International Plant Nutrition Colloquium
(University of California, Davis)

Year 2009 *Paper* 1329

Distribution of water extractable heavy metals (Cd, Co, Mn and Mo) in the topsoil of Osijek-Baranja County (Eastern Croatia)

Vladimir Ivezic *   Åsgeir R. Almås †
Zdenko Loncaric ‡   Bal Ram Singh **

*University of Life Sciences (UMB), Norway
†University of Life Sciences (UMB), Norway
‡University of J.J.Strossmayer, Osijek, Croatia
**University of Life Sciences (UMB), Norway

Distribution of water extractable heavy metals (Cd, Co, Mn and Mo) in the topsoil of Osijek-Baranja County (Eastern Croatia)

Abstract

Based on the pedological map of Osijek-Baranja County in eastern Croatia 74 soil samples were collected and analyzed for water extractable heavy metals (Cd, Co, Mn and Mo). By using GIS technique (ArcView software), different set of maps showing the water extractable metals were created. The maps indicate the correlation of water extractable fraction of heavy metals with soil pH, further statistical analysis will be preformed to confirm these assumptions. In addition analysis of variance was conducted to examine the influence of land use and different soil types on water extractable metals. Land use has shown significance for Cd, Co and Mn while soil type for Mo. These results also seem to be pH dependent, as land use and soil type differ in pH which is the factor causing the difference in the concentration of water extractable metals.

Introduction

Osijek-Baranja County is the main agricultural region of Croatia and therefore food quality and soil quality is of great importance in this area. However, as there is no heavy industry in the area very little attention is addressed to the concentration of heavy metals in these soils. Nevertheless, due to the agricultural importance of the region, information on the heavy metal concentration is necessary, as traffic and inappropriate usage of fertilizers can, to some extent, contribute to elevated levels of heavy metals in the soil (Alloway, 1992). The main objective of this research is to evaluate the soil of the area regarding the water extractable heavy metals and to create a comprehensive overview of the County on the subject of heavy metal availability. Such overview can be a base line for further research of soil contamination, soil-plant relationship and influence of different fertilization methods. To visualize the distribution of plant available heavy metals in the area, GIS technique will be used.

Materials and methods

The study area (Osijek-Baranja County) covers 4 144 km^2, it is a flat area part of the Pannonian valley that stretches through Hungary, Serbia and Croatia. Based on the pedological map 74 sites were randomly chosen so that all soil types and different land uses are included (agricultural field, pasture and forest). From each site 10 subsamples with 5 meters away from each other were taken and combined in one sample of approximately 500 grams. Samples were than sieved through the 2-mm mesh and such samples were used for the determination of soil pH, DOC and water extractable heavy metals, for soil organic carbon (TOC) samples grind to finer particles were used. TOC was determined by a dry combustion method on Leco Carbon Determinator EC12 (Nelson, D.W. & Sommers, L.E. 1982). Soil pH was done with pH-meter with KCl electrode (Mc Lean, 1982) and the water extractable metals were determined by ICP-OES and ICP-MS instrument. The statistical analysis was done by using PC application software Minitab.

Results and discussion

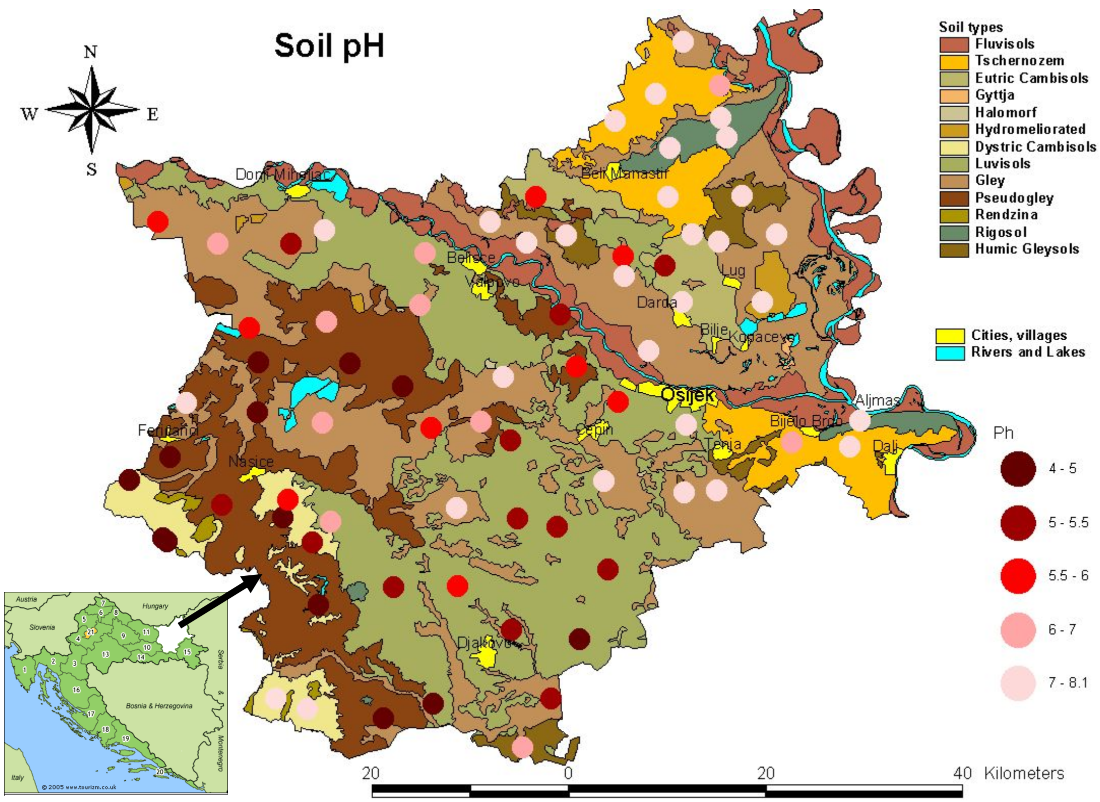
Water extraction of four heavy metals (Cd, Co, Mn and Mo) was analyzed by ICP-OES and ICP-MS obtaining the following statistical data (Table 1.). The values are in µg/l, some of the Mo samples had concentrations below the limit of quantification.

Table 1. Descriptive statistics

Variable	Mean	SE Mean	StDev	Minimum	Median	Maximum	
Cd	0,06378	0,00941	0,08094	0,00312	0,03328	0,52293	µg/l
Co	1,123	0,212	1,821	0,058	0,566	10,487	µg/l
Mn	129,8	31,6	271,7	0,3	26,1	1592,0	µg/l
Mo	0,707	0,106	0,916	0,039	0,199	4,625	µg/l

Cd: Cadmium, Co: Cobalt, Mo: Molybdenum and Mn: Manganese

The results were analyzed for two factors: land use (agriculture field, pasture and forest) and soil type (Pseudogley, Dystric Cambisols, Luvisols, Gley(Eugley), Tschernosem, Fluvisols, Eutric cambisols, Humic Gleysols, Rigosol and Hydromeliorated soils). Analysis of Variance (ANOVA) has shown that land use is significant factor for water extractable fraction of Co, Cd and Mn. Tukey pairwise comparison test showed that there is no difference between pasture and agriculture field, but the difference is between forest and agriculture or pasture. The concentration of water extractable metals was always higher in forest, which is mainly related to the fact that average pH of forest soil is smaller than the one of agriculture field and pasture, and pH has shown to be an important factor correlated with the availability of metals as it was also shown in the research of Loncaric et al. (2008) when examining extraction methods of plant available micronutrients in continental Croatia by EDTA and HCl. From the map of soil pH (Figure 1.) it can be seen that the lower pH is in the southern part of the County, and maps of Co, Cd and Mn indicate higher concentrations in southern part, while map of Mo indicates higher concentrations in northern part where pH is higher, these maps imply that higher pH causes higher values of water extractable Mo while for Co, Cd and Mn the situation is opposite, lower pH causes higher water extractable concentrations. Statistical analysis of correlation between the elements and soil properties such as pH, TOC, DOC and total metals will be provided later.



Croatia (white: Osijek-Baranja County)

Figure 1. Map of Soil pH of the Osijek-Baranja County

Results for different soil types showed no significance for Cd, Co and Mn but significant for Mo. Even that some of the soils had quite lower averages in pH from the others, for example: Pseudogley (5,3) and Dystric Cambisols (5,4) had quite lower averages from Gley(Eugley) (6,7) and Tschernosem (7,2). All ten soil types were included in the research and some covering smaller area than others did not have the same number of samples which resulted with unbalanced design (for example, two soil types were represented with only one sample) which makes the ANOVA regarding the soil types questionable. When number of examined soil types is reduced to only five of them, the main five that cover around 80% of the area, than the ANOVA results show the significant influence of the soil types on water extractable fraction of Cd, Mn and Mo, which is once again mainly due to the pH, as it was show earlier, the average pH for these five soils is between 5,3 - 7,2, so the soils with lower pH have higher values of Cd and Mn and soils with higher pH have higher values of Mo.

Using GIS we can present the data more visually, however statistical analysis of correlation between these metals and soil properties is necessary to confirm what can be seen from the maps and as it was mentioned before this analysis will be provided later. GIS technique will especially be beneficial for the future research since each sampling site was recorded by GPS, future changes in heavy metal concentration can be monitored and source, location and extent of heavy metal impact can be identified (Bolstad, 2008). This will specially contribute in examining the changes due to building of a new highway that will go through the area from north to south and most likely have an impact on agricultural fields in its vicinity.

Reference list

- Alloway, B.J., 1995. Heavy Metals in Soils, 2nd edition. Blackie Academic and Professional, Glasgow.
- Bolstad, P. 2008. GIS Fundamentals: A first text on geographic information systems, 3rd edition. Eider Press, White Bear Lake, Minnesota.
- Loncaric, Z., Karalic, K., Popovic, B., Rastija, D. and Vukobratovic, M. 2008. Total and Plant Available Micronutrients in Acidic and Calcareous Soils in Croatia. VII. Alps-Adria Scientific Workshop. Vol. 36, 2008, Suppl.
- Mc Lean, E.O, 1982. Soil pH and Lime Requirement. I: Page, A.L. et al. Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy no. 9, Madison, Wisconsin, USA: p 199-224
- Nelson, D.W. & Sommers, L.E. 1982. Total Carbon, Organic Carbon and Organic Matter. I: Page, A.L. et al. Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties. 2nd ed. Agronomy no. 9, Madison, Wisconsin, USA: p 539-579

APPENDIX 1.

Maps of water extractable Cd. Co, Mn and Mo in Osijek-Baranja County (all of the data is in µg/l)