38]. The soil Fe content was determined using the FAAS method after extraction in M3 solution.

Table 3. Characteristics of the soil P tests.

Soil Test	Extraction Solution Components	Solution pH	Soil/Solution Ratio	Extraction Time
Egner–Riehm DL	0.02 M $Ca(C_3H_5O_3)_2$ + 0.02 M HCl	3.7	1:50	90 min
Mehlich 3	0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA	2.5	1:10	5 min

All analyses were performed in the Central Laboratory of the Institute of Soil Science and Plant Cultivation in Pulawy, certified by the Polish Centre of Accreditation (certificate no. AB 339) according to PN-EN ISO/IEC 17025 [39].

2.3. Statistics

Statistical analysis of the results was performed using Statgraphics Centurion XVI software (Version 16.2.04, StatPoint Inc., Warrenton, VA, USA). The data sets were characterized using descriptive statistical methods (mean, minimum, maximum, and standard error). Pearson correlation coefficients between (1) soil features; (2) soil P_{DL} and soil P_{M3}; and (3) plant P and soil P_{DL} or soil P_{M3} were calculated. Correlations were assumed to be statistically significant at $p < 0.05$. Furthermore, to express the relationship between the P extracted using the Egner–Riehm DL and Mehlich 3 tests, linear regression was used and equations were derived for conversion from one extractant to another.

3. Results and Discussion

3.1. Factors Affecting Soil Tests

The solubility and mobility of phosphorus in the soil depend on the properties of the soil. Among the most important characteristics are pH, $CaCO_3$ content, soil texture, organic matter, and Fe and Al oxides. These parameters also influence the extractability of P and the efficiency of extraction solutions. Authors generally study the influence of texture (sand, silt, and clay), organic matter, and pH on soil tests [25,29], in addition to the influence of Ca, Mg, Al, and K [40].

In our study, we investigated the effects of pH, soil fraction with particles less than 0.02 mm in diameter (Fr < 0.02), total organic matter (TOC), and Fe content on extraction results with Egner–Riehm DL (DL) and Mehlich 3 (M3) solution. The Fr < 0.02 adopted for this study represents the soil texture well, as it is the sum of clay and fine silt. According to this parameter, soils in Poland are classified into very light (≤10%), light (11–20%), medium (21–35%), and heavy (≥36% Fr < 0.02).

It was found that the DL extraction results were mostly influenced by soil pH; in comparison, the M3 results were influenced by soil texture (represented by Fr < 0.02) and Fe content (Table 4). The significant positive correlation between the DL test and soil pH was confirmed by the results of Kabala et al.'s study [29]. Verification of our results regarding M3 can be seen in the research of Wuenscher et al. [23]. In a study examining 14 soil P extraction methods and their correlation with 13 soil parameters, the authors proved that M3 was most highly correlated with soil texture. They found a significant negative correlation of M3 with clay and silt and a positive correlation with sand at $p < 0.001$. A slightly smaller positive correlation coefficient was obtained with Fe at $p < 0.01$.

In order to accurately assess the influence of soil pH and texture on P extraction efficiency, the entire set of samples was divided into groups according to pH and Fr < 0.02 (Table 5). As a result, four groups related to pH were formed, acidic, very acidic, neutral, and alkaline soils, in addition to four groups related to texture, traditionally referred to in Poland as very light, light, medium, and heavy soils.

Table 4. Pearson correlation coefficients between soil features and P in soil determined using Egner–Riehm DL and Mehlich 3 tests (n = 237).

Soil Feature	P_{DL}	P_{M3}
pH	0.21 **	ns
Fraction < 0.02 mm	ns	−0.35 ***
TOC	0.14 *	ns
Fe	0.16 *	0.34 ***

P_{DL} and P_{M3}—P in soil determined using the Egner–Riehm DL or Mehlich 3 tests; p-value: * ≤ 0.05, ** ≤ 0.01, and *** ≤ 0.001; ns—not significant; TOC—total organic carbon.

Table 5. Collection of soil samples divided into groups by pH and texture.

Soils (pH)	*n*	Soils (% of Fraction with Particles <0.02 mm in Diameter)	*n*
Acidic (≤5.5)	62	Very light (≤10%)	36
Slightly acidic (5.6–6.5)	90	Light (11–20%)	111
Neutral (6.6–7.2)	59	Medium (21–35%)	73
Alkaline (≥7.3)	26	Heavy (≥36%)	17
All	237	All	237

n—number of samples.

In Polish conditions, very light and light soils are generally acidic. In the case of our soil collection, the correlation between pH and Fr < 0.02 in each of the individual groups was insignificant (Table 6). These results allowed for an independent assessment of the effect of these two features on P extraction efficiency using the DL and M3 extractants.

Table 6. Correlation between pH and soil fraction < 0.02 mm depending on soil acidity and texture.

Soils	Range of Fraction <0.02 mm (%)	Pearson Coefficient	Soils	Range of pH	Pearson Coefficient
Acidic	4.3–37.0	ns	Very light	4.06–7.61	ns
Slightly acidic	5.0–39.3	ns	Light	4.06–7.57	ns
Neutral	2.6–37.0	ns	Medium	4.10–7.67	ns
Alkaline	3.6–37.2	ns	Heavy	4.10–7.57	ns
All	2.6–39.3	ns	All	4.06–7.67	ns

ns—not significant.

3.2. Extraction Efficiency

A number of authors report that more P is extracted from soil using the M3 test than using the DL test [8,29,31]. Vucāns et al. [30], conversely, claim that both tests extract almost the same amount of P from the soil. According to these authors, the difference in favor of M3 amounts to only 4%. In our study, the average efficiency of both tests for the entire soil set was also similar, with a difference of roughly 6% in favor of M3 (Table 7). Nevertheless, it should be noted that the amount of P extracted using the DL and M3 tests varied according to soil pH (Figure 2). In acidic and slightly acidic soils, more P was extracted using the M3 test than the DL test, and the difference between them was 54 and 29 mg kg^{-1}, respectively (Table 7). For neutral soils, the test values were similar while, for alkaline soils, with the DL test, 33 mg kg^{-1} more P was extracted than with the M3 test. The higher efficiency of the M3 test than the DL test from acidic soils may be explained by the presence of ammonium fluoride (NH_4F) in the M3 extractant, which facilitates the release of P from Al oxides into the extraction solution [15]. However, in the study by Eriksson et al. [32], the M3 test was more efficient for acidic than for alkaline soils, compared to the DL test, only in a few cases. In other cases, the M3 test extracted more P from alkaline soils than the DL test. These results mean that it is not possible to clearly indicate which test has higher efficiency because this depends not only on pH but also on other factors.

Table 7. Phosphorus concentration in soil determined using the Egner–Riehm and Mehlich 3 tests depending on pH and soil texture.

Soils	P_{DL}	P_{M3}	P_{DL}-P_{M3}	P_{M3}/P_{DL}	Soils	P_{DL}	P_{M3}	P_{DL}-P_{M3}	P_{M3}/P_{DL}
	mg kg^{-1}					mg kg^{-1}			
Acidic	156	210	−54	1.3	Very light	163	265	−102	1.6
Slightly acidic	169	198	−29	1.2	Light	177	209	−32	1.2
Neutral	233	225	8	1.0	Medium	200	167	33	0.8
Alkaline	203	170	33	0.8	Heavy	222	165	57	0.7
All	190	201	−11	0.9	All	190	201	−11	0.9

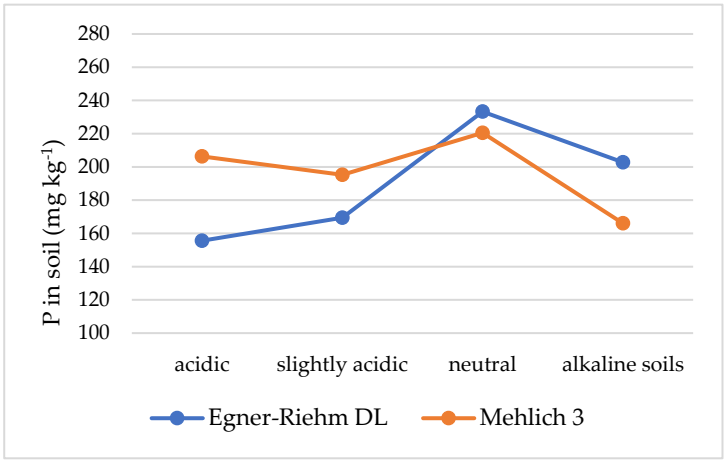


Figure 2. Phosphorus concentration in soil determined using the two soil tests depending on soil pH. Acidic: pH ≤ 5.5, slightly acidic: pH 5.6–6.5, neutral: pH 6.6–7.2 and alkaline soils: pH ≥ 7.3.

In our study, the efficiency of the tests was also compared in relation to soil texture (Figure 3). The biggest difference between M3 and DL occurred for very light soils, for which the M3 test showed 102 mg kg^{-1} more phosphorus than the DL test (Table 7). For light soils, the difference was much smaller at 32 mg kg^{-1}. It is interesting to note that, for the other soils, the relationship was reversed. The DL test extracted 33 mg kg^{-1} more P from medium soils and 57 mg kg^{-1} more P from heavy soils than the M3 test.

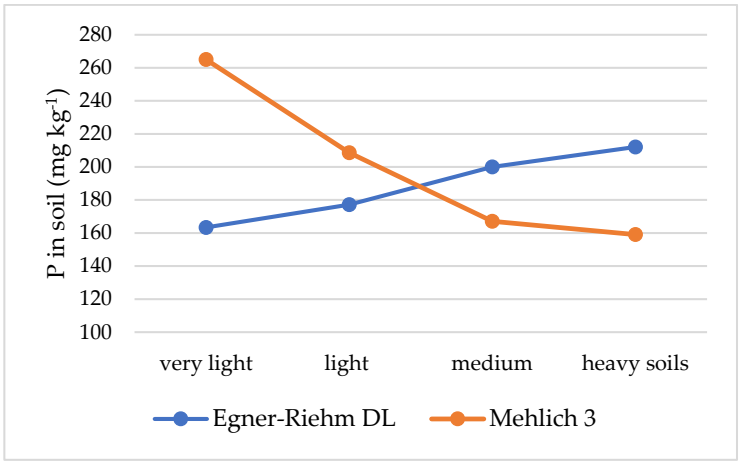


Figure 3. Phosphorus concentration in soil determined using the two soil tests depending on soil fraction < 0.02 mm. Very light: fraction < 0.02 mm is ≤ 10%, light: 11–20%, medium: 21–35%, and heavy soils: ≥35%.

Some authors calculate the reciprocal ratios of P using different extractants, which could possibly be used to convert the results of one test to another. Kabała et al. [29], based on a collection of 200 soil samples collected from Poland, showed that the ratio of P_{M3}/P_{DL} was 1.9 on average. The results of a study by Zbiral and Nemec [31] show that, for soils collected from the Czech Republic (1173 samples), the ratio reached a value of 1.3. In a study examining soils from the Baltic catchment areas (99 samples), the ratio of P_{M3}/P_{DL} ranged from 0.8 to 1.6 [32]. In contrast, from the data presented in the work of Vucāns et al. [30], it can be calculated that, for soils collected from Latvia (145 samples), the ratio of P_{M3}/P_{DL} was close to the value of 1.0. In our study, on average, for 237 samples, this ratio amounted to 0.9; however, it varied depending on the group of soils separated by pH and Fr < 0.02 (Table 7). The ratio decreased from 1.3 for acidic soils to 0.8 for alkaline soils and from 1.6 for very light soils to 0.7 for heavy soils. However, a more precise method of converting P_{DL} extraction results into P_{M3} is to use regression equations that take into account the soil properties which affect phosphorus solubility.

3.3. The Relationship Between Soil Tests

The Pearson correlation coefficients (r) between the DL and M3 tests differed depending on the soil group separated based on pH or Fr < 0.02 (Table 8). The best correlation was obtained for acidic soils (r = 0.79 ***) or medium soils (r = 0.85 ***). Regression equations for converting the test results into one another, containing only the variables P_{M3} and P_{DL} and the intercept, presented too low an R^2 coefficient, which indicated an unsatisfactory fit of the model to the data (in most cases R^2 approx. 40%). Figure 4 shows, as an example, the simple regression equations for soil groups separated according to pH.

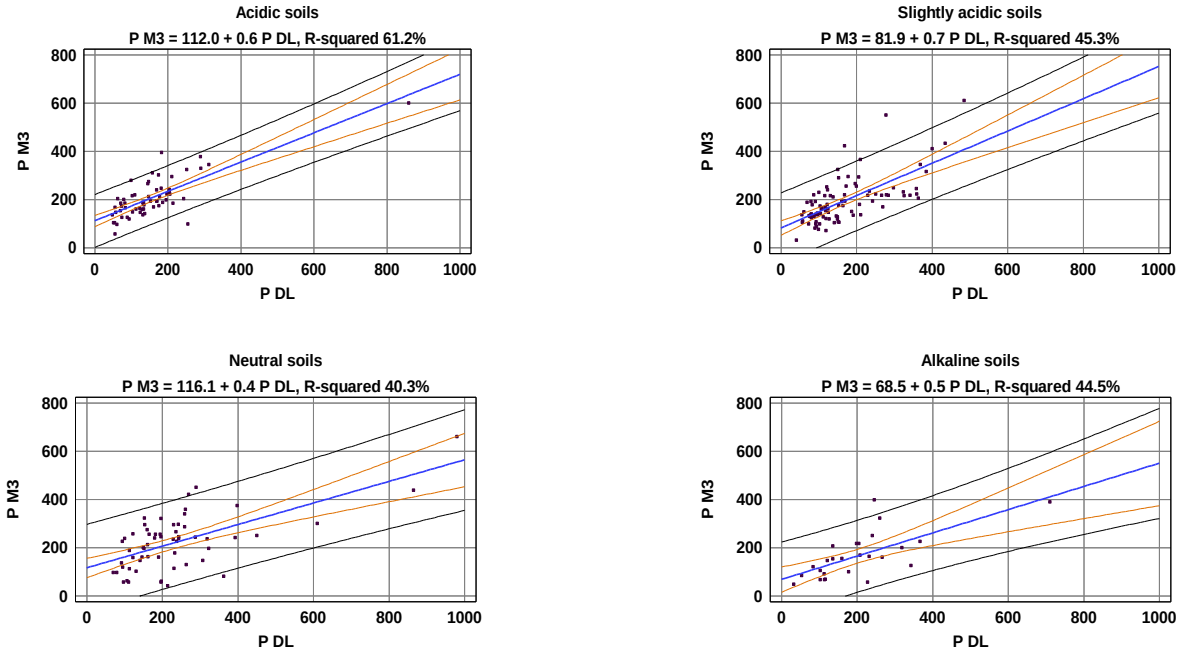


Figure 4. Simple regression equations for converting the DL test to the M3 test for soil groups separated by pH.

Therefore, in the next step, multiple regression equations were derived for each soil group, taking into account the soil features influencing phosphorus solubility (Tables 9 and 10). The dependent variable was P_{M3}, and the independent variable was P_{DL}, in addition to soil features such as pH, Fr < 0.02, TOC and soil Fe.

Table 8. Pearson correlation coefficients between P in soil determined using the Egner–Riehm and Mehlich 3 tests.

Soils	*n*	Coefficient	Soils	*n*	Coefficient
Acidic	62	0.786 ***	Very light	36	0.708 ***
Slightly acidic	90	0.678 ***	Light	111	0.692 ***
Neutral	59	0.643 ***	Medium	73	0.850 ***
Alkaline	26	0.684 ***	Heavy	17	0.568 ***
All	237	0.664 ***	All	237	0.664 ***

n—number of samples; *p* value: *** $\leq$ 0.001.

Table 9. Linear regression equations for the conversion of the Egner–Riehm test to the Mehlich 3 test regarding pH group.

Soils	*n*	Equation	R^2
Acidic	62	P_{M3} = 154.9 + 0.7 P_{DL} − 2.8 Fr < 0.02	68.2 ***
Slightly acidic	90	P_{M3} = 181.3 + 0.7 P_{DL} − 5.0 Fr < 0.02	66.3 ***
Neutral	59	P_{M3} = 223.8 + 0.5 P_{DL} − 6.3 Fr < 0.02	61.6 ***
Alkaline	26	P_{M3} = 141.6 + 0.6 P_{DL} − 4.4 Fr < 0.02	62.4 ***
All	237	P_{M3} = 291.6 + 0.6 P_{DL} − 17.8 pH − 4.6 Fr < 0.02	66.4 ***

Fr < 0.02—fraction < 0.02 mm in %; TOC—total organic carbon; *** $p \leq 0.001$.

Table 10. Linear regression equations for the conversion of the Egner–Riehm test to the Mehlich 3 test regarding texture group.

Soils	*n*	Equation	R^2
Very light	36	P_{M3} = 111.6 + 0.9 P_{DL}	48.6 ***
Light	111	P_{M3} = 209.4 + 0.5 P_{DL} − 16.2 pH	49.5 ***
Medium	73	P_{M3} = -30.9 + 0.5 P_{DL} + 0.3 Fe	77.9 ***
Heavy	17	P_{M3} = 24.2 + 0.3 P_{DL} + 0.2 Fe	40.1 **
All	237	P_{M3} = 291.6 + 0.6 P_{DL} − 17.8 pH − 4.6 Fr < 0.02	66.4 ***

Fr < 0.02—fraction < 0.02 mm in %; *p*-value: ** $\leq$ 0.01; *** $\leq$ 0.001.

For the entire set of soils (*n* = 237), an equation with a regression coefficient R^2 = 66.4*** was derived, which included soil properties such as pH and Fr < 0.02. For soil groups separated on the basis of pH, the R^2 coefficients were similar and ranged from 62.4 *** to 68.2 *** (Table 9). R^2 values above 60.0 indicate that conversion of P_{DL} to P_{M3} is possible in any pH group. However, the best model was obtained for acidic and slightly acidic soils. All the equations included only P_{DL} and Fr < 0.02.

For the groups of soils separated based on texture, the range of R^2 was much higher than for the pH groups (Table 10). These results were confirmed by the graphical interpretation of the P extraction results (Figures 2 and 3). Noteworthy is the group of medium soils for which the equation has the highest R^2 = 77.9 *** and includes Fe content. For the remaining groups, the R^2 ranged from 40.1 ** to 49.5 ***. The equation for very light soils, excluding P_{DL}, does not include any soil features. For light soils, pH was included in the equation, and for heavy soils Fe content was included. Based on the R2 value, it should be assumed that the conversion of P_{DL} results to P_{M3} is only possible for soils that contain from 21% to 35% of the fraction with particles less than 0.02 mm in diameter (medium soils).

Zbiral and Nemec [31], using 1173 soil samples, tested the possibility of converting the DL test results/Mehlich 3 test results. The authors derived a linear regression equation with R^2 = circa 50.0, a value too low for conversion. However, no soil features were included in the calculation. The authors only divided the entire set of soils into non-carbonate and carbonate and derived equations for these groups, which did not significantly improve the R^2. In contrast, Eriksson et al. [32] obtained R^2 = 79, high enough to convert the DL

test results to M3 test results. However, this model too does not take into account any soil properties.

3.4. Evaluation of Soil Tests with Plant Features

The results of a soil P test should provide information on the plant-available P content, based on which P accumulation by the plant can be predicted. However, this is not an accurate assessment, as P uptake is also influenced by microbial processes, weather conditions, such as drought, and even species traits. Nevertheless, an assessment of the diagnostic value of the test should be made based on the test's correlation with plant features, such as the yield, P in the leaves, or P content in the grains/seeds.

The main factor influencing the speciation and availability of P ions in arable soils is pH [41]. At soil pH below 7.2, the dominant ion in the soil solution is $H_2PO_4^-$, while at pH above 7.2, HPO_4^{2-} dominates. Soil acidification increases the content of Al and Fe ions, which can precipitate along with $H_2PO_4^-$ and HPO_4^{2-}, reducing the amount of plant-available phosphorus in the soil [42]. Chemicals used in soil tests to extract P can often release P forms into the solution that are not actually available to plants. For example, in the Mehlich 3 procedure, ammonium fluoride releases P from aluminum phosphates by forming AL–F complexes, which may be partially unavailable to plants [23]. Researchers who evaluate soil P tests generally compare their efficiency and the possibility of replacing one test with another. Unfortunately, the issue of correlation of the test result with plant features is omitted in these studies. However, few authors have evaluated the usefulness of soil P tests based on their correlation with plant features. Haefele et al. [27] evaluated the M3 test for predicting the P concentration in the grains of five crop species. As a result, they found that the test showed good agreement with the P content in the grains of most of the species tested.

In our study, we used the P concentration in the shoots of young plants as a plant feature to assess the diagnostic value of soil P tests. Our results showed that the DL test was better at assessing plant-available P than the M3 test. Although the correlation coefficients between P_{DL} and plant P (PP) were not high (average r = 0.26 *), they were higher than those between P_{M3} and PP, which were generally insignificant (Table 11). In the soil groups separated by pH, the DL test showed the best diagnostic value for alkaline soils (r = 0.58 **) and the worst for slightly acidic soils (r = 0.22 *). In contrast, the M3 test results correlated significantly with PP only in the acidic soil group (r = 0.27 *). For soils divided by texture (Fr < 0.02), both tests showed the best diagnostic value for light soils; moreover, the Pearson coefficient of P_{DL} with PP was higher and more significant than P_{M3} with P_P (r = 0.36 *** vs. r = 0.26 **).

Table 11. Pearson correlation coefficients between plant P and soil P determined using the Egner–Riehm and Mehlich 3 tests.

Soils	P_{DL}	P_{M3}	Soils	P_{DL}	P_{M3}
Acidic	0.30 *	0.27 *	Very light	ns	ns
Slightly acidic	0.22 *	ns	Light	0.36 ***	0.26 **
Neutral	0.32 *	ns	Medium	0.25 *	ns
Alkaline	0.58 **	ns	Heavy	Ns	ns
All	0.26 *	ns	All	0.26 *	ns

P_{DL} and P_{M3}—P in soil determined using the Egner–Riehm or Mehlich 3 tests; other notes as for Table 3. *p*-value: * ≤ 0.05; ** ≤ 0.01; *** ≤ 0.001, ns—not significant.

4. Conclusions

Based on our research, it cannot be clearly stated which soil test, Egner–Riehm DL (DL) or Mehlich 3 (M3), extracts more P from the soil. The efficiency of these tests depended on the soil properties, in particular on pH and texture, represented here by the soil fraction < 0.02 mm (Fr < 0.02). The M3 test extracted more P from acidic soils than the DL, while the DL test was more efficient for neutral soils. Furthermore, M3 test extracted

significantly more P from light soils (Fr < 0.02 to 20%), and the DL test from heavy soils (Fr < 0.02 ≥ 36%).

In general, the conversion of DL test to M3 test can be performed using an equation with pH and Fr < 0.02 (P_{M3} = 291.6 + 0.6 P_{DL} − 17.8 pH—4.6 Fr < 0.02). This model explains 66% of the variation of the results (R^2 = 66.4***) and can be used for soils in the entire pH range (4.1–7.7). The reliability of the test conversion depended more on the soil fraction < 0.02 mm than on pH. The best conversion reliability was obtained for medium soils with the fraction < 0.02 mm ranging from 21% to 35% (R^2 = 77.9 ***), regardless of their pH. For medium soils, the equation that takes into account the Fe content in the soil should be used (P_{M3} = −30.9 + 0.5 P_{DL} + 0.3 Fe).

Another aim of our study was to assess the diagnostic value of the tested tests based on the correlation between soil P and plant P. It was found that the DL test gave more reliable results of the plant-available P content than the M3 test, especially for alkaline soils. In future studies, we intend to focus on the evaluation of these tests in relation to plant yield.

Author Contributions: Conceptualization, J.K. and E.S.-G.; methodology, J.K. and E.S.-G.; investigation, J.K. and E.S.-G.; data curation, J.K.; writing—original draft preparation, J.K. and E.S.-G.; writing—review and editing, J.K. and E.S.-G.; project administration, J.K. All authors have read and agreed to the published version of the manuscript.

Funding: Work was funded by the Polish Ministry of Agriculture and Rural Development under the 2.33 Scientific Research Program of the Institute of Soil Science and Plant Cultivation—State Research Institute in Pulawy.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Barrow, N.J. The effects of pH on phosphate uptake from the soil. *Plant Soil* **2017**, *410*, 401–410. [CrossRef]
2. Penn, C.J.; Camberato, J.J. A critical review on soil chemical processes that control how soil pH affects phosphorus availability to plants. *Agriculture* **2019**, *9*, 120. [CrossRef]
3. Cordell, D.; Drangert, J.; White, S. The story of phosphorus: Global food security and food for thought. *Glob. Environ. Change* **2009**, *19*, 292–305. [CrossRef]
4. Bartosova, A.; Capell, R.; Olesen, J.E.; Jabloun, M.; Refsgaard, J.C.; Donnelly, C.; Arheimer, B. Future socioeconomic conditions may have a larger impact than climate change on nutrient loads to the Baltic Sea. *AMBIO* **2019**, *48*, 1325–1336. [CrossRef] [PubMed]
5. Svendsen, L.M.; Gustafsson, B. Waterborne Nitrogen and Phosphorus Inputs and Water Flow to the Baltic Sea 1995–2018. HELCOM Baltic Sea Environmental Fact Sheet 2020. Available online: https://helcom.fi/wp-content/uploads/2020/06/BSEFS-Waterborne-nitrogen-and-phosphorus-inputs-and-water-flow-to-the-Baltic-Sea.pdf (accessed on 17 October 2024).
6. Buczko, U.; van Laak, M.; Eichler-Löbermann, B.; Gans, W.; Merbach, I.; Panten, K.; Peiter, E.; Reitz, T.; Spiegel, H.; von Tucher, S. Re-evaluation of the yield response to phosphorus fertilization based on meta-analyses of long-term field experiments. *AMBIO* **2018**, *47*, 50–61. [CrossRef] [PubMed]
7. Higgins, S.; Keesstra, S.D.; Kadziuliene, Ž.; Jordan-Meille, L.; Wall, D.; Trinchera, A.; Spiegel, H.; Sandén, T.; Baumgarten, A.; Jensen, J.L.; et al. Stocktake study of current fertilisation recommendations across Europe and discussion towards a more harmonised approach. *Eur. J. Soil Sci.* **2023**, *74*, 13422. [CrossRef]
8. Steinfurth, K.; Börjesson, G.; Denoroy, P.; Eichler-Löbermann, B.; Gans, W.; Heyn, J.; Buczko, U. Thresholds of target phosphorus fertility classes in European fertilizer recommendations in relation to critical soil test phosphorus values derived from the analysis of 55 European long-term field experiments. *Agric. Ecosyst. Environ.* **2022**, *332*, 107926. [CrossRef]
9. Tóth, G.; Guicharnaud, R.A.; Tóth, B.; Hermann, T. Phosphorus levels in croplands of the European Union with implications for P fertilizer use. *Eur. J. Agron.* **2014**, *55*, 42–52. [CrossRef]
10. Jordan-Meille, L.; Rubæk, G.H.; Ehlert, P.A.I.; Genot, V.; Hofman, G.; Goulding, K.; Recknagel, J.; Provolo, G.; Barraclough, P. An overview of fertilizer-Precommendations in Europe: Soil testing, calibration and fertilizer recommendations. *Soil Use Manag.* **2012**, *28*, 419–435. [CrossRef]
11. Egnér, H. Neue Beiträge zur chemischen Bodenuntersuchung unter besonderer Berücksichtigung der Laktatmethode. *Landwirtsch. Forsch.* **1954**, *SH6*, 28–32.

12. Egner, H.; Kohler, G.; Nydahl, F. Die Laktatmethode zur Bestimmung leicht-loslicher Phosphorsa ure in Ackerboden [The lactate method for determination of easily dissolved phosphorus in agricultural soils]. *Lantbrukshogsk. Ann.* **1938**, *6*, 1227–1234.
13. Riehm, H. Bestimmung der laktatloslichen Phosphorsaure in karbonathaltigen Boden. *Phosphorsaure* **1943**, *1*, 167–178.
14. Schüller, H. Die CAL-Methode, eine neue Methode zur Bestimmung des pflanzenverfügbaren Phosphates in Böden. *Z. Pflanzenernähr. Bodenkd.* **1969**, *123*, 48–63. [CrossRef]
15. Mehlich, A. Mehlich 3 soil test extractant: A modification of the Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [CrossRef]
16. Olsen, S.R.; Watanabe, F.S.; Cosper, H.R.; Larson, W.E.; Nelson, L.B. Residual phosphorus availability in long-time rotations on calcareous soils. *Soil Sci.* **1954**, *78*, 141–152. [CrossRef]
17. Bray, R.H.; Kurtz, L.T. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* **1945**, *59*, 39–45. [CrossRef]
18. Dyer, B. On the analytical determination of probably available mineral plant food in soils. *J. Chem. Soc.* **1894**, *65*, 115–167. [CrossRef]
19. Vuorinen, J.; Makitie, O. The method of soil testing in use in Finland. *Agrogeol. Publ.* **1995**, *63*, 1–44.
20. Schick, J.; Kratz, S.; Rückamp, D.; Shwiekh, R.; Haneklaus, S.; Schnug, E. *Comparison and Inter-Calibration of Different Soil P Tests Used in the Baltic Sea Countries*; Julius Kühn-Institut, Federal Research Center for Cultivated Plants (JKI) Institute for Crop and Soil Science: Braunschweig, Germany, 2013.
21. Kesik, K.; Jadczyszyn, T.; Lipinski, W.; Jurga, B. Adaptation of the Mehlich 3 procedure for routine determination of phosphorus, potassium and magnesium in soil. *Przem. Chem.* **2015**, *6*, 973–976.
22. Korzeniowska, J.; Stanislawska-Glubiak, E.; Lipiński, W. New limit values of micronutrient deficiency in soil determined using 1 M HCl extractant for wheat and rapeseed. *Soil Sci. Annu.* **2020**, *71*, 205–214. [CrossRef]
23. Wuenscher, R.; Unterfrauner, H.; Peticzka, R.; Zehetner, F. A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. *Plant Soil Environ.* **2015**, *61*, 86–96. [CrossRef]
24. Vona, V.; Centeri, C.; Biró, Z.; Vona, M.; Kalocsai, R.; Jakab, G.; Kauser, J.; Kulmány, I.M.; Kovács, A.J.; Milics, G. Comparing different phosphorus extraction methods: Effects of influencing parameters. *Sustainability* **2022**, *14*, 2158. [CrossRef]
25. Dari, B.; Rogers, C.W.; Leytem, A.B.; Schroeder, K.L. Evaluation of soil test phosphorus extractants in Idaho soils. *Soil Sci. Soc. Am. J.* **2019**, *83*, 817–824. [CrossRef]
26. van Laak, M.; Klingenberg, U.; Peiter, E.; Reitz, T.; Zimmer, D.; Buczko, U. The equivalence of the Calcium-Acetate-Lactate and Double-Lactate extraction methods to assess soil phosphorus fertility. *J. Plant Nutr. Soil Sci.* **2018**, *181*, 795–801. [CrossRef]
27. Haefele, S.M.; Mossa, A.W.; Gashu, D.; Nalivata, P.C.; Broadley, M.R.; McGrath, S.P.; Thomas, C.L. Mehlich 3 as an indicator of grain nutrient concentration for five cereals in sub-Saharan Africa. *Field Crops Res.* **2024**, *307*, 109243. [CrossRef]
28. Watson, M.; Mullen, R. *Understanding Soil Tests for Plant-Available Phosphorus Fact Sheet*; Ohio State University: Columbus, OH, USA, 2007; Available online: https://agcrops.osu.edu/sites/agcrops/files/imce/fertility/Soil_Tests.pdf (accessed on 17 October 2024).
29. Kabala, C.; Galka, B.; Labaz, B.; Anjos, L.; de Souza Cavassani, R. Towards more simple and coherent chemical criteria in a classification of anthropogenic soils: A comparison of phosphorus tests for diagnostic horizons and properties. *Geoderma* **2018**, *320*, 1–11. [CrossRef]
30. Vucans, R.; Lipenite, I.; Livmanis, J. Comparison of methods determination of phosphorus in carbonatic soil. *Agron. Vestis.* **2008**, *11*, 229–304.
31. Zbíral, J.; Němec, P. Comparison of Mehlich 2, Mehlich 3, CAL, Egner, Olsen, and 0.01 M $CaCl_2$ extractants for determination of phosphorus in soils. *Commun. Soil Sci. Plant* **2002**, *33*, 3405–3417. [CrossRef]
32. Eriksson, A.K.; Ulén, B.; Berzina, L.; Iital, A.; Janssons, V.; Sileika, A.S.; Toomsoo, A. Phosphorus in agricultural soils around the Baltic Sea–comparison of laboratory methods as indices for phosphorus leaching to waters. *Soil Use Manag.* **2013**, *29*, 5–14. [CrossRef]
33. Iho, A.; Valve, H.; Ekholm, P.; Uusitalo, R.; Lehtoranta, J.; Soinne, H.; Salminen, J. Efficient protection of the Baltic Sea needs a revision of phosphorus metric. *AMBIO* **2023**, *52*, 1389–1399. [CrossRef]
34. Sánchez-Alcalá, I.; Del Campillo, M.C.; Torrent, J. Critical Olsen P and $CaCl_2$-P levels as related to soil properties: Results from micropot experiments. *Soil Use Manag.* **2015**, *31*, 233–240. [CrossRef]
35. *PN-R-04023*; Chemical and Agricultural Analysis Determination of the Content Available Phosphorus in Mineral Soil. Polish Standards Committee: Warszawa, Poland, 1996. (In Polish)
36. *PN-ISO 14235:2003*; Soil Quality: Determination of Organic Carbon in Soil by Sulfochromic Oxidation. Polish Committee for Standardization: Warsaw, Poland, 2003. (In Polish)
37. *PN-EN ISO 10390:2022-09*; Soil, Treated Biowaste and Sludge—Determination of pH (ISO 10390:2021). Polish Committee for Standardization: Warsaw, Poland, 2022. (In Polish)
38. *PN-R-04033:1998*; Soil and Mineral Soil Materials—Particle Size Distribution on Soil Classes. Polish Committee for Standardization: Warsaw, Poland, 1998. (In Polish)
39. *PN-EN ISO/IEC 17025:2018-02*; General Requirements for the Competence of Testing and Calibration Laboratories. Polish Committee for Standardization: Warsaw, Poland, 2018. (In Polish)

40. Mumbach, G.L.; Gatiboni, L.C.; Dall'Orsoletta, D.J.; Schmitt, D.E.; Pessotto, P.P.; de Oliveira, C.M.B. Phosphorus extraction with soil test methods affected by soil P sorption capacity. *J. Soil Sci. Plant Nutr.* **2020**, *20*, 1882–1890. [CrossRef]
41. Lindsay, W.L. *Chemical Equilibria in Soils*; John Wiley & Sons: New York, NY, USA, 1979; p. 449.
42. Ziadi, N.; Whalen, J.K.; Messiga, A.J.; Morel, C. Assessment and modeling of soil available phosphorus in sustainable cropping systems. *Adv. Agron.* **2013**, *122*, 85–126.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.