

POTASSIUM CONTENTS IN POST-MINING SOILS AFTER 35-YEAR-LONG FIELD EXPERIMENT: THE EFFECT OF PHYSICAL-CHEMICAL COMPOSITION OF SOILS

Summary

The paper discusses the contents and chemical forms of potassium in post-mining soils after 35-year-long experimental cultivation. In the experiment the post-mining dump deposits were fertilized with N, P, K, NK, NP, PK or NPK. Wheat and rape were sowed on the fields. The control field was left unfertilized. In the years 2014-2016 surface (0-30 cm) and subsurface (30-60 cm) layers of fertilized and unfertilized soils were sampled for chemical analyzes. In <2 mm fraction of these soils we determined pH, C and N contents as well as the following K forms: H₂O-soluble K (K-H₂O), active K (K-CaCl₂), bioavailable K (K-DI), exchangeable K (K-CH₃COONH₄), fixed K (K-HCl) and non-exchangeable K (K-HNO₃). We demonstrated that effect of fertilizing on the K fractionation in the soils was statistically significant. The most favorable chemical changes in the cultivated soils occurred due to NPK treatment. The NPK fertilizing resulted in the highest increase in H₂O-soluble K and exchangeable K contents.

Key words: post-mining lands, reclamation, fertilization, forms of K, K availability, nonexchangeable K, K fixation

ZAWARTOŚĆ FORM POTASU W GLEBIE ROZWIJAJĄCEJ SIĘ Z GRUNTÓW POGÓRNICZYCH PO 35 LATACH PROWADZENIA DOŚWIADCZENIA NA TLE WYBRANYCH WŁAŚCIWOŚCI FIZYKO-CHEMICZNYCH

Streszczenie

W pracy przedstawiono wyniki badań dotyczące zawartości form potasu w próbkach glebowych pobranych z doświadczenia polowego założonego na gruntach pogórnicych po przeszło 35 latach jego prowadzenia. Czynnikiem doświadczenia były następujące kombinacje nawożenia mineralnego: N, P, NK, NP, K, PK, NPK oraz kontrola – brak nawożenia. Na polatkach uprawio pszenicę i rzepak. Do badań pobrano próbki średnie wiosną w latach 2014-2016 z poziomu 0-30 cm oraz 30-60 cm. W powietrnie suchych częściach ziemistych oznaczono odczyn (pH), C i N oraz następujące formy potasu: wodno rozpuszczalny K-H₂O, aktywny – K-CaCl₂, przyswajalny wg Egnera-Riehma – K-DI, wymienny – K-CH₃COONH₄, uwsteczniony – K-HCl oraz rezerwowy K-HNO₃. Wykazano statystycznie istotny wpływ stosowanych w doświadczeniu kombinacji nawożenia mineralnego na zawartość analizowanych form potasu zarówno w próbkach glebowych pobranych z warstwy 0-30 cm jak i z 30-60 cm. Spośród analizowanych form potasu największy wzrost zawartości w stosunku do kontroli, pod wpływem zastosowanego nawożenia mineralnego zaobserwowano w przypadku potasu: wodnorozpuszczalnego oraz wymiennego. Największą zawartość analizowanych form potasu stwierdzono w glebach poletek, na których stosowane było nawożenie w kombinacji NPK. Stosowanie nawożenia mineralnego w kombinacji NPK spowodowało najkorzystniejsze zmiany właściwości chemicznych tworzących się gleb.

Słowa kluczowe: grunty pogórnicy, rekultywacja, nawożenie, formy potasy, potas przyswajalny, niewymienny, fiksacja potasu

1. Introduction

Potassium occurs in soils in remarkable abundance [1] between 0,9 and 2,3% [8]. Fertilizing has a profound effect on chemical composition of soils including the content and bioavailability of potassium [2, 3, 7, 19]. The speciation of potassium is heavily affected by the long-term static experiments [7, 9, 15].

The bioavailable forms of potassium are those occurring in soil solution as well as weakly sorbed onto the sorption complex. These forms contain up to 1-3% of total potassium [20]. Many authors claim that the excess potassium (unutilized by plants) is prone to leaching and/or unchangeably bound by the soil complex [8, 9]. The potassium in soils was thoroughly studied, however most of studies were performed on agricultural areas 4, 18]. Much less attention was drawn to the soils formed due to reclamation of post-mining dump deposits [12, 13]. Therefore the present study aimed at determining potassium speciation in post-mining soils undergoing 35-year long experimental reclamation.

We have compared the potassium contents and speciation in two horizons (0-30 cm and 30-60 cm).

2. Materials and methods

The static experiment on an inner mine waste dump of the Pątnów brown coal mine was set up in 1978 [14].

The soil samples were taken in spring 2014, 2015 and 2016 from the surface (0 – 30 cm) and subsurface (30-60 cm) layers using soil sampler. Each sample was composed of 25-30 injections. For chemical analyzes the samples were air-dried and the fraction <2 mm was separated. Organic C and total N contents were analyzed via elemental CN analyzer. Prior to the analysis carbonates were removed with 1 mol·dm⁻³ HCl. The pH was measured potentiometrically in distilled H₂O and 1MKCl (soil:solution = 1:2,5). The speciation of potassium was determined using procedure described in detail in Tab. 1. The grain size distribution was analyzed with areometric method.

Tab. 1. Analytical procedures to determine K forms in soils
 Tab. 1. Zestawienie procedur oznaczania form potasu

K forms	Chemical reagent	Symbol	Method of extraction
H ₂ O-soluble	H ₂ O	K - H ₂ O	100g of soil + 100cm ³ H ₂ O (1:1) → shaking for 1.5 h → filtering → K determination with Varian FS 220
Active	0,01 mol·dm ⁻³ CaCl ₂	K - CaCl ₂	2g soil + 100 cm ³ 0,01 mol·dm ⁻³ CaCl ₂ (1:50) → shaking for 1.5 h → filtering → K determination with Varian FS 220
Bioavailable (Egner-Riehm)	(C ₂ H ₂ OHCOO) ₂ Ca + HCl pH 3,6	K - DI	2g soil + 100 cm ³ acidified Ca lactate (Egner-Riehm soln.) → shaking for 1.5 h → filtering → K determination with Varian FS 220
Exchangeable	1 mol·dm ⁻³ NH ₄ OAc o pH 7,0	K - CH ₃ COONH ₄	2g soil + 50 cm ³ CH ₃ COONH ₄ (1:25) → shaking for 1.5 h, centrifuging for 10 min at 3600 rpm → residuum treated with 50 cm ³ CH ₃ COONH ₄ → filtering → K determination with Varian FS 220
Fixed	2 mol·dm ⁻³ HCl	K - HCl	2g soil + 100 cm ³ 2 mol·dm ⁻³ HCl → shaking for 2 h → filtering → K determination with Varian FS 220
Non-exchangeable	1 mol·dm ⁻³ HNO ₃	K - HNO ₃	2g soil + 100 cm ³ 1mol·dm ⁻³ HNO ₃ → extraction at 80°C → shaking → filtering → K determination with Varian FS 220

Source / Źródło: Spsychalski et al. 2016

The potassium speciation in treated and non-treated soil samples was compared using one factor analysis of variance. The significance of the differences was tested with Tukey's test at $p < 0.05$. The correlation coefficients between potassium chemical species were established. The calculations were performed using Statistica 12.

3. Results and discussion

The 35-year-long agricultural reclamation of a waste dump of the Pańków brown coal mine led to considerable differentiation of chemical composition of the newly formed soils. The observed changes are shown in Tab. 2. The content of clay in the samples from 0-30 cm and 30-60 cm layers was rather high and ranged from 13 to 16%. The changes during the experiment were minor. The organic C in the surface layer increased from 0.39% at the onset of the experiment to 0.75% in the NPK fertilized soils. The P, K and PK fertilizing resulted in the overall increase in organic C to 0.49%, 0.49% and 0.56%, respectively. However, these changes were statistically insignificant. The NP, N and NK treatment gave significant organic C increase to 0.59%, 0.62% and 0.67%. However, the highest increase in organic C (to 0.75%) occurred due to NPK fertilization. On the other hand, in the subsurface (30-60 cm) the organic C was much lower than in the surface layer and ranged from 0.23% in control field to 0.52% in K-fertilized field.

Long-term fertilizing resulted in remarkable changes in N content in soils. The N contents in the surface layer of

soils varied from 0.043% in control field to 0.080% in the NPK-fertilized soils. Statistically significant enrichment in N occurred in soils treated with P, K, PK, and NPK fertilizers. In the latter case the N content was twice as high as in a control field. Similar results for post-mining soils were obtained earlier [11, 12, 13].

The pH in the 0-30 cm layer of the analyzed soils was alkaline and ranged from 7.76 to 8.05 for pH_(H₂O) and from 7.31 to 7.55 for pH_(KCl). Long-term fertilizing with NPK, NP and NK significantly lowered the pH in most experimental fields. On the other hand, the change in pH in the subsurface layer was different and showed dependence on the mode of fertilization. pH_(H₂O) showed statistically significant decline owing to N, P, NK, NP, PK, and NPK fertilization, while pH_(KCl) dropped owing to NP treatment.

Bioavailable P content varied from 47.5 to 105.1 mg P·kg⁻¹ in the surface layer and from 6.30 to 55,10 mg P·kg⁻¹ in the soil subsurface. Statistically significant increase in P abundance in the surface layer occurred due to PK fertilizing, however, the fertility class of the soil changed from III to II. The highest increase in bioavailable P resulted from P, NP, and NPK fertilizing. The change in P content was associated with a shift from the IIIrd to the Ist fertility class of the soils. The content of P in the subsurface layer increased largely from 7.90 to 55.1 mg P·kg⁻¹ owing to NP fertilizing. Thus, the reclamation resulted in a shift from the Vth to the IIIrd fertility class in the subsurface layer of the studied soil.

Tab. 2. Physical-chemical composition of 0-30 cm layer of studied soils

Tab. 2. Podstawowe właściwości chemiczne i fizyczne analizowanych próbek glebowych pobranych z warstwy 0-30 cm (wartości średnie z trzech lat)

Fertilizing applied	Clay	C-org	N-tot	C:N	pH		P-DI mg·kg ⁻¹	Class of abundance
	%	%	%		H ₂ O	KCl		
0NPK (control sample)	16c	0,39a	0,043a	9	8,05c	7,55b	47,5a	III
N	15bc	0,62bc	0,070c	9	7,95bc	7,51b	51,5a	III
P	14ab	0,49ab	0,054b	9	7,99bc	7,50b	110,0c	I
N K	14ab	0,67bc	0,068c	10	7,89ab	7,43ab	48,7a	III
N P	14ab	0,59bc	0,067c	9	7,88ab	7,41ab	94,5c	I
K	13a	0,49ab	0,055b	9	7,99bc	7,45b	57,3a	III
P K	13a	0,56abc	0,052b	11	8,00bc	7,51b	78,1b	II
N P K	15bc	0,75c	0,080d	9	7,76a	7,31a	105,1c	I

The lower case letters denominate groups of significantly different values

Source: own data / Źródło: praca własna

Tab. 3. Physical-chemical composition of 30-60 cm layer of studied soils

Tab. 3. Podstawowe właściwości chemiczne i fizyczne analizowanych próbek glebowych pobranych z warstwy 30-60 cm (wartości średnie z trzech lat)

Fertilizing applied	Clay	C-org	N-tot	C:N	pH		P-DI	Class of abundance
	%	%			H ₂ O	KCl	mg·kg ⁻¹	
0NPK (control sample)	15bc	0,23a	0,025a	9	8,22c	7,71b	7,90a	V
N	14ab	0,35abc	0,034abc	10	8,05ab	7,64ab	12,50ab	V
P	14ab	0,33abc	0,036bc	9	8,10ab	7,65ab	38,30c	IV
N K	15c	0,44bcd	0,051d	9	8,04ab	7,57ab	39,60c	IV
N P	13a	0,45cd	0,042cd	11	8,01ab	7,53a	55,10d	III
K	14bc	0,52d	0,035abc	15	8,12bc	7,66ab	21,70b	V
P K	15bc	0,29ab	0,030ab	10	8,10ab	7,63ab	20,90b	V
N P K	15bc	0,30abc	0,027ab	11	8,00a	7,61ab	6,30a	V

The lower case letters denominate groups of significantly different values

Source: own data / Źródło: praca własna

Tab. 4 Potassium content in the subsurface (0-30 cm) layer of the studied soils

Tab. 4. Zawartość form potasu w analizowanych próbkach glebowych pobranych z warstwy 0-30 cm

Fertilizing mode	K-H ₂ O	K-CaCl ₂	K-DI	K-CH ₃ COONH ₄	K-HCl	K-HNO ₃
	mg K·kg ⁻¹					
0	10,25a	119,22a	126,24a	119,10a	285,09a	744,46a
N	16,22b	146,58b	150,76b	176,74b	334,65b	720,62a
P	17,15b	153,21b	154,40b	180,36b	355,87bc	869,27b
NK	26,60d	177,45c	190,54c	244,69cd	445,60d	944,82bc
NP	20,68c	188,47cd	195,61c	217,11c	382,42c	910,73b
K	23,40cd	197,94de	200,82c	247,57cd	433,35d	1020,65cd
PK	24,21d	211,89ef	203,90c	254,45d	440,05d	1053,31d
NPK	34,69e	225,18f	245,04d	310,98e	490,83e	1087,80d

The lower case letters denominate groups of significantly different values

Source: own data / Źródło: praca własna

The distribution of the speciation forms of K in the surface and subsurface layers of soils for different modes of fertilization is presented in Tab. 4 and Tab. 5, respectively. The H₂O-soluble K had the lowest abundance and ranged from 10.25 mg K·kg⁻¹ to 34.69 mg K·kg⁻¹. The abundance of H₂O-soluble K increased significantly owing to long-term fertilizing, and the highest increase occurred in the NPK-fertilized soils. In the latter the content of H₂O-soluble K was c.a. three times higher than in control samples. In the subsurface the H₂O-soluble K was lower than in surface layer, however, owing to K fertilization its abundance increased. This increase argues for the downward migration of the excess K in the soils. Similar observations were reported from soils displaying positive K balance [8, 9, 15].

Active K was significantly more abundant in fertilized soils than in control sample and ranged from 119.22 to 225.18 mg K·kg⁻¹ in the surface layer and from 100.11 to 194.91 mg K·kg⁻¹ in the subsurface. The highest content of the active K of 225.2 mg K·kg⁻¹ was obtained in the surface layer of the NPK-fertilized soils. However, statistically significant enrichment in active K in relation to control samples occurred in NPK, PK, K, and NP-fertilized soils. In the subsurface, the active K was lower than in the surface layer. However, fertilization led to enrichment in active K in the subsurface and in K- and PK-fertilized soils the content of active K was twice as high as in control sample.

Bioavailable K varied from 126.24 to 245.04 mg K·kg⁻¹ in the surface layer and from 115.56 to 188.94 mg K·kg⁻¹ in the subsurface layer of the analyzed soils. From our data it emerged that K, NK, PK, and NPK fertilizing resulted in statistically significant enrichment in bioavailable K in topsoil and subsoil. However, the NPK fertilizing had the most important contribution to this enrichment. Owing to 35 years of NPK fertilizing in the surface layer the content of bioavailable K doubled and in the subsurface layer it increased by half. Consequently, the fertility of both soils layers changed from the IIIrd

(medium) class to the Ist (very high) class. Stępień & Mercik [16] argued that such high increase in bioavailable K in the whole soil profile results from accumulation of K unused by plants and/or its migration towards the subsoil.

Exchangeable K was between 119,10 and 310,98 K·kg⁻¹ in 0-30 cm layer and between 109,29 and 205,81 mg K·kg⁻¹ in 30-60 cm layer (tab. 4, 5). Similarly to H₂O-soluble and bioavailable K, exchangeable K increased its abundance markedly during our experiment. Statistically significant changes in exchangeable K in the studied soils were obtained for each fertilizing mode, however, the NPK fertilizing gave the best results. In the surface layer of the NPK-fertilized soils the exchangeable K in the surface and subsurface layers was 2.6 and 1.9 times higher than respective contents in a control sample.

The content of fixed K varied between 285,09 and 490,83 mg K·kg⁻¹ in the surface layer and between 235,41 and 410,29 mg K·kg⁻¹ in the subsurface (Tab. 4, 5). In the 0-30 cm layer fixed K increased owing to each fertilizing mode applied. On the other hand, in the 30-60 cm statistically significant increase in fixed K resulted from K, NP, NK, PK, and NPK fertilizing. In the latter case the increase in fixed K was most significant and the obtained contents in both layers were 1.7 times higher than in the control sample.

Non-exchangeable K was the most abundant form of K in the analyzed soils. In the surface layer non-exchangeable K was between 744,46 and 1087,80 mg K·kg⁻¹ and in the subsurface layer it varied from 679,7 to 951,53 mg K·kg⁻¹ (Tab. 4, 5). The N fertilizing caused only minor and statistically insignificant change in non-exchangeable K in the post-mining soils. On the other hand P, NK, NP, K, PK, and NPK fertilizing caused marked enrichment in non-exchangeable K. Owing to these fertilizing modes the non-exchangeable K showed 1.3-1.4-fold and 1.2-1.5-fold increase in the surface and subsurface layers, respectively.

Tab. 5. Potassium content in the subsurface (30-60 cm) layer of the studied soils

Tab. 5. Zawartość form potasu w analizowanych próbkach glebowych pobranych z warstwy 30-60 cm

Fertilizing mode	K-H ₂ O	K-CaCl ₂	K-DI	K-CH ₃ COONH ₄	K-HCl	K-HNO ₃
	mg K·kg ⁻¹					
0	9,77a	100,11a	115,56a	109,29a	235,41a	679,66a
N	12,80b	128,56b	119,30a	138,16b	276,26a	723,84a
P	12,72b	137,20b	128,61a	143,34b	292,08a	830,77b
NK	20,84d	162,57c	188,38c	210,10c	410,59b	933,78b
NP	17,20c	187,19d	154,48b	187,64c	373,55b	897,12bc
K	17,90c	194,81d	166,75b	201,40c	421,00b	916,56c
PK	22,15d	188,40d	159,13b	189,81c	397,97b	932,77c
NPK	29,22e	170,63c	188,94c	205,81c	410,29b	951,53c

The lower case letters denominate groups of significantly different values

Source: own data / Źródło: praca własna

Tab. 6. Correlation coefficients between the forms of potassium in the analyzed soil samples

Tab. 6. Współczynniki korelacji pomiędzy analizowanymi formami potasu

	K-H ₂ O	K-CaCl ₂	K-DL	K-CH ₃ COONH ₄	K-HCl	K-HNO ₃
	K-H ₂ O	-	0,67	0,89	0,84	0,83
K-CaCl ₂		-	0,73	0,89	0,92	0,89
K-DL			-	0,93	0,91	0,91
K-CH ₃ COONH ₄				-	0,99	0,96
K-HCl					-	0,96

Source: own data / Źródło: praca własna

The speciation forms of determined K showed strong mutual correlations (Tab. 6). The obtained r values were between 0.67 and 0.96. The covariance between bioavailable and active potassium was reported by Fotym et al. [5].

4. Conclusions

1. Long-term fertilization of post-mining soils resulted in statistically significant enrichment of the soil in organic C, N, bioavailable P and K as well as the increase in pH;
2. Long-term fertilizing led to increased contents of H₂O-K and exchangeable K;
3. The highest contents of the analyzed forms of potassium were obtained in the samples from NPK fertilized soils;
4. The NPK treatment resulted in the most favorable changes in chemical composition of the topmost (0-30 cm) layer of post-mining soils;
5. The NPK treatment led to enrichment of the analyzed forms of potassium in the subsurface (30-60 cm) layer.

5. References

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