Trace elements in soils planted with sunflower from Maritsa East region and Borovan-Banitsa village area in NW Bulgaria

Редки елементи в почви, засяти със слънчоглед, от района на Марица-Изток и селата Борован и Баница в СЗ България

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Keywords: trace elements, soil, ICP-MS, mineral composition.

Introduction

The chemical composition of soils from the area of mining and power producing enterprise Maritsa East were studied in order to determine, whether the mining and power producing industry have environmental impact on them. The results were also compared to contents of elements in soils from area distant from the Maritsa East in NW Bulgaria. All studied samples were planted with sunflower.

Materials and methods

Composite samples of cultivated soil were collected from topsoil (0–25 cm) in summer (July 2012, 2013) from 3 different places in the area of Maritsa East coal basin: 1) 2 km N of thermo electric power station (TEPS) Maritsa East 2 (1S); 2) 3 km NE of TEPS Brickel (4S) and 3) 2 km NW of TEPS Maritsa East 3 Contour Global (2S). Two samples (7S, 8S) were collected 32–40 km SSW from Kozloduy (N from villages of Borovan and Banitsa) for geochemical comparison. Samples 2S and 4S are from terrains underwent reclamation during 1990s and 1980s respectively. Soils in the vicinity of Maritsa East coal basin are classified as vertisols (FAO classification), while those in Borovan and Banitsa – phaeozems (Ninov, 2002). Both types are varieties of chernozem soil. Samples were dried at room temperature and later on sieved to fractions <1mm (S) and <0.63 μm (SF) in order to determine trace element and mineral distribution. The pH of soils was determined in accordance with BDS ISO 10390:2002 (Table 1). Concentrations of trace elements were determined in Bureau Veritas Minerals (previously known as Acme Laboratories) at their Canadian and Turkish branches. The analyti-

Table 1. Element contents in samples and respective MPC for pH range 6.0–7.4 (according to Regulation No. 3)

Element	MPC	1S	1SF	2S[1,*]	2SF[1,*]	4S[2]	4SF[2]	7S	7SF	8S	8SF
Cr, ppm	200	22.5	20.0	12.9	14.1	25.8	27.2	38.8	26.9	37.6	24.7
Ni, ppm	110	23.0	21.3	12.3	13.3	25.2	25.4	40.3	29.1	28.5	20.3
Cu, ppm	150	27.1	63.4	16.1	25.8	35.4	23.5	27.1	25.6	18.3	20.3
Zn, ppm	320	44.6	60.9	28.4	30.0	44.8	44.3	77.9	49.6	51.9	39.1
As, ppm	25	5.9	5.2	3.2	3.8	5.8	5.7	10.5	7.2	12.5	7.5
Cd, ppm	2	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.1	0.2	0.1
Hg, ppb	1500	25.0	41.0	26.0	26.0	28.0	27.0	30.0	22.0	40.0	40.0
Pb, ppm	100	24.7	39.4	15.8	16.7	21.6	18.6	19.6	14.5	30.0	16.1
pH	6.0–7.4	6.9		6.7		7.1		6.8		6.0	

[1] reclamated land in 1990s; *[2]* reclamated land in 1980s; [*] sample taken in 2012
Detection limits: Cr 0.5 ppm; Ni, Zn, As 0.1 ppm; Cd, Cu, Pb 0.01 ppm; Hg 5 ppb

cal procedure was a standard Aqua Regia digestion of 0.5 g pulverized soil and analysis by ICP-MS. Total carbon and sulphur were measured by Leco method. Major elements were determined by wet chemical analysis. Mineral composition of each sample fraction was characterized by powder X-ray diffraction (XRD) using a PANalytical Empyrean equipped with a multi-channel detector (Pixel 3D).

Results

The major minerals (>3 vol.%) in all soil samples are quartz, muscovite and albite. Orthoclase, microcline and feldspar are presented as major, minor (1–3 vol.%) or accessory (<1 vol.%) minerals in some of the samples. Montmorillonite, calcite and dolomite are characteristic for soils in Maritsa East area, while chlorite and kaolinite – for Borovan and Banitsa soils. Illite is detected in soils from Maritsa East as well. Clay minerals were determined in both fractions.

A total of 70 elements were analyzed in soils: lithophilic metals – Li, Be, Na, Mg, Al, K, Ca, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, REE, Hf, Ta, W, Re; non-metals – B, C, Si, P, S; siderophilic metals – Sc, Ti, V, Cr, Mn, Fe, Co, Ni; chalcophilic metals – Cu, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi; radioactive elements – Th, U; noble metals – Pd, Ag, Pt, and Au. Data for B, W, Ge, Ta, Re and Pd is below detection limits. The concentrations of all other elements were compared to values for maximum permissible concentrations of harmful elements in cultivated soil (MPC) for respective pH range (Regulation No. 3, 2008), published data for concentrations in chernozem soils (Kabata-Pendias, 2001) and contents in Upper Crust (Grigoriev, 2009). The contents of Cr, Ni, Cu, Zn, As, Cd, Hg and Pb of all soil samples (measured pH in the range 6–7) are significantly lower than MPC values for this pH range (Table 1).

Comparison of trace elements to published data (minimum values) of Kabata-Pendias (2001) shows that only 12 elements have enrichment factor (EF) ≥2: Be, Ti, Mn, Co, Ni, Cu, In, Sn, Tl, Pb, Th, and Au (Fig. 1). Gold has highest EF with concentrations in the range of 1.3–72.3 ppb, as it is higher in Maritsa East soils than Borovan and Banitsa. Thallium also shows elevated EF in all samples. Fraction 1SF (<0.63 µm) has maximum elements with EF ≥2, which might be due to presence of discrete phases. Comparison with values for Upper Crust shows that only C, Se, Sn, Te, Pb, and Au have EF ≥2, as Au and Te are highest.

Conclusions

Based on our results for contents of monitored harmful elements (Cr, Ni, Cu, Zn, As, Cd, Hg, and Pb) pollution in soils from Maritsa East region (cultivated land and reclamation terrains) and Borovan-Banitsa area is not determined. Some elements (Be, C, Ti, Mn, Co, Ni, Cu, In, Sn, Se, Te, Tl, Pb, Th, and Au) show enrichment in the studied samples in comparison with published data for Upper Crust and chernozem soils. Considerable variations in trace element concentrations in soils from the two areas were not observed. Major mineral composition of soils from both studied areas is similar with the exception of carbonate and different clay mineral content. The soil media with circum neutral pH is less reactive therefore migration of elements is limited.

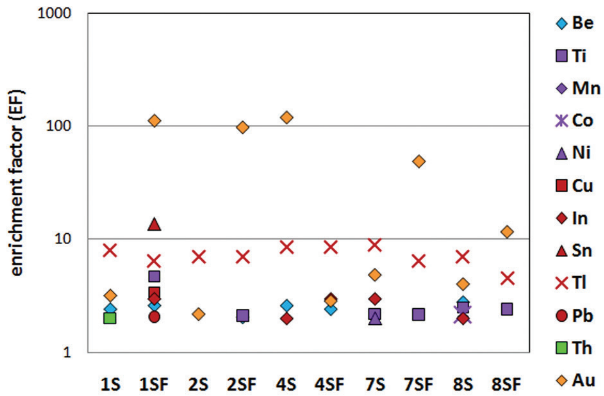

Fig. 1. Elements with enrichment factor (EF) ≥2 in soil samples compared to minimum values of Kabata-Pendias (2001)

Acknowledgements: This study is financially supported by the DNTS China 01/7 grant of the Bulgarian Science Fund. The authors thank "Mini Maritza Iztok" geological department for their assistance in sample collection on site and to prof. Doncho Karastanev for collecting samples from the Borovan and Banitsa village area.

References

Grigoriev, N. A. 2009. *Chemical Eelement Distribution in the Upper Continental Crust*. Ekaterinburg, Institute of Geology and Geochemistry, 301 p. (in Russian).

BDS ISO 10390:2002. *Soil Quality. Determination of pH*. 8 p.

Kabata-Pendias, A. 2001. *Trace Elements in Soils and Plants*. 3rd Edition. CRC Press, 432 p.

Ninov, N. 2002. *Soils*. – In: Kopralev, I. (Ed.). *Geography of Bulgaria. Physical and Social-economical Geography*. Sofia, Institute of Geography, BAS, ForKom, 277–315.

Regulation No. 3. 2008. Guideline values for maximum permissible contents of harmful substances in soils. *Bulgarian State Newspaper*, *71* (in Bulgarian).