



CONDITIONS PROMOTING AND RESTRAINING AGRONOMIC EFFECTIVENESS OF WATER-INSOLUBLE PHOSPHATE SOURCES, IN PARTICULAR PHOSPHATE ROCK (PR): I. INDICES OF PHOSPHATE ROCK USE OPPORTUNITY (PRUOIS) AND OF PHOSPHATE ROCK SUITABILITY FOR DIRECT USE (PRSIDU)

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Abstract. Several issues of phosphate rock (PR) use are discussed in this paper. Maize for green fodder (*Zea mays* L) and ryegrass (*Lolium multiflorum* Lam.) were grown in 7 kg of dry soil and in small pots of 1.25 kg dry soil capacity, respectively, on several base unsaturated soils belonging to Hapludoll and Hapludalf soil groups. The amount of phosphate rock (PR) to apply was based on experimental data considering soil adsorbed acidity (A_h), humus content (H^2), cation exchange capacity (T), sum of exchangeable bases (SEB) and mobile (easily soluble) phosphate content (P_{AL}) in the soil. The factors were combined in a rock phosphate use, opportunity index of the soil (PRUOIS):

$$PRUOIS = \frac{A_h * H^2 * T * 100}{SEB * 10^{0.0245 * P_{AL}}}$$

Rock phosphate suitability for direct use was evaluated by means of the rate of PR-P dissolution (PRPRS) in a 0.6% ammonium heptamolybdate in 0.01M calcium chloride solution (ppm P) and by carbonate content (%CaCO₃) in PR. Both of these parameters combined provided a phosphate rock suitability index for direct use (PRSIDU):

$$PRSIDU[ppmP/min] = PRPRS * (1 - 0.03 * CaCO_3)$$

Water insoluble P sources studied were PR from Kola-Russia, Morocco, Kneifiss-Siria, El Hassa-Jordan, Gafsa-Tunisia, North-Carolina (USA), and Arad-Israel. All PRs were compared with TSP applied at the same rate of P. Neither PRUOIS or PRSIDU considered separately could satisfactorily explain the variance of PR efficiency. An index obtained by multiplicative combination of PRUOIS x PRSIDU did correlate significantly with indices on the agronomic efficiency of PR.

1. INTRODUCTION

The famous Russian scientist Mendeleev (1834-1907), discoverer of the periodic law in chemistry, was actively engaged in coordinating a network of field trials throughout famine affected Russia in the early sixties of the previous century. The experimental results recorded at that time could not be understood and explained with reference to soil and PR intrinsic properties.

Contemporary soil-plant-PR interaction studies and their understanding could probably be traced from a couple innovative activities and publications [1, 2]. Physico-chemical interactions of phosphates in soils as understood at the beginning of thirties of this century were summarised by Buehrer [3].

An important turning point in plant-PR-soil interaction was the introduction of X ray diffraction technology in studies on crystal lattice of apatite minerals in PR of various geographical areas. Advances from this technology were especially significant after the precision of measurements by x ray diffraction was raised to 10⁻¹¹ cm [4-6], permitting accurate measurements of the length of the *a* axis of apatite crystal lattice. Such an advancement in crystallographic studies on apatites permitted establishment of an inverse relationship between the length of the axis and CO₃:PO₄ molar

substitution ratio in PR apatites. The PO₄ substitution for CO₃ in apatite lattice proved to be positively correlated with dissolution of PR-P in neutral ammonium citrate and in 2% formic acid and also with PR agronomic efficiency [7, 8].

Plant-soil-PR interaction studies conducted by means of old classical methods of field trials and chemical soil and plant testing have been summarized [9] by pointing to the role of base saturation (V value) and cation exchange capacity (T value) of the soils in the mobilization of PR-P for crops. Klecikovsky [10] synthesized these studies to show the role of adsorbed acidity in addition to V and T. Golubev and Klecikovsky [9, 10] both established the importance of soil V, T and Ah values to establish whether PR of unspecified P content and solubility were inferior, equal, or superior to soluble P fertilizer sources.

2. PROCEDURES AND METHODS BASED ON CLASSICAL METHODS OF ASSESSING EFFICIENCY OF PHOSPHATE ROCK (PR)

Five double crossed maize plants (*Zea mays* L, CVR DKH 120) were grown until the 10 to 12 leaf stage on 7 kg dry soil in Mitscherlich type pots on three hapludalf soils dressed with 1.25 g of P₂O₅ per pot from all studied P sources. One g of N from ammonium nitrate and 1.0 g K₂O from potassium sulfate were also studied per pot. Four successive crops of maize were grown in this system on 3 soils (Ilișești, Suceava and Ițcani) using 5 PR sources of P (TSP; Kola — Russia FA; Morocco; El Hasa — Jordan, and Kneiffiss — Siria Prs) and water-soluble TSP.

Chemical properties of the soils suspected of being relevant to PR dissolution were adsorbed acidity (Ah), capacity for cation adsorption as a sum of Ah and of exchangeable bases (T), degree of base saturation (V), humus content (H), and mobile P extractable with ammonium lactate-acetic acid (P_{AL}). These parameters were analyzed by official and standardized Romanian methods (STAS 7184/12-88 for determination of Ah, T, SEB and V; STAS 7184/19-82 for P_{AL} and STAS 7184/21-82 for Humus content) are recorded in Table I.

Some of the chemical properties of the phosphate rocks influencing their P bioavailability were established in concordance with Rom. Patent nr.75241/1980 and are recorded in Table II.

After about 7 weeks of growth the plants were harvested by cutting at the soil surface, fixed at 105°C for 30 minutes and dried at 70°C, milled in fine powder and analyzed for total P. Plant material was digested with 9 H₂SO₄ + 1 HClO₄. Phosphorus was determined by the molybdo-vanadate yellow method [11, 12]. Variance of analyses was applied on all plant pot experimental analytical data [13].

TABLE I. SOME OF THE CHEMICAL PROPERTIES OF THE SOILS BELONGING TO HAPLUDALF GREAT SOIL GROUP (PLOUGHED LAYER 0–25 cm) USED IN PR STUDIES WITH MAIZE

Soils	PH of 1:2.5 soil water suspension	Clay content < 0.002 mm (%)	Ah (meq/ 100 g soil)	SEB (meq/ 100 g soil)	V (%)	H (%)	P _{AL} (ppm)	PRUOIS ¹
Ilișești	5.5	19.0	4.5	10.5	70.0	2.0	10.0	14.7
Suceava	5.6	35.0	5.0	17.0	77.5	3.0	12.0	29.8
Ițcani	7.5	29.0	0.3	25.5	99.0	2.5	45.0	0.2

¹ PRUOIS = Phosphate rock use opportunity index of the soil = (Ah x H² x 100) / (V x 10^{0.0245xP_{AL}}).

TABLE II. SOME OF THE CHEMICAL PROPERTIES OF THE PRs USED IN THE STUDY WITH MAIZE

P sources	Total P content (%)	Rate of PR-P ¹ solubilization (ppm P/min)	Free CaCO ₃ ² content (%)	PRSIDU ³ (ppm P/min)
Fluorapatite (FA), Kola, Russia	16.6	1.0	3.5	0.89
Morocco PR	14.3	4.5	4.5	3.90
El Hasa Jordan PR	13.9	8.5	5.0	4.25
Kneifiss Siria PR	14.5	9.0	5.2	4.39

¹ Rate of PR-P solubilization = $P_{120} - P_{60} / 60$. ² CaCO₃ content in PR determined as loss weight when PR was treated with 2NHCl in an aeration device. ³ PRSIDU, ppm P = $(P_{120} - P_{60}) \times (1 - 0.03 \times \text{CaCO}_3) / 60$

3. RESULTS AND DISCUSSION

3.1. Phosphate rock use opportunity index of the soil (PRUOIS)

The mobilization of PR-P for crops is strictly dependent on soil agrochemical properties and without exception has occurred only as a result of PR interaction with the soil. Also, the effect of PR as a source of P for plants cannot be explained by considering only a single soil or PR chemical property.

Graphical schemes, proposed by Golubev [9] and by Klecikovsky [10], have shown adsorbed acidity (Ah), degree of base saturation (V) and cation exchange capacity (T) as important soil properties involved in PR solubilization. At that time no algorithms or formulas were proposed to substantiate relationships. Combining the relevant soil and PR chemical properties in a synthetic index to predict PR efficiency in a soil was not proposed in Eastern Europe at the time of Golubev [9] and Klecikovsky [10].

In the course of studies for working out a PRUOIS, humus (H) and easily soluble phosphate contents in the soil ploughed layer were considered to be parameters that should be included with Ah, V and T soil values considered by Golubev [9] and Klecikovsky [10]. Introduction of humus content in the PRUOIS formula has been encouraged by experimental data with maize for green fodder (Table III). The consideration of easily soluble phosphate (P_{AL}) has its background in chemistry of common ion effects due to orthophosphate anions whose activity in the solution is directly related to easily soluble soil P content. Apart from the humus contribution to CEC of the soil (about 1.5 meq per 100 g of soil for each percent of humus content increase), humus content influences mobilization of PR-P in the soil by complex physico-chemical and biological processes.

Soil CEC (cation exchange capacity) effect on PR-P mobilization is explained by the activity of calcium ions being lower in the soil solution at higher CEC. The lower Ca activity favors the dissolution of PR and mobilization of its P in the soil. Variation of ion binding strength with CEC of soil colloids may be made evident and quantified by a methodology described by Barber [14]. Some of these aspects benefit from an explicit presentation of the formula as shown below:

$$PRUOIS = \frac{Ah * H^2 * 100}{SEB * 100 * 10^{0.0245 * P_{AL}}} = \frac{Ah * H^2 * (SEB + Ah)}{SEB * 10^{0.0245 * P_{AL}}} = \frac{(Ah^2 + Ah * SEB) * H^2}{SEB * 10^{0.0245 * P_{AL}}} \quad (1)$$

The presence of the T value ($CEC = (SEB + Ah)$) in its interaction with adsorbed acidity (Ah) and humus content (H^2) in the numerator of the PRUOIS formula indicates agronomic effectiveness of PR with increased P is due to interactions of adsorbed acidity, CEC and humus content in the plow layer of the soil. The interaction of the sum of exchangeable bases (SEB) with mobile phosphorus (P_{AL}) placed in the denominator of the PRUOIS formula reflects the negative influence of these soil properties on PR dissolution in the soil and on PR-P mobilization for crops.

TABLE III. CORRELATION COEFFICIENTS (R) OF PR EFFICIENCY IN MAIZE FOR GREEN FODDER ($Y_1 =$ DRY MATTER YIELD FORMATION; $Y_2 =$ P UPTAKE IN EPIGEIC PARTS OF PLANTS) WITH PRUOIS X PRSIDU SYNTHETIC INDICES¹

PRUOIS x PRSIDU	y_1	y_2
PRUOIS without humus (H)	0.885	0.889
PRUOIS with humus (H)	0.884	0.862
PRUOIS with humus (H^2)	0.956	0.963
PRUOIS with humus (H^3)	0.961	0.965

¹ 4 successive crops of maize (DKH 120) on 3 soils (Ilișești, Suceava and Ițcani) dressed with equal rates of P from TSP, Kola, Morocco, Jordan and Siria PR. Number of correlated pairs were 10.

3.2. Phosphate rock suitability index for direct use (PRSIDU)

The PR-P solubility rate was determined in a 0.6% solution of ammonium heptamolybdate in 0.01 M calcium chloride solution (MoCa 0.6 solution) at ambient temperature (20°C) after 60 and 120 minutes incubation at 1:200 PR: MoCa 0.6 solution ratio. From these two extractions, PR-P solubility rate was determined as ppm P/min by dividing the difference of P at 120 and 60 minutes by 60. Due to the formation of complex phosphate-coordinated dodeca-molybdenum hetero polyions, the equilibrium of P extraction is continuously shifted to the right so that PR-P solubilization-rate is actually an average for the time period from 60 to 120 minutes. The PR-P solubilization rate is inversely related to the length of the a-axis of apatite mineral in PR and directly related to PR solubility. In the course of preliminary research on PRSIDU, it was considered proper to adjust the PR-P rate of solubility in MoCa 0.6 according to free carbonate content of PR:

$$PRSIDU [ppmP/min] = PRPRS * (1 - 0.03 * CaCO_3) \quad (2)$$

This adjustment was thought necessary because any significant mobilization of PR-P in the soil may start only after removal of alkaline earth carbonates from PR particles. The solubility of basic alkaline earth phosphates is hampered by the presence of calcium carbonates in PR particles through the common-ion effect.

According to Chien and Menon [8] and Lehr and McClellan [7], solubility of P-PR in different conventionally chosen reagents, such as 2% formic acid, is in an inverse relationship with the $CO_3:PO_4$ molar substitution ratio in the crystal lattice of the apatite mineral of PR. The $CO_3:PO_4$ molar substitution ratio is inversely related to the length of the crystal lattice a axis according to the following equation:

$$\frac{CO_3}{PO_4} \cong 0.36431 - 0.0049906 * a \quad (3)$$

For an a axis of 10^{-11} cm and x substituted for $\text{CO}_3:\text{PO}_4$ molar ratio in PR apatite mineral, then Eq. 3 becomes:

$$P_{AF}^{PR} = 86.15 * x - 9.2 \quad (4)$$

It has also been estimated that PR-P solubility in 2% formic acid is in direct relationship with PRSIDU according to the following equation:

$$\text{PR-P solubility in 2\% formic acid} \approx 3.15 * \text{PRSIDU} \quad (5)$$

3.3. Synthetic index of PR reactivity in the soil and of agronomic effectiveness of PR as resulted from multiplicative combination of PRSIDU and PRUOIS

From numerous pot and field experiments it has been noticed that high reactive PR (like North Carolina-USA, Gafsa-Tunisia and others) could be satisfactory sources of P for plants even on soils having less favorable conditions for PR-P mobilization. Less reactive PR under comparable conditions proved to be adequate sources of P for plants only on soils with favorable PR-P mobilization properties. It has also been noticed that no single chemical property of soil or of PR was able to explain the variation of PR efficiency as a source of plant available P.

There is some mutual compensation between soil and PR chemical properties involved in P mobilization processes to such an extent that less reactive PR might be satisfactory sources of P on soils with soil chemical properties favorable for dissolution and PR-P mobilization. Linear correlation coefficients (r) of maize dry matter yields and phosphorus absorption versus PR-PRSIDU, soil-PRUOIS and PRSIDU x PRUOIS are given in Table IV. Values for dry matter and P absorption relative to TSP (triple superphosphate) in three successive maize crops as dependent on PR-PRSIDU x soil-PRUOIS indices are depicted in Figs. 1 and 2 (first two crops) and in Fig. 3 (the last crop of maize for green fodder). The Mitscherlich-type pot experiments with maize were performed using old, classical difference methodology.

TABLE IV. CORRELATION COEFFICIENTS OF MAIZE DRY MATTER YIELD WITH PR-PRSIDU, SOIL PRUOIS AND PRSIDU x PRUOIS

Dependent variables (y) ¹	Independent variables (x) ²		
	PRSIDU	PRUOIS	PRSIDU x PRUOIS
Maize for green fodder, first cut			
y ₁	0.465	0.739	0.859
y ₂	0.473	0.759	0.883
Second cut			
y ₁	0.465	0.872	0.898
y ₂	0.413	0.783	0.873
Third cut			
y ₁	0.459	0.811	0.925
y ₂	0.459	0.810	0.924
Fourth cut			
y ₁	0.526	0.725	0.885
y ₂	0.490	0.768	0.902

¹ y₁ = dry matter yield of maize for green fodder, y₂ = P uptake in maize plant (mg of P / pot).

² number of correlated pairs was 10.

From the correlation data displayed in Table V and from graphical presentations relative to TSP dry matter yield and P absorption in plants displayed in Figs. 1 and 2, it follows that multiplicative combination of PRSIDU and PRUOIS gave rise to significant improvement of plant-soil and PR correlations. The determination of variation in PR efficiency in maize for green fodder was raised up to 86% with the use of PRSIDU \times PRUOIS. This improvement of PR efficiency correlation with combined PRSIDU and PRUOIS indices is certainly due to mutual compensations, which have intervened between PR and soil chemical properties [3]. The mutual compensation substantially enlarges the area of agronomic effectiveness of an increased number of suitable areas for direct use of PR. Also, regularities of relative TSP and PR effects on maize dry matter yield and on P absorption in maize plants, as displayed in Fig. 3, are subject to laws of statistical distribution and should be evaluated by means of their resultant averages. These need to be further substantiated by means of accurate pot and field plant trials, both by classical non-isotope methodology and by ^{32}P isotope dilution techniques.

3.4. Using PRSIDU and PRUOIS synthetic indices as aids in solving aspects of soil fertilization with TSP and PR

The significance of the PRSIDU \times PRUOIS synthetic index for PR direct use in soil P fertilization can be used to assess the probability of P use efficiency according to the values outlined in Table VI. The PRSIDU \times PRUOIS index can also be used to evaluate PR application rate to use instead of soluble P fertilizers. In order to reach the highest probability of PR being efficient as a P source, the rates of P from PR should be increased so to compensate for their water insoluble P and for their slow or retarded interaction in the soil. It was considered proper to recommend the PR-P rate increase as a complex function of the PRSIDU index of PR and PRUOIS of the soil subject to PR direct use:

$$X = A \times \left(0.55 + \frac{19.0}{\text{PRSIDU} \times \text{PRUOIS}} \right) \times C \quad (6)$$

where X = rate of P_2O_5 from PR, A = economically sound rates of P_2O_5 from soluble P fertilizers, and C = degree of soluble P fertilizer substitution with PR.

The formula presented above implies the possibility of natural PR and soil compensation to such an extent that PR with favorable reactivity may compensate for less favorable PR mobilization soil chemical properties. The rate of P_2O_5 from water-soluble P fertilizers (D) is:

$$D = A - (1 - C) \quad (7)$$

As far as the economical aspect of using PR as direct P sources is concerned, one should first consider the ratio of water soluble P fertilizer and PR cost per unit of P_2O_5 , and the physical efficiency of the P fertilizer in each soil. The cost per unit of P_2O_5 has averaged around 2.22. The physical efficiency may be estimated from plant response to P curve parameters, considering also the state of soil mobile P supply, the efficient amount of P supplied by soil and the degree of growth factors favored for a given crop in a certain soil climate situation. If C is considered to be 0.67 (represents two thirds of the economically sound P rate, application costs being considered equal), one may arrive to the conclusion that combining PR with TSP fertilization amounts fertilization costs at 70 to 85% of using TSP alone. Combining PR (0.67 parts) with TSP (0.33 parts) does not significantly differ from full fertilization with TSP. This is especially true when following the official technological recommendations to incorporate two thirds of P rate into soil by plowing as a basal dressing and to apply the remaining one third of P as "starter NP fertilizer" at planting time. From such an economical estimation, one discovers that within the range of 70 to 85% the higher the PRSIDU and PRUOIS the lower the cost of combined PR and TSP fertilization. In fact, the economical evaluation of PR use for partial or complete substitution of water-soluble P fertilizers may be more complicated due to differences in mobile soil P dynamics under the influence of TSP and PR P sources.

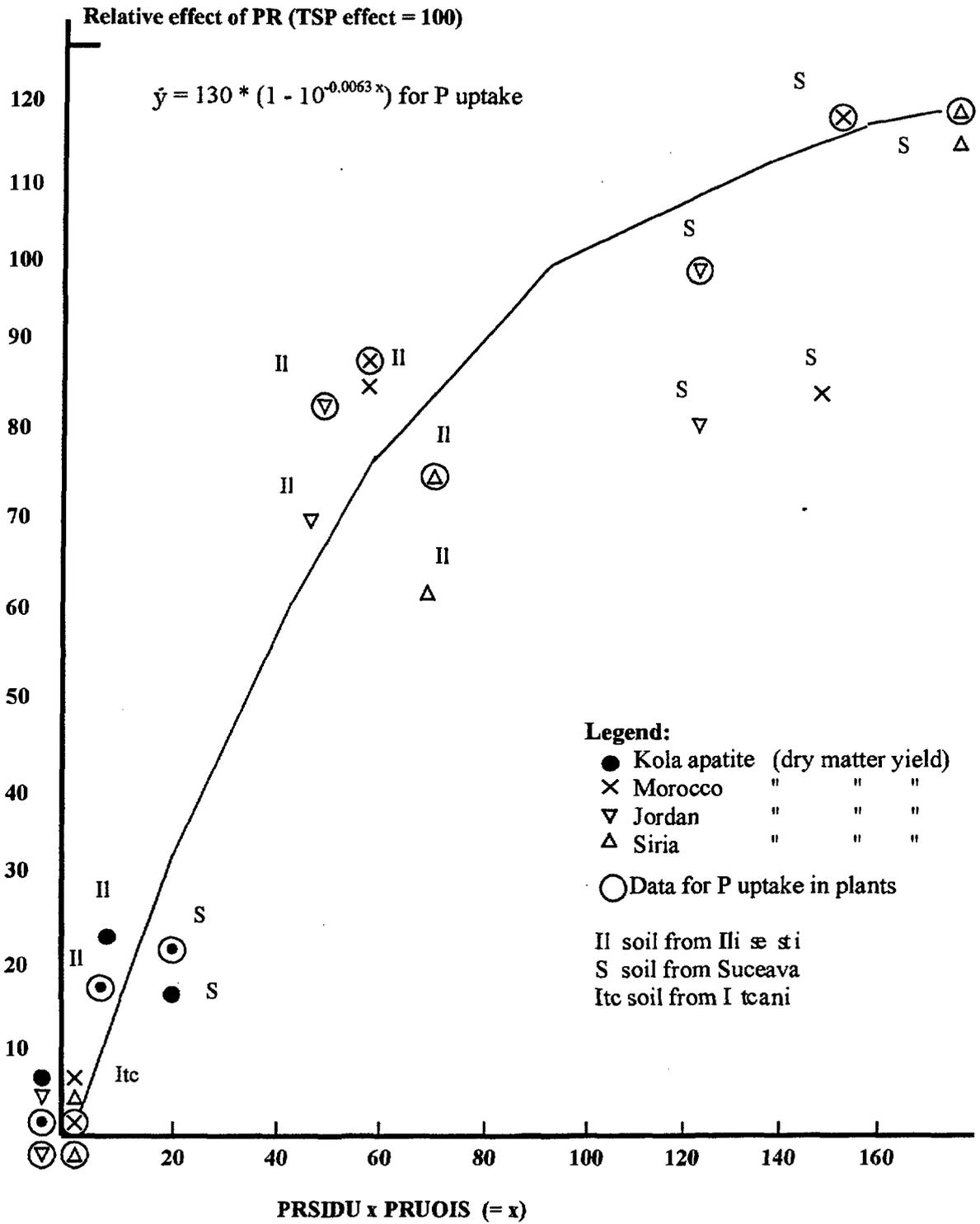


Fig. 1. Relative effect of PR on maize (DKH 120) dry matter yield and on plant P uptake in 1-st year, 2-nd crop versus the composite synthetic index obtained by multiplying PRSIDU x PRUOIS (7 kg dry soil pot experiment on 3 soils).

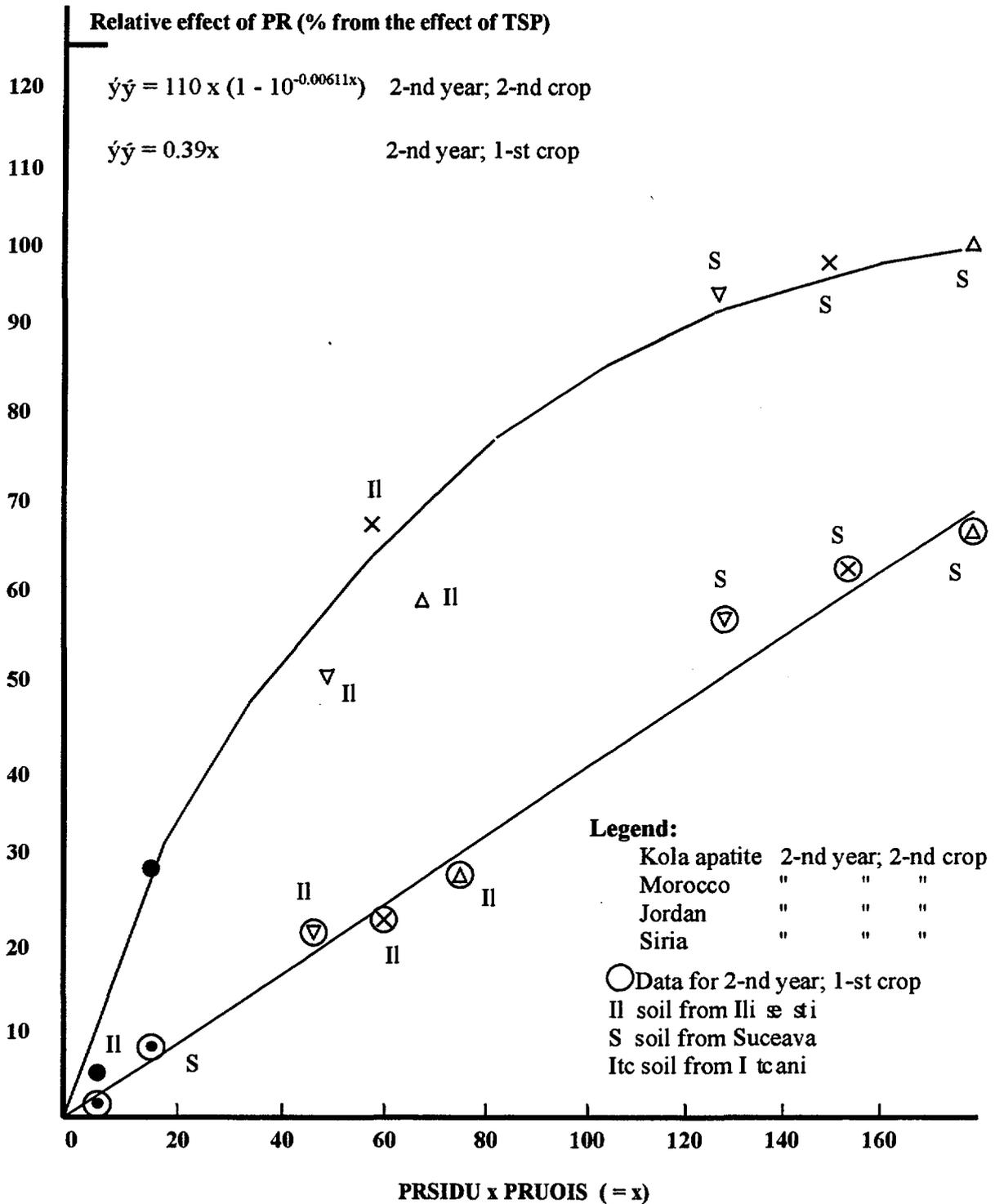


Fig. 2. Relative effect of PR on maize (DKH 120) dry matter yield versus a composite synthetic index obtained by multiplying PRSIDU x PRUOIS (the later calculated with H^2) (7 kg soil pot experiment). Symbols for PR same as used in Fig. 1.

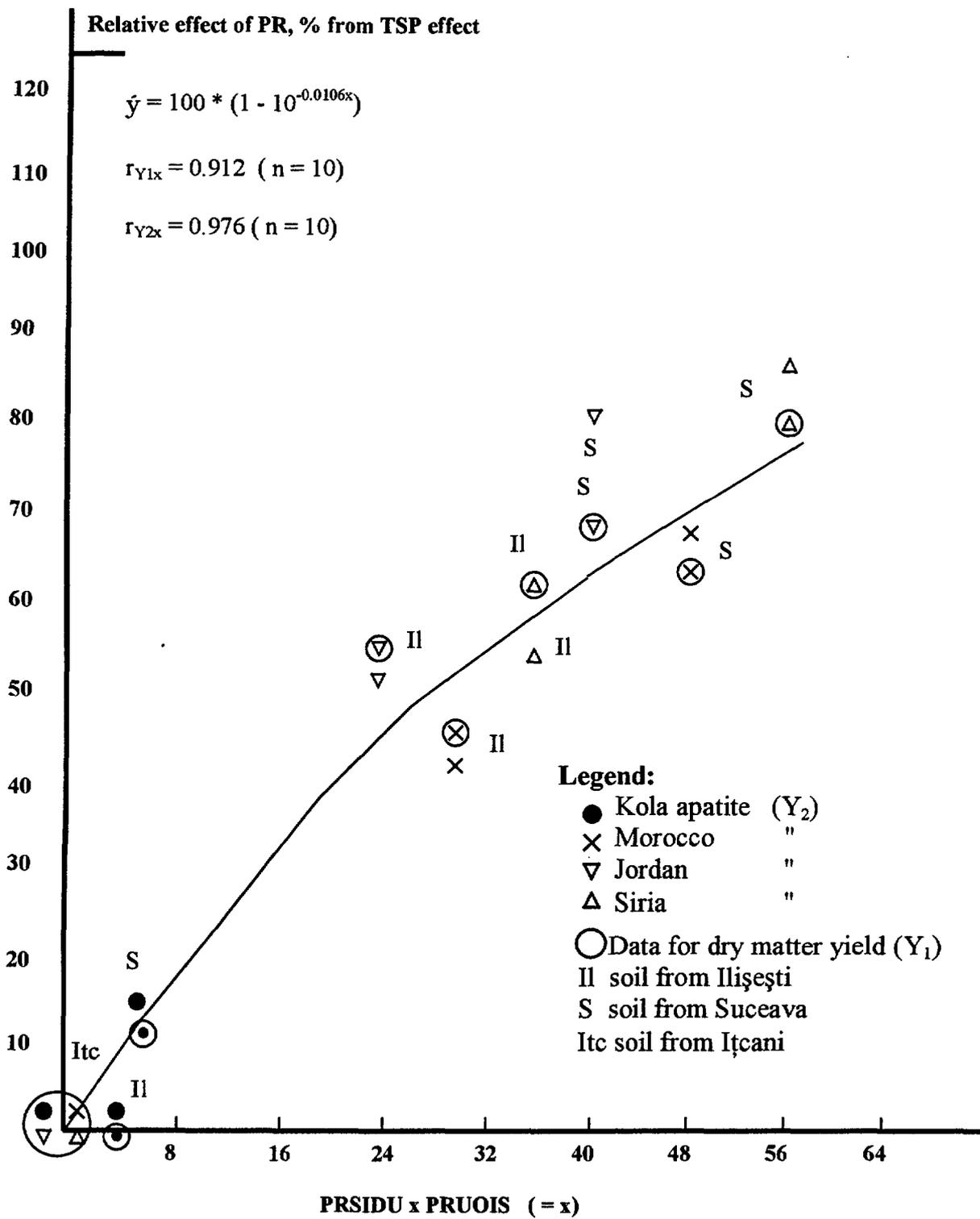


Fig. 3. Relative effect of PR on dry matter yield and on plant P uptake in maize (DKH 120), versus PRSIDU x PRUOIS composite synthetic index. (7 kg soil pot experiment).

TABLE V. SOIL, PR AND PLANT (RYEGRASS) CORRELATION STUDIES INCLUDING ALSO A COMPARISON OF ³²P ISOTOPE DILUTION TECHNIQUE WITH NON-ISOTOPE DIFFERENCE METHOD

Independent variables (X)	Y ₁ =PdfPR as % from total plant P	Dependent variables (Y)		
		Y ₂ =PdfPR/PdfCSP ¹	Y ₃ =PdfPR/PdfCSP ²	Y ₄ =(PuPR-PuCheck)/(PuCSP-PuCheck) ³
X ₁ =PRUOISxPRSIDU	0.9311	0.8903	0.7956	0.6317
X ₂ =PRUOISxPRSIDUxRBCIS	0.9312	0.8909	0.8332	0.6544
Statistical significance of correlation ratios				
YX ₂ compared with YX ₁	n.s.	n.s.	n.s.	n.s.
X ₃ =PRSIDU alone	0.5729	0.6431	0.7105	0.7530
YX ₃ compared with YX ₁ and YX ₂	ooo	ooo	n.s.	n.s.
X ₄ =PRUOIS alone	0.7089	0.6080	0.3625	0.2351
YX ₄ compared with YX ₁ and YX ₂	ooo	ooo	ooo	o
X ₅ =RBCIS alone	0.6250	0.5655	0.4503	0.2800
YX ₅ compared with YX ₁ and YX ₂	ooo	ooo	ooo	o
YX ₅ compared with YX ₄	n.s.	n.s.		
X ₆ =RBCISxPRSIDU	0.7521	0.7976	0.9696	0.8104
YX ₆ compared with YX ₁ and YX ₂	ooo	n.s.	n.s.	x
YX ₆ compared with YX ₃	n.s.	n.s.	xx	n.s.
YX ₆ compared with YX ₄ and YX ₅		n.s.	xxx	xxx

¹ Pdf P sources as % from total plant P.

² Pdf P sources as mg of P per pot.

³ P uptake in P treatments -P uptake in no P check, established by non-isotope, difference method.

⁴ In all cases, number of correlated pairs was 60.

n.s. = non significant; x and o = significant; xx and oo distinctly significant; xxx and ooo very significant positive and negative, respectively.

TABLE VI. PROBABLE MEANING OF (PRSIDU * PRUOIS) SYNTHETIC INDEX IN TERMS RELATIVE TO TSP EFFICIENCY

PRSIDU x PRUOIS	Probability of PR being efficient as P sources in field crops	Probable efficiency ¹ (relative to TSP) in field crops %
Below 10	very small	Below 20
10-20	small	20-60
20-40	medium	40-80
40-80	considerable	70-90
Over 80	high	Over 80

¹ subject to considerable variation from crop species to another, depending on their physiological peculiarities of mineral nutrition.

4. CONCLUSIONS

Several aspects of theoretical and practical interest of PR use as a P source on low P and base unsaturated soils have been tackled in the course of our participation in the IAEA Co-ordinated research program on phosphorus: "The use of nuclear and related techniques for evaluating the agronomic effectiveness of phosphate fertilizers in particular rock phosphates".

1. Opportunity of using PR, of adequate quality, directly as a P source depending on adsorbed acidity (Ah), humus (H), degree of base saturation (V) and easily soluble (mobile) P content in the upper layer of soils (PRSIDU).
2. Characterization of PR reactivity in view of its direct use by means of PR-P rate of solubility in 0.6% ammonium molybdate in 0.01 M calcium chloride solution (PRSIDU).
3. A multiplicative combination of PR reactivity index with the opportunity of PR use index of soil in a synthetic index of phosphate rock reactivity and opportunity of PR use (PRSIDU x PRUOIS). Such a combination implies a mutual compensation of PR and of soil properties involved in PR-P mobilization. It also implies a new understanding of PR-P mobilization occurring in the soil as a result of prolonged contact and chemical interaction of PR and soil particles. Some results obtained in plant soil correlation studies when working out PRUOIS and PRUOIS x PRSIDU synthetic indices are recorded in Tables III to V while the regression of P absorption in plants and PR relative efficiency on synthetic PRUOIS * PRSIDU synthetic indices are given in Figs. 1-3.
4. A tentative procedure of interpretation of PRUOIS * PRSIDU from a practical view point so as to predict the probability of PR being efficient as P sources on a particular soil and the necessary rate of PR-P at any given degree of TSP (soluble P fertilizers) replacement with PR.
5. A tentative evaluation of economical aspects of PR direct use as the only P source for partial replacement of water-soluble P fertilizers. This evaluation has pointed out the higher the PRUOIS * PRSIDU the better the economical outcome of PR use.
6. In all these aspects the authors have arrived at sound conclusions and recommendations of practical interest, which certainly may support the use of reactive PR as sources of P for field crops on about one-third of the arable land in Romania.

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