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Multivariate statistical and GIS-based approach to identify heavy metal sources in soils of the Drama plain, Northern Greece

Многовариантен статистически и GIS-подход за идентификация на източниците на тежки метали в почвите на района на Драма, Северна Гърция

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Soil contamination by heavy metals (HM) has become a widespread serious problem in many parts of the world. Heavy metals in agricultural soil may originate from weathering of soil and rocks and a variety of human activities. Among these, mining and ore processing are considered as the most dangerous anthropogenic activities in the world (Acosta et al., 2011). The knowledge of the regional variability, the background values and the anthropic vs. natural origin for potentially harmful elements in soils is of critical importance to assess human impact and to fix guide values and quality standards.

The present study was undertaken on agricultural soil contamination at the western part of the Drama plain (N Greece) which lies very close to the main establishment of the 25 km Drama-Kato Nevrokopi abandoned manganese mine. A grid-type (cell-size 1x1 km) sampling scheme was applied and a total of 148 surface soil samples were collected. Samples from the mining wastes as well as stream sediments from the Xiropotamos, which passes through the mine place and drains the Drama plain, were also collected for comparison. The aims of the study were to: 1) determine average regional concentrations of some heavy metals (Mn, Pb, Zn, Cu, Cr, Ni and As); 2) find out their spatial variability; 3) define their natural or artificial origin; and 4) identify possible relationship among soil heavy metals contamination and the heaps of waste materials in the abandoned manganese mine. Descriptive statistics (mean, median, standard deviation and range) of metals in soils, sediments and heaps were performed applying the Excel for Windows software package. The Pearson correlation coefficient was used to measure the relationship between the metals in soils, sediments and heaps; Factor Analysis (FA) was adopted for data treatment, allowing the identification of the main factors controlling the heavy metals variability in cultivated soils. Geostatistics were used to construct regional distribution maps using GIS software.

Total metal concentration ranges (in mg/kg) of soils observed were: 245–130 013 for Mn, 11–1996 for Pb, 23–2140 for Zn, 5–153 for Cu, 0.4–28 for Cd, 5–137 for Ni, 4–98 for Cr, 2–1077 for As, 29–406 for Ba and 5–358 for Sr with mean values of 4149, 183, 134, 33, 2, 32, 34, 43, 127 and 33 respectively.

Extremely high concentrations of metals were found in the Xiropotamos sediments and in the waste heaps with mean values (in mg/kg) of: 149 594 and 226 080 for Mn, 1993 and 1819 for Pb, 3172 and 2474 for Zn, 159 and 107 for Cu, 26.3 and 26.4 for Cd, 673 and 650 for As, 541 and 593 for Ba and 153 and 469 for Sr respectively.

Pearson correlation analysis among the heavy metals concentrations in soils showed a very significant positive correlation ($p=0.01$) of Cd with Zn and As; Mn with Zn, As, Cd, Pb and Cu; Pb with Cu, Zn and Cd; Cu with Cd and As, as well as significant positive correlation ($p=0.05$) of Mn with Sr and Ba. The high correlations between soils HM may reflect similar pollution level and similar pollution sources. Overall, Mn, Pb, Zn, Cu, Cd, As, Ba and Sr are grouped together, indicating that the anthropogenic sources of these HM are closely related to the soil of the study area.

The same happens, but with different values for p and r, with the total concentration of these heavy metals in the stream sediments and the tailing heaps. This suggests that the natural soils could have been influenced by the abandoned mining materials (Martínez-Martínez et al., 2013).

Factor Analysis (FA) has been applied for a total of 12 elements to separate groups of metals from different sources (Ghrefat et al., 2012). Besides, maps were constructed showing the geographical distribution of the factor scores.

The FA results demonstrated that elements concentrations could be grouped into a three-factor model, which accounted for 85.03% of all the data variation. The first factor (F1), which explains 44.5% of the system variance, has high positive factor loadings on Mn, Pb, Zn, Cu, Cd, As, Ba and Sr. The second factor (F2) accounted for 29.9% of the total variance and is characterized by high positive loadings on Fe, V, Th, La, Ni and Cr. The third factor (F3) accounted for 10.7% of the total variance and is mainly characterized by high levels of Ni and Cr. The rotation of the matrix contributes to clarify the ambiguities for Ni and Cr. Thus, Mn, Pb, Zn, Cu, Cd, As, Ba and Sr were associated because of high values of F1. Iron, V, Th and La are well attributed to F2. The Ni and Cr are represented only in F3.

The first component includes elements existing in structure of the Mn-ore minerals (Michailidis et al., 1997; Sofianska et al., 2008). The geographical distribution of this component is around Xiropotamos stream. This suggests an anthropogenic input, related to the transfer and redistribution of the mining wastes by the Xiropotamos stream.

The variability of the elements associated in the second component is controlled by soil parent rocks.

The third factor, including the elements Ni and Cr, is located in a narrow zone at the western part of the Drama plane. Because of the low concentration of these elements in the parent rocks, they are also considered to be anthropogenic.

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References

Acosta, J., A. Faz, S. Martínez-Martínez, R. Zornoza, D. Carmona, S. Kabas. 2011. Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. – *J. of Geochem. Expl.*, *109*, 1–3, 8–17.

Ghrefat, H., N. Yusuf, A. Jamarh, J. Nazzal. 2012. Fractionation and risk assessment of heavy metals in soil samples collected along Zerqa River, Jordan. – *Environ. Earth Sci.*, *66*, 1, 199–208.

Martínez-Martínez, S., J. Acosta, A. Faz Cano, D. Carmona, R. Zarnoza, C. Cerda. 2013. Assessment of the lead and zinc contents in natural soils and tailing ponda from the Cartagena-La Unión mining district, SE Spain. – *J. of Geochem. Expl.*, *124*, 166–175.

Michailidis, K., K. Nicholson, M. Nimfopoulos, R. Patrick. 1997. An EPMA and SEM study of the Mn^{4+}oxide mineralisation of Kato Nevrokopi, Macedonia, northern Greece: Control on formation of the Mn^{4+}-oxides. – In: Nicholson, K. I., J. R. Hein, B. S., Bühn, S. Dasgupta (Eds.). *Manganese Mineralisation: Geochemistry and Mineralogy of Terrestrial and Marine Deposits.* Geological Society of London, Spec. Publ. 119, 265–280.

Sofianska, E., K. Michailidis, G. Trontsios, A. Kassoli-Fournaraki. 2008. Contamination of the Xiropotamos stream sediments (Drama district, Western Rhodope massif, Northern Greece) by mining and manganese ore processing activities. – *Rev. Bulg. Geol. Soc.*, *69*, 1–3, 39–47.