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Arsenic concentration in the soils of the Brenta Plain (Northern Italy): mapping the probability of exceeding contamination threshold.

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In the last decades the increase of industrial activities and the introduction of new technologies applied to activities traditionally characterised by a low environmental impact such as agriculture, enhanced the risk of soil contamination by pollutants. Among these, heavy metals, due to their persistence, accumulate in soils possibly reaching concentrations above regulatory contamination thresholds.

In the frame of soil survey carried out in Veneto Region (North Eastern Italy) most of the Brenta alluvial plain (1350 km^2) was investigated at the scale 1:50,000; in the northern part of the plain soils developed on a Pleistocenic surface, while in the southern area soils developed on a younger Holocenic surface. For 212 representative profiles topsoil and subsoil were analyzed for heavy metals. The total content of As, Cd, Co, Cu Cr, Hg, Ni, Pb and Zn was determined through acid extraction with *aqua regia* (ISO 11466) and detection by ICP (Inductive Coupled Plasma). As concentrations were generally high, frequently above regulatory thresholds. Concentrations above 10 $mgkg^{-1}$ are commonly found in the recent alluvial deposits and above 20 $mgkg^{-1}$ in the older ones as the result of a different origin of the deposited alluvial materials, but concentrations above 50 $mgkg^{-1}$ are locally observed as the result of anthropogenic pollution. Differently from any other heavy metal investigated in the area, As concentrations are higher for subsoil samples (depth $>$70 cm) than for topsoil samples (depth$<$40 cm). The upper limit of the pedo-geochemical background value defined for subsoil samples following the ISO international standards (ISO/DIS 19528) is higher (36 $mgkg^{-1}$) than the regulatory threshold (20 $mgkg^{-1}$). The same

happen for the upper limit of the background content defined for topsoil sample (30 mgkg^{-1}).

In order to assess the natural variability of As concentrations, to detect the areas affected by possible anthropogenic pollution and to quantify and map the probability to exceed environmental thresholds a non-parametric geostatistical approach was adopted. A non-stationary simple kriging with varying local means based on the soil map 1:50,000 was used to infer the local conditional cumulative distribution function (*ccdf*) of As concentration for topsoil and subsoil. The use of local uncertainty models based on the estimated *ccdf* allowed the assessment of the probabilities to exceed critical thresholds. At a probability level of 65%, corresponding to the observed marginal probability of values above the regulatory threshold, it was found that the regulatory threshold for As in the topsoil was exceeded at 13% of the interpolated locations covering about 165 $\text{km}^2$of the study area. In the case of subsoil, the extent of As values above 20 mgkg^{-1} appeared to be more relevant: at a probability level of 50%, corresponding to the observed marginal probability of value $>$20 mgkg^{-1}, the regulatory threshold for As was exceeded at 57% of the interpolated locations covering about 757 $\text{km}^2$of the study area. Despite the high background level for As, areas of probable anthropogenic As contamination are clearly detectable at both depths. The risk to identify locations below or above a given threshold is quantified in both cases, identifying locations where additional As samples should be collected in order to improve the classification into safe and contaminated locations and plan reclamation priorities.