Geochemical patterns of soils in the Bobov dol valley, Bulgaria. Assessment of Cu, Pb and Zn contents

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Abstract

The content of Si, Al, Fe, Ti, Mn, Mg, Ca, Na, K, S, P, C, Cu, Pb and Zn were determined in order to reveal geochemical patterns of soils in the Bobov dol valley, Bulgaria. Since the Bobov dol Thermal-electric Power Plant (TPP) is situated in the valley this paper pays attention to the geospatial distribution of Cu, Pb, and Zn due to their diverse vital significance. Elements assemblages and geospatial distribution pathways are also discussed in the light of the past 40 years of operation of the Thermal Power Plant. According to the results obtained the average content of Cu (27.04 mg kg^{-1}), Pb (21.96 mg kg^{-1}) and Zn (57.95 mg kg^{-1}) is higher than the average content of elements in local soil parent rocks: Cu (20.03 mg kg^{-1}), Pb (6.07 mg kg^{-1}) and Zn (46.60 mg kg^{-1}). Compared to the precautionary threshold concentrations adopted for assessing the soil contamination in Bulgaria the elements contents are lower including their maximum values. However, the geoaccumulation indexes reveal an initial stage of contamination of soils with Pb. Lead tends to follow a separate mode of geospatial distribution which is controlled by both the geogenic factors and the aerosol emissions of TPP. Copper accumulation is more strongly affected by technogenic depositions and dominated in urban and technogenic zones under the form of oval spots. Konyavska Mountain is the domain of Zn revealing an altitudinal gradient of distribution. Its accumulation proceeds slowly in topsoil, but still, Zn is the most abundant element in studied soils from the Bobov dol valley. The petrogenetic pattern of geochemical suits still predominated in studied soils wherein the iron has the greatest affinity for studied elements. Soil medium reaction (pH) and organic carbon do not control the processes of distribution and accumulation of Cu, Pb and Zn. The lack of statistical correlation with organic carbon resulted from the siliciclastic nature of soil parent rocks and also reveals the prevailing geogenic origin of studied elements.

Key words: Pedoecology, Trace Elements, Distribution, Geochemical Diversity, Background Values

Introduction

Geochemical assay ensures the knowledge of phenomena governing the trace elements distribution in soils. Different geochemical standards such as the average element content in the main types of rocks in the Earth's crust – the continental crust and lithosphere

(Turekian and Wedepohl, 1961; Vinogradov, 1962; Dobrovolskii, 1983; Yaroschevskii, 1990; Wedepohl, 1995; Rudnick and Gao, 2003) are widely used in this study to overcome a geospatial irregularity in soil elemental composition (Vinogradov, 1957; Dobrovolskii, 1983; Alekseenko and Alekseenko, 2013). The last are reference values reflecting the average content of chemical elements over the globe and are consider for one of the most significant achievements of geochemistry during the 20th century. The average content of the elements is an important geochemical characteristic presenting a background amount of elements. The global values, known as "Clarkes" (Vernadskii, 1954) assists in assessing the degree of dispersion or concentration of trace elements in soils. Of special significance are those coefficients, showing the relative enrichment of a chemical element in studied geochemical systems in comparison to its average content in the Earth’s crust, i.e. concentration coefficients. The Clarke concentration (CC) is one of the first introduced coefficients and represents the ratio of the element content in the studied material and the Clarke value of the same element in the Earth's crust. Nowadays, other coefficients are also used to evaluate the geochemical (re)distribution of trace elements in diverse terrestrial environments (Helz et al., 1983; Muller, 1969).

Along with the average content, the establishment of the most important element assemblages determining the specificity and the nature of the geochemical system has a very important methodological role in soil geochemistry. The criterion of this determinative or typomorphic association is the element concentration coefficient regarding the standard which is genetically related to the studied system, i.e., soil forming (parent) materials. It is well known that the composition of the soil parent materials determines the chemistry, mineral composition, structure and characteristics of soils. For this reason, soil parent materials (rocks and sediments) are considered for the genetic standard in soil study. Often the information on the geochemical composition of parent rocks is either incomplete or missing and impedes the study of the diversity of elements and the contributing processes. This information is especially important today when human activity already became a powerful geochemical factor that appreciably affects the distribution of chemical elements in the geosphere.

Thermoelectric Power Plants, (TPP), utilizing solid fuels are one of the major providers of trace elements in the environment, due to the emission of gases and fine ash particles, which contain a number of elements: C, S, H, K, Ca, Al, Cl, Si, Mg, Zn, Mn, Mo, Rb, Ti, Cu, Co, Cr, Br, Pb, Hg, Sb, Cd (Raikov et al., 1984). These emissions contribute not only to the environment pollution but directly affect human health. Therefore, the knowledge of processes governing the accumulation, solubility and cycling of trace elements is nowadays of global importance.

The present study focuses on the geochemical patterns of soils located in the vicinity of the Bobov dol Thermoelectric Power Plant, Bulgaria. The special attention is paid to the amount and geospatial distribution of Cu, Pb and Zn in order to reveal their geochemical behavior, associations, and origin in soils.

Material and methods

Site description

The studied region represents a valley surrounded by Konyavska Mountain. The valley hosts the Bobov dol Thermoelectric Power Plant, which is the main source of trace elements in the region since the early 70s of the 20th century. In the TPP is utilizing mainly lignite and sub-bituminous coal from Bobov dol, Beli Breg, Staniantsi, Chukurovo and Pernik coalfields (Zdravkov et al., 2012). Due to the high ash content in coal, the TPP annually produces about 900 000 t ash (Donchev et al., 2001). Although the Bobov dol Plant works on a program approved to limit the negative impact on the environment, it has only an ash-capture equipment.

The soil cover is generally uniform with few soil varieties presented: Vertic Luvisols, Albic Luvisols, Endocalcic Cambisols, Chromic Cambisols and Luvisols, Eutric Fluvisols, Umbric Leptosols, Colluvic Regosols (WRB, 2014).

In the Bobov dol valley predominate siliciclastic rocks (conglomerate, sandstone, siltstone, and shale) of Paleogene age, which to the North of the TPP contain sub-bituminous coal layers of the Bobov dol coalfield (Marinova, 1993). The Eastern hillsides of the mountain consist of Paleozoic diorite belonging to the Struma Diorite Formation (Marinova, 1993).

Sampling

Soil sampling procedure is based on an irregular site-specific network designed to cover an area of about 8 km^2 around the Bobov dol TPP (Fig. 1). Eighty-five soil samples were taken to a depth of 30 cm in accordance with Bulgarian State Standard (BSS) ISO 10381-1, 2, 4.

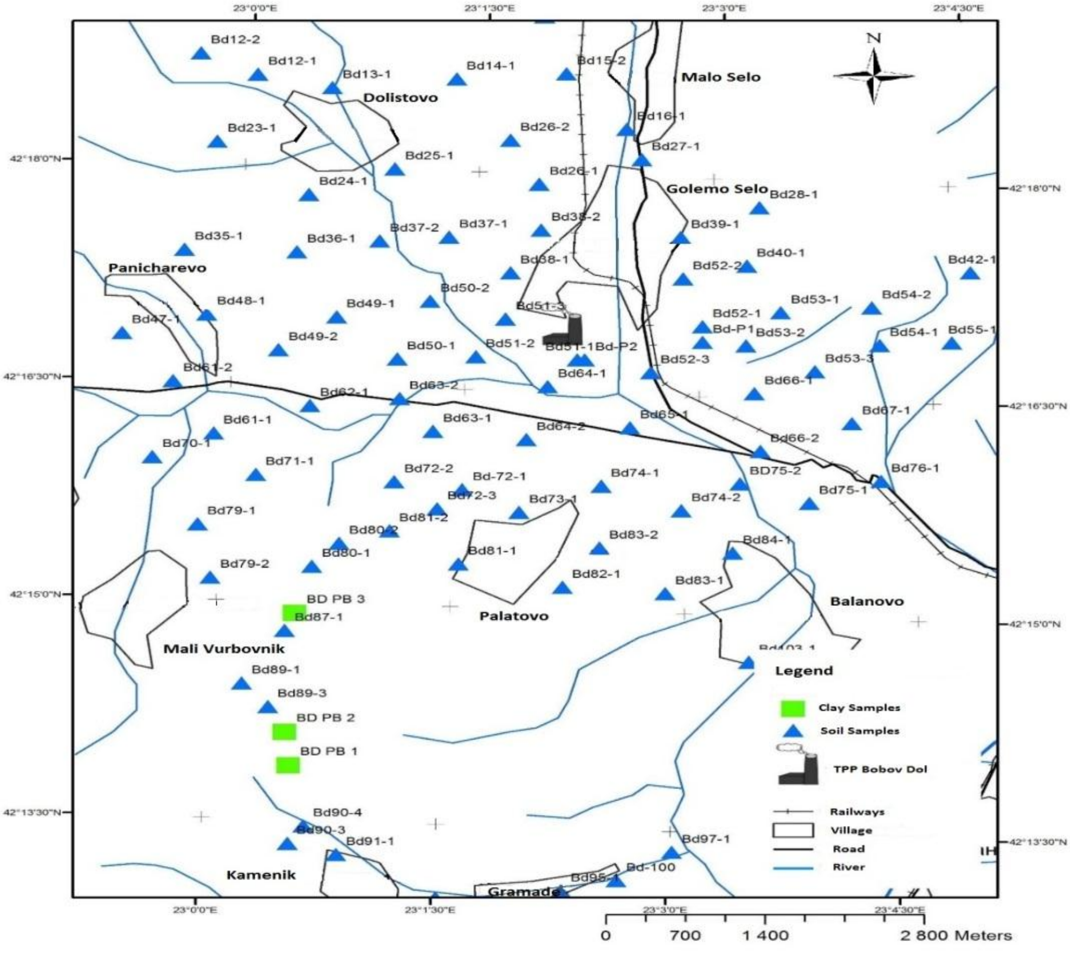

Figure 1. *Location of sampling points*

Three sites disclosed along the conveyor belt transporting the ash to the tailing pond "Kamenik" (Fig. 1) are additionally sampled in order to determine the background content of trace elements in the indigenous soil parent rocks. Although the three rock samples are insufficient to fully characterize the variety of rocks, the results nonetheless present some insights on the concentration of these elements. However, the very similar rock lithology allows us to tentatively accept that the data are sufficiently representative for the studied region. Rock samples were collected from the outcrops by rock hammer and drill to penetrate to 20 cm depth.

Fly ash samples are collected from the intermediate storage tank using surface techniques in duplicate.

Analyses

The content of Cu, Pb, and Zn was determined in all eighty-five samples by the method of soil extraction with aqua regia (ISO 22036:2012). A subset comprising sixty-eight soil samples, representative for all soil varieties has undergone full silicate analysis using lithium metaborate fusion sample preparation as described in the inter-laboratory method CLING BM-2:2013. Soil samples were pre-treated according to ISO 11466:2010 and analyzed in the laboratory of "Geochemistry" (the University of Mining Geology "St. Ivan Rilski", Sofia) by ICP - OES (ICP 720-ES Agilent Technologies). Quality assurance samples (blank and SMR - SOC001-30G) were analyzed every 15 samples. Accuracy and precision for all samples were below 10% and 15% respectively. Determination of pH corresponded to ISO 10390:2010. The modified method of Turin (Kononova, 1963) was applied for organic carbon content analysis.

Table 1. Threshold concentrations (precautionary, maximum permissible and intervention concentrations) of heavy metals in Bulgarian soils

Elements	pH (H_2O)	Precautionary concentrations (A)	Maximum permissible concentrations (B)		Intervention Concentrations (C)
			Arable Lands	Permanent grasslands	
Cu	<6.0	60	80	80	500
	6.0 – 7.4		150	140	
	>7.4		300	200	
Pb	<6.0	45	60	90	500
	6.0 – 7.4		100	130	
	>7.4		120	150	
Zn	<6.0	160	200	220	900
	6.0 – 7.4		300	390	
	>7.4		400	450	

Assessment of trace elements content

The assessment of Cu, Pb, and Zn content is based on the ISRIC methodology applied in SOVEUR's project which uses three degree scale (Van Lynden, 2000): light degree of pollution (L) – concentration of pollutant(s) between A and B values; moderate (M) - concentration of pollutant(s) between B and C values; strong (S) - concentration of pollutant(s) above C. Generally, soils with concentration of pollutant(s) below A value (precautionary concentrations) are unpolluted and considered ―clean". The threshold concentrations (determined in aqua regia as total concentrations, in mg kg^{-1}) adapted to Bulgarian legislation (Regulation 3/2008) are listed in Table 1.

Several concentration coefficients are calculated in order to assess the abundance of Cu, Pb, and Zn in soils: i) the concentration coefficient reflecting the abundance of element in soils compared to the local rocks (local geochemical background) – it is marked with Ccl and is calculated by dividing the average content of each element in studied soils with its average content in local rocks, ii) Ccr reflecting the element abundance compared to its median content (or the average value if the number of samples <100) in main types of Bulgarian rocks (Kuikin et al. 2001) iii) Ccs reflecting the ratio of element content in studied soils and the average element content in Bulgarian soils (Atanasov et al. 2000), and iv) Clarkes (global values estimated for the Earth's crust), coefficient CC (http://www.webelements.com/periodicity/abundance_crust).

In order to provide another approach for evaluation of metal contamination of soils a geoaccumulation index (Muller, 1969) is also calculated (equation 1):

$$I_{geo} = \log_2[Cn/1.5Bn] \qquad (1),$$

Where Cn is the measured concentration of the metal n in soils, Bn is the background value for the metal n. The mean of the content of element n in indigenous rocks was accepted as Bn. Igeo values are evaluated by a 7 point scale of Förstner et al. (1993) where: Igeo <0 = practically unpolluted, class 0; 0-1 = unpolluted to moderately polluted, class 1; 1-2 = moderately polluted, class 2; 2-3 = moderately to strongly polluted, class 3; 3-4 = strongly polluted, class 4; 4-5 = strong to very strong pollution, class 5 and > 5 = very strong pollution, class 6.

The range of geochemical background was introduced to reflect the natural variety of content of elements in indigenous rocks and is calculated by traditional formula, equation 2 (Gałuszka et al., 2015):

$$\text{Range of geochemical background} = \text{Mean value} \pm 2 \text{ standard deviations} \qquad (2)$$

Geoinformation

Software packages ENVI and ArcGIS are used for the analysis of satellite images ASTER and Digital Elevation Model and mapping. The methodology is described in detail by Ruskov et al. (2012) and involves data obtained by ASTER (Advanced Spaceborne Thermal Emission and Reflection Radiometer) Level 1B scene (ID ASTL1B 0207040929070208060920) calibrated with radiometric and geometric corrections. The image is georeferenced and digital SRTM (shuttle radar topographic mission) model of the relief with a resolution of 90 m is applied for 3D visualization of terrain. The ordinary kriging and spherical model of variogram function are used for data interpolation. The directions of anisotropy are 51 (Cu), 102 (Zn) and 106 (Pb) degrees.

Statistics

Statistical analysis of data was accomplished by Microsoft Excel™ statistical package. Standard error of the mean (SEM) is calculated by the formula of Browne (1979) (equation 3):

$$SEM = \sigma/\sqrt{n} \qquad (3)$$

Where, σ is the standard deviation (SD) of the sample; n – sample size.

Results and Discussion

Copper geochemistry

Abundance in litho - and pedosphere. The diversity drivers

The average Cu content in the Earth' crust is 68 mg kg^{-1} (www.webelements.com). In lithosphere, Cu is associated with medium acidic to mafic rocks, although increased copper content is also found in some sedimentary rocks, e.g. shales, sandstones. Further distribution of the element is dominated mainly by anthropogenic factors although the naturally occurring surface copper mineralization or active volcanism also takes place. Among human-induced distribution, the processing of copper ores and coal utilization are of dominant importance. Nriagu and Pacyna (1988) found that the annual man-induced mobilization of Cu into the biosphere can reach 150 thousand tons year^{-1}. According to Yudovich and Ketris (2005) the atmospheric emissions of copper, which mostly due to coal utilization in thermo-electric power plants amount to about 32%.

Distribution of technogenic copper in studied area depends not only on the content and the nature of Cu chemical bond in coal but also on combustion technology. Copper is mainly related to organic matter in coal used in the Bobov dol TPP (Kortenski, 2011) and quantitatively exceeds the Clarke concentration for coal (Table 2). Chukurovo coalfield is remarkable for high Cu content which is about 55-fold higher than Clarke's.

Table 2. *An average content of trace elements in coal utilized in the Bobov Dol TPP (mg kg^{-1})*

Parameter	Beli breg coalfield[1]	Stanyantsi coalfield[1]	Chukurovo coalfield[1]	Pernik coalfield[1]	Bobov dol coalfield[2]	**Average**	**Clarke[3]**
Cu	25,9	7,47	835,0	71,1	50,0	**197,9**	**15,0**
Zn	15,5	36,0	449,0	90,3	133,0	**144,8**	**18,0**
Pb	6,0	21,5	94,2	30,3	15,0	**33,4**	**6,6**

Legend: [1] – Kortenski (2011) data; [2] - Vassilev (1994) data; [3] - Ketris and Yudovich (2009)

Vassilev and Vassileva (1997) investigated the contents of trace elements in the coal and the deposited ash of eleven TPPs in Bulgaria, including Bobov dol TPP, and estimated that between 40 and 60% of the total copper content in coal is emitted into the atmosphere as a aerosol phase. This fact shows the TPP is a driver of the geochemical diversity in the region.

The copper content in studied soils varies in the range from 13.89 up to 53.72 mg kg^{-1} and is higher than 20.03 mg kg^{-1} (the local geochemical background) in 67% of the sampled sites (Table 3).

Regardless of the accumulation trend found in this study copper content is lower that the precautionary level, A (Table 1) revealing the attenuated development of contamination process. The negative mean value of geoaccumulation index (Igeo) also reveals the negligible input of technogenic copper (Table 4).

Table 3. *Basic statistical data on the content of microelements, organic carbon and pH in studied samples from the Bobov dol valley (n = 85, 2 and 3 respectively)*

Parameter	pH	Org. C (%)	Cu	Zn	Pb
			mg kg^{-1}		
Soils					
MIN	4.00	0.43	13.89	21.89	5.68
MAX	7.70	4.41	53.72	102.93	32.82
AVERAGE	5.94	1.29	27.04	57.93	21.96
MEDIAN	5.80	1.23	26.30	56.44	22.91
SD	1.04	0.55	6.99	14.89	5.93
SEM	0.11	0.06	0.76	1.61	0.64
Fly ash from TPP					
AVERAGE	7.7	0.82	32.40	32.21	10.50
Indigenous soil forming rocks					
AVERAGE	Not determined		20.03	46.60	6.07
MEDIAN			22.2	42.2	5.7
SD			5.41	7.68	1.29
Range of geochemical background			9.22 - 30.85	31.24 - 61.96	3.48 - 8.65

Data summarized in Table 4 portray the relative enrichment of the top soil with Cu. The average copper content in studied soils does not significantly diverge from the background content in Bulgarian soils (Ccs), but well displays the element accumulation. The content of Cu in local rocks coincides with a mean reference value for Bulgarian rocks which is an indication of the lack of Cu geochemical anomaly in the Bobov dol valley. Local rocks contained an equal amount of Cu with all types of metamorphites in Bulgaria (Kuikin et al., 2001) and, therefore, Cu content cannot be use as indicative in geologic-petrogenetic context.

Table 4. *Copper average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Para-meter	Content in studied soils	Local Back-ground value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Cu	27.04	20.03	1.35	20.0	1.35	24.0	1.13	68	0.40	-0.10

Legend: Ccl – concentration coefficient of element in studied soils accounting its average content in local rocks as reference value; Ccr – coefficient of concentration showing element abundance in soils compared to its median reference value in Bulgarian rocks; Ccs – element concentration coefficient in studied soils versus its background value (median) in Bulgarian soils; CC – concentration coefficient indicating the degree of element accumulation over the Clarke value; Igeo – index of geoaccumulation

Geospatial distribution and associations in studied soils

The geospatial distribution of copper within the studied area (Fig. 2) is characterized by frequently alternating zone with different element content. Enhanced concentrations of the element are observed in urban sites located on different distance from TPP. These cumulative areas shaped like islands are presumably owing to anthropogenic inputs originated from the domestic use of coal for heating. The technogenic objects as the fly-ash storage tank located close to TPP (next to Bd51-1 in the area of Vertic Luvisols) and the zone for ashes transfer to the tailing pond (points Bd89-1 and 89-3 located on Chomic Cambisol) are also richer in Cu, and reveal the formation of separate Cu-rich areas due to the influence of the TPP activity. Although Cu content in these areas is still lower than the average content in the Earth's crust it is up to 2-fold higher than the local background.

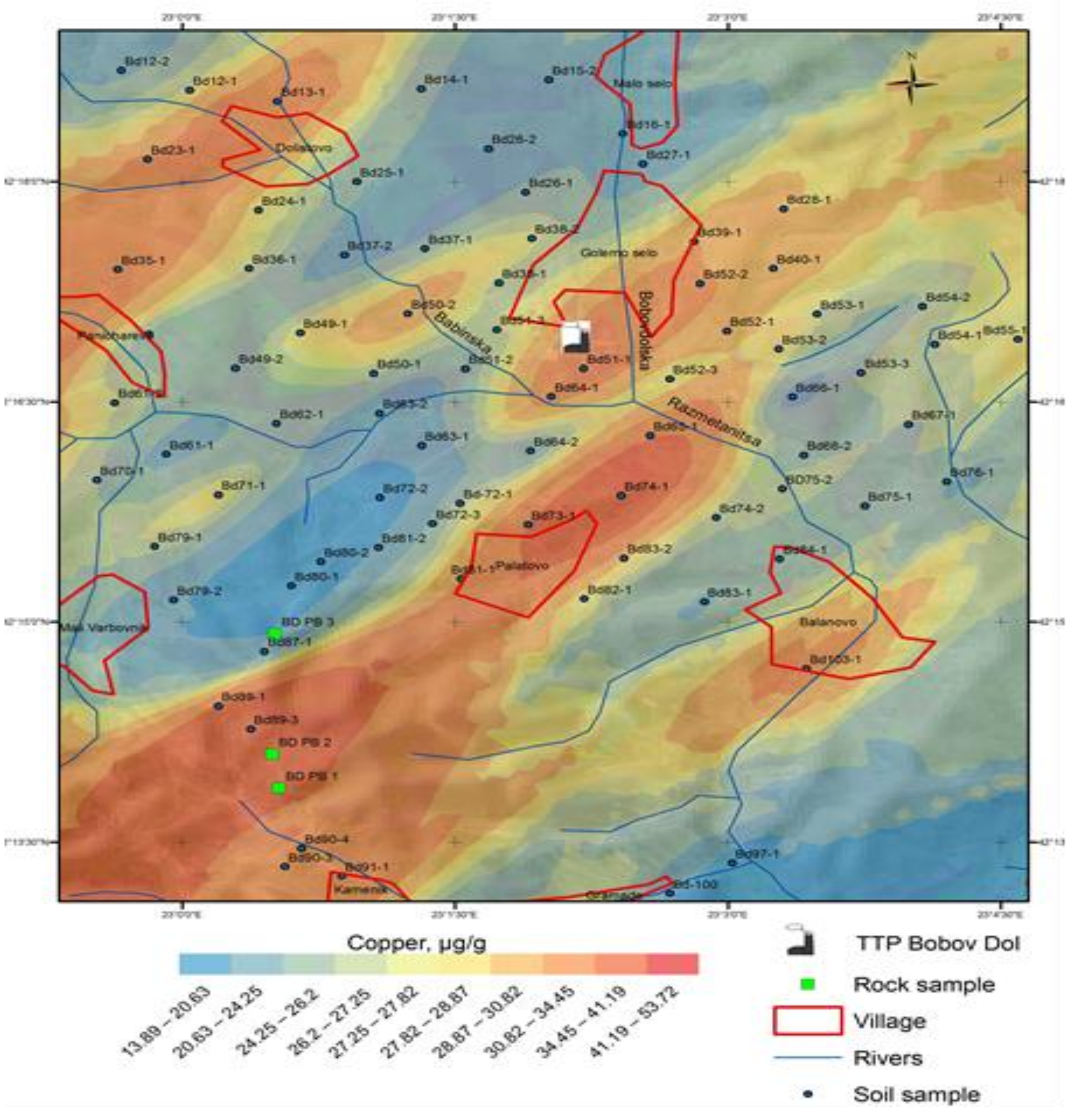

Figure 2. *Geospatial variability of Cu content in the surface layer of studied soils*

Copper distribution seems linked with few elements (Tables 5 and 6; Fig. 3). The content of total copper strongly correlates with the total contents of zinc and iron which are its major alloys in nature and ensure the simultaneous presence of these elements.

Table 5. *Correlation matrix of the content macro- and microelement (n = 68 points sampled)*

Parameter	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SO_3	SiO_2	TiO_2	Cu	Zn	Pb
Al_2O_3	1.00													
CaO	-0.56	1.00												
Fe_2O_3	0.70	-0.24	1.00											
K_2O	0.45	-0.57	0.35	1.00										
MgO	-0.25	0.50	0.05	-0.30	1.00									
MnO	0.25	-0.24	0.39	0.10	-0.13	1.00								
Na_2O	-0.17	-0.23	-0.29	0.28	-0.14	-0.10	1.00							
P_2O_5	0.13	0.22	0.30	0.02	0.18	0.24	0.11	1.00						
SO_3	-0.40	0.80	-0.18	-0.40	-0.01	-0.11	-0.22	0.16	1.00					
SiO_2	0.29	-0.86	-0.06	0.43	-0.70	0.13	0.31	-0.37	-0.57	1.00				
TiO_2	0.64	-0.56	0.58	0.28	-0.29	0.53	-0.01	0.02	-0.35	0.43	1.00			
Cu	0.48	-0.16	0.66	0.21	0.03	0.30	-0.15	0.21	-0.11	-0.04	0.40	1.00		
Zn	0.46	-0.25	0.57	0.39	-0.05	0.37	0.05	0.24	-0.18	0.08	0.49	0.74	1.00	
Pb	0.36	-0.44	0.26	0.33	-0.33	0.40	-0.02	-0.20	-0.32	0.44	0.54	0.38	0.59	1.00

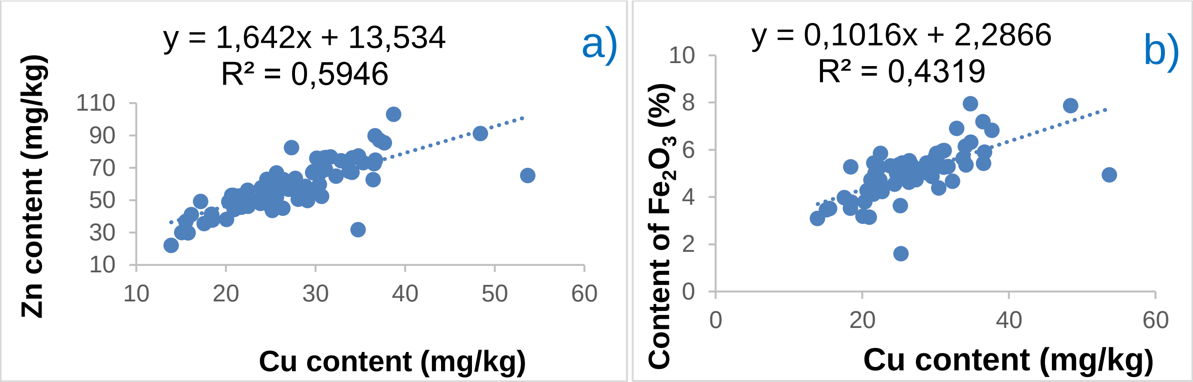

Fig. 3. The correlations between the contents of Cu and Zn (a) and Cu and total Fe (b)

The metal well correlated with iron extractable with aqua regia (Table 6) and hence discovers another analytical way to study Cu association in soils.

Table 6. Correlation matrix of the content of microelement and diversity drivers (n = 85)

Parameter	Cu	Zn	Pb	Fe	pH	Corg
Cu	1.00					
Zn	0.77	1.00				
Pb	0.37	0.45	1.00			
Fe	0.74	0.79	0.50	1.00		
pH	0.20	0.15	-0.36	-0.02	1.00	
Corg	-0.01	-0.02	-0.26	-0.12	0.19	1.00

The weaker correlation with Al suggests that the metal occurs in a non-diffuse form which is the most stable form of this metal in soils (Kabata-Pendias, 2000). The element occurs predominantly in the form of mineral compounds as revealed by the lack of correlation with organic carbon. Having in mind that siliciclastic rocks spread in the region are formed by inorganic processes the lack of correlation with organic carbon is not surprising. Moreover, it also accentuates the prevailing petrogenetic origin of Cu in studied soils. No statistical correlation was found between the content of total copper and pH (Table 6), which can be explained by the weak dependence of Cu geochemistry on pH. Baker and Senft (1995), Adriano (1986) and Kabata-Pendias (2000) suggest that the adsorption and mobility of copper (and lead) in uncontaminated soil is less dependent on pH, which partly explains Cu accumulation in studied soils.

Zinc geochemistry

Abundance in litho- and pedosphere. The diversity drivers

The average zinc content in rocks of the Earth's crust is 79 mg kg^{-1}. Increased concentrations are found in basic igneous rocks (100 mg kg^{-1}) and argillaceous sedimentary rocks (120-200 mg kg^{-1}, Alloway, 2008).

In unpolluted soils, the total zinc content is largely dependent upon the geochemical composition of the parent rock materials and fluctuates between 10-300 mg kg^{-1} at an average of 50 mg kg^{-1} (Kiekens, 1995). Zinc accumulates in soils as a result of both natural and anthropogenic processes, but the latter has a greater share. Many studies reported on pollution of soils located near the plants of metallurgical industry or ameliorated with fertilizers containing zinc (Kabata-Pendias and Mookherjee, 2007; Alloway, 2008). Nicholson et al. (2003) announced that Zn is the most cumulative element among all trace elements monitored in soils which accumulation rate could reach 217 g/ha $year^{-1}$.

Emissions from coal burning can influence lithogenic background of Zn in studied area (Table 2). Compared to the elements such as As, Co, Pb, which are highly volatile and almost completely pass into gaseous form, the formation of zinc gaseous phase is a complex process and depends on more factors - the combustion temperature, the excess of oxygen, and Zn chemical form (Yudovich and Ketris, 2005). For these reasons, the amount of emitted zinc varies considerably (Yudovich and Ketris, 2005) and can result in variable levels of zinc dressed soils (Alloway, 2008).

The content of zinc in studied soil surface layers widely varies from 21.89 to 102.93 mg kg^{-1} and in 79% of the analyzed samples exceeds the average content in the local bedrocks. However, compared with the soil background and precautionary values in Bulgaria studied soils are poorer in zinc (Tables 1, 3, 7).

Table 7. *Zinc average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Parameter	Content in studied soils	Local Background value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Zn	57.93	46.6	1.24	45.0	1.29	69.0	0.97	79	0.73	-0.05

High values of SD (Table 3) compromise to some extent the homogeneity of results but zinc accumulation in studied soils is still demonstrated (Table 7). Zinc is another element that tends to accumulate in studied soils but the degree of accumulation still slightly exceeds the background values according to the data in Table 7.

Geospatial distribution and associations in studied soils

Zones of zinc accumulation are located on hillsides of the Konyavska Mountain while the plane part of the area is occupied by sedimentary materials with low zinc content (Fig. 4).

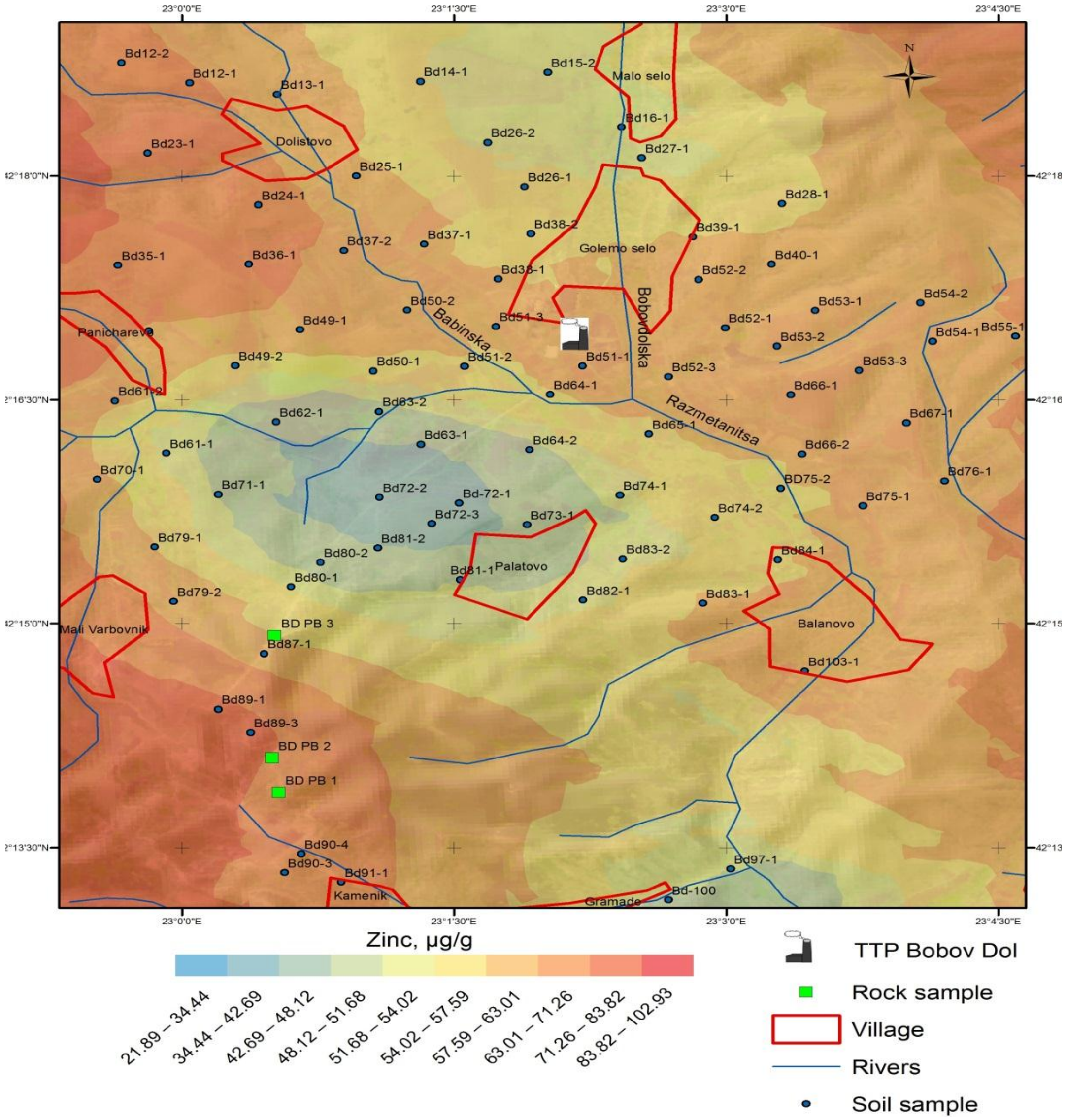

Figure 4. Geospatial variability of Zn content in the surface layer of studied soils

The area of Bobov dol TPP characterized with Zn content higher than the average but soils (Chomic Cambisol) surrounded the transfer facilities for ash (Bd89-1 and 89-3) are the most enriched. This shows again that TPP is a modern driver of geochemical diversity in the region.

Zinc also occurs in inorganic form - the correlation coefficient with organic carbon is negligible (Table 6). It linkage with Fe (Fig. 5), including iron extracted by aqua regia (Fig. 5b) seems stable and franklinite ($ZnFe_2O_4$), which contains both Fe^{3+} and Fe^{2+} (Lindsay, 1972), could be the mineral controlling the mobility of zinc in studied soils irrespectively of the other adsorption mechanisms.

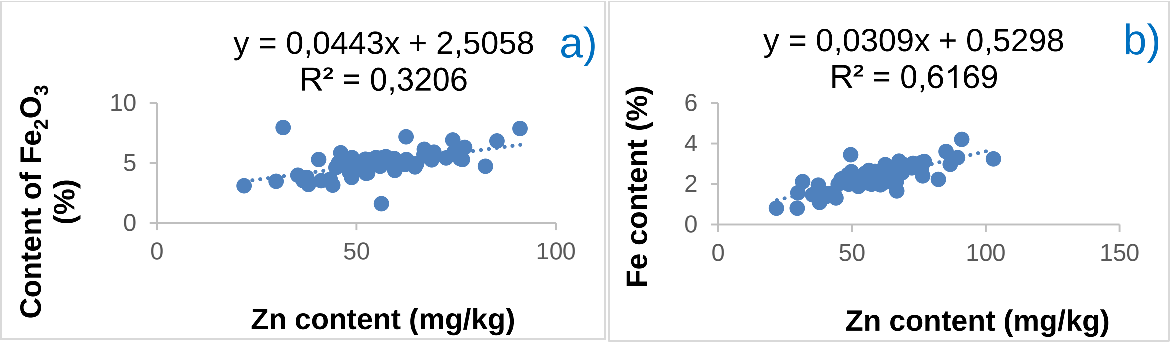

Figure 5. *The correlations between the contents of Zn and total Fe (a) and Zn and AR-extractable Fe (b)*

The association of Zn and Cu, which is the only one between trace metals is also a hallmark of studied pedogeochemical system (Fig. 3a). No correlation was found between the content of zinc and pH (Table 6), which could be regarded as a complex result of the specific sorption of the element (Orlov, 1995; Alloway, 2008) and low content of organic matter.

Lead geochemistry

Abundance in litho- and pedosphere. The diversity drivers

Lead content in the Earth's crust is not high (10 mg kg^{-1}, Table 8). The metal usually is prone to concentrate in acidic and moderately acidic igneous rocks (Kuikin et al., 2001; Kabata-Pendias and Mookherjee, 2007). In fact, regardless of the concentration, it occurs in almost all types of rocks (Aubert and Pinta, 1977).

Many processes in pedosphere immobilize Pb and retain it in soils and sediments (Davies, 1995; Pais and Benton, 1997; Kabata-Pendias, 2000), although the prime source of Pb in soils is parent rocks. Soil lead content widely varies and in some European soils reaches 970 mg kg^{-1} at an average of 32.6 mg kg^{-1} (Salminen et al., 2005). Kabata-Pendias (2000) reckoned 25 mg kg^{-1} for baseline concentration in top soil on the global scale.

Nowadays, lead accumulation in soils is irreversible process contributing to unparalleled perturbations of its biogeochemical cycle (Davies, 1995; Nriagu, 1990). The most significant anthropogenic sources of lead are metallurgical enterprises and thermal power plants utilizing fossil fuel (Pacyna, 1987; Kabata-Pendias and Mookherjee, 2007). The lead content in the TPP’s emission depends on the element content in coal, and on its chemical form (Xu et al., 2003; Yudovich and Ketris, 2005). The average concentration of an element in coal, the Clarke, is usually low - 6,6 mg kg^{-1} in lignite and brown coal and 9 mg kg^{-1} in black and anthracite (Ketris and Yudovich, 2009). Among coal that is utilized in the Bobov dol TPP predominated ones with lead content exceeding Clarke’s (Table 2).

3.3.2. Geospatial distribution and associations in studied soils

Lead content ranges from 5.68 to 32.82 mg kg^{-1} (Table 3) in studied soils and in 77% of sampled sites exceeds 18 mg kg^{-1}, i.e., the background (average) content of the element in Bulgarian unpolluted soils (Table 8).

Table 8. *Lead average content in different materials (mg kg^{-1}) and accumulation rates in studied soils*

Para-meter	Content in studied soils	Local Back-ground value	Ccl	Content in Bulgarian rocks	Ccr	Content in Bulgarian soils	Ccs	Content in the Earth's crust	CC	Igeo
Pb	21.96	6.07	3.62	21.0	1.05	18.0	1.22	10	2.20	0.39

This range indicates the lack of pollution according to ISRIC methodology but an assessment based on geoaccumulation index reveals the initial stage of contamination – Igeo class 1. Very high level of Pb accumulation is displayed by Ccl coefficient showing the enrichment rate of soils compared to background concentration in parent rocks.

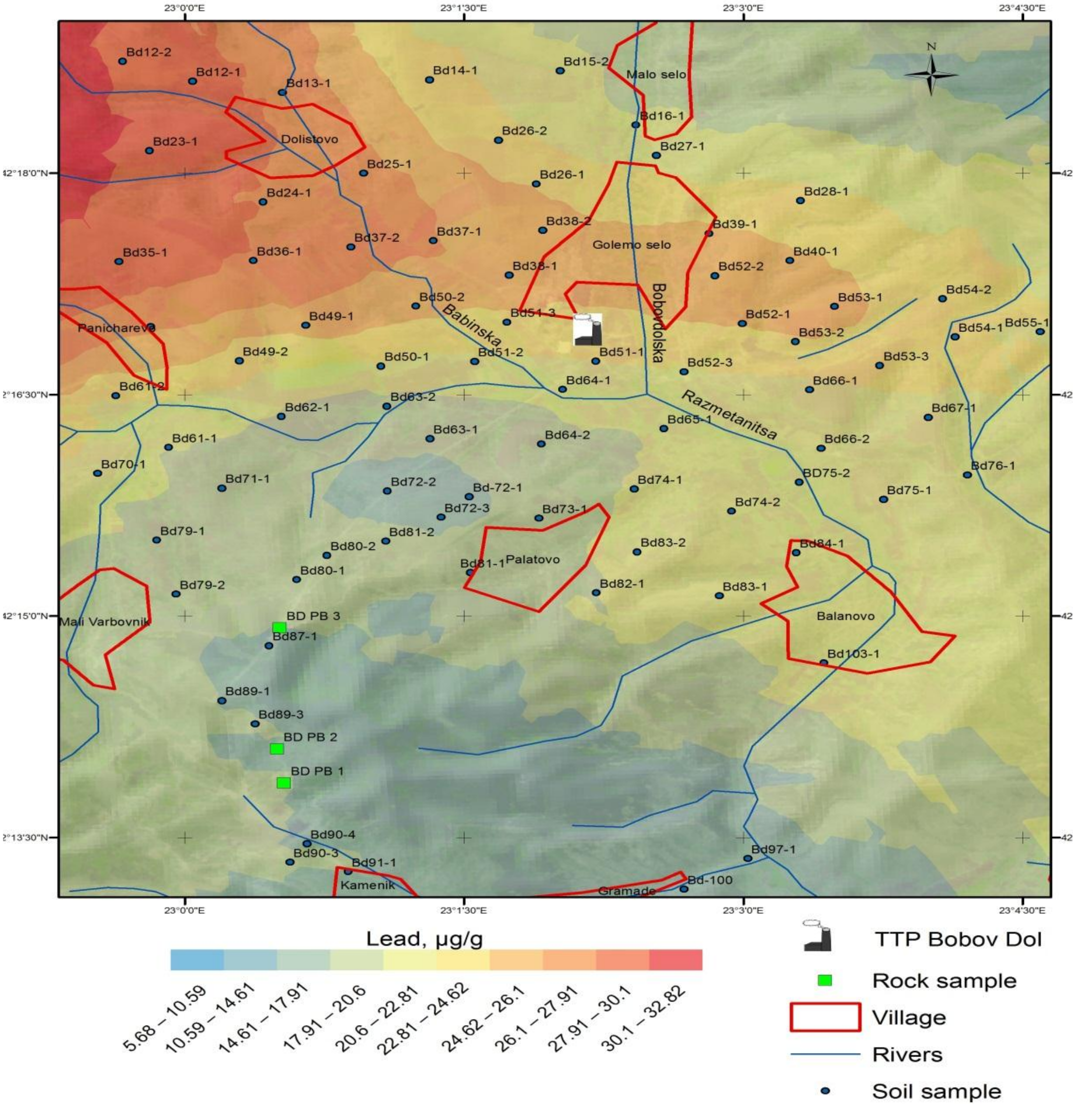

Figure 6. *Geospatial variability of Pb content in the surface layer of studied soils*

The higher content of Pb in soils located in various coal regions of Bulgaria established in previous studies validates the lower baseline level of the element in studied soils (Tsolova et al., 2014). Therefore, local geochemical hallmarks of rocks could better reflect the abundance of lead in studied region.

In geospatial aspect lead content decreased after the Razmetanitsa catchment and along the technogenic "corridor" for ash transport is close to the average value in studied soils. The highest concentrations are established northwest of Bobov dol TPP on the hillsides of the Konyavska Mountain (Fig. 6) where Chromic Luvisols prevailed. Besides the lithogenic nature, these concentrations may have a modern origin that could be assigned to human-induced redistribution of elements within the research area and beyond as well.

The lack of significant correlations with studied microelements is the reason to assume that Pb is distributed with other geologic suits in the Bobov dol valley. The calculated correlations between the content of lead and major elements give an indication of the prevalence of its inorganic forms, mainly associated with titanium, AR-extracted iron, silicon and negatively with calcium oxide (Tables 5, 6).

Obviously, Pb's affinity for Fe is stronger than the interactions with base metals such as Cu ($r = 0.37$) and Zn ($r = 0.45$). Dominant distribution of the mineral lead is confirmed by the lack of correlation with organic carbon. There is also no correlation accounted between the lead amount and pH (Table 6).

It should be noted that the aqua regia is maybe not the most appropriate reagent for analysis of technogenic lead originated in coal combustion. Czaplicka and Buzek (2011) while studied the dust emitted from Non-Ferrous Metallurgy Processes, found that the element presents mainly in two chemical forms: as salts, soluble in an alkaline solution or as compounds that produce plumbites (Na_2PbO_2) in reaction with sodium hydroxide.

Conclusions

The indigenous soil parent rocks create a negative geochemical anomaly with a lower content of studied elements compared to Clarkes (element content in the Earth's crust). In surface horizons of studied soils – different varieties of Luvisols, Cambisols, Fluvisols, Leptosols and Regosols the accumulation of Cu, Pb and Zn is verified by concentration coefficients accounting the element average contents in soil forming rocks.

Lead quickly accumulates in soils and becomes the only element with a positive index of geoaccumulation. It weakly associates with most of the studied elements but occurs allied to iron compounds extractable with aqua regia. Lead, therefore, tends to follow a separate mode of geospatial distribution which is influenced by geogenic factors and the aerosol emissions of TPP as well.

Copper accumulation is also evidenced by geochemical hallmarks included in the study. It, however, is more strongly affected by technogenic receipts and dominated in urban and technogenic zones under the form of oval spots. Konyavska Mountain is the domain of Zn revealing an altitudinal gradient of distribution. Its accumulation proceeds slowly in topsoil, but Zn is still the most abundant element in studied soils from the Bobov dol valley.

The litho-petrogenetic pattern of geochemical assemblages still predominated in studied soils wherein iron manifests the greatest affinity for studied elements. Soil medium reaction (pH) and organic carbon do not distinctly control the distribution and accumulation of Cu, Pb, and Zn. The lack of statistical correlation with organic carbon resulted from the siliciclastic nature of soil parent rocks and also reveals the prevailing geogenic origin of studied elements.

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