

Earthworm casts as a sampling medium – a case study from highly contaminated Hg roasting site Pšenk (Idrija area, Slovenia)

Deževnikovi iztrebki kot vzorčno sredstvo – primer uporabe na močno onesnaženem območju Hg žgalnice Pšenk (Idrijsko, Slovenija)

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Prejeto / Received 8. 11. 2013; Sprejeto / Accepted 18. 11. 2013

Key words: earthworm casts, soil, Hg contamination, enrichment factor, Idrija
Ključne besede: deževnikovi iztrebki, tla, onesnaženje, faktor obogatitve, Idrija

Abstract

In this study an interesting sampling medium - earthworm casts was examined in a highly Hg contaminated area. Enrichment factor (EF) has been applied to assess elevated concentrations of analyzed elements in earthworm casts and to determine elevated concentrations of these elements in soils and casts with regard to European average concentrations in topsoil. In a previous study (TERŠIČ & GOSAR, 2012) it was shown that Hg contents and dispersion in casts from studied roasting site are comparable to those in soil, which indicates that soil contamination is substantially reflected in contamination of earthworm casts. Therefore the comparison between elemental concentrations in earthworm casts and soil was investigated with the intention to assess the reflection of possible soil contamination in casts. Besides Hg contamination, elevated concentrations of As, Ca, Cd, Mo, Pb and U were also determined in earthworm casts. The calculated EFs show moderate enrichment of casts with Ca, Sr and P and minimal enrichment with Mg, Zn and Cu. Cast, SOM (surface organic matter rich soil layer) and soil enrichments with regard to the European averages show extreme enrichment of all studied media with Hg, followed by significant enrichment with Mo and Cd and moderate enrichment with As. Spatial distributions of analyzed elements in casts mostly show similar pattern as in soil, however, because of the different nature of different earthworm species and specific properties of different elements, the data about cast contamination can only serve as an approximate prediction about the dispersion and distribution of contaminant in soil.

Izvleček

Na močno obremenjenem okolju živosrebrne žgalnice v okolici Idrije smo raziskovali zanimiv vzorčni medij - deževnikove iztrebke. Faktor obogatitve (EF) smo uporabili za oceno povišanih vsebnosti analiziranih elementov v deževnikovih iztrebkih in tleh ter za primerjavo s povprečnimi vsebnostmi v tleh Evrope. Predhodna (TERŠIČ & GOSAR, 2012) in ta študija sta pokazali, da so Hg vsebnosti in prostorska porazdelitev v deževnikovih iztrebkih dobro primerljive z vsebnostmi in porazdelitvijo v tleh na raziskovanem ozemlju, kar kaže da se onesnaženje tal dobro odraža v vsebnostih v deževnikovih iztrebkih. Primerjavo med vsebnostmi kemijskih elementov v deževnikovih iztrebkih in tleh smo raziskovali z namenom, da bi ocenili stopnjo ujemanja vsebnosti elementov v deževnikovih iztrebkih in tleh. Poleg povišanega Hg smo določili tudi povišane koncentracije As, Ca, Cd, Mo, Pb in U v deževnikovih iztrebkih. Izračunani faktorji obogatitve (EF) so pokazali zmerno obogatitev v iztrebkih z Ca, Sr in P ter rahlo obogatitev z Mg, Zn in Cu. Vsebnosti v deževnikovih iztrebkih, vrhnjem z organsko snovjo bogatem sloju tal in tleh so glede na evropsko povprečje izjemno obogatene s Hg, sledijo obogatitve z Mo in Cd ter rahla obogatitev z As. Prostorske porazdelitve analiziranih elementov v deževnikovih iztrebkih kažejo večinoma podoben vzorec kot v tleh. Zaradi različne narave različnih vrst deževnikov in specifičnih lastnosti nekaterih elementov, lahko podatke o vsebnostih v deževnikovih iztrebkih uporabimo le kot približne napovedi o vsebnostih in porazdelitvi onesnaževal v tleh.

Introduction

Soils are the major sink for heavy metals released into the environment by anthropogenic activities; most metals released to the environment do not undergo microbial or chemical degradation,

and their total concentration in soils persists for a long time after their introduction (ADRIANO, 2003). Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem; the disturbance of the natural biogeochemical cycle of metals can lead to toxic effects on flora and fauna.

Earthworms are an essential part of the soil fauna, representing up to 80 % of the total biomass of the soil fauna and play an important role as decomposers, especially in forest ecosystems and in chemical element transformations (EDWARDS, 2004; ERNST et al., 2008; SIZMUR & HODSON, 2009). They can survive and reproduce in anthropogenically metal-contaminated soil (SPURGEON et al., 1994) and have a demonstrated ability to efficiently accumulate heavy metals from soils (NAHMANI et al., 2007; HOBBELEN et al., 2006).

It is well known that earthworms are of special importance for nutrient cycling, soil structure and transport processes. The first scientific observations on the effects of earthworms on soil structure were conducted by DARWIN (1881). He showed that earthworms have an ability to displace large amounts of soil and that by affecting the rate of weathering of rocks, humus formation and differentiation of the soil profile, they play a major role in soil formation. By feeding, burrowing and casting activities they contribute to the incorporation of organic residues or waste into the soil promoting decomposition and the release of nutrients to plants (KIZILKAYA, 2004). Earthworms consume organic matter and mineral particles and many of the species egest casts that are microbially very active and contain nutrients, which are readily usable by plants (EDWARDS, 2004). Earthworms are also known to significantly influence soil aggregate stability. They regulate SOM (soil organic matter) decomposition and soil erosion (JOUQUET et al., 2008).

Different species of earthworms have different life histories, occupy different ecological niches, and have been classified, on the basis of their feeding and burrowing strategies, into three ecological categories: epigeic, anecic, and endogeic (BOUCHÉ, 1977; FELLER et al., 2003; LEE, 1985). Anecic species live in deep burrows and feed primarily on decaying surface organic residues. The organic materials are mixed with minerals and lead to formation of stable organo-mineral structures within the casts. Endogeic earthworm species burrow extensively belowground and feed on soil enriched with organic matter. Portions of their burrows are often occluded with their casts, and occasionally they cast on the surface (SHIPITALO & LE BAYON, 2004; SIX et al., 2004). Epigeic species of earthworms have little effect on the structure of mineral soils. They live in organic soil horizons, in or near the surface litter, and feed primarily on coarse particulate organic matter. They ingest large amounts of undecomposed litter and excrete holorganic fecal pellets (DOMINGUEZ & EDWARDS, 2011). Generally, all three ecological groups of earthworms increase the mobility and availability of metals and metalloids in soils (SIZMUR & HODSON, 2009).

Recently, earthworms in contaminated soils have been a topic of many studies (ERNST et al., 2008; KAMITANI & KANEKO, 2007; UDOVIČ & LEŠTAN, 2007; ZHANG et al., 2009). Some laboratory experi-

ments with earthworms were also performed (BURTON et al., 2006; CHENG & WONG, 2002; DOMINGUEZ-CRESPO et al., 2012; KIZILKAYA, 2004; NAHMANI et al., 2005; ZORN et al., 2005), while investigations in non-contaminated sites are not so frequent (ERNST et al., 2008; RIEDER et al., 2011). Earthworms were proved to be a good biological indicator. They can be sampled easily, have a wide distribution range and strongly accumulate pollutants. However, the accumulation of metals varies between ecological categories and species (JÉGOU et al., 2001; KAMITANI & KANEKO, 2004). Earthworms are important for bioturbation as they bring to the surface minerals and soil materials from lower soil horizons and are depositing them on the soil surface as earthworm casts (JORDAN et al., 1997).

Earthworm casts as sampling medium

Casting occurs when earthworms ingest soil and leaf tissue to extract nutrients, and then emerge from their burrows to deposit the fecal matter (casts), as mounds of soil on the surface. 99.9 % of ingested material is egested as casts. Earthworm cast consists of mixed inorganic and organic materials from the soils that are voided after passing through the earthworm intestine (CHAUDHURI et al., 2009). Earthworm casts offer micro-environmental conditions very different from those occurring in the surrounding soil, resulting from both food selection and digestion process (KIZILKAYA, 2004). Casts, deposited on the burrow walls, within the burrow, or on the soil surface, usually contain more clay and less sand than the surrounding soil because of selective ingestion (SHIPITALO & LE BAYON, 2004). Earthworm casts also usually have higher bulk density than the soil (EDWARDS & BOHLEN, 1996; GÖRRES et al., 2001), and are higher in pH, contain more available nutrients, and have higher levels of microbial activity (SHIPITALO & LE BAYON, 2004).

Surface castings can serve as a direct indicator of earthworm activity. Environmental factors such as soil temperature, soil moisture and annual rainfall greatly influence cast production (CHAUDHURI et al., 2009).

Chemical and physical properties of casts have been investigated in many studies (BITYUTSKII & KAIDUN, 2008; BUCK et al., 1999; CHAUDHURI et al., 2009; JÉGOU et al., 2001; JOUQUET et al., 2008; OYEDELE et al., 2006; SCHRADER & ZHANG, 1997; ZORN et al., 2008). CHAUDHURI et al. (2009) reported that nutrient enrichment and physical properties of casts compared to the surrounding soil differed among the species. They suggested that the elevated levels of cations (K^+ , Ca^{2+} , Mg^{2+} and Na^+) often observed in earthworm casts in the field (JOUQUET et al., 2008; OYEDELE et al., 2006) are probably due to selective feeding by earthworms on materials enriched in those cations (CHAUDHURI et al., 2009). Higher pH and organic carbon content were also observed in earthworm casts as compared to parent soil (BISHT et al. 2006; JOU-



Fig. 1. Example of surface earthworm cast at investigated roasting site Pšenk

QUET et al., 2008; OYEDELE et al., 2006; REDDY et al., 1997; SCHRADER & ZHANG, 1997). It was reported that casts are less water-stable than natural soil aggregates (SCHRADER & ZHANG, 1997) and that they contain finer textured materials compared with the parent soil in A horizon (OYEDELE et al., 2006).

Studies on metal contents in earthworm casts compared to surrounding soil are few (KIZILKAYA, 2004; SIZMUR et al., 2011; UDOVIČ & LEŠTAN, 2007; UDOVIČ et al., 2007; ZHANG et al. 2009; ZORN et al., 2005; TERŠIČ & GOSAR, 2012). Generally, an increased mobility of metals in earthworm casts was reported (KIZILKAYA, 2004; SIZMUR et al., 2011; UDOVIČ & LEŠTAN, 2007; UDOVIČ et al., 2007).

In this study we examined the applicability of earthworm casts as a sampling medium for estimating the soil contamination. The investigation was carried out at the ancient Hg ore roasting site Pšenk in the surroundings of Idrija, where extremely high total mercury concentrations in soils (up to 8,600 mg/kg) and soil organic matter (SOM) (up to 4,200 mg/kg) were determined in previous investigations (GOSAR & ČAR, 2006; TERŠIČ, 2010a; TERŠIČ et al., 2011; TERŠIČ & GOSAR, 2009). The contents and spatial distributions of 37 elements were determined in earthworm casts and compared to the contents in SOM and soil (0–15 cm) from investigated area.

The results of this investigation were partly published in TERŠIČ & GOSAR (2012) where Hg con-

tents and Hg spatial distribution in earthworm casts were compared to the Hg values in SOM and soil (0–15 cm) from the same highly contaminated area. Highly elevated Hg concentrations were determined in earthworm casts reaching as much as 4300 mg/kg; the contents were in the following order: soil > cast > SOM. It was shown that the contents and distribution in soil are strongly reflected in Hg contents and dispersion in earthworm casts, and that earthworm casts could be a suitable sampling medium for determining Hg soil contamination at this particular area (TERŠIČ & GOSAR, 2012).

In this work, enrichment factor (EF) has been applied to assess elevated concentrations of analyzed elements in earthworm casts at the small historical Hg roasting site (Pšenk) and to determine elevated concentrations of these elements in soils and casts with regard to European average concentrations in topsoil. Besides, we focused on the comparison of spatial distributions of analyzed elements in casts and soil in order to assess the reflection of soil contamination in casts.

Materials and methods

Sampling

Earthworm casts, deposited on top of the soil (Fig. 1), were collected at the ancient roasting site area Pšenk. Sampling was performed at the area of approximately 150 x 150 m (Fig. 2). Earthworm cast samples were collected at 32 sampling points in the research grid 30 x 30 m. At each sampling location on average 5 – 10 casts were collected in the 2.5 m radius to create the composite sample.

The detailed descriptions of the sampling area, sampling locations and elemental distribution in SOM and soil from the investigated area are given in the preliminary geochemical study at the Pšenk roasting site (TERŠIČ & GOSAR, 2009) and in the study of environmental influences of historical small scale ore processing at Idrija area (TERŠIČ, 2010a, TERŠIČ, 2010b, TERŠIČ et al., 2011). Earthworm cast sampling and elemental contents in casts as well correlation between elemental contents in earthworm casts, soil and SOM are presented in TERŠIČ & GOSAR (2012).

Soil characteristics

The prevailing soil types are Cambisols with typical A-B-C/R layers sequence. Visibly observed, soils are generally rich in organic matter to the depth of about 30 cm; deeper the clayey loam prevails. Depth to the parent material is mainly about 50 cm. At the surface there is a loose leafy litter resting on a brown granular horizon containing numerous earthworm casts. Boundaries between A and B horizon are mostly gradual and irregular. The more detailed description of soil characteristics can be found in TERŠIČ (2010b).

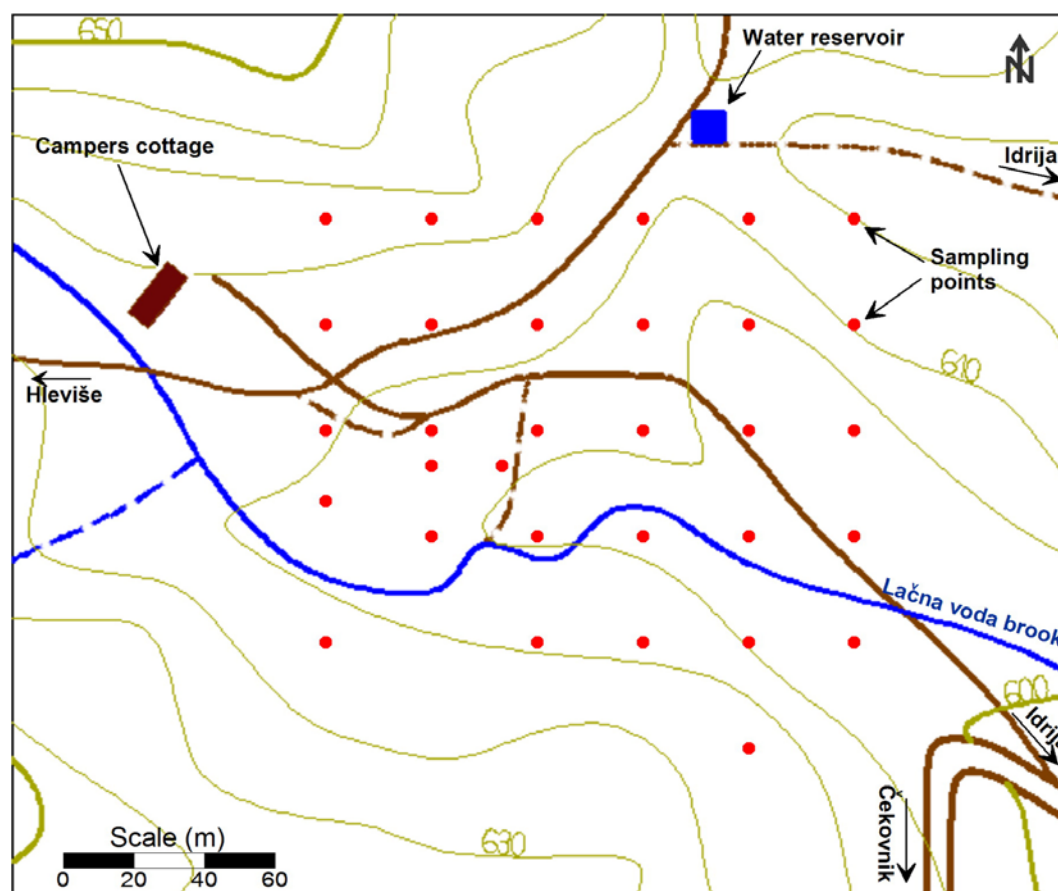


Fig. 2. Investigated roasting site at Pšenk with earthworm cast and soil sampling locations (reprinted from Teršič & Gosar, 2012, with permission from Elsevier)

Earthworm cast preparation

Earthworm cast samples were prepared in the same manner as SOM and soil samples in a previous investigation (TERŠIČ et al., 2011). The samples were air-dried and afterwards gently crushed in a ceramic mortar, sieved through a 2 mm mesh sieve and pulverized prior to chemical analysis (TERŠIČ & GOSAR, 2012).

Multielemental analysis

The powdered earthworm cast samples were submitted for chemical analysis to ACME Analytical Laboratories in Vancouver (Canada) accredited under ISO 9001:2000. Analysis for Hg and 36 chemical elements (Ag, Al, As, Au, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Sr, Te, Th, Ti, Tl, U, V, W, Zn) was performed with inductively coupled plasma mass spectrometry (ICP-MS) after aqua regia digestion. Samples with more than 50 mg/kg Hg were analyzed with ICP emission spectrometry (ICP-ES). Analysis of soil and SOM samples was performed in ACME laboratories in the same manner in 2008. Detailed description of soil and SOM samples analyses is given in TERŠIČ et al. (2011).

The accuracy and precision of the analytical methods were verified against standard reference materials (standards GXR-2 (Park City, Summit Co., Utah), GXR-5 (Somerset Co., Maine), GXR-6 (Davidson Co., North Carolina) and SJS-1 (San

Joaquin Soil)) (ABBEY, 1983; EPSTEIN, 1990) and duplicate samples in each analytical set. The shipment of samples, duplicates ($n=4$) and geological standards ($n=4$) to the laboratory was carried out in a random succession to distribute evenly any errors due to laboratory performance. This procedure ensured an unbiased treatment of samples and a random distribution of possible drift of analytical conditions for all samples. Objectivity was assured through the use of neutral laboratory numbers.

Detection limits were 1 mg/kg for Ba, Cr, Ga, La, Mn, Sr and Zn, 0.5 mg/kg for As and Se, 0.2 mg/kg for Te, 0.1 mg/kg for Ag, Bi, Cd, Co, Cu, Mo, Ni, Pb, Sb, Sc, Th, Tl, U, and W, 0.01 mg/kg for Hg, 0.01 % for Al, Ca, Fe, K and Mg, 0.05 % for S, 0.001 % for Na, P and Ti, 2 mg/kg for V, 20 mg/kg for B and 0.5 µg/kg for Au.

Accuracy (A) of the analytical method was estimated by calculating the absolute systematic error between the determined (X_a) and recommended values (X_p) of geological standards using equation (MEIER & ZÜND, 2000):

$$A = \frac{|x_a - x_p|}{x_p} 100 [\%]$$

Most elements determined in standards differ on average by less than 15 % from their recommended values in the sample concentration range. Only La has higher average deviation (31.4 %).

Precision (P) was tested by relative differences between pairs of analytical determinations (x_1 , x_2) of the same sample using equation (MEIER & ZÜND, 2000):

$$P = \frac{2|x_1 - x_2|}{(x_1 + x_2)} 100 [\%]$$

The precision of analytical determinations is acceptable and is <20 % for all analyzed elements. The reliability of analytical procedures was considered adequate for using the determined elemental contents in further statistical analyses.

Statistical analysis

In order to better describe and interpret analytical results, descriptive statistics (mean, median, standard deviation, first and third quartile, maximum, minimum, frequency histogram and Kolmogorov and Lilliefors test for normality) were determined using Statistica 6.1 software to the database of earthworm cast, soil and SOM samples results. Although 37 elements were analysed, only 32 were considered in the statistical analysis. The rest of variables (Ag, B, Na, Ti, and Te) were excluded for having more than 30 % of observations below the method's detection limit and for not being considered relevant for this study.

Statistical normality of elemental distributions was estimated with Kolmogorov and Lilliefors test for normality and visually with the examination of shapes of histograms of natural and logarithmic values, with tests of skewness and kurtosis, and with comparison of average and geometric mean value with the median value.

Mapping/Kriging

Data analysis and production of maps were performed on a PC using the Statistica (ver. 6.1; StatSoft, Inc., USA), Autocad (ver. 2000) and Surfer (ver. 8.0; Golden Software, Inc., Colorado) software. The universal kriging with linear variogram interpolation method (DAVIS, 1986) was applied to construct the maps of spatial distribution of analyzed elements in earthworm casts and soil (0–15 cm). For class limits the percentile values of the elemental distribution in investigated samples were chosen. Seven classes of the following percentile values were selected: 0–10, 10–25, 25–40, 40–60, 60–75, 75–90 and 90–100.

The determined elemental contents in analyzed cast samples were compared to elemental contents in SOM and soil (0–15 cm) determined in previous investigation of environmental impact of historical ore roasting at Pšenk area (TERŠIČ et al., 2011). In order to perform an unbiased research, only the SOM and soil samples (n=32) taken from the same sampling locations as cast samples were used in comparison of descriptive statistics and construction of maps of spatial distribution of analyzed elements.

Enrichment factors

Enrichment factors (EF) of chemical elements in earthworm casts with respect to SOM and soil (0–15 cm) as also the cast, SOM and soil enrichment factors with respect to European soil averages (0–25 cm; SALMINEN et al., 2005) (EF_{Europe}) were calculated. The enrichment factor permits to classify the chemical elements in sample materials with regard to their origin – natural or man produced (FERGUSON & KIM, 1991). For the calculation of enrichment factors (EF) the following equations were used:

$$EF_{\text{SOM}} = C(\text{cast}) / C(\text{SOM})$$

$$EF_{\text{soil}} = C(\text{cast}) / C(\text{soil})$$

$$EF_{\text{Europe}} = C(\text{Pšenk area}) / C(\text{Europe})$$

$$C = C(\text{examined element}) / C(\text{reference element})$$

In the calculation of enrichment factor we used a reference element in order to obtain a more accurate result. An element is regarded as a reference element if it is of low occurrence variability and is present in the environment in trace amounts. The most common reference elements are Sc, Mn, Al and Fe (LOSKA et al., 1997).

Elements which are naturally derived have an EF value of nearly unity. The degree of contamination can be described using 5 categories: <2 depletion to minimal enrichment, 2–5 moderate enrichment, 5–20 significant enrichment, 20–40 very high enrichment and >40 extremely high enrichment (SUTHERLAND, 2000).

Certain shortcomings of using EFs as a means of recognizing and quantifying anthropogenic interference relative to natural element fluxes were stressed out by REIMANN & DE CARITAT (2000). EFs have been widely used in environmental sciences to derive the origin of elements in the atmosphere, seawater, soils, lake sediments or peat (REIMANN et al., 2005). Usually, the EF for a given element was calculated as the concentration of that element, divided by the concentration of the same element in the Earth's crust, normalized to a reference element (REIMANN & DE CARITAT, 2000). REIMANN & DE CARITAT (2000) demonstrated that due to the variation in the composition of the Earth's crust and the various processes of rock and soil formation, the EF is not precise enough to differentiate between geogenic and anthropogenic element sources.

In our investigation, the EF was calculated at each sampling location for all analyzed elements as the ratio between total element concentration in casts and SOM or soil from the same sampling location, normalized by concentrations of a reference element measured in the same media and the same sampling location. Besides, EF_{Europe} was applied in order to determine elevated concentrations of analyzed elements with respect to European average concentrations. Although European average elemental concentra-

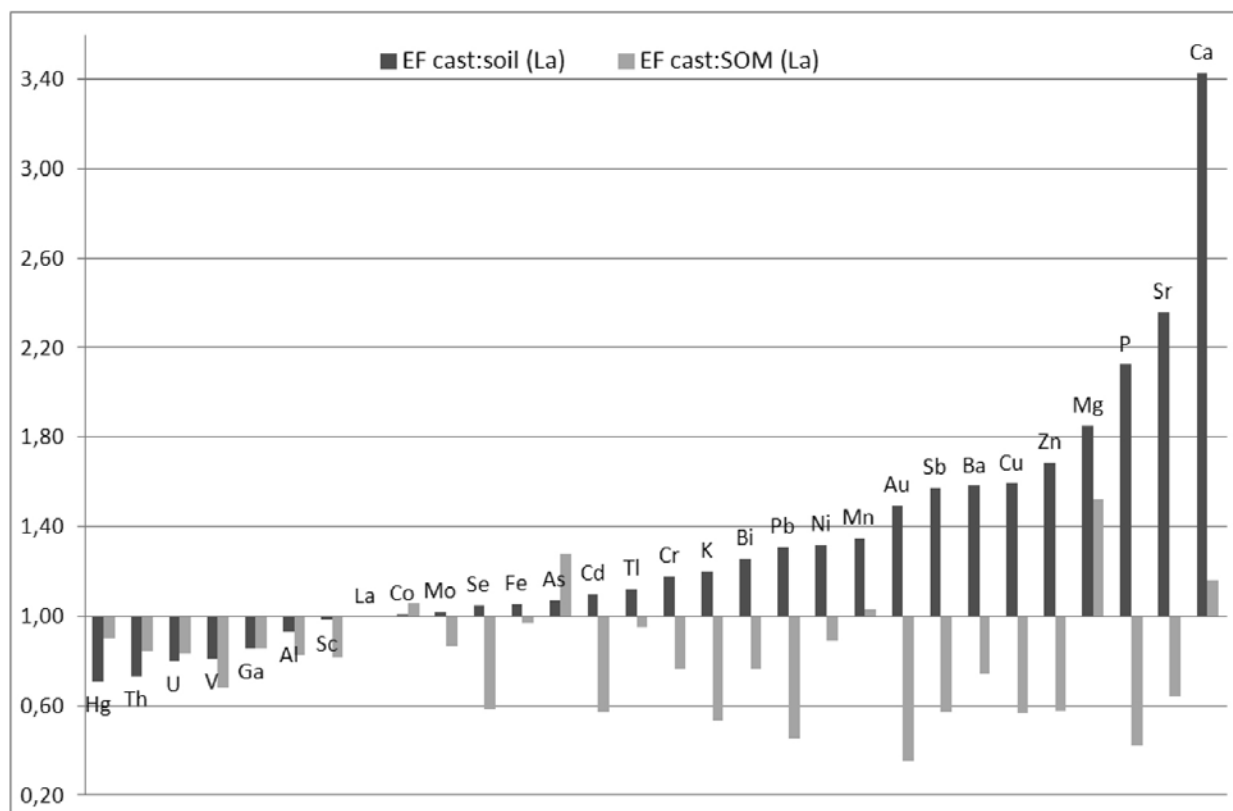


Fig. 3. Enrichment factor (EF) in earthworm casts with respect to soil and SOM

tions cannot be regarded as baseline elemental concentrations for this particular study, the comparison is needed for highlighting the importance of our results and for placing the study in a wider context.

Results and discussion

The univariate statistical results for all analysed elements in earthworm casts, SOM and soil (0–15 cm) of studied roasting site Pšenk and the comparison to Slovenian and European averages of chemical elements in soil are presented in TERŠIČ & GOSAR (2012). On the basis of the results of normality tests and visual inspection of distribution histograms for all elements in earthworm casts, as also with comparison of average and geometric mean values with the median values it was estimated that natural values of the following elements show normal distribution: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Ga, La, Mn, Ni, P, Pb, Sc, Sb, Th, V and Zn. For the rest of the elements (Au, Bi, Ca, Hg, K, Mg, Mo, S, Se, Sr, Ti, U and W) the logarithms of elemental contents were considered normally distributed.

Highly elevated Hg contents were determined in earthworm casts varying between 5.4 and 4,330 mg/kg with the median of 31 mg/kg. These values were lower than in soil where they reach the maximum of 8,600 mg/kg. Highly significant correlation between Hg contents in casts and soil was found ($r^2=0.75$). It was shown that Hg contents and distribution in casts are comparable to those in soil (TERŠIČ & GOSAR, 2012).

Beside Hg, elevated concentrations of As, Ca, Cd, Mo, Pb and U were also determined in earthworm casts. All of these elements except Ca express elevated concentrations also in soil and SOM samples from investigated roasting site (TERŠIČ & GOSAR, 2012). We do not have an explanation for elevated concentrations of As, Cd, Mo and Pb. Idrija ore deposit is classified as a monometal deposit (MLAKAR & DROVENIK, 1971); mercury is the only metal found in the Idrija ore deposit in economically important quantities, while other elements appear only in traces or insignificant quantities. Therefore high contents of above mentioned elements in studied soils are probably not the consequence of historical ore roasting, with the exception of uranium, whose increased concentrations might be the result of roasting extremely rich cinnabar ore from Skonca beds, which contain on average up to 7 times the average contents of radioactive elements such as uranium, radium, thorium and potassium, and also radon as a consequence of radioactive decay (MLAKAR & DROVENIK, 1971).

Contents of the rest of analyzed chemical elements in the earthworm casts are within the normal values for soils as also within Slovenian (ŠAJN, 2003) and European (SALMINEN et al., 2005) averages for soil.

For most of the analyzed elements the determined concentrations were in the order of soil > cast > SOM. Only Ca, Mg, P, Sr, Cu and Zn contents were higher in earthworm casts compared to soil and SOM. Contents of Pb were the lowest

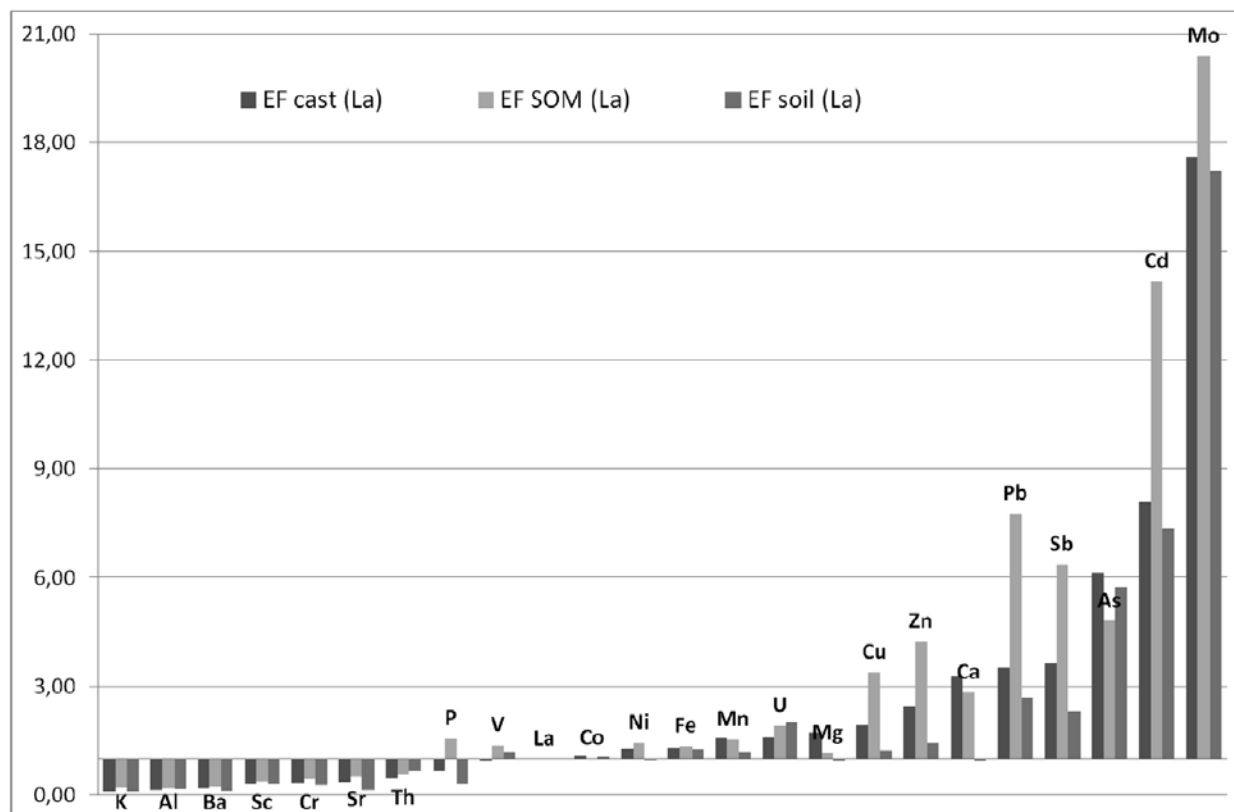


Fig. 4. Enrichment factors (EF) in cast, SOM and soil with regard to the European averages

in casts and the highest in SOM, while Se and K were the lowest in casts and the highest in SOM (TERŠIČ & GOSAR, 2012).

Enrichment factor

After the examination of spatial distributions of analyzed elements in casts and soil we decided to use La as a reference element in the calculation of enrichment factors, because it is not anthropogenically enriched and it represents a good example of the natural component of elemental distribution in the discussed area.

The factors of cast enrichment with regard to SOM and soil are shown in Fig. 3. The average enrichment factor (EF) in earthworm casts with respect to soil is the highest for Ca (3.4) followed by Sr (2.4) and P (2.1). These elements are moderately enriched with regard to soil. Minimal enrichment was calculated for Mg (1.85), Zn (1.69) and Cu (1.59). EFs above 1 were calculated also for Ba, Sb, Au, Mn, Ni, Pb, Bi, K, Cr, Tl, Cd, As, Fe, Se, Mo and Co. The lowest enrichment factors were calculated for Hg (0.71), Th (0.73), U (0.80), V (0.81), Ga (0.86), Al (0.93) and Sc (0.98). Enrichment factors with regard to SOM are low. EFs above 1 were calculated only for Mg (1.52), As (1.28), Ca (1.16), Co (1.06) and Mn (1.03).

Enrichment of earthworm casts with Ca and Mg contents compared to the soil was reported earlier (OYEDELE et al., 2006; JOUQUET et al., 2008). OYEDELE et al. (2006) and SCHRADER & ZHANG

(1997) ascribed the high Ca content of casts to the presence of calcite spheroids originating from earthworms' calciferous glands and to the incorporation of decomposed plant and animal debris which are usually rich in bases. However, CHAUDHURI et al. (2009) reported lower Ca values in casts compared to surrounding soil, suggesting that the elevated levels of Ca often observed in earthworm casts in the field are probably due to selective feeding by earthworms on materials enriched in those cations. Increase in P, particularly available P in the casts relative to that of surrounding soil was observed in investigations by BISHT et al. (2006), CHAUDHURI et al. (2009) and REDDY et al. (1997) and was assigned to enhanced phosphatase activities in the casts. Cu and Zn were also found to be enriched in casts compared to the soil (KIZILKAYA, 2004); it was shown that earthworms accumulate Cu and Zn when exposed to contaminated soil (ASH & LEE, 1980; KIZILKAYA, 2004).

Cast, SOM and soil enrichments with regard to the European averages (SALMINEN et al., 2005) are shown in Fig. 4. Extremely high EFs were calculated for Hg – the average is amounting to 1400 in casts, almost 1600 in SOM and almost 2000 in soil. Hg is followed by Mo (17 in casts and soil and 20 in SOM) and Cd (EF is 14 in SOM, 8.1 in casts and 7.4 in soil). In casts EFs above 2.0 were calculated also for As (6.1), Sb (3.6), Pb (3.5), Ca (3.3) and Zn (2.5). Similarly, in SOM Pb (7.8), Sb (6.4), As (4.8), Zn (4.2), Cu (3.4), Ca (2.8), and in soil As (5.7), Pb (2.7), Sb (2.3) and U (2.0) have EF above 2.0.

Calculated values of cast, SOM and soil EFs with respect to European averages do not indicate appreciable anthropogenic influences except for Hg which is highly enriched owing to ore processing activities. For Mo, a relatively wide range of average soil abundance (0.013 to 17 mg/kg) was reported (KABATA-PENDIAS & PENDIAS, 2001). Enrichment of Mo in cast, SOM and soil from the studied site with regard to European average Mo concentration in topsoil, could probably be explained with the known enrichment of Mo in soil on limestone in Slovenia, while low Mo values occur in central Finland, in the glacial drift area from the Netherlands to Poland and Lithuania, in eastern Hungary, south-western France, and small areas in Portugal, Spain and Greece with different geological substrates, which lowers the average European concentration (SALMINEN et al., 2005).

The average content of Cd in soil varies between 0.06 to 1.1 mg/kg, whereas the global mean for surface soil has been estimated to be 0.53 mg/kg, and apparently all higher values may reflect anthropogenic influences (KABATA-PENDIAS & PENDIAS, 2001). In investigated samples, the highest concentrations were measured in soils, where the maximum determined concentration was 2.8 mg/kg. In casts and SOM all determined concentrations were below the Slovenian warning value of 2 mg/kg (OFF. GAZ. RS 68/96). Enrichment of Cd in investigated samples with regard to European averages could be to some extent explained by geological characteristics. Cd enrichment could not be associated with anthropogenic sources such as industry or fertiliser use in agriculture, because the studied location lies in the remote forest area about 700 m height above sea level.

Of special interest and concern are elevated concentrations of As in all studied media at investigated roasting site (up to 65 mg/kg in casts and 116 mg/kg in soil). Global As contents in soil vary from 4.4 to 9.3 mg/kg; the lowest As levels are found in sandy soil and, in particular, those

derived from granite, whereas higher As concentrations often occur in alluvial soil rich in organic matter (KABATA-PENDIAS & PENDIAS, 2001). Naturally elevated levels of arsenic in soils may be associated with geological substrata such as sulphide ores. Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Historically, the use of arsenic containing pesticides has left large tracts of agricultural land contaminated (WHO, 2001). The median of soils presented in Geochemical Atlas of Europe is 6.02 mg/kg for subsoils and 7.03 mg/kg for topsoils (SALMINEN et al., 2005; Table 1). High As values in soils in certain parts of Europe are mainly associated with geology and mineralisation or with mining activities (SALMINEN et al., 2005). In Idrija and its surroundings As enrichments (concentrations from 7 to 57 mg/kg) were found in some areas in previous investigations (GOSAR & ŠAJN, 2005). No correlation with Hg was found, which was also the case in our study, so the origin of As in investigated area is still unknown.

Spatial distribution of analyzed elements in earthworm cast and soil

Contents of Ca, As and U in cast and soil of the studied roasting site show interesting distribution patterns. Besides, these elements are of interest because they show elevated concentrations in one or both of the studied media.

Spatial distribution of Ca in soil (Fig. 5a) shows the lowest concentrations (above 0.88 %) in the centre of the investigated area, where the highest Hg concentrations were determined (TERŠIČ et al., 2011). The highest values are in the SW part of the investigated area. Comparing spatial distribution of Ca in casts (Fig. 5b) we can see much higher concentrations, above 0.88 % over the whole investigated area; however, the values in casts do not reach the maximum concentration class above 7.84 %.

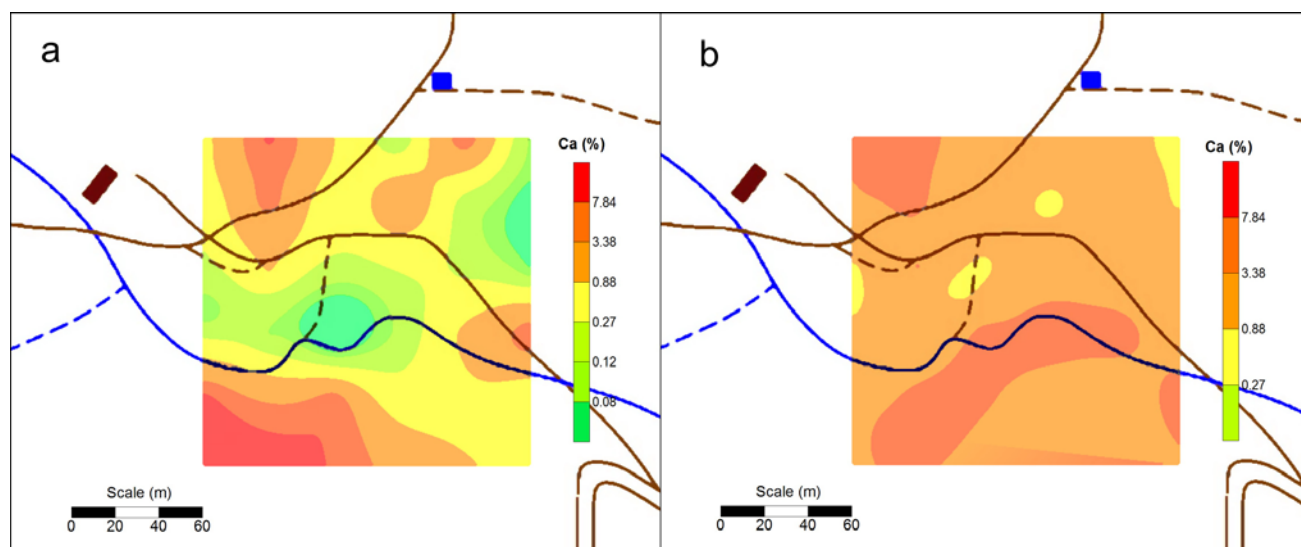


Fig. 5. Spatial distribution of Ca in earthworm cast (a) and soil (b) at Pšenk roasting site

Table 1. Elemental concentrations in earthworm casts, SOM and soil (0–15 cm) from Pšenk roasting site, Slovenian and European averages of elements in soil, casts enrichment factors with respect to SOM and soil and cast, SOM and soil enrichments with respect to European soil averages.

Pšenk (after Teršič & Gosar, 2012)			Slo- venija	Europe	Enrichment factor (EF)					
earthworm cast (n=32)		SOM (n=32)	soil (0-15 cm) (n=32)	soil (0-5 cm)	soil (0-25 cm)	EF		EF _{Europe}		
Md (min-max)		Md (min-max)	Md (min-max)	(Šajn, 2003)	(Salminen et al., 2005)	cast: SOM	cast: soil	cast	SOM	soil
Al	1.0 (0.53–1.7)	0.79 (0.16–1.42)	1.8 (0.72–2.8)	6.90	11.10	0.83	0.93	0.16	0.19	0.17
As	26 (6.1–65)	12 (2.0–39)	40 (3.3–116)	/	7.03	1.28	1.07	6.14	4.81	5.74
Au	1.9 (0.50–8.9)	4.2 (0.50–300)	1.6 (0.50–194)	/	/	0.35	1.49	/	/	/
Ba	41 (20–62)	32 (11–62)	42 (13–59)	358.00	375.00	0.74	1.58	0.18	0.25	0.12
Bi	0.40 (0.20–5.6)	0.30 (0.10–3.6)	0.55 (0.30–1.0)	/	/	0.76	1.26	/	/	/
Ca	1.8 (0.61–6.3)	0.81 (0.35–5.3)	0.40 (0.02–12)	0.70	0.92	1.16	3.43	3.30	2.84	0.96
Cd	0.70 (0.20–1.2)	0.70 (0.20–1.5)	0.90 (0.10–2.8)	0.40	0.15	0.57	1.10	8.10	14.18	7.37
Co	5.0 (2.3–11)	2.7 (0.20–7.4)	7.5 (2.6–29)	16.00	7.78	1.06	1.01	1.08	1.02	1.07
Cr	12 (2.0–22)	9.5 (3.0–25)	19 (3.0–42)	90.90	60.00	0.76	1.18	0.34	0.44	0.28
Cu	15 (5.5–24)	15 (9.0–48)	14 (3.3–30)	30.60	13.00	0.57	1.59	1.93	3.39	1.21
Fe	1.3 (0.66–2.1)	1.04 (0.20–1.6)	1.9 (0.25–3.9)	3.50	1.69	0.97	1.05	1.31	1.36	1.25
Ga	3.0 (2.0–5.0)	2.5 (1.0–6.0)	6.0 (2.0–19)	/	/	0.86	0.86	/	/	/
Hg	31 (5.4–4330)	20 (1.5–4200)	68 (6.28–8600)	0.065	0.037	0.90	0.71	1410	1590	1970
K	0.13 (0.08–0.28)	0.14 (0.08–0.26)	0.15 (0.07–0.45)	1.60	1.92	0.53	1.20	0.11	0.21	0.09
La	14 (4.0–22)	9.0 (1.0–15)	21 (5.0–44)	32.10	23.50	1.00	1.00	1.00	1.00	1.00
Mg	0.80 (0.21–3.3)	0.33 (0.11–2.2)	0.64 (0.22–6.8)	0.70	0.77	1.52	1.85	1.74	1.14	0.94
Mn	611 (408–1615)	346 (74–1025)	714 (69–2013)	1054.00	650.00	1.03	1.35	1.58	1.53	1.17
Mo	6.5 (0.80–83)	4.9 (0.80–74)	9.8 (1.9–137)	0.80	0.62	0.86	1.02	17,60	20,37	17,23
Ni	14 (5.8–25)	9.7 (2.7–18)	18 (3.9–39)	49.50	18.00	0.89	1.32	1.28	1.44	0.97
P	0.05 (0.02–0.07)	0.07 (0.05–0.12)	0.03 (0.01–0.08)	0.10	0.13	0.42	2.12	0.66	1.56	0.31
Pb	47 (26–91)	59 (31–106)	57 (38–113)	41.70	22.60	0.45	1.31	3.52	7.77	2.69
S	0.11 (0.07–0.21)	0.18 (0.09–2.1)	0.16 (0.03–5.7)	/	/	0.35	1.08	/	/	/
Sb	1.3(0.60–3.0)	1.4 (0.40–4.4)	1.3 (0.40–10)	1.10	0.60	0.57	1.57	3.64	6.36	2.31
Sc	1.5 (0.10–2.5)	1.0 (0.30–4.7)	2.6 (0.60–4.9)	12.00	8.21	0.82	0.98	0.31	0.38	0.31
Se	1.1 (0.60–26)	1.2 (0.50–12)	1.6 (0.50–100)	/	/	0.58	1.05	/	/	/
Sr	18 (9.0–28)	16 (9.5–36)	10 (1.0–57)	77.00	89.00	0.64	2.36	0.34	0.53	0.14
Th	2.1 (1.0–3.2)	1.5 (0.20–3.6)	4.7 (1.15–7.6)	10.60	7.24	0.84	0.73	0.49	0.58	0.66
Tl	0.50 (0.20–3.2)	0.40 (0.10–4.0)	0.70 (0.20–1.4)	/	/	0.95	1.12	/	/	/
U	1.9 (0.60–12)	1.4 (0.20–25)	3.6 (1.0–37)	/	2.00	0.84	0.80	1.59	1.91	2.00
V	34 (13–85)	33 (8.0–119)	74 (17–2397)	102.00	60.40	0.68	0.81	0.94	1.39	1.17
W	0.20 (0.10–0.90)	0.20 (0.10–2.0)	0.20 (0.05–8.7)	/	/	0.57	1.57	/	/	/
Zn	76 (44–93)	76 (42–103)	74 (35–115)	124.00	52.00	0.58	1.69	2.45	4.24	1.45

* Al, Ca, Fe, K, Mg, P and S in %, Au in mg/g, all other elements in mg/kg

Md = median, min = minimum, max = maximum

Spatial distribution of As in soil (Fig. 6a) shows the highest concentration at the N and S parts of investigated area, while the lowest values prevail in the central part, just opposite from the spatial distribution of Hg in soil (TERŠIČ et al., 2011). High As concentrations (above 50 mg/kg) are continuing across NW and SE margin of investigated area. Distribution of As in casts (Fig. 6b) is similar and shows the lowest concentrations in the central part of the studied area, while higher concentrations (above 26 mg/kg) appear in the N and S. Concentrations in casts are lower than in soil, which probably implies that either earthworm species at this area do not accumulate As in their bodies or they do accumulate As, but do not excrete it efficiently. Further investigations on heavy metal concentrations in the tissues of earthworms are needed to confirm this assumption.

The highest concentrations of U in soil from Pšenk roasting site (Fig. 7a) appear in the centre of the investigated area, with the highest anomaly

in the region similar to the highest anomaly of Hg in soil (TERŠIČ et al., 2011). High concentrations are then continuing in the medium-sized zone towards the NW and SE. Interestingly, the lowest values prevail at the flat surface in the central western margin of the studied area, where large amount of roasting vessels were found and highly elevated Hg contents were determined. This suggest that U is not linked only to roasting of ore from radioactive Skonca beds and that there might perhaps exist another source of elevated U in this area. Spatial distribution of U in earthworm cast (Fig. 7b) shows the highest contents in the same region as in soil, only the anomaly is smaller; the contents rapidly decrease with the distance from this central part and reach the contents of below 3.1 mg/kg in the major part of investigated area.

Conclusions

Comparison of elemental concentrations in earthworm casts and soils and elemental enrichments with regard to European average concen-

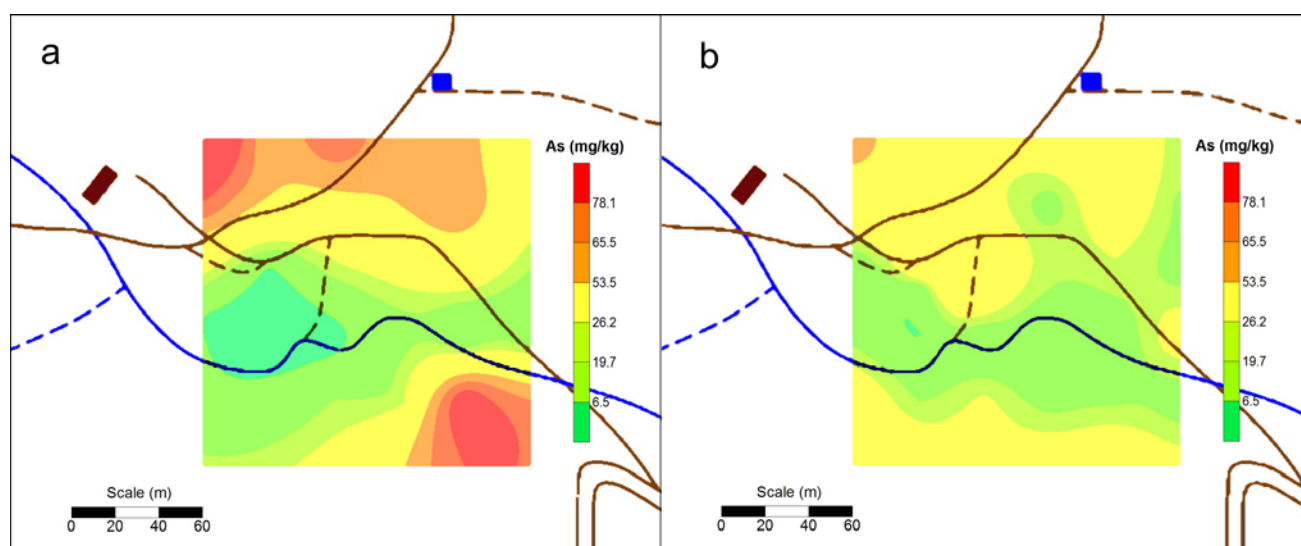


Fig. 6. Spatial distribution of As in earthworm cast (a) and soil (b) at Pšenk roasting site

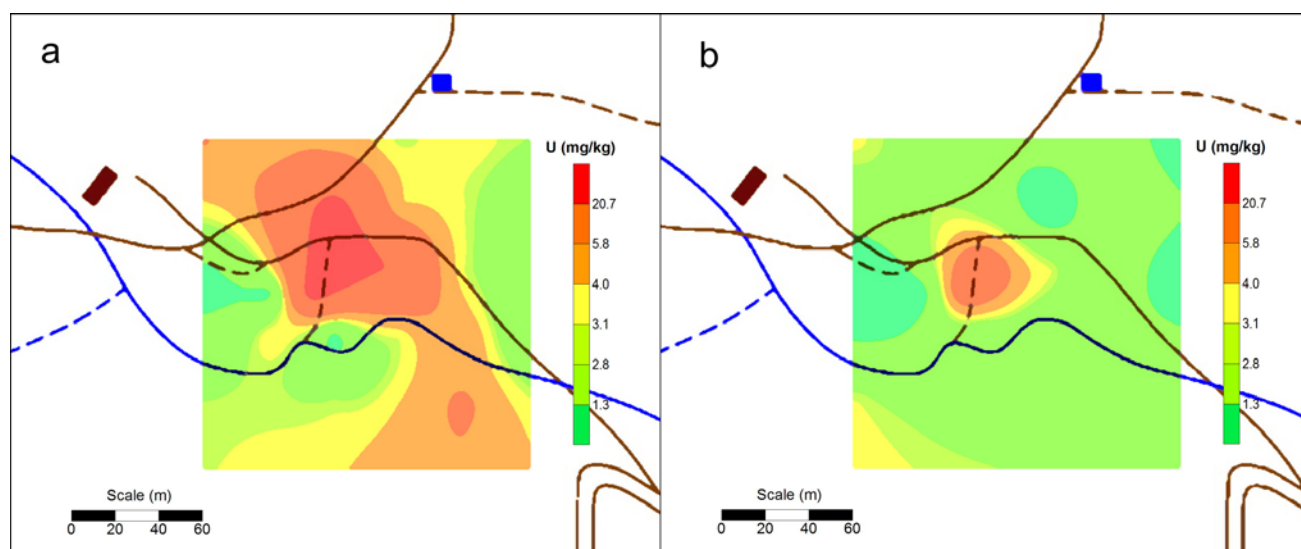


Fig. 7. Spatial distribution of U in earthworm cast (a) and soil (b) at Pšenk roasting site

trations in topsoil were studied at highly Hg contaminated roasting site Pšenk. Beside extreme contamination with Hg, elevated concentrations of As, Ca, Cd, Mo, Pb and U were also determined in earthworm casts. Of these, only elevated U can be explained and are probably linked to roasting of extremely rich cinnabar ore from Skonca beds, which contain high U. Of concern are also elevated concentrations of As in all studied media. Additional investigations are needed in order to explain these anomalies.

Calculated EFs show moderate enrichment of casts with Ca, P and Sr and minimal enrichment with Mg, Zn and Cu. Enrichment of Ca, P, Cu and Zn in casts compared to that in the surrounding soil was observed also by other researchers. Cast, SOM and soil enrichments with regard to the European averages show extreme enrichment of all studied media with Hg, followed by significant enrichment with Mo and Cd and moderate enrichment with As. Calculated values of cast, SOM and soil EF_{Europe} do not indicate appreciable anthropogenic influences except for Hg which is highly enriched owing to ore processing activities.

Spatial distributions of analyzed elements in casts mostly show similar pattern as in soil. Results of this study have confirmed the findings of previous investigation which proved that earthworm casts could be an appropriate sampling medium for determining soil contamination with Hg at the investigated area. Various species of earthworms have different feeding and digestion characteristics and different elements are accumulated and egested in specific way; therefore, elemental concentrations in casts can be a useful supplementary data but caution is needed when using the dispersion and distribution of contaminant in casts for prediction of soil contamination.

Acknowledgments

The presented research and preparation of the paper are funded by the Slovenian Research Agency (ARRS) in the frame of the research program Groundwater and Geochemistry (P1-0020) which is performed at the Geological Survey of Slovenia.

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