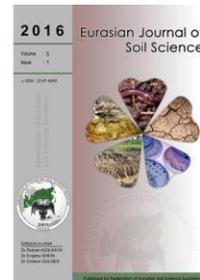




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Geochemical pattern of soils in Bobovdol valley, Bulgaria. Assessment of Cd and Co contents

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Abstract

The chemical composition of soils spread in the Bobov dol valley was studied in order to reveal the natural and anthropogenic patterns of Cd and Co spatial distribution. A sampling procedure based on the irregular grid of points and validated analytical methods were used in the field and laboratory studies. It is found that Cd content varies from 0.21 to 0.90 mg kg⁻¹ in studied soils and the average value of 0.55 mg kg⁻¹ coincides with concentration demarcating soil pollution (0.5 mg kg⁻¹). Co content ranges from 2.22 to 15.76 mg kg⁻¹ and in 70 % of sampled points exceeds the natural background content of 7.8 mg kg⁻¹ found in local rocks. Still, Cd enrichment of studied soils is more significant than Co's with coefficient of Clarke concentration of 3.67. Hence, the secondary deposition of studied elements as a result of the Bobov dol Thermal power plant air emissions is verified by results obtained. The spatial distribution of Cd and Co is featured with an altitudinal gradient in deposition and a trend of quantitative depletion in the South of Plant. Soil organic matter and pH have no influence on the content and spatial distribution of studied elements. Elements iron affinity governs their geochemical linkage in soils although cobalt occurs allied with aluminum and titanium.

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Introduction

The study of distribution of trace elements in soils of Bulgaria is still concentrated in areas affected by industrial activities, such as mining (Marinkina, 1999; Jeleva, 2008; Hristova, 2013) and processing of mineral resources (Misheva et al., 2007; Nikova et al., 2013). Most of these studies are designed to assess soil contamination and include the surface 30-40 cm of soil profile (Petrova, 2009; Dinev, 2012). This approach is used in monitoring programs, but does not provide enough information for three-dimensional (3-D) geochemical characteristics of soils and the cycles of trace elements in pedosphere.

Geochemical maps designed by the grid sampling procedure to reflect the spatial distribution of chemical elements in soils may be used for predicting the extension of soil degradation and its negative impact on the interacting environmental components. Detailed information on the natural variability of background concentrations of chemical elements in soils and the quantitative database allow imaging the geochemical diversity (Jurlik, 2001). In this regard, the elements cadmium and cobalt are of great interest in Bulgaria where there is a limited knowledge of their distribution and availability in the pedosphere.

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A large number of studies reveal the role of cadmium in geochemical processes (Krauskopf, 1956; Jones, 1973). However, its geochemical fate in pedosphere and especially in soil surface layer is still not well understood (Gong et al., 1977). It is known that cadmium persists only in the +2 valence state in soils and goes readily into solution on weathering. The enrichment of soils with cadmium occurs primarily through the adsorption and/or complexation of cadmium onto organic matter followed by the accumulation of organic debris in the depositional environment. Cd mobility is affected mainly by the pH and oxidation potential (Kabata-Pendias and Pendias, 1984). It is most mobile in acidic soils within the pH range 4.5 - 5.5 and is rather immobile in alkaline soils, wherein CdHCO_3 prevails. Studies of cobalt geochemistry in terrestrial environments have also received a lot of attention. However the case studies of cobalt variability and accumulation in soils could contribute to the better knowledge of element global cycling. This article deals with the geochemical patterns of soils located in the vicinity of the "Bobov dol" Thermal power plant, Bulgaria, emphasizing on the amount and spatial distribution of Cd and Co in order to determine their geochemical behavior, associations and origin in soils.

Material and Methods

Site description

The present study is initiated to determine the influence of Bobov dol Thermal power plant (TPP) on Cd and Co contents and distribution in soils surrounding the Plant (Figure 1). The choice of this area is consistent with a few facts:

- 1) "Bobov dol" TPP is the only major source of trace elements in the researched area, which excludes the cumulative effect of other industrial pollutants. This plant is one of the oldest in Bulgaria (it was working at full capacity since 1975) and its impact on the geochemical status of surrounding soils is of incontestable interest.
- 2) Soils are mainly developed on sandy clay conglomerates from motley under-coal-bearing formation of Bobov dol graben and thus provide very similar lithology and geochemistry of soil parent materials.
- 3) The geochemical composition of lignite and brown coal burned in "Bobov dol" TPP is already known as well as the Clarkes – the average element contents in coal (Kortenski, 2011).
- 4) Almost all agricultural lands there are cultivated, which determines the socio-economic importance of the region.

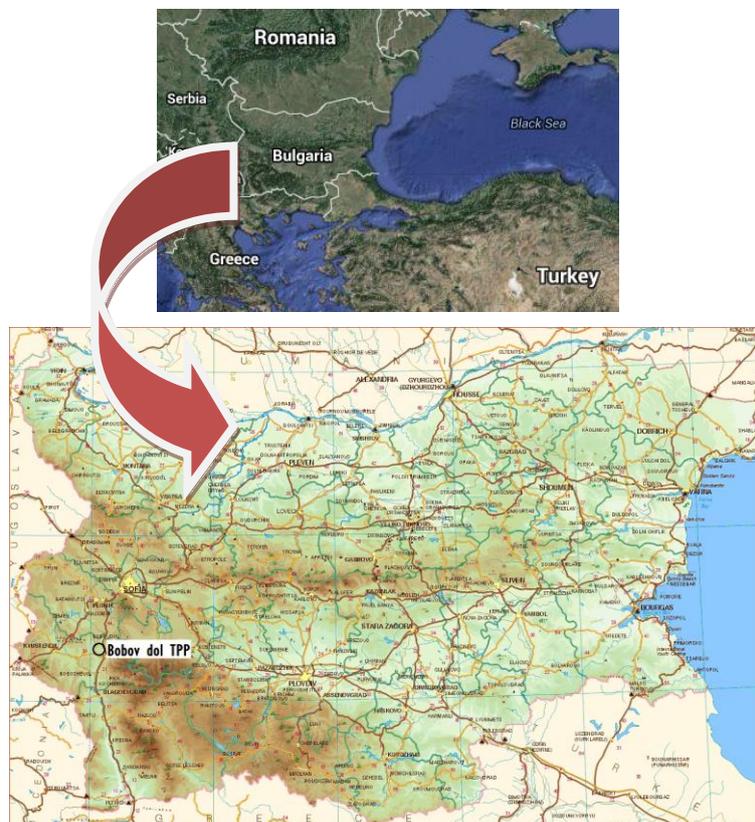


Figure 1. Location of the Bobov dol TPP

Sampling

The spatial distribution of trace elements in soils is studied by irregular network. The grid tightly covers about 5 km zone around the TPP. Soil cover is present by: Endocalcic Chromic Luvisols; Chromic Cambisols, Vertic Luvisols, Umbric Leptosols, Eutric Fluvisols and Colluvic Regosols ([WRBSR, 2014](#)).

Samples were taken at a depth of 30 cm, since the surface 30 cm soil layer is the most vulnerable to anthropogenic enrichment with heavy metals ([Dinev et al., 2008](#)) and is the most active part of the soil. For the determination of background elements contents in indigenous (soil parent rocks) three samples located in the southern part of the region, near by a conveyor belt to a tailings pond "Kamenik" were taken.

Analyses

The concentration of Cd and Co was determined by the method described in ISO 22036:2012. Analysis of samples pre-treated according to the ISO 11466:2010 was carried out in the laboratory of "Geochemistry" (University of Mining Geology "St. Ivan Rilski", Sofia). 30 soil samples were set for full silicate analysis implemented in agreement with the inter-laboratory method CNILG BM-2: 2013. The content of macroelements was determined by the ICP 720-ES (Agilent Technologies) after lithium metaborate fusion sample preparation.

The pH was determined potentiometrically in compliance with ISO 10390:2005. Organic carbon content was analyzed by the modified method of Turin ([Kononova, 1963](#); [Filcheva and Tsadilas, 2002](#)).

Assessment of trace elements content

The concentration coefficients of Cd and Co are calculated with the average elements content in local rocks (local geochemical background) marked as Ccl, as well as in Bulgarian rocks using data of [Kuikin et al. \(2001\)](#) - marked as Ccr, in Bulgarian soils - Ccs with data of [Atanasov \(2003\)](#), and in the Earth's crust - Cc - data from www.webelements.com.

Geoinformation

Remote sensing data: 11 ASTER (Advanced Space borne Thermal Emission and Reflection Radiometer) Level 1B scenes obtained on 2002/07/04 is used. The calibrated ASTER Level 1B data represent the TOA (top of atmosphere) radiance with radiometric and geometric corrections. ASTER scene ID is ASTL1B 0207040929070208060920. The image is georeferenced in projection UTC North Zone 35, WGS-1984. Digital model of the relief created by the space shuttle Terra in February 2000, known as SRTM (shuttle radar topographic mission) with a resolution of 90 m is applied for 3D visualization of terrain.

Geostatistical methods are used for spatial interpolation of points with unknown contents. Preliminary assessments of the difference between the values were made with variogram analyses using directional semivariograms. The ordinary kriging and spherical model of variogram function are used for interpolation. For each element were investigated the statistical properties of dataset and the global trend (second order) in data was removed. It was also made assessments of the output surfaces. Soil geochemical maps were made with ArcGIS.

Statistics

Microsoft Excel software is used for statistical analysis of data. Standard error of the mean (SEM) is calculated by commonly accepted formula.

$$SEM = \frac{\sigma}{\sqrt{n}}$$

Where, σ is the standard deviation of the population; n - a population size.

Results and Discussion

The levels of cadmium in soil widely vary from 0.06 mg kg⁻¹ in weak developed soils to hundreds of mg/kg in the vicinity of pyro metallurgical Plants ([Waldron, 1980](#)). The highest amount with average level of 7.5 mg kg⁻¹ are found in soils developed on shale ([Lund et al., 1981](#)) contrary to soils on sandstone and basalt, which have the lowest average concentration of 0.84 mg kg⁻¹. [McBride \(1994\)](#) announced the concentrations of soil Cd exceeding 0.5 mg kg⁻¹ suggest a soil contamination.

The average cadmium content in studied soils slightly differs from the lithogenic threshold of 0.5 mg kg⁻¹, but in all grid points is higher than its average value in Bulgarian soils (Table 1, 3).

Table 1. Statistic data of studied parameters

	C _{org}	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SO ₃	SiO ₂	TiO ₂	Cd	Co	Zn	pH
Min	0.42	8.86	1.18	3.01	1.41	0.80	0.04	0.97	0.07	0.03	36.58	0.36	0.24	2.22	21.6	4.0
Max	4.41	16.46	3.48	7.32	2.74	11.38	0.11	2.50	0.22	0.88	70.46	0.86	0.90	15.76	96.5	7.9
Average	1.21	14.28	3.01	4.62	2.26	2.08	0.07	1.77	0.12	0.06	63.44	0.65	0.55	8.71	54.0	6.0
Median	1.15	14.74	1.66	4.64	2.29	1.70	0.07	1.80	0.11	0.03	65.49	0.67	0.51	8.90	52.7	5.9
SD	0.54	0.96	2.36	0.59	0.22	0.89	0.02	0.39	0.03	0.06	4.80	0.08	0.13	2.14	13.60	1.04
SEM	0.06	0.17	5.48	0.11	0.17	0.16	0.00	0.07	0.01	0.01	0.88	0.01	0.01	0.23	1.45	0.11

The spatial distribution of Cd is characterized by frequently alternating zones with different element content (Figure 2). The highest accumulation of Cd goes off on the hillsides of Konyavska Mountain showing an altitudinal gradient in deposition. The last trend is also documented by (Van de Velde et al., 2000; Planchon et al., 2002; Barbante et al., 2003; Lee et al., 2008). It is reasonable to assume that the areas of higher content (> 0.5 mg kg⁻¹) reflect a technological abundance of Cd while lower in concentrations areas are its lithogenic zones. In the nearest to the Plant area with lowest cadmium content is situated the old reclaimed ash-pond (Bd 72-1, Bd 72-2 and Bd 72-3). Zinc content is also low in reclaimed zone (21.60-30.70 mg kg⁻¹) and reveals the lithological pattern of soils existed in the valley prior to ash-pond construction. Furthermore, due to the similarity in their geochemistry, Cd²⁺ usually replaced Zn²⁺ in zinc minerals which are the most important host for cadmium (Adriano, 1986; Alloway, 1995; Minkina et al., 2014). This process catalyzed by the additional supplement of Cd (as a result of Plant emissions) could explain the established spatial fluctuations in Cd content (Figure 2).

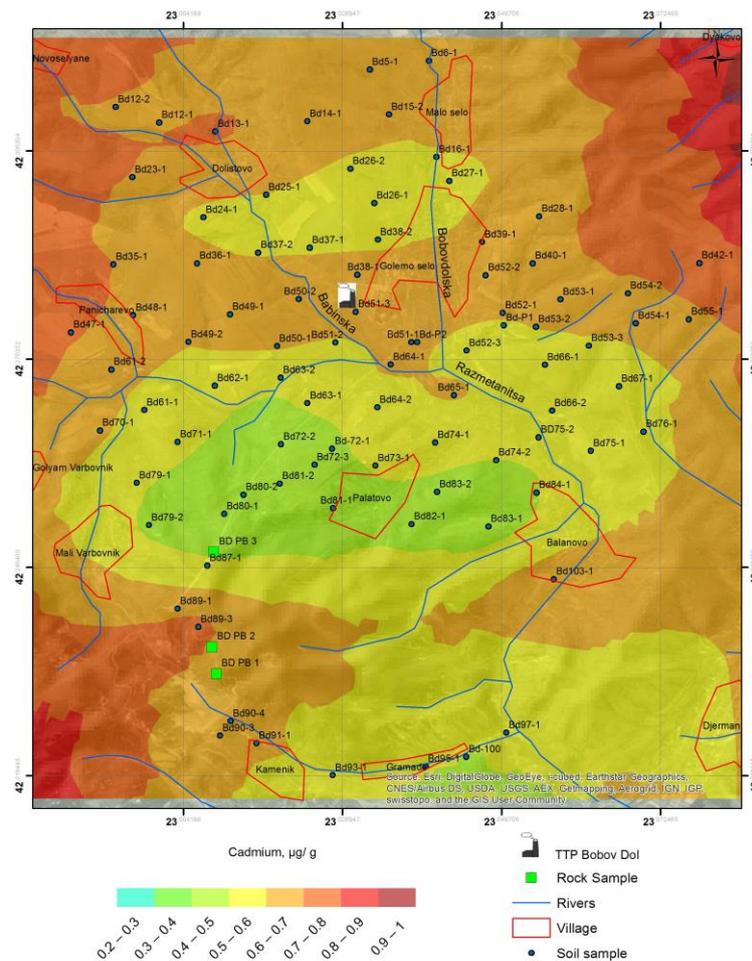


Figure 2. Spatial variability of Cd content in the surface layer of studied soils

Although, the correlation between Cd and Zn is not high ($R^2=0.34$), probably due to the technogenic origin of Cd accumulation established in surface layers of studied soils (Figure 3).

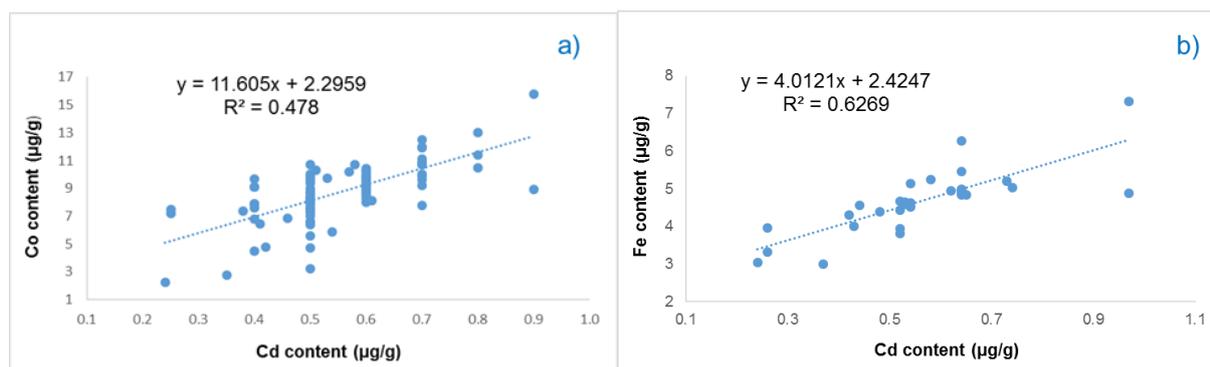


Figure 3. Correlation between the content of Cd and Co (a), Cd and Fe (b)

Cadmium shows slight affinity to Al (expressed as Al_2O_3 content, $R^2=0.44$) and Ti (TiO_2 , $R^2=0.46$) but well correlates with Fe (Figure 3). With Co whose distribution is managed by secondary processes Cd does not significantly correlated (Figure 3).

In order to evaluate the content of trace elements in studied soils various concentration coefficients are calculated (Table 2). Data obtained in this study were compared with the average content of these elements in Bulgarian soils and in the Earth's crust - Clarke values (Table 2).

Table 2. Average contents of trace elements in various objects (mg/kg) and concentration coefficients in studied soils

	Content in studied soils	Local background	Ccl	Content in rocks	Ccr	Content in soils	Ccs	Content in the Earth's crust	Cc
Cd	0.55	0.0	-	2.3	0.24	0.21	2.62	0.15	3.67
Co	8.71	7.8	1.12	10.0	0.87	13.0	0.71	30.0	0.29

Legend: Ccl – coefficient of concentration accounting local rocks content; Ccr – coefficient of concentration accounting average content in main rock types; Ccs- concentration coefficient accounting soil content; Cc- Clarke coefficient

The results in Table 2 show that Cd is not found in local rocks presuming that soil cadmium content has not lithogenic origin and can be consider as a result of technogenic deposition. According to Ccs the accumulation of Cd in studied soil varieties is well pronounced and exceeded the background values in Bulgarian soils. These data confirms the findings of [Lalor et al. \(1995\)](#) that cadmium is predominantly accumulated in soil surface layers and the processes responsible for its accumulation are: adsorption by soil humus and deposition of atmospheric sediments, fertilizers and plant debris.

Regardless of Cd low average content in the Earth's crust it is extensively distributed in the lithosphere - in shale, igneous rocks, coal, sandstone, limestone, lake and ocean sediments and soils ([Waldron, 1980](#)). Its levels in igneous and metamorphic rocks widely vary but rarely exceed 0.5 mg kg^{-1} . Nowever, in sedimentary rocks, carbonate and sandstone it occurs in the lowest values (0.035 mg kg^{-1}). The accumulation of Cd to potentially hazardous concentrations in some coal and crude oil deposits may also occur ([Ketris and Yudovich, 2009](#); [Kortenski, 2011](#)).

Table 3. Average content of trace elements in coal burned in TPP "Bobov Dol" (in mg kg^{-1})

Parameter	Beli breg coalfield ¹	Stanyantsi coalfield ¹	Chukurovo coalfield ¹	Pernik coalfield ¹	Bobov dol coalfield ²	Average	Clarke ³
Cd	1.4	2.2	1.6	3.2	nd	2.1	0.24
Co	0.8	2.2	12.4	43.1	8.0	13.3	4.2

Legend: ¹ – [Kortenski \(2011\)](#) data; ² - [Vassilev \(1994\)](#) data; ³ - [Ketris and Yudovich \(2009\)](#); nd – no data

The cadmium content in coal is cursory studied. This is a consequence of low Cd content which requires sophisticated techniques for determining the parts per billion levels of concentration especially as routine analysis ([Lee and Tebo, 1994](#)). The average Cd content in coal varies between 0.2 and 0.24 mg kg^{-1} , depending on the degree of coalification ([Ketris and Yudovich, 2009](#)). In coal incinerated in TPP Bobov dol, cadmium content exceeds Clarke value 6 to 13 times and could provoke a danger to the environment (Table 3). During the high temperature combustion of coal cadmium forms volatile compounds and is released into

the atmosphere, either in the form of gas (metallic Cd and oxides), or condensed onto the submicron dust particles (Yudovich and Ketris, 2005; Kabata-Pendias and Mukherjee, 2007). In soils technogenic cadmium forms simple inorganic compounds (oxides, hydroxides, chlorides, sulfates depending on the soil pH and Eh) or organo-metallic complexes which are accessible to plants (Kabata-Pendias and Mukherjee, 2007). Some plants, such as lettuce, carrots, tobacco accumulate significant quantities of Cd and became a serious threat to human's health.

Sources of cadmium in the atmosphere are quite diverse and can be either natural (volcanic activity, forest fires, wind transported soil or rock particles) or anthropogenic (mining and processing of lead and zinc ores, combustion of coal, oil and waste products, the production of batteries and pigments, Hutton, 1982; Kabata-Pendias and Mukherjee, 2007). Among them, metallurgical and thermal power plants utilizing solid or liquid fuel are the most significant Cd emitters in the atmosphere (Kabata-Pendias and Mukherjee, 2007).

With relation to Co geochemistry a few features should be noted.

Cobalt displays chalcophile and siderophile properties and associates with the iron sulphides, arsenopyrite and pyrrhotite. It is also present as an accessory component in olivine, pyroxene, amphibole, mica, garnet and sphalerite and in oxide accessory minerals, such as magnetite (Ure and Berrow, 1982). It forms several rare minerals: smaltite (Co,Ni)As_{2-2.5}, cobaltite (Co,Fe)AsS and linnaeite (Co,Ni)₃S₄.

Cobalt, together with Cr and Ni, is indicative of mafic rocks. It replaces Fe²⁺ and Mg²⁺, which are similar in charge and ionic radius, and hence accumulates in mafic rocks (Wedepohl, 1978). Generally, the average abundances of Co in different rocks types cited by Mielke (1979) is: ultramafic - 150 mg kg⁻¹; basaltic - 48 mg kg⁻¹; granitic 1-7 mg kg⁻¹; syenite 1 mg kg⁻¹; an average bulk continental crust abundance of 29 mg kg⁻¹, and 10 mg kg⁻¹ in the upper continental crust (McLennan and Murray, 1999).

Cobalt is immobile during metamorphism (Condie, 1976; Nicollet and Andriambololona, 1980). Minerals such as quartz, feldspar and pure calcium carbonate contain low amounts of Co (<2 mg kg⁻¹), as well as sandstone and limestone. In sedimentary rocks, Co is concentrated in the fine-grained fractions and tends to vary with the Fe and Mn content (Vine and Tourtelot, 1970). Formation of organo-metallic complexes is not an important enrichment mechanism for Co in sedimentary processes.

Cobalt is most mobile in the surface environment under acidic and reducing conditions (Qian et al., 1998). Cobalt does not form residual silicate minerals in soil. The average concentration of Co in European soils is quoted as 8.91 mg kg⁻¹ (extracted with aqua regia) with a range from <1 to 255 mg kg⁻¹ (Salminen et al., 2005). Koljonen (1992) announced 10 mg kg⁻¹ as a total content in soil worldwide.

Human induced sources of cobalt include coal combustion, special steels production, fertilizers, lead, iron and silver mining and processing (Reimann and Caritat, 1998). Ecological problems arose from pollution with technogenic Co are generally less significant than those associated with some other heavy metals (Cole and Carson, 1981). Atmospheric cobalt, derived from combustion sources is assumed that exists primarily in oxide form (Schroeder, 1987). Cobalt and its inorganic compounds are not volatile.

Yudovich and Ketris (2005) adduced data of coal with high amount of Co. The influence of rich in Co coal on the element spatial distribution strongly depends on the form of its presence in the coal and the temperature in the combustion chamber. Cobalt as a siderophilic metal has high affinity to sulfur and in coal often participates as isomorphic alloy of sulphide minerals (mainly pyrite). In some coal cobalt is also present in association with organic matter (Kortenski, 2011). Yudovich and Ketris (2005) noted that in low temperature combustion (1000-1200°C) the element is separated from organic matter and partly from sulfides, and then usually condensed in the form of Co-containing spinel in cinder-slag portion of the ashes. At high temperature combustion (1200-1600°C) cobalt goes into the gaseous phase, where either partially condenses on fine ash particles, or is emitted into the atmosphere. Vassilev and Vassileva (1997) found that Co amount in the volatile fraction ranges between 10 and 20 % of the concentration of cobalt in the coal.

Data summarized in Table 3 show that some of coal burned in the Plant are characterized with high concentrations of cobalt and its average contents exceeds over 3 times Clarke, determined by Ketris and Yudovich (2009).

In studied soils Co content ranges from 2.22 to 15.76 mg kg⁻¹ and the extension of values is greater than 4.5 to 12 mg kg⁻¹ issued by Kabata-Pendias and Mukherjee (2007) for soil surface horizons. Soils containing

<0.5–3 mg kg⁻¹ are considered cobalt-deficient and risky to ruminants breeding (Becker and Smith, 1951; Boikat et al., 1985; Keener et al., 1949)

The content of cobalt is higher than in local rocks and in 70 % of points exceeds 7.8 mg kg⁻¹ (Table 1). Compared to the average content in Bulgarian soils it is somewhat lower reflecting the negligible impact of TTP "Bobov dol" emissions (Table 2).

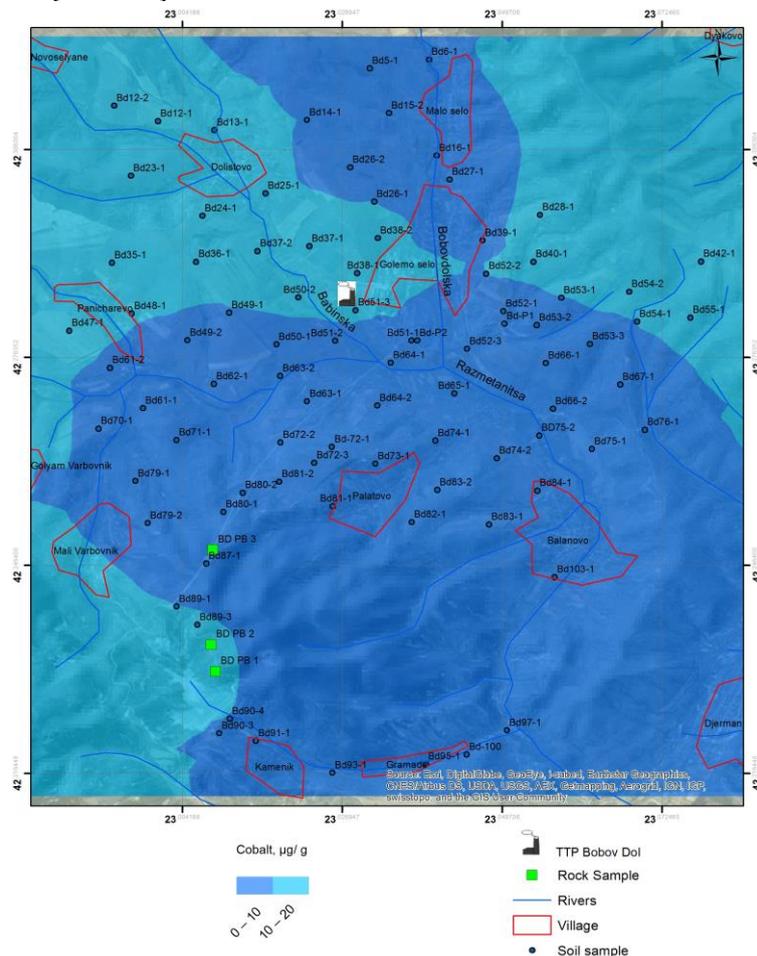


Figure 4. Spatial variability of Co content in the surface layer of studied soils

Cobalt slightly accumulates in studied soils (Ccl, Table 2), and this reflected in its quite uniform spatial distribution along the studied area. In general, cobalt content decreases from North to South and likewise Cd its lowest amount is found in the reclaimed area.

Several significant correlations of Co are found with: aluminum ($R^2=0.63$), titanium ($R^2=0.65$) and iron (Figure 5). Its association with zinc (Figure 5) presumably originates from the secondary processes or diagenesis.

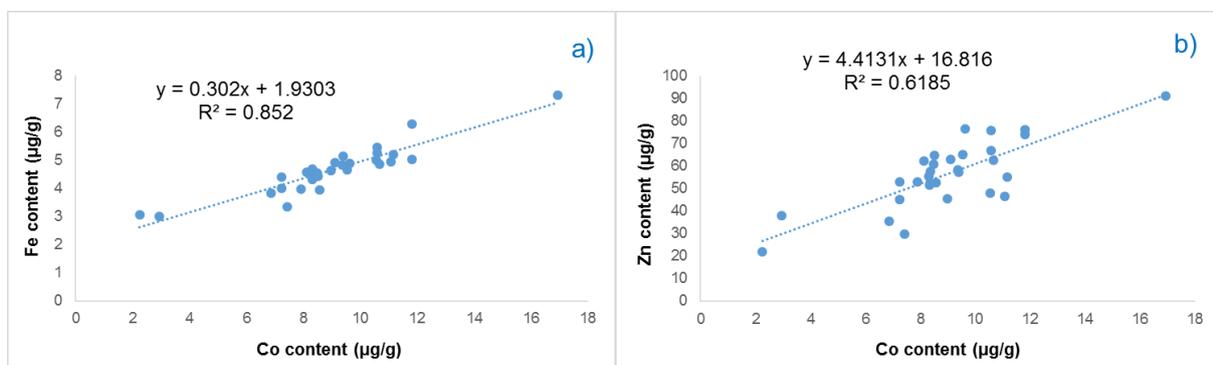


Figure 5. Correlation between the content of Co and Fe (a), Co and Zn (b)

Soil chemical factors, such as pH and organic matter have no influence on the content and spatial distribution of cobalt.

Conclusion

Cadmium is exogenous element in studied soil varieties supplied by anthropogenic activities. It is distinctly accumulates in soil surface layers regardless of the soils organic carbon content and pH. The element iron affinity governs its geochemical linkage in soils although it occurs allied with aluminum, titanium and cobalt.

Cobalt, likewise cadmium forms the same geochemical associations, but the correlations between elements are much stronger. Cobalt more slightly accumulates in studied soils but its content is somewhat lower than Clarke and background value for Bulgarian soils. It prevails in the northern part of the area occupied by Konyavska Mountain and gradually disperses to the South.

Great differences between the content of cadmium and cobalt in soil parent rocks from researched area and the summarized average values of the rocks in Bulgaria does not allow a firm conclusion about elements typomorphic accumulation to be made.

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