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Mapping Zn, Cu and Cd contents at the small catchment level after dispersion of contaminants by agricultural practices

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Dispersion of trace metals into the rural environment through the use of sewage sludge, fertilizers and manure has been worldwide reported. In El Abelar (Coruña province, Spain), pig slurry was discharged during years intensively into an agricultural field by means of a device which constituted a point source of contamination. The application point was located near the head of an elementary basin, so that slurry was dispersed by runoff into neighboring grassland and maize fields. In addition, diffuse pollution was also present in the study area as a consequence of cattle grazing. Water quality was monitored during and after slurry application at the outlet of a small catchment (about 10.7 ha in surface) draining the study fields. High levels of nutrients, including heavy metals, were found in drainage water. The main objectives of this paper are to determine the spatial variability of Cu, Zn and Cd as extracted by NO_3H, EDTA and Ca_2Cl and to evaluate the risk of accumulation of these heavy metals at the small catchment level. A set of 55 soil samples were taken from the top soil layer (0-20 cm) of the studied catchment, following a random sampling scheme. Fe, Mn, Cu, Zn and Cd contents were determined i) after digestion by nitric acid in a microwave (USEPA-SW-846 3051) ii) after extraction with EDTA and iii) after extraction with Cl_2Ca. Element contents in the extracts were determined by ICP-MS. Summary statistics indicate that variability in Cu, Zn and Cd contents over the study area was very high. For example, after NO_3H digestion Zn contents ranged from 29.66 to 141.77 3 mg kg^{-1} and Cu contents varied from 10.45 to 72.7 3 mg kg^{-1}. High Cu and Zn contents result from accumulation as a consequence of slurry discharge. Also, some hot spots with high levels of Cd ($>$ 3 mg kg^{-1} after NO_3H) with respect to background values were recorded. Geostatistics provides all necessary tools to analyze the spatial variability of soil properties over a landscape. The spatial dependence of the extracted heavy metals was assessed by semivariogram analysis. When a pattern of spatial dependence was found, kriging was used to construct contour maps of metal contents. Indicator kriging was also used to map the probability that a local threshold is exceeded. This probability map can also be used for decision making processes such as the determination of areas where additional samples should be collected. In cases where extractable trace elemet contents did not show spatial structure at all, hence, non-geostatistical techniques such as the inverse distance method were used to attempt to interpolate these metal fractions. The used mapping methods illustrate how poor the studied site was managed from an environmentally point of view. The spatial distribution of the study soil elements appear to depend largely on both, the discharge pattern and the morphological characteristics of the area where slurry was applied.

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