Speciation Analysis of Elements in Soil Samples by XRF

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Abstract

This paper presents results of speciation analysis of soils coming from Silesia. In examinations a five-step extraction procedure has been applied. Direct analysis of sediments and analysis of extracts was carried out by the X-ray fluorescence spectrometry with wavelength dispersion. Examinations were carried out with the use of soil CRM S-l.

Introduction

In natural conditions soil plays a very important buffer role protecting against excessive translocation of compounds and substances of anthropogenic origin to groundwaters and plants. Pollution of the environment has an unfavourable effect on physicochemical properties of soil and could delimit its protective function. Observation of changes in chemical composition of soil plays a very important role in estimating its pollution grade and permits choosing such methods of agricultural exploitation which delimit excessive passage of trace elements from soils to plants. Nowadays there exists a need to determine not only total concentration of elements in examined samples, but also concentrations of various forms in which these elements could exist. Bioaccumulation and influence on living organisms of these elements depends on their physicochemical forms. Examination of element distribution in soil is very important because under environmental conditions it can accumulate or release them [1]. Various methods have been proposed for speciation analysis of soils. We can meet methods based on calculation of element speciation, thanks to application of ready counting programs, such as: MICROQL [2, 3] and WHAM program [4]. These methods are based on

knowledge of total concentration of elements, ligands and thermodynamic stability constants. NMR [5], XAFS and SEM/EDX [6] are often in use as direct methods for speciation analysis of elements, whereas single and sequential extraction procedures are applied as indirect methods. H_2O [7], 0.01 M KNO_3 [8] and a mixture of phosphate buffer K_2HPO_4 with aluminium sulfate $Al_2(SO_4)_3$ [10] were applied as solvents in single extraction procedures. Most often however sequential extraction is proposed. In particular steps (usually 3-6) the following electrolytes: neutral ($CaCl_2$, $MgCl_2$), weak acids buffers, chelating agents (EDTA, DTP A), redox compounds (NH_2OH), strong acids and bases are frequently in use as extraction solvents. Applying this type of extraction we can get distribution over various fractions, e.g. free ions, coprecipitated with carbonates, adsorbed on oxide surface, organically bound and ions closed in crystal structure of minerals. Obtained extracts are examined with methods designed for multielement analysis. Al, Fe, Zn, Mn for instance were examined using AAS [11-24]; S by IC [25], Pb by DPASV [8, 9], Cr by photometric method [10].

Soil extracts were also examined using coupled methods, like HPLC-ICP-MS [26-30], IE or ED with AAS [31], FPLC with ET-AAS; SE, UV with ICP-AES

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[32]. The XRF method was used for analysis of an element's total concentration in examined soils [18].

Experimental Procedures

Apparatus

In examining X-ray fluorescence a spectrometer with wavelength dispersion PW 2400 Philips and centrifuge Hermle were used.

Materials

Soil samples from various places of Silesian province: Dabrowa Gornicza, Ruda Slaska, Będzin, Bielsko Biala, Lipowa Bugaj, Pyskowice and from grounds of different character, such as housing estates, fields, forests, parks, meadows, main roads, petrol stations and neighbourhoods of steelworks were analysed. Samples were collected from surface layer of soil (20 cm) and next were air-dried and sifted (fraction below 2 mm).

Standard solutions were used: Fe, Mn, Zn, Pb and Si of concentration 1 mg/ml (Merck), HNO_3, NaOH, HC1, $NH_2OH \cdot HCl$ and NH_4OAc (POCh). All reagents were of analytical grade.

Methods

Samples of soils were ground in a mill with input of silicon carbide to reach graining below 63 μm and next 2 g of sample with binder was tableted under a pressure of 2 t/cm^2, then a direct XRF analysis were carried out.

pH of analysed soil samples was measured potentiometrically in water and KCl suspension. Obtained results are gathered in Table 1.

Samples after 5-step extraction (5 g of sample) were also examined [33, 34]. The following solvents were applied: 1 M NH_4OAc (pH 5), 1 M NH_2OHHCl with 25% AcOH (1:1), 0.1 M HC1, 0.5 M NaOH and 8 M HNO_3. The blank test was carried out in parallel. Concentrations of elements in extracts (solutions A-E) were analysed by XRF with the use of hel arrangement, suitable for analysis of liquid samples. Applied measurement parameters are depicted in Table 2.

Examinations were carried out on the basis of calibration curves which were made with the use of certified reference material: CRM of soil S-l. Correction for mutual multi-element interactions was calculated for calibration curves. For Mg and Rb determination the α factor to correct the effect of Na was introduced, for P, Ca, Fe and Zn determination α factor to correct the effect of Al, for S determination α factor to correct the effect of Si and for Mn, Sr and Pb determination a factor to correct the effect of Fe. In Table 3 regression parameters of analytical curves for analysed elements are gathered.

Results of direct analysis of sediment samples obtained by calibration curves are presented in Table 4. Results of extract analysis (A, B, C, D, E) are presented in graphic form in Fig. 1.

A chosen X-ray spectra of sample 1 are shown in Fig. 2.

Table 1. pH of examined soils.

Soil	pH (H₂O)	pH (KCl)
1 (housing estate, Dąbrowa Górnicza)	6.88	6.76
2 (housing estate, Będzin)	7.26	7.24
3 (park, Dąbrowa Górnicza)	**5.92**	**5.70**
4 (main road, Sosnowiec)	7.32	7.28
5 (housing estate, Ruda Śląska)	7.12	7.04
6 (meadow, Lipowa Bugaj)	**5.28**	**4.52**
7 (forest, Lipowa Bugaj)	**5.24**	**4.42**
8 (field, Lipowa Bugaj)	**4.16**	**3.68**
9 (petrol station, Dąbrowa Górnicza)	7.14	6.96
10 (steelworks, Dąbrowa Górnicza)	8.16	8.04
11 (petrol station, Bielsko Biała)	6.92	6.80
12 (main road, Bielsko Biała)	7.86	7.58
13 (park, Pyskowice)	7.38	7.38
14 (field, Pyskowice)	7.52	7.12
15 (main road, Pyskowice)	8.26	8.10
16 (allotment, Pyskowice)	**5.92**	**5.34**

Table 2. Parameters of measurement program.

Lp.	Element	Crystal	Collimator	Detector	kV	mA
1	Zn, Sr, Pb, Rb	LiF 200	150 μm	Scintillation	60	50
2	Fe, Mn	LiF 200	150 μm	Flow	60	50
3	Ca, K, S	LiF 200	150 μm	Flow	40	75
4	Si, Al, P	PE 002	550 μm	Flow	40	75
5	Mg	PX 1	550 μm	Flow	40	75

Table 3. Regression parameters of analytical curves for liquid (a) and solid (b) standards.

	(a)			(b)
Mg	y = 1.08x + 0.150		**Mg**	y = 6.88x – 0.58
Al	y = 0.04x + 0.028		**Al**	y = 1.54 + 2.10
Si	y = 0.07x – 0.019		**Si**	y = 1.41x + 8.59
S	y = 0.16x + 0.049		**S**	y = 15.32x + 8.95
K	y = 0.25x + 0.003		**K**	y = 1.44x + 0.35
P	y = 0.10x + 0.025		**P**	y = 4.10x – 0.06
Ca	y = 0.36x – 0.016		**Ca**	y = 5.25x – 2.67
Fe	y = 0.47x – 0.012		**Fe**	y = 9.74x + 10.88
Mn	y = 104.62x – 45.22		**Mn**	y = 0.01x – 0.37
Zn	y = 10.73x – 0.59		**Zn**	y = 0.04x + 0.48
Rb	y = 3.67x – 0.70		**Rb**	y = 0.09x + 1.26
Sr	y = 4.19x + 0.92		**Sr**	y = 0.09x + 1.83
Pb	y = 15.07x + 90.16		**Pb**	y = 0.03x + 0.93

Results and Discussion

Soils coming from various places of Silesian province and from areas of different character, like: housing estates, parks, fields, forest, meadow, main roads, petrol stations, allotments and neighbourhood of steelworks were analysed using the XRF method.

Results of direct XRF analysis showed that examined soils can be divided into two groups:

1. contaminated soils submitted to various an thropogenic influences, like soils coming from Dabrowa Gornicza, Ruda Slaska, Sosnowiec, where concentrations of Pb, Mn and Zn are high, and

2. unpolluted soils like those coming from Lipowa Bugaj and from Pyskowice with low concentrations of these elements.

Taking the concentration of Pb and Zn into account we can classify them into various groups of soil chemical quality. Soils coming from areas of high anthropogenic activity, like soils 1-5 and 10 (housing estates, parks, main roads, steelworks in Dabrowa Gornicza, Bedzin, Ruda Slaska, Sosnowiec) belong to III and IV class and could be only afforested or used for cultivation of industrial plants. Unpolluted soils from Lipowa Bugaj (samples 6-8) and from Pyskowice (samples 13-16), where these elements exist in natural content, belong to 0 and I class and can be used for cultivation of various plants.

We can observe high contents of Rb (90-150 μg/g) in mountain soils originating from granites and gneiss. In some analysed soils concentration of Rb and Sr increases with an increase of K and Ca concentration due to the same weathering process as in the case of Ca and K. In soils coming from fields, allotment (samples 8 and 16) and meadow (sample 6) increasing concentration of P is observed, which is probably connected with fertilization of these soils.

On the basis of pH measurement it is possible to divide analysed samples into the following groups: acid and sub-acid soils (samples 3, 6-8, 16), neutral soils (samples 1-5, 9 and 11) and alkaline soils (samples 10,12-15). Acid soils belong to the sandy soils, neutral to the sandy-loamy soils and alkaline ones to the loamy soils. Acid soils are prone to increased leaching of important components and decreased assimilation of such macroelements as P, K and Mg by plants. Plants growing on alkaline soils can have troubles with assimilation of Fe, Cu and Mn. The effect of acidifying of soils is visible in decreasing their saturation with exchangeable cations and successive loss of Ca and Mg and simultaneous activation of toxic compounds of Al, Mn, Fe and accumulation of heavy metals (Pb) by plants.

It was found that the greater difference between pH (H_2O) and pH (KCl) causes an increase of soil sorption capacity in what can be observed especially for acid soils (sample 3, 6-8, 16).

Taking into account results of speciation analysis we can ascertain that:

Mg and Ca in all samples occur mainly in the extraction residue closed in mineral structure or in fraction of carbonates in easy exchangeable form. In some samples there exist pretty large participation of Mg and Ca in oxide fraction, which could be connected with character of their matrix and their origin. In acid soils there appears worse bioaccumulation of Mg by plants. Mg could create mixed hydroxide minerals with other cations like Zn, Mn, Al and Fe, which influence mobility and bioaccumulation. In samples 13, 14 and 16 from Pyskowice we can observe larger content of Ca in organic matter and the humic compounds fraction. This could be connected with a presence of clay and high content of organic matter.

Al and Si were found mostly in the residue in the form of aluminosilicates and silica. In soils from Pyskowice, Sosnowiec and Lipowa Bugaj low content of free ions and carbonates fraction is found. Both fractions take part in physicochemical and biochemical soil processes and could be accumulated by plants. A low content of Al and Si in oxide fraction, in fraction of the humic compounds (especially in soil from forest-7) and in organic matter fraction (sample 10 from steelworks and 12 from Bielsko Biala main road) has been found. A certain content of Al and Si in sulphide fraction was determined in forest soil (Lipowa Bugaj), soils from Bielsko Biala petrol station, Dabrowa Gornicza steelworks and Pyskowice field and allotment. In acid soils, especially in forest soils Al could force out other cations from sorption complex and leads to its degradation. Al could exist in various soluble forms, like: AL^{3+}, Al-OH, Al-SO_4 (especially in forest soils). Si in soluble form can occur as orthosilicic acid, whose solubility increases with increase of pH, but the influence of P, Al, Ca and Fe here is important, too.

S in examined soils occurs mainly in the residue and in sulphide fraction. In some samples S occurs in the form bound to carbonates (9-15%), especially in soils from fields, due to fertilizers, soils from main roads (sample 4,12,15), where the soil is exposed to intensive traffic. In samples 3 and 8 about 10% of S exists in oxide
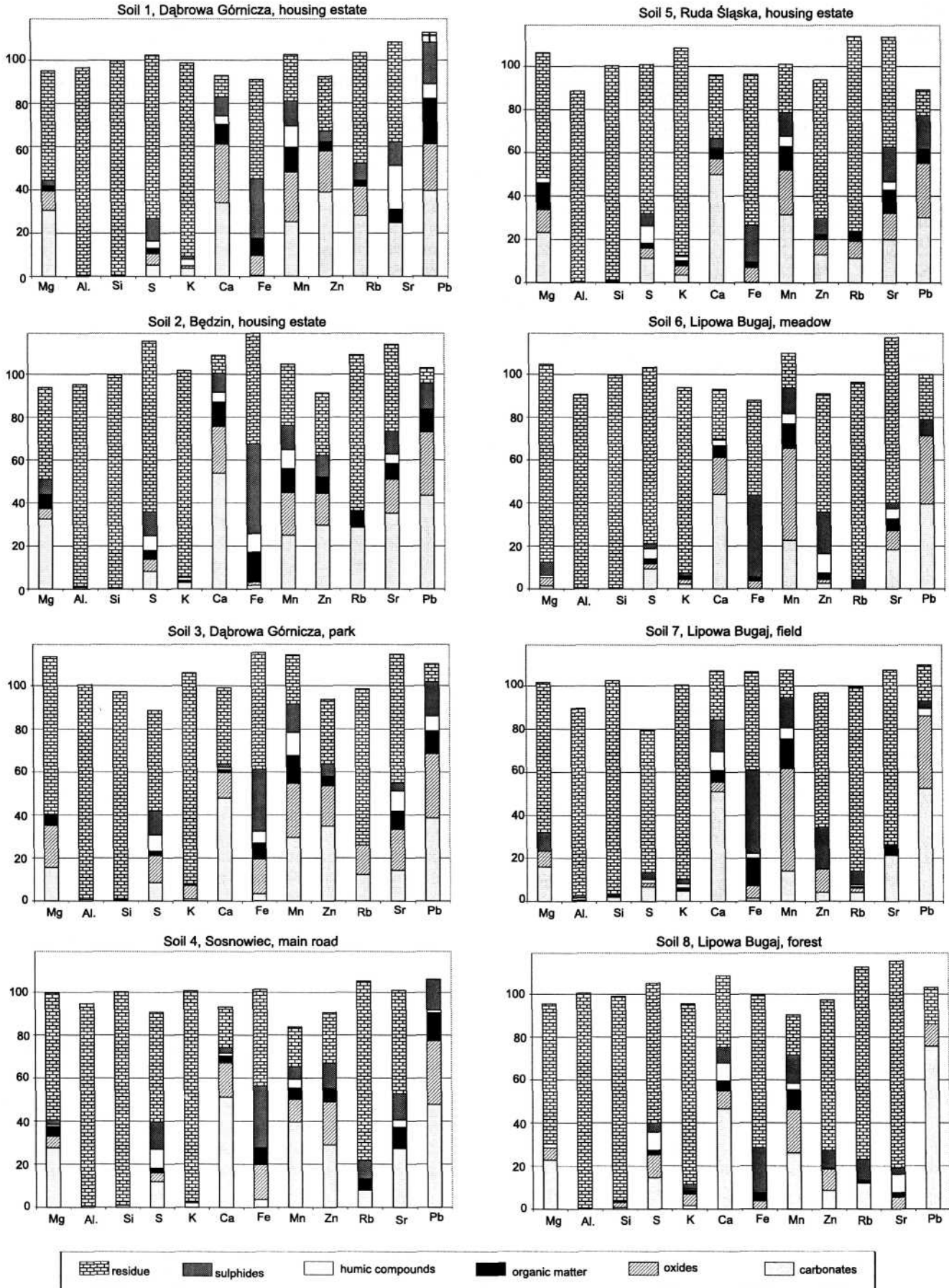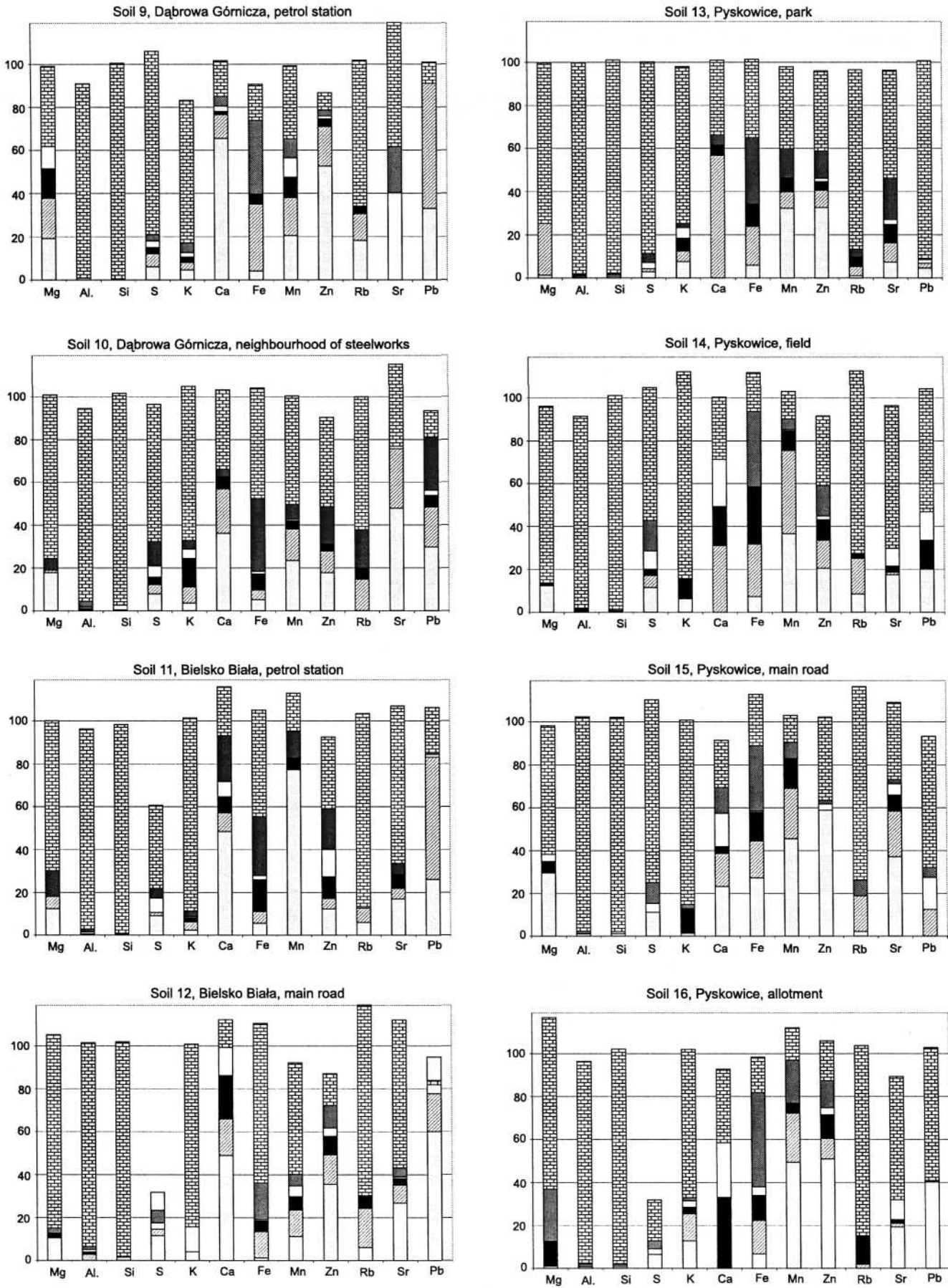
Fig. 1. Distribution of the elements over various fractions in examined soils.

Soil 9, Dąbrowa Górnicza, petrol station

Soil 13, Pyskowice, park

Soil 10, Dąbrowa Górnicza, neighbourhood of steelworks

Soil 14, Pyskowice, field

Soil 11, Bielsko Biała, petrol station

Soil 15, Pyskowice, main road

Soil 12, Bielsko Biała, main road

Soil 16, Pyskowice, allotment

(Fig. 1 – continuation)

Table 4. Results of direct analysis of soil samples obtained by calibration curves (for n = 6).

	mg/g						
	Mg	Al	Si	P	S	K	Ca
1 (housing est., Dąbrowa Górnicza)	2.42±0.18	43.71±2.43	249.84±6.13	1.54±0.03	0.76±0.02	8.81±0.26	16.53±1.09
2 (housing est., Będzin)	3.52±0.05	37.59±0.39	236.47±2.75	0.72±0.01	0.72±0.01	7.43±0.04	25.29±0.26
3 (park. Dąbrowa Górnicza)	1.60±0.02	37.91±0.29	249.61±1.49	1.07±0.01	1.00±0.01	8.79±0.02	11.53±0.07
4 (main road. Sosnowiec)	7.46±0.13	58.29±0.33	218.37±0.99	1.14±0.01	0.99±0.01	12.82±0.04	35.97±0.24
5 (housing est., Ruda Śląska)	2.67±0.28	40.44±2.88	234.65±7.66	0.75±0.08	0.63±0.02	10.17±0.50	6.85±0.49
6 (meadow. Lipowa Bugaj)	9.36±0.07	94.29±0.38	281.52±0.69	1.03±0.01	0.42±0.01	20.28±0.06	5.41±0.02
7 (forest. Lipowa Bugaj)	9.59±0.11	89.21±0.53	288.83±1.18	0.67±0.01	0.59±0.01	21.87±0.07	4.85±0.03
8 (field. Lipowa Bugaj)	3.19±0.04	69.74±0.55	335.887±1.98	1.05±0.01	0.47±0.01	16.41±0.09	2.12±0.02
9 (petrol stat., Dąbrowa Górnicza)	1.02±0.02	21.76±0.28	387.33±9.65	0.22±0.01	0.49±0.01	6.09±0.08	3.69±0.04
10 (steelworks. Dąbrowa Górnicza)	5.36±0.04	35.43±0.12	212.14±0.46	0.49±0.01	1.14±0.01	7.32±0.02	76.32±0.15
11 (petrol station. Bielsko Biała)	4.34±0.07	63.54±0.38	315.21±1.63	0.73±0.01	0.66±0.01	17.12±0.07	7.09±0.05
12 (main road. Bielsko Biała)	2.08±0.04	29.93±0.39	307.02±2.52	0.65±0.01	0.68±0.01	8.76±0.09	16.74±0.22
13 (park. Pyskowice)	3.94±0.08	65.75±0.27	202.26±0.63	1.57±0.03	1.41±0.02	13.97±0.07	17.99±0.18
14 (field. Pyskowice)	2.02±0.02	45.53±0.37	357.32±1.89	0.64±0.02	0.17±0.01	11.24±0.08	5.54±0.04
15 (main road. Pyskowice)	2.46±0.04	30.03±0.23	347.21±1.54	0.44±0.03	0.36±0.01	9.28±0.09	21.22±0.18
16 (allotment. Pyskowice)	1.11±0.02	29.98±0.20	378.84±1.34	1.08±0.03	0.94±0.03	10.41±0.07	3.92±0.08
CRM S–1	1.98±0.05	38.79±0.17	368.51±0.92	0.45±0.01	0.61±0.02	12.28±0.05	2.59±0.02
Cert. Value	1.85±0.34	–	–	–	–	12.05±0.58	2.60±0.60
LKSD–2	10.6±0.10	65.73±3.20	269.77±2.68	1.38±0.01	1.68±0.07	21.40±0.10	16.61±0.10
Cert. Value	10.25	65.12	275.36	1.31	1.4	21.58	15.72

|	mg/g	µg/g				
	Fe	Mn	Zn	Rb	Sr	Pb
1 (housing estate. Dąbrowa Górnicza)	19.84±0.52	365.62±9.57	4973.96±91.30	20.89±0.78	38.05±0.61	398.73±4.59
2 (housing estate. Będzin)	19.89±0.03	396.70±2.19	5218.95±21.93	14.42±0.56	39.14±0.25	523.98±5.81
3 (park. Dąbrowa Górnicza)	14.40±0.04	336.84±1.63	1408.51±6.58	27.93±0.56	30.87±0.89	343.13±2.49
4 (main road. Sosnowiec)	35.95±0.12	854.64±4.99	1339.18±6.37	50.97±0.41	119.49±0.59	549.97±2.93
5 (housing estate. Ruda Śląska)	31.28±1.16	759.13±34.24	4664.39±139.29	32.15±0.85	90.99±2.02	1451.53±20.66
6 (meadow. Lipowa Bugaj)	40.03±0.09	769.19±2.91	193.89±1.08	130.23±0.74	82.58±0.37	56.55±5.19
7 (forest. Lipowa Bugaj)	36.92±0.06	673.01±4.00	142.72±2.19	174.11±0.32	75.97±0.35	38.57±4.03
8 (field. Lipowa Bugaj)	24.96±0.14	458.29±4.57	145.26±1.51	87.14±0.97	68.85±1.02	76.31±1.63
9 (petrol station. Dąbrowa Górnicza)	2.58±0.02	114.19±1.31	380.87±1.13	13.29±0.50	13.09±0.46	150.83±3.29
10 (steelworks. Dąbrowa Górnicza)	27.09±0.03	2391.45±3.25	1145.83±2.83	17.98±0.91	214.12±0.58	496.18±8.58
11 (petrol station. Bielsko Biała)	24.92±0.05	492.73±2.07	206.43±1.23	81.88±0.53	76.95±0.44	107.68±1.86
12 (main road. Bielsko Biała)	11.91±0.04	192.75±2.06	268.22±2.58	36.11±1.07	91.05±0.86	38.13±4.19
13 (park. Pyskowice)	30.85±0.08	591.50±1.87	247.29±1.57	72.75±0.52	312.76±1.23	57.53±3.82
14 (field. Pyskowice)	15.10±0.14	516.37±1.46	247.61±1.32	40.60±0.88	53.94±0.29	59.50±3.14
15 (main road. Pyskowice)	8.34±0.11	1284.45±5.23	103.70±0.89	27.81±1.11	73.65±0.42	48.24±2.24
16 (allotment. Pyskowice)	7.22±0.12	346.10±0.93	199.59±0.96	31.74±0.93	40.60±0.29	53.42±2.89
CRM S-1	9.45±0.04	251.50±1.03	37.35±0.97	50.43±0.61	52.34±0.54	14.36±2.45
Cert. Value	9.88±0.45	266.00±18.00	35.00±3.30	52.00±2.20	55.00±2.42	15.00±3.60
LKSD-2	38.93±0.55	2077.20±7.14	210.50±3.70	83.80±0.71	211.60±0.80	39.50±1.40
Cert. Value	43.36	2020.00	209.00	85.00	220.00	44.00
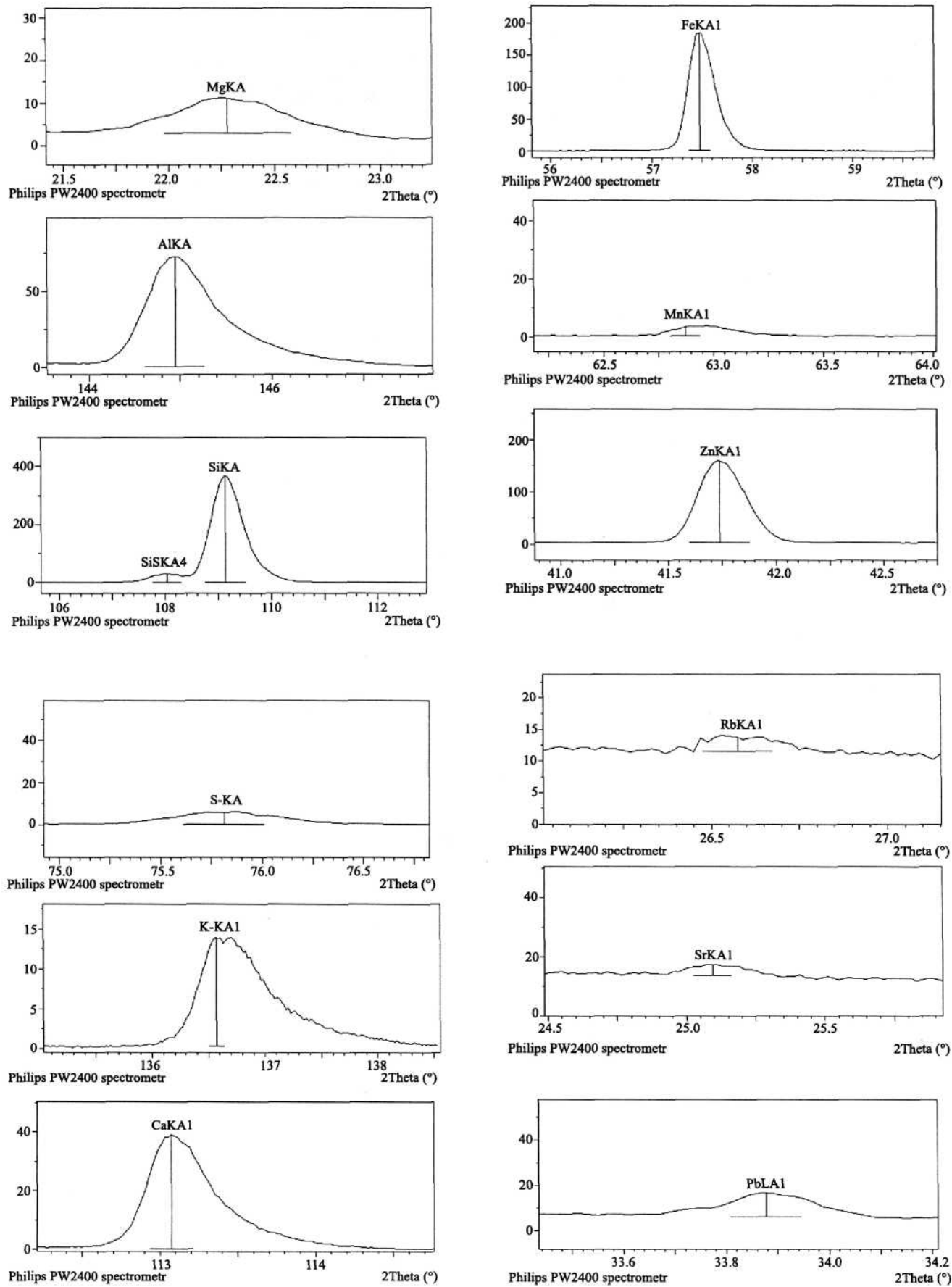
Fig. 2. X-ray spectra of soil 1 (Dąbrowa Górnicza, housing estate).

fraction and especially in samples 7, 11, 12, 16 there occurs loss of sulphur (40-65%) on account of AVS.

K was found mostly in the residue, so in the form bound with minerals. A certain percentage of K occurs in sulphide fraction, especially in soils from Dabrowa Gornicza and Lipowa Bugaj, which is probably connected with their origin. In soil from Pyskowice (sample 16-acid soil) we can ascertain increased (~ 10%) content of free ions and carbonates fraction. In some acid soils, like soil from the park and steelwork in Dabrowa Gornicza, from Lipowa Bugaj field and from Pyskowice allotment we can observe a certain content (5-7%) of K in oxide fractions. In alkaline soil 10, 14 and 15 K exists in organic fraction and in sample 12 in the humic compounds fraction. K is an element which could undergo increased leaching in acid soils and for potassium Mg has an antagonistic influence on its bioaccumulation by plants.

Fe in soils occurs mainly in the residue (16-74%) and in sulphide fraction (17-44%). Fe exists also in other fractions like: fraction of free ions and carbonates and organic matter (Fe introduced with organic fertilizers after mineralization could be bound to organic matter) and can be met in soils from Pyskowice (sample 14 and 15), Bedzin and Bielsko Biata. In fraction of oxides Fe occurs in samples from Pyskowice and Dabrowa Gornicza (samples 9 and 14). Fractions of humic compounds have an importance in distribution of Fe, especially in soils from park in Dqbrowa Gornicza and from housing estate in Bedzin. Sollubility of Fe compounds increases with the decrease of pH. Compounds and minerals of Fe and its complex with organic matter are very important in soil-forming processes and they influence other elements. All Fe minerals have a large sorption capacity for other metals. Organic compounds increase mobility of Fe and its bioavailability for plants.

Mn exists mainly in 3 fractions: the residue (minerals), free ions and bound to carbonates (soils from Ruda Slaska, Sosnowiec, main roads in Bielsko Biala and Pyskowice, where there exists a large influenece of anthropogenic activity) and in oxides fraction (especially in soils from Bielsko Biala and Pyskowice, depended on origin of these soils). Mn also occurs in organic matter fraction in soils of forest and fields, in humic compounds fraction in soils from housing estate and park in Dabrowa Gornicza and in sulphide fraction in all examined soils. Chemistry of Mn is very complicated under the influence of pH and Eh. It also forms its own oxides and hydroxides, bounds with organic matter and decides about redox reactions of other elements. Excessive pollution of soils by Mn could occur after fertilization with liquid manure, for instance in field soil from Pyskowice.

Zn and Pb are elements which we could meet mainly in residue (especially in soils from Ruda Slqska, Lipowa Bugaj and Pyskowice) and in carbonate fraction (soils from Pyskowice and Bielsko Biala). In soils from industrial areas (Dabrowa Gornicza, Sosnowiec, Ruda Slaska and Bedzin) we can observe a great participation in oxide and free ions fraction. Fraction of organic matter we can meet in Bielsko Biala and steelwork soil from Dabrowa

Gornicza and humic compounds fraction in the soil from the Bielsko Biaia petrol station and Pyskowice. Sulphides occur mainly in soils from Lipowa Bugaj, the petrol station in Bielsko Biata and steelworks in Dabrowa Gornicza (depending on the form in which compounds of Pb and Zn are introduced to the soil during pollution of the environment with compounds of Zn and Pb). Zn and Pb could create stable bounds with organic matter, strong compounds with Fe and Mn oxides. Their mobility increase with decreasing pH, but in alkaline soils Zn could be mobile, because of its ability to create mineral-organic compounds and anion complexes. High participate of Pb free ions in field soil from Lipowa Bugaj could be connected with fertilization of this soil. Pb is submitted to sorption by the loamy minerals, hydroxides of Fe and Al and by organic matter. In acid soils in some cases organic compounds of Pb could dominate, which could increase or decrease its mobility. Sollubility of Pb increases in acid soils and Pb could exist as Pb^{2+}, $PbHCO_3^+$ and organic complexes, while in alkaline soils $PbOH^+$ and $Pb(CO_3)_2^{2-}$ dominate. P introduced to soil (for instance with fertilizers) decreases the content of easy soluble form of Pb bounded to carbonates and oxides and increases organic fractions and the residue (like in sample 13 and 16 from Pyskowice).

Rb and Sr are observed mainly in the residue after extraction (especially in mountain soils from Lipowa Bugaj, Bielsko Biala and in soils from Pyskowice, which could be connected with character of their matrix). In some samples, especially coming from areas of high pollution, like housing estates, parks, petrol stations of Dabrowa Gornicza, Bedzin, Ruda Slaska and Sosnowiec we can observe a certain percentage (10-30%) in fraction of free ions and carbonates, which indicate its mobility. In soils from Dabrowa Gornicza, Bielsko Biala, Bedzin and soils from field and main road in Pyskowice oxide fraction amounts to 10-20%. Organic matter plays a certain role in soil from Dabrowa Gornicza, Bedzin, and in allotment from Pyskowice and fraction of humic compounds in forest soil (sample 7). In the end sulphide fraction appears in steelworks and petrol station soil from Dabrowa Gornicza and from Pyskowice park. So the distribution of Rb and Sr over various fractions depends on the origin of the soil, the influence of anthropogenic activity (in soils from areas of high pollution Rb exists in easy exchangeable form) and pH. Increasing Rb content in organic matter fraction could be connected with a large content of organic matter, its acidity and fertilization. Distribution depends on the origin of the soil and the pH value. In the light acid soils Sr is easy leachable while in alkaline soils it could be initiated and bioaccumulated by plants (sample 10).

Fe, Mn, Zn, Pb, Rb and Sr in acid soils are easily leachable and, worse: bioaccumulated by plants. Their organic and mineral-organic compounds are very important in soil-forming processes and influence other elements. Some of them have a good mobility in alkaline soils because of their ability to create mineral-organic compounds and anion complexes.

A large precipitation of carbonate and oxide fraction could be connected with acidity of used reagent, which

could cause releasing of metals from clay, which are then associated with another fractions, like carbonates and oxides. Occurrence of larger association of metals with humic compounds could be connected with the presence of clay high content and with advanced processes of mineralization and creating humic compounds. In some soil samples we ascertain a larger content of organic matter fraction, which could be connected with a high content of organic matter and with the ability of some elements to create stabile bonds with organic compounds. However, occurrence of a large residue in examined samples is possible in mineral soils with high content of clay where elements (Zn) have the ability to penetrate crystal structure of silicates.

Conclusions

Summarizing the obtained results it was found that:

- application of the XRF method gives us the possibility to realize quick multielement soil analysis and speciation analysis

- owing to application of the 5-step extraction we have the possibility to obtain fractions of the humic compounds, organic matter and sulphides (unlike with other generally used extraction procedures)

- in particular fractions examined elements occurred in the form of free ions and carbonates (Mg, Ca, Mn, Zn, Pb, Rb and Sr), bound with oxides (Mg, Ca, Mn, Fe), organic matter and the humic compounds (Fe, Zn, Pb, Rb and Sr), sulphides (Fe, S) and in the residue (all elements)

- obtained results give us information on the main contents of the soil, anthropogenic activities which influence soils, natural soil-forming processes and hazards, connected with changes of elements chemical form under environmental conditions and their influence on living organisms.

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