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Title: **STUDY ON ANOMALIES IN HEAVY METALS IN DIFFERENT ENVIRONMENTAL MATRICES OF THE TYRRHENIAN COASTAL AREA BETWEEN THE CORNIA VALLEY AND BRUNA VALLEY**
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Southern Tuscany hosts a number of ore deposits which have been actively exploited since the Etruscan period until very recent time. Natural processes of rocks weathering led to the dispersion in the environment of toxic elements.
The Department of Earth Sciences of University of Florence has conducted over the past ten years, numerous studies about the distribution of arsenic and heavy metals in mineralized areas of Tuscany, particularly in the Pecora basin. The Pecora river drainage-basin is located in the SW part of Colline Metallifere. The area hosts several polymetallic ore bodies and a pyrite ore deposit. The studies have identified several geochemical anomalies (As, Cu, Pb, Zn…) both in the areas which host the ore bodies and in the coastal plain (Scarlino Plain). The studies suggest that in Scarlino Plain the primary geogenic geochemical anomalies have been overprinted by an anthropogenic input. The anomaly in As is not limited to the surface portion of the deposits Neogene - Quaternary outcropping (ARPAT-DST/UNIFI, 2003), but also extends in the deep sediments of the complex Neoautoctono explored in La Botte and Vetricella boreholes which have reached the substrate of the complex (Fontani, 2005; ARPAT-DST/UNIFI, 2005, 2006; Fontani, 2007; ARPAT-DST/UNIFI, 2008; Dughetti, 2009; Rossato et al., 2011). If the model is defined to explain the origin of the anomaly in the Val di Pecora As (associated with the presence of Cu, Pb and Zn) is valid, in reference to the origin geogenic, then it is plausible that a similar situation can also be found in any other basin where the river network draining mining areas (O'Shea et al., 2007, Pfeifer et al., 2004, Romero et al., 2003).
In this regard therefore, the coastal basins similar to the Scarlino Plain, filled with unconsolidated sediments and mineralized areas inside the basin, are those of Brown and Cornia.
The analysis have focused on soils and stream sediments, to better understand the correlations between the downstream transport of rivers and the soils.
Sampling sites were chosen on the basis of the distribution of different types of soils as reported in the map of Regione Toscana. The soils are subdivided on the basis of the origin of sediments, related to different areas (recent channel, alluvial fan or lagoon). Surface (0-10 cm) and subsurface (40-80 cm) soil samples were collected from each site. Deep horizons were therefore sampled in order to characterize, if possible, the natural local pedo-geochemical background (Baize and Sterckeman, 2001).
Air dried soil samples were sieved (to construct granulometric curves and classify them), and analyzed for chemical-physical properties. We have made mineralogical analysis for X-ray power diffraction and for SEM-EDS, and chemical analysis for the determination of major elements (XRF) and for the determination of 35 minor elements and traces (ICP-ES). Were also carried out analysis of 7 samples of groundwater relating to Val di Cornia, for the determination of the major ionic species and traces. Finally, we have made sequential extraction and leaching tests to evaluate the mobility of the As, Cu, Pb, Zn.
Chemical data indicate that the Pian d'Alma presents a compositional homogeneity with the surrounding areas and low levels of heavy metals and As. It can therefore be considered as "background microbasin " for studies of the geochemistry of southern Tuscany coast. Analysis of the data obtained in this work, together with previous data in the area, show that Cornia Valley, Pecora Valley and Bruna Valley have differentiated enrichment in As (Cu, Pb and Zn) associated with metasomatic and hydrothermal phenomena. The isotopic data (Cortecci et al., 1985; Pennisi et al., 2006; Muti, 2006) confirm the hypothesis of a common origin for the geothermal fluids in the area of Larderello-Travale and, pyrite and polymetallic deposits present in the Colline Metallifere.
The origin of different enrichments in the three basins is therefore common, even if the enrichment processes are differentiated. In fact, while in the Pecora Valley and in the Bruna Valley the process of enrichment in As (Cu, Pb, Zn) is mainly due to sediment deposits from alteration and dismantling of outcropping mineralization, in the basin of the Cornia the primary enrichment process of As (B) seems to have been the aqueous phase (through interaction with deep geothermal fluids), which then led also to the enrichment of the solid phase.