Influence of climate factors on soil heavy metal content in Slovenia

Nina Zupančič[1,2]

Abstract

Purpose In spite of equal lithology, the local climate can affect soils' geochemical characteristics. We investigated the dependence of heavy metal content on climatic factors according to a hierarchical nested analysis of variance design (ANOVA).

Materials and methods We examined the heavy metal content in soils developed on the Upper Triassic dolomite at six locations situated at increasing distances from the Adriatic Sea towards inland. We tested the influence of the locations' position, i.e. climate, vegetation cover, small-scale variability and analytical error. Co, Cr, Cu, Ni, Pb and Zn contents were determined by emission spectrometry.

Results and discussion An initial increase in annual precipitation towards inland is followed by a steady decrease. Very high small-scale variability prevented statistically significant differences from being established at the location level due to the high variance components exhibited. However, the simpler one-way and non-parametric varieties of ANOVA confirmed significant differences in Co, Cr and Ni among locations. The differences are more pronounced in grassland soils where the Cu and Pb contents also differ between locations. There is a positive correlation among annual precipitation, Co,

Cr and Ni, and it seems that the prevailing winds can also influence their content in soils.

Conclusions The Co, Cr, Cu and Ni values are readily the highest in those locations with the greatest precipitation, possibly due to their resistance to leaching. The soils could be additionally enriched by an eolian contribution from the SW located outcropping flysch rocks. The established variability could be due to somewhat different dolomite composition. The reasons for the observed geochemical variability are complex and only partly due to climate.

Keywords Analysis of variance · Climate factors · Dolomite · Eolian contribution · Enrichment by leaching

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1 Introduction

The composition of soils is governed by many different factors (Kabata-Pendias and Pendias 2011). In the first stages of soil development, the landscape position and topography can affect the element content (Sharma et al. 2005), but most commonly, parent material is crucial for soils' mineralogical and geochemical characteristics (Palumbo et al. 2000; Streckeman et al. 2006; Nael et al. 2009; Galán et al. 2008; Garrett 2009; Kabata-Pendias and Pendias 2011). Trace elements are generally associated with the clay minerals and Fe, Mn and Al oxides and hydroxides of the soil (Streckeman et al. 2004) or bound in heavy minerals.

The influence of the parent material on trace elements tends to decrease with soil development (Zhang et al. 2002), and the effect of climate, i.e. temperature and precipitation conditions, plays a key role. The soil-forming processes impact the content and mobilisation of trace elements (Nael et al. 2009), modify the basic geochemical composition and redistribute the content of metals within the soil profile (Bini et al.

2011). During these processes, topsoil can be enriched in trace elements (Reimann et al. 2001) due to bio-geochemical cycles and/or anthropogenic sources (Streckeman et al. 2004). It is generally recognised that climate is the most important factor regulating soil organic matter (Homann et al. 1995; Alvarez and Lavado 1998). With higher temperatures, the carbon content in soil decreases due to more intense organic matter mineralisation (Cole et al. 1993; Kirschbaum 1995). With increasing precipitation and temperature, the soil clay content increases due to rock weathering and clay neoformation (Jenny 1941).

The geochemical mapping of an area is quite often preceded by pilot studies in which soils are sampled in regular grids and/or transects (Pirc et al. 1991; Reimann et al. 2007; Drew et al. 2010) to evaluate the geospatial variability of the elements. The results help to identify patterns related to profound differences in soil parent materials and climate effects (Woodruff et al. 2009). Eberl and Smith (2009), for example, confirmed that the distribution of selected minerals in soils across the continental USA depends on soil parent materials and precipitation patterns. Dai and Huang (2006) established the soil organic matter concentration's relationship with climate and altitude in different regions of China. Reimann et al. (2007) concluded that climate is an important factor behind the enrichment of quite a number of metals, which is often attributed to human activities in the organic soils of Scandinavia.

It should be noted that soil formation is a relatively slow process, taking thousands of years for the soil profile to form. The observed soil profiles could have formed in different climatic conditions than those observed currently. Our study of vegetation cover's influence on the heavy metal content in soils (Zupančič 2012) has already drawn attention to their spatial variability, which could be caused by different regionally variable climatic conditions. In Slovenia, climatic conditions vary from the continental climate in the northeast, the severe Alpine climate in the high mountain regions and the sub-Mediterranean climate in the coastal region, with the three climatic systems strongly interacting in most of the country. A variety of conditions occurs in the presence of different weather types. Heavy southwest winds regularly bring precipitation to the west of Slovenia, while dry weather prevails in the eastern part (Cegnar 2016). These specific local conditions can also probably influence the geochemical characteristics of the soils. The main purpose of the present study was to establish possible statistically significant systematic spatial variation and the influence of present climatic differences on heavy metal contents in soils.

2 Materials and methods

For the sampling, an analysis of variance (ANOVA) stratified random sampling design was employed, which aimed to estimate the variability of heavy metals in soil among six general locations, within each site between two types of vegetation cover and the position of individual sample sites, and the analytical error. The meteorological data show that climatic changes would be the most pronounced in the NE direction from the seaside to the interior of Slovenia. To minimise the number of other probable factors that could affect the heavy metal content as much as possible, the topsoil samples were taken on the same parent rock—Upper Triassic dolomite, the same soil type—rendzina, at the same elevation—around 600 m a.s.l., on the same SW insolation of the slope and on each location in soils covered with two vegetation types—forest and grassland. The sampling locations were chosen to be as equally spaced and distant enough (10–40 km) as possible to detect the present local climatic variations. Six sampling locations roughly met these conditions: Postojna, Zaplana, Stična, Dole, Nazarje and Zg. Dolič (Fig. 1).

Although the sampled locations are positioned on slopes where more pronounced colluvial processes are possible, we presumed that the surrounding geological units are sufficiently far away to make their direct influence on the soil composition unlikely. However, it is worth noting that in the SW of Postojna, the carbonate rocks are exposed next to outcropping flysch rocks; in the central area, they are in contact with clastic siliceous sedimentary rock; and in the north of Nazarje and Zg. Dolič, igneous and metamorphic rocks are found in the broader surroundings (Pleničar et al. 2009). In addition, in all grassland locations, some contamination due to agriculture is possible. For every location, basic climatic data—average annual, January and July temperatures, annual precipitation, days with snow cover and prevailing wind direction—were obtained (Table 1) from official data sources, i.e. the Environmental Agency of the Republic of Slovenia (ARSO–Atlas okolja 2016) and by taking the advice of meteorologists into account. The meteorological stations are not exactly at the same sites as our sampling areas, but they are close enough to be representative and to allow some patterns to be established. There is a slight decrease in temperature (annual, January and July) and increase in annual precipitation and days with snow cover from the first to second locations, mainly due to the flat terrain that is open to the sea in the direction towards Postojna and hilly thereafter. Zaplana is thus the coolest and wettest location. In continuation of the traverse, there is a significant temperature rise at the next location, Stična. It also exhibits the highest temperatures on the traverse. The temperatures tend to decline thereafter with a slight oscillation at Nazarje, where they are higher than in the previous location. However, the most distant location, Zg. Dolič, is again cooler, with temperatures comparable to Zaplana or even lower. The pattern of days with snow cover is just opposite to that of temperatures. From Zaplana, there is a constant downward trend in annual precipitation. The most inland location, Zg. Dolič, is therefore the driest and the second coolest location. In Postojna,
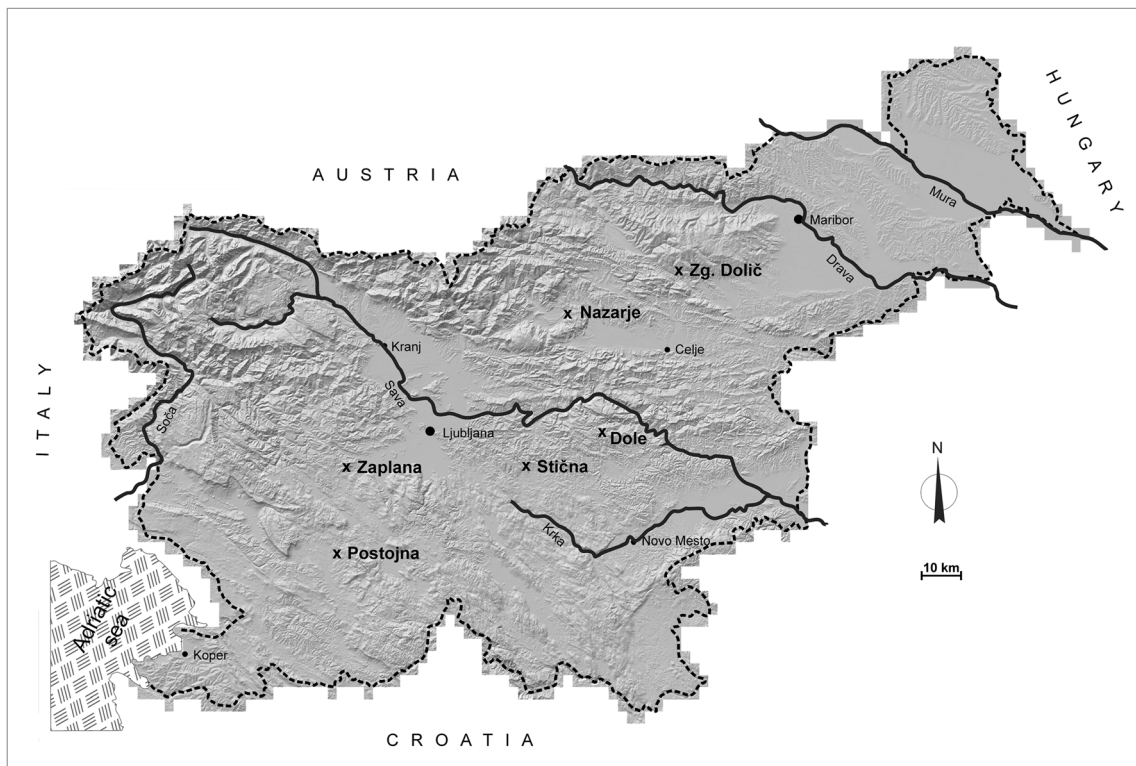
Fig. 1 Sampling locations on the NE traverse from the Adriatic Sea inland

Zaplana and Dole, the prevailing winds come from SW, in Nazarje and Zg. Dolič from NW and in Stična from ENE.

A total of 60 topsoil (0–15 cm) samples without the organic horizons, each weighing 1.5–2 kg, were collected. At each general sampling location, four samples were taken from the grassland and four from a forest-covered area with the single exception of the Nazarje location, where only forest soils could be sampled. To assess the local scale variability of the soil's geochemical composition at each location, sampling sites were appointed on randomly positioned 100-m long traverses at the starting point, at 1, 10 and 100 m. Further, at four locations at the randomly selected vegetation profile (forest—Postojna, Dole pri Litiji, Nazarje and Zg. Dolič; grassland—Stična), a

1000-m distant sample site was also added. Each sample collected at the zero site was split into two, with the replicate sample serving to control the analytical precision. The described design permits the use of an unbalanced hierarchical nested analysis of variance (ANOVA) scheme to estimate the variability sources and their significance (Garrett 2009).

The soil samples were air-dried. About 1 kg of every sample material was first passed through a 2-mm sieve and then 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.

Table 1 Data regarding actual climatic conditions and distance from the sea

Soil sampling location	Weather station	Mean annual T (°C)	Mean January T (°C)	Mean July T (°C)	Annual precipitation (mm)	Mean days with snow cover	Prevailing wind direction	Distance from the sea (km)
Postojna	Postojna	8.4	−0.9	17.7	1578	47	SW	35
Zaplana	Rovte nad Logatcem	7.8	−1.9	17.3	1867	86	SW	50
Stična	Grosuplje	10.6	0.7	21	1361	54	ENE	60
Dole	Sevno	9	−1.1	18.3	1215	57	SW	100
Nazarje	Velenje	9.7	0	19.2	1211	43	NW	115
Zg. Dolič	Šmartno pri Slovenj gradcu	8	−3.4	17.6	1139	73	NW	135

(http://gis.arso.gov.si/atlasokolja/profile.aspx?id=Atlas_Okolja_AXL@Arso)

The evaluation of the analytical quality was carried out independently using the replicate analysis and standard reference material data by comparing the obtained results against accepted norms. For the accuracy control of the analysis, five standard materials (GXR-2, GXR-5 (Allcot and Lakin 1978), SO-1, SO-2, SO-3 (Abbey 1983)) were added. The accuracy of the Co, Cr and Zn determinations was established as good (less than 10% deviation) and that of Cu, Ni and Pb as satisfactory (less than 20% deviation). Precision was estimated by ANOVA from all raw data and by coefficients of variation (CV) for the five replicate analyses of each standard material. Generally, the analytical error is acceptable (less than 15% of total variance); only Zn occasionally indicated a somewhat higher analytical variation (17–30%, also see Table 3).

Since for the parametric statistics, the data should be normally distributed, the distribution of the whole data set was checked visually from the histograms 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). With respect to these criteria, the distribution can be considered normal for Cr and Ni and close to it for Co. The skewed distribution of Cu, Pb and Zn is mainly caused by some extreme values. Since it was uncertain whether the extreme values are part of the real population, or perhaps just a consequence of some error, we transformed all the heavy metal data to a more symmetric distribution with a Box-Cox transformation (Box and Cox 1964). The transformation improved the closeness to a normal distribution for all elements. For Cu and Pb, they remained slightly non-normal according to the Shapiro-Wilk test but sufficiently close to normality to allow the use of parametric ANOVA.

Classical parametric ANOVA is based on assumptions concerning the homogeneity of variance and normality of data. The homogeneity of variance is the condition in which the variances of data subsets across the data range are similar. If this condition does not hold, the data require a transformation so that the variances are similar (Bartlett 1947). Levene's and Brown-Forsythe's tests confirmed the homogeneities of variances of the Box-Cox transformed data of each vegetation group. As the climatic variables exhibit just approximate values, they were used only in the non-parametric Spearman correlation calculations. Non-parametric tests were also performed on the raw data set to confirm the results of the parametric statistics calculated on the Box-Cox transformed data. To enable a better visual presentation, original data are used in the box-whisker diagrams.

3 Results and discussion

3.1 Geochemical characterisation

The majority of the data used together with the ANOVA scheme and comments on the heavy metal contents are presented in Zupančič (2012). Therefore, in Table 2, only the descriptive statistics of the whole raw data set and short comments on the observed values are given.

Common characteristics of all samples are very high Co, Cr and Ni contents. They are much higher than the Mediterranean baseline values (Micó et al. 2007) and contents reported by Bini et al. (2011) for Trentino area (Italy) soils developed on limestones and dolomites. The Cr and Ni averages exceed the Slovene median values (Pirc and Šajn 1997), and all three of them are above the Slovene directive limit value; Cr is even above the action value (Uradni list RS 1996). In spite of that, they are natural (Oze et al. 2007), typical of karstic soils in Slovenia. The comparison with the data of two soil profiles developed on the dolomite, reported by Zupan et al. (2008), shows that observed values are very similar. They are even slightly lower than values reported for karst soils in neighbouring Croatia and comparable to the ones in Slovakia (Miko et al. 2003). In the Mediterranean area, all three elements are related to mineralised ophiolitic rocks and sedimentary rocks derived from them and/or to bauxites and residual soils over carbonate rocks (De Vos and Tarvainenen 2006). These three elements are highly correlated (Pearson r and Spearman's r' ~0.8), indicating their common behaviour. Bini et al. (2011) observed the same strong correlation between Cr and Ni and associated it with mafic minerals. Their relatively low CV values are in accordance with their prevailingly geogenic source. Their correlation with Cu is statistically significant ($p < 0.05$) but not very high (correlation coefficients 0.3 with Ni, 0.5 with Co and 0.6 with Cr). A high correlation between Cu and Cr is typical of European topsoils (De Vos and Tarvainen 2006).

The observed outliers and relatively higher CV could indicate some anthropogenic influence on Pb and Zn and to a smaller extent on the Cu content. The Cu, Pb and Zn average values are quite low and within the normal range for Slovenia (Pirc and Šajn 1997) and Europe (De Vos and Tarvainen 2006). The Pb content is slightly above the Mediterranean baseline (Micó et al. 2007), and Cu and party Zn are higher

Table 2 Descriptive statistics for the 60 raw topsoil samples' (non-transformed) data

	Mean	Geo	Me	Min	Max	s	CV
Co	24.9	20.7	23.0	3	65	14.29	57
Cr	117.3	101.7	108.0	20	250	57.00	49
Cu	26.8	23.4	25.0	4	117	16.76	63
Ni	59.3	49.2	59.0	7	133	31.31	53
Pb	41.4	32.7	34.5	2	255	37.45	91
Zn	77.5	58.8	57.0	12	710	95.45	123

All values in milligrams per kilogram, except CV in percent

Mean arithmetic mean, *Geo* geometric mean, *Me* median, *Min* minimum, *Max* maximum, *s* standard deviation, *CV* coefficient of variation

than observed in soils developed on carbonate rocks in Italy (Bini et al. 2011) and comparable to the data on Croatian and Slovakian karst soils (Miko et al. 2003). Cu contents are similar to the values reported in Zupan et al. (2008), while the average Pb and Zn contents are even lower. High CV values over 50 could indicate, together with the skewed distribution of these elements, some local enrichment. Indeed, the Cu content is close to 100 mg/kg in one forest sample from the Postojna and one from the Stična. Still, the elevated Cu content could be natural, as soils' Cu might be related to mafic detritus, secondary Fe and Mn oxides (Forbes et al. 1976), clay minerals (Heydeman 1959) and organic matter (Stevenson and Ardakani 1972). In one forest sampling site at Zg. Dolič and one meadow sampling site at Postojna, Pb and Zn are elevated (255 and 165 mg/kg Pb, 275 and 270 mg/kg Zn). Further, one Stična grassland sampling site shows very high Zn content (710 mg/kg), and one Zg. Dolič forest sampling site has Pb content just over 100 mg/kg. The elevated Pb content could be associated with organic matter and by fauna activity (Baize and Sterckeman 2001). Natural Zn content in soil ranges from 10 to 300 mg kg^{-1} (Mihaljević 1999) and is often accumulated in the surface horizons (Kabata-Pendias and Pendias 2011). However, Miko et al. (2003) have ascribed high Cu, Pb and Zn contents in Slovakian soils to airborne pollution. In none of the abovementioned locations was any obvious pollution source established; thus, we retained the outliers in the data set and interpreted them as natural enrichment. The correlation between Pb and Zn is statistically significant at the <0.5 level but quite low ($r = 0.5$).

3.2 Influence of local climate conditions on heavy metal content

A hierarchical nested analysis of variance was performed on the whole data set by taking account of the influence of the geographical position of the sampling location (Postojna, Zaplana, Stična, …), the vegetation (forest, meadow), the place of the sample in each sampling traverse (1, 10, 100 or 1000 m) and analytical replications. Since a previous study (Zupančič 2012) indicated that forest soils were poorer in all heavy metals considered except Pb, the data for both vegetation types were also checked separately for climate/location influence according to the same design but excluding the vegetation level. The summarised results are presented in Table 3.

ANOVA of the complete data set including vegetation as the second level of variance source indicates that the different sampling locations contribute a statistically significant 52% of the total variance for Ni. The variance component at the location level is not statistically significant but also quite high for Co and Cr. It seems that the climate effect is more pronounced in meadow soils than in forest soils. Namely, variance components at the location level of the separate vegetation data sets are quite high for Co, Ni and Pb in forest soils and for all elements in meadow soils. However, nowhere did the location level prove to be statistically significant due to high variability at the 100 m and especially the 1 m distances. In the case of Zn, the high analytical error prevents the contribution of other levels to the total variance from being evaluated. Therefore, the data in Figs. 2 and 3 are presented using the median values, which are less sensitive to outliers (Garrett 2009). The patterns of all elements show pronounced oscillations between the locations with no obvious trend.

Next to the described hierarchical nested ANOVA, we performed a simple one-way ANOVA to compare only the different locations, regardless of the sampling sites' position in the location traverses. However, ANOVA only explains the significance of the variances, in our case of the difference between the location means. A statistically significant difference at a certain level only means that at least two means, and not necessarily more, are different. The forest locations exhibit statistically significant differences between Co, Cr and Ni contents (Tables 4 and 5). The differences between locations are even more pronounced for the grassland profiles, as they were statistically significant for all elements except Zn (Tables 4 and 5). In addition, the simple one-way ANOVA

Table 3 Hierarchical nested ANOVA

	All							Forest						Meadow					
	L	V	1000	100	10	1	Err	L	1000	100	10	1	Err	L	1000	100	10	1	Err
Co	27	25	0	26*	8	10*	5	30	0	45*	2	15	8	52	4	16	18	7	3
Cr	36	3	25	13	0	17*	6	16	38	19*	0	25*	2	49	0	9	18	10	14
Cu	12	0	20	0	0	65*	2	0	15	0	0	82*	3	44	0	25	0	28*	3
Ni	52*	0	10	12	0	24*	2	40	2	20	0	35*	3	71	11	0	7	9*	2
Pb	0	34	0	19	0	37*	10	25	0	12	0	55*	8	48	0	30	4	4	14
Zn	1	19	0	46*	3	0	31	9	0	46*	0	0	45	28	0	43	12	0	17

L location, *V* vegetation type, *1000*, *100*, *10*, *1* positions at 1000, 100, 10 and 1 m sampling sites in the traverse, *Err* Analytical error

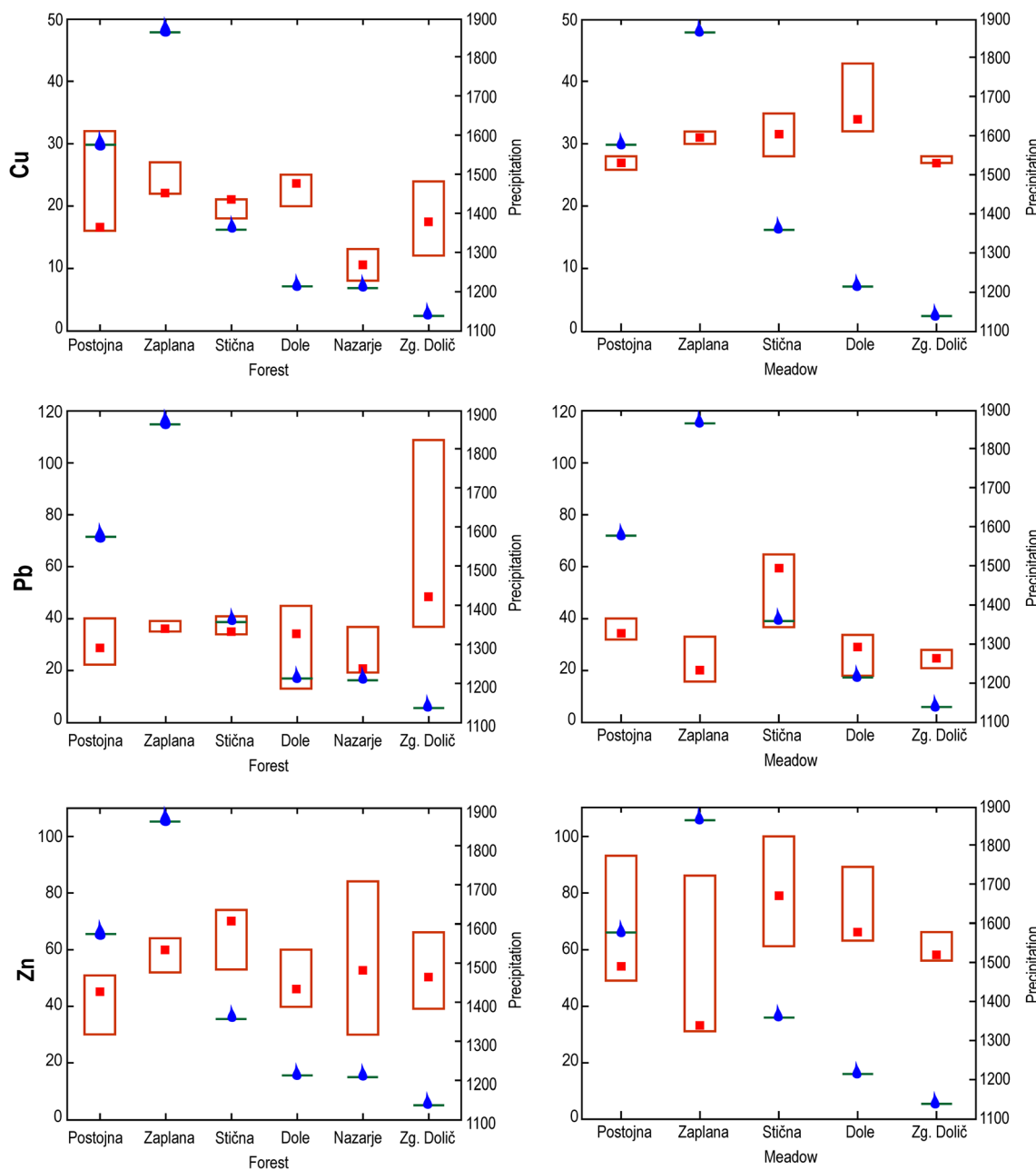*95% statistically significant values
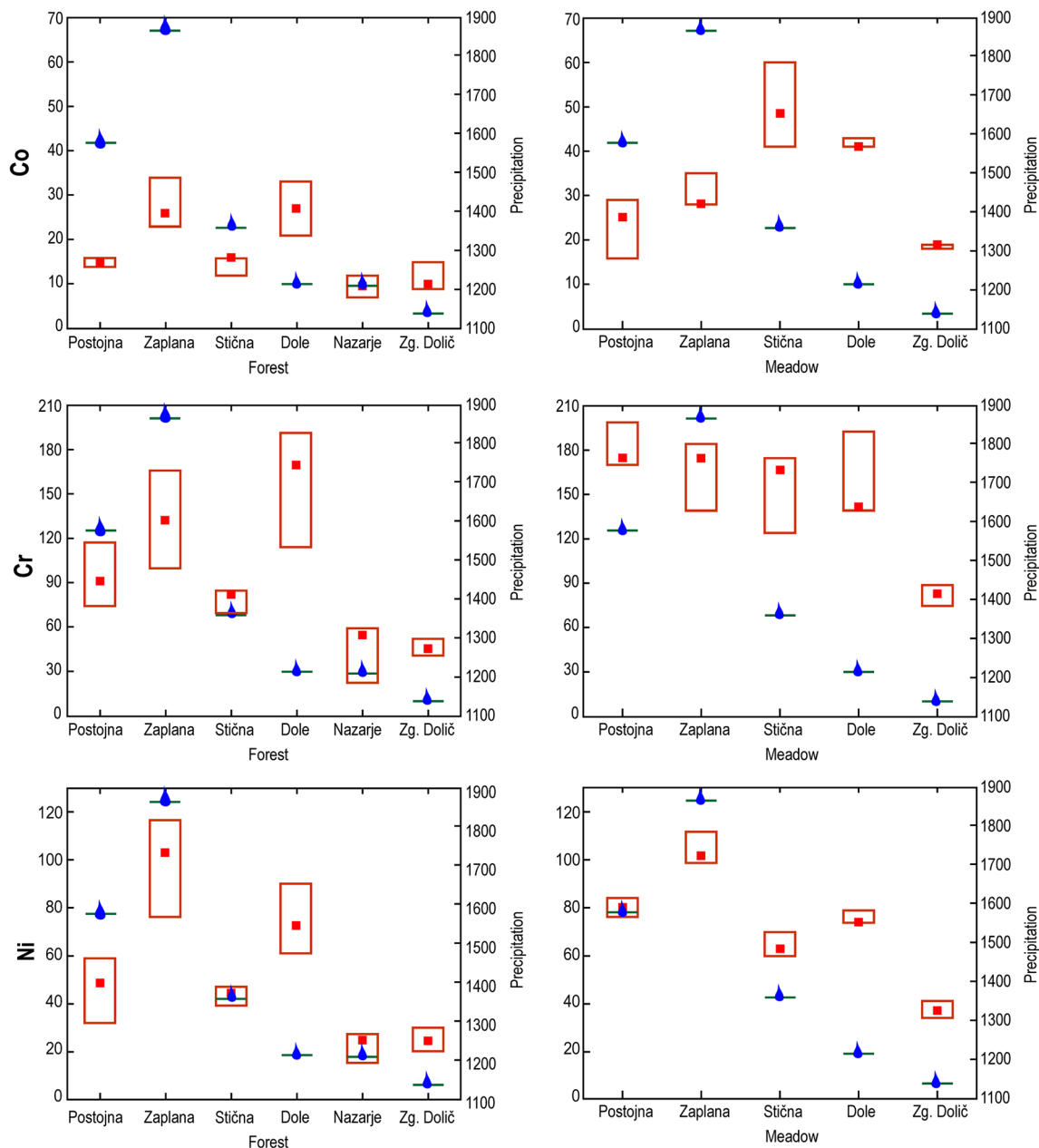
Fig. 2 Co, Cr and Ni median (*central point*), interquartile deviation (*box*), minimum-maximum (*whisker*) plots of forest and meadow soils comparing different locations (in mg/kg on left *y*-axis) and annual precipitation data (*drops*; in mm on the right *y*-axis)

indicates statistically significant differences for Co, Cr, Cu and Ni among locations even if the vegetation type is not considered (Table 4). The post-hoc Tukey HSD test shows that the low contents of all elements at Zg. Dolič are the main reason for the established significance of differences.

Moreover, the non-parametric varieties of ANOVA, i.e. the Kruskal-Wallis and Median test, support the hypothesis of statistically different Co, Cr and Ni contents among different locations in forest and grassland soils. In addition, soils overgrown with grass also differ in their Cu and Pb contents. The multiple comparison Z-test indicates that the primary reason for the established significant differences among locations is

the difference between values of Cr and Ni in the forest and meadow soils between Zaplana and Zg. Dolič and between the same two locations for Co in forest soils. The site Zaplana often exhibits the highest and Zg. Dolič the lowest values. The Zg. Dolič and Dole locations contribute to the significance of the difference in Cr content in forest soils, with Zg. Dolič having the lowest and Dole the highest values. The same two locations, along with Zg. Dolič—Stična and Postojna—Stična, are the reason for the statistically significant difference in the Co concentration in the meadow soils. The variation in the Pb content is chiefly due to the Stična and Zaplana locations.

Fig. 3 Cu, Pb and Zn median (*central point*), interquartile deviation (*box*), minimum-maximum (*whisker*) plots of forest and meadow soils comparing different locations (in mg/kg on left *y*-axis) and annual precipitation data (*drops*; in mm on the right *y*-axis)

Table 4 F values of the one-way ANOVA results

	F all data	*F* forest	*F* meadow
Co	8.9*	6.3*	12.6*
Cr	11.6*	10.4*	6.9*
Cu	5.2*	2.3	3.3*
Ni	16.5*	7.9*	29.1*
Pb	1.5	1.5	3.3*
Zn	0.8	0.4	1.1

*95% statistically significant differences between locations

Regardless of the type of vegetation cover, and excluding the Nazarje location, as only forest profiles were sampled there, the only feature in common is that the Co, Cr and Ni values are always the lowest in the most distant locality from the sea, i.e. Zg. Dolič, which is the driest and the second coolest (Table 1, Figs. 2 and 3). The enrichment factor (EF), calculated as the ratio between the average elemental values observed in Zg. Dolič and the other locations, showed that the Co content is 2.3 times higher in Dole and very close to it in Stična (2.2 times) and Zaplana (2.1 times). Similarly, the EF for Cr is 2.3 for Zaplana and Dole, 2 for Postojna and 1.9 for

Table 5 Mean and median values of heavy metals in forest and meadow soils at the different localities locations (in mg/kg)

	Co		Cr		Cu		Ni		Pb		Zn	
	Mean	Me	Mean	Me	Mean	Me	Mean	Me	Mean	Me	Mean	Me
Forest												
Postojna	18	15	96	92	35	17	50	49	33	29	43	45
Zaplana	29	26	133	132	24	22	98	103	38	36	59	60
Stična	16	16	77	82	33	21	37	43	40	35	71	70
Dole	26	27	148	169	24	24	69	73	29	34	50	46
Nazarje	10	10	47	55	12	11	23	25	28	21	56	53
Zg. Dolič	12	10	52	46	19	18	28	24	85	49	82	50
Meadow												
Postojna	23	25	168	175	26	27	78	80	59	34	100	54
Zaplana	33	28	174	175	30	31	103	102	25	20	54	33
Stična	50	49	168	168	31	32	65	63	57	60	180	79
Dole	42	41	161	142	38	34	79	74	31	29	76	66
Zg. Dolič	18	19	80	83	26	27	36	37	26	24	77	58

Stična. The highest EF is observed for Ni, i.e. 3.1 in Zaplana, followed by 2.3 in Dole and 2 in Postojna. For Cu, the EF is 1.4 for Postojna, Stična and Dole and 1.2 for Zaplana. In comparison to values obtained in Zg. Dolič, soils from other locations are depleted in Pb. The same is true for Zn, with the exception of Stična soils, which are 1.6 times richer in Zn than soils sampled in Zg. Dolič.

The Spearman's rank order correlations indicate statistically significant connections of Co, Cr and Ni with annual precipitation and of Co and Ni also with days of annual snow cover (Table 6); there are practically no correlations among the other meteorological parameters and elemental contents. It again seems that the high narrow-scale variability of the data hinders the establishment of correlations.

The observed high spatial variability at different scales is in line with observations from Norway (Reimann et al. 2007; Anderson and Kravitz 2010), Poland (Karczewska et al. 2006) and the USA and Canada (Garrett 2009). For the neighbouring Mediterranean area of Croatia, Vrbek et al. (2010) explained various values of lead, copper and zinc content with the structure and position of samples in the karst area. Some authors (Marzaioli et al. 2010; Nanos and

Rodríguez Martín 2012; Rodríguez Martín et al. 2013) actually reduced the high variability at a small-scale level when sampling by thoroughly mixing several subsamples (e.g. 5 to 21) to obtain a final composite 1-kg sample.

There are several possible reasons for the observed small- and large-scale variability. First, it might reflect the natural heterogeneity of the parent rock. Although the dolomite seems quite uniform, Ogorelec and Rothe (1993) report that Upper Triassic dolomite might have various content (0.8–4.5%) of insoluble residual. Assuming that the soil is formed exclusively as an insoluble residual, a slight variation in the content and composition of the dolomite detrital minerals could affect the soil's geochemical characteristics.

The second explanation could be the sampling method. Samples taken at a fixed depth might consist of different proportions of organic and mineral horizons. Samples with more organic matter are therefore richer in some elements, especially Cu and Zn.

The third option is the non-homogenous release of different heavy metals during soil formation, mainly due to a varying degree of eluviation. High precipitation could favour faster leaching of the soil profile, which results in the concentration of elements, bound in minerals resistant to weathering, as also noted by other authors (Reimann et al. 2001, Nael et al. 2009). Bini et al. (2011) consider that yearly rainfall over 1200 mm, typical for all locations except Zg. Dolič, intensifies the leaching of top horizons, decarbonation and acidification. Under basic conditions, typical for calcareous parent material in situ alterations, most elements are slightly mobile and accumulate at the surface. This would explain the low Co, Cr and Ni contents in Zg. Dolič and their high concentrations in Zaplana. The interpretation is supported by the fact that higher contents of all elements, except Pb, are found in meadow soils.

Table 6 Spearman's rank order correlation matrix of meteorological data and heavy metals in soils

All	Co	Cr	Cu	Ni	Pb	Zn
Mean T	0.04	−0.05	−0.02	−0.27	0.15	0.17
T January	0.08	0.07	−0.02	−0.09	0.15	0.12
T July	0.04	−0.05	−0.02	−0.27	0.15	0.17
Annual precipitation	0.39	0.53	0.24	0.64	0.03	−0.06
Days with snow	0.27	0.18	0.25	0.35	−0.02	0.01

However, Fig. 2 reveals that even for elements that correlate with precipitation, the relationship is not so simple. Very high Co, Cr and Ni contents are also often observed at the Dole location, where precipitation is much lower than in Zaplana.

The next option is the unequal contribution of allochthonous material to the topsoil. Perhaps at least for some observed differences, a part of the explanation could lie in the prevailing SW wind direction that is typical of Postojna, Zaplana and Dole. For soils developed on flysch alluvium, Zupančič and Skobe (2014) recorded very high Cr (215 mg/kg) and Ni (80 mg/kg) and somewhat lower Co (18 mg/kg) content. Detrital Cr-spinels are widespread in the Eocene flysch basins SW of the sampled area (Lenaz et al. 2003). Therefore, some eolian contribution to soils from nearby flysch beds should be considered, at least for Cr and Ni, as they are higher in meadow soils, which are more exposed and subjected to the effects of wind. In fact, in the Alpine and Mediterranean areas, several authors have already demonstrated the airborne input of detrital mineral fragments to the soils from carbonate terrains (Durn 2003; Küfmann 2003; Skaberne et al. 2009; Babić et al. 2013).

4 Conclusions

The study focused on evaluating how certain climatic factors, vegetation cover and small-scale variability influence the content of six heavy metals (Co, Cr, Cu, Ni, Pb, Zn) in soils developed on Upper Triassic dolomite. The climate influence on the spatial distribution of studied elements could not be unambiguously confirmed. It has been indicated for Co, Cr and Ni and interpreted by the enhanced leaching of soil owing to higher precipitation and by wind transport from neighbouring flysch rocks. For Cu, Pb and Zn, no variability with climate could be established. The value of the statistical approach has been confirmed, which permitted the results to be obtained with minimum expenditure of efforts and means.

Meteorological data confirmed changes in climate parameters in the NE direction from the coast to the inland area, further influenced by local topography. The locations differ in their temperature, annual precipitation, days with snow cover and prevailing wind direction, but there are no simple trends. However, the most inland location is the driest, and three of the locations are exposed to strong SW winds.

Co, Cr and Ni are all probably of geogenic origin, regardless of their likely allochtonous source. On the other hand, Cu, Pb and Zn seem to be connected and are possibly at least partly influenced by biological factors—organic matter content and/or pollution. However, no obvious human contamination source was established.

The heavy metal content in soil is very heterogeneous on a small scale (i.e. at distances of 1 and 100 m). Therefore, in future sampling strategies, it is advisable to sample several subsamples in the 1–100 m range and mix them to obtain a composite sample that is representative of the given location. The sampling of separate horizons is preferred over fixed depth, as higher organic matter content could affect Cu and Zn accumulation.

The observed narrow-scale variations hinder the establishment of differences due to climate. Nevertheless, we noticed that the climate effect on heavy metal content in soils is more pronounced in meadow soils than in forest ones, as trees restrict the impact of heavy rainfall and wind. The differences between locations on the climate traverse are statistically significant for Co, Cr and Ni in the whole data set and sets comprised of separate vegetation types. In addition, all data sets also differ in Cu and soils sampled on grassland in Pb.

The lowest Co, Cr, Ni and partly Cu contents are observed in the coolest and driest locality, situated most inland, which contributes the most to the variability among the locations. The high contents of the abovementioned geogenic elements, especially Cr and Ni, seem to be connected with high precipitation, which causes more intense eluviation and acidification of soils. The relatively wetter climate could influence the faster development of the soil profile, i.e. leaching, and the concentration of the elements, bound in more resistant minerals. Further, the exposed flysch rocks SW of the sampling traverse could be an additional source of the elevated Cr and Ni contents, as prevailing heavy SW winds could relocate fine-grained minerals that are carriers of Cr and Ni further inland.

However, the observed variabilities could also be due to the somewhat heterogeneous dolomite composition. We may conclude that the factors and processes affecting heavy metal distribution in soils are very complex, rendering an unambiguous interpretation difficult.

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