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THE INFLUENCE OF A LONG-TERM RECLAMATION ON THE CONTENT OF PHOSPHORUS FORMS IN SOILS FORMED FROM POST-MINING LANDS

Summary

The paper contains the results of the research on the content of phosphorus and its speciation in the soils formed from post-mining lands after over thirty years of their reclamation. Experimental factors included two crop rotations: frumentaceous-rapeseed and fodder-frumentaceous, and three fertilization levels: 0NPK, 1NPK and 2NPK. Fractioning was conducted with Hedley's method. Total content of phosphorus oscillated between 397,2 and 935,8 mg P · $kg^{-1}$of soil. The content of all the analysed forms of phosphorus increased along with the growth of fertilization level and was between 6,27 and 24,6 mg P · kg^{-1} of soil – for water-soluble phosphorus, 5,5 and 50,8 mg P · kg^{-1} of soil for 0,5 mole · dm^{-3} $NaHCO_3$ extracted phosphorus, 5,2 and 44,4 mg P · $kg^{-1}$of soil for 0,1 mole · dm^{-3} NaOH extracted phosphorus, 227,0 and 649,2 mg P · $kg^{-1}$of soil for 1 mole · dm^{-3} HCl phosphorus and 60,9 and113,5 mg P · $kg^{-1}$of soil for residual phosphorus. Statistically important differences have arisen between the same combinations of mineral fertilization implemented in the analysed crop rotations. Higher content of phosphorus both in total and the majority of analysed fractions, was found in the samples collected from the fields with fodder-frumentaceous crop rotation.
***Key words**: post-mining lands, sequential extraction, fraction of phosphorus, fertilization*

WPŁYW WIELOLETNIEJ REKULTYWACJI NA ZAWARTOŚĆ FORM FOSFORU W GLEBACH TWORZĄCYCH SIĘ Z GRUNTÓW POGÓRNICZYCH

Streszczenie

W pracy przedstawiono wyniki badań dotyczące zawartości fosforu oraz jego specjację w glebach wytworzonych z gruntów pogórniczych po przeszło trzydziestu latach ich rekultywacji. Czynnikami doświadczenia były dwa płodozmiany: zbożowo-rzepakowy oraz paszowo-zbożowy oraz trzy poziomy nawożenia:0NPK, 1NPK oraz 2NPK. Frakcjonowanie przeprowadzono metodą Hedleya. Całkowita zawartość fosforu wahała się od 397,2 do 935,8 mg P · kg^{-1}gleby. Zawartość wszystkich analizowanych form fosforu zwiększała się wraz ze wzrostem poziomu nawożenia i wahała się w przedziale dla fosforu wodnorozpuszczalnego od 6,27do 24,6 mg P · kg^{-1} gleby, ekstrahowanego 0,5 mol · dm^{-3} $NaHCO_3$ od 5,5 do 50,8 mg P · kg^{-1}gleby, ekstrahowanego 0,1 mol · dm^{-3} NaOH od 5,2 do 44,4 mg P · kg^{-1}gleby, ekstrahowanego 1 mol · dm^{-3} HCl od 227,0 do 649,2 mg P · kg^{-1}gleby, fosforu rezydualnego od 60,9-113,5 mg P · kg^{-1}gleby. Wystąpiły statystycznie istotne różnice pomiędzy tymi samymi kombinacjami nawożenia mineralnego zastosowanymi w analizowanych płodozmianach. Większe ilości fosforu zarówno całkowitego, jak i w większości analizowanych frakcji stwierdzono w próbkach pobranych z poletek płodozmianu zbożowo-rzepakowego. Tylko frakcja fosforu rezydualnego dominowała w glebach pobranych z poletek płodozmianu paszowo-zbożowego.
***Key words**: grunty pogórnicze, ekstrakcja sekwencyjna, frakcja fosforu, nawożenie*

1. Introduction

Brown coal mining conducted in Konin-Turek basin leads to land geo-mechanical transformations. Sedimentary rocks left over an excavation on inner and outer spoil dumps, are reclaimed in this area either in an agricultural or forest direction [2, 3]. Agricultural reclamation is conducted in accordance with the model of Polish Academy of Science created by professor Bender [1]. Main idea of this model is to regulate the chemistry of the parent material (rock). Mineral fertilization and the implementation of agriculture plants are used to achieve this objective [10]. Phosphorus fertilization is o.ne of the reclamation methods. Phosphorus is necessary for the growth and proper development of organisms. Mineral soils are dominated by its inorganic compounds which are 70-95% of its total content [9]. They are a component of a parent rock and usually occur in the sparingly soluble form. When implemented into soil, phosphorus combined with mineral fertilizers in the form of easily dissolving monocalcium phosphates, undergoes chemical sorption. This phenomenon occurs in soils of both, acid and alkaline reaction. This prevents its elution and therefore limits the share of this particle in so called eutrophication process. Egner's – Riehm's method is a widely used method for the determination of soil's abundance in this particle's available forms in Poland, however, it does not provide information about the process dynamics of so called phosphates retardation [19]. Such information is provided when methods of sequential extractions are implemented, where phosphorus is extracted with stronger and stronger extractors [4, 17, 18].

The aim of the paper was to determine the content of phosphorus forms with Hedley's method in soil samples collected from an arable horizon formed from post-mining lands under the conditions of differentiated level of mineral fertilization and to crop rotations after over thirty years of reclamation.

2. Materials and methods

The research was conducted on medium samples collected in the year 2013 in 15 fields from top soil horizons from a reclaimed outer spoil dump which were an area of long- term experiments for more than 30 years. Experimental factors included two crop rotations (frumentaceous-rapeseed and fodder-frumentaceous) and three levels of mineral fertilization (0 NPK, 1 NPK and2 NPK). Laboratory analyses were conducted on air-dried material passed through a sieve of 2 mm meshes. Fractioning was done with Hedley's method [6] (Tab. 2), whereas phosphorus concentration in the obtained extracts was marked with a colorimetric method with blue-staining ammonium molybdate and ascorbic acid and emetic (antimonyl-phosphate tartrate) according to Murphy's and Riley's method [8]. Reading was done on Cary 60 apparatus. The results were put under variance analysis and the importance of differences between the averages was verified with Tukey's test at reliance (p = 0,05).

Table 1. Mineral fertilization doses in accordance with 1 NPK combination ($kg \cdot ha^{-1}$)
Tab. 1. Dawki nawożenia mineralnego zgodne z kombinacją 1 NPK ($kg \cdot ha^{-1}$)

Plant species	Chemistry remediation used for the first 10 years			Mineral fertilization used from the 11th year until now		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O
Winter wheat	160	270	140	160	40	80
Rapeseed	200	460	150	200	70	90
Lucerne with grasses	170	380	260	170	70	150

Source: own studies / Źródło: badania własne

3. Results and discussion

After thirty years of agricultural reclamation conducted within the established experience on an outer spoil dump of Pątnów lignite exposure, chemical composition of soils which formed there changed. Investigations concerning basic physical and chemical properties were conducted by Spychalski et al. [11]; mentioned authors also analysed changes in phosphorus compounds [12]. The authors reported that after thirty years of reclamation, the texture of forming soils was weakly differentiated, characteristic for sandy loams. The humus content in these soils depended on the dose of mineral fertilization and cultivated plants. Spychalski et al. [13] also conducted research on phosphorus speciation in these soils. Appreciation analysis was led in accordance with Chang's and Jackson's method [4] by separating six fractions of mineral phosphorus. The obtained results proved that soils formed from post-mining materials were highly differentiated in the content of phosphorus, both total and connected with individual elements of soil solid phase. The results of total phosphorus content and its fractions are present in table 3.

3.1. Phosphorus soluble in water

In the analysed soil samples collected from top horizons of soil formed from post-mining lands, the average content of phosphorus soluble in water oscillated between 6,27 mg $P \cdot kg^{-1}$ – fodder-frumentaceous crop rotation –0NPK fertilization and 24,60 – frumentaceous-rapeseed crop formation –2NPK fertilization (Tab. 3). The differentiation of content of this phosphorus form relatively high and depended on the dose of mineral fertilization and crop rotation. The highest differences in the content of phosphorus soluble in water (P-H_2O) were observed especially in the samples collected from fields with rapeseed-frumentaceous crop rotation where fertilization of 0NPK in relation to 2NPK was implemented. The content of this form of phosphorus doubled. Along with the increase of fertilization, the content of this form of phosphorus grew. Percentage share of average values of P-H_2O obtained from each fertilization combination for two crop rotations was not high in relation to its total content and oscillated from 1,96% - 0NPK fodder-frumentaceous crop rotation to 2,84% - 2NPK rapeseed-frumentaceous crop rotation (Fig. 1). Fertilization of 1NPK dose in fodder-frumentaceous crop rotation did not statistically lead to any crucial changes in the content of phosphorus soluble in water. Similar and not significantly differentiated values of 7,95 and 8,31 mg $P \cdot kg^{-1}$ were obtained. The implementation of mineral fertilization in 2NPK dose caused statistically significant growth in P-H_2O content. In the soils of the crop rotation, fertilization doses of 1NPK and 2 NPK led to a statistically important increase of this ingredient. When analysing the influence of a crop rotation on changes in the content of this form of phosphorus, statistically significant differences between the same fertilization combinations in rapeseed-frumentaceous and fodder-frumentaceous crop rotations were found (Tab. 4).

Table 2. Sequential fractioning of phosphorus according to Hedley's method [6]
Tab. 2. Frakcjonowanie sekwencyjne fosforu wg metody Hedleya [6]

Fractions name	Extractant	Procedure	Specification
P- H_2O	H_2O	2 grams of soil + 40 cm^3 H_2O, shaking for 16 h	P-active – labile forms of phosphorus in soil solution
P – $NaHCO_3$	0,5 mole $\cdot dm^{-3}$ $NaHCO_3$	0,5 mole $\cdot dm^{-3}$ $NaHCO_3$ shaking for 16 h	Replaceable and loosely absorbed phosphorus compounds
P - NaOH	0,1 mole $\cdot dm^{-3}$ NaOH	0,1 mole $\cdot dm^{-3}$ NaOH shaking for 16 h	Phosphorus compounds connected with hydroxides of iron, aluminium and with organic matter
P- HCl	1 mole $\cdot dm^{-3}$ HCl	40 cm^3 1 mole $\cdot dm^{-3}$ HCl shaking for 16 h	Difficult to solve phosphorus compounds – apatites
P - Residual	Concentrated HCl	Burning at 500^0C +15 cm^3 + concentrated HCl + boiling	Organically stable organic and inorganic P

Table 3. Content of phosphorus fractions in the soils formed from post-mining lands

Tab. 3. Zawartość frakcji fosforu w glebach wytworzonych z gruntów pogórniczych

Crop rotation (A)	Plant	Level NPK (B)	P- H_2O	P- $NaHCO_3$	P- NaOH	P- HCl	P- residual	P- sum of fractions	P- Total
			mgP·kg^{-1}						
Fodder-frumentaceous	Wheat after lucerne	0 NPK	6,27	5,47	5,18	299,67	75,53	392,12	485,17
		1 NPK	6,97	9,57	10,72	309,70	113,53	450,49	474,57
		2 NPK	7,93	14,33	15,78	332,50	85,70	456,24	521,20
	Lucerne in the 1st year	0 NPK	10,00	5,70	6,68	245,63	73,03	341,04	397,77
		1 NPK	9,50	16,20	14,77	349,10	82,10	471,67	482,47
		2 NPK	12,57	23,43	19,28	416,50	85,40	557,18	622,20
	Lucerne in the 2nd year	0 NPK	7,57	5,77	8,30	227,00	76,83	325,47	483,13
		1 NPK	8,47	14,80	20,30	328,47	83,43	455,47	479,47
		2 NPK	13,97	36,30	44,38	554,90	99,17	748,72	917,77
Rapeseed-frumentaceous	Rapeseed	0 NPK	12,40	13,50	15,40	342,80	69,13	453,23	397,23
		1 NPK	18,60	44,50	30,10	535,40	90,67	719,27	813,10
		2 NPK	24,60	44,97	33,68	649,23	92,83	845,31	935,80
	Wheat	0 NPK	11,13	13,23	12,28	419,60	60,93	517,17	422,30
		1 NPK	16,30	29,73	24,53	426,17	76,27	573,00	614,63
		2 NPK	23,23	50,80	37,23	638,53	89,57	839,36	864,50

Source: own studies / Źródło: badania własne

Table 4. Average content of phosphorus fraction in soils formed from post-mining lands in mg P·kg^{-1}

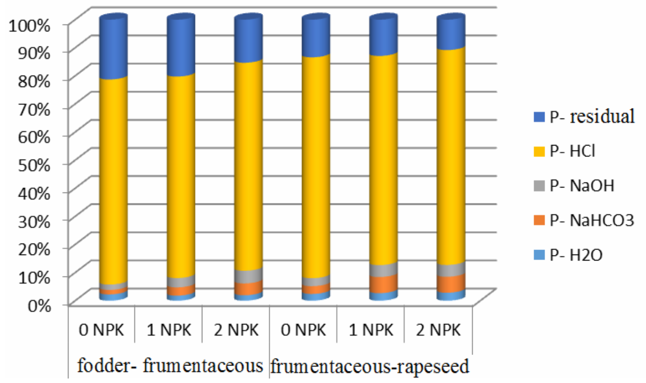
Tab. 4. Średnie zawartości frakcji fosforu w glebach wytworzonych z gruntów pogórniczych mg P·kg^{-1}

Crop rotation (A)	NPK Level (B)	P-H_2O	P-$NaHCO_3$	P-NaOH	P-HCl	P- residual	P- sum of fractions	P- Total
		mgP·kg^{-1}						
Fodder	0 NPK	7,95	5,65	6,72	257,43	75,13	352,88	455,36
	1 NPK	8,31	13,52	15,26	329,09	93,02	459,21	478,84
	2 NPK	11,49	24,69	26,48	434,63	90,09	587,38	687,06
Frumentaceous-rapeseed	0 NPK	11,77	13,37	13,84	381,20	65,03	485,20	409,77
	1 NPK	17,45	37,12	27,32	480,79	83,47	646,14	713,87
	2 NPK	23,92	47,89	35,46	643,88	91,20	842,34	900,15
NIR B/A		1,48	4,18	2,08	60,57	9,16	73,87	72,85
NIR A/B		1,21	3,43	1,71	49,71	7,52	60,61	59,78

Source: own studies / Źródło: badania własne

3.2. Phosphorus solubale in $NaHCO_3$

According to numerous authors [5, 16], phosphorus extracted in 0,5 mole·dm^{-3} $NaHCO_3$ is defined as a exchangeable and loosely connected fraction with soil, stays in balance with P-H_2O and is a reservoir of phosphorus which is easily available for plants. In the analysed soil samples, the content of phosphorus in this fraction oscillated between 5,47 and 36,30 mg P · kg^{-1} (on rapeseed-frumentaceous crop rotation fields) and between 13,23 and 50,80 mg P · kg^{-1} (on fodder-frumentaceous crop rotation fields) (Tab. 3). It was found that, similarly to phosphorus soluble in water, the higher content of implemented mineral fertilization, the more phosphorus (P- $NaHCO_3$) the analysed soils samples contained. This fraction oscillated from 1,60% (0NPK) to 4,20% (2NPK) in fodder-frumentaceous crop rotation and accordingly in rapeseed-frumentaceous from 2,75% (0NPK) to 5,74% (1NPK) of total phosphorus (Fig. 1). Average values of this form of phosphorus in samples collected from each fertilization combination and crop rotation showed high differentiation. Statistically significant influence of mineral fertilization on the increase of this form of phosphorus both in rapessed-frumentaceous and fodder-frumentaceous crop rotation soils was observed (Tab. 4). When comparing the same established combinations implemented in both analysed crop rotations, a statistically higher content of this form of phosphorus was found in the samples collected from the frumentaceous-rapeseed crop rotation.



Source: own studies / Źródło: badania własne

Fig. 1. Percentage share of individual forms of phosphorus marked with Hedley's method in relation to its total content (sum of fractions).

Rys. 1. Procentowy udział poszczególnych form fosforu oznaczonego metodą Hedleya w stosunku do jego całkowitej zawartości (suma frakcji)

3.3. Phosphorus soluble in NaOH

Phosphorus extracted in 0,1 mole · dm^{-3} NaOH, includes the hardly soluble combinations of phosphorus with iron, aluminium and organic matter. Its content in the analysed soil samples oscillated from 5,18 mg P · kg^{-1} (fodder-frumentaceous crop rotation – control -0NPK) to 44,38 mg

P · kg^{-1}(fodder-frumentaceous crop rotation – control – 2NPK) (Tab. 3). The implementation of growing mineral fertilization doses caused a statistically significant increase of this form of phosphorus both in frumentaceous-rapeseed crop rotation and in fodder-frumentaceous one. When comparing the same mineral fertilization combinations in both crop rotations, a statistically higher growth if this form of phosphorus in the soils of fodder-frumentaceous crop formation was found (Tab. 4). This fraction oscillated between 1,90% and 4,51% in the fodder-v crop rotation and between 2,85% and 4,21% of total phosphorus (Fig. 1).

3.4. Phosphorus soluble in HCl

Phosphorus extracted in 1 mole · dm^{-3} HCl constitutes a stock of its hard available compounds. These forms are mostly combined with calcium [5,17,18]. Its content oscillated from 227,00 mg P · kg^{-1} (fodder-frumentaceous crop rotation – control - 0NPK) to 649,23 mg P · kg^{-1} (frumentaceous-rpeseed crop rotation - 2NPK) (Tab. 3). When analysing the impact of mineral fertilization on the content of this phosphorus fraction, it was found that the implementation of mineral fertilization both in 1NPK and 2NPK doses statistically significantly influenced the growth of the content of this phosphorus form in soils of both crop rotations. A percentage share of this phosphorus fraction in relation to its total content was between 71,66% (1NPK) and 74,00% (2NPK) (Fig.. 1), which was on average 72,87% in fodder-frumentaceous crop rotation), and between 74,41% (1NPK) to 78,57% (0NPK), which was an average of 76,47% in soils of fodder-rapeseed crop rotation. Statistically significant differences were found in the content of this phosphorus forms in soil samples collected from the same fertilization combinations in frumentaceous-rapeseed and fodder-frumentaceous crop rotations. Higher values of P-HCl were found in the soils of frumentaceous-rapeseed crop rotation

3.5. Residual phosphorus

Remains from the sequential extraction are a pool of mineral and organic phosphorus which is not available for plants. Its content in the analysed soil samples oscillated between 60,93 mg P · kg^{-1} (rapeseed-frumentaceous crop rotation - control - 0NPK) and 113,53 mg P · kg^{-1} (fodder-frumentaceous crop rotation – control - 1NPK) (Tab. 2). Mineral fertilization implemented in the experiment in 1NPK dose caused a statistically significant increase of this element in the analysed soil samples from both crop rotations. Further increase of fertilization did not result in any statistically significant growth in the content of this phosphorus form. Comparison of the same fertilization combinations in both crop rotations showed that significantly higher content was found in the fields with a fodder-frumentaceous crop rotation which were not fertilized - 0NPK – and fertilized with the dose of 1NPK (Tab. 4). Whereas none statistically significant differences were found in the content of residual phosphorus between crop rotations in which fertilization with 2NPK dose was implemented. A percentage share of residual phosphorus in relation to its total content in soils of fodder-frumentaceous crop rotation oscillated from 15,3% - 2NPK dose to 21,3% -control 0NPK, and in the soils of frumentaceous-rapeseed crop rotation - 13,4% and 10,8% (Fig. 1), respectively.

3.6. Total phosphorus

The content of total phosphorus in the analysed soil samples was between 397,2 and 935,8 mg P · kg^{-1} (Tab. 3); the same regularities in the changes of total phosphorus as in the case of its previously described fractions were observed. Significant differences in case of total phosphorus were observed in the soils with frumentaceous-rapeseed crop rotation between the implemented levels of fertilization. In the soils of fodder-frumentaceous crop rotation, the implementation of 1NPK dose did not cause a statistically significant growth in the content of this phosphorus form; the similar results were obtained in case of 0NPK- 455,4 mg P · kg^{-1} and 1NPK 478,8 mg P · kg^{-1} doses. The implementation of 2NPK dose in this crop rotation caused a significant increase of the content of total phosphorus.

4. Discussion

The paper covered the research on various amounts of phosphorus forms in the soil formed from post-mining lands as a result of reclamation processes. A systematic, over-30 year-long implementation of mineral fertilization increased the content of the analysed phosphorus forms when compared to the control. Even fertilization with such a minor dose as 1NPK increased the content of the analysed phosphorus forms in soil samples collected from both crop rotations. Numerous investigations conducted on arable lands by various authors proved an impact of fertilization on the content of more or less easily available forms of phosphorus [5, 7, 9, 14 15, 20]. In the investigated soils, the dominating fraction was the compound of phosphorus and calcium, which on average summed up to 73% of total phosphorus in the soils of fodder-frumentaceous crop rotation and 77% in the soils of frumentaceous-rapeseed crop rotation. It confirms what numerous authors have previously claimed about the susceptibility of phosphorus to chemical sorption. On the basis of various research, Spychalski et al. [13] pay attention to the proneness of soils formed on post-mining lands to strong chemical sorption of this element, especially to forming compounds with calcium. The authors emphasize that in alkaline soils, which are rich in $CaCO_3$, easily soluble forms of phosphorus defined as labile forms and present in such compounds as $CaH_4(PO_4)_2$, CaH_4PO_4, they undergo a process of retardation, if not retrieved by plants. Mineral fertilization caused the highest possible growth of phosphor in the extracted fraction of 0,5 mole·dm^3 $NaHCO_3$. The increase of this fraction in relation to the control was from more than doubled to almost four-times higher.

5. Conclusions

The obtained results allowed to define final conclusions:

1. Factors implemented in the experiment (NPK fertilization and crop rotation) significantly influenced the quantity and quality changes of phosphorus compounds in the soil.
2. With increasing level of NPK fertilization also the increase of the total phosphorus and all the investigated fractions content marked with Hedley's method, were observed. The average content of the analysed phosphorus forms are in gradation order: $P_{H2O} < P_{NaOH} < P_{NaHCO3} < P_{residual} < P_{HCl}$.
3. High share of phosphorus forms combined with calcium was observed – on average 75% of its total content.
4. Small increase of the most analysed phospohorus, was observed in the soils of fodder-frumentaceous crop rotation.

6. References

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