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Assessment of soil Cu concentration and background threshold value in terra rossa of Dalmatia

Procjena koncentracije Cu u tlu i vrijednost pozadinskog praga u Crvenici iz Dalmacije

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ABSTRACT

The aims of this study were (i) to assess the soil Cu concentration in the mineral A horizon and cambic Bw horizon, (ii) to determine the background threshold value (BTV), and (iii) to quantify the differences between the horizons in terra rossa soil from Dalmatia. A total of 128 samples from 64 soil profiles located on terrains used for non-agricultural purposes were analysed for aqua regia soluble Cu concentration. The soils were classified according to the Croatian Soil Classification System and World Reference Base for Soil Resources as terra rossa soil and Chromic and Rhodic Cambisols. The median value of Cu concentration in A horizon (Cu_A) and cambic Bw horizon (Cu_B) were 34.9 and 36.1 mg/kg, respectively, and ranged between 16.2 and 69.5 mg/kg in the Cu_A and from 17.0 to 73.0 mg/kg in the Cu_B horizon. The estimated BTV for Cu_A varied between 43.6 and 58.4 mg/kg depending on the calculation method applied. The median ratio Cu_A/Cu_B of 0.96 was close to identical. The Wilcoxon matched pairs signed rank test and the Hodges-Lehmann estimator showed that the median difference in Cu concentration between the Cu_A and Cu_B was very small (-1.78 mg/kg). Mentioned statistical evidence on the small differences in Cu concentration between the horizons suggests that Cu concentrations measured in the Bw horizon can be considered a “local background” for the samples collected in A horizon and its utilization in screening terra rossa soil contamination can be suggested.

Keywords: background threshold value, cambic horizon, matched pair testing

SAŽETAK

Ciljevi ovog istraživanja bili su (i) odrediti koncentraciju bakra u mineralnom A i kambičnom Bw horizontu, (ii) odrediti pozadinsku vrijednost praga (PVP) te, (iii) kvantificirati razlike između horizonata u Crvenici iz Dalmacije. Ukupno 128 uzoraka iz 64 profila tla lociranih na terenima koji se koriste u nepoljoprivredne svrhe, analizirano je na koncentraciju topljivog Cu u zlatotopki. Tla su klasificirana prema Hrvatskom sustavu klasifikacije tala i Svjetskoj referentnoj bazi za resurse tla kao Crvenica, odnosno Chromic i Rhodic Cambisol. Vrijednosti medijane za koncentraciju Cu u A horizontu (Cu_A) i kambičnom Bw horizontu (Cu_B) bile su 34,9, odnosno 36,1 mg/kg, a kretale su se između 16,2 i 69,5 mg/kg u Cu_A i od 17,0 do 73,0 mg/kg u Cu_B horizontu. Utvrđeni PVP za Cu_A varirao je između 43,6 i 58,4 mg/kg, ovisno o primjenjenoj metodi određivanja. Medijana omjera Cu_A/Cu_B od 0,96 bila je blizu identičnom. Wilcoxonov test usklađenih parova i Hodges-Lehmann metoda su pokazali da je razlika medijana Cu koncentracija između Cu_A i Cu_B bila vrlo mala (-1,78 mg/kg). Navedeni statistički dokazi o malim razlikama u koncentraciji Cu između horizonata sugeriraju da se koncentracije Cu izmjerene u kambičnom horizontu mogu smatrati "lokalnom pozadinom" za uzorke prikupljene u A horizontu i može se predložiti njihova upotreba u probiranju onečišćenja Crvenica.

Ključne riječi: pozadinska vrijednost praga, kambični horizont, testiranje usklađenih parova

INTRODUCTION

Assessment of soil heavy metal background concentration and threshold values derivation is an important task to correctly evaluate the chemical status of soils in regard to the national Soil Protection Regulation. A review of worldwide national legislation and approaches to determining threshold values is outside the scope of this work, but we find it useful to bring up some examples from Finland, the Netherlands, the United Kingdom and Croatia. The Finland Government Decree on the Assessment of Soil Contamination and Remediation Needs (214/2007) (Finnish Government Decree, MEF, 2007) defines a geochemical baseline as being the natural geochemical background concentration. The upper limit of geochemical baseline variation or threshold value is determined as Tukey inner fence (Tukey,1977) for some elements. In areas where metal concentration exceeded the threshold value further assessment is needed. The United Kingdom Statutory Guidance on soil quality (Defra, 2012) defines normal background concentration (NBC) as the "content of a substance in a soil resulting from both natural geological and pedological processes and including diffuse source inputs". The upper limit of NBCs, at or below which contaminant levels can be considered to be normal is defined as the upper 95% confidence limit of the 95th percentile (mg/kg) (Ander et al., 2013). In the Netherlands, every exceedance of background values represents contamination of soil that affects its quality (Crommentuijn et al., 1997). According to the Dutch Soil Protection Act (Ministry of VROM, 2006), the background values (BVs) are the concentration of the compounds in topsoil from undisturbed, clean soils. The BVs were derived as the 95-percentile values of topsoil (0-10 cm) concentrations. The Croatian Ordinance on protection of agricultural land from pollution (Official Gazette, NN 71/19) prescribed maximum admissible concentration (MAC) taking into account pH values. However, no actions are envisaged in the case when Cu concentration exceeds the MAC.

Copper (Cu) is an essential micronutrient for the growth of plants and animals, with average levels in natural worldwide soils that ranged between 13 and 24 mg/kg (Kabata-Pendias, 2011). An impact on human health and biota related to deficiency as well as the excess of Cu are well known. The contamination of soils with copper, especially due to agriculture, is a process that can lead to serious environmental problems (Desaules, 2012; Sacristan and Carbo, 2016), especially in terms of adverse effect on soil biota (Merrington et al., 2002; Diaz Ravina et al., 2007). An assessment of the Cu soil contamination is of practical importance, especially in the Mediterranean area.

In the Croatian Adriatic coastal region dominant crops are vine and olives whose management implies the use of copper-based fungicides. The median Cu concentration of 35.5 and 45.0 mg/kg reported by Halamić et al. (2009) and Miko et al. (2001) in soils of this region are more than twice elevated compared to Cu concentration at the continental scale of 14.5 mg/kg (Albanese et al., 2015). Unfortunately, the data on background concentrations for Cu is still missing. The knowledge of the background (naturally occurring) metal concentration in soil is important to quantify the level of contamination (Baize and Steckerman, 2001; Bini et al., 2011), to better distinguish sources of metals contamination (Reimann and Garret, 2005) and to develop and improve guidelines for environmental legislation (Dung et al., 2013; Ander et al., 2013).

In the current study, background concentration is defined as the „concentration of an element or a substance characteristic of a soil type in an area or region arising from both natural sources and anthropogenic diffuse sources such as atmospheric deposition" (ISO, 2018). There is an increased focus both on the national as well as on the international level on how to determine 'background' concentrations of contaminants to manage land. On the importance and necessity of knowledge of the background content of heavy metals (HMs) in the evaluation of the contamination of soils reported numerous authors (i.e. Hawkes and Webb, 1962; Reimann and Garret, 2005; Baize and Sterckeman, 2001). The concentration above background values indicates contamination that may limit particular soil function to a various extent (Reganold and Wachter, 2016) and require attention in environmental risk assessment in terms of further monitoring/control (Labaz et al., 2019). Contamination assessment is performed by comparing the HM content in the contaminated soil with the background concentration. Therefore, without knowing the background value of HM correct evaluation of the contamination cannot be made.

The background concentrations vary significantly from one place to another depending on the geological setting (Gallan et al., 2008; Jarva et al., 2010; Albanese et al., 2015; Birke et al., 2016) and soil type (Baize and Steckerman, 2001; Bini et al., 2011). This indicates that estimates of backgrounds are very dependent on location and scale as pointed out by several researchers (e.g., Matschullat et al., 2000; Reimann and Garrett, 2005; Tarvainen and Jarva, 2011). So, the use of guidelines defined in national regulations for an assessment of soil contamination is not sufficiently reliable for application in the whole country. Therefore, the determination of background metal concentration in soil at the regional level is needed. The factors controlling the Cu content - lithology and soil type can vary on a small scale and then neither a regional background concentration will be locally appropriate, and in such cases, it is necessary to determine the local background. However, at the site where local background content cannot be established an assessment of soil Cu contamination is not easy. Therefore, some authors (e.g., Steinnes and Njåstad, 1995; Blaser et al., 2000) suggest that element concentrations measured in a bottom soil horizon can be taken as local background for the topsoil horizons. Many authors (Blaser et al., 2000; Fachinelli et al., 2001; Reimann et al., 2001; Reimann et al., 2007; Yang et al., 2009; Massaas et al., 2009; Reimann et al., 2009; Bini et al., 2011) have used the concentration of heavy metals in the bottom horizon as a local background of topsoil (top/bot ratio) as a proof of anthropogenic impact. However, the results of using this ratio were very different in terms of the reliability of such evidence of soil contamination. These can be related to the fact that the soil characteristics (soil type, morphology, and their functioning) are most often not taken into account.

In this study, we are focused on the most widespread soil type of the Adriatic coastal region of Croatia known as terra rossa. Since data on Cu concentrations in natural terra rossa soil are missing the first goal was to assess soil Cu concentration in the mineral A horizon and cambic Bw horizon and to determine regional background threshold value (BTV) for terra rossa using various statistical techniques and compare it with soil quality standards as defined in Croatia and some of the national systems in Europe. The second goal and the main focus of the study were to quantify and test the difference in Cu between the topsoil (A horizon) and bottom (Bw) horizon. More precisely, the second goal was to explore the reliability of using the concentration of Cu in the bottom horizon (Cu_B) as the background in the topsoil (Cu_A) of natural terra rossa soil. The basic assumption is that there is a strong relationship between the Cu concentrations in the mineral A horizon and Bw horizon of terra rossa soil. To test whether there was enough statistically significant evidence for an assumption of dependency in Cu between the A horizon and Bw horizon we used approaches as follow (i) measuring the differences between the distribution of the Cu_A and Cu_B samples by Kolmogorov-Smirnov (KS) test, (ii) calculation and analyzing Cu_A/Cu_B ratio (top/bot) on the whole distribution scale, and (iii) testing the differences between the Cu concentration in the matched pairs of the A horizon and Bw horizon using the Wilcoxon matched pairs signed-rank test and Hodges–Lehmann estimator.

MATERIAL AND METHODS

Study area

The study area is located in the Middle Adriatic region of Croatia, Figure 1. Geologically, the area is built of the Cretaceous limestones and dolomites characterized by typical karst geomorphology and hydrology. According to the Köppen classification (Köppen, 1918), the climate is Mediterranean with warm summers (Cs) and temperate humid with warm summers (Cf). According to the plant-geographical division of the vegetation of Croatia

(Trinajstić, 1998), this area belongs to the Mediterranean-littoral vegetation zone of wild forests olives, forests of evergreen oak (*Quercus ilex* L.), pubescent oak (*Quercus pubescens* Willd.), and hornbeams (*Ostrya carpinifolia* Scop. and *Carpinus orientalis*, Mill.). The primary forests have been lost and today their various degradation forms dominate, including maquis, garrigue, scrubs, sparsely vegetated areas, natural grassland, and bare rock. Terra rossa soil is the most represented soil type. It has clayey or silty clayey texture, excellent soil aggregate stability and therefore a high water infiltration rate and internal drainage.

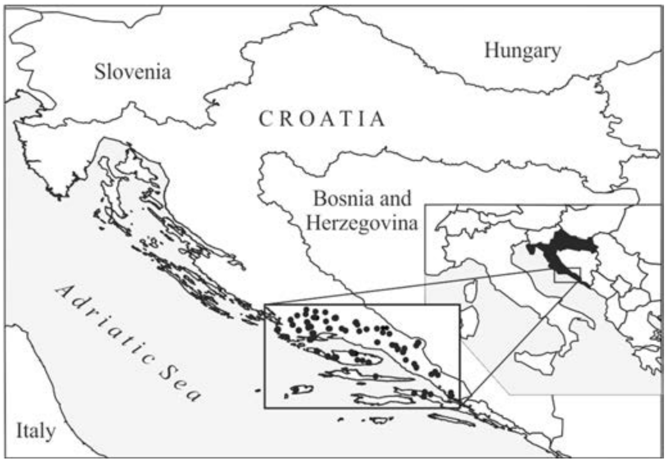

Figure 1. Map showing the locations of the soil sampling sites

The Croatian Soil classification system (Škorić et al., 1985) puts terra Rossa soil in the class of Cambic soils. According to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014, update 2015), the mentioned soil type is Leptic Chromic or Rhodic CAMBISOLS (Clayic, Colluvic) or Leptic Chromic Rhodic LUVISOLS (Clayic, Colluvic).

Data sources and laboratory analysis

Data for a total of 64 soil profiles of natural terra rossa used for non-agricultural purposes were selected from the database of heavy metals in the soils of Dalmatia (Miloš, 2015), comprised of different pedological studies conducted in Middle Dalmatia, Croatia (Figure 1). In the mentioned studies, a horizon-based sampling was performed, including mineral A horizon also signed as topsoil and cambic Bw horizon also signed as bottom horizon. The thickness of A horizon ranged between 10 and 26 cm with a mean value of 18.5 cm. The thickness of the Bw horizon was on average 45.1 cm and varied between 25 and 71 cm. The detailed information on basic soil properties including pH, carbonates, soil organic carbon (SOC) content, and particle size distribution in A and Bw horizon has been presented in the study of Miloš and Bensa (2020). The analyzed terra rossa soils had acid to alkaline, in average neutral pH reaction throughout the entire soil profile and mostly are non-calcareous. A few calcareous samples, with up to 18.4% $CaCO_3$, can be connected to colluviation and mixing of soil material and carbonate rock fragments. It is characterized by a wide range and medium average SOC content in A and Bw horizons of 52.1 and 27.6 g/kg, respectively. The A horizon is a silty clay loam with an average of 38.6% of clay particles. The Bw horizon is silty clay and clay with an average of 45.8% clay.

In a total of 128 soil samples grounded and sieved (0.50 mm) the Cu was extracted by aqua regia (ISO, 1995) using microwave techniques, and its concentration was determined by the inductively coupled plasma - optical emission spectrometry (ICP OES). Accuracy was controlled by participating in the ISE Wepal (Wageningen University) proficiency testing scheme, as well as using CRMs for internal quality control and it was within range of ±15% of the certified values. Analytical precision was controlled by repeating the analysis of individual samples three times and it was satisfactory (relative standard deviation < 5%).

Statistical analysis

The statistical analysis included: mean, median, standard deviation, minimum and maximum values, and skewness. The kernel density estimation (KDE) is used to estimate the probability density function (PDF). KDE is the most common nonparametric technique for visualizing and comparing the data distribution. For more details see Wand and Jones (1995) and Bowman and Azzalini (1997). The kernel smooths the probabilities across the range for a random variable such that the sum of probabilities equals one. The normality of the data distributions is tested by the one-sided Kolmogorov-Smirnov (KS) test. To test whether two empirical distribution functions are the same the two-sided KS test was used. This non-parametric technique quantifies a maximum distance (D) between the cumulative distribution functions (CDF). That is, defined as:

$$D_{n,m} = \sup | F_{1,n}(x) - F_{2,m}(x) |,$$

where $F_{1,n}(x)$ and $F_{2,m}(x)$ are the empirical distribution functions of the first and the second sample respectively, and sup is the supremum function.

In the determination of the upper limit of variation in Cu concentrations or threshold value of Cu concentration the following approaches were used: the median +2 median absolute deviations [median+2MAD], the Tukey inner fence (TIF), the mean + 2 standard deviations [mean+2SD], and the percentile-based approach in cumulative probability distributions that includes the 95th percentile of a given dataset.

The median absolute deviation (MAD) in the [median+2MAD] rule is defined (Huber, 1981) as follows:

$$MAD = b * M_i (| x_i - M_j (x_j |)$$

where the x_j is the n of original observations M_j is the median of the series and b is the outlier multiplying factor of 1.5 based on the assumption of asymmetrical data distribution.

For determining outliers in a sample we used a method referred to as Tukey fences (Tukey, 1977).

The Tukey (upper and lower) inner fence (TIF) is defined as follows:

$$\text{upper TIF} = Q_3 + 1.5 * IQR \text{ and}$$
$$\text{lower TIF} = Q_1 + 1.5 * IQR$$

where, IQR = (Q_3-Q_1) is the interquartile range; Q_3 is the 75th percentile and Q_1 is the 25th percentile.

Fences we used to illustrate outliers in box plots. To compare two paired samples a non-parametric Wilcoxon matched-pairs signed-rank test and the Hodges-Lehmann estimator (Hodges and Lehmann, 1963; Conover, 1999) were used. The Wilcoxon signed-rank test computes the difference between two matched pairs of variables and analyses these differences to establish if they are statistically significantly different from one another. It's used when the data are not normally distributed. The null hypothesis for this test is that the medians of two paired samples are equal. The assumptions are that paired samples are random and independent and that the distribution of differences is symmetrical. For more details of the Wilcoxon test see Pratt and Gibbons (1981). The Hodges–Lehmann median difference between two paired samples with sample size *n* is calculated as follows: first the n paired differences are calculated. For each possible set of 2 differences, the average is calculated. The Hodges-Lehmann median difference is the median of all $n \times (n+1) / 2$ averages. Statistical analyses were performed using MedCalc software and AMC statistical software for Excel.

RESULTS AND DISCUSSIONS

Statistical analysis of Cu concentration

Statistical summary of Cu concentration in 64 soil samples of A horizon and 64 samples of Bw horizon of terra rossa soil signed as Cu_A and Cu_B are given in Table 1. The mean value of Cu_A and Cu_B were 37.0 and 38.8 mg/kg, respectively. The Cu_A and Cu_B varied in a wide range from 16.2 to 69.5 mg/kg and between 17.1 and 73.0 mg/kg, respectively. The interquartile range (IRQ) of Cu_A was small (9.46 mg/kg; Table 1) and showed the closer together and slightly spread out the data with six outliers (Figure 2b). The Cu_B sample has a wider IQR (12.51 mg/kg; Table 1) and only two outliers. The medians in Cu_A and Cu_B samples have similar values of 34.9 and 36.1 mg/kg, respectively, which are generally close to the mentioned mean values (Table 1). The skewness coefficients of Cu_A (0.87) and Cu_B (0.96) indicate a moderately skewed distribution with a right tail.

The Cu concentration in probability density function (PDF) plot estimated via Kernel density estimation (KDE), Figure 2a illustrates the mentioned skewness and a high level of similarities in the distribution pattern of analysed Cu_A and Cu_B samples. The PDF plot (Figure 2a) shows the small differences in the mean values and spread between the Cu concentrations in the topsoil and bottom horizon.

Table 1. Descriptive statistics of Cu concentration in A horizon (Cu_A) and Bw horizon (Cu_B), mg/kg

Variable	Mean	Min	Max	Range	First Q_1	Median Q_2	Third Q_3	IQR	S.D.	Skew
Cu_A	37.03	16.24	69.50	53.26	32.47	34.88	41.92	9.46	9.93	0.87
Cu_B	38.81	17.01	73.00	55.99	31.78	36.14	44.29	12.51	10.76	0.96

Mean; Min: minimum; Max: maximum; Range; First quartile (Q_1): 25th percentile, Median (Q_2): 50th percentiles, Third quartile (Q_3): 75th percentile; IQR: Interquartile range; SD: Standard deviation and Skew: Skewness

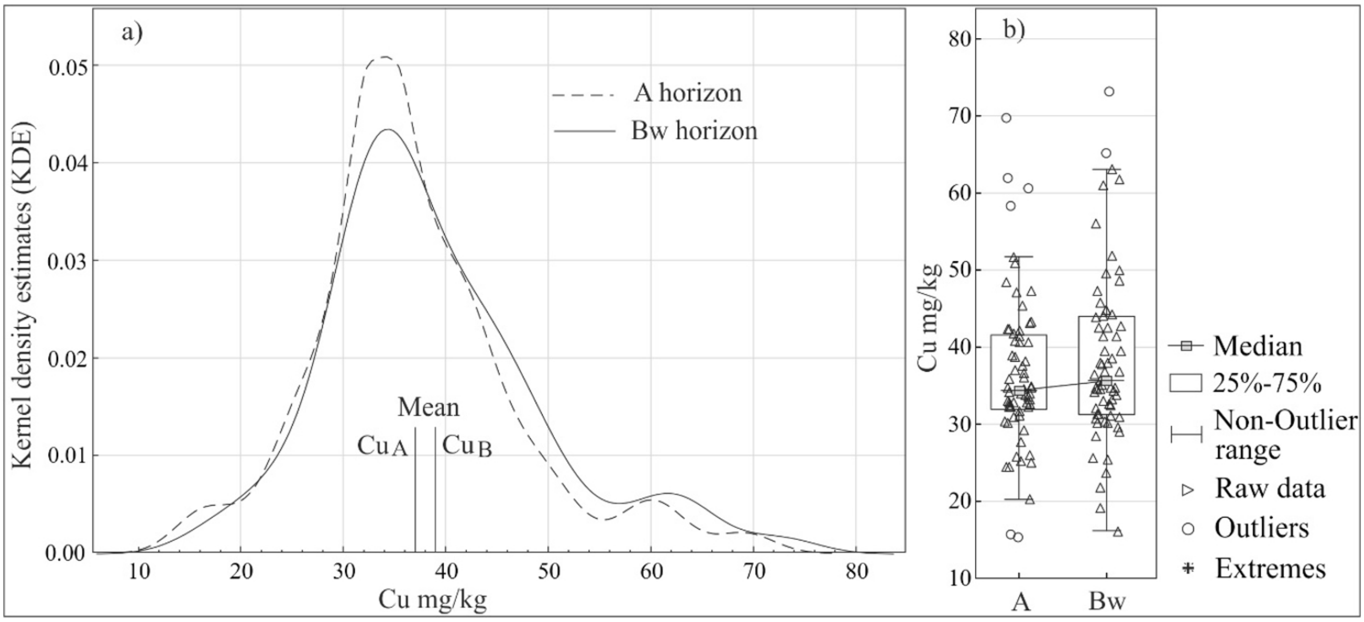

Figure 2. Probability Density Function (PDF) plot estimated via Kernel density estimation for a Cu_A and Cu_B sample (a), and box-plot diagram of Cu concentration in A horizon and cambic Bw horizon (b)

In the PDF plot, the probability is given by the area under the probability density function for the specified range. The probability between two values of Cu concentration, 'x_1' and 'x_2', is the integral of the probability density function that is the area under the curve between the lowest and greatest values of the range. Mathematically this is $\int_{x2}^{x1} f(x)dx = P\,(x_1<X<x_2)$. For any PDF, the area under the curve must be 1. This allows determination of the probability, for example what is the probability (P) that the newly sampled value of the Cu concentration in topsoil (Cu_A) will achieve the value of the Cu greater than 35 mg/kg and less than 50 mg/kg Cu, [P (35<X<50)]. According to the PDF plot (Figure 2a) the expected probability is 41%.

The distribution pattern based on a five-number summary statistics ("minimum", first quartile (Q_1), second quartile (Q_2) median, third quartile (Q_3), and "maximum", displayed in Table 1 and belonging box-plot (Figure 2b) indicates a small difference between analysed samples and suggests that overall (Cu_A and Cu_B) data set have a high level of similarities with each other.

Summary results of the one-sample Kolmogorov-Smirnov hypothesis test used to determine whether a sample Cu_A and Cu_B comes from a population that is normally distributed are given in Table 3. The maximum difference (D - value) between the observed and theoretical cumulative distribution function for Cu_A and Cu_B samples of 0.129 and 0.123, respectively, is higher than their asymptotic p-values of 0.010 and 0.017 at the significance level of 0.05. These test results mean that the null hypothesis should be rejected (the assumption of normality not supported) suggesting that the distributions of both samples do not follow the normal distribution.

The median values of Cu concentration for A and Bw horizon (35.8 and 36.5 mg/kg, respectively; Table 1) are in agreement with published data for natural terra rossa soils in Italy (Bellanca et al., 1996 and Vingiani et al., 2018) and Turkey (Temur et al., 2009). Also, it is comparable to median Cu concentration for terra rossa soils in Istria, Croatia (Peh et al., 2003), and coastal Croatia (Halamić et al., 2009) dominated by terra rossa, although the data on land use in mentioned studies are missing. However, in comparison to average Cu levels in natural worldwide soil that vary from 13 to 24 mg/kg (Kabata Pendias, 2011) or with the median value of 14.5 mg/kg established in the GEMAS project for grazing land (Albanese et al., 2015), mean and median Cu concentrations in the current study are higher.

The reasons for elevated Cu concentrations in terra rossa soils are not entirely clear and related to the geological structure - the hard limestones and dolomites characterized by high $CaCO_3$ content and very low insoluble residues (<2%) (Durn et al., 1999, Temur et al., 2009) which implies a lengthy process of weathering and accumulation with the release of high amounts of iron oxides closely bound to clay minerals. Also, these soils have been affected by various external materials such as long-range transported eolian dust from Sahara (Yallon, 1997; Muhs et al., 2012) and loess sediments from the early Middle Pleistocene (Durn, 1999). Also, it is well-known that Cu has a high affinity for binding to Fe and Mn oxides (Boujelben et al., 2009; Cerqueira et al., 2011) and clay minerals (Al-Qunaibit et al., 2005) which terra rossa abounds, so great retention and accumulation of Cu in these soils are expected.

Background threshold values for Cu concentration

The results of the determination of the background threshold values for Cu concentration are given in Table 2 and in the cumulative probability (CP) plot (Figure 3). The obtained results show a wide range of possible threshold values depending on the chosen method of calculation. The [Median+2MAD] method achieved the lowest threshold value for Cu of 43.6 mg/kg and classified more outliers (total 12) than any other method (Figure 3).

Table 2. Threshold value estimated by a variety of methods

Variable	Threshold values (mg/kg)			
	[Median+2MAD]	TIF	95^{th}	[Mean+2SD]
Cu_A	43.6	56.1	58.4	56.9

Mean + 2 standard deviations [Mean+2SD]; Tukey upper inner fence (TIF); Median + 2 median absolute deviation [Median+2MAD] and 95^{th} percentile

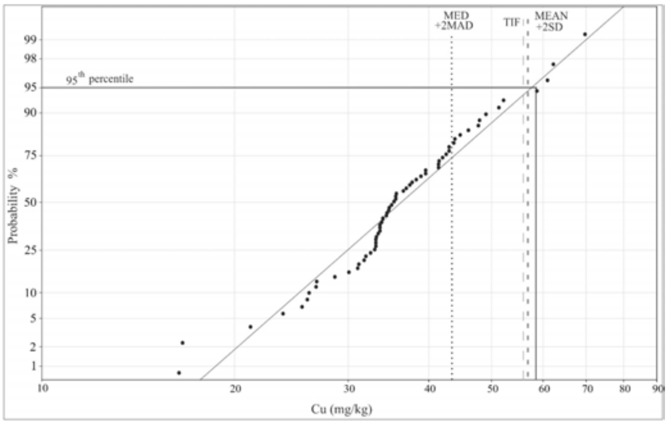

Figure 3. Cumulative probability (CP) plot for Cu concentration in the A horizon. The threshold values in Cu concentration: median +2 median absolute deviations [Median+2MAD] is indicated by the vertical dotted line; the Mean + 2 standard deviations [Mean+2SD] is indicated by vertical dashed black lines; Tukey inner fence (TIF) is shown as a vertical dashed grey line; the 95^{th} percentile are indicated by the black line. Data plotted on a logarithmic scale equivalent to a logarithmic transformation

It is recognised (Reimann et al., 2018; Miloš and Bensa, 2019) that this method gives the most conservative estimates. The [Median+2MAD] procedure is followed by Tukey's inner fence (TIF), the Mean + 2 standard deviations [Mean+2SD], and the 95^{th} percentile according to the calculated threshold value of 56.1, 56.9, and 58.4 mg/kg, respectively. The CDF plot (Figure 3) and Table 2 show that the background threshold values established by the TIF method, [Mean+2SD] method, as well as by the method of 95^{th} percentile, which achieved the highest Cu value, sit close to each other.

European countries have various approaches to define threshold values and prescribed actions if concentrations of contaminants exceeded them (Carlon et al., 2007; Reimann et al., 2018). Therefore, a direct comparison of established BTV in the current study with threshold values set in national legislation is not quite possible. This is illustrated by the wide range of soil guidelines (SGV) for Cu in EU countries (40-1000 mg/kg) as pointed out by Reimann et al. (2018). Nevertheless, it should be noted that the BTV in the current study, established using various statistical techniques (43.6-58.4 mg/kg; Table 3), are significantly lower than MAC prescribed in Croatian Ordinance (NN 71/19). In this ordinance the MACs are set taking into account pH values: < 5, 5-6 and > 6 and amount 60, 90 and 120 mg/kg, respectively. Most of the analysed samples have pH > 6 and only a few samples have pH 5-6 (Miloš and Bensa, 2020) so they were undergoing MAC of 120 and 90 mg/kg, respectively. The established BTVs are also lower in comparison to the threshold value of 100 mg/kg prescribed in the Finnish legislation (MEF, 2007). In comparison to the Cu upper limit of NBC of 62 mg/kg prescribed for Principal domain soils in the United Kingdom (Ander et al., 2013), the BTVs in the current study is slightly lower. The background value (BV) for Cu in agricultural soils of 36 mg/kg prescribed by the Ministry of VROM (2006) in the Netherlands is lower compared to the Cu BTVs in this study.

Quantification and testing the differences in Cu between the A and Bw horizon

This analysis aims to answer the following question: How are the two soil horizons similar in their Cu concentration? To answer this question, we used the following approaches: (i) measuring the differences between empirical cumulative distribution function (ECDFs) of the Cu_A and Cu_B samples, (ii) analysing Cu_A/Cu_B ratio signed also as "top/bot" ratio, and (iii) analyzing and testing the differences between the Cu concentration in the matched-pairs of the Cu_A and Cu_B samples using Wilcoxon matched pairs signed-rank test and Hodges-Lehman estimator.

The comparison of the distribution function of the Cu concentration in A and Bw horizon

To compare the distribution function of the Cu_A and Cu_B samples we used a two-sided Kolmogorov-Smirnov (KS) test. It is based on the idea that if two sample sets belong to the same population their empirical cumulative distribution functions (ECDFs) must be similar. This means that we can evaluate their similarity by measuring the differences between the ECDFs. The maximum difference (D-value) between two empirical cumulative distribution functions Cu_A and Cu_B was lower (D=0.125) compared with their asymptotic p-value of 0.669 at the significance level of 0.05 (Table 3).

This test result suggests that the null hypothesis should be retained and the assumption of equality is supported, meaning that the distributions of analysed sample sets are similar (come from the same distribution). These results are in line with the visualization of Cu concentrations in the A and Bw horizon shown in the probability density plot (Figure 2a).

Analysis of Cu_A/Cu_B ratio

The results of the analysis of the relationship between Cu concentration in A and Bw horizon (Cu_A/Cu_B ratio) calculated for each of the 64 paired samples (soil profiles) are given in Table 4. The mean and median value of Cu_A/Cu_B ratio was close to identical (0.96) and it ranged from 0.72 to 1.16 (Table 4). The median Cu_A/Cu_B ratio was close to unity and amounted to 0.84, 0.91, 0.96, 1.02, and 1.07 for the 5th percentile, first quartile (Q_1), median

Table 3. Kolmogorov-Smirnov hypothesis test summary

CDFs Samples	Maximum difference (D)	Asymptotic two-tailed (p-value)	Decision
Cu_A	0.129	0.010	Reject null hypothesis
Cu_B	0.123	0.017	Reject null hypothesis
Cu_A and Cu_B	0.125	0.699	Retain null hypothesis

Maximum difference (D), Asymptotic p-value (p), and decision for the normal distribution of independent Cu_A Cu_B samples and equality of distributions (CDFs) of Cu_A and Cu_B samples Asymptotic significance The significance level is 0.05

(Q_2), third quartile (Q_3), and 95th percentile, respectively. The mentioned values indicate an almost symmetrical distribution in line with the corresponding skewness value of 0.02. For the reliability of the top/bot ratio assessment, the number of points at which the comparison will be made is important. A common use of top/bot ratio in literature findings implies a simple ratio between the mean (or median) value of topsoil and the one from the bottom horizon. It is rather modest and rough data that does not provide relevant insight in relationships among element concentrations in topsoil and underlying horizon. A more detailed analysis conducted in the current study involving the calculation of the top/bot ratio at two percentiles (5th and 95th) and quartiles (Q_1, Q_2, and Q_3) across the entire distribution ensures a more reliable conclusion regarding the relation among Cu concentrations in A and Bw horizon.

Top/bot ratio has been widely used for some time (Fachinelli et al., 2001; Reimann et al., 2001; Reimann et al., 2007; Yang et al., 2009; Massaas et al., 2009; Reimann et al., 2009; Bini et al., 2011) as a proof of anthropogenic impact. However, the results of these studies were very different in terms of the reliability of such evidence, so Sucharova et al. (2012) suggested its rejections. Some of the reasons for poor reliability can be found in the comparison of HMs concentrations among horizons that are not related (O and C horizons), as well as in the analysis of large data sets without distinguishing different soil types and respecting their differences. However, in cases when soil properties of analysed horizons are similar, i.e. do not vary significantly with depth, top/bot is effective as an indication of relative enrichment or depletion of elements in the top-soil layer as stressed out by Blaser et al. (2000), Bini et al. (2011), and Miloš and Bensa (2019).

Analysis and testing differences in Cu concentration between matched paired samples

Even more accurate data on relations among Cu concentration in A horizon and Bw horizon provide the results of the analysis of the differences between the paired samples of the Cu concentration in Cu_A and Cu_B (Cu_A-Cu_B) given in Table 4 and graphic plot (Figure 4). The mean value of the paired sample differences Cu_A-Cu_B was -1.78 and ranged between -9.81 and 6.01 (Table 4). These differences in Cu concentrations on the first quartile (Q_1), second quartile (Q_2) median, and third quartile (Q_3) were -4.07, -1.75, 1.02 mg/kg, respectively. The difference between Cu_A and Cu_B on the 5th percentile and the 95th percentile was -7.43, and 3.74 mg/kg, respectively, Table 4.

The mentioned differences in the probability density function (PDF) plot and the belonging boxplot (Figure 4) gives a good insight into how the values in the data are spread out. These graphs show an almost symmetrical distribution of data that is also confirmed by the corresponding skewness value of 0.01. The PDF plot (Figure 4b) of the differences between the concentration of Cu in A (Cu_A) and Bw horizon (Cu_B) specify the probability of differences in Cu_A and Cu_B falling within a particular range of values. This allows determination of the probability, for example, what are the probability (P) that a new sampling would achieve a value of the difference of the paired samples greater than -4 mg/kg and less than 2 mg/kg Cu, [P (-4<X<2)].

Table 4. The mean value and five number statistics of Cu concentration for the ratio Cu_A/Cu_B and the difference between Cu_A and Cu_B paired samples

Variable	Mean	Min	Max	Range	First Q_1	Median Q_2	Third Q_3	IQR	Skew	Percentiles	
										5th	95th
Ratio Cu_A/Cu_B	0.96	0.72	1.16	0.49	0.91	0.96	1.02	0.13	0.02	0.84	1.07
Difference Cu_A-Cu_B	-1.78	-9.81	6.01	15.81	-4.07	-1.75	0.64	4.71	0.01	-7.43	3.74

Min: minimum; Max: maximum; Range; First (Q_1): 25th percentile, second quartile (Q_2) Median; third quartile (Q_3): 75th percentile; IQR: Interquartile range; Skew; Skewness; 5th and 95th percentiles of Cu concentration for the ratio Cu_A/Cu_B and the difference between Cu_A and Cu_B paired samples

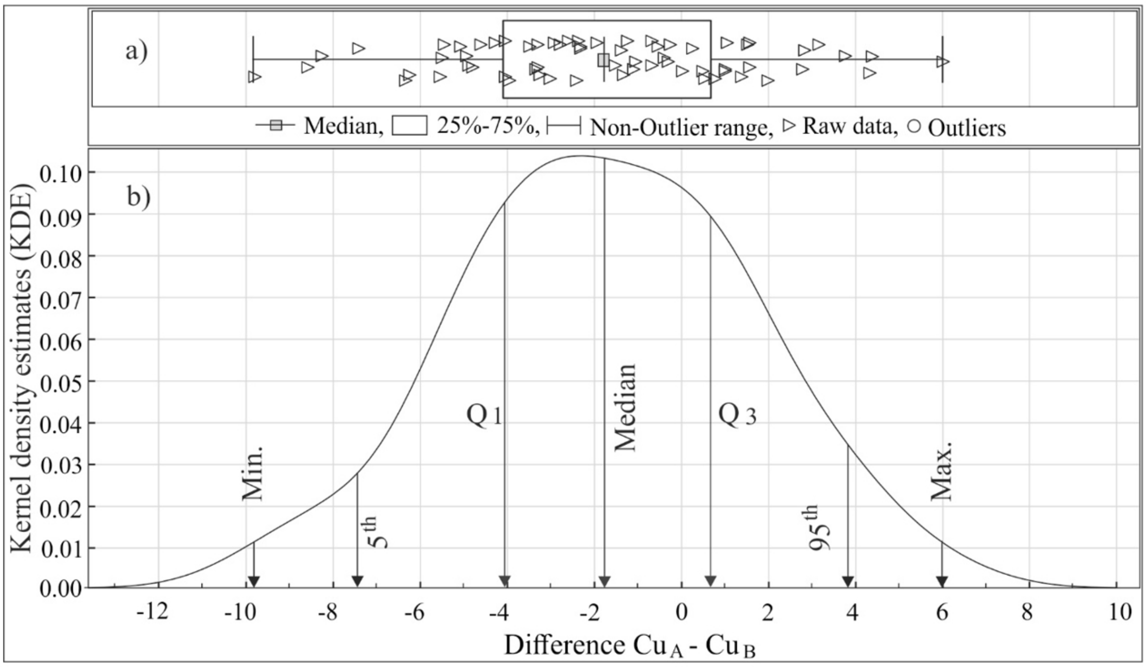

Figure 4. The box plot of the differences between the Cu concentration in the matched pairs of the A and Bw horizon Cu_A and Cu_B (a) and probability density function - PDF (b)

According to the mentioned PDF plot (Figure 4b), the calculated probability is 67%. The probability determined in this way provides information on how likely it is that the new sampling will have the value of the difference between Cu_A and Cu_B within a specified range.

Summary statistics for the Wilcoxon matched pairs signed-rank test given in Table 5 resulting in the two-tailed p-value of 0.0002 is less than the specified risk of 5 per cent (P<0.05). Therefore, we reject the null hypothesis that the median difference in Cu concentration between the matched-pairs is significantly different from zero. Since the null hypothesis was rejected, we cannot know which of the paired sample (or all) is not consistent with the sample outcome indicating that the test provided no straightforward estimate of the magnitude of the difference between the matched pairs Cu_A and Cu_B. The median difference between matched paired samples estimated using the Hodges-Lehmann methodology was small (-1.78 mg/kg Cu) and its 95% confidence interval is likely to be between -2.65 to -0.91 mg/kg (Table 5). The small median difference and confidence interval between paired samples (Table 5), an equal distribution across Cu_A and Cu_B (KS test, Table 3), and top/bot ratio close to unity across the entire distribution (Table 4) suggest that the established differences between the two samples being compared have no practical meaning. Therefore, we believe that the difference in concentration of Cu between topsoil and the bottom horizon has no practical significance although the Wilcoxon test showed that they are statistically significant. In other words, although there were large differences in some paired samples, in most samples the difference was rather small (IQR 4.71 mg/kg; Table 4).

Table 5. Wilcoxon signed-rank test, Hodges-Lehmann median difference between matched-pairs Cu_A and Cu_B and its confidence interval 95%

Pair of variables	Number of differences		p-value	Hodges-Lehmann median difference estimate	Confidence interval 95%	
	positive	negative			Lower	Upper
Cu_A and Cu_B	44	20	0.0002	-1.78	-2.65	-0.91

A specified significance level at P<0.05; P-value is two-sided

CONCLUSIONS

The median values of Cu concentration in A horizon (Cu_A) and cambic Bw horizon (Cu_B) of terra rossa soil were 34.9 and 36.1 mg/kg, respectively. The Cu_A and Cu_B varied in a wide range from 16.2 to 69.5 mg/kg in A horizon and between 17.1 and 73.0 mg/kg in the Bw horizon. Both Cu_A and Cu_B samples had a small interquartile range and slightly spread out of data. The background threshold value (BTV) of Cu concentration ranged between 43.6 mg/kg determined by the [Median+2MAD] method and 58.4 mg/kg by the method of 95th percentile. The Cu_A and Cu_B samples had an equal distribution function, ratio close to identical across the entire distribution, and small median difference and confidence interval between paired samples. The mentioned statistical evidence on the small differences between Cu_A and Cu_B suggests that Cu concentrations measured in a cambic Bw horizon can be considered a “local background” for the samples collected in A horizon and its utilization in screening terra rossa soil contamination can be suggested.

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