Analysis of Heavy Metal Concentrations in Soil Profiles: Necessity of a Typology

Luis Rodríguez-Lado[1] , Florence Carré & Luca Montanarella

[1] Land Management and Natural Hazards Unit. Joint Research Centre. Ispra, 21020 (VA) Italy (luis.rodriguez-lado@jrc.it) Tel. +39 0332 789977; Fax. +39 0332 786394

Institute for Environment and Sustainability

EUROPEAN COMMISSION DIRECTORATE-GENERAL Joint Research Centre

INTRODUCTION

Among the negative impacts related to human activities, the mobilization of heavy metals from their naturals reservoirs to the aquatic and terrestrial ecosystems has become a generalized problem in almost worldwide (Han et al., 2002; Koptsik et al., 2003; Salemaa et al., 2001). At the present, it is considered that a great proportion of soils in developed countries present concentrations of some elements and compounds higher than their expected natural concentration (Jones, 1991). Nevertheless, in some areas, natural factors as parent material, climate, vegetation, volcanoes, etc. are highly influencing heavy metal contents in soils (Nriagu, 1989; Nriagu and Pacyna, 1988).

This problem is also recognized in the recent EU "Thematic Strategy for Soil Protection" (COM, 2002), where contamination is identified as one of the main threats for soils in the Europe. This Strategy constitutes the basis for maintaining and improving soil resources quality along Europe. The working group on "Contamination and Land Management" (Van Camp et al, 2004) states the needs for measuring heavy metal concentrations in soils, determining the sources of pollution, establishing background values and critical loads of pollutants for each soil type and determining the risk of pollution as basis for the development of soil quality standards.

Decisions on the remediation of polluted soils are one of the most difficult management issues for environmental state agencies. The cost of the assessment of soil contamination status at regional or national level is high and, in most of the cases, this assessment is uncertain. The economic implications of ensuring soil quality are multiple, thus understanding the spatial distribution of contaminants is a crucial point for policy making at the EU level.

This paper presents a general method to link pollutants to soil types that can be helpful to perform a quick analysis of the distribution of pollutants over soils. It can be used as a tool for decision makers to make a faster delineation of problematic areas and to analyze the probable sources of pollution in such areas.

STUDY AREA

The study was carried out in soils from Natura 2000 protected areas in the Italian Peninsula. We used a database containing 218 soil profiles, with a total amount of 664 soil horizons described. Their spatial distribution is shown in Figure 1.

Figure 1.- Location of soil profiles.

Soil profile descriptions include geographic information (location, geology, vegetation type, aspect, slope, altitude), and pedological information as soil type, number and description of the horizons, soil texture.

Total contents of heavy metals (Hg, Cd, Cr, Cu, Ni, Pb, Zn) were determined by atomic absorption spectroscopy. Threshold values for HM in ***agricultural soils*** coming from European legislation and descriptive statistics for these samples are reported in Table 1.

Element	Threshold Value Soil pH < 7	Threshold Value Soil pH > 7	Minimum	Maximum	Average	SD
Cadmium	1	3	0.01	160.6	5.15	19.02
Copper	50	210	1.5	156.2	33.1	21.2
Nickel	30	112	3	774.6	46	46.1
Lead	50	300	0.3	284.2	37.5	35
Zinc	150	450	5.4	3039.7	132.7	222
Mercury	1	1,5	0.21	20150	178.09	1120.47
Chromium	100	150	3.3	866.5	76.9	60.3

Table 1.- Threshold values and descriptive statistics for HM.

METHODOLOGY

We adopted a Three-Step strategy in order to make a risk assessment of pollution with HM in these areas.

- Firstly we compared the HM concentration in these samples against threshold values for coming from the European legislation. This allows to identify soils at risk according to such values.

- Although the geographical distribution of heavy metals in soils may be dependent on environmental factors like geology, topography, etc, and thus may be linked to soil types, it may be also highly related to climatic variables (precipitation, dry deposition rates, wind, etc). and land use. For this reason it is necessary to determine the sources of heavy metals (geogenic and anthropogenic) on soils and their partial contribution to the overall heavy metal concentrations.

In this sense Principal Component Analyses (PCA) were carried out to understand the association between different heavy metals, to try to explain their distribution into the soil profile and to identify the possible sources of contamination. PCA with Varimax Rotation were performed on standardized data, and the analyses were done on the correlation matrix. The four main principal components were retained based on their Eigenvalues. In bibliography, these analyses are the most used to distinguish geogenic (concentrations that are inherent to soil types due to their pedogenetic origin) and anthropogenic (mainly derived from atmospheric deposition or land management practices) sources of HM.

- Finally we used both a Matrix Cluster Classification and a automated K-means algorithm in order to introduce two new dimensions in the analysis: taxonomy and location of soil observations. All observations are then classified according to each other on the basis of heavy metal concentrations in each horizon within each soil type.

Bibliography:

Han, F.X., A. Banin, Y. Su, D.L. Monts, M.J. Plodinec, W.L. Kingery, and G.E. Triplett, 2002. Industrial age anthropogenic inputs of heavy metals into the pedosphere. Naturwissenschaften 89, 497-504.

Jones, K.C., 1991. Contaminant trends in soils and crops. Environ Pollut 69, 311-25.

Koptsik, S., G. Koptsik, S. Livantsova, L. Eruslankina, T. Zhmelkova, and Z. Vologdina, 2003. Heavy metals in soils near the nickel smelter: chemistry, spatial variation, and impacts on plant diversity. J Environ Monit 5, 441-50.

Nriagu, J.O. 1989. A Global Assessment of Natural Sources of Atmospheric Trace Metals. Nature,v.338, p.47-49.

Nriagu, J.O. and Pacyna, J.M. 1988. Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace Metals. Nature, v. 333, p.134-139.

Salemaa, M., I. Vanha-Majamaa, and J. Derome, 2001. Understorey vegetation along a heavy-metal pollution gradient in SW Finland. Environ Pollut 112, 339-50.

Van-Camp. L., Bujarrabal, B., Gentile, A-R., Jones, R.J.A., Montanarella, L., Olazabal, C. and Selvaradjou, S-K. (2004). Reports of the Technical Working Groups Established under the Thematic Strategy for Soil Protection. EUR 21319 EN/4, 872 pp. Office for Official Publications of the European Communities, Luxembourg.

RESULTS

Heavy metal contents in this soil is heterogeneous. Since the soils include in this study are mainly derived from lime rocks, we observed that most of the samples have HM concentrations lower than the thresholds fixed in the European legislation for soil pH > 7. There are also many samples with high contents of heavy metals. This occurs in some samples for Cd (Lazio, Molise), Hg (Lazio) Cr (Basilicata, Toscana, Lazio and mainly Sardinia), Ni (Basilicata, Sardinia), Zn (Basilicata, Toscana, Lazio, Calabria and Sardinia). We must note that these thresholds were defined for agricultural soils, so they are not really applicable to natural soils as those presented in this study and they are merely presented just as a reference values.

PCA analyses reveals four groupings of heavy metals. The four-component model accounts for 83% of the data variation. The first factor well discriminates Ni, and Cr (Figure 2). It can be considered that the origin of these elements in soils is geogenic. The second factor separates Pb and Cu. These elements are usually related to human activities, so their concentration in soils is mainly anthopogenic. In the third axis is represented Zn, also controlled by lithology. The fourth axis represents Hg. In this case, the origin of this element in soils is also anthropic. For Cd we found an ambiguous situation, it is represented equally in both the 2nd and 3rd axes. Seems that its presence in soils can be due to both human and natural inputs.

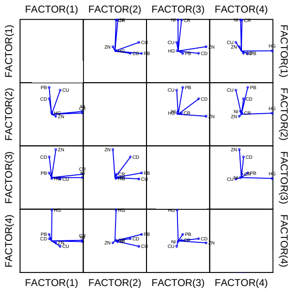

Figure 2.- Factor Loadings Plot

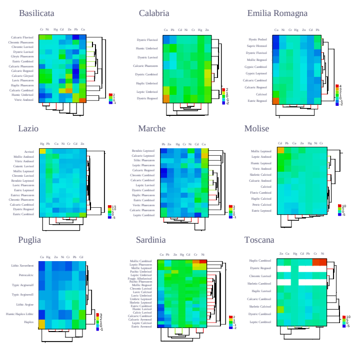

Figure 3.- Cluster analyses for HM contents

Hierarchical cluster analyses were performed for both heavy metals and soil types. These analyses were performed by administrative regions. Permuted data matrices on standardized data (Figure 3) show both the cluster trees for elements and soils and a colored matrix indicating the standard deviations of HM content for each soil type. Rows and columns are ordered according to the overall similarity to help interpretation.

In general we observe the same pattern of associations between HM as those obtained in the PCA using the whole dataset. We observe that soils in regions like Basilicata and Marche have a higher content in Cu, probably due to vine cultivation. In Lazio the most evident is the higher contents in Pb derived from the emissions of the road transport. In Molise, leptic soils trend to exhibit higher contents of Cd, Pb, Cu and Zn. These analyses also permit to identify special situations. In Sardinia, Cr and Ni contents in Phaeozems and in Mollic Cambisols/Leptosols can be related to the presence of vitric materials. Minning activities were reported in these areas. Vitric Andosols in Basilicata present very high contents in Cu.0

However the presence of noncristaline materials and the high contents of organic matter provides a high capacity to retain HM so their bio availability is probably low. The higher Hg contents are located in soil samples from Tuscany and North of Lazio. Industrial activities in these areas as well as pollution coming from geothermal plant can be the origin of this pollution.

Finally, cluster K-means classification reveals the three main groups of soils according to their HM contents (Figure 4). The first group includes 94% of the soils. It is a highly homogeneous group, with all metal contents distributed around the mean values and low dispersion of the data that probably represents the characteristics of the main natural soils in Italy. The second group includes five soil profiles. It is characterized by higher contents of Cd and Zn, probably due to specific natural conditions, to anthropogenic inputs or to a mix of both . The third group includes three cases with very high contents of Hg, Cr and Ni. In these cases specific studies on HM pollution are convenient to better understand the real problem of contamination in these areas.

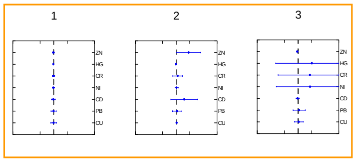

Figure 4.- Cluster K-means groups

CONCLUSIONS

Soil vulnerability to heavy metals are influenced by the diversity, distribution and specific vulnerability of soils across Europe. In this study we presented a method to perform a simple multi-evaluation on the status of pollution with heavy metal in soils. In this case we used natural soils coming from Natura 2000 sites in Italy. This approach allows to identify areas at risk, determine the possible sources of pollution and to find links between heavy metal contents. On the other hand, soil types were ranked and clustered according to their heavy metal content. To find a typology of polluted soils would help decision makers to protect specific areas minimizing costs of evaluation in order to protect natural ecosystems and human health. Accurate results can be obtained by means an adequate soil sampling design covering the most significant soil types and also taking into account their spatial distribution in the study area. These results can be improved by adding information on land management practices, location of point sources of pollution, evaluation of deposition rates, etc. We must note that toxicity risk for heavy metals is not dependent only on the total metal content in soils but also in the speciation forms they are present and in their mobility. For more detailed studies deepen surveys are needed.