Journal of Agricultural Sciences
Vol. 55, No. 2, 2010
Pages 157-163

DOI: 10.2298/JAS1002157M
UDC: 631.42:546.47(497.11-11) ; 631.42:546.49(497.11-11)
Original scientific paper

BACKGROUND LIMIT OF Zn AND Hg IN SOILS OF EASTERN SERBIA

Vesna V. Mrvić*, Ljiljana M. Kostić Kravljanac, Mirjana S. Zdravković, Branka Ž. Brebanović, Dragan B. Čakmak, Biljana B. Sikirić and Elmira R. Saljnikov

Institute of Soil Science, Teodora Drajzera 7, Belgrade, Serbia

Abstract: The objective of the present study was to point out different approaches for background limits assessment of Zn and Hg. Background limits obtained by graphical methods (cumulative probability plot-CDF and boxplot) were similar for Zn (about 100 mg/kg^{-1}), while background limits for Hg were different (from 0.2 mg kg^{-1} to 0.3 mg kg^{-1}). For three empirical methods, besides natural data, log-transformed ones were used. Results from log-transformed limits were higher than from natural (except classical methods for Hg). The most of the territory of Eastern Serbia has low content of these elements, whose background limits calculated using log-transformed data by [Median+2MAD] methods (73 mg kg^{-1} for Zn and 0.15 mg kg^{-1} for Hg) are the most suitable (MAD-median of the absolute deviations from the data′s median). On the part of area with elevated elements content, background limits were determined using log-transformed data by methods with the highest values: for Zn it was [Mean+2Sdev], and for Hg box-plot (166 mg kg^{-1} and 0.41 mg kg^{-1} for Zn and Hg respectively).

Key words: background limits, Zn, Hg, soil.

Introduction

Risk assessment of trace elements in soils requires prediction of site-specific background limit (Reimann et al., 2005). Several methods for assessing background limits have been used so far. Results of [Mean+2Sdev] method are not always satisfying, thus [Median+2MAD] and Tukey-s boxplot are commonly used, usually with log-transformed values (Gil et al., 2004; Reimann and Garrett, 2005; Galan et al., 2008). Graphical methods, EDA (histogram, boxplot and cumulative probability plot-CDF) enable better insight into data structure, inflection points and background limits (Bech et al., 2010). Results obtained by these procedures are different and subsequent application of those values on geochemical maps enables assessment of background limits more accurately. This paper presents results from

*Corresponding author: e-mail: vesnavmrvic@yahoo.com

survey of background limits of Hg and Zn in Eastern Serbia. Due to anthropogenic influences, background limits have approximate values.

Materials and Methods

In all, 979 surface (0-25cm) soil samples were taken, by grid system at each 3.3 x 3.3 km between 2005-2006 (Figure 1). Content of the hot acid extractable form of Zn was determined after extraction with HNO_3 and H_2O_2, while samples for Hg determination were additionally prepared by hydride technique. AAS was used for determination, with VGA system for Hg. SPSS.10.0 was used for statistical analysis and graphs (descriptive statistics, cumulative probability plot-CDF and boxplot). Background limits were determined by several methods, described in Reimann et al. (2005): classic [Mean+2Sd], [Median+2MAD], boxplot-upper whisker (Tukey, 1977) and graphics-CDF and boxplot (Tukey, 1977). For background assessment natural and log-transformed data were used. The software used for mapping was ESRI′ Arc View 8.3.

Figure 1. Investigated area.

Results and Discussion

Content and distribution of trace elements

Content of Hg is below maximum allowable concentration (2 mg kg^{-1}), while Zn concentration exceeds MAC (300 mg kg^{-1}) in two samples. Median values are 39.3 mg kg^{-1} and 0.06 mg kg^{-1} for Zn and Hg respectively (Table 1). Elements have positive Skewness and Kurtosis coefficients, which means that elements are right-skewed and that observations cluster has longer tails then those in the normal distribution.

Table 1. Statistical summary of Zn and Hg (mg kg^{-1}).

Element	Mean	Sdev	CV %	Skewness	Kurtosis	Min.	Max.	Percentiles				
								25	50	75	95	98
Zn	46.53	32.54	70	2.9	14.8	0.10	330.00	29.50	39.30	54.90	104.00	149.00
Hg	0.09	0.13	143	6.1	48.7	0.00	1.67	0.04	0.06	0.10	0.23	0.50

Graphical methods

In CDF graph the first inflection point for Zn is at 20 mg kg^{-1} (Figure 2). The second part of the curve (20 mg kg^{-1} to 70 mg kg^{-1}) is significantly prone, which means that data are homogenous in about 70% of samples. In the part of the curve from 70 mg kg^{-1} to 100 mg kg^{-1} curve slope is gentler, e.g. differences in Zn content are significantly higher. Background limit (point on which core data were separated from outliners) is set at 100 mg kg^{-1}, and above this value the curve remains the same, but points are sparse. CDF for Hg shows that in the first part of the curve, Hg content is increasing slowly, thus in about 95% samples Hg values are up to 0.2 mg kg^{-1}. In part of the curve, from 0.2 mg kg^{-1} to 0.3 mg kg^{-1}, a slope is gentler. Background limit is 0.3 mg kg^{-1}, and values above these are correspondent to individual points with the highest Hg concentration. Background limits from boxplot for Zn are similar as CDF, while for Hg is 0.2 mg kg^{-1}.

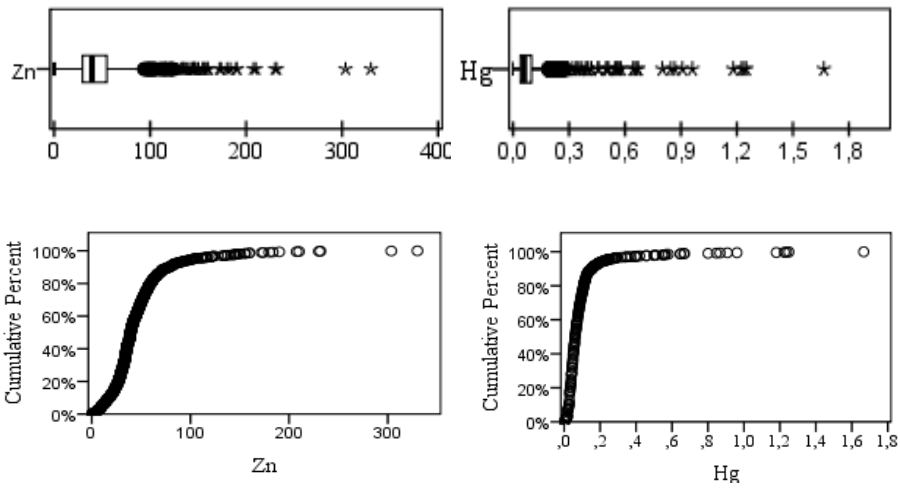


Figure 2. Graphical description of Zn and Hg contents: a) Zn boxplot, b) Hg boxplot, c) Zn CDF, d) Hg CDF. *Boxplot (2a and 2b) shows statistical values: lower whisker, lower hinge (25%), median (50%), upper hinge (75%), upper whisker (background limit), outliers, far outliers (extreme) and maximum.

Empirical (calculated methods)

Three methods were used in this effort: classic [Mean+2Sdev], [Median+2MAD] and box-plot-calculated value of upper whisker (Table 2).

Table 2. Background concentrations of Zn and Hg determined by different empirical methods (mg kg^{-1}).

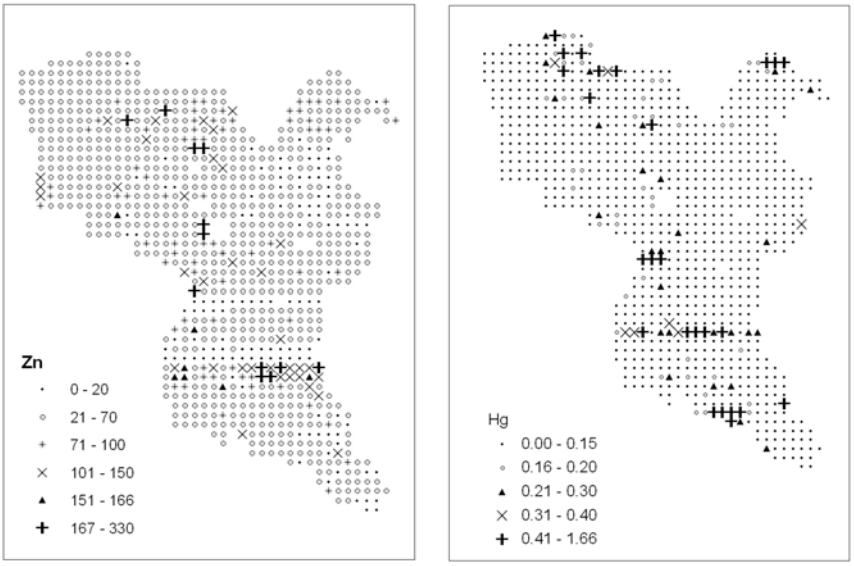
	Mean		Sdev		Median		MAD		[Mean+2Sdev]		[Median+2MAD]		Upper whisker	
Elements	Natural	Log10	Natural	Log10	Natural	Log10	Natural	Log10	Natural	Antilog	Natural	Antilog	Natural	Antilog
Zn	46.5	1.57	32.5	0.32	39.3	1.59	12.0	0.13	111	166	63.3	73.0	92.7	139.6
Hg	0.09	1.19	0.13	0.33	0.06	1.21	0.03	0.19	0.35	0.30	0.11	0.15	0.19	0.41

Values from the [Median+2MAD] procedure for Zn and Hg result in the lowest background limits. In natural simulation classical [Mean+2Sdev] rule presents the highest background limit (large Sdev). In logarithmic simulations the highest values is for boxplot for Hg and for Zn classical methods. Results from antilogarithmic values are higher than from natural, with the exception of classical methods for Hg (the highest dispersion values).

Since background limits are different for different methods, results should be checked on maps in order to determine which methods are the most suitable for local characteristics.

Maps

Maps were drawn according to inflection points from CDF graphs and antilogarithmic background limits obtained by three methods (Figures 3 and 4).



Figures 3 and 4. Spatial distribution of Zn and Hg in soils of Eastern Serbia. *Values for Zn: 0 mg kg^{-1}=min, 20 mg kg^{-1}=1st inflection point, 70 mg kg^{-1}=2st inflection point and background (BC) from [Median+2MAD], 100 mg kg^{-1}=BC from graphical methods, 140 mg kg^{-1}=BC upper whisker, 166 mg kg^{-1}=BC from [Mean+2Sdev]. Values for Hg: 0 mg kg^{-1}=min, 0.15 mg kg^{-1}=BC from [Median+2MAD], 0.20 mg kg^{-1}=1st inflection point and BC from boxplot, 0.3 mg kg^{-1}=BC from CDF and [Mean+2Sdev], 0.4 mg kg^{-1}=BC from upper whisker.

There is elevated Zn concentration in some individual samples from the Kucajsko-Beljanicki and Homoljsko-Neresnicki crystalline complex, in the Cretaceous and Jurassic carbonate rocks with the occurrence of magmatism, and in the zone south from Zajecar (Kalenić et al., 1973). Assuming that this Zn content is of natural origin, the most suitable background limits are those with the highest values e.g. [Mean+2Sd]. Higher Hg contents are found in Ramsko-Golubacka sandpit, alluvial sediments of the river Pek, Leptosol of Kljuc area, in southern part in individual samples formed on carbonate substrate and on contact part between carbonated and silicated substrate. On those parts the best fitting background is boxplot, upper whiskers.

Conclusion

The objective of the study was to point out different approaches for assessment of background limits of Zn and Hg in soils of Eastern Serbia. According to graphical methods (CDF and boxplot) background limit for Zn is 100 mg kg^{-1}, and for Hg is within interval from 0.2 mg kg^{-1} to 0.3 mg kg^{-1}. Results from antilogarithmic values are significantly higher than from natural ones (except classical methods for Hg). Background limits from the [Median+2MAD] procedure are the lowest in both simulations. Maps showed that the largest part of territory has low concentrations of elements whose background limits are corresponding with the values obtained by [Median+2MAD] methods. On those parts of territory with elevated content, where there is presumption of natural origin, background limits are corresponding with [Maen+2Sd] for Zn and boxplot, upper whisker for Hg.

We applied different background limits (from different methods) on maps, and according to these maps, we chose method that is the most suitable for the given territory. Investigation shows that there is not a universal method that would be appropriate for all conditions and that the right method is a matter of local natural and anthropogenic characteristics.

Acknowledgements

This paper presents the part of data from the Project: “Control of fertility and determination of harmful and dangerous substances in the soils of Republic of Serbia” financed by the Ministry of Agriculture, Forestry and Water Management, Serbia.

References

Bech, J., Reverter, F., Tume, P., Sanchez, P., Longan, L., Bech, J., Oliver, T. (2010): Pedogeochemical mapping of Al, Ba, Pb, Ti and V in surface soils of Barcelona Province (Catalonia, NE Spain): relationships with soil physicochemical properties. Journal of Geochemical Exploration. Article in press: doi:10.1016/j.gexplo.2010.10.002.

Galán, E., Fernández-Caliani, J.C., González, I., Aparicio, P., Romero, A. (2008): Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. Journal of Geochemical Exploration 98:89-106.

Gil, C., Boluda, R., Ramos, J. (2004): Determination and evaluation of cadmium, lead and nickel in greenhouse of Almería (Spain). Chemosphere 55:27-34.

Kalenić, M., Hadži-Vuković, M., Dolić, D., Lončarević, Č., Rakić, M. (1973): Tumač za list Kučevo L 34-128. Osnovna geološka karta 1:100 000. Zavod za geološka i geofizička istraživanja, Beograd.

Reimann, C., Garrett, R.G. (2005): Geochemical background: concept and reality. Science of the Total Environment 350:12-27.

Reimann, C., Filzmoser, P., Garrett, R.G. (2005): Background and threshold: critical comparison of methods of determination. Science of the Total Environment 346:1-16.

Tukey, J.W. (1977): Exploratory data analysis. Addison-Wesley, Reading.

Received: September 29, 2010
Accepted: December 3, 2010

BACKGROUND GRANICA Zn I Hg U ZEMLJIŠTU ISTOČNE SRBIJE

Vesna V. Mrvić*, Ljiljana M. Kostić Kravljanac, Mirjana S. Zdravković, Branka Ž. Brebanović, Dragan B. Čakmak, Biljana B. Sikirić i Elmira R. Saljnikov

Institut za zemljište, Teodora Drajzera 7, Beograd, Srbija

R e z i m e

U radu su istraživane različite metode određivanja gornje granice prirodnog nivoa Zn i Hg. Granica prirodnog nivoa određena grafičkim metodama (CDF i boxplot) je ista za Zn (100 mg kg^{-1}), dok se razlikuje za Hg (od 0,2 mg kg^{-1} do 0,3 mg kg^{-1}). Za tri empirijske metode, pored prirodnih, korišćeni su i log-transformisani podaci. Log-transformisane vrednosti su veće od prirodnih (osim kod klasične metode za Hg). Najveći deo teritorije istočne Srbije ima nizak sadržaj ovih elemenata, gde je granica prirodnog nivoa izračunata metodom [Median+2MAD] najprikladnija. Na delu teritorije sa povećanim sadržajem elemenata, više odgovara granica prirodnog nivoa određena metodama: [Mean+2Sd] za Zn i box-plot 'gornji brk' za Hg.

Ključne reči: granica prirodnog nivoa, Zn, Hg, zemljište.

Primljeno: 29. septembra 2010.
Odobreno: 3. decembra 2010.

*Autor za kontakt: e-mail: vesnavmrvic@yahoo.com