Soil geochemistry of the Mediterannean agricultural karst catchment (Vrana Lake, Croatia)

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The Vrana Basin, located in the central part of Croatian Adriatic Sea coast, is a typical cryptodepression formed by tectonic activities, with 6830 ha of agricultural land and Lake Vrana situated in the very basin. The area is ecologically highly sensitive and it is characterised by intensive vegetable production in a karst environment where, due to geological and climatic conditions as well as anthropogenic influence, it is easy for harmful substances to enter the food chain or penetrate ground water or open watercourses. This threatens the largest Croatian lake, Lake Vrana, as well, which is a large potential source of water for agriculture, possibly also drinking water, as well as for tourism and leisure activities. Because it is one of the rare natural habitats of waterbirds as well as because of its fresh water springs and biodiversity, the Vrana Lake and its surroundings have been declared a nature park. To evaluate the impact of agricultural practices on trace metals accumulation and behaviour in soils a multi-element geochemical survey was carried out. The objectives of this study were: (i) to determine contents of trace metals in soils and (ii) to assess their natural or anthropogenic source using multivariate statistical analysis. Topsoil (0-30 cm) and sub-soil (30-60 cm) samples were taken from 74 locations following regular square sampling grid with 1x1 km distances. Element contents (Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Zn) were determined by ICP-OES after aqua regia extraction, while Hg was determined using the CV AAS technique. A GIS geospatial database was compiled. Furthermore, after statistical and geostatistical analyses, trace metal distribution maps have been produced. The trace metal contents do not exceed threshold value established by the Croatian government regulation, with exception of copper. The practice of using Cu-sulphates and other copper containing fungicides to protect mostly grapevine, resulted in significant Cu accumulation in soils worldwide. A high chromium and nickel concentration in spots seems to be of geogenic origin. By applying factor analysis (FA), complex linear correlations between metal concentrations in soils were determined which enabled the interpretation of correlations of elements in the studied area. Considering the influence they exerted on the determined distribution of elements, the said multielement factors were divided into three groups: (1) factors caused by predominantly natural geogenic and pedogenic processes, (2) factors caused by specific long-term agricultural practice, mainly fertilization and (3) soil organic matter and nitrogen contents variation. The identification of factors is based on the dominant influence. The distribution of individual associations of elements in topsoils was determined by principal components method. Based on eigenvalues, three main factors explained 72.6% of the total variance.

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