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Original scientific paper

DISTRIBUTION OF COBALT IN SOIL FROM KAVADARCI AND THE ENVIRONS

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A b s t r a c t: The results of the study of spatial distribution of cobalt in surface soil and subsoil over of the Kavadarci region, Republic of Macedonia, are reported. From the investigated region (360 km^2) in total 344 soil samples from 172 locations were collected. At each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil soil (20–30 cm). Inductively coupled plasma – mass spectrometry (ICP-MS) was applied for the determination of cobalt. Data analysis and construction of the map were performed using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. It was found that for both topsoil and subsoil the median and average values are 15 mg/kg, ranges between 6.7 and 58 mg/kg. The highest content of cobalt is present in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and Flysch (E) – Eocene upper flysch zone (on the northern part) and the lowest in the soils from the Holocene alluvium of the rivers Crna Reka and Vardar. There are no significant differences between the surface and subsoil in terms of its average quantities. It was found that the critically high contents are related primarily to high contents of cobalt in the sampling points from the western part of the investigated region. The contents of cobalt are higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

Key words: soil; cobalt; pollution; Kavadarci; Republic of Macedonia

INTRODUCTION

Soils differ widely in their properties because of geologic and climatic variation over distance and time. Even a simple property, such as the soil thickness, can range from a few centimeters to many meters, depending on the intensity and duration of weathering, episodes of soil deposition and erosion, and the patterns of landscape evolution. Beside this, soils have a unique structural characteristic that distinguishes them from mere earth materials and serves as a basis for their classification: a vertical sequence of layers produced by the combined actions of percolating waters and living organisms (Kabata-Pendias and Pendias, 2001). The presence of substances in soil that are not originated from naturally processes is of great public concern. Many of these chemicals have been found to be carcinogens or may accumulate in the environment with toxic effects on the ecosystems. Although human exposure to these substances is primarily through inhalation or drinking water, soils play an important role because they affect the mobility and biological impact of these toxins.

The abundance of heavy metals in soil has been increased dramatically by the accelerated rate of extraction of minerals and fossil fuels and by highly technological industrial processes. Most of the metals were typically found at very low total concentrations in pristine waters – for this reason they often are referred to as trace metals. Rapid increases of trace metal concentrations in the environment are commonly coupled to the development of exploitative technologies. Soils contain trace elements of various origin (Kabata-Pendias and Pendias, 2001): lithogenic elements which are directly inherited from the lithosphere, pedogenic elements which are of lithogenic origin, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes or anthropogenic elements which are all those deposed into soil as direct or indirect results of man's activities. The behaviour of trace elements in soil and in consequence their bioavailability differs as to their origin. However, regardless of the forms of the anthropogenic heavy metals in soil, their phytoavailability is significantly higher than those of pedogenic origin.

Urban pollution with heavy metals has recently become a subject of many studies (Šajn et al., 1998; Šajn, 2004; Chen et al., 2005; Bretzel and Calderisi, 2006; Diawara et al., 2006; Kaur and Rani, 2006; Davidson, 2006; Stafilov et al., 2008). The regional contamination of soil occurs mainly in industrial regions and within centres of large settlements where factories, motor vehicles and municipal wastes are the most important sources of trace metals (Kabata-Pendias and Pendias, 2001). Because of heterogeneity and ceaseless changing of urban areas, it is necessary first to understand the natural distribution and the methods for distinguishing man-made anomalies in nature. However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities can increase the pollution. It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination (Razo et al., 2004; Li et al., 2005, 2006; Tembo et al., 2006; Cappuyns et al., 2006), including soil contamination due to nickel smelter plants or another industrial activities (Krishna et al., 2005; Simeonov et al., 2005; Everhart et al., 2006; Mico et al., 2006).

The subject of this study is to present the results of a spatial distribution of cobalt in surface and subsurface soil over of the Kavadarci region, Republic of Macedonia, known for its ferronickel industrial activity in the nearest past. This smelter plant uses the nickel ore from the Ržanovo mine, about 30 km south of the plant. The Ržanovo ore body has the following lithological rock types: hematite, magnetite-ribecite schists, dolomite-talc schists, talc schists and serpentine (Maksimović, 1982; Boev and Janković, 1996). In the last 4 years beside ore from Ržanovo mine, ore mainly from Gebe nickel mine, Indonezia (saprolite-limonite type), reach in nickel (2–2.5 %), is used. It is well known that the nickel ores contain cobalt as well (in average of 0.05 % for Ržanovo ore) (Maksimović, 1982; Boev and Janković, 1996). Therefore, the dust from this plant has the same content like ore used as a raw material including some of the heavy metals like nickel, cobalt and chromium (Maksimović 1982, Boev and Jankovic 1996). For that reason, the goal of this work was to determine the content of cobalt in the soil from the town of Kavadarci and its surroundings and to assess the size of the area eventually affected by the ferronickel smelter plant situated near the town.

STUDY AREA

Town Kavadarci is located in Tikveš valley, Republic of Macedonia (Fig. 1). The city is known by its vineyards and it is main vine production region in Macedonia. The urban area is located on 200–300 m altitude, surrounded with hills from east and south sides of the valley (with height difference between 300 and 770 m). The climate in Kavadarci is of a continental type of climate with a reduced Mediterranean climate and with hot summer and cold winter (Lazarevski, 1993). The major wind direction is from the north and northwest.

The study area is large 18 (W-E) × 20 (S-N) km (Fig. 2) and is located in the south-central part of Macedonia, which is limited with coordinates (Gauss Krueger zone 7) 7574000 (W) – 7592000 (E) and 4582000 (S) – 4602000 (N). Of the total 360 km^2 of the study area (Fig. 2), the water surface (rivers and lakes) covers 6 km^2 (2 %), cultivable land 221 km^2 (61 %), non-cultivable area (mainly forests) 120 km^2 (33 %) and urbanized area (settlements, industry zones, archaeological sites, quarries and tailings) 13 km^2 (4 %).

The complete investigated region (360 km^2) is covered by a sampling grid of 2×2 km^2; in the urban zone and around the ferronickel smelter plant (117 km^2) the sampling grid is denser, 1×1 km^2. All together, in 172 locations 344 soil samples were collected. At each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil (20–30 cm).

Two divisions of soils were determined in the investigated region: automorphyc and hydromorphic soils.

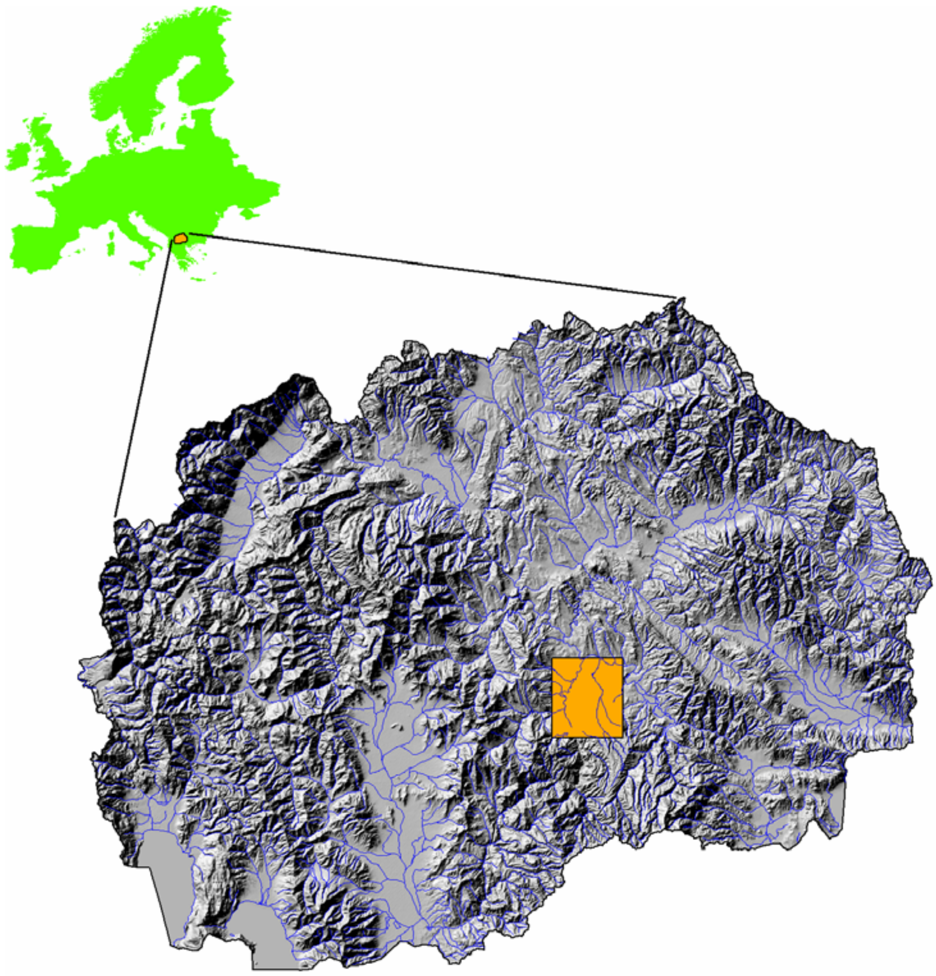

Fig. 1. Location of the study area

SOIL CONDITIONS

Automorphic soils

Several types of automorphic soils were established: lithosols , regosols, different soil complexes (regosols-lithosols, lithosols-regosol-rendzinas, lithosols-regosols-rankers), deluvial (coluvial) soils, rendzinic soils, vertisols, chernozems, and cinnamonic forest soils.

Lithosols with (A)-R_1-R_2 type of soil profile are undeveloped or weakly developed soils with maximum soil depth of 20 cm, formed on a solid or slightly defragmented rock. These soils have a low productive capability, due to the shallow solum and small amount of clay and have no importance for agricultural production.

Regosols with (A)-C type of soil profile are formed on a loose substrates. They are formed with severe erosion of the soil profile of the formerly developed soils and with an initial process of pedogenesis which leads to formation of an undeveloped top layer (A). These soils are prone to surface or dice erosion, so antierosive measures should be implemented. Regosols are characterized with low soil fertility in comparison with the adjacent soil types, which were transformed into regosols with severe erosion.

Soil complex: regosols-lithosol. In the Tikveš region these two soil types alter on a very small distances and it's very difficult to delineate then as separate cartographic units. This complex is spread on sloppy terrains west of the Tikveš Lake in the districts of Debrište, Kamen Dol and Kruševica villages and north-west of Dolno Čičevo village.

Soil complex: lithosol, regosols and rendzinas. Series of lithosol-regosols-rendzinas can be often noticed in the region of Tikveš valley. Lithosols occupy the highest parts of the terrain. Very often the solid rock can be noticed on the surface. Regosols are developed on inclined terrains where due to the erosion processes the solum is constantly in its initial phase of development, while the rendzinic soils are developed on amore flat terrains at foothills and are altering with regosols on very small distances. This soil complex is extended over the districts of Drenovo, Sirkovo, Kamen Dol, Mrzen Oreovec, Debrešte and east of Gradsko settlement on the left side of Vardar river.

Soil complex: Lithosols, regosols and rankers. This series is delineated on the highland Vitačevo, nearby Kavadarci. Lithosols and rankers are formed on compact volcanic rocks, while regosols are developed with erosion processes and degradation of the top soil of rankers.

Deluvial (coluvial) soils with (A)-C type of soil profile are undeveloped or weakly developed soils with (A) or Ap top layer, formed with erosion of the material from the upper part of the terrain with surface and torrent erosion and its deposition in the foothill. The hor. (A) contains a bit higher amounts of organic matter than hor. C, but still there are no obvious signs of formations of soil structure. Deluvial soils posses big spatial and vertical (in depth soil profile) heterogeneity of all its properties. In comparison with the bordering alluvial soils, deluvial soils have lower productivity.

Rendzinic soils with an A-AC-C type of profile are formed on a loose silicate-carbonate substrate, with mollic A horizon. The depth of the top soil is up to 40 cm, with dark gray, dark brown or black color with well developed soil structure. Carbonates are present from the surface or deeper in the soil profile. The major part of these soils is used for intensive agricultural production, while a small part is under pastures. On the soil map these soils are indicated as a complex of lithosols-regosols-rendzinas. The complex of rendzinas and regosols covers the biggest part of the investigated area. In the area of village Dolno Čičevo on a small area a complex of cinnamonic forest soils and regosol is presented.

Vertisols are formed on a clay sediment (mostly carbonate) with more than 30 % of clay content with ability for swealing (smectites) or on basic or ultrabasic rocks which with decaying derives such type of clay. Vertisols at the examined area are formed on clay tercier sediment on moderately wavy landscape with small inclination. The profille type is A-AC-C. The soil contains more than 30 % clay and hor. A hase vertical character: cracks, and specific prismatic structure. The aggregate surface is shiny („slickensides”). Hor. A is deaper than 30 cm, while the AC hor. is on 20–30 cm depth. In the examined area vertisols are detached as a separate soil type. These soils are spread in the adjacent surroundings of the Ribarci, Trstenik and Vozarci, northern of the city of Kavadarci.

Chernozems are commonly developed in semi-arid steppe regions with typical molic hor. Amo thicker than 40 cm and an intermediate hor. AC (25–30 cm). This soil contains carbonates which appears from the soil surface, in some cases from the lower part of hor. A or from hor. AC. Hor. A has a well developed, stabile granular soil structure. In the examined area chernozems contains carbonates at its surface, while in some cases carbonates are washed out at certain depth of the soil profile. Chernozems are delineated as a separate carthographic unit (Fig. 3). On the soil map a big areas are detached north from Rosoman village, and some small units east from Palikura village and between villages Timjanik and Dolni Disan.

Cinnamonic forest soils with Ap-$(B)_v$-C or Ap-$(B)_v$-$(B)_v$C-C type of profile are characterized with the presence of clay cambic hor. (B). The cambic hor. (B) always contains more clay than the hor. A. It is denser with reduced capillary porosity and stability of the structural aggregates and lower water conductivity. Production capability is medium due to the bad soil structure, low humus content, insufficient quantities of nutrients and appearance of erosion on sloppy terrains.

Hydromorphic soils

Alluvial soils are recent layers of river or lake sediments, and usually have hor. (A) or Ap, hor. C and in some cases hor. G. Unlike deluvial soils, they have good fractionation of the parent material. The alluvial sediments which serve as a parent material for formation of this soil have hetero-organic mineralogical composition. In terms of its mechanical composition these are light soils, with weakly emphasized soil structure and high dependence of the physical characteristic to the mechanical composition. They are characterized with good air, water and temperature regime. These are very fertile soils with intensive agricultural production. They are represented as a separate soil type along the river beads of the rivers Vardar, Crna Reka and Luda Mara.

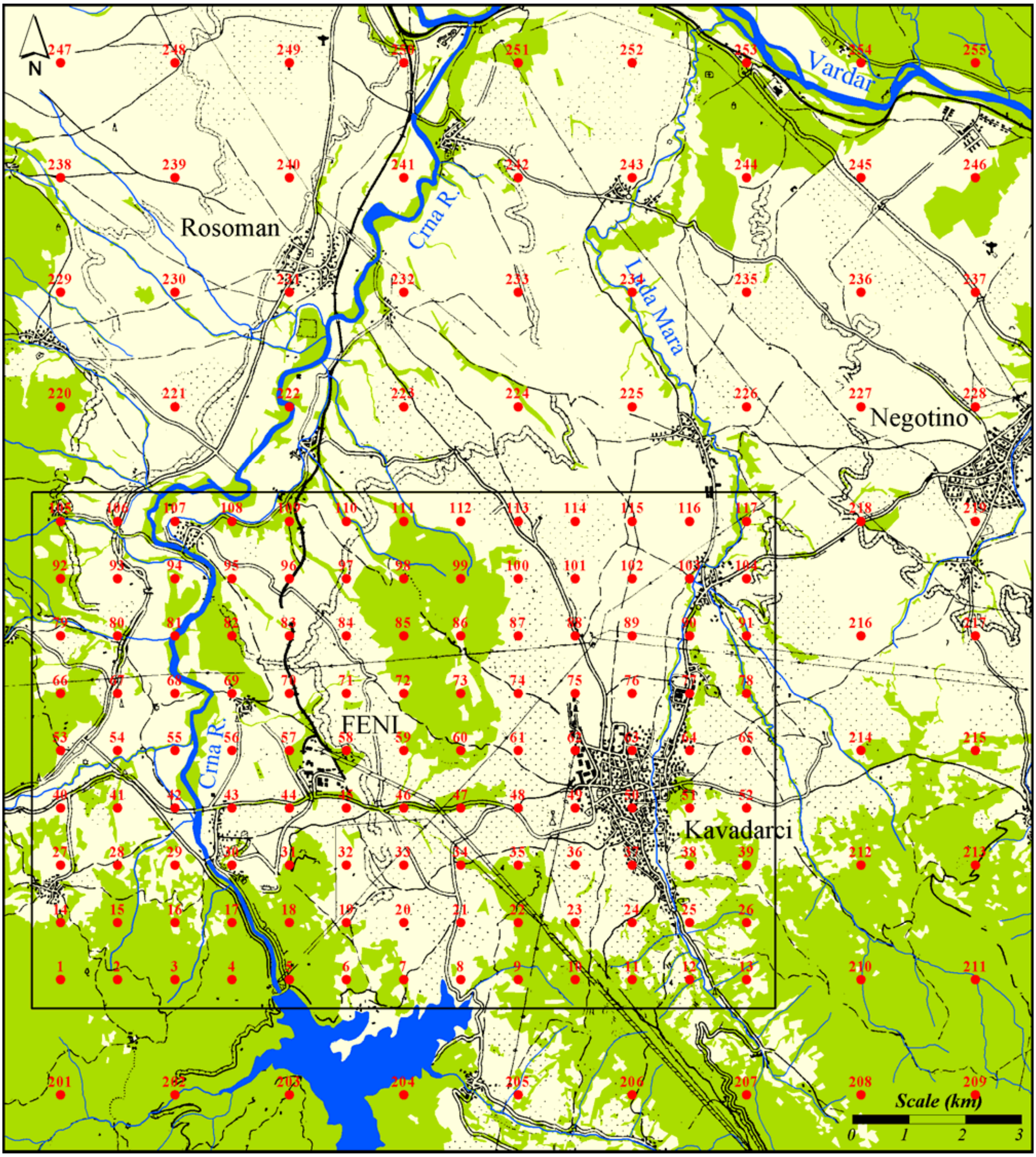

Fig. 2. Land use map and soil samples locations in the Kavadarci area

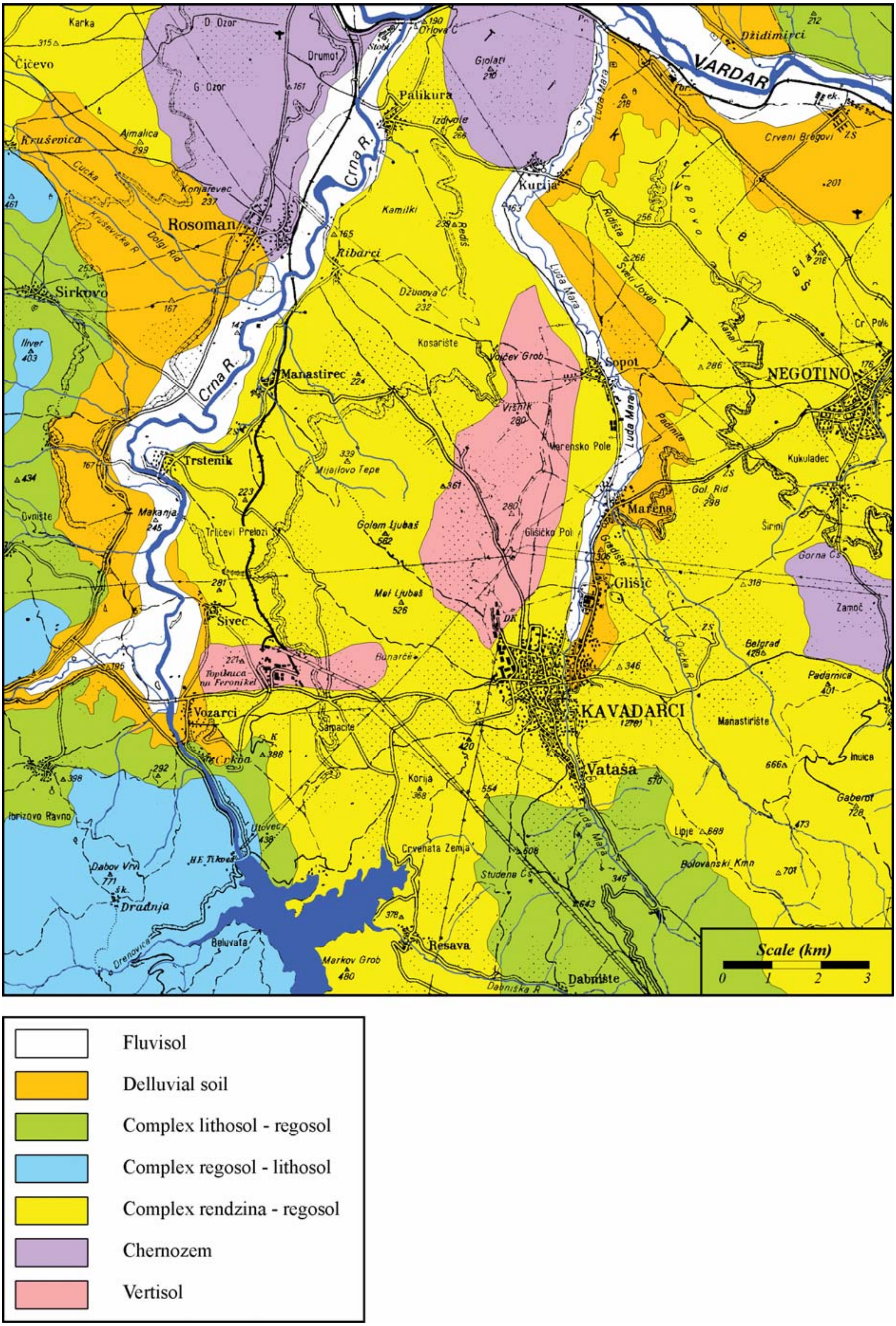

Fig. 3. Soil map of Kavadarci area

MATERIAL AND METHODS

Sampling

Soil samples in the town of Kavadarci and the surrounding region were collected according to the European guidelines for soil pollution studies (Theocharopoulos et al. 2001; Darnley et al. 1995; Šajn 2004, Reimann et al. 2008). The complete investigated region (360 km^2) was covered by a sampling grid 2×2 km^2, but in urban zone of Kavadarci and around the ferronickel smelter plant (117 km^2), the sampling grid was denser, 1×1 km (Fig. 2). Altogether 344 soil samples were collected from 172 locations. In each sampling point soil samples were collected at two depths, topsoil (0–5 cm) and subsoil (20–30 cm). The possible organic horizon was excluded. One sample represents the composite material collected at the central sample point itself and at least four points within the radius of 10 m around it towards N, E, S and W. The mass of such composite sample was about 1 kg (Darnley et al. 1995).

With regard to the basic lithological units, 24 location of sampling are located on the area of Paleozoic and Mesozoic rocks (39 km^2), 10 on the Eocene upper flysch zone (34 km^2), 90 on the Pliocene sandy series (182 km^2), 29 on the Pleistocene tuff, Holocene deluvium and Holocene alluvium of the river Luda Mara (46 km^2), 10 on the Holocene river terraces (23 km^2) and 9 on the Holocene alluvium of the rivers Crna and Vardar (21 km^2).

Preparation

The soil samples were air dried indoors at room temperature for about two weeks. Then they were gently crushed, cleaned from extraneous material and sifted through a plastic sieve with 2 mm mesh (Salminen et al., 2005). The shifted mass was quartered and milled in agate mill to an analytical grain size below 0.125 mm.

Chemical analyses

Mass spectrometry with inductively coupled plasma (ICP-MS) determination of cobalt was performed in the laboratory of ACME Ltd. in Vancouver, Canada, after aqua regia digestion (mixture of HCl, HNO_3 and water at 95°C – 1DX method).

Data processing and construction of maps

Data analysis and production of maps were performed on a PC using the Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) and Surfer (ver. 8.09) software. The methods of parametric and nonparametric statistics were used for the data analysis (Snedecor and Cochran, 1967; Davis, 1986). On the basis of the results of the normality tests and visual inspection of the distribution histograms the logarithms from the content for the normal distribution was used.

The universal method kriging with linear variogram interpolation (Davis, 1986) was applied for construction of the areal distribution map of cobalt in topsoil (0–5 cm) and subsoil (20–30 cm). The basic grid cell size for interpolation was 20×20 m. For class limits the percentile values of distribution of the interpolated values were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

RESULTS AND DISCUSSION

The basic data obtained from the descriptive statistics for cobalt content in the soil in the investigated area are given in Table 1 and the averages of the cobalt content in the soil according to basic lithological units for both topsoil and subsoil are given in Table 2. It can be seen (Table 1) that the median and average values are the same (15 mg/kg) and that the content of cobalt in the whole investigated area ranges between 6.7 and 58 mg/kg. From data given in Table 2 it can be concluded that the highest content of cobalt is present in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and flysch (E) – Eocene upper flysch zone (on the northern part), and the lowest in the soils from the Holocene alluvium of the rivers Crna and Vardar.

On the Fig. 4 the spatial distribution of cobalt in topsoil (left) and subsoil (right) is presented. It can be seen that the spatial distribution of cobalt in both soil layers is closely dependent on the lithogenesis. The highest contents were found in areas of Paleozoic and Mesozoic rocks and Eocene upper flysch zone and the lowest values in area of the Pleistocene tuff, Holocene deluvium (W from the town of Kavadarci) and Holocene alluvium of the rivers Luda Mara, Crna Reka and Vardar.

The ferronickel smelter plant, in spite of the obvious environmental pollution has not contributed significantly to the measured amount of this element, which occurs in high concentrations in the background. It was found (Fig. 4) that the critically high concentrations are related primarily to high concentrations of cobalt in the sampling points from the western part of the investigated region. In some cases the content of this element is higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

Table 1

Descriptive statistics of measurements for cobalt content in top and subsoil layers the investigated area (data given in mg/kg)

Number of samples	344
Distribution (Log – lognormal)	Log
Md – Median	15
X_g – geometrical mean	15
s_g – geometrical standard deviation	1.4
A – skewness	0.98
E – kurtosis	1.96
Minimum	6.7
Maximum	58
P_{10} – 10 percentile	11
P_{90} – 90 percentile	24

Table 2

Average of the cobalt content in the soil according to basic lithological units (in mg/kg)

Soil layer/	Mean	Rocks	Flysch	Sand	Tuff	Terraces	Alluvium
number of samples (*n*)	All	(Pz-Mz)	(E)	(Pl)	(Q)	(Q)	(Q)
n	172	24	10	90	29	10	9
Topsoil (depth 0–5 cm)	16.2	26	10	14	13	15	12
Subsoil (depth 20–30 cm)	17.2	29	22	14	14	16	13

Mean (EU) – European topsoil average (Salminen et al., 2005); Rocks (Pz-Mz) – area of Paleozoic and Mesozoic rocks (39 km^2); Flysch (E) – Eocene upper flysch zone (34 km^2); Sand (Pl) – Pliocene sandy series (182 km^2); Tuff (Q) – Pleistocene tuff, Holocene deluvium and Holocene alluvium of the river Luda Mara (46 km^2); Terraces (Q) – Holocene river terraces (23 km^2); Alluvium (Q) – Holocene alluvium of the rivers Crna and Vardar (21 km^2)

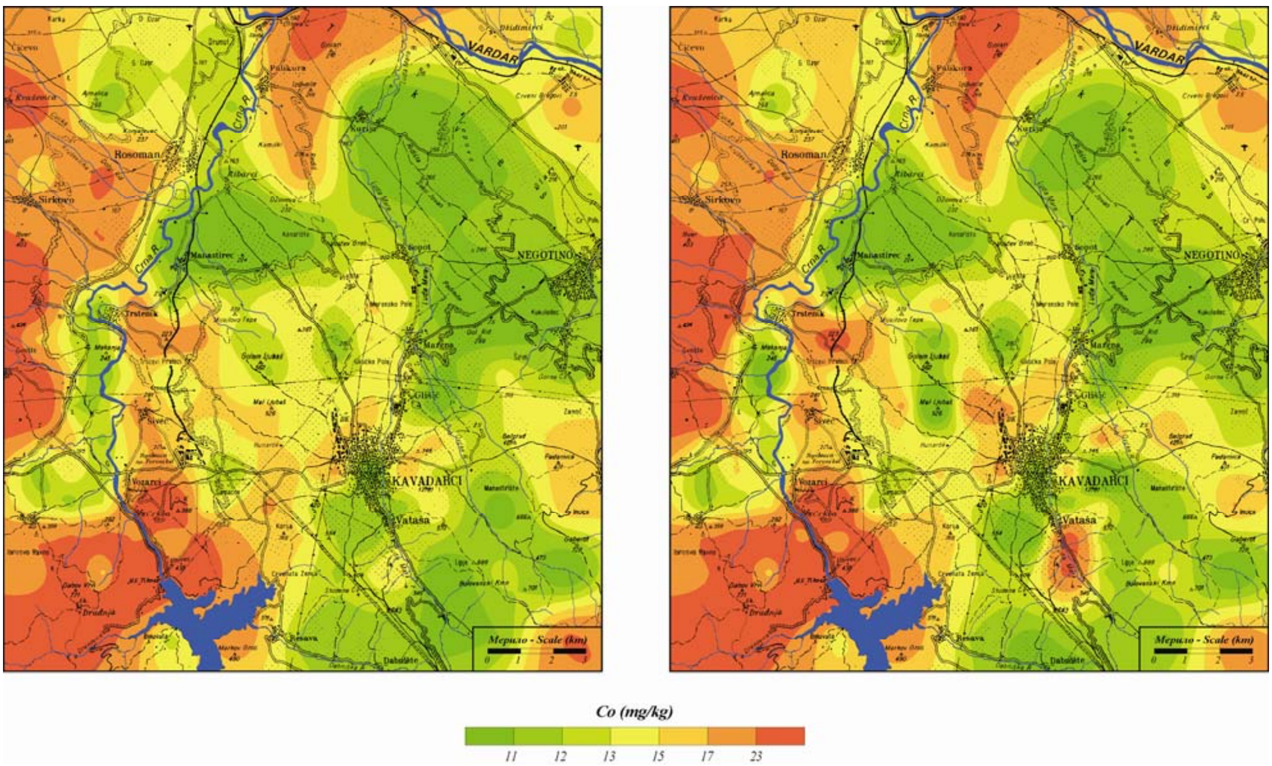

Fig. 4. Spatial distribution of cobalt in topsoil (left) and subsoil (right)

Average and border contents (max. and min.) of Co in different soil types of the investigated region are presented in Table 3. Average contents of Co in topsoil of the complex regosols-lithosols is significantly higher (24.2 mg/kg) comparing with the Co content in the topsoil of all other soil types which vary in the ranges of 12.0–17.8 mg/kg. There are no significant differences between the surface and subsoil in terms of its average quantities. The differences of quantities between the soil types are following the same logic as in the surface layer. The highest quantities are noticed in the complex regosols-lithosols (25.3 mg/kg) while the lowest values are detected in the subsoil of fluvisols. Maximum and minimum contents of Co differ in broad ranges in all soil types, either in the surface or in a subsurface layer.

Generally speaking, the average contents in almost all soil types are slightly higher in subsoil (20–30 cm), which again leads to a conclusion that there is no human induced surface accumulation of Co in soils in Kavadarci region.

Table 3

Average of the cobalt content in the soil according to basic pedological units (in mg/kg)

Soil layer	Co content	All samples	Complex regosol-lithosol	Complex lithosol/regosol	Delluvial soil	Fluvisol	Complex rendzina-regosol	Chernozem	Vertisol
No of samples (*n*)		172	13	23	19	13	80	8	16
Topsoil (depth 0–5 cm)	Average	16.2	24.2	17.8	16.0	12.0	15.0	13.9	14.5
	Max.	54.3	54.3	47.9	26.9	16.7	28.6	20.3	17.3
	Min	7.6	11.8	10.4	10.9	9.3	7.6	7.9	10.1
Subsoil (depth 20–30 cm)	Average	17.2	25.3	19.2	17.9	12.4	15.0	15.2	15.2
	Max.	57.8	57.8	55.7	30.9	17.6	29.3	21.1	21.0
	Min	6.7	12.9	9.9	10.7	8.2	6.7	11.3	9.3

CONCLUSION

It was found that the averages of the cobalt content in the soil according to basic lithological units for both topsoil and subsoil with the median and average values of 15 mg/kg, ranges between 6.7 and 58 mg/kg. The highest content of cobalt is present in the soil from the area of Paleozoic and Mesozoic rocks (Pz-Mz) on the western part of the investigated area and Flysch (E) – Eocene upper flysch zone (on the northern part) and the lowest in the soils from the Holocene alluvium of the rivers Crna and Vardar. It was also found that the average contents of Co in topsoil of the complex regosols-lithosols is significantly higher (24.2 mg/kg) comparing with the Co content in the topsoil of all other soil types which vary in the ranges of 12.0–17.8 mg/kg. There are no significant differences between the surface and subsoil in terms of its average quantities. The ferronickel smelter plant, in spite of the obvious environmental pollution, has not contributed significantly to the measured amount of this element, which occurs in high concentrations in the background. It was found that the critically high concentrations are related primarily to high concentrations of cobalt in the sampling points from the western part of the investigated region. The contents of this element are higher in subsoil than in topsoil from which it can be concluded that the occurrence is natural.

REFERENCES

Boev B., Janković S., 1996: *Nickel and nickeliferrous iron deposits of the Vardar zone (SE Europe) with particular references to the Ržanovo–Studena Voda ore-bearing series*, Faculty of Mining and Geology, Special issue No. 3, Štip, p. 103–126.

Bretzel F., Calderisi M., 2006: Metal contamination in urban soils of coastal Tuscany (Italy), *Environ. Monit. Assess.*, **118**, 319–335.

Cappuyns V., Swennen R., Vandamme A., Niclaes M., 2006: Environmental impact of the former Pb-Zn mining and smelting in East Belgium, *J. Geochem. Explor.*, **88**, 6–9.

Chen T. B., Zheng Y. M., Lei M., Huang Z. C., Wu H.T., Chen H., Fan K. K., Yu K., Wu X., Tian Q. Z., 2005: Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China, *Chemosphere*, **60**, 542–551.

Darnley A. G., Björklund A., Bolviken B., Gustavsson N., Koval P. V., Plant J. A., Steenfelt A., Tauchid M., Xuejing X., Garrett R. G., Hall G. E. M., 1995: *A global geochemical database for environmental and resource management*. Recommendations for international geochemical mapping. Final report of IGCP project 259, UNESCO Publishing, Paris.

Davidson C. M., Urquhart G. J., Ajmone-Marsan F., Biasioli M., Duarte A. D., Diaz-Barrientos E., Grcman H., Hossack L., Hursthouse A. S., Madrid L., Rodrigues S., Zupan M., 2006: Fractionation of potentially toxic elements in urban soils from five European cities by means of a harmonised sequential extraction procedure, *Anal. Chim. Acta*, **565**, 63–72.

Davis J. C. 1986: *Statistic and Data Analysis in Geology*, Willey in Sons, New York, pp. 651.

Diawara M. M., Litt J. S., Unis D., Alfonso N., Martinez L. A., Crock J. G., Smith D. B., Carsella J., 2006: Arsenic, cadmium, lead, and mercury in surface soils, Pueblo, Colorado: implications for population health risk, *Environ. Geochem. Health*, **28**, 297–315.

Everhart J. L., McNear Jr. D., Peltier E., Van der Lelie D., Chaney R. L., Sparks D. L., 2006: Assessing nickel bioavailability in smelter-contaminated soils, *Sci. Total Environ.*, **367**, 732–744.

Kabata-Pendias A., Pendias H. 2001: *Trace elements in soil and plants*, Third Edition, CRC Press, Boca Raton.

Kaur R., Rani R., 2006: Spatial characterization and prioritization of heavy metal contaminated soil-water resources in Peri – Urban areas of National Capital Territory (NCT), Delhi, *Environ. Monit. Assess.*, **123**, 233–247.

Krishna A. K., Govil P. K., 2005: Heavy metal distribution and contamination in soils of Thane-Belapur industrial development area, Mumbai, Western India, *Environ. Geol.*, **47**, 1054–1061.

Lazarevski A., 1993: *Climate in Macedonia*, Kultura, Skopje.

Li J., Xie Z. M., Zhu Y. G., Naidu R., 2005: Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine, *J. Environ. Sci.– China*, **17**, 881–885.

Li Y., Wang Y. B., Gou X., Su Y., Wang G., 2006: Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China, *J. Environ. Sci.– China*, **18**, 1124–1134.

Maksimović Z., 1982: *Mineralogical Study of the Ore from Ržanovo Mine*, Faculty of Geology and Mining, Belgrade.

Mico C., Reatala L., Peris M., Sanchez J., 2006: Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis, *Chemosphere*, **65**, 863–872.

Reimann C., Albanese S., Batista M. J., Bel-Lan A., Birke M., Cicchella D., Demetriades A., de Vivo B., de Vos W., Dinelli E., Duris M., Dusza-Dobek A., Ernstsen V., Flight D., Gilucis A., Gosar M., Gregorauskiene V., Gulan A., Hayoz P., Halamic J., Haslinger E., Hratovic H., Ion A., Ivanovna Y., Johnson C., Jordan G., Kisivilla J., Klein P., Kwecko P., Lax K., Lima A., Locutura J., Malyuk B.I., Maquil R., Marku S., Martins L., Mazreku A., Messina A., O'Connor P., Ottesen R.T., Pasieczna A., Petersell W., Reeder S., Salpeteur I., Schedl A., Sefcik P., Slaninka I., Sorsa A., Selinus O., Stafilov T., Tarvainen T., Trendavilov V., Utermann J., Valera P., Vidojevic D., Volden T., 2008: *Eurogeosurveys geochemical mapping of agricultural and grazing land soil of Europe (GEMAS)*, Field manual. NGU Report 2008.038. Geological Survey of Norway.

Razo I., Carrizales L., Castro J., Diaz-Barriga F., Monroy M., 2004: Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico, *Water Air Soil Poll.*, **152**, 129–152.

Šajn R., Bidovec M., Andjelov M., Pirc S., Gosar M., 1998: *Geochemical Atlas of Ljubljana and Environs*, Institute of Geology, Geotechnique and Geophysics, Ljubljana.

Šajn R., 2004: Distribution of mercury in surface dust and topsoil in Slovenian rural and urban areas, *RMZ-Geol. Geoenviron.*, **51**, 1800–1803.

Salminen R., Batista M. J., Bidovec M., Demetriades A., De Vivo B., De Vos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'Connor P. J., Olsson S. Å., Ottesen R. T., Petersell V., Plant J. A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfelt A., Tarvainen T., 2005: *Geochemical Atlas of Europe*, Part 1, *Background Information, Methodology and Maps*. Geological Survey of Finland, Espoo.

Simeonov V., Einax J., Tsakovski S., Kraft J., 2005: Multivariate statistical assessment of polluted soils, *Cent. Europ. J. Chem.*, **3**, 1–9.

Snedecor G. W., Cochran W. G., 1967: *Statistical Methods*, The Iowa State University Press, Ames, Iowa, pp. 575.

Stafilov T., Šajn R., Boev B., Cvetković J., Mukaetov D., Andreevski M., 2008: *Geochemical Atlas of Kavadarci and the Environs*, Faculty of Natural Sciences and Mathematics, Skopje.

Tembo B. D., Sichilongo K., Cernak J., 2006: Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia, *Chemosphere*, **63**, 497–501.

Р е з и м е

ДИСТРИБУЦИЈА НА КОБАЛТ ВО ПОЧВИТЕ ВО КАВАДАРЦИ И НЕГОВАТА ОКОЛИНА

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Клучни зборови: почви; кобалт; загадување; Кавадарци; Република Македонија

Во трудот се презентирани резултатите од просторната распределба на кобалт во почвите во Кавадарци (Република Македонија) и неговата околина. Од испитуваната област (360 km^2) се земени вкупно 344 примероци од 172 локации. На секоја локација се земени почви од две длабочини, површински слој почва (0–5 cm) и потповршински слој (20–30 cm). Определувањето на кобалтот е вршено со индуктивно спрегната плазма со масена спектрометрија (ICP-MS). Обработката на податоците и конструирањето на картата на дистрибуција се вршени со примена на софтверите Paradox (ver. 9), Statistica (ver. 6.1), AutoDesk Map (ver. 2008) и Surfer (ver. 8.09). Утврдено е дека вредноста за медијаната и средната вредност на содржината на кобалт во површинските и потповршинските почви изнесува 15 mg/kg (од 6,7 до 58 mg/kg). Највисоки содржини се најдени во областите на палеозојските и мезозојските стени и во зоната на горноеоценскиот флиш, а најниските вредности во обласа на плеистоценскиот туф, холоценскиот делувиум (западно од градот Кавадарци) и холоценскиот алувиум на реките Црна Река и Вардар. Не е забележана значителна разлика помеѓу содржините на кобалт во површинските и потповршинските почви. Утврдено е дека високи вредности за кобалт се најдени во примероците почва од западниот дел на испитуваното подрачје. Исто така, утврдено е дека во овие примероци повисоки вредности на кобалт се најдени во потповршинските почви во однос на површинските, што укажува на природната застапеност на кобалтот во овие почви.