Original scientific paper
Journal of Central European Agriculture, 2020, 21(3), p.633-648
DOI: /10.5513/JCEA01/21.3.2588

Lead and zinc concentration in genetic horizons of Terra rossa soil at a local scale. How these concentrations differ?

Koncentracije olova i cinka u genetskim horizontima crvenice na lokalnoj razini. Kako se te koncentracije razlikuju?

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Received: July 4, 2019; accepted: January 2, 2020

ABSTRACT

The goals of this study were to (i) determine the concentration of the Pb and Zn in Terra rossa soil, (ii) reveal its origin and (iii) establish how the concentration of these elements between genetic horizons differ. In a total of 128 soil samples collected from the genetic A and B horizon of 64 Terra Rossa soil profiles were analyzed for aqua regia soluble concentration of lead (Pb_A and Pb_B) and zinc (Zn_A and Zn_B) as well as soil properties: pH in KCl, $CaCO_3$, soil organic carbon (SOC) and particle size distribution. The median value of Pb_A, Pb_B, Zn_A, and Zn_B were 41.6, 33.8, 106.1 and 103.8 mg/kg, respectively. The principal component analyses have shown that the Pb and Zn contribute most to the variability of A horizon and have the same and natural origin – they are accumulated by geochemical weathering and soil-forming processes. Using non-parametric techniques (the two-sided Kolmogorov-Smirnov test (K-S) and a shift function (SF) we estimated that (i) the Pb_A and Pb_B distribution differ in spread and median and (ii) the Pb_B distribution need to be progressively shifted, at the whole range starting from 2.8 mg/kg for the first decile; 7.2 mg/kg for the fifth decile (median) to 12.2 mg/kg for the ninth decile to match Pb_A distribution. In the case of Zn, there is no evidence that the distribution of Zn_A is in any way different than the distribution of Zn_B. This implies that the Zn_A and Zn_B have a remarkably similar shape of their distribution functions and a noticeable slight shift with a value of 2.3 mg/kg at fifth decile. The analysis presented here illustrated why detailed statistical descriptions can help to better understand how and by how much lead and zinc distributions in Terra rossa genetic horizon differ.

Keywords: cumulative distribution function, heavy metals origin, potentially toxic elements, shift function

SAŽETAK

Ciljevi ovog istraživanja bili su (i) odrediti koncentracije olova i cinka u crvenici, (ii) otkriti njihovo porijeklo i (iii) utvrditi kako se koncentracije tih elemenata razlikuju između genetskih horizonata. Analizirano je ukupno 128 uzoraka tla sakupljenih iz genetskog A i B horizonta u 64 profila crvenica, na koncentracije olova (Pb_A i Pb_B) i cinka (Zn_A and Zn_B) u zlatotopki, kao i na svojstva tla: pH u KCl-u, $CaCO_3$, organski ugljik i mehanički sastav tla. Vrijednosti medijane za Pb_A, Pb_B, Zn_A, i Zn_B iznosile su: 41,6, 33,8, 106,1 i 103,8 mg/kg. Analiza glavnih komponenti pokazala je da varijabilnosti A horizonta najviše doprinose Pb i Zn koji imaju isto, prirodno porijeklo – akumulirani su geokemijskim trošenjem i pedogenetskim procesima. Korištenjem neparametrijskih tehnika (dvostranog Kolmogorov- Smirnov testa (K-S) i funkcije pomaka) ustanovljeno je (i) da se raspodjele Pb_A i Pb_B razlikuju u disperziji i medijani i (ii) da Pb_B distribuciju treba postupno pomaknuti po cijelom rasponu počevši od 2,8 mg/kg na prvoj decili preko 7,2 mg/kg na petoj decili (medijani) do 12,2 mg/kg na devetoj decili da bi se podudarala s Pb_A raspodjelom. U slučaju cinka, nema dokaza da se raspodjela Zn_A na bilo koji način razlikuje od raspodjele Zn_B. To implicira da Zn_A i Zn_B imaju upadljivo slične oblike funkcija raspodjele uz zamjetan blagi pomak od 2,3 mg/kg na petoj decili. Ovdje prikazana analiza ilustrira zašto detaljni statistički opisi mogu pomoći u boljem razumijevanju kako i koliko se razlikuju distribucije olova i cinka u genetskim horizontima crvenice.

Ključne riječi: kumulativna funkcija raspodjele, porijeklo teških metala, potencijalno toksični elementi, funkcija pomaka

INTRODUCTION

Lead is heavy metal very toxic to plants, animals, and microorganisms that cannot be biodegraded but can be accumulated in living organisms, whereas zinc is an essential element for all organisms. Lead and zinc occur in Earth´s crust at the mean content of 15 mg/kg (Kabata Pendias and Pendias, 2001) and 78 mg/kg (Alloway, 2008), respectively. The mean values of Pb in limestones reported by Wedepohl (2004), Halamić et al. (2009) and Faust and Aly (1981) were 5, 9 and 16 mg/kg, respectively. Zinc concentration in limestones is more uniformed e.g. Alloway, (2008), Halamić et al. (2009) and Wedepohl (2004) reported the mean value of 20, 21 and 23 mg/kg, respectively. An overall mean value of Pb and Zn in topsoil on the global scale have been estimated 25 and 55 mg/kg, respectively (Kabata Pendias and Pendias, 2001; Alloway, 2008).

Continental studies of the Pb and Zn concentrations in Europe (Salminen et al., 2005; Reimann et al., 2018), Australia (Reimann and Caritat, 2017) and North America (Smith et al., 2014) have established median Pb value of 15, 16, 7 and 18 mg/kg, respectively and median Zn value of 48, 45, 26 and 58 mg/kg, respectively. World soils have been seriously polluted by Pb and slightly by Zn (Adriano 2001; Kabata Pendias and Pendias, 2001) due to accumulation from different anthropogenic sources. The identification and quantification of potentially toxic elements (PTEs) in the soil are important for understanding and assessing the environmental condition of the whole environment. It is one of the major threats to soil quality and therefore is the subject of many studies around the world (Salminen et al., 2005; Reimann et al., 2014; Smith et al., 2014; Reimann and Caritat, 2017). The concentration of metals in pristine soil is primarily influenced by the lithology and secondly, by the soil-forming processes, that modify and redistribute its content within the soil profile. The basic geochemical composition is modified by the human impact that makes the difference between the topsoil and subsoil concentrations of metals. If the concentration of some element in the topsoil samples were known, the contamination could be determined by comparing its contamination distribution with the pristine background distribution of the same element in subsoil samples. This comparison makes sense because the subsoil generally is less influenced by anthropogenic contamination, and distribution shapes of some element in the subsoil and the topsoil are remarkably similar. That is why the comparative analysis of PTEs in topsoil and deeper horizons are used to recognize and quantify the natural and anthropogenic sources (Facchinelli et al., 2001; Massas et al. 2009; Yang et al., 2009). Reliability of using these differences expressed as top/bottom ratio depends on the similarities between soil properties in the top and bottom horizon as well as tools used in analyzes.

The different statistical methods have been used to detecting and quantifying differences between the content of some element in the topsoil sample with the same element in the subsoil. An approaches like a high mean or median top/bottom-soil ratios (i.e. Facchinelli et al., 2001; Yang et al., 2009) or different high values of "enrichment factors" (i.e. Blaser et al., 2000; Manta et al., 2002; Singh et al., 2010) as a proof of anthropogenic impact on soil, were not shown as a reliable indication of the human interference with the global environment (Reimann and Caritat, 2000, 2005; Sucharova et al., 2012). So, in the new approaches to this topic, there is a withdrawal from the concept of the descriptive statistics and using non-parametric methods based on the analysis of the cumulative distribution functions (CDFs) of the PTEs. Recently, Fabian et al. (2017), Reimann et al. (2019a) and Reimann et al. (2019b) were used the CDF and cumulative probability (CP) plot for the detecting and quantifying several types of contamination with PTEs at the continental to regional scale. These authors used CDF analysis to compare the observed topsoil CDF to the CDF of the same element from samples taken at a subsoil horizon from the same area. They demonstrated that the effects of different sources of contamination can be identified on CP curves.

In this study we are focused to (i) determine the concentration of the Pb and Zn in Terra rossa soil from Dalmatia, Croatia, (ii) reveal its origin by analyzing the relationships of these metals and soil properties in a multivariate manner and (iii) establish how and by how much Pb_A and Pb_B, as well as Zn_A and Zn_B, differ by comparing their overall CDF using Kolmogorov–Smirnov test and its CDF at particular points (quantiles) using the shift functions.

MATERIAL AND METHODS

Study area

The study area is located in the middle Dalmatia, Croatia (Figure 1). This area is built of the Cretaceous limestones and dolomites that belong to the Adriatic–Dinaridic Carbonate Platform (Pamić et al., 1998). It is characterized by the most typical karst geomorphology and hydrology. A prevalent climate is the Mediterranean. According to the Köppen climate classification (Koppen, 1918) on the islands and in coastal area there is an olive climate (Csa) with the dry period in the warm part of the year, whereas inland has moderately hot humid climate (Cfa) characterized by more precipitation and its more balanced distribution. This area is covered by eumediterranean forests of the evergreen oak (Quercus ilex), submediterranean forests of pubescent oak (Quercus pubescens Willd.) and hornbeams (Ostrya carpinifolia Scop. and Carpinus orientalis, Mill). The long-lasting devastation of mentioned vegetation cover resulted in various degradation vegetation stages including maquis, garrigue, scrubs, sparsely vegetated areas, natural grassland, and bare rock. These human activities have resulted in deep changes in the soil cover and its physical, chemical and biological properties. However, in this area, there is no significant human impact in terms of contamination by potentially toxic elements except through diffuse contamination from large-scale atmospheric transport.

The Terra Rossa soil is a typical soil in Mediterranean region, easily recognizable by reddish and reddish-brown color, clayey and silty clayey texture. These soils are mainly shallowly interrupted by large rock outcrops that cause discontinuity of the soil cover. According to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014) investigated soils were classified as Chromic cambisols and Rhodic cambisols. The Croatian classification (Škorić et al., 1985) puts Terra Rossa soil in the class of Cambic soils.

In a total of 64 soil profiles of Terra Rossa soil were selected from various pedological studies conducted in the middle Dalmatia, Croatia (Figure 1). In mentioned studies, sampling depth was defined by genetic horizons: topsoil - mineral horizon signed as A and bottom - cambic horizon signed as B horizon.

Figure 1. Soil sampling locations in middle Dalmatia

Laboratory methods

In a total of 128 soil samples were analyzed for basic soil properties and Pb and Zn concentration in both A and B horizon. Laboratory analyses were carried out on air-dried and sieved (< 2-mm) soil samples by following methods: pH was measured potentiometrically on a suspension of soil and KCl (c=1M) in 1:5 ratio (ISO, 2005);

carbonate content was obtained volumetrically (ISO, 1995a), soil organic carbon content by oxidation digestion in chromium-sulfuric acid according to ISO (1998) and particle size distribution was analyzed by pipette-method (ISO, 2009), with wet sieving and sedimentation after dispersion with sodium- pyrophosphate ($Na_4P_2O_7$, c=0.4M). For determination of Pb and Zn concentration, the rest of the samples were ground in the mortar and sieved through a 0.50 mm nylon sieve. Both elements were extracted by aqua regia (ISO, 1995b) with microwave techniques. Concentrations of Pb and Zn were 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%).

The statistical analysis

The statistical analysis included: mean, median, standard deviation, minimum and maximum values, and skewness. The normality of the Pb and Zn concentration distribution is tested by the Shapiro-Wilk test. To characterize how two distributions differ we used non-parametric tests: the two-sided Kolmogorov-Smirnov test (K-S), the kernel density estimation (KDE) and a technique called a shift function (SF). The K-S test is used to compare the overall shape of the two empirical distribution functions and to test whether two distributions are different. The K–S statistic quantifies a distance between the cumulative distribution functions of two samples. 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. D is the maximum absolute difference between the two cumulative distribution function. The kernel density estimation (KDE) is a non-parametric way to estimate the probability density function. This technique we used as a tool for visualizing and comparing the data distribution. The KDE plots are essentially smooth histograms of used datasets that nicely reveals the shape of the data distribution and retain the overall structure. For more details see Wand and Jones (1995) and Bowman and Azzalini (1997). The shift function (SF) is the technique for comparing two distributions which was originally proposed by Doksum (Doksum,1974; Doksum and Sievers, 1976). It consists of plotting the difference between two group quantiles as a function of the quantiles in one group. Essentially, the shift function illustrates how and by how much one distribution should be re-arranged or shifted to match the other one. This technique is both a graphical and an inferential method. Sample size in this study is small to define confidence intervals of the quantile differences; hence the generalizations are based on intuitive plausibility rather than statistical inference.

RESULTS AND DISCUSSION

Description of soil properties

Analyzed soil samples are acid to alkaline, in average neutral in both horizons, with slightly higher values of pH in A compared to B horizon, Table 1. These results are in agreement with literature data for Terra Rossa soil of Croatia (Škorić et al., 1987; Peh et al., 2003), Italy (Vingiani et al., 2018) and Spain (Conde et al., 2007). The $CaCO_3$ content varies in range 0-18.5% in A horizon and 0-14.0% in B horizon with a mean value of 1 and 1.5%, respectively. The $CaCO_3$ data distribution is highly skewed with a long tail to the right (Skew: 4.92 and 2.99, Table 1). The soil organic carbon (SOC) content in A horizon is twice as high as in B horizon (mean value 54.20 and 27.58 g/kg, respectively Table 1). The both A and B horizon are characterized by a wide range of SOC content. These results correspond to literature findings for Terra rossa soil of Dalmatia, Croatia (Miloš and Bensa, 2017).

Table 1. Summary statistics (mean, minimum, maximum, range and skewness: Skew) for soil properties: pH KCl, $CaCO_3$, soil organic carbon (SOC) and particle size distribution: sand, silt, and clay in A and B horizon

Properties	Hor.	Mean	Minimum	Maximum	Range	Skew
pH KCl	A	6.73	5.21	7.51	2.30	-1.47
	B	6.71	5.06	7.40	2.34	-1.07
$CaCO_3$ (%)	A	1.0	0.0	18.5	18.5	4.92
	B	1.5	0.0	14.1	14.1	2.99
SOC (g/kg)	A	52.12	17.73	114.30	96.57	1.04
	B	27.58	4.88	72.79	67.91	0.46
Sand (0.05-2.0 mm)	A	10.5	4.0	27.0	23.0	1.17
	B	8.9	2.0	29.0	27.0	1.64
Silt (0.002-0.05 mm)	A	50.9	33.0	77.0	44.0	0.09
	B	45.3	21.0	68.0	47.0	0.03
Clay (<0.002 mm)	A	38.6	14.0	59.0	45.0	0.28
	B	45.8	23.0	70.0	47.0	0.30
Thickness A (cm)		18.5	10.0	26.0	16.0	0.07
Soil depth (cm)		45.1	25	71	46	0.25

The A horizon is composed predominantly of silt size particles followed by clay (mean values 50.9 and 38.6% respectively, Table 1). The B horizon comprises in average 45.8% clay, 45.3% silt, and 8.9% sand. According to the USDA textural triangle (Soil Survey Division Staff, 1993), the A horizon is silty clay loam, whereas the B horizon is silty clay. Established texture classes of both horizons are typical for Terra rossa soils, proven in many studies (Škorić et al., 1987; Bellanca et al., 1996; Vingiani et al., 2018). The thickness of A horizon ranged between 10 and 26 cm, on average 18.5 cm, Table 1. The analyzed soils are shallow to deep (25-71 cm, Table 1), that is well known and characteristical variability in the depth for the soils developed on karstified limestone in the Mediterranean region.

According to a general rule of thumb, if skewness is less than -1 or greater than 1, the distribution is highly skewed. If skewness is between -1 and -0.5 or between 0.5 and 1, the distribution is moderately skewed. If skewness is between -0.5 and 0.5, the distribution is approximately symmetric. If we follow these rules SOC, silt, clay, soil depth and thickness of A horizon are approximately symmetrically distributed; sand and $CaCO_3$ are highly skewed distributed with a long tail to the right, whereas pH is negatively highly skewed distributed with a long tail to the left (Table 1).

Statistical analysis of Pb and Zn concentrations

Statistical summary of Pb and Zn concentration in 64 soil samples of A and B horizon signed as Pb_A, Pb_B, and Zn_A, Zn_B of Terra Rossa soil are given in summary statistics (Table 2) and graphically (Figure 2). The median value of Pb_A and Pb_B were 41.6 and 33.8 mg/kg, respectively. The Pb_A ranged from 28.3-67.4 mg/kg and Pb_B from 25.5-51.8 mg/kg. The distributions of the mentioned element in both horizons have moderately right-skewed distribution (Skew. = 0.68 and 0.90 for Pb_A and Pb_B, respectively; Table 2). The KDE plot (Figure 2a) shows the significant difference in the median and spread between the Pb_A and Pb_B data distribution. The Shapiro-Wilk test indicates that the Pb_A and the Pb_B are normally distributed.

Table 2. Summary statistics (mean, median, minimum: min, maximum: max. and range in mg/kg, standard deviation: SD and skewness: Skew) and Shapiro-Wilk test for Pb and Zn concentration in A and B horizon

Element/Horizon	Mean	Median	Min	Max	Range	SD	Skew	Shapiro-Wilk	
								Stat.	Sig.
Pb_A	42.9	41.6	28.3	67.4	39.1	8.89	0.68	0.96	0.06
Pb_B	35.2	33.8	25.5	51.8	26.3	5.51	0.90	0.97	0.09
Zn_A	108.7	106.1	55.4	185.7	130.3	24.11	0.49	0.97	0.11
Zn_B	105.3	103.8	50.8	176.2	125.4	23.64	0.47	0.98	0.57

The significance level is 0.05

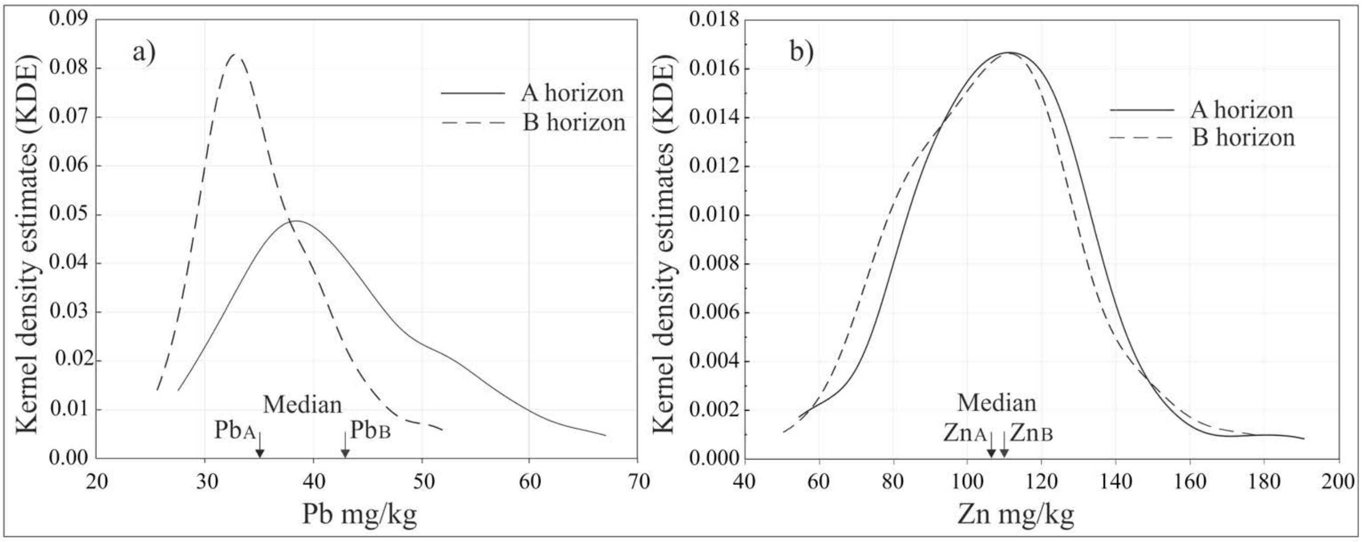

Figure 2. Kernel density plot of Pb_A and Pb_B (a) and Zn_A and Zn_B (b)

Established elevated Pb concentrations in the current study are in agreement with those reported by Bellanca et al. (1996), Vingiani et al. (2018) and Yamasaki et al. (2013) for Terra rossa soils on limestones (Table 3). Peh et al. (2003) also have established very similar mean values of Pb in Terra rossa soil (Table 3). It is important to note a much wider range of Pb in mentioned studies that related to mixed land use. Anomalous high Pb values in Terra rossa soil Reimann et al. (2012) linked to the mineralization of the Triassic carbonates.

Comparison of the statistical descriptions of the Pb concentrations established in this study conducted on a local scale with those at the continental scale can help to better understand the factors and processes that contribute to variation. The median value of Pb concentration in the A horizon (Pb_A) of 41.6 mg/kg (Table 2) is more than twice as high as median values of Pb in the topsoil samples of above mentioned continental projects (Table 3). The range of Pb_A variation (Table 2) in this study is much narrower in comparison to the Pb ranges in topsoil established in the continental studies as follows: Forum of European Geological Surveys – FOREGS (Salminen et al., 2005); Geochemical Mapping of Agricultural Soil – GEMAS (Reimann et al., 2014); National Geochemical Survey of Australia – NGSA (Caritat et al., 2011a and 2011b) and North American Soil Geochemical Landscapes – NASGL (Smith et al., 2014) listed in Table 3.

The Pb concentration in mentioned studies has a highly skewed distribution with a right tail, i.e. skewness coefficient for Pb concentration in the topsoil and subsoil established in the FOREGS project (Salminen et al., 2005) were 11.4 and 14.2 mg/kg, respectively.

Table 3. Minimum (Min), maximum (Max), mean and median (Med) values of Pb (mg/kg) in topsoil and subsoil from literature data

	Topsoil			Subsoil		
Author/Project	Min-max	Mean	Med	Min-max	Mean	Med
Salminen et al. (2005) /FOREGS[1]	<3-886	23.9	15.0	<3-749	15.5	10.0
Reimann et al. (2014) /GEMAS[2]	1.6-1309	-	16.0	-	-	-
Caritat et al. (2011a, b) /NGSA[3]	<0.1-1090	-	7.2	<0.1-789	-	7.4
Smith et al. (2014) /NASGL[4]	<0.5-12400	-	18.1	<0.5-681	-	14.9
Peh et al. (2003)	27-233	40.7	38	-	-	-
Bellanca et al. (1996)	18-51	34.7	-	14-38	29.8	-
Vingiani et al. (2018)	32.3-58.7	47.7	-	29.3-52.4	41.7	-
Yamasaki et al. (2013)	34.8-54.8	46.4	-	-	-	-

[1] Forum of European Geological Surveys; [2] Geochemical Mapping of Agricultural Soil; [3] National Geochemical Survey of Australia; [4] North American Soil Geochemical Landscapes

It´s expected considering great differences in geology and anthropogenic activities (industrialization, urbanization, traffic, and agriculture) in the large scale projects comparing to the uniform soil type and parent material as well as an absence of the human impact in this study.

The median value of the Zn_A and Zn_B were 106.1 and 103.8 mg/kg, respectively, Table 2. The Zn_A varied in the range 55.4-185.7 mg/kg and Zn_B in the range 50.8-176.2 mg/kg. The skewness coefficients <0.5 pointed to the approximately symmetrical distribution of Zn_A and Zn_B (Table 2). The kernel density estimation (KDE) plot (Figure 2b) shows symmetrically bell-shaped Zn_A and Zn_B distribution and illustrates that there are no differences between its distributions and median values. The Shapiro-Wilk test indicates that the Zn_A and Zn_B are normally distributed. The mean value and range of Zn (Table 2) in this study are comparable to those in the studies of Terra rossa soils conducted by Peh et al. (2003), Bellanca et al. (1996) and Vingiani et al. (2018), Table 4. Yamasaki et al. (2013) have reported a higher mean value and a wider range of Zn concentration in topsoil (Table 4) compared to Zn_A in the current study, Table 2. This can be connected to the anthropogenic impact recognized through mixed land use. The median Zn_A value of 106.1 mg/kg (Table 2) in the current study is almost twice as high as the median value in the FOREGS, GEMAS and NASGL project and four times higher than those found in the topsoil of NGSA project (Table 4). The Zn concentration in these projects varied in much wider ranges in comparison to range in this study. The distributions of Zn concentrations in mentioned continental projects are highly skewed with the right tail i.e., skewness coefficient of the Zn concentration in topsoil and subsoil in the FOREGS project were and 18.3 mg/kg respectively. A highly skewed distribution of the Zn concentration in the large scale projects is connected to the great differences in geology and anthropogenic activities, whereas the normal distribution of Zn_A and Zn_B in the current study (Table 2) reflects uniform parent material and lack of direct human interference.

It is important to note that a comparison of the data from different studies/projects has its limits due to the methodological differences. Namely, most of the studies on the continental scale (FOREGS, GEMAS, NGSA) used depth-based sampling, including different soil depths. Smith et al. (2014) in NASGL project used a combination of depth-based and horizon based sampling, whereas local studies (Bellanca et al., 1996; Vingiani et al., 2018) used sampling according to pedogenetic horizons. In addition, there are differences in methods of sample preparation (sieving).

Table 4. Minimum (Min), maximum (Max), mean and median (Med) values of Zn (mg/kg) in topsoil and subsoil from literature data

	Topsoil			Subsoil		
Author/Project	Min-max	Mean	Med	Min-max	Mean	Med
Salminen et al. (2005) /FOREGS[1]	4-2270	60.9	48.0	5-2280	54.6	44.0
Reimann et al. (2014) /GEMAS[2]	2.8-1396	-	45	-	-	-
Caritat et al. (2011a, b) /NGSA[3]	<0.1-262	-	26.3	<0.1-330	-	26.1
Smith et al. (2014) /NASGL[4]	<1-11700	-	58	<1-653	-	54
Peh et al. (2003)	59-186	97.0	92	-	-	-
Bellanca et al. (1996)	56-164	112.8	-	35-158	109.5	-
Vingiani et al. (2018)	57-146	95.0	-	54-139	98	-
Yamasaki et al. (2013)	98.6-331	175	-	-	-	-

[1] Forum of European Geological Surveys; [2] Geochemical Mapping of Agricultural Soil; [3] National Geochemical Survey of Australia; [4] North American Soil Geochemical Landscapes

The top/bottom ratio

Many authors (Facchinelli et al., 2001; Massas et al., 2009; Yang et al., 2009) have suggested that the calculation of ratios of element concentrations observed in topsoil to those in the subsoil from the same location - top/bottom ratio (TOP/BOT) may provide a proof of contamination caused by anthropogenic impact. The ratio between topsoil and the bottom horizon is effective as an indication of relative enrichment of elements in the uppermost soil layer only if the soil properties in both horizons are similar i.e. do not vary significantly with depth as stressed out by Blaser et al. (2000) and Bini et al. (2011).

The top/bottom ratio of Pb in this study calculated for mean and median values (1.23 and 1.22, respectively) indicates poor enrichment of Pb in A horizon. It is comparable with TOP/BOT for the mineral horizons of soil established in previous studies conducted in the Mediterranean region e.g. Bellanca et al. (1996) and Vingiani et al. (2018) founded TOP/BOT for Terra rossa soils in Italy of 1.16 and 1.14 respectively (Table 3), whereas Cohen et al. (2012) reported a higher value of 1.57 in Geochemical Atlas of Cyprus. In the condition of even more arid climate and lower organic matter content in Australian soil this ratio amounts only 0.97 (NGSA project, Table 3). Contrary, soils with organic (O) - top horizons and mineral bottom horizons have a much higher values of TOP/BOT e.g. Reimann et al. (2001), Reimann et al. (2007), Reimann et al. (2009), Reimann et al. (2015) obtained 12.8, 7.6, 8.7 and 4.0 respectively. Mentioned differences in top/bot ratio can be connected with a similarity in the mineralogy and with a high enrichment factor of Pb explained with a strong affinity of Pb to organic binding (Goldschmidt, 1937; Reimann et al., 2109). The top/bottom ratio calculated for mean and median values of Zn_A and Zn_B in this study (1.03 and 1.02, respectively) do not point to any specific process of the enrichment or depletion. Similar values of top/bottom ratio for Zn concentrations close to the unit were established in all projects listed in Table 4. Possibility of using TOP/BOT as proof of anthropogenic impact cannot generally be rejected as suggested by Reimann and Caritat (2005) and Sucharova et al. (2012). It can be used as a rough indicator of anthropogenic impact in cases where top and bottom horizons have similar properties, as in this study.

Principal component analysis

Due to the nature of the soil characterized by very complex and longlasting processes of the weathering and pedogenesis, often interrupted, the identification and quantification of human influence, such as heavy metal (HM) contamination, is demanding and complicated.

The principal component analysis (PCA) can provide a comprehensive view of the relationships of HMs and soil properties. It can help to identify the origin of HMs and to highlight those soil properties that contribute most to their variability. This approach has been widely used (Facchinelli et al., 2001; Mico et al., 2006; Wei et al., 2011; Lovrenčić Mikelić et al., 2011; Sun et al., 2010; Kelepertzis, 2014) to identify the origin of HMs and quantify the anthropogenic impact. Facchinelli et al. (2001) associated Pb to road transport, urban and industrial areas and Zn with long term agronomic practices in wine growing. Mico et al. (2006) listed the vehicle and industrial fumes and irrigation water as a potential source of Pb, whereas for Zn stated mixed source both from lithogenic and anthropogenic input. Sun et al. (2010) attributed Pb to anthropic activities (industrial fumes, coal- burning exhaust, and domestic waste) and Zn to lithogenic sources. Lovrenčić Mikelić et al. (2011) and Kelepertzis (2014) highlighted the impact of anthropogenic activities on Pb and Zn concentrations in soil.

The PCA was conducted to analyze relationships of the HMs and soil properties in a multivariate manner and to reveal the dominating characteristics of the A and B horizon that contribute most to their variability. The PCA included the following variables: the Pb and Zn concentration, pH, SOC, $CaCO_3$ and soil particles: sand, silt and clay and it was performed in both A and B horizon. The results of the PCA for A and B soil horizon are shown in Table 5. and loading plots in Figure 3. that gives a graphical projection of all experimented variables on the plan of the first two principal components. The number of significant principal components were three and it is selected using the Kaiser criterion (Kaiser, 1960) with an eigenvalue higher than 1.

The first two principal components for the experimented variables in A horizon explained 47.80%, the first three together account for 62.38% of the total variance (Table 5). In mentioned results, the first principal component has large negative associations with Pb, Zn, and SOC. This component can be interpreted as an indicator of HMs in top-soil. The principal component 2 (PC2) had the greatest contribution from the particles of clay and sand. Clay content has large negative loading, whereas sand has a large positive loading on component 2 (PC2). So, this component can be interpreted as an indicator of the soil texture. In addition, in the plot (Figure 3a) can be seen a close co-ordinate loadings of the Pb and SOC. It can be linked to the well-known strong association of the Pb with organic matter, proven in many studies (Goldschmidt, 1937; Alloway 1995; Fujikawa and Fukui, 2001; Kabata Pendias and Mukherjee, 2007; Reimann et al., 2015). Furthermore, adsorption of soil organic matter to oxide minerals eg. Fe oxides which are abundant in the Terra rossa soil can lead to synergistic effects of Pb adsorption to oxide surfaces as stressed by Heidman et al. (2005). The higher complexation of Pb with Fe oxides caused by elevated organic carbon is confirmed in many studies (Xiong et al., 2015; Tang et al., 2015; Wan et al., 2018).

The results of PCA for B horizon (Table 5; Figure 3b) show that the largest contribution to PC1 that accounted 36.07% variance is given by clay and silt content, whereas the largest contribution to PC2 that explained 19.56% variances gives Zn and Pb. The first principal component has a large positive association with clay content and large negative associations with silt, pH, and SOC. So, this component can be interpreted as an indicator of the basic soil properties. The principal component 2 (PC2) has large positive associations with Pb and Zn and it can be interpreted as a status indicator of HMs in the B horizon. In loading plots (Figure 3a and Figure 3b) Pb and Zn in A and B horizon have a close coordinate loadings that can be connected with the fact that both horizons are mineral and quite similar regarding the soil texture, pH and $CaCO_3$ content. Close co-ordinate loading of Pb and Zn in B horizon and its perpendicular position according to the coordinate locations of all soil properties, except sand (Figure 3b), indicates a strong association of Pb_B and Zn_B and its weak interaction with soil properties. The mentioned relations suggest that Pb and Zn have the same origin – they are accumulated in the soil by similar processes. These include geochemical weathering and soil-forming processes characterized by longlasting and polygenetic origin.

Table 5. Principal component loadings for the experimented variables (soil properties and concentration of Pb and Zn in A horizon and B horizon), eigenvalues, total and cumulative variance

Experimented variables	PC loadings of the variables in A horizon			PC loadings of the variables in B horizon		
	PC1	PC2	PC3	PC1	PC2	PC3
pH KCl	-0.52	-0.44	0.22	-0.71	0.08	0.08
$CaCO_3$	-0.52	-0.02	0.71	-0.53	0.08	0.51
SOC	-0.57	0.10	-0.61	-0.68	-0.01	-0.41
Sand	0.31	0.67	0.25	-0.16	-0.48	-0.62
Silt	-0.41	0.28	0.28	-0.89	-0.01	0.18
Clay	0.31	-0.78	0.02	0.89	0.25	0.07
Pb	-0.77	0.17	-0.29	-0.10	0.69	-0.61
Zn	-0.79	-0.12	0.07	-0.17	0.88	0.06
Eigenvalues	2.43	1.39	1.16	2.88	1.56	1.22
Total variance (%)	30.43	17.37	14.58	36.07	19.56	1.3
Cumulative (%)	30.43	47.80	62.38	36.07	55.63	70.93

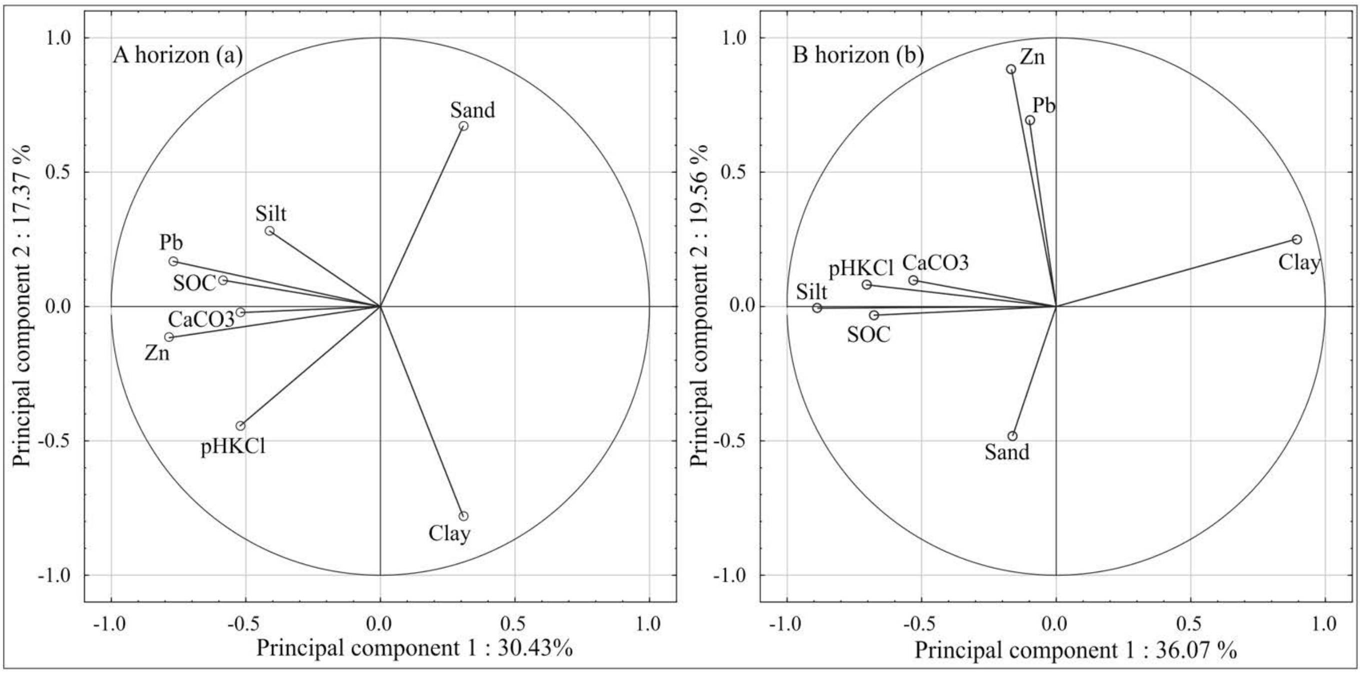

Figure 3. Projection of the soil properties and concentration of Pb and Zn in A horizon (a) and B horizon (b) on the plan of the first two principal components

Comparing CDFs

A cumulative probability (CP) plot of Pb and Zn concentration in A and B horizon (Figure 4a and Figure 4b), respectively provide a graphical view of the relation between these two cumulative distribution functions. By definition, the CDF is showing the probability that a variable (i.e. Pb) is less than or equal to some value (x). So, using the CDF we can pose and easily answer to the following type of question: what percentage of top-soil and bottom samples have a lower content, eg. Pb of 40 mg/kg. The vertical line at 40 mg/kg (Figure 4a) shows us that 40% of Pb_A and 80% of Pb_B have less than 40 mg/kg. This means that the probability of the Pb_B scoring below 40 mg/kg is higher than the probability of Pb_A for the same scoring. If we look at the CDFs as whole this suggests that the Pb_A score is higher than Pb_B.

In the cumulative probability (CP) plot (Figure 4a) the Pb_A and the Pb_B samples fall on a straight line without changing its slope or shape of a distribution. This shows that the Pb data are normally distributed and outside of the local contamination source that could distort the CP plot and reflecting the fact that the analyzed element comes from the same sources. This suggests that the increase in Pb concentration is primarily due to the soil formation processes.

Comparing the observed topsoil CDF to a reference CDF of the same element from samples taken in a subsoil horizon that was unaffected by emissions Fabian et al. (2017), Reimann et al. (2019a) and Reimann et al. (2019b) used to quantify the anthropogenic emissions at the continental to regional scale. The basic idea is to identify distortion of the observed topsoil CDF with respect to a reference CDF. They demonstrated that the effects of the different sources of contamination can be identified on CP curves. So, the diffuse contamination will distort the low- concentration end of a topsoil CDF, whereas the effect of the high concentrations at a local scale will distort the CP plot resulting in a bump or bulge in the CDF. Based on a comprehensive analysis of continental and regional studies Fabian et al. (2017) estimated diffuse Pb contamination to be 1-3 mg/kg.

The differences in the CP plots of Pb_A and Pb_B (Figure 4a) demonstrate a pronounced shift with an increasing deviation in the Pb distributions toward higher concentrations. This can be connected to a high SOC in the A horizon and strong Pb and OM binding. The differences between more organic topsoil and minerogenic subsoil, and the affinity of Pb to organic matter (Goldschmidt, 1937; Alloway, 1995; Fujikawa and Fukui, 2001; Kabata Pendias and Mukherjee, 2007; Reimann et al., 2015), lead to an increase in the shift. For example, in the continental scale NASGL project as in the regional scale NTR project Fabian et al. (2017) have been established a pronounced shift between the topsoil samples that are substantially more organic than the bottom minerogenic C horizon,

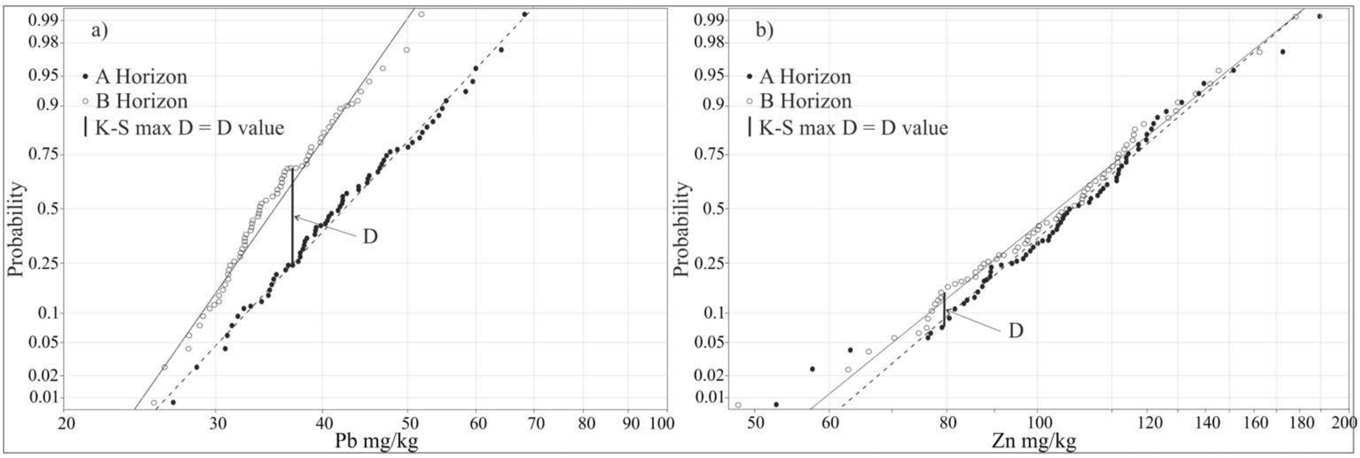

Figure 4. Cumulative distribution functions (CDFs) of Pb_A and Pb_B (a) Zn_A and Zn_B (b) with the best linear fit for both horizons and Kolmogorov Smirnov maximum distance (D value) between two CDFs. Data plotted on a logarithmic scale

but their CDF shapes are remarkably similar. For the Australian topsoil samples (NGSA project) that generally are not substantially more organic than the subsoil, Fabian et al. (2017) founded a remarkably similar shape of their CDFs and a very slight shift displayed at the whole distribution range.

The Zn_A and Zn_B display remarkably similar shapes of their CDFs. When shifting the CDF of the Zn_B to match the CDF of Zn_A noticeable is the slight shift displayed at the whole distribution range. The median difference of 2.3 mg/kg is in agreement with Reinman et al. (2019b) that estimated input of Zn to soil at the continental (European) scale, taking into account diffuse contamination and a possible biogenic input, lies in the 1–5 mg/kg range.

Kolmogorov-Smirnov test

Difference between concentrations of Pb and Zn in soil horizons are given by comparing their overall cumulative distribution functions (CDFs) using Kolmogorov – Smirnov test and CDFs at particular points (quantiles) using the shift functions. The statistical similarity between Pb_A and Pb_B, as well as Zn_A and Zn_B CDFs using its CP plots, was tested using the Kolmogorov-Smirnov test. The results of the K-S test are given in Table 6. The K-S test statistic (absolute distance - D value) between CDF of the Pb_A and Pb_B (Figure 4a) is the difference between the probability of Pb_A (Prob. ≈0.24) and Pb_B (Prob. ≈0.70) and occur at the Pb concentration of 37.1 mg/kg. The established D value of 0.46 (Prob. 0.70-0.24) is greater than the corresponding asymptotic significance (critical) P<0.001 (Table 6). It can be concluded that the hypothesis that the Pb concentration in both A and B horizons have the same distributions should be rejected based on the available data. The P<0.001 for Pb implies that <1% of samples will have a D statistically higher than the one obtained from the test (0.46). The K-S test for Zn_A and Zn_B probability distributions (Table 6) show that D value of 0.10 (Prob. ≈ 0.17-0.07; Figure 4b) is lower than the corresponding asymptotic significance p-value of 0.925. In this case, there is no evidence that the distribution of Zn_A is in any way different than the distribution of Zn_B. This implies that the Zn concentration in both A and B horizon has the same probability distributions. The P of 0.925 for Zn implies that 92.5% of samples of the sample set, will have a D statistic less than the one obtained from the test (0.10).

Table 6. Absolute difference (D), asymptotic significance (p-value) of Kolmogorov- Smirnov test and decision (the null hypothesis is samples of Pb_A and Pb_B, Zn_A and Zn_B have same probability distribution)

CDFs	Absolute difference D	Asymptotic significance	Decision
Pb_A and Pb_B	0.46	P<0.001	Reject the null hypothesis
Zn_A and Zn_B	0.10	P=0.25	Retain the null hypothesis

The significance level is 0.05

The shift function

The shift function is the plot of the differences between quantiles of the two distributions against the quantiles of one group. The quantiles divide a set of data into two, four, ten or hundred equal parts. Such values are referred to as median, quartiles, deciles, and percentiles, respectively. The quantiles function is also called the percent-point function or inverse cumulative distribution function. The Pb and Zn quantiles are obtained from the cumulative distribution functions. The shift functions of Pb and Zn are shown in Figure 5a and Figure 5b. Figure 5a illustrates how much need to shift the Pb_B distribution to match the Pb_A distribution. The first decile difference between Pb_A and Pb_B shows that to match the first deciles of Pb_A, the Pb_B first decile needs to be shift up 2.8 mg/kg. Deciles 2, 3 and 4 show the same direction with progressively stronger effect sizes. Decile 5 is median, suggesting that the two distributions in central tendency differ by 7.2 mg/kg. At the ninth decile, the shift is 12.2 mg/kg. As we move away from the first decile, we observe progressively larger positive differences, indicating that to match the Pb_A, Pb_B distribution (Figure 4a) needs to be shifted to the right. The mentioned differences between Pb_A and Pb_B distribution can be also illustrated by kernel plot (Figure 2a) and confirmed with results of the K-S test (Table 6). The increasing differences between Pb_A and Pb_B

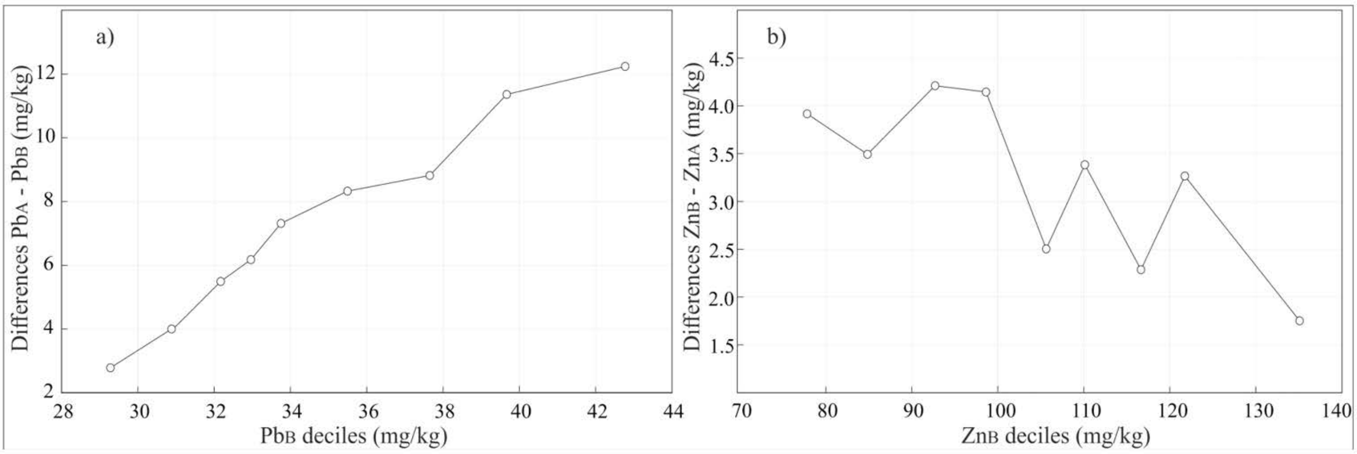

Figure 5. The plot of the deciles differences between the Pb_A and Pb_B against deciles in Pb_B (a); and the deciles differences of the Zn_A and Zn_B against deciles in Zn_B (b)

toward higher values of Pb_B resulting in a steeper gradient of the shift function (Figure 5a) that can be explained by (i) fact that the soil samples with higher content of the Pb in B horizon have a higher content of the SOC in the A horizon and (ii) the aforementioned a well-known strong binding the Pb and organic matter.

The shift function for the Zn (Figure 5b) shows a small difference between Zn_A and Zn_B distribution as well as its a slightly and ununiform decreasing of the deviations toward a higher Zn_B concentration. These differences suggest that Zn_B to match Zn_A distribution needs to be shifted at the first decile 3.9 mg/kg; at the fifth decile (median) 2.3 mg/kg and 1.7 mg/kg at the ninth decile. Decile 5 (median) amounted 2.3 mg/kg, suggesting that the two distributions do not differ in central tendency. The very slight shift at each decile implies that the Zn_A and Zn_B have a remarkably similar shape of their distribution and indicate that there no clear differences between Zn_A and Zn_B distribution. The described relationships between the two distributions are in agreement with the results of K-S test (Table 6) and also can be illustrated by two similarly shaped distribution in CP plot (Figure 4b) and kernel density estimation plot (Figure 2b).

CONCLUSIONS

The established concentrations of the Pb and Zn in the Terra rossa soil are typical for this soil type and several times higher compared to the values established in the geochemical research on the global and continental scale. The PCA has shown that (i) the Pb and Zn contributes most to the variability of A horizon and highlighted well-known strong association of the Pb with organic matter, (ii) the variability of B horizon is mainly defined by basic soil properties, and (iii) the Pb and Zn have the same and natural origin – they are accumulated by geochemical weathering and soil-forming processes. The top/bottom ratio of the Pb and Zn close to 1 can be connected with the fact that both horizons are mineral and quite similar regarding the soil texture, pH and $CaCO_3$ content. A slightly higher ratio established for Pb compared to Zn can be linked-to binding Pb and organic matter in A horizon. Using non-parametric techniques (the two-sided Kolmogorov-Smirnov test and a shift function) we estimated that the distribution curve of Pb in topsoil (Pb_A) and subsoil (Pb_B) differ in spread and median. Distributions of Pb_A and Pb_B differ at overall CDF, as well as at particular points - deciles of its CDFs. The Pb_B at the whole distribution range needs to be progressively shifted to match Pb_A distribution. In the case of the Zn_A and Zn_B, there is no statistical evidence that the overall distribution of Zn_A is in any way different than the distribution of Zn_B that implies they are a remarkably similarly shaped. Considering the difference in particular points (deciles) Zn_B needs to be a slightly, and ununiform increased towards higher values to match the Zn_A distribution. The analysis presented here illustrates why detailed descriptions of the distributions can be vital to make sense of a dataset.

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