Methods for Assessment of Background Limit of Ni and Cr in Soils of Eastern Serbia

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Summary: The primary objective of the present study was to point out different approaches to background limits assessment. The content of selected trace elements is relatively low, and elements have right-skewed asymmetrical distribution, with high dispersion. Background for Cr and Ni (60 mg kg^{-1}) which are obtained by graphical methods cumulative probability plot (CDF) and box-plot are similar. Natural and log-transform data are used for empirical methods. Results from antilogarithmic values are significantly higher than from natural ones. Background limits obtained by empirical methods are different. Maps show that the largest part of territory has a relatively low concentration of investigated elements, whose background limits calculated by [Median+2MAD] methods are the most suitable. On the part of area with elevated elements content, where natural origin of elements had previously been proven, background limits are determined with box-plot method.

Key words: background limit, Cr, Ni, soil

Introduction

Content of trace elements depends on pedogeological and anthropogenic factors. Therefore, it is advisable to determine the background concentration, the content in trace elements in soils without the influence of human activity, although it is very hard, almost impossible to find territory without any influences of that kind (Sekulić et al. 2004, Čuvardić et al. 2004, Mrvić et al. 2009). Risk assessment of trace elements in soils is a key to many environmental protection measures and requires prediction of site specific background limit (Reimann & Garrett 2005). Determination of a unique background concentration for a large area (on a regional scale) does not take into account spatial variation of soil type and properties, so background limits for large area (e.g. for a whole state or a region) may cause either overestimation or underestimation of trace elements contamination and the associated risk for a particular soil (Diez et al. 2009). Thus, background limits evaluation is necessary on a local level. This approach enables development

of monitoring system, risk assessment and determination of trace elements levels, which require protection, remediation and sanation measures.

Several methods for assessing background limits have been used so far: classical [Mean $\pm$ 2Sd], [Median $\pm$ 2MAD], Tukey-s boxplot and cumulative probability plot - CDF graph (Gil et al. 2004, Galan 2008, Mico et al. 2008, Pérez-Sirvent et al. 2009) (Sd-standard deviation, MAD- median of the absolute deviations from the data's median).

Results from classical method are not always satisfying for unequal data sets, and methods [Median $\pm$ 2MAD] and Tukey-s boxplot give better results (Reimann et al. 2005, Diez et al. 2009). Very often, geochemical data are right-skewed, thus besides natural values, logtransform values are used in order to get symmetric normal distribution (Reimann et al. 2005, Diez et al. 2009). On the other hand, graphical methods, EDA (histogram, and especially box plot and CDF) enable much better insight into data structure, inflection points and possible background limits (Bech et al. 2005, 2008).

There are significant differences between results obtained by different methods. Results or limits obtained by selected procedures and subsequent

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application of those limits on geochemical maps enable clearer insight in spatial distribution of trace elements and enable more accurate assessment of background limits. Although some methods have an obvious advantage, neither of them can clearly be distinguished as satisfying for all conditions.

This paper presents results from investigation of Eastern Serbian soil, which has very heterogenic properties. The primary objective of the present study was to point out different approaches for determination of background limits. Due to high anthropogenic influences at the investigated area, background limits for Cr and Ni have approximate values.

Materials and Methods

Soil sampling was performed in 2005-2006. Total of 979 surface (0-25cm) soil samples were taken by grid system at each 3.3 x 3.3 km (Fig. 1).

Fig. 1. Geographical characteristics of Eastern Serbia
Slika 1. Geografske karakteristike istočne Srbije

Analytical methods included determination of content of the hot acid extractable forms (“pseudototals”) of trace elements Cr, Hg, Ni and Zn, extracted with HNO₃ and H₂O₂ with AAS. SPSS.10.0 was used for statistical analysis. Background values were determined by several methods, described in Reimann et al. (2005): classic [Mean ± 2Sd], [Median ± 2MAD], boxplot - upper whisker (Tukey 1977) and graphics - cumulative probability plot (CDF) and boxplot (Tukey 1977). For background assessment natural and logtransformed data were used. The software used for mapping was ESRI' Arc View 8.3.

Results and Discussion

Contents and Distribution of Trace Elements

Compared to the interquaternary values, the content of the selected trace elements is relatively low (Tab. 1). The values of Ni in about 93% of samples are below 50 mg kg⁻¹, which is the maximal allowed concentration (MAC) for agricultural soils (SG RS 1994, BBodSchV 1999), while the values of Cr are below the critical (100 mg kg⁻¹) in about 99% of samples.

Statistical analyses for all trace elements show that Skewness coefficient has a positive value (above zero) which means that elements have right-skewed asymmetrical distributions. There are positive Kurtosis coefficients, which means that the observations cluster has longer tails than those in the normal distribution. These elements show similar distribution patterns.

Graphical Methods

Cumulative probability plot (CDF) and box-plot methods provide a valuable tool for describing elements distribution, inflection points and can be used for setting up background limits (Reimann et al. 2005).

CDF graphs are suitable because points at which line trends are changing, i.e. inflection

Table 1. Statistical summary of selected soil properties and Ni and Cr concentrations (mg kg⁻¹)
Tabela 1. Statistički pokazatelji karakteristika zemljišta i sadržaja Ni i Cr (mg kg⁻¹)

Parameters	Percentiles												
	Mean	Std.Dev.	CV %	Skewness	Kurtosis	Min	Max	5	25	50	75	95	98
Cr	23.75	19.20	80.8	2.81	13.92	0.20	185.79	2.8	11.8	21.0	31.1	52.6	74.1
Ni	24.34	22.60	92.9	3.06	14.25	0.06	208.19	3.6	9.8	19.8	31.6	59.0	110.0

points, are clearly visible. At the same time, background limits also point at which core data separated from outliers can be accessed. Values of inflection points from CDF graph are similar for Ni and Cr. First point is approximately at 40 mg kg^{-1} , and second is at 60 mg kg^{-1} , which is background limit at the same time (Fig. 2).

Since assessment of background limits from CDF graph is to a large extent based on subjective assessment, obtained values are not entirely reliable, thus it is advisable to use CDF graph in combination with other EDA graphs (box-plot, histograms, one-dimensional scattergram). Box-plot was used in this effort. For every element box-plot shows statistical

be used. Three methods were used in this effort: classic [Mean+2Sdev], [Median+2MAD] and boxplot – mathematically calculated value upper whiskers.

Classic [Mean+2Sdev] method is commonly used, but it is greatly influenced by outliers and extremes and thus results in unrealistically high background limits for geochemical data, and it is not suitable for calculating action levels or clean-up goals in environmental legislation (Reimann et al., 2005).

Influences of extremes are much smaller in [Median+2MAD] method. MAD is a robust measure of the variability of a univariate sample of quantitative data. For a univariate data set $X_1, X_2, \dots, X_n$, the MAD is defined as the median of

Fig. 2. Graphical description of Cr and Ni contents through box-plot and CDF diagram

Slika 2. Grafički prikaz sadržaja Cr i Ni (*box-plot* i CDF dijagram)

values (mathematically calculated): minimum, lower whisker, lower hinge (25%), median (50%), upper hinge (75%), upper whisker, outliers, far outliers (extreme) and maximum. Combination of these methods enables better assessment of background limits and percentage of samples which are above this values which belong to outliers and extremes. Application of both of these methods on realistic data sets gives equal background limits for Cr and Ni (60 mg kg^{-1}).

Empirical (Calculated Methods)

Besides graphical assessment of background limits, empirical (calculated) method may also

the absolute deviations from the data's median: $\text{MAD} = \text{Median } i (|X_i - \text{Median } j (X_j)|)$.

Besides these methods, box-plot is also useful for the identifications of extreme values. Two parameters are calculated: upper inner fence (UIF), which is lower bounder of outliers appearance, and upper whisker, which is background limit. UIF is defined as the box extended by 1.5 times the length of the box towards the maximum: $\text{UIF} = \text{upper hinge } (x) + 1.5 \cdot \text{HW}(x)$. Upper whisker = $\max (x | x < \text{UIF})$, where HW (hinge with) is the difference between the hinges (upper hinge - lower hinge).

Table 2. Background concentrations of Ni and Cr determined with different methods (mg kg⁻¹)
Tabela 2. *Background* koncentracije Ni i Cr u zemljištu određene različitim metodama (mg kg⁻¹)

Elements	Mean		Sdev		Median		MAD		[Mean+2Sd]		[Median+2MAD]		Upper whisker		98th percentile	Outer limit - graphics methods
	Natural	Log10	Natural	Log10	Natural	Log10	Natural	Log10	Natural	Anti-log	Natural	Anti-log	Natural	Anti-log		
Cr	23.7	1.23	19.2	0.41	21.0	1.32	9.5	0.19	62.1	111.2	40.0	50.9	58.9	131.8	74.1	60
Ni	24.3	1.23	22.6	0.41	19.8	1.30	10.6	0.24	69.5	113.2	41.0	60.8	64.0	184.1	110.0	60

Assessment of background limits by the above mentioned method with natural data is possible because they have small variability. If variability is higher, logtransformation of data is required. According to Reimann et al. (2005) if the CV is between 70% and 100%, the use of logarithmical scale will likely be informative. If the CV>100% logarithmical scale should be used. This rule is applied on our data sets, since they are highly diverse (CV> 70%), as shown in table 2.

In natural simulations values from the [Median+2MAD] procedure results in the lowest background limits, followed by the boxplot. The

classical [Mean+2Sdev] rule presents the highest background limit, duo to large standard deviation. Similar results are obtained by other researchers (Reimann et al. 2005, Galan 2008). Results from logtransformed values are significantly higher then from natural values. Background limits from the [Median+2MAD] procedure remain the lowest, while the highest is for boxplot. Logtransformed background limit for [Median+2MAD] methods is similar to background values from graph.

Since background limits are different for different methods, results should be checked on maps. Only after this checking, it is possible to

Fig. 3. and Fig. 4. Spatial distribution of Cr and Ni in soils of Eastern Serbia (mg kg⁻¹)
Slika 3. i Slika 4. Prostorni raspored Cr i Ni u zemljištu istočne Srbije (mg kg⁻¹)

propose which methods are the most suitable for local characteristics.

Maps

Border values of maps present inflection points from CDF graphs and logtransformed background values obtained by three methods (Fig. 3 and Fig. 4).

Spatial distribution of Ni shows that the highest levels of nickel are in alluvial of Velika Morava, and on slopes of Deli Jovan. For these areas previous investigation showed that Ni is of natural origin (Kalenić et al. 1976, Jakovljević et al. 1997, Antić-Mladenović 2003). On these areas proposed background concentrations are above 60 mg kg^{-1} . For this region the method which best corresponds with local condition is box-plot, which in relation to other methods gives the highest values of background limits. On the other areas background limits are smaller, below 60 mg kg^{-1} . For this area the best methods are CDF and [Median+2MAD] method. Similar to Ni, naturally elevated concentration of Cr content is on the slopes of Deli Jovan and for this area background is set by box-plot, which is 130 mg kg^{-1} . In Velika Morava valley, content of Cr is smaller compared to those from Deli Jovan (40 mg kg^{-1} to 110 mg kg^{-1}), so for this valley the most suitable method is [Mean+2Sdev].

Conclusions

This paper presents results from investigation of Eastern Serbian soil, which is of very heterogeneous properties. The primary objective of the present study was to point out at different approaches for assessment background limits. Due to anthropogenic influences in this region, calculated values have orientation values. Statistical analyses show that content of the selected trace elements is relatively low, and they have right-skewed asymmetrical distributions, with high dispersion. According to graphical methods, CDF and box-plot, background limits for Cr and Ni are equal (60 mg kg^{-1}). Natural and logtransformed data were used in empirical methods. In natural simulations, values from the [Median+2MAD] procedure result in the lowest background limits, followed by the boxplot. Results from logtransformed values are significantly higher than from natural and the values of background limits from the [Median+2MAD] procedure remain the lowest, while the highest are for box-plot.

Border values of maps present inflection points from CDF graphs and antilogarithmic background values obtained by three methods. Maps show that the larger part of territory has relatively low concentrations of investigated elements whose background limits correspondent with limits obtained by [Median+2MAD] methods. On those parts of territory with elevated content, where there was previously established natural origin, background limits correspond with methods which give the highest values, i.e. box-plot.

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Metode za procenu Background Limita Ni i Cr u zemljištima istočne Srbije

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Izvod: U radu su prikazane različite metode određivanja *background limita*. Sadržaj ispitivanih elemenata u tragovima je relativno nizak, a distribucija elemenata je desno asimetrična, sa visokom disperzijom. Primenom grafičkih metoda (kumulativna kriva - CDF i box-plot) dobijene su slične vrednosti *background limita* za Cr i Ni (60 mg kg^{-1}). Za empirijske metode korišćeni su prirodni i log-transformisani podaci. Vrednosti log-transformisanih podataka su znatno veće nego prirodne. *Background limiti* dobijeni empirijskim metodama su različiti. Karte pokazuju da najveći deo teritorije ima relativno niske koncentracije ispitivanih elemenata čiji *background limiti* najviše odgovaraju vrednostima izračunatim metodom [Median+2MAD]. Na delovima teritorije sa povećanim sadržajima, uslovljenim prvenstveno geohemijskim sastavom, *background limit* odgovara metodi sa najvećim vrednostima - box-plot.

Ključne reči: *background limit*, Cr, Ni, zemljište