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Spatial distribution of elements in soils of experimental area, Ružomberok - X-ray analysis

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Abstract. In this work we focused on the presence and spatial distribution of chemical elements in soil. Field research was conducted in the town of Ružomberok and its surroundings, from July to August 2016. In total 100 samples were processed and analysed with X-ray spectrometry. In some cases, detected values exceed ID Criteria of the Ministry of Environment of the Slovak Republic. We found significantly higher concentrations of lead (Pb) at higher altitudes as well as elevated concentrations of certain elements such as S, Cl, Cr, Cu, Zn, Mo, Ba and Hg in the city's surrounding areas and near the pulp and paper factory. Our findings suggest that some elements and heavy metals may be transferred through the food chain to plants, animals and people.

Key words: soil, metals in soils, heavy metals, X-ray analysis

Introduction

The most polluted soils are situated near roads and its surroundings. As a result of anthropogenic materials (exhaust fumes, oil residues, tire particles, weathered parts of roads), the influence of urbanization, solid fuel combustion, construction of roads, buildings and also biological materials (fallen leaves, plant materials) soils on the surface absorb diverse elements and dust. These materials (dust), do not only pose a in soils near roads, but also in the broader environment (Omar *et al.* 2007).

In this work we focused on the quality of soils in Ružomberok and its surroundings. Ružomberok is a district town in the Žilina region, located in the west part of basin - Liptovska kotlina, and surrounded by mountains - Low Tatras, Great Fatra and Chočské hills. This area was chosen because Ružomberok and its surroundings are known as one of the most polluted area in the Slovak republic. Today the biggest factory in Ružomberok is a pulp factory and it is also the largest paper and pulp processing factory in the Slovak Republic. The company´ s production capacity is 560,000 tons of uncoated paper and 100,000 tons of dried pulp. The company also employs about 1,500 employees (MONDI 2017). Industry provides many opportunities for the region, but at what cost? What impact do these manufacturing processes have on the environment and on our health? In this study we focused on the concentration and dispersion of chemical elements. From natural content found in soils (Fe,Ca,K,Mg,...) through hazardous elements (Cd,Zn,Cu,...), to heavy metal content (Hg,Pb,Ag,...). The main aim of this research was the description and analysis of the spatial distribution of elements in the soils around Ružomberok.

Material and Methods

For our study of spatial distribution of elements and contamination of soils we chose the town of Ružomberok and its surroundings. The study area was located in the western part of Slovakia and belongs to Podtatranská basin. It is one of the largest and longest depressions in the Central Carpathians (Gross *et al.* 1980). From a geological zoning point of view, it is a zone of limestone-dolomite rocks and claystone-limestone rocks. The study area belongs to the mild climate zone. Lapin *et al.* (2002) state that it is moderately warm, humid, with cool to cold winter, and moderately cool. The average annual temperature ranges from 6 to - 2 degrees (www.ruzomberok.sk 2017). In our study area, rendzic leptosols, eutric cambisols, calcaric cambisols, calcaric fluvisols and albic luvisols mainly occur (Šály and Šurina 2002). Mean annual soil temperature ranges from 7 - 9 ˚ C (Tomlain and Hrvoľ 2002). Retention capacity and permeability of soils in the study area arecharacterized as soils with medium permeability, and medium to high retention capacity (Cambel and Rehák 2002). Depending on the soil texture we can find in this region loamy and clay-loamy soils, somewhat loamy-sandy soils and also moderately stony soils (gravelled) (Čurlík and Šály 2002). Using GIS (ArcGIS 10) we created a square grid of sampling sites (10x10 km) which we have divided into 10 columns and 10 rows. In total, 100 sampling places were created in a distance of 1 km (Fig. 1). For the most precise location of sampling places, we used GPS Tracker Etrex 20. Into this GPS, we uploaded coordinates of sampling places. Collection of samples was conduced in summer months, from July to August in 2016. After localization by GPS, we used a small shovel to collect samples of soil. We took soil samples from the upper layers (10 cm), and put it into a closable PVC bag. Volume of sampled soils was around 0.125 l. Our work continued in laboratory. After samples were sorted, we continued with weighing of samples on labora-

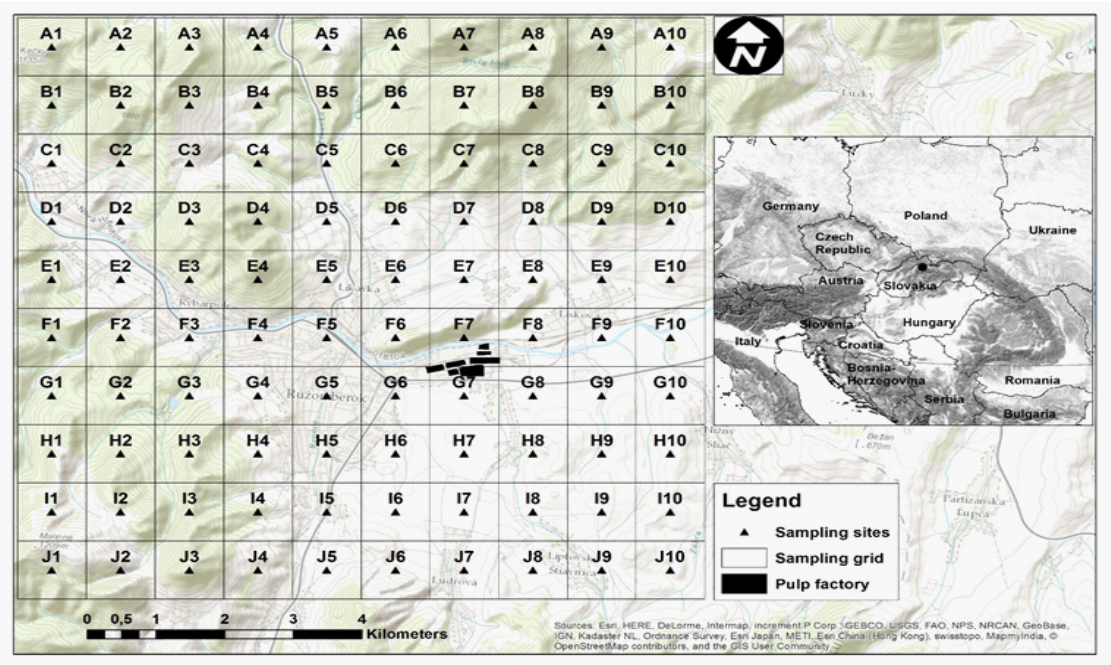

Fig. 1 Study area with sampling grid (10x10 km) and sampling sites (from A1 to J10).

tory scales. For drying process we useda Memmert IF 160 Plus desicator, set for a 12 hour drying program, with temperature set to 75° C and 70% ventilator speed rotation. After drying, samples were weighed again for dryness control. Afterward, soil samples were homogenized in a CryoMill (Retsch GmbH 2015) set for 30/sec. frequency. The samples were analysed by X-ray fluorescence (Stephens and Calder 2004) using the hand-held XRF spectrometer DELTA CLASSIC (USA), set 3 repeatitions in 30 seconds. The following elements were determined in soil samples: P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Sn, Sb, Ba, Pb. The original matrix from X-ray measurement was added to other variables such as distance form urban area, distance from road and distance from pulp factory pulp (center of chimney). These variables were processed in GIS by the Euclidian distance function (in Spatial analysis toolset, ArcGis). Spatial analysis (ArcGis) surface variables were also calculated including elevation, slope and aspect. This data was calculated with Land cover 2012 (from European Environment Agency EEA) and was added to the original matrix (by function Extract value from raster, ArcGis). Spatial distribution of element concentrations was simulated by the interpolation technique IDW (Inverse distance weighted) in ArcGis by 3D Analysis toolset. For statistical analysis, Statistica 8 was used. According to the Shapiro-Wilk test of normality all data were not normally distributed, except Fe, Rb and distance from pulp factory. Correlation analysis was used for detection of how elements in soil are connected with altitude, slope, distance from roads, distance from urban areas and distance from pulp factory. Because the variations of the data often showed a skewed distribution in some of the sample groups, a non-parametric approach to the analysis of the data was necessary. Significant differences between groups were verified using a Kruskal-Wallis test ($p < 0.05$). Principal component analysis was used to extract potential relationships between the variables. The first four principal components were tested using a non-parametric approach to assess the effect of the land cover to main phenomena. Some elements such as Co, Ag were not detected in all sites. Therefore, these elements were excluded from the statistics

Results

Average values of element concentrations and other measured elofical variables are presented in Table 1.

Principal component analysis

From principal component analysis we determined several main phenomena (Table 2).

The first factor (PC1) represents the interaction of P, K, Ti, Cr, Fe, Mn, Ni, Rb, Ba, Cu versus Cl and Ca. Generally speaking, if the level of the first elements increases then the level of Cl and Ca decreases or vice versa. The effect is not statistically significant among different types of habitats (land cover classes - p=0.713) although the ratio of first elements (P, K, etc.) to Cl, Ca tends to be higher in industrial than other areas (Fig. 2). Spatial distribution of this group of elements is presented in Fig. 3a.

The second factor (PC2) is a phenomenon of S concertation with Cu, Zn, As, Pb and Sr. According to Kruskal-Wallis test (p=0.045), the effect of S and other element increase is strongly connected to industrial areas (Fig. 4 and 3b).

The third factor (PC3) describes the presence of Sr and Ca in relation to Pb and Cd. This relationship does not significantly reflect any differences among types of land (p=0.386; Fig. 5). Spatial distribution of this element relationship is presented in Fig. 7a.

The fourth factor (PC4) describes the interaction of Mn and Ni when compared to Zr, Mo and

	Valid N	Mean	Minimum	Maximum	Std. Dev.
P	100	343.72	0.00	1032.00	325.17
S	100	458.82	0.00	1952.00	382.48
Cl	100	78.84	0.00	562.00	174.00
K	100	16187.84	3200.00	25841.00	5126.84
Ca	100	71923.96	1045.00	387668.00	80083.00
Ti	100	3549.57	75.00	5897.00	1319.18
Cr	100	92.48	14.00	228.00	8.41
Mn	100	761.62	85.00	3106.00	479.01
Fe	100	24835.57	2036.00	49333.00	9833.76
Ni	100	46.36	0.00	218.00	34.61
Cu	100	32.67	11.00	87.00	14.37
Zn	100	120.36	27.00	797.00	90.98
As	100	18.42	0.00	132.00	15.66
Se	100	1.28	0.00	4.30	1.61
Rb	100	85.15	6.30	152.00	31.62
Sr	100	122.69	2.00	864.00	97.32
Zr	100	234.37	10.00	1327.00	149.55
Mo	100	2.53	0.00	9.20	1.68
Cd	100	1.53	0.00	16.00	4.20
Sn	100	3.97	0.00	27.00	8.33
Sb	100	4.17	0.00	29.00	7.45
Ba	100	517.86	25.00	1215.00	197.44
Hg	100	2.27	0.00	10.00	3.04
Pb	100	41.45	6.00	131.00	23.56
Altitude	100	676.97	456.00	1190.00	188.48
Slope	100	14.58	0.00	44.10	10,95
Dist. f. urban areas	100	988.67	0.00	4110.00	1018.86
Dist. f. roads	100	323.95	0.00	1467.40	340.47
Dist. f. pulp factory	100	4061.50	450.00	8173.30	1769.82

Table 1. Average values of element concentrations and other ecological variables (elements in ppm; Altitude in m.a.sl.; Slope in degree; Distance from urban areas, roads and pulp factory in metres).

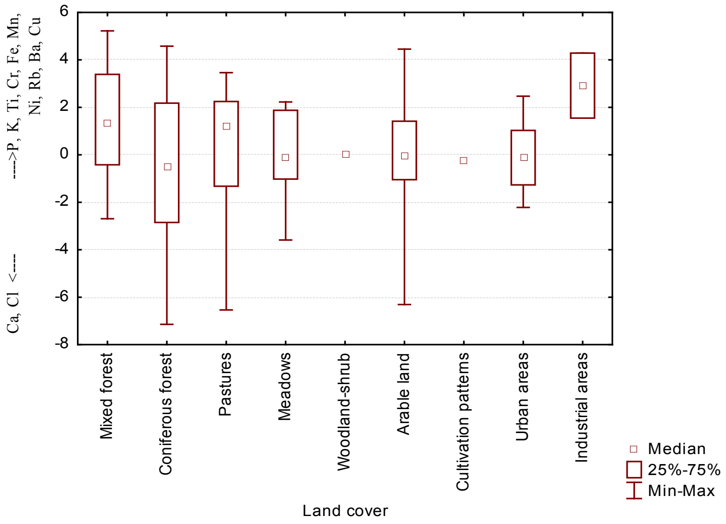

Fig. 2. Effects of P, K, Ti, Cr, Fe, Mn, Ni, Rb, Ba, and Cu versus Ca and Cl concertations in relation to land cover classes [Kruskal-Wallis test: H (8, N=100) = 5.413, p=0.713].

	PC 1	PC 2	PC 3	PC 4
P	0.776	0.119	0.079	-0.031
S	-0.206	-0.757	0.129	0.117
Cl	-0.507	-0.220	0.141	-0.009
K	0.759	0.356	0.247	-0.098
Ca	-0.718	-0.016	0.417	0.097
Ti	0.856	0.199	-0.040	-0.244
Cr	0.821	-0.295	-0.090	0.268
Mn	0.644	-0.200	0.111	0.472
Fe	0.939	-0.063	-0.011	0.131
Ni	0.669	0.096	0.287	0.457
Cu	0.529	-0.508	0.379	-0.160
Zn	0.388	-0.636	0.184	-0.256
As	0.119	-0.467	0.050	-0.306
Se	-0.140	0.125	0.397	-0.044
Rb	0.907	0.176	-0.015	0.164
Sr	-0.122	-0.424	0.524	-0.007
Zr	0.418	0.343	-0.340	-0.449
Mo	0.200	-0.362	-0.442	-0.529
Cd	-0.012	-0.229	-0.519	0.234
Sn	0.093	0.039	-0.202	0.092
Sb	-0.074	-0.384	-0.340	0.016
Ba	0.913	-0.188	0.020	-0.131
Hg	0.179	0.006	0.355	-0.480
Pb	0.011	-0.455	-0.523	0.225
Eigenvalue	7.542	2.742	2.130	1.671
Total variance %	31.427	11.424	8.875	6.962
Cumulative Eigenvalue	7,542	10,284	12,414	14,085
Cumulative %	31,427	42,851	51,726	58,688

Table 2. Principal component (PC) vectors (loadings), indicate mutual interaction of trace elements in the examined soils. (Factor coordinates of the variables are derived from the correlation matrix).

Hg in the study area. According to Kruskal-Wallis test (p=0.001), proportionally more Mn and Ni and less Zr, Mo and Hg was found in forest areas. Conversely, more Zr, Mo, Hg and less Mn, and Ni was found in urban and industrial areas (Fig. 6), mainly in the eastern region of the study area (Fig. 7b).

Spatial distribution

Phosphorus (P) in our study area (Fig. 8) shows diverse distribution. Higher concentrations are mainly found on west and northwest sides of slopes, at higher altitudes. In some cases, the high concentrations were also foud near main roads. Sulphur (S) in our study area occurs mainly at low altitudes. However in five cases we detected increased values of sulphur in the soil of the Chočské hills (Fig. 8). Increased presence of sulphur was also recorded on west and northwest slopes.

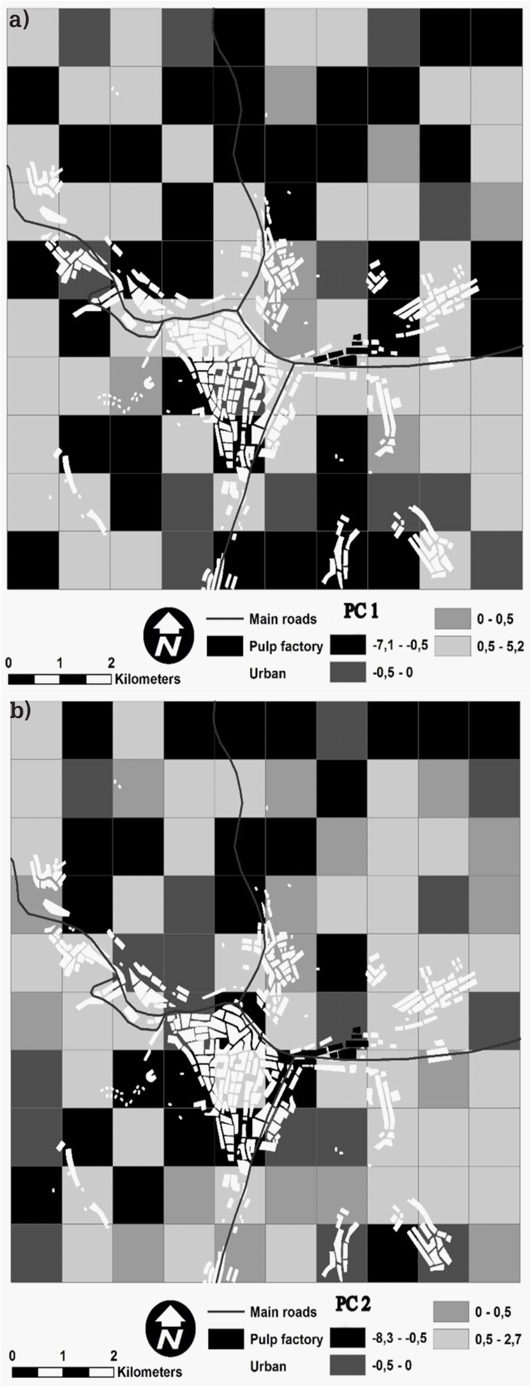

Fig. 3. Spatial distribution of selected elements defined PC1 a) and PC2 b) scores in study area (PC1: grey is an effect of increasing mutual concentration of P, K, Ti, Cr, Fe, Mn, Ni, Rb, Ba, and Cu and decreasing of Cl and Ca, black - is an effect of increasing concentrations of Ca and Cl while P, K, Ti, Cr, Fe, Mn, Ni, Rb, Ba, Cu decrease, PC2: grey is an effect of increasing concentration of Cu, Zn, As, Pb and Sr; black - is an effect of decreasing concentration of Cu, Zn, As, Pb and Sr).

Iron (Fe) was dispersed thorughout the whole study area (Fig. 9). Highest concentrations were detected on south and southwest slopes, in high as well as low altitudes. Slope in these localities was around 30-35 degrees and dominated by forest habitats. Concentrations of nickel (Ni) were mainly detected on the west side of the study area (Fig. 9). Higher values tended to occur at higher altitudes, with

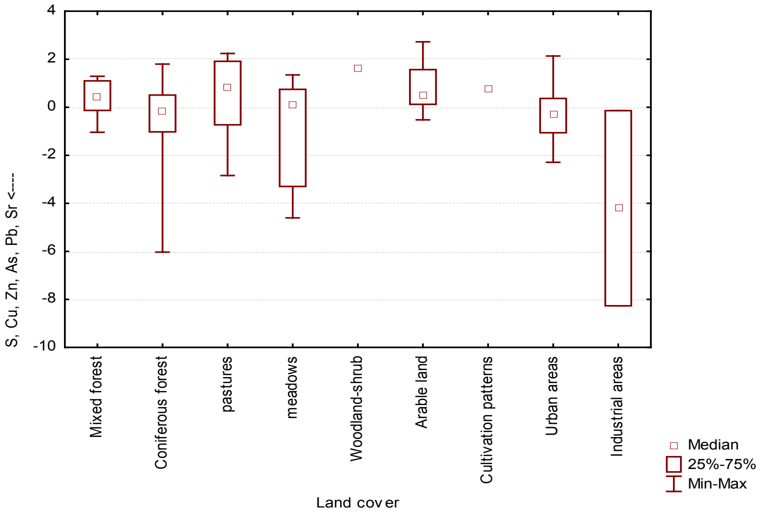

Fig. 4. Effect of S concertation together with Cu, Zn, As, Pb and Sr in relation to land cover classes [Kruskal-Wallis test: H (8, N=100) =15.819, p=0.045].

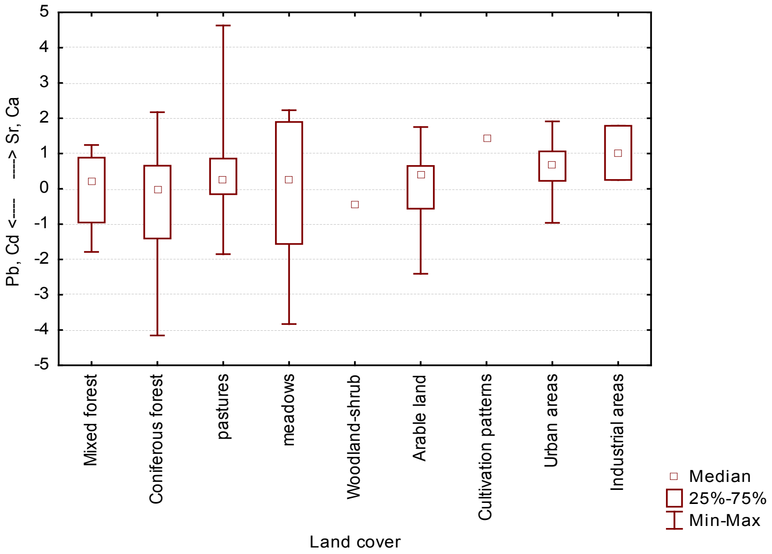

Fig. 5. Effect of Sr and Ca versus Pb and Cd concertation in relation to land cover classes [Kruskal-Wallis test: H (8, N=100) = 8.498, p=0.386]. The differences in the element relationship were not statistically significant among the land classes.

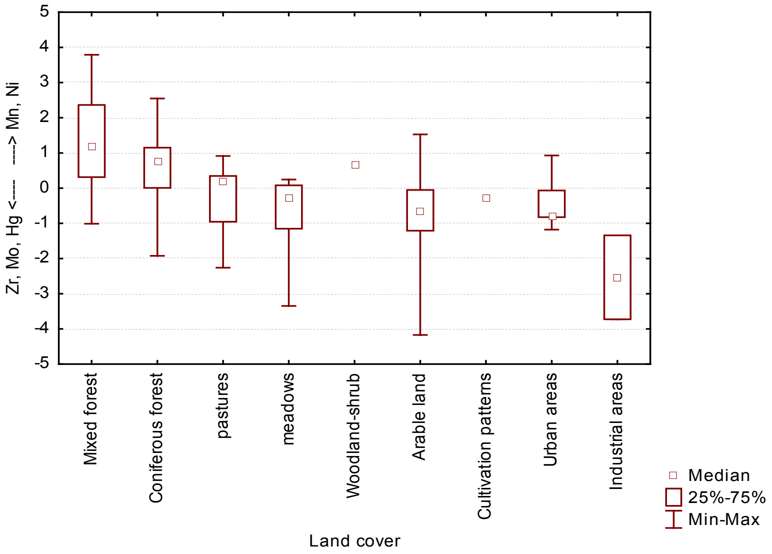

Fig. 6. Effect of Mn and Ni versus Zr, Mo and Hg concertation in relation to land cover classes [Kruskal-Wallis test: H (8, N=100) = 34.51702, p=0.001]. For detailed description see text.

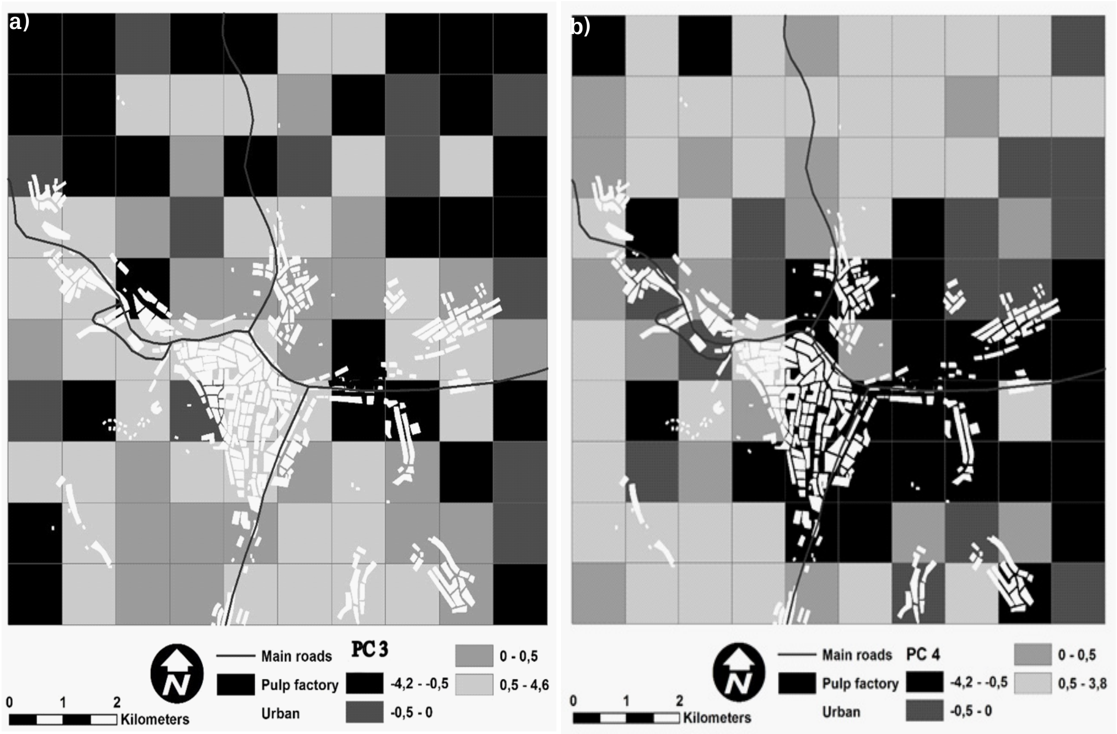

Fig. 7. Spatial distribution of selected elements defined PC3 a) and PC4 b) scores in study area (PC3: grey is an effect of increasing mutual concentration of Sr, Ca and decreasing of Pb,Cd, black - is an effect of increasing concentrations of Pb, Cd while Sr,Ca decrease, PC4: grey is an effect of increasing mutual concentration of Mn, Ni and decreasing of Zr, Mo, Hg, black - is an effect of increasing concentrations of Zr, Mo, Hg while Mn, Ni decrease).

slopes of 25 to 35 degrees as well as onsouth-southeast slopes dominated by coniferous forests. The highest concentrations of copper (Cu) and zinc (Zn) in the study area were detected mainly in town and its surroundings (Fig. 10). Both were found at low altitudes and on gentle slopes, located westerly or northwesterly. Cadmium (Cd) and tin (Sn) were very unevenly distributed (Fig. 11). Localities with higher concentrations have some common attributes, including middle altitudes, slopes between 20 and 30 degrees, south, southwest slopes, and coniferous forests. Arsenic (As) is dispersed almost everywhere (Fig. 12), but in some places its concentrations are high. This occurs at lower altitudes, slopes around 20-30 degrees, north-northeast. In comparison to As, selenium (Se) has very specific and uneven distribution. From places with almost zero concentration directly to places with high concentrations (Fig. 12). In general, higher concentrations occur at lower altitudes, slope from 15 to 30 degrees, dominated coniferous forest and pastures. Higher concentrations were detected in east and northeast slope sites. Mercury (Hg), similar to barium is mainly located near the town, roads and their surroundings (Fig. 13). Higher concentrations are found in low altitudes with slopes around 5-15 degrees, urban areas and arable lands. Lead (Pb) in the study area is mainly accumulated at high altitudes where coniferous forests dominate (Fig. 13). Highest concentrations are foudn on the north side of town, on steep slopes of 30-40 degrees. Spatial distribution of all elements is summarized in Table 1. Concentration of chlorine (Cl) is relatively specific, and it is mainly located at low altitudes. Considerably higher values were detected near urban areas and roads (Fig. 14). Potassium was almost evenly distributed, regardless of urban areas or roads (Fig. 14) but it is more concentrated at low altitudes. Rubidium (Rb) is distributed throughoutthe whole study area on slopes around 25-35 degrees with west, northwest, south and southeast slope sites, in areas dominated by coniferous and mixed forests (Fig. 15). Strontium (Sr) is presenteverywhere in lower concentrations, and only occurs in few a localities in higher concentrations. This includesmiddle and low altitudes, slopes from 5 to 20 degrees, west, northwest and northeast slopes, are where coniferous forests and pastures dominate (Fig. 15). Antimony (Sb) is relatively unevenly dispersed (Fig. 16). It can be found at middle altitudes with slopes around 20-30 degrees,with northeast and southeast slopes in coniferous forests. Highest concentrations of barium (Ba) are around town, roads and their surroundings (Fig. 16). These localities are at lower altitudes with slope from 10 to 20 degrees. The highest concentrations of chromium (Cr) were detected mainly in higher altitudes, steep slopes and the west slopes of study area. In town and its surroundings only moderately higher values of chromium in soils were detected (Fig. 17). The highest concentrations of manganese (Mn) were detected mainly at higher altitudes withsteep wet facing slopes. At low altitudes only moderate values of chromium were detected (Fig. 17). Increased values of calcium (Ca) in the study area are sporadic (Fig. 18), but mainly occur on west slope with meduim inlcination atlower. Titanium (Ti) is also relatively dispersedthorughout the study area, but its highest concentrations occured at lower altitudes. Much higher f concentrations of titanium were detected near the pulp factory

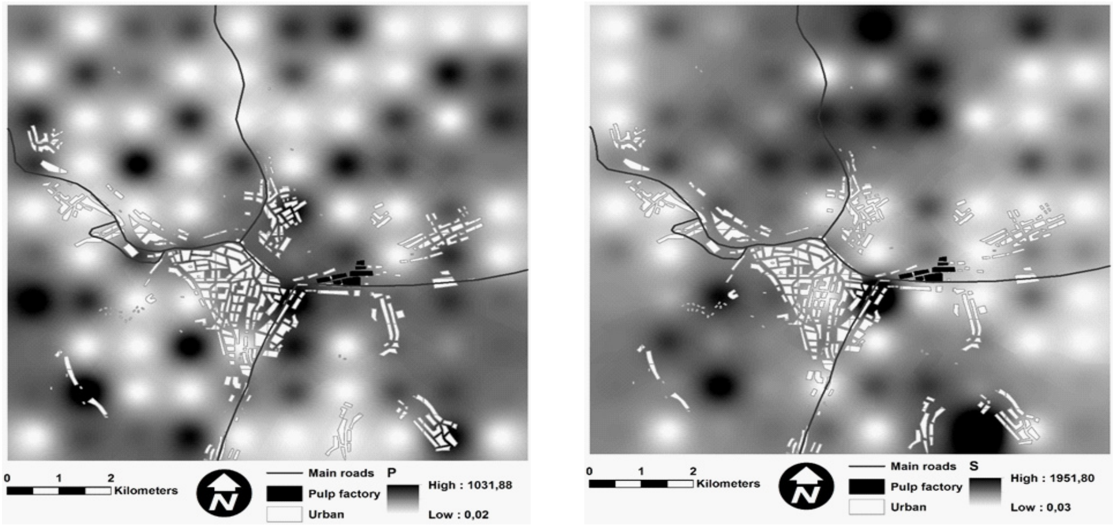

Fig. 8. Spatial distribution of P and S concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

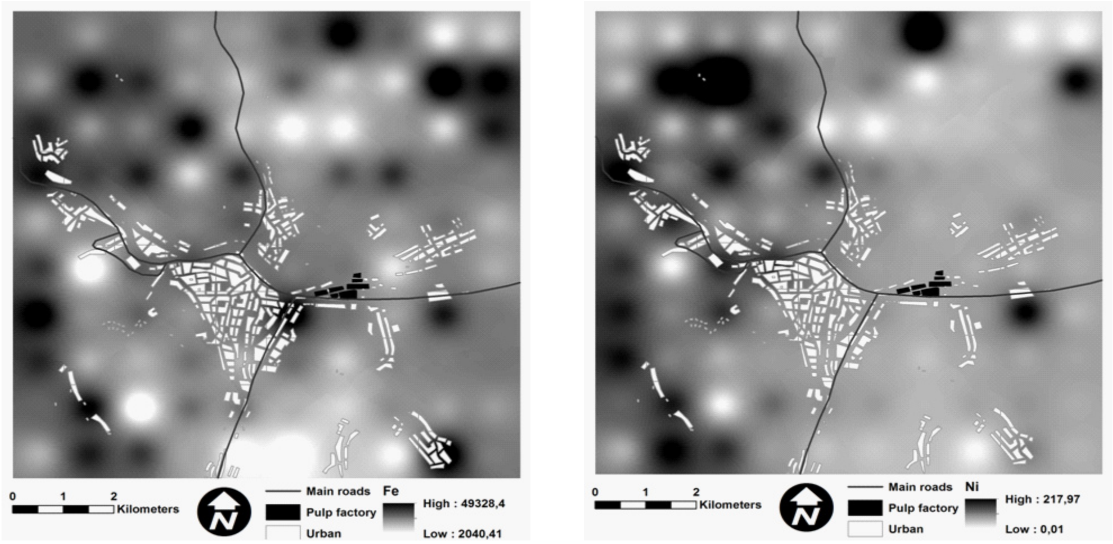

Fig. 9. Spatial distribution of Fe and Ni concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

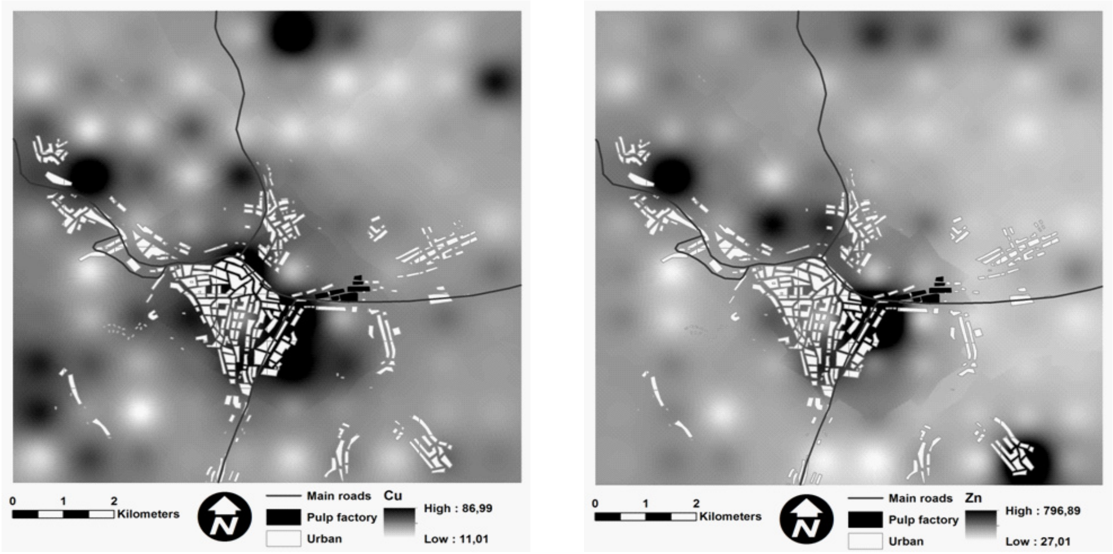

Fig. 10. Spatial distribution of Cu and Zn concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

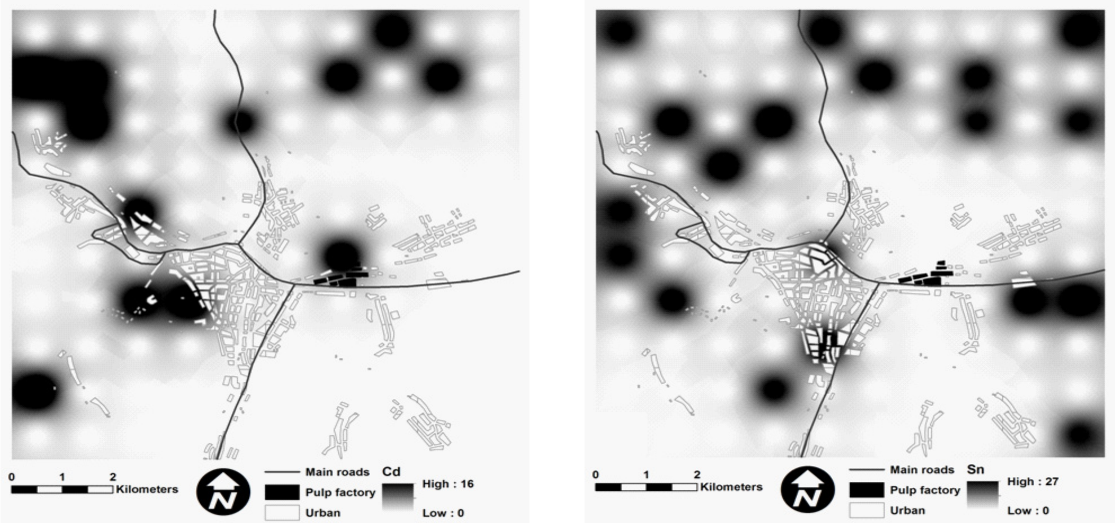

Fig. 11. Spatial distribution of Cd and Sn concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

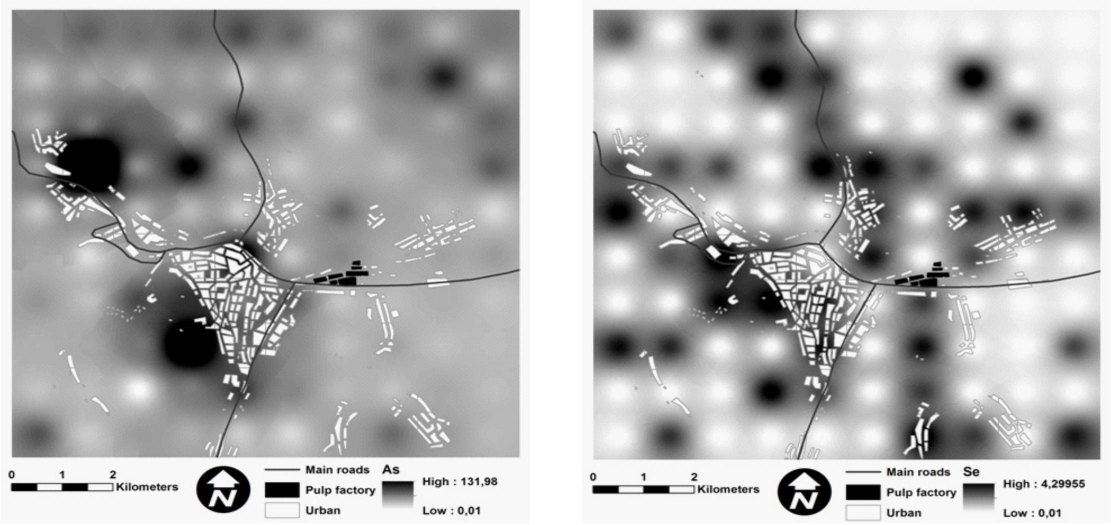

Fig. 12. Spatial distribution of As and Se concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

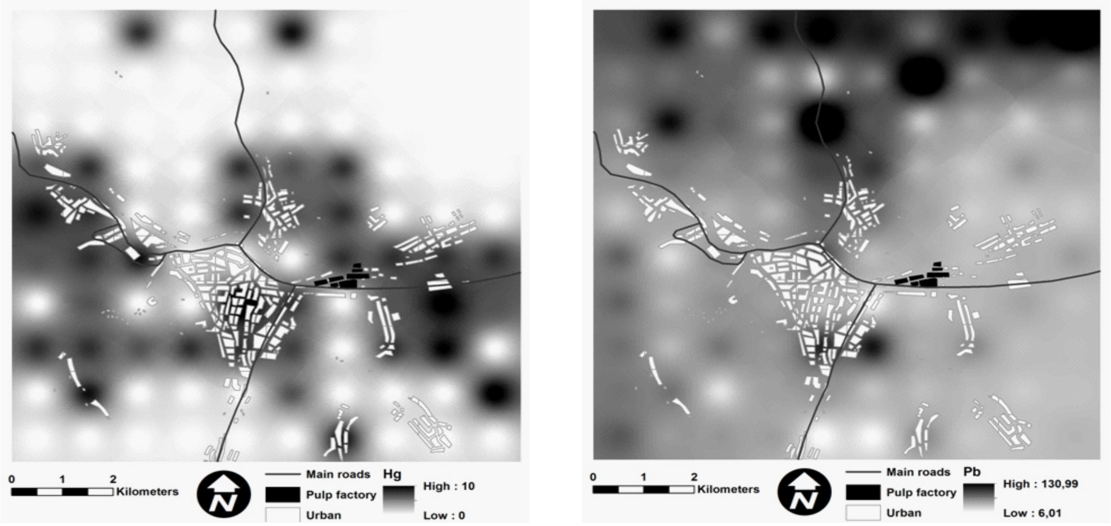

Fig. 13. Spatial distribution of Hg and Pb concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

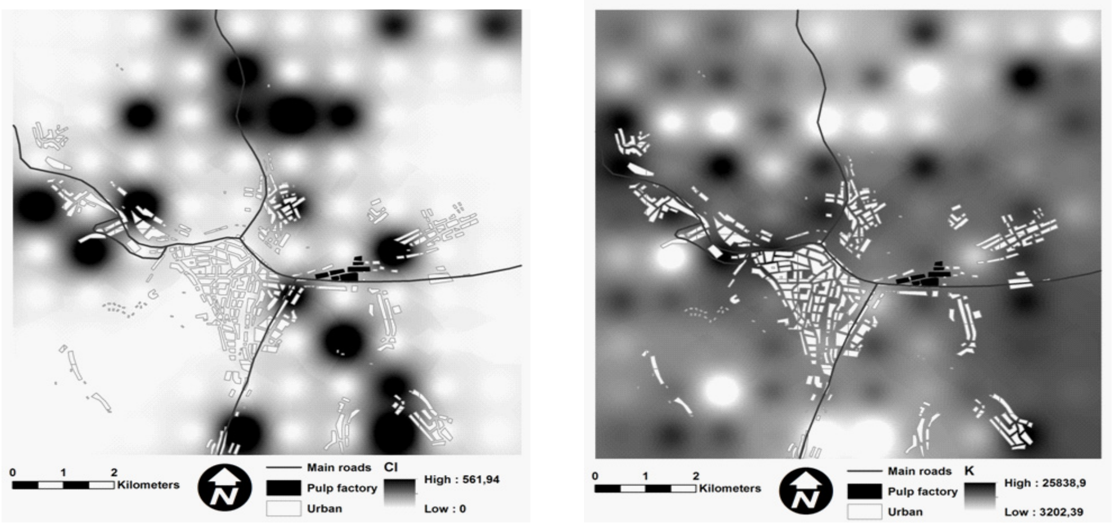

Fig. 14. Spatial distribution of Cl and K concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

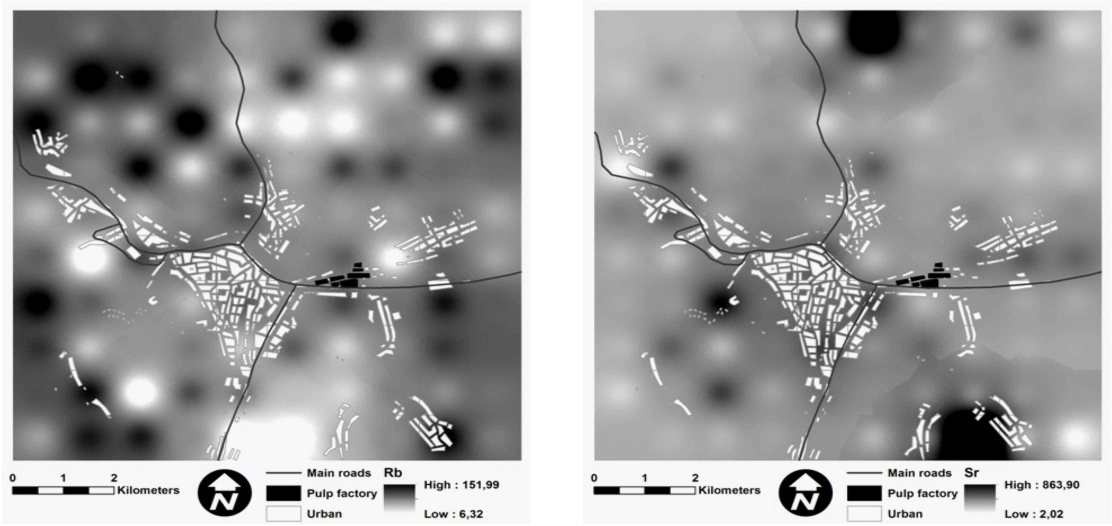

Fig. 15. Spatial distribution of Rb and Sr concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

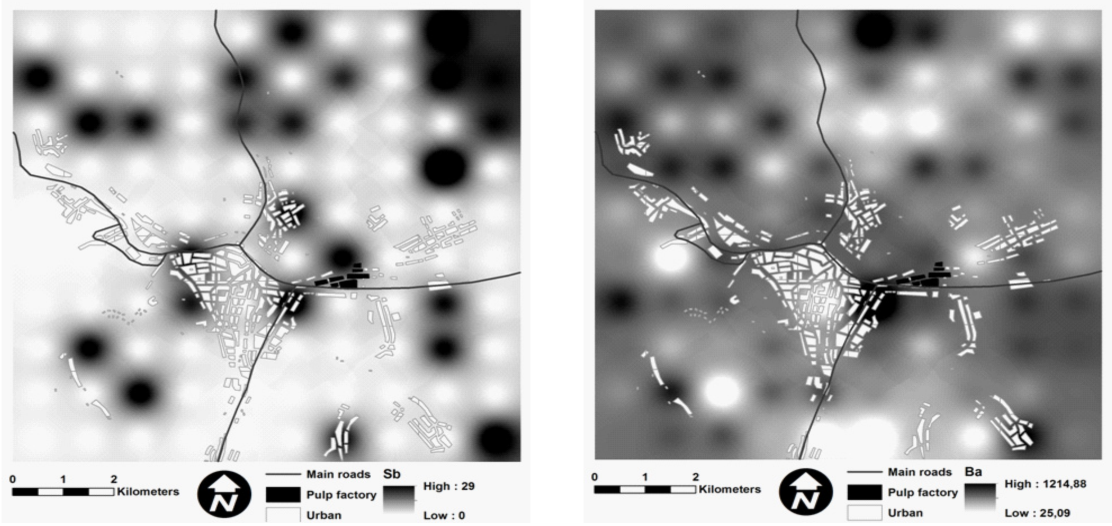

Fig. 16. Spatial distribution of Sb and Ba concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

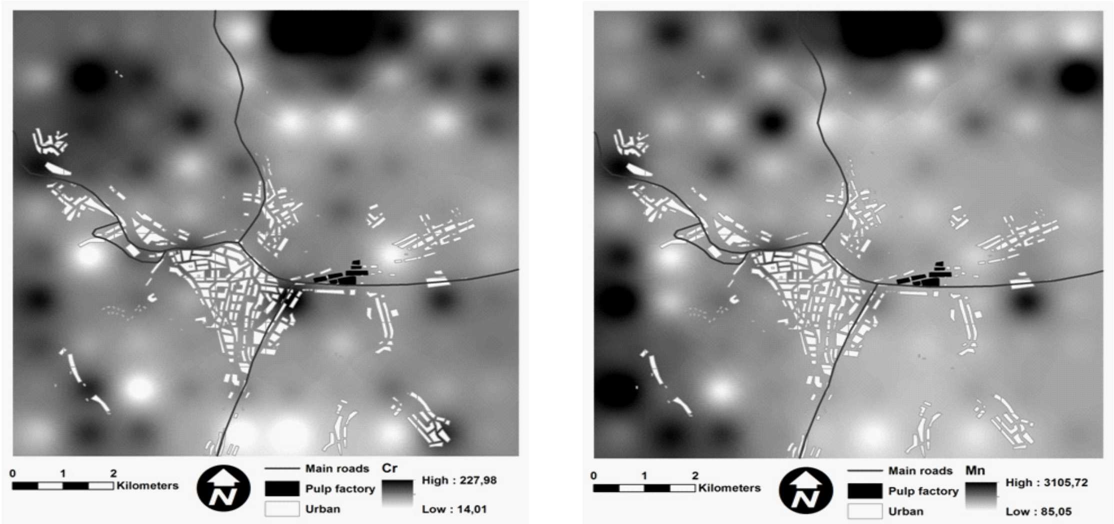

Fig. 17. Spatial distribution of Cr and Mn concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

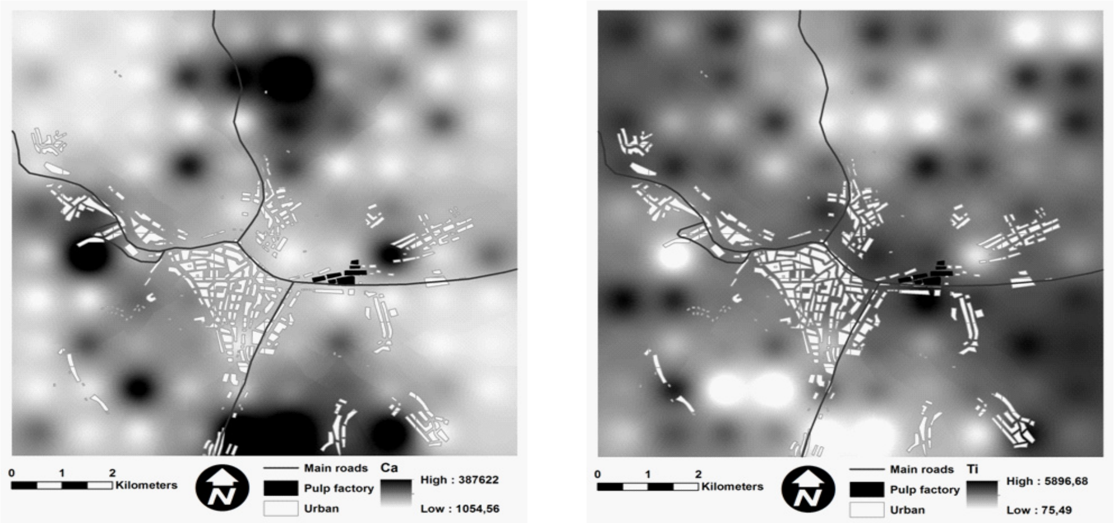

Fig. 18. Spatial distribution of Ca and Ti concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

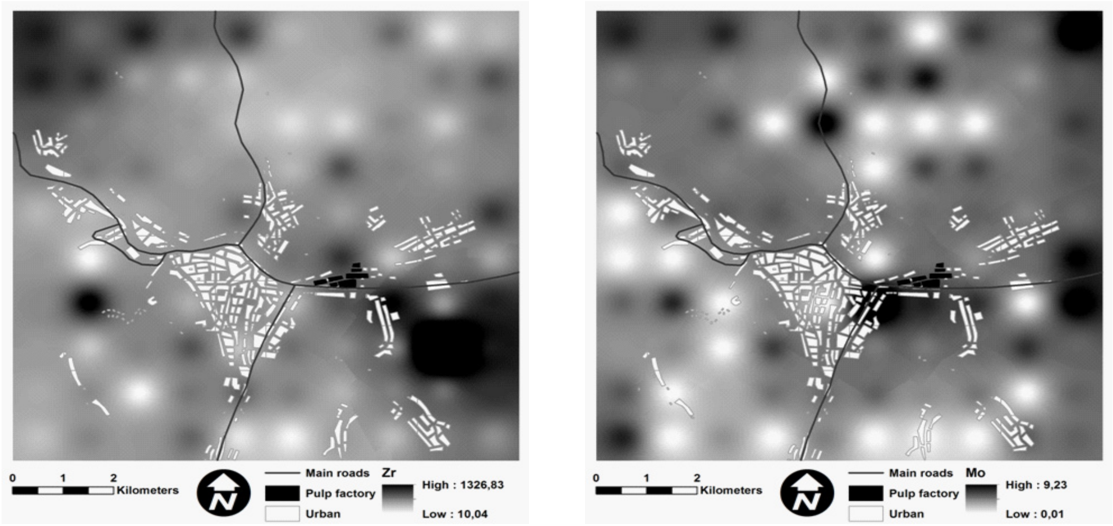

Fig. 19. Spatial distribution of Zr and Mo concentrations in the soils – surroundings of Ružomberok (high concentrations are in black).

(Fig. 18). Zirconium (Zr) is present in all parts of the study area, but high values were discovered (Fig. 19) in areas of arable land at lower altitude, with northwest and northeast slopes of 15-30 degrees. High values were also found near the pulp factory. Higher values of molybdenum (Fig. 19) were detected near the pulp factory, town and its surroundings these corresponded with areas of arable land at lower altitudes with slopes from 5 to 25 degrees.

Discussion

The Ministry of Agriculture, Environment and Regional Development of the Slovak Republic implemented indication and intervention criteria for the appraisal of dangerous concentrations of chemical elements in soil, water and rocks. Indication criteria (ID) means that when the concentration of contaminants exceed the limit value which is given, pollutants could threaten human or animal health and the environment. In this situation monitoring of the endangered area would be warranted.

Intervention criteria (IT) Is a critical value wherein concentrations of contaminantsexceed determined limitsand there is a high probability of threat to human or animal health and the environment. This situation requires a detailed geological monitoring of the endangered environment and analysis of risks (MŽP SR 2015).

For our study of contaminated soils and spatial distribution of elements, we chose Ružomberok town and surroundings, because it is known as one of the most polluted towns in Slovakia (SAZP 1996). The environment of this town is influenced by agricultural practices, and transport, but most significantly by industry. In general, concentration and spatial distribution of individual elements in our study area differ due to parent rock soil horizons, altitude, and distance from roads, the town and the pulp and paper factory.

Arsenic (As) in soils

Arsenic is very distributed in the environment. In the upper horizons of soil, concentration varies from 0.5 to 2.5 mg.kg^{-1}. Arsenic is located mainly in shale, coal, and peat deposits (Kabata-Pendias and Mukherjee 2007). In general, concentrations of As range from 0.5 to 7.5 mg.kg^{-1}, but could be also higher if influenced by human activities (Alloway 2013). Concentrations of arsenic in soil and its accumulation are different in different habitats, and usually each country has own criteria for concentration of arsenic in soils. Chernozems of Siberia have As concentrations from 18 to 32 mg.kg^{-1}, Polish soils have concentrations of As from 0.9 to 3.4 mg.kg^{-1}, in other European soils, concentrations range from 100 to 115 mg.kg^{-1} (Kabata-Pendias and Mukherjee 2007). Arsenic in soils is very well associated with primary and secondary minerals, including oxides and hydroxides of iron. Organic arsenic mainly occurs from throughfall and plant residues (Alloway 2013). Arsenic and its compounds are mobile in alkaline and neutral environments, and are used in agriculture as pesticides. Microorganisms also have a large influence on the mobility and the fleetingness of arsenic in soils (Suchá 2010). It is well known that some plants have a close connection to arsenic in soilssuch as inin oats and tobacco, where we can find the highest arsenic concentrations (Melicherčík and Melicherčíková 2006). In general, concentration of arsenic (As) in Swedish topsoils varies from 0.4 to 10.5 mg.kg^{-1} (Eriksson 2001), while USA soils have values around 5.8 mg.kg^{-1} (Kabata-Pendias and Mukherjee 2007). In Poland, the highest values were detected in shale soils, where the concentration of arsenic ranges from 0.9 to 3.4 mg.kg^{-1}. However, in some industrial parts of Poland much higher concentrations wre discovered, over 650 mg.kg^{-1} (Kabata-Pendias and Pendias 1999). According to Kabata-Pendias and Mukherjee (2007) soils near industrial areas, or soils which are exposed to the impact of fertilizers, pesticides or sludges showed values of arsenic higher than 20,000 mg.kg^{-1}. In our study, we detected that the average value of arsenic was 18.4 mg.kg^{-1}. Higher values were recorded near roads and the town. Our highest detected value of arsenic was 132 mg.kg^{-1} near Hrboltová in meadow soil samples taken 25 meters from the road (in the past this was arable farmland). This high value could be caused by excessive fertilization or by transport.

Barium (Ba) in soils

Barium is a soft metal, which likely concentrates in acid igneous rocks and argillaceous sediments. Concentrations of barium in soils range from 100 to 1,200 mg.kg^{-1}. It has no specific role in plants or animals, but is easily taken up by plants from soils. Some species of plants, such as sunflowers, absorb barium from contaminated soils very well (Alloway 2013). For a study of radon activities and its migration to soils, barium is the best indicator as it has similar ionic radii (Alloway 2013). Barium and potassium are attended on geochemical processes and accumulate in soils and acid rocks. (Frankovská *et al.* 2010). Because of its low solubility, barium is not very mobile but it is very easily absorbed by oxides and hydroxides in most types of soils (Kabata-Pendias and Mukherjee 2007). Concentration of barium (Ba) in surface layers of soils is strongly dependent on organic matter (Kabata-Pendias and Mukherjee 2007). USA´ s soil values are around 265 mg.kg^{-1}. In Polish soils the concentration of barium ranges from 20 to 130 mg.kg^{-1} (Terelak *et.a*l 2001). Higher values occur Swedish soils around 778 mg.kg^{-1} (Eriksson 2001). For agricultural soils in Canada there was an established limit of 750 mg.kg^{-1} (Jaritz 2004). In Slovakia, the limit is 900 mg.kg^{-1}, but this number is not limited to agricultural soils (Table 1). In our study area we detected values from 25 (in forest) to 1,215 mg.kg^{-1} (in a town near industrial area). Higher values were detected mainly near roads.

Cadmium (Cd) in soils

Cd is a white metal which is insoluble in water, but soluble in acids. It is a dangerous element because of its ability to produce organic compounds (Dadová 2013). Its concentrations range from 0.1 to 1.0 mg.kg^{-1} (Alloway 2013). All Cd compounds are toxic and dangerous for human and plant health, and deposits can beocme visible on vegetation. Rice as a crop is the best accumulator of cadmium (Alloway 2013). Cadmium is on the list of pollutants from the Large Water Program of the Environmental Protection Agency (Frankovská *et al.* 2010). Cadmium is recognized as being one of the most toxic metals, which affects all biological processes and environments. Because of the mobility of cadmium in soils, it often has a high influence on oxidation-reduction reactions (Kabata-Pendias and Mukherjee 2007). In contaminated areas, the highest concentration of cadmium is in the upper three centimetres of soils. Mobility of cadmium increases with pH and humidity of soil (Suchá 2010). Concentration of cadmium (Cd) in surface soils around the world varies from 0.06 to 1.1 mg.kg^{-1}. In some European countries concentrations range as follows: Switzerland - 1.7 mg.kg^{-1} (Herter and Kuelling 2001), Denmark 0.3 mg.kg^{-1}, France 4.4 mg.kg^{-1} (Eckel *et.al* 2005). The highest concentrations of Cd in soils were detected near industries. For example, 270 mg.kg^{-1}, in Poland, 1,500 mg.kg^{-1}, in the USA or 1,781 mg.kg^{-1}, in Belgium (Kabata-Pendias and Pendias 2001). In our study area, we detected the highest value at the level of 16.0 mg.kg^{-1}, the average value was 1.53 mg.kg^{-1}.

Chromium (Cr) in soils

Cr is commonly accumulated in the top layer of soils (Kabata-Pendias and Mukherjee 2007). It is often used in industry, but moreso in the pulp and paper and wood preservation and metallurgy industry than in the textile industry. Low concentrations of Cr could play an essential role in the environment and for organisms, but higher concentrations are toxic and can cause death (Alloway 2013). Mobility of chromium depends mainly on the quantity of organic matter, clay minerals and pH. Acidic and alkaline environments are the best for mobility of chromium in soil (Suchá 2010). The average value of chromium (Cr) in Swedish soils is 22 mg.kg^{-1} (Eriksson 2001). In Japanese soil concentrations vary from 56 to 70 mg.kg^{-1} (Takeda *et al.* 2004). The main factors attributed to increased pollution of soils are agricultural practices and different types of wastes, including sludge and municipal waste (Kabata-Pendias and Mukherjee 2007). In some polluted parts of Portugal chromium values were were detected 27.000 mg.kg^{-1} (Morgado *et al.* 2001). In surface soils in our study area, we detected values from 14 to 228 mg.kg^{-1}. Our detected values did not exceed indicator values, which are 450 mg.kg^{-1} in Slovakia (Table 1).

Mercury (Hg) in soils

Mercury naturally occurs only in a low quantity. Anthropogenic sources of mercury include exploitation of fossil fuels, industry, wastes and gold production. In agriculture, soil contamination is caused use of fertilizers and fungicides (Alloway 2013). Lower concentrations occur in loamy and sandy soils, and higher concentrations occur in organic soils (Kabata-Pendias and Mukherjee 2007). Increase of mercury in the environment is related to industrial development. Hg in soil would be present in its solid state or as a volatile element. Higher participation of organic matter in soils decreases the ability of mercury mobility (Suchá 2010). Hg is also very well absorbed by plants, but all forms of mercury are toxic (Frankovská *et al.* 2010). Mercury gets into the environment mainly through the burning of fuel, wastes, and also by bad processes in industry and agriculture (Dadová 2014). In the world, the concentration of mercury (Hg) ranges from 0.001 to 212 mg.kg^{-1} (Kabata-Pendias and Mukherjee 2007), in China soil concentrations of mercury vary from 0.015 to 0.294 mg.kg^{-1} (Govindaraju 1994), but much higher concentrations of Hg in China were detected near industrial areas. In Swedish forest soils average values around 0.24 mg.kg^{-1} were detected (Andersson 1987). In surface layer soils in our study area we detected an average value of Hg 2.27 mg.kg^{-1}. Higher values of mercury in soils were, comparable to those in China were detected near roads and industry areas, but did not exceed a value of 2.25 mg.kg^{-1} (Table 1).

Nickel (Ni) in soils

Nickel is a hard metal which has a wide range of concentrations in the environment. In the surface of soil horizons Ni occurs mainly as an organically bound form. The presence of nickel in soil is a result of parent rocks, but also comes from natural sources such as volcanic activity, forest fire or meteoric dust (Frankovská *et al.* 2010). Nickel in the upper soil horizon reflects the impact of air pollution. Concentrations range from 3 to 48 mg.kg^{-1} (Alloway 2013). The more acidic the environment, the lower nickel concentration is found in soil. Mobility of Ni in soil is not large, but it is very well associated with Fe and Mn oxides and their minerals (Kabata-Pendias and Mukherjee 2007). Although nickel is considered one of the heavy metals, in low concentrations it plays an essential role for fungi, some bacteria and microorganisms (Alloway 2013). In the world, values of Nickel (Ni) in surface layers of soils range from 0.2 to 450 mg.kg^{-1}. In Poland, agricultural soils showed concentrations from 6.2 to 18 mg.kg^{-1} (Terelak *et al.* 2000), these values are dependent on parent material (Kabata-Pendias and Mukherjee 2007). In Swedish soils the values fall around 13 mg.kg^{-1} (Eriksson 2001). Russian soils showed values from 28 to 34 mg.kg^{-1} (Protasova and Kopayeva 1985). According to Kabata-Pendias and Mukherjee (2007) the higher values of nickel could be attributed to the presence of other elements, which naturally exist in soils, such as iron and manganese. The average value of nickel in our study area was 46.36 mg.kg^{-1}, the highest detected value was 218 mg.kg^{-1} (Table 2). In some samples values higher than the indicator value were detected (Table 1).

Lead (Pb) in soils

Lead is a very soft metal, with a good resistance to corrosion. It has one of the lowest levels of mobility in the environment. It is an extensive polluter of soil, and hasan impact on microbiological activity in soil that subsequently reduces soil productivity (Frankovská *et al.* 2010). Elemental Pb is considered toxic, but its oxides and salts are also toxic. Toxicity of lead depends on soil type, soil species and soil reaction (Suchá 2010). The natural way that lead gets into the soil, is from parent rocks. Lower concentrations of Pb occur in sands, sandstones and limestones. The higher concentrations of Pb occur in argillaceous sediments. Lead is very well associated with oxides, including Fe and Mn (Kabata-Pendias and Mukherjee 2007). The concentration of lead (Pb) in the world soils ranges 0.1 to 16,388 mg.kg^{-1} (Kabata-Pendias and Mukherjee 2007). For example in Ireland, values range from 0.5 to 138 mg.kg^{-1} (Dickson and Stevens 1983), while in Wales from they range from 35 to 16 388 mg.kg^{-1}, and in Poland they range from 0.1 to 5,000 mg.kg^{-1} (Terelak and Pietrowska 1998). In our study area we recorded an average value of 41.45 mg.kg^{-1} (Table 2.– surface layer). Higher values were detected at high altitudes, where the deposition of lead may depend on air flows. Our detected values did not exceed the indicator value (Table 1).

Sulphur (S) in soils

Natural sulphur occurs as afree element near volcanos, hot springs and meteorites. Large-scale deposits of sulphur wwere found in soils in Texas and Louisiana, in the USA (Winter 2014). Sulphur concentrates in organic matter and is found in top layers of soils (Barančíková *et al.* 2009). Sulphur is essential for plants and animals, and no negative effects due to higher concentrations were mentioned. In other districts of Slovakia, the amount of sulphur was recorded at a level of 113.4 to 329.1 mg.kg^{-1} (Jedlovská and Feszterová 2008). In our study area we detected that average values of sulphur in the upper horizons of soils were 458.82 mg.kg^{-1}. Our highest detected value was 1,952 mg.kg^{-1}. These higher values were detected near roads and urban sites.

Chlorine (Cl) in soils

Chlorine accumulates well in mafic rocks, sandstone and calcareous rocks, and not well in organic matter. It has a good mobility in many types of soils and it is well transported by water. Cl is concentrated mainly in surface layers of arid and semiarid climate zones (Kabata-Pendias and Mukherjee 2007). At some concentrations, chlorine is essential for mammals and plants (Winter 2014). Higher concentrations of Cl in soils have deleterious effects on vegetation and soil properties (Kabata-Pendias and Mukherjee 2007). Chlorine in Japanese forest soils was detection at values from 91 to 486 mg.kg^{-1}, in Japanese soils in upland fields the average was 114 mg.kg^{-1} (Kabata-Pendias and Mukherjee 2007). Our samples measured 78.84 mg.kg^{-1} on average, with the highest detected value at 562.0 mg.kg^{-1}. Chlorine in our study area was distributed very unevenly. High values were detected near some roads.

Rubidium (Rb) in soils

Generally, rubidium occurs in acid-igneous rocks and sedimentary-argillaceous rocks, but is also present in lower concentrations in sandy and organic soils. Heavily textured soils contain relatively high concentrations of rubidium (Kabata-Pendias and Mukherjee 2007). Concentrations of rubidium in topsoils range from 80 to 390 mg.kg^{-1} (Alloway 2013). In general, rubidium does not play any specific role in organisms, but it is useful in metabolic processes and can help with the accumulation of potassium in muscle (Winter 2014). Rubidium is preferably accumulated by tobacco, sugar beet and vines. According to Govindaraju (1994) in the US, rubidium concentrations in soil ranged from 69 to 1,141 mg.kg^{-1}. In China the concentration of rubidum in surface soils wasbetween 15 and 140 mg.kg^{-1}, and in Swedish soils the concentrations varied from 2.5 to 53 mg.kg^{-1} (Eriksson 2001). We measured from 6.3 to 152 mg.kg^{-1} (Table 2).

Zirconium (Zr) in soils

The lowest concentrations of Zr are found in ultramafic rocks and calcareous sediments. The main source of zirconium in soils is parent material. Similarly to titanium, Zr is also used as a soil index. Some Zr minerals play a significant role in the technological industry (Kabata-Pendias and Mukherjee 2007). In the environment, Zr is slightly mobile due to its resistance to weathering. Zirconium does not represent a serious threat for the environment (www.lenntech.com 2017). Concentrations of zirconium (Zr) in Russian soils vary from 200 to 500 mg.kg^{-1} (Protasova and Kopayeva 1985). In Japan, surface layers of agricultural soils showed average values of 85 mg.kg^{-1}was (Takeda *et al.* 2004). In Swedish soil zirconium ranges from 308 to 757 mg.kg^{-1} (Eriksson 2001). In our samples we found surprisingly high values ranging from 10 to 1.327 mg.kg^{-1} (Table 2).

In our work we've shown that higher concentrations of chemical elements occur near Ružomberok and its surounding area. These elements, including heavy metals, can have harmful effect on soil, plants and subsequently on human health. In general, we have detected higher values of sulphur, chlorine and mercury mainly near the town and main roads. Chromium, rubidium, zirconium and barium were relatively equally distributed in the whole study area and lead was found to be specifically dispersed. Higher concentrations of this element were detected at higher altitudes in the northern part of the town.

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