Waldemar SPYCHALSKI[1], Andrzej MOCEK[1], Dariusz KAYZER[2]
Poznań University of Life Sciences, Poland
[1] Department of Soil Science and Land Protection
[2] Department of Mathematical and Statistical Methods
e-mail: spychal@up.poznan.pl

TEXTURE AND CHEMICAL COMPOSITION OF THE SELECTED ADDITIONAL FORMATIONS OF BROWN COAL AND SOILS ORIGINATING FROM THEM

Summary

This thesis contains the research on the chemical composition of top horizons of soils originated from post-mining ground and selected rocks from the addition of brown coal. The analyzed soils originated from the mixture of the following additional sedimentary rocks of brown coal: glacial till (Würm), glacial till (Riss-grey till), sands and Poznan clays. Experimental factors were crop rotations (rape-grain and fodder) and three levels of mineral fertilization (0 NPK, 1 NPK and 2 NPK). The content of following elements was examined: Si, Al, Fe, Mn, Ca, K, Mg, Ti, Mn, Sr, Pb, Cd, Cr, Ni, Co, Zn, Cu. The total amount of all the listed elements was marked with two methods. The first was digestion method in HF with which the total amount of all the elements was determined, the latter was a method of extraction with aqua regia with which the content of elements close to the total was marked. The results proved that the mixture of the mentioned rocks has got impact on the properties of soils which originate from it. The average contents of the components determined in HF in g·kg^{-1} were: Si-347,35; Sr-0,3; Ca-29,0; Al-24,2; Na-4,1; Mg-6,0; Fe-11,6; K-11,8; Mn-0,3; Ti-2,1 whereas macroelement in aqua regia in g·kg^{-1}: Sr-0,16; Ca-26,72; Al-9,78; Na-0,32; Mg-5,75; Fe-8,65; K-3,06; Mn-0,16; microelements Zn-25,87; Pb-3,6; Co-3,5; Cd-0,064; Cr-12,37; Ni-10,97; Cu-7,018. The amounts of various components differed in various extracts, yet the results were strictly correlated. Statistical analysis showed that graining of the originating soils was most similar to glacial till of Würm and Riss.

***Key words**: post-mining grounds, soils, brown coal, chemical composition, research*

UZIARNIENIE I SKŁAD CHEMICZNY WYBRANYCH UTWORÓW NADKŁADOWYCH WĘGLA BRUNATNEGO ORAZ WYTWORZONYCH Z NICH GLEB

Streszczenie

W niniejszej pracy przedstawiono badania składu chemicznego wierzchnich poziomów gleb wytworzonych z gruntów pogórniczych oraz wybranych skał nadkładu węgla brunatnego. Analizowane gleby wytworzyły się z mieszaniny następujących skał nadkładowych węgla brunatnego: glin polodowcowych zlodowacenia bałtyckiego, szarych zlodowacenia środkowopolskiego, piasków oraz iłów poznańskich. Czynnikami doświadczenia były dwa płodozmiany (rzepakowo-zbożowy i paszowy) oraz trzy poziomy nawożenia mineralnego (0 NPK, 1 NPK i 2 NPK). W pracy badano zawartość takich pierwiastków jak: Si, Al, Fe, Mn, Ca, K, Mg, Ti, Mn, Sr, Pb, Cd, Cr, Ni, Co, Zn, Cu. Ogólną ilość wszystkich wymienionych pierwiastków oznaczono dwoma metodami. Pierwszą z nich była metoda trawienia w HF, w której oznaczono całkowitą zawartość poszczególnych pierwiastków, a drugą metoda ekstrakcji wodą królewską, w której oznaczono zawartość pierwiastków zbliżoną do całkowitej. Uzyskane wyniki badań dowiodły, iż mieszanina wcześniej wspomnianych skał ma wpływ na właściwości gleb z nich powstających. Średnia zawartość składników oznaczona w HF wyrażona w g·kg^{-1} była następująca: Si-347,35; Sr-0,3; Ca-29,0; Al-24,2; Na-4,1; Mg-6,0; Fe-11,6; K-11,8; Mn-0,3; Ti-2,1 natomiast w wodzie królewskiej makroelement (g·kg^{-1}: Sr-0,16; Ca-26,72; Al-9,78; Na-0,32; Mg-5,75; Fe-8,65; K-3,06; Mn-0,16; mikroelement Zn-25,87; Pb-3,6; Co-3,5; Cd-0,064; Cr-12,37; Ni-10,97; Cu-7,018. Uzyskane zawartości różnych składników oznaczone w różnych ekstraktach różniły się , lecz wyniki te były ze sobą ściśle skorelowane. Analiza statystyczna pokazała, że uziarnienie tworzących się gleb było najbardziej zbliżone do gliny lodowcowej – zlodowaceenia - Vistulian oraz Riss.

***Słowa kluczowe**: grunty pogórnicze, gleby, węgiel brunatny, skład chemiczny, badania*

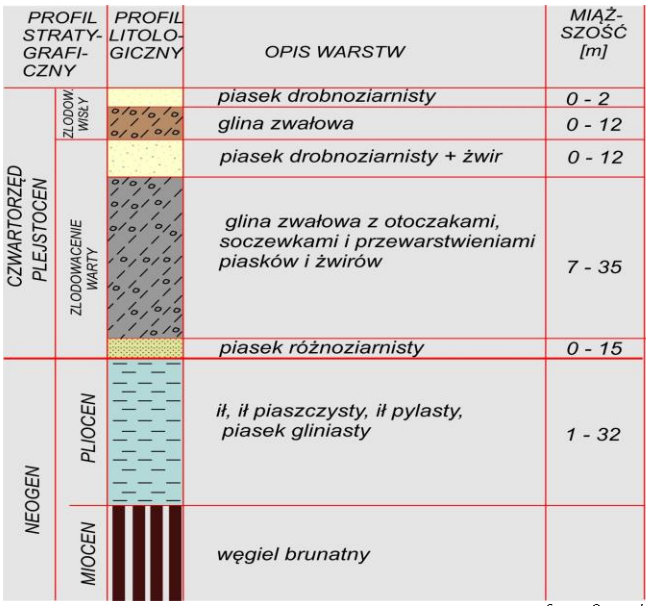
1. Introduction

Opencast mining in Konin-Turek Coalfield has functioned for over 60 years and led to relatively significant geomechanical and hydrological changes. Exposures result in the origination of inner and outer spoil tips which require technical and biological reclamation, usually in an agricultural or forest direction [1, 2]. Choice of the direction depends mainly on the type of rocks in the addition of the mineral. Among the most important parameters there are graining and chemical composition. In Konin Coalfield, the addition of brown coal is dominated by quaternary formations (Pleistocene) which include tills of the Ice Age – Würm, of Riss (till), glacial sands, quaternary sands and neogene formations – Poznan clays and, rarely, Miocene sands often polluted with coal dust [7, 11, 12,13, 14].

The aim of this research was the determination and comparison of graining and chemical composition of the rocks in the addition of brown coal and of anthropogenic soils developing from them.

2. Material and methods

The research was conducted on the samples of sedimentary rocks from the addition of brown coal in Konin Coalfield. A generalized geological profile of these rocks was presented in Fig. 1.



Source: Own work

Fig. 1. Generalized geological profile of Konin

Source: Own work

Fig. 2. Extraction device with a reflux condenser

Coalfield the samples were collected from Kleczew exposure. The following sedimentary rocks were represented: glacial till - Riss, glacial till (Würm), quaternary sand, miocene sand, glacial sand, Poznan clays. Furthermore, medium samples from 30 fields were collected from topsoil horizons of a reclaimed spoil tip, where long-term research has been conducted for more than 30 years. Experimental factors were two crop rotations (rape-grain and fodder) and three levels of mineral fertilization (0 NPK, 1 NPK i 2 NPK). Laboratory analysis were conducted on a dry material sifted with a sieve of 2 mm mesh diameter. The following parameters were determined with the methods:

- texture (Proszynski's aerometric method)
- chemical composition of the rocks and soils - in HF according to Lim's and Jackson's method [10]. The determination of total elements distribution was done in the following stages:

– soil samples of 5 g surplus weight were being burnt for 4 hours in a stove in the temperature of 850°C;
– next 0,2 g of ash was weighed out into plastic containers with HDPE (resistant to HF);
– 1 ml of *Aqua regia* was added to the bottles (1 ml HCl + HNO_3, proportion 3:1 v/v) and shaken for 1 hour;
– after initial digestion, 6 ml of hydrofluoric acid was added to the bottles and, in order to avoid fluorosilicates, the bottles were tightly closed with a Teflon tape and shaken for 24 hours;
– next 10 ml of hot (~85°C), saturated solution of boric acid was added, the bottles were again tightly closed and shaken for 24 hours;
– the solution was diluted to 50 cm^3.

The following parameters were marked in the solution:

– the content of Fe, Mg, K, Na, Mn – marked with AAS method with Varian Spectra 220 FS in an acetylene- air flame whereas Si, Ti, Al, Sr i Ca were marked with an atomic spectrophotometric method in an acetylene flame with nitrous oxide.

The chemical composition was also done with acid extraction – aqua regia – in accordance with ISO – 11466 procedure [4]: soil samples were ground in an agate mortar and 3 g of soil was weighed out to each flask of 250 ml;
– 21 ml of concentrated HCl acid and next – 7 ml of concentrated HNO_3 acid were added;
– such flasks were shelved for at least 16 hours in an ambient temperature;
– next, samples were boiled for over 2 hours in a fractionating column with a reflux condenser – Fig. 2;
– 0,5 mole nitric acid from a scrubber was taken to a reaction flask through a condenser and left for cooling;
– the solution was put into 100 ml volumetric flasks and filled with distilled water;
– the samples were filtrated to plastic containers;
– in such an extract, content of the following elements was marked: Pb, Cd, Cr, Ni, Co, Sr, Ca, Al, Na Mg, Fe, Cu, K, Mn, Zn with the application of the atomic absorption spectroscopy (AAS); the markings were done on an atomic absorption spectrometer Varian Spectra 220 FS.

The results of the elemental composition of soils were analyzed using tools of multivariate analysis of variance Lejeune and Caliński [9]. The analyses conducted to determine the trace elements in soils made it possible to present the position of selected rocks in the space of the two first canonical variables. This method, which makes possible a graphical presentation of the results of multidimensional experiments, consists in the transformation of the original set of variables into a set of new variables, which carry similar information, but are distributed in a multivariate Euclidean space [3, 6]. In this case, canonical variable analysis is based on the matrix include differences between mean values of elements for the particular rocks and the mean value obtained from all experimental plots.

3. Results and discussion

The results of texture analysis of the examined samples and addition rocks of Brown coal were presented in table 1. Their graining differed and depended on geological origin. The obtained results were in the range given by Rząsa et al.[12] and Wasilewski [15]. What is significant, is that after over 30 years of field experience, graining of the analyzed samples differed. According to the FAO/USDA distribution, they were placed in one texture group – sandy loam (SL) and the content of clay fraction on average was 14% (10-16%), silt fraction – 19% (15-23%) and sandy fraction - 67% (60-73%). Similar results in this area were obtained by Spychalski and Gilewska [13, 14]. According to them, the unification (homogenization) of graining was partly a result of mining activities connected with brown coal excavation, namely – collecting the addition, its transport and selective binging. Further homogenization of top layers was a result of agrotechnical activities e.g. tillage.

On the basis of the results of a multidimensional analysis of variances it was claimed that the graining of soil samples collected from experimental field was very similar to the graining of last glacial period till (table 2). When analyzing a percentage content of each fraction statistically determined as Mahanalobis' Δ distance, it was ascertained that when graining is concerned, Poznan clay differed the most from soil texture from all the experimental fields.

Table. 1. Graining of tested samples

Sedimentary Rock	The percentage of the fraction			Textural-group FAO/USDA
	Sand	***Silt***	***Clay***	
Vistulian loam	61	22	17	**Sandy loam (SL)**
Miocen sand	93	6	1	**Sand (S)**
Pliocen Clay (Poznan)	10	23	67	**Clay (C)**
Riss loam	46	26	28	**Sandy Clay loam (SCL)**
Quaternary sand	96	3	1	**Sand (S)**
Glacial sand	66	29	5	**Sandy loam (SL)**
Experimental plots	67	19	14	**Sandy loam (SL)**

Source: Own work

Table 2. The differences in grain size of the analyzed samples of lignite overburden between the mean value for each rock and the mean value obtained from all experimental plots

Sedimentary Rock	The differences in the percentage of the fraction			Δ
	Sand	***Silt***	***Clay***	
Vistulian loam	-6	3	3	2.90
Miocen sand	27**	-14**	-13**	59.47**
Pliocen Clay (Poznan)	-57**	3	54**	354.4**
Riss loam	-21**	9**	13**	37.60**
Quaternary sand	30**	-17**	-13**	76.2**
Glacial sand	-2	10**	-8**	18.8**

** difference significant at Δ=0.05 *Source: Own work*

Taking into consideration percentage content of the analyzed texture fractions, it was noted that a significant differentiation was observed in the content of sand fraction. It was much lower in Poznan clay when compared to the analyzed soil samples collected from experimental fields, whereas the content of clay fraction was much higher. The results of a multidimensional analysis of the variance were presented graphically in the space of canonical variables in Fig. 3. It can be observed, that the graining of soil samples from experimental fields was close to the graining of last glacial period loam and next – to the graining of bing sand and grey till (Riss).

Chemical composition of the analyzed additional rocks of brown coal was also varied. It turned out that Pliocene Poznan clays were the richest in necessary nutrition components, where Si was low in comparison to – mainly – sands. Similarly, Riss till, whose part in the addition is significant, had a very good chemical composition, from the agricultural point of view. Elemental composition of the analyzed rocks was in the range given by Ratajczak et al. [11] and Kabata-Pendias and Pendias [5]. Table 3 contains descriptive statistics of the content of macro elements in the soil samples collected from experimental fields. Low values of most of the variable coefficients (usually below 10%) prove minor differentiation of the components. It was ascertained that soils from rocks of various geological origin (i.e. different when mineralogical composition and, what is connected with it, chemical one are concerned) are very homogeneous after 30 years of tillage. Among the analyzed elements, only the content of sodium in soil samples was highly differentiated. The value of a variable coefficient for this component was 45,5%. The content of such elements as Al, Mn, K and Na was at a similar level as in top horizons of many soils in Wielkopolska examined by Komisarek [8], however, the content of Fe given by this author was 2,5 times lower. Such low content of this element may be explained with the fact that soils originating form post-mining grounds are "young" when compared to the soils analyzed by Komisarek – the latter have undergone the processes of pedogenesis. As a result of these processes, top horizons became poorer in clay minerals and nutrition components.

Table 3 contains the comparison of the total content of elements in the analyzed sedimentary rocks in the addition of brown coal in Konin Coalfield with the soils originating from the mix of these rocks. The content of the examined elements was marked in HF extract. When analyzing Mahanalobis' distances it was ascertained that the analyzed soil samples collected from a long-term experiment differed significantly from the additional sedimentary rocks. Elemental composition of these soils was most similar to such additional rocks as last glacial period till or grey glacial till (Riss) (table 4). Among the examined elements marked in HF extract, there was no reason to claim that the content of Al, Mn, Fe, K, Ca, Na, Sr differed significantly between the soil samples and grey till (Riss). Therefore, it can be assumed that the content of these elements in the analyzed soil samples which originated from post-mining grounds was similar to the content in grey loam. Furthermore, large similarity was proved between the content of Al, Mn, Fe, Ca, Na and Sr in the analyzed samples and last glacial period till (Würm). On the other hand, among the analyzed sedimentary rocks, Poznan clay showed significant differences in mineralogical composition and, what follows, chemical composition. On the basis of the results and their statistical analysis, differences in the content of the analyzed elements (apart from potassium and sodium) in the originating soils were proved when compared to Poznan clay. The highest differences were visible in the content of Al, Fe, Ti and Ca. Fig. 4 shows graphical combination of the research results for the first two canonical coordinates. What can be observed is that the chemical composition of Poznan clay, quaternary sand and Miocene sand were different from the soils. The differences were mostly visible in the content of Si, Fe, Al and Ca in the samples of analyzed rocks and originating soils.

The characteristics of soils which originated from the post-mining grounds when the content of the selected elements in the extract of *aqua regia* is concerned was presented in table 5. Although the analyzed sedimentary rocks and soils originating from them contain toxic elements such as Cd and Pb, their content does not exceed the norms and is not harmful to the environment. The results concerning the content of heavy metals confirmed numerical data given by Terelak i Motowiecka-Terelak [16]. The values of variable coefficients for the content of the most of analyzed components marked in the extract was lower than 15%. The content of admium and potassium differed most and the variable coefficients for these elements were, respectively,

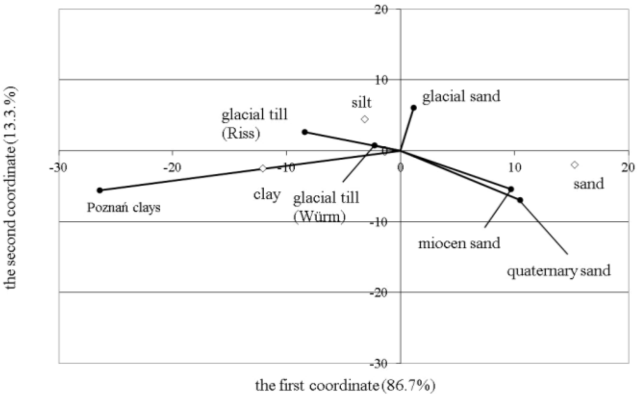


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Fig. 3. Position of selected rocks differing in grain size in the space of the first two canonical variates and spacing of the fractions in the dual space of canonical variates (values of dual canonical coordinates multiplied by 0.15)

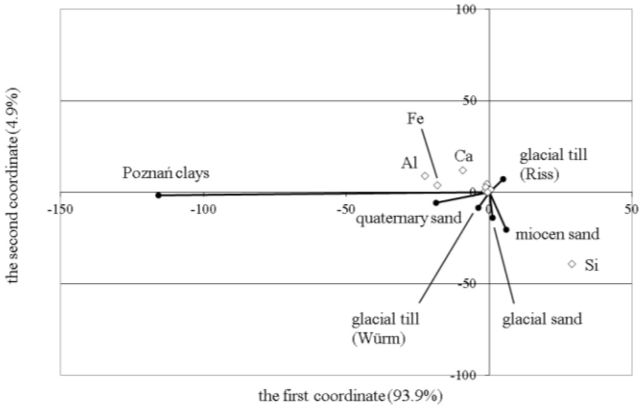

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Fig. 4. Position of selected rocks differing in the elemental composition in the space of the first two canonical variates and spacing of the components in the dual space of canonical variates (values of dual canonical coordinates multiplied by 0.25, extraction of acid - HF)

Table 3. Elemental composition of soils developed from land mining (extraction of acid - HF)

Descriptive statistics	Si	Ti	Al	Mn	Fe	K	Mg	Ca	Na	Sr
	g·kg^{-1}									
Minimum	282.5	1.43	21.34	0.24	9.30	9.45	4.78	23.59	3.23	0.24
Maximum	371.8	2.41	26.7	0.32	14.83	15.21	7.12	33.91	13.55	0.34
Mean	347.3	2.07	24.19	0.28	11.59	11.78	6.02	29.00	4.09	0.28
Standard deviation	19.4	0.23	1.44	0.02	1.21	1.22	0.64	2.91	1.86	0.02
Coefficient of variation	5.6	10.9	6.0	6.6	10.4	10.4	10.6	10.0	45.5	7.1

Source: Own work

Table 4. Differences in the elemental composition of the soil samples between the mean value for each scale and the mean value obtained from all experimental plots (extraction of acid - HF)

Sedimentary Rock	**Si**	**Ti**	**Al.**	**Mn**	**Fe**	**K**	**Mg**	**Ca**	**Na**	**Sr**	**Δ**
	g⊙kg^{-1}										
Vistulian loam	-57.8**	-0.690*	-7.923	-0.096	-2.03	-4.480**	-3.867**	-18.21	-0.536	-0.117	59.2**
Miocen sand	74.1**	-1.520**	-23.62**	-0.166**	-10.33	-10.435**	-5.202**	-23.92	-3.786*	-0.255	226.1**
Pliocen Clay (Poznan)	-87.7**	3.650**	61.81**	0.154**	50.51**	1.435	3.428**	27.48*	-1.856	1.528**	6515**
Riss loam	-98.5**	0.520	1.672	0.064	-0.09	1.270	2.968**	10.67	0.069	0.073	62.1**
Quaternary sand	34.2	-0.085	7.072	-0.066	8.23	-5.675**	-2.307**	-23.20	-1.471	-0.107	217.5**
Glacial sand	71.5**	-1.150**	-14.71**	-0.126*	-7.83	-6.890**	-4.417**	-11.00	-1.291	-0.077	102.1**

Source: Own work

Table 5. Elemental composition of soils developed from land mining (extraction of acid - aqua regia)

Descriptive statistics	**Na**	**Mg**	**Fe**	**Al**	**K**	**Mn**	**Ca**	**Sr**	**Pb**	**Cd**	**Cr**	**Ni**	**Co**	**Zn**	**Cu**
	g·kg^{-1}							mg⊙kg^{-1}							
Minimum	0.212	4.35	7.00	6.30	1.716	0.145	22.92	0.126	2.57	0.000	9.640	8.840	2.810	21.46	6.03
Maximum	0.420	6.87	9.74	13.7	4.646	0.184	30.45	0.183	4.23	0.160	16.33	14.04	4.710	34.04	8.30
Mean	0.317	5.75	8.65	9.78	3.057	0.164	26.72	0.157	3.65	0.066	12.37	10.97	3.534	25.87	7.02
Standard deviation	0.060	0.62	0.73	2.18	0.822	0.011	1.68	0.013	0.40	0.043	1.735	1.323	0.469	2.53	0.61
Coefficient of variation	19.0	10.8	8.4	22.3	26.9	6.5	6.3	8.3	11.0	65.3	14.0	12.1	13.3	9.8	8.7

Source: Own work

Table 6. Differences in the macroelements of the soil samples between the mean value for each scale and the mean value obtained from all experimental plots (extraction of acid - aqua regia)

Sedimentary Rock	**Na**	**Mg**	**Fe**	**Al**	**K**	**Mn**	**Ca**	**Sr**
	g⊙kg^{-1}							
Vistulian loam	-0.018	-3.82**	-8.61	-1.88	-1.198	-0.069	-11.69	-0.08
Miocen sand	-0.176**	-5.27**	-7.76	-9.48**	-2.97**	-0.136*	-20.24*	-0.12
Pliocen Clay (Poznan)	0.416**	-1.71*	55.27**	25.0**	6.02**	0.189**	10.74	1.34**
Riss loam	0.216**	5.55**	7.41	3.97	3.34**	0.036	26.64**	0.09
Quaternary sand	0.053	-4.19**	7.83	11.23**	0.453	-0.079	-17.40*	-0.06
Glacial sand	-0.095	-4.12**	-5.30	-8.41*	-2.639**	-0.094	-0.59	-0.03

Source: Own work

Table 7. Differences in the microelements composition of the soil samples between the mean value for each scale and the mean value obtained from all experimental plots (extraction of acid - aqua regia)

Sedimentary Rock	**Pb**	**Cd**	**Cr**	**Ni**	**Co**	**Zn**	**Cu**	**Δ**
	mg⊙kg^{-1}							
Vistulian loam	-1.61	-0.011	-2.342	-1.620	-0.314	-8.978**	-1.99	186**
Miocen sand	-3.59**	-0.041	-11.32*	-10.71**	-3.139**	-21.13**	-6.02**	255**
Pliocen Clay (Poznan)	13.32**	0.059	34.85**	25.16**	5.166**	66.92**	18.9**	39164**
Riss loam	0.90	-0.031	4.453	2.835	0.801	2.337	1.79	179**
Quaternary sand	-1.61	-0.031	7.768	6.020*	0.731	4.752	0.56	774**
Glacial sand	-2.26*	-0.026	-8.762	-7.245**	-1.479	-14.33**	-4.23**	156**

Source: Own work

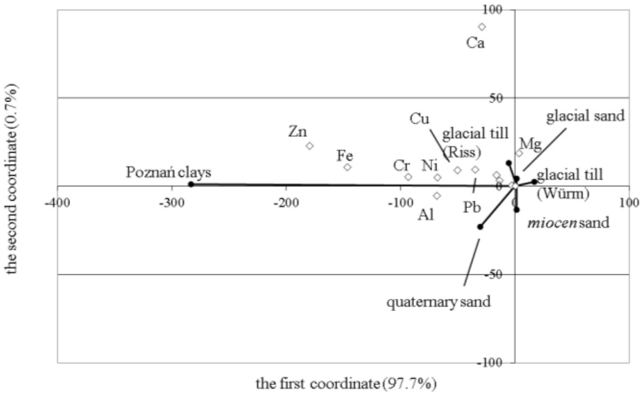

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Fig. 5. Position of selected rocks differing in the elemental composition in the space of the first two canonical variates and spacing of the fractions in the dual space of canonical variates (values of dual canonical coordinates multiplied by 0.25, extraction of acid - aqua regia)

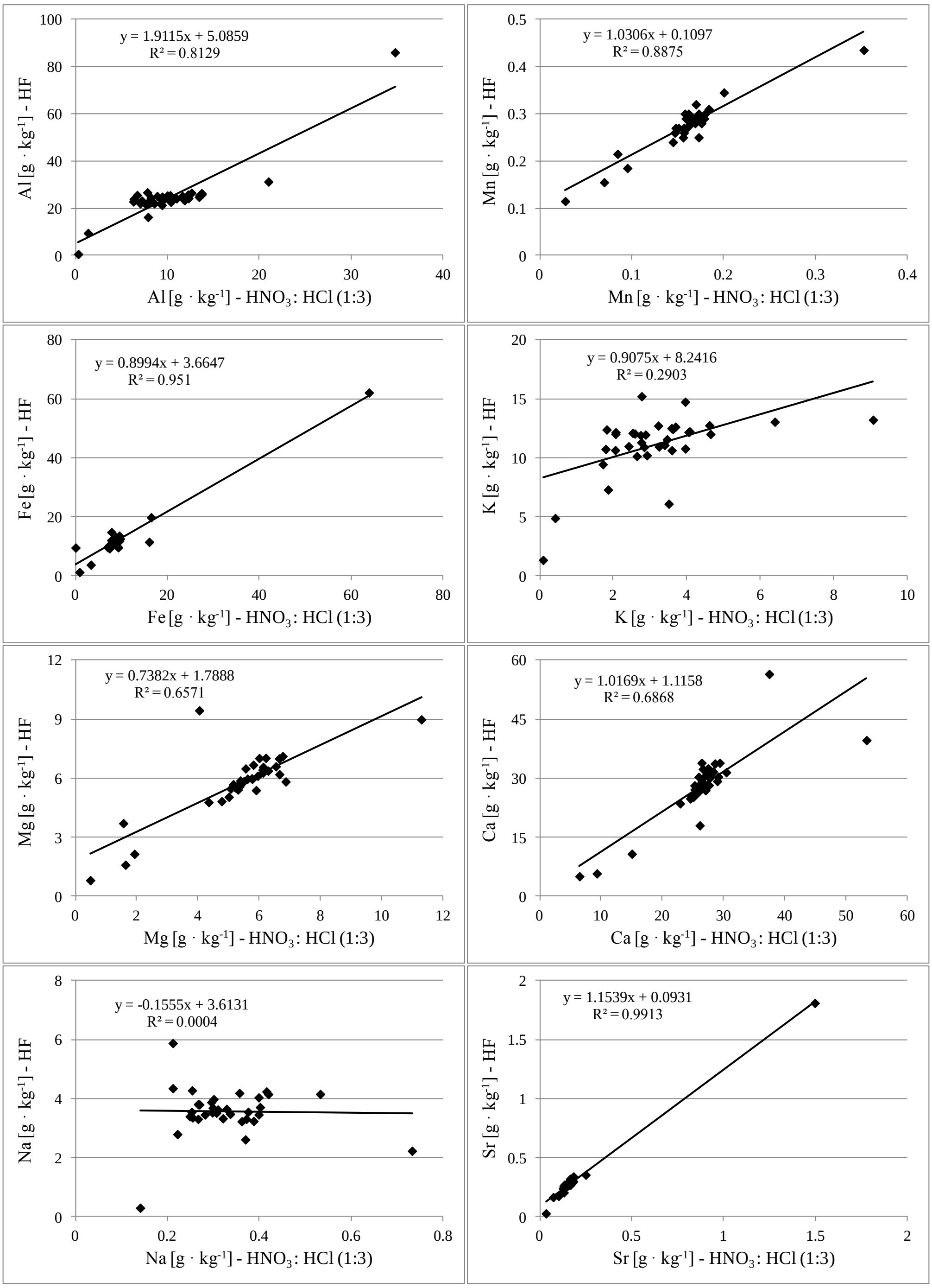

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Fig. 6. Macro-and microelements determined HF in dependence on elements determined at aqua regia

65,3% and 26,9%. Such large differentiation may have been caused by various doses of phosphorus-potassium fertilization used in the field experience.

The results of a multi-directional analysis of variance showed that the amount of elements marked in the extract of *aqua regia* differed significantly form their amount in the additional rocks in brown coal. The smallest differences in chemical composition were observed between the soil samples and bing sand, glacial till (Würm) and glacial till (Riss) (table 5 and 6). Table 5 contains the comparison of total content of macroelements of the analyzed sedimentary rocks in the addition of brown coal whereas table 6 – the comparison of microelements. The content of each element was marked in the extract of *aqua regia.* High similarity was found among the content of Na, Al, Cd, Cr, Ni and Co in last glacial period till, the content of Mn, Pb and Zn glacial till (Riss) and the content of Fe, Ca and Sr in bing sand and the samples collected from experimental fields. The results of the analysis were presented graphically in the space of canonical variables (Fig. 5). The largest differences were observed in the content of zinc and iron.

The reliance of total elements content in the analyzed sedimentary rocks and the soils originating from the mixture of these soils marked in HF extract and those marked in the extract of *aqua regia* was presented in line regression. The assessment of the parameters of regression and a graphical illustration of the curves was presented in Fig. 6. The values of determination coefficients prove high predictive ability of Al, Mn, Fe, Mg and Sr according to the model of line regression. It means that the analyzed models allow a prediction of an average content of these elements marked in HF extract at the assessed single content of these elements in *aqua regia,* whereas the values of the determination coefficient (0.0004 and 0.2903 for Na and K, respectively) show no possibility of the prediction of the average content of these elements in both methods.

4. Conclusions

The results of the research allow the formulation of such conclusions:

1. Graining and chemical composition of the soils originating from post-minig grounds was a resultant of the chemical composition of sedimentary rocks and their reliance in the post-mining material.
2. The analyzed soil samples were qualified as sandy loams according to FAO/USDA when their texture was concerned and were closest to last glacial period till (Würm).
3. Positive yet minor impact of the mineral fertilization was proved for such elements as K and Cd.
4. Elemental composition of the analyzed soils was similar to such sedimentary rocks as last glacial period till (Würm) and grey till (Riss).
5. The research proved that the elemental content in the analyzed soils depended on the marking method. The content of element extracted with *aqua regia* were lower than with HF extract.
6. The method of *aqua regia* extraction was strictly correlated with the extraction in HF solution and may be suggested as a substitution of HF, which is more toxic.

5. References

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