The influence of vegetation type on metal content in soils

Vpliv vrste vegatacije na vsebnost težkih kovin v tleh

Nina Zupančič[1, *]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva 12, SI-1000 Ljubljana, Slovenia

*Corresponding author. E-mail: nina.zupancic@ntf.uni-lj.si

Received: August 31, 2012 **Accepted:** September 14, 2012

Abstract: Human influence on soil contamination with metals can only be established when the real background values are known. Besides parent rock type and climate, vegetation cover can be one of the factors influencing soil properties. Fifty samples of soils developed on Upper Triassic dolomite at an elevation of around 600 m and on slopes with SW insulation were collected. At each of the five locations, four samples and one replicate were taken from forest-covered area and from area covered by grass. The Co, Cr, Cu, Ni, Pb and Zn content was analysed by emission spectroscopy. Very high Co, Cr and Ni values are natural, typical for karstic soils in Slovenia. An analysis of variance showed a high analytical error for Pb and Zn, and high variability at small distances (1 m, 10 m, and 100 m) for Co, Cr, Cu and Ni. This is the reason why vegetation influence on the metal content was only proven for Cu. On the contrary, a t-test indicates lower values of all elements in the forest soils, except Pb, where there seems to be no difference between soils covered by grass or forest. The reason for the higher metal content in the meadow soils could be the application of manures. Vegetation cover should be considered when designing the sampling and interpreting the data.

Izvleček: Vpliv človeka na onesnaženost tal s kovinami lahko ugotovimo le, če poznamo prave vrednosti ozadja. Poleg matične podlage in podnebja je eden od dejavnikov, ki vplivajo na lastnosti tal, lahko tudi vegetacijski pokrov. Na nadmorski višini 600 m smo na pobočjih vzorčili 50 vzorcev tal, razvitih na zgornjetriasnem dolomitu. Na vsakem od petih področij smo odvzeli štiri vzorce in eno ponovitev na delu, pora-

---

Original scientific paper

ščenem z gozdom, in delu, poraščenem s traviščem. Vsebnost Co, Cr, Cu, Ni, Pb in Zn je bila določena z emisijsko spektroskopijo. Izredno visoke vsebnosti Co, Cr in Ni so naravne in značilne za kraška tla v Sloveniji. Analiza variance je pokazala visoko analitsko napako Pb in Zn ter veliko spremenljivost Co, Cr, Cu in Ni na majhni razdalji (1 m, 10 m in 100 m). Zato je vpliv vegetacije na vsebnost težkih kovin z analizo variance potrjen le za Cu. Nasprotno, t-test kaže v gozdnih tleh nižje vsebnosti vseh prvin, razen Pb, kjer je videti, da ni razlik med tlemi, poraščenimi z gozdom ali traviščem. Razlog za višje vsebnosti kovin v tleh bi lahko bilo gnojenje. Pri načrtovanju vzorčenja in interpretaciji rezultatov bi morali upoštevati vrsto rastlinske poraščenosti.

Key words: soil, metals, vegetation
Ključne besede: tla, težke kovine, vegetacija

INTRODUCTION

The distribution of most elements in soils shows a pattern related to geology. Geochemical surveys reveal patterns of a geochemical signature on the scale of the selected area, and indicate the different factors influencing these patterns, notably bedrock geology, climate and human influences (De Vos & Tarvainen, 2006). With time, soil-forming processes modify the basic geochemical composition and redistribute the content of metals within the soil profile (Bini et al., 2011). In their study of the FOREGS database, Imrie et al. (2008) reported that the overall distribution of geochemical elements in European topsoils follows diverse patterns that can be explained by various processes occurring on different spatial scales. They concluded that the geochemical variation on short scales chiefly depends on local variations of lithology, land use, weathering processes and organic matter content.

Vegetation is a well-known key factor governing soil-forming processes. A diversity of vegetation can lead to different stages of soil formation, soil profiles and soil types (Küfmann, 2003). In certain climatic conditions, vegetation influences the status of trace elements by affecting their release, migration, transformation and transportation (Zhang et al., 2002). Some authors try to eliminate at least some effects of pedogenic processes by, for example, sampling just forest soils (De Vos & Tarvainen, 2006; Bini et al., 2011), which is not always possible. Others seek to establish how different land use and/or vegetation cover may influence metal accumulation in soils (Bai et al., 2010; Baize & Sterckeman, 2001; Zhang et al., 2002; Xia et al., 2011). Zhao et al. (2007) even proposed that vegetation would best proxy the delineation of the single attribute of urban soils and can be used as a basis for soil regionalisation in urban and peri-urban environments.

To establish anthropogenic soil pollution it is necessary to know what the real background values are. It is therefore very important to evaluate not only the geologic and climatic effect on soil geochemistry, but also the biologic one. The presented study was part of a project to geochemically map Slovenia which was designed and conceptually guided by Prof. Dr. Simon Pirc. The aim of this paper is to present possible differences in the content of six metals (Co, Cr, Cu, Ni, Pb, and Zn) in soils developed on the same parent rock but covered by forest or grassland in Slovenia.

Materials and methods

As the main purpose of the study was to establish the influence of vegetation cover on metal contents in soils, we tried to minimise all other possible factors which could affect their content. Slovenia is prevailingly a carbonate country so we decided to sample on Upper Triassic dolomite, which is supposed to be spatially quite uniform. The sampling locations were selected from five different parts of Slovenia (Postojna, Zaplana, Stična, Dole pri Litiji, Dolič pri Mislinji) representing variations of climatic conditions in terms of distance from the sea, but always at approximately the same elevation (600 m) and the same inclination of the slope (SW).

At each sampling location, four soil samples were taken from the grassland and four from the forest. At Postojna, the vegetation type was *Carici humilis – Centaureetum rupestris* for grassland and *Querco – Carpinetum* for the forest. At Zaplana, the meadows were mainly cultivated (*Brometalia erecti*) and the forest type was *Ostryo – Fagetum*. At Stična, the grassland was covered with *Arrehno – thetrtum medioeuropeum* and the woods with *Fagetum submontanum praedinaricum*. The same forest type prevails at Dole pri Litiji, where the grassland is *Bromo – brachypodietum*. Dolič was vegetated with *Arrehno – theretum medioeuropeum* on the meadows and with the only type of coniferous forest – *Genisto – Pinetum*. At all of the grassland locations contamination due to agriculture was possible to some extent.

Four samples at each location were arranged in randomly positioned 100 m long profiles, with samples taken at

0 m, 1 m, 10 m and 100 m from the starting point. Each sample from the starting location was split into two to provide replicate samples to serve as a control over the accuracy of the analyses. This sampling strategy enabled a hierarchical nested analysis of variance (ANOVA) design to be used along with an estimation of the variability source and its significance.

A total of 50 soil samples weighing 1.5–2 kg were collected. All organic soil horizons were removed, and soil down to a depth of 15 cm was taken. The soil samples were air dried. About 1 kg of every sample was ground, split and sieved to produce a 20 g sample with a grain size of less than 0.063 mm. The chemical composition of the samples was determined at the Kemijski inštitut (National Institute of Chemistry, Ljubljana, Slovenia) by emission spectroscopy.

To control the accuracy of the analysis five standard materials (GXR-2, GXR-5 (Allcot & Lakin, 1978), SO-1, SO-2, SO-3 (Abbey, 1983)) were added. The Co, Cr and Zn accuracy was established good, Cu, Ni, and Pb satisfactory. Precision was estimated from ANOVA of repeated soil samples and a calculation of the coefficients of variation (*CV*) for five replicate analyses of each standard material. Generally, analytical error is below 10 % for Co, Cr, Cu and Ni and close to 30 % for Pb and Zn. The interpretation of the last two elements requires some caution.

RESULTS

Analytical results with the ANOVA scheme are presented in Table 1, whereas descriptive statistics of all samples and both vegetation groups are shown in Table 2.

Table 1. Analysis of variance (ANOVA) design and metal content (mg kg^{-1}) for 50 soil samples from Upper Triassic dolomite from Slovenia.

sample	vegetation	location	100 m	10 m	1 m	anaytics	Co	Cr	Cu	Ni	Pb	Zn
s1	forest	Postojna	1	1	1	1	14	75	17	40	33	51
s2	forest	Postojna	1	1	1	2	16	67	13	32	65	30
s3	forest	Postojna	1	1	2	1	12	117	117	7	40	49
s4	forest	Postojna	1	2	1	1	14	102	16	59	11	22
s5	forest	Postojna	2	1	1	1	37	135	32	102	22	65
s6	forest	Zaplana	1	1	1	1	20	98	17	59	30	52
s7	forest	Zaplana	1	1	1	2	23	100	22	76	49	60
s8	forest	Zaplana	1	1	2	1	34	165	27	117	39	64
s9	forest	Zaplana	1	2	1	1	26	132	22	103	35	34

s10	forest	Zaplana	2	1	1	1	43	170	34	133	36	84
s11	forest	Stična	1	1	1	1	16	70	21	47	25	35
s12	forest	Stična	1	1	1	2	10	82	21	48	34	53
s13	forest	Stična	1	1	2	1	12	85	85	9	41	123
s14	forest	Stična	1	2	1	1	16	87	18	43	65	74
s15	forest	Stična	2	1	1	1	24	62	18	39	35	70
s16	forest	Dole	1	1	1	1	33	190	22	70	29	49
s17	forest	Dole	1	1	1	2	25	170	25	75	39	43
s18	forest	Dole	1	1	2	1	33	167	25	90	2	40
s19	forest	Dole	1	2	1	1	29	190	36	93	48	90
s20	forest	Dole	2	1	1	1	21	114	20	61	13	18
s21	forest	Dolič	1	1	1	1	10	42	17	22	45	53
s22	forest	Dolič	1	1	1	2	9	42	18	20	52	12
s23	forest	Dolič	1	1	2	1	3	25	33	13	14	66
s24	forest	Dolič	1	2	1	1	15	50	10	26	37	47
s25	forest	Dolič	2	1	1	1	10	53	12	30	255	275
s26	meadow	Postojna	1	1	1	1	25	175	27	80	34	93
s27	meadow	Postojna	1	1	1	2	29	171	28	76	26	49
s28	meadow	Postojna	1	1	2	1	32	200	26	89	40	54
s29	meadow	Postojna	1	2	1	1	12	90	19	59	32	34
s30	meadow	Postojna	2	1	1	1	16	205	32	84	165	270
s31	meadow	Zaplana	1	1	1	1	28	140	33	99	16	33
s32	meadow	Zaplana	1	1	1	2	35	185	32	112	42	86
s33	meadow	Zaplana	1	1	2	1	28	140	24	102	13	31
s34	meadow	Zaplana	1	2	1	1	27	175	30	85	33	100
s35	meadow	Zaplana	2	1	1	1	48	230	31	119	20	21
s36	meadow	Stična	1	1	1	1	51	160	28	61	37	61
s37	meadow	Stična	1	1	1	2	46	175	24	60	37	49
s38	meadow	Stična	1	1	2	1	65	250	31	85	58	65
s39	meadow	Stična	1	2	1	1	60	175	38	70	62	100
s40	meadow	Stična	2	1	1	1	41	125	35	65	80	710
s41	meadow	Dole	1	1	1	1	43	193	32	74	34	66
s42	meadow	Dole	1	1	1	2	41	142	34	72	29	119
s43	meadow	Dole	1	1	2	1	52	202	50	79	58	89
s44	meadow	Dole	1	2	1	1	41	140	43	95	16	42
s45	meadow	Dole	2	1	1	1	32	130	29	74	18	63
s46	meadow	Dolič	1	1	1	1	18	75	28	34	35	58
s47	meadow	Dolič	1	1	1	2	19	95	27	37	24	66
s48	meadow	Dolič	1	1	2	1	19	89	29	41	28	155
s49	meadow	Dolič	1	2	1	1	25	83	27	42	21	56
s50	meadow	Dolič	2	1	1	1	10	57	17	26	20	50

Table 2. Descriptive statistics of metals (mg kg^{-1}) for all 50 soil samples, and for the forest and meadow subgroups. Corrected Mean – Mean of data where outliers were replaced by the average of the element, SD – Standard Deviation, CV – Coefficient of Variation, Skew. – Skewness, Kurt. – Kurtosis, S-W – normality according to Shapiro-Wilk's test.

All	Mean	Corrected Mean	Median	Min	Max	SD	CV	Skew.	Kurt.	S-W
Co	26.96	26.96	25	3	65	14.293	53.0	0.68	–0.05	yes
Cr	127.84	127.84	131	25	250	55.233	43.2	0.09	–0.93	yes
Cu	29.04	26.12	27	10	117	17.137	59.0	3.53	15.63	no
Ni	64.68	64.68	68	7	133	30.873	47.7	0.04	–0.69	yes
Pb	41.44	34.70	35	2	255	39.160	94.5	4.06	19.60	no
Zn	81.58	60.54	57	12	710	103.739	127.2	4.96	28.43	no
Forest										
Co	20.20	20.20	16	3	43	10.210	50.55	0.55	–0.47	yes
Cr	103.60	103.60	98	25	190	49.569	47.85	0.36	–1.01	yes
Cu	27.92	22.08	21	10	117	23.463	84.04	3.05	9.64	no
Ni	56.56	56.56	48	7	133	35.008	61.90	0.51	–0.58	yes
Pb	43.76	35.32	36	2	255	46.574	106.43	4.15	19.31	no
Zn	62.36	51.40	52	12	275	50.398	80.82	3.35	13.80	no
Meadow										
Co	33.72	33.72	32	10	65	14.752	43.75	0.36	–0.56	yes
Cr	152.08	152.08	160	57	250	50.470	33.19	–0.14	–0.65	yes
Cu	30.16	30.16	29	17	50	6.817	22.60	0.90	2.43	yes
Ni	72.80	72.80	74	26	119	24.145	33.17	–0.17	–0.39	yes
Pb	39.12	34.08	33	13	165	30.831	78.81	3.10	11.76	no
Zn	100.80	69.68	63	21	710	136.610	135.53	4.06	17.90	no

The metal abundance sequence varies somewhat regarding all the data or separate groups and also if we take mean or median values as a measure of it. Most commonly, it is Cr > Zn or Ni > Pb > Cu or Co. The highest values of Co, Cr and Zn are found in the Stična grasslands, Ni in the Zaplana forest and Pb in the Dolič forest. The lowest values of all elements are always found in forests – Co, Cr, Cu and Zn in Dolič, Ni in Postojna and Pb in Dole. The variation sequence according to CV also differs for all data, forest and grassland, but the values are very high in all cases. For all data, it is Zn > Pb > Cu > Co > Cr > Ni, for forest Pb > Cu > Zn > Ni > Co > Cr and for grassland Zn > Pb > Co > Cr > Ni > Cu.

Most statistical analyses demand a normal distribution of the data. The normality of the distribution was tested visually from histogram and normal probability plots, with comparisons of the mean, geometric mean and median, testing of skewness and kurtosis and with Shapiro-Wilk's test, as proposed by Madansky (1988). The distribution is not normal for Co, Cr and Ni and extremely positively skewed for Cu, Pb and Zn. For all three elements, the deviation from normality is mainly caused by five outliers (s3, s13, s25, s30 and s40), with three of them being in forests (Postojna, Stična, Dolič) and two in meadows (Postojna and Stična). Except in outlier s3 where only the Cu, and s40 where only the Zn content is very high, in the rest of them two elements exhibit extreme values – in s13 Cu and Zn, in s25 and s30 Pb and Zn. Omitting outliers from the datasets improves the distribution to normal. Coefficients of variation remain around 30 due to the very low values recorded for every analysed element. As it was uncertain if the extreme values are real or perhaps just the consequence of an error, we transformed all the data to a more symmetric distribution with a Box-Cox transformation (Box & Cox, 1964). This transformation improved the normality of the distribution of all variables except Pb, which remained a little skewed. If we replace the outliers of critical elements with mean values for the appropriate vegetation type (forest Cu 28, Pb 44, Zn 62, and meadow Pb 39, Zn 101), the distributions become normal for all elements except Zn. All of the statistical analyses were performed with parametric statistics for the Box-Cox transformed data and the data with outliers changed by mean values – so-called corrected data. The results with the original data are presented in the box-whisker diagrams.

The correlations were computed on raw data (Table 3), mean-replaced outliers data, and Box-Cox transformed data with a nonparametric Spearman correlation coefficient as proposed by Swan & Sandilands (1995). All three matrices are similar, showing a really good correlation among Co – Cr – Ni and a less persuasive one of Cu with this group of elements, and Zn and between Pb, and Zn.

Table 3. Nonparametric Spearman correlation coefficients of raw data ($n = 50$). The 95 % statistically significant values are in bold.

	Co	Cr	Cu	Ni	Pb
Cr	**0.79**				
Cu	**0.54**	**0.54**			
Ni	**0.73**	**0.78**	**0.39**		
Pb	0.01	0.08	0.05	–0.12	
Zn	0.18	0.18	0.**46**	0.01	**0.45**

The comparison of the metal content in soils covered with different types of vegetation was first assessed with a t-test. The Box-Cox transformed data results (Table 4) indicate statistically significant differences in Co, Cr, Cu and Ni content between the forest and grassland soils. Data with the replaced outliers (Table 4) give the same result for Co, Cr and Cu as the Box-Cox transformed data, but show no differences in Ni and in addition differences in Zn.

Raw data (Table 2, Figure 1) generally show a lower mean content of all elements, except Pb in the forest soils and the high variability of Cu and Pb in the forest and Zn in the meadow soils. Enrichment in meadow soils is most pronounced for Co (1.7-times), followed by Zn (1.6-times), Cr (1.5-times), Ni (1.3-times) and Cu (1.1-times). If we disregard the outliers, the sequence is Co (1. 7-times), Cr (1.5-times), Cu (1.4-times) = Zn (1.4-times) and Ni (1.3-times). In both cases, the Pb values are just a little higher in the forest soils.

Table 4. t-test and F-test results of Box-Cox transformed (first row) and corrected (second row) data. Statistically significant results are in bold.

	t	p	F	p
Co	**–3.76**	**0.00**	1.14	0.76
	–3.77	**0.00**	2.09	0.08
Cr	**–3.44**	**0.00**	1.16	0.72
	–3.43	**0.00**	1.04	0.93
Cu	**–2.55**	**0.01**	**5.53**	**0.00**
	–4.14	**0.00**	1.05	0.91
Ni	**–2.03**	**0.05**	2.26	0.05
	–1.91	0.06	2.10	0.07
Pb	0.04	0.97	1.90	0.12
	0.28	0.78	1.12	0.78
Zn	–1.73	0.09	1.08	0.85
	–2.47	**0.02**	**2.64**	**0.02**

The high variability of the data and/or the existence of outliers seem to hinder the interpretation so a hierarchical nested analysis of variance was performed taking the influence of not only vegetation into consideration, but also the geographical position of the sampling location, the place of the sample in each sampling profile and analytical replications. A method using the expected MS and a Type III calculation of SS was applied. The results for the Box-Cox transformed data and corrected data are presented in Table 5 and Figure 2. It is obvious that the vegetation type is never the main source of variation for any element. The influence of vegetation is highest for corrected values of Cu (28 %), where it is also statistically significant. For Co and Cr, the proportion for the vegetation level is around 15 %, but not significant, for corrected Zn around 10 %, and practically 0 for Ni, Pb and non-corrected Zn. The statistical significance of the corrected Zn is unreliable due to high analytical error. The same is true for the corrected Pb and non-corrected Zn results so any further statistical inference regarding these two elements is limited. A quite obvious feature of the data is the statistically significant variability at a small scale, i.e. comparison of 0 m and 1 m, for Co, Cr, Cu, Ni and it seems that it could also hold true for Pb and Zn. It is significant and within a range of between 10 % for Co to 75 % (50 % for corrected data) for Cu. For Co, the next statistically significant source of variance is variability on a 100 m scale, and for Cr and Ni it is location. For all of them, variance at the location level comprises 20–60 %.

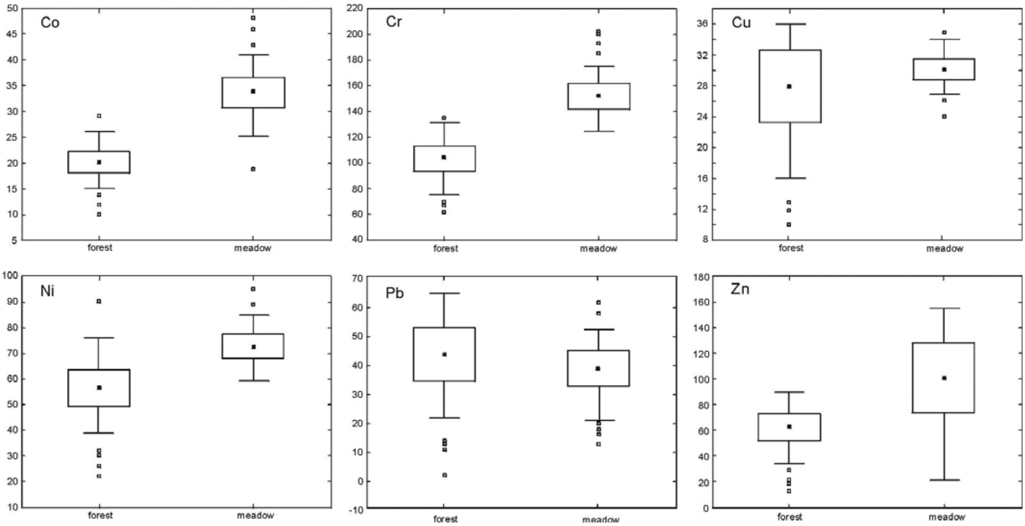

Figure 1. Box-whisker graphs of metals (mg kg^{-1}) in the forest and meadow soils. Entral dot – Mean, box – Mean ± Standard error, whisker – Non-Outlier Range, external dots – outliers.

Table 5. Hierarchical nested ANOVA results for Box-Cox (first row) and replaced outliers (second row) data. Statistically significant differences at 95 % probability are shown in bold.

	Vegetation	Location	100 m	10 m	1 m	Analytics
Co	13.8	41.4	**24.4**	5.6	**9.8**	5.0
	15.2	37.9	**32.2**	0.0	**10.2**	4.5
Cr	15.6	**47.6**	14.0	0.4	**15.1**	7.3
	16.3	**42.5**	16.0	0.0	**16.8**	8.4
Cu	8.6	12.2	0.0	0.0	**75.1**	3.7
	28.0	5.0	14.9	0.0	**47.9**	4.2
Ni	0.0	**57.1**	15.4	0.0	**25.3**	2.3
	0.0	**57.2**	17.7	0.0	**22.7**	2.4
Pb	0.0	8.5	29.4	0.0	**47.9**	14.2
	0.0	33.2	0.0	10.2	25.5	31.1
Zn	1.5	0.0	**56.0**	3.4	0.0	39.2
	9.7	0.0	0.0	19.4	18.9	52.0

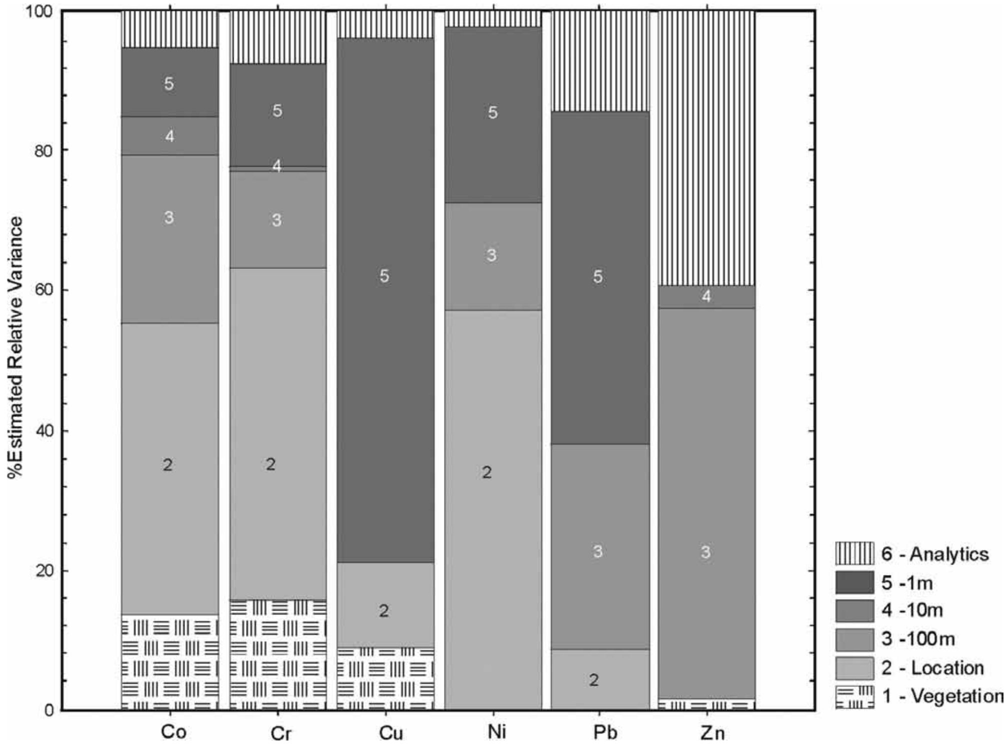

Figure 2. Estimated relative variance (%) the contributions of vegetation, location, 100 m, 10 m, 1 m and analytical error factors for metals in soils.

DISCUSSION

Before making any conclusions about the role of vegetation cover in metal content in soils, it is important to establish that we are dealing with natural values and that the soils are not polluted due to human activity.

The observed Co, Cr and Ni values are quite high. Their mean values for both vegetation types and even median values for the meadows are above the Slovenian legal limit (Uradni list RS, 1996) and in the case of Cr and Ni even above the action value (Table 6). They are also above the Slovenian (PIRC & ŠAJN, 1997) and European median values (DE VOS & TARVAINEN, 2006). For Cu, Pb and Zn the mean and median values are within the normal range for Slovenia and Europe (Table 6).

Only 19 individual Co values are below 20 mg kg^{-1}, with the majority of them being sampled in forest at the Dolič location. Four values higher than 50 mg kg^{-1} were all sampled in Stična (three) and Dole (one) grasslands. The high Co values in soil are very often geogene, related to mafic or ultramafic rocks, but they could also be the result of adsorption and coprecipitation processes with Fe and/or Mn from lithologies rich in these metals. Co may also bind to humic and fulvic acids and inorganic colloids (Qian et al., 1998). The karst soils of Slovenia exhibit a high Co content > 14.4 mg kg^{-1} that is probably related to the bauxite and Fe-Mn rich rocks (De Vos & Tarvainen, 2006).

Nearly the same 19 samples have Cr values above the limit value of 100 mg kg^{-1} and 19 samples, again mainly sampled in the meadows, have values above the action value of 150 mg kg^{-1}. In soils, Cr behaviour is governed by pH, Eh and organic matter. Its adsorption by clays is also highly dependent on pH. The dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} to Cr^{3+}, the rate of which increases with soil acidity (Kabata-Pendias & Pendias, 2001). De Vos & Tarvainen (2006) reported that high Cr values in Slovenia are found over carbonate rocks so the observed contents seem to be natural.

Also for Ni, only 17 values below the limit (50 mg kg^{-1}) are observed mainly in the forest soils and at the Dolič location. Twenty-five values mainly from the Zaplana and Dole forests and grasslands are even above the action value (70 mg kg^{-1}). Organic matter can contain Ni concentrations in excess of 50 mg kg^{-1}, but high values of Ni (>37.4 mg kg^{-1}) are found in Slovenia in residual soils over carbonate rocks (De Vos & Tarvainen, 2006).

Several authors (De Vos & Tarvainen, 2006; Zhang et al., 2002) have established a strong correlation between Co, Ni, Cr and Cu, which is also the case in our study. Spearman's correlation coefficients above 0.7 support a similar geochemical behaviour and origin of Co, Cr and Ni. The observed high values seem to be natural and not influenced by human activity.

Cu content is above the limit value of 60 mg kg^{-1}only in one forest sample from Stična and one from Postojna. In both sampling areas no obvious pollution source was documented and the nearby samples also do not exhibit any Cu increase. The reason for the elevated Cu could be analytical error or natural local concentration due to one or a combination of reasons. In unmineralised sediments, Cu concentrations are principally determined by mafic detritus, secondary Fe and Mn oxides (Forbes et al., 1976), clay minerals (Heydeman, 1959) and organic matter (Stevenson & Ardakani, 1972). Further, the affinity of Cu for natural organic matter has been widely documented (Rashid, 1974; Rippey, 1982).

Table 6. A comparison of the forest and meadow soils' metal content (mg kg^{-1}) with other work. All values are rounded off to the nearest integer value: a – Uradni list RS, 68/96 (1996), b– PIRC & ŠAJN (1997), c – DE VOS & TARVAINEN (2006)

		Co	Cr	Cu	Ni	Pb	Zn
This study	Me forest	16	98	21	48	36	52
	Me meadow	32	160	29	74	33	63
This study	Mean forest	20	104	28	57	44	62
	Mean meadow	34	152	30	73	39	101
Slovene Law[a]	Limit Value	20	100	60	50	85	200
Slovene Law[a]	Action value	50	150	100	70	100	300
Slovene Law[a]	Critical Value	240	380	300	210	530	720
Slovenia[b]	Me		42	23	31	34	77
Europe[c]	Me	8	60	13	18	23	52

The quality of the Pb and Zn analytics is not sufficient to allow any serious interpretation. In spite of this, some comments are presented. Just two Pb values, one from a Postojna meadow and the other from a Dolič forest, are above the Slovenian legal action value. In both cases, this could be just an analytical error or a natural reason. Pb in soils is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles (KABATA-PENDIAS & PENDIAS, 2001).

In the same two samples the Zn limit value is also exceeded. In one sample from the Stična meadows the Zn content is very close to the critical value. Zn content in soil depends on the nature of the parent rocks, texture, organic matter and pH, and ranges from 10 mg kg^{-1} to 300 mg kg^{-1} (MIHALJEVIĆ, 1999). Since Zn is easily adsorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons (KABATA-PENDIAS & PENDIAS, 2001). High Zn values (>76 mg kg^{-1}) occur in karstic Slovenia (DE VOS & TARVAINEN, 2006). The three observed values are above this, but could still be just a coincidence and do not prove pollution. No possible contamination was established at the mentioned locations and the samples from very near positions have a normal Zn content.

In subsoil and topsoil Pb is strongly correlated with Zn (BAIZE & STERCKEMAN, 2001), which is also true for our data.

A simple comparison of the forest and meadow metal contents in the soils indicates lower values of Co, Cr, Cu, Ni and Zn in forest soils and the nearly equal content of Pb in both types. For the first four elements, the difference is statistically significant at a 95 % probability level. An analysis of variance was unable to confirm the result, except for Cu, due to the very high variability at lower levels, especially the location, 100 m and 1 m. Our results are in line with Bai et al. (2010) who established a relatively large difference in the effect of the accumulation of Cr, Ni, Cu, and Zn in soils under different land use patterns (i.e. greenhouse, vegetable field, maize field and forest field), except Pb, with less accumulation in the forest soils. The agricultural chemical compound and application of manures, especially the quantity and quality of the applied fertilisers, is a main factor leading to the different accumulation of metals in soils (Bai et al., 2010), which could at least also hold true for the meadows.

On the contrary, in their study Zhang et al. (2002) claimed that the total concentrations of trace elements followed the pattern: farmland ≈ shrub > forests > meadow > prairie > marsh and others. Also some other authors have found higher values of some elements in forest compared with grassland or agricultural soils, for example Baize & Sterckeman (2001) for Zn and Cd and Rusjan et al. (2006) for Cd and Co. In the latter case, the differences were not statistically significant. Baize & Sterckeman (2001) explain the difference as a consequence of unequal inheritance between the thinner very clayey soils below the wood, and the thicker less clayey soils of the cultivated part. It seems that to make a detailed interpretation of metals in soils a precise determination of the pedological and mineralogical characteristics should also be considered, i.e. the type and content of clay minerals, organic matter and soil pH.

Conclusions

The influence of vegetation cover, i.e. forest and meadow, on the Co, Cr, Cu, Ni, Pb and Zn content in soils was tested at five locations where four samples were taken at different distances from the starting point. According to the added standard materials and replicate samples, the analytics proved satisfactory for Co, Cr, Cu, and Ni, but was less good for Pb and Zn.

The metal abundance sequence is in most cases Cr > Zn or Ni > Pb > Cu or Co. The data variation is quite high with extremely low and high values. When considering the whole dataset it is Zn > Pb > Cu > Co > Cr > Ni.

Due to the outliers, the distribution of no elements for all samples is normal. Normality was achieved by a Box-Cox transformation and by replacing extremely high values with mean values for selected elements in appropriate soils, i.e. grass or forest covered.

Although Co, Cr and Ni exhibit very high absolute values, which even exceed the limits permitted by Slovenian law in the majority of samples, one can be relatively confident that they are not caused by pollution. They are probably related to bauxite and Fe-Mn rich carbonates, which are typical for some karstic soils developed on carbonates. They are also highly correlated, which could support their common origin.

The Cu, Pb and Zn values are higher than expected just in a few cases. We could not establish any pollution source so we interpret these values as accidental. It is unsure if the observed values are some kind of analytical error or just natural variability in clay and/or organic matter content in soils.

The analysis of variance helped reveal very variable geochemical conditions on a small scale, i.e. the statistically different element content of samples from the same location and under the same vegetation cover in the profiles where samples were just 1 m, 10 m or 100 m apart. Moreover the variance component due to different sampling locations (Postojna, Zaplana, Stična, Dole and Dolič) is quite high (approximately 30 % to 60 %) for Co, Cr, Ni and Pb, but statistically significant only for Cr and Ni, as for the other three elements the high variability at lower levels (Co on 100 m, Cu on 1 m, Pb on 1 m or analytics and Zn on 100 m and analytics) prevented any statistically significant confirmation of higher factors.

The high variability at lower levels is also a reason why the analysis of variance did not prove the influence of vegetation cover on metal content in soil, except for Cu in the case of corrected data. The share of variance in the case of the corrected Cu data is nearly 30 %, but half of that for Co and Cr, practically zero for Ni and Pb, and around 10 % for the corrected Zn. In spite of this, a t-test managed to show statistically significantly higher values of all elements, except Pb, in the soils covered by grassland. The reason for the higher metal content in the meadow soils could be the application of manures. In our study, the meadow soils are 1.7-times enriched with Co, 1.6-times with Zn, 1.5-times with Cr, 1.3-times with Ni, and 1.1-times with Cu regarding the forest soil. If we disregard the outliers, the sequence is Co (1.7-times), Cr (1.5-times), Cu (1.4-times) = Zn (1.4-times) and Ni (1.3-times). In both cases, the Pb values are just a little higher in the forest soils. In the case of Pb and Zn, the results are merely indicative due to the low analytical quality. We can still conclude that, where possible, vegetation cover should be considered when designing the sampling and interpreting the data.

References

Abbey, S. (1983). Studies in "Standard Samples" of silicate rocks and minerals 1969–1982. Geological Survey of Canada, Ottawa, 114 p.

Allcot, G. & Lakin, H. (1978): Tabulation of geochemical data furnished by 109 laboratories for six geochemical exploration reference samples. United States Department of the Interiory Geological Survey, Washington, 199 p.

Bai, L., Zeng, X., LI, L., Pen, C. & Li, S. (2010): Effects of land use on heavy metal accumulation in soils and sources analysis. Agricultural Sciences in China, Vol. 9, pp. 1650–1658.

Baize, D. & Sterckeman, T. (2001): Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. Science of the Total Environment, Vol. 264, pp. 127–139.

Bini, C., Sarton, G., Wahsha, M. & Fontana, S. (2011): Background levels of trace elements and soil geochemistry at regional level in NE Italy. Journal of Geochemical Exploration, Vol. 109, pp. 125–133.

Box, G. E. P. & Cox, D. R. (1964): An analysis of transformations. Journal of the Royal Statistical Society (B), Vol. 26, pp. 211– 252.

De Vos, W. & Tarvainenen, T. (Chief editors) (2006): Geochemical Atlas of Europe, Part 2. Inetrpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications. Geological Survey of Finland. Espoo, 690 p.

Forbes, E. A., Posner, A. M. & Quivk, J. P. (1976): The specific adsorption of divalent Cd, Co, Cu, Pb, Zn on goethite. Journal of Soil Science, Vol. 27, pp. 154–165.

Heydeman, A. (1959): Adsorption aus sehr verdunnten Kupferlosungen an reinen Tonmineral. Geochimica et Cosmochimica Acta, Vol. 15, pp. 305–329.

Imrie, C. E., Korre, A., Munoz-Melendez, G., Thornton, I. & Durucan, S. (2008): Application of factorial kriging to the FOREGS European topsoil geochemistry database. Science of the Total Environment, Vol. 393, pp. 96–110.

Kabata-Pendias, A. & Pendias, H. (2001): Trace Elements in Soils and Plants. 3th ed. CRC Press, Boca Raton, 413 p.

Küfmann, C. (2003): Soil types and eolian dust in high-mountainous karst of the orthern Calcareous Alps (Zugspitzplatt, Wetterstein Mountains, Germany). Catena, Vol.53, pp. 211–227.

Madansky, A. (1988): Prescriptions for Working Statisticians. Springer-Verlag, New York, 295 p.

Mihaljević, M. (1999). Zinc. In: Marshall, C. P. & Fairbridge, R. W. (eds.), Encyclopedia of Geochemistry. Kluwer Academic Publishers, Dordrecht, Germany, 51 p.

Pirc, S. & Šajn, R. (1997): Vloga geokemije v ugotavljanju kemične obremenitve okolja. – Kemizacija okolja in življenja – Do katere mere?. Zbornik projekta Evropskega leta varstva narave 1995, Slovensko ekološko gibanje, Ljubljana, pp. 165–186.

Qian, J., Xue, H. B., Sigg, L. & Albrecht, A. (1998): Complexation of cobalt by natural ligands in fresh water. Environmental Science and Technology, Vol. 32, pp. 2043–2050.

Rashid, M. A. (1974): Adsorption of metals on sedimentary and peat humic acids. Chemical Geology, Vol. 13, pp. 115–123.

Rippey, B. (1982): Sediment-water interactions of Cu, Zn and Pb discharged from a domestic waste source into a bay of Lough Neagh, Northern Ireland. Environmental Pollution (B), Vol. 3, pp. 199–214.

Rusjan D., Strlič M., Pucko D., Šelih V. S. & Korošec-Koruza Z. (2006): Vineyard soil characteristics related to content of transition metals in a sub-Mediterranean winegrowing region of Slovenia. Geoderma, Vol. 136, pp. 930–936.

Stevenson, F. J. & Ardakani, M. S. (1972): Organic matter reactions involving micronutritiens in soils. In: Mortveldt, J. J., Giordano, P. M. & Lindsay, W. L. (Eds.), Micronutritiens in agriculture. Soil Science Society of America, Madison, Wisconsin, pp. 79–104.

Swan, A. R. H. & Sandilands, M. (1995): Introduction to Geological Data Analysis. Blackwell Science, Oxford, 446 p.

Uradni list RS (68/1996): Uredba o mejnih, opozorilnih in kritičnih emisijskih vrednostih nevarnih snovi v tleh, Ljubljana.

Xia, X., Chen, X., Liu, R. & Liu, H. (2011): Heavy metals in urban soils with various types of land use in Beijing, China. Journal of Hazardous Materials, Vol. 186, pp. 2043–2050.

Zhang, X. P., Deng, W. & Yang, X. M. (2002): The background concentrations of 13 soil trace elements and their relationships to parent materials and vegetation in Xizang (Tibet), China. Journal of Asian Earth Sciences, Vol. 21, pp. 167–174.

Zhao Y. G., Zhang G. L., Zepp H. & Yang J. L. (2007): Establishing a spatial grouping base for surface soil properties along urban–rural gradient – A case study in Nanjing, China. Catena, Vol. 69, pp. 74–81.