

THE PEDOGEOCHEMICAL MAP AS A SUPPORT FOR ENVIRONMENT PLANNING STRATEGIES IN EMILIA-ROMAGNA

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ABSTRACT

A reliable evaluation of metal contents in soils, under both natural and anthropogenic conditions, is a fundamental issue. In this work, we show our methodology applied to the case study of the western Emilia-Romagna plain in determining the pedogeochemical contents of heavy metals and their anomalies. In this context, where natural values of some metals (Cr and Ni) for several soil types exceed the threshold limits indicated by the law, the application of an adequate methodology in geochemical anomalies evaluation assumes a significant role.

Key words: soil, pedogeochemical content of heavy metals, geochemical anomalies, analytical methods, threshold limits

1. INTRODUCTION

According to the Italian Legislative Decree 152/06 of 3rd April 2006, concerning the consolidated law governing environmental issues ("Testo Unico recante le Norme in Materia Ambientale"), the Contamination Threshold Value is defined as follows (at art.240 comma 1 letter b): *"threshold values are the values of contamination of environmental matrix above which the characterization and specific risk analysis of the contaminated site, as described in the Appendix 5 at part four of the present law, becomes necessary. In the event the potentially polluted site is located in an area where geogenic or anthropogenic factors are responsible for the exceeding of threshold values for some parameters, the background content of these parameters is assumed as threshold.*

The background content of a substance in a soil is the concentration "resulting from both natural geological and pedological processes and including diffuse source inputs" (ISO/DIS 19258). Without an accurate knowledge of the background content of metals in soils, it is not possible to assess their contamination state.

The pedogeochemical content in a soil is the concentration "resulting from both natural geological and pedological processes excluding any addition of human origin" (ISO/DIS 19258)

Between 2004 and 2008, in accordance with ISO/DIS 19258, 2005 Soil quality - Guidance on the determination of background values, Regione Emilia-Romagna in collaboration with Bologna University (Department of Earth Sciences) produced the pedogeochemical maps of Cr, Pb, Ni, Zn and Cu for the Sheet 181 (Parma Nord) at 1:50,000 scale and of two pilot areas in the western part of Emilia-Romagna alluvial plain at 1:250.000 scale. The

geochemical characterization of soils in the southern Po Plain has shown that the three major factors controlling natural metal distribution in soils are: (i) sediment provenance (Amorosi et al., 2002; Bianchini et al., 2002), (ii) grain size (Amorosi & Sammartino, 2005; 2007), and (iii) the degree of alteration of primary minerals (Sammartino et al., 2007). A similar approach, but on a considerably wider area (from Tidone River to Secchia River), is now in progress, and will lead to the construction of the Pedogeochemical Map of Cr, Pb, Ni, Zn and Cu of Emilia alluvial plain to 1:250,000 scale, by December 2009. This project will also provide new data relative to the background content of some other elements, such as As, Cd, Sb and Sn. The following sections explore the methodological aspects and the major results of this project.

2. METHODS

2.1. Sampling

The project is based on 280 sites of observation and sampling with density of 1 site/16,3 km². Two samples were collected by hand-drillings, using Eijkelpamp Agrisearch equipment, for each site chosen in green areas with agriculture management and far from contaminated sites (on the basis of Land Use maps from 1976 to nowadays): i) top-soil (20-30 cm deep) samples (*i.e.*, the upper part of a non-contaminated soil which is generally dark coloured and has a higher organic carbon and nutrient content when compared with the sub-soil below), and ii) sub-soil (120-130 cm deep) samples (*i.e.*, the partially decomposed layer of rock underlying the top-soil and overlying the solid parent rock beneath). The content at the depth of 120-130 cm for the subsoil samples represents the pedogeochemical content because prevents from the influence by anthropogenic activities in areas with agriculture ordinary management. In order to make a typological sampling instead of a simple grid, the pedological criteria was used with the support of Regione Emilia-Romagna Soil Maps to 1:50,000 scale. The aim is the geochemical characterization of the different drainage basins and their compositional variability in the correspondent soil units.

2.2. Analytical Techniques

Samples at both depths were analyzed through the XRF method in order to evaluate the total metal contents, while analyses of topsoil samples also availed of aqua regia digestion and the ICP-MS (EPA 6020 A, 1998) method, which is the more commonly adopted and that prescribed by the law (official method published in the Official Gazette n° 2498 of 21/10/99, ARPA Ravenna laboratories). Total metal contents can best be calculated through XRF analysis, while aqua regia digestion measures only a percentage as it does not completely destroy silicates. The aqua regia digestion permits to evaluate the long-term releasable content of elements in soil, the one more easily increased by anthropogenic activity; for this reason in the top soil both analytical methods were applied. XRF analyses, including major and trace elements, were conducted in the Department of Earth Sciences (University of Bologna). Samples for XRF-analysis were not sieved, but analyzed as bulk. They were analyzed in a Philips PW 1480 spectrometer with a Rh tube. Aqua regia analyses were obtained by microwave assisted acid digestion in microwave MILESTONE MLS 1200 Mega, by aqua regia attack of the solid fraction. Digests have been analysed by ICP-MS (ICP-MS 7500 CE Agilent). The data obtained were within the linear calibration range (between 0.1 µg/L e 200 µg/L).

3. RESULTS AND DISCUSSION

3.1. Metal distribution in soils as a function of sediment provenance

Similarly to what recently documented from the Romagna coastal plain (Amorosi & Sammartino, 2005; 2007) and Sheet 181 (Sammartino et al., 2007), this study shows that the natural concentration of selected elements, such as Cr and Ni, is strongly dependent upon sediment provenance. Specifically, soils deriving from rivers that drain ophiolitic complexes, such as Po River and several Apenninic rivers, may display pedogeochemical contents of Cr and Ni that exceed the maximum concentrations admitted by Italian legislation for parks and residential areas (150 ppm for Cr and 120 ppm for Ni, D. M. 152/06). This is clearly shown in Figure 1, where boxplots related to five rivers of Parma alluvial plain (Parma, Stirone, Ongina, Taro and Po) show significantly contrasting values. Sediments supplied by Po and Taro rivers exhibit the highest Cr and Ni contents, while pedogeochemical contents within sediments derived from Parma, Ongina and Stirone are remarkably lower.

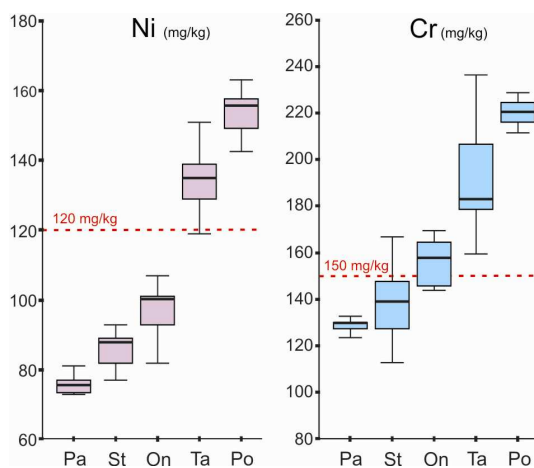


Figure 1: Boxplots showing the influence of sediment provenance on natural metal distribution for selected Emilia rivers of Parma alluvial plain. On: Ongina River, St: Stirone River, Ta: Taro River, Po: Po River, Pa: Parma River. The red line is the threshold limit indicated by D.M 152/2006.

3.2. Metal distribution in soils as a function of grain size

In addition to sediment provenance, grain size appears to represent another important factor controlling geochemical composition of soils. Geochemical analyses of different grain size fractions (sand, silt and clay) enable the distinction of different pedogeochemical contents for Zn, Cu and Pb (Fig. 2). In particular, these metals are generally concentrated within the finer-grained fraction, whereas they attain lower values in the sands.

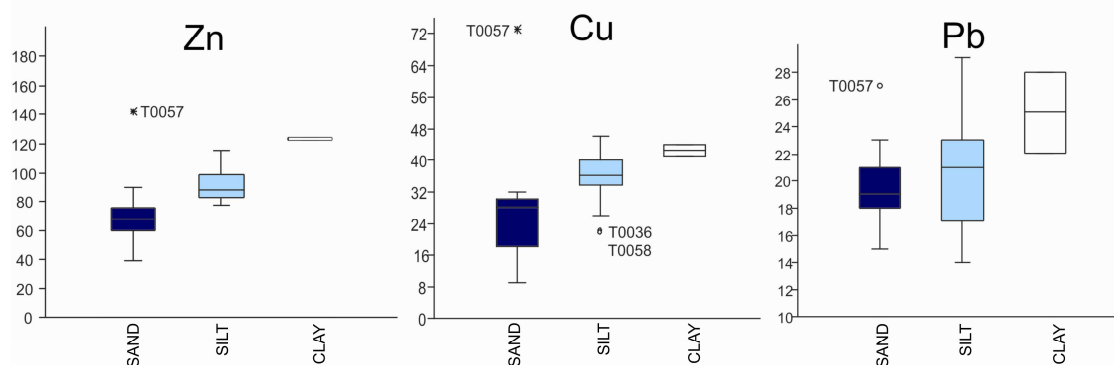


Figure 2: Boxplots showing the influence of grain size on natural metal distribution for Emilia soils.

3.3. Metal distribution in soils as a function of soil alteration

Recent work on Emilia-Romagna soils (Sammartino et al., 2007) has documented that concentration of selected geochemical indicators (Ca, Fe, Al, Zr, Ti, V) varies as a function of the degree of soil alteration, confirming processes seen in other context study (Feaks & Retallack, 1988). The extent to which metals are involved in this process is being studied. Although it is likely that pedogeochemical contents of certain metals may vary from a soil to another as a function of its degree of alteration, the magnitude of this fluctuations is by far lower than the one due to sediment provenance and grain size.

3.4. Geochemical anomalies

The spatial distribution of element concentration at the depth of 120-130 cm represents the pedogeochemical content: from the statistical treatment of data the 90th percentile is the numeric value that represent the pedogeochemical content in a specific area (Provincia di Milano, 2003; .

On the same base we can calculate the background value (pedogeochemical plus anthropogenic content according to ISO 19258 definition) of the top soil, as the Italian Legislative Decree 152/06 of 3rd April 2006 suggests.

In order to evaluate the potential state of contamination in a soil or sediment is even effective to know the enrichment of a determinate element nearby the surface in comparison with the natural content at a certain depth (Top Enrichment Factor - TeF, Index of Geoaccumulation - Igeo, Förstner & Müller, 1981) and to know its bioavailability beside its toxicity. As for chromium and nickel, they are much more concentrated in the soils of basins where ultramafic rocks are outcropping, and for vast areas of the Po Plain their content exceeds the threshold limits. This elevated geogenic content does not correspond to an elevated level of pollution of the area, as comparison between the subsoil and the topsoil contents demonstrates (Igeo), nor does it pose a danger for human health (only few sites are contaminated), as shown by a number of bioavailability tests performed in the Romagna coastal plain (Sammartino, 2004), where sediments deriving from ultramafic rocks are largely diffused, too.

On the basis of Igeo, the pollution status of soils can be differentiated into seven classes (Table 1), from < 0 to 6. The highest value of Igeo (see class 6 in Table 1) reveals metal concentrations 100 times higher than pedogeochemical concentrations.

| I _{geo} | I _{geo} class | Designation of soil quality |
|------------------|------------------------|--|
| < 0 | 0 | Unpolluted |
| 0-1 | 1 | From unpolluted to moderately polluted |
| 1-2 | 2 | Moderately polluted |
| 2-3 | 3 | From moderately to strongly polluted |
| 3-4 | 4 | Strongly polluted |
| 4-5 | 5 | From strongly to extremely polluted |
| > 5 | 6 | Extremely polluted |

Table 1: Soil quality evaluation on the basis of the Index of geoaccumulation of Müller (1979) and Förstner and Müller (1981).

A different behaviour from Cr and Ni is observed for other metals, in particular for Cu and Pb. In these instances, although metal concentrations are far below from threshold values, several sites show anthropogenic enrichment in the topsoil and the area is consequently slightly contaminated. Figure 3 shows an example of geochemical anomaly map for two elements with contrasting behaviour. Despite its high natural levels (exceeding threshold limits, as shown by concentrations indicated in red), nickel does not display any anomaly, as indicated by the presence of green dots (= no accumulation in

topsoils). In contrast, copper demonstrates diffuse contamination despite low concentration, as documented by the abundance of yellow and red dots.

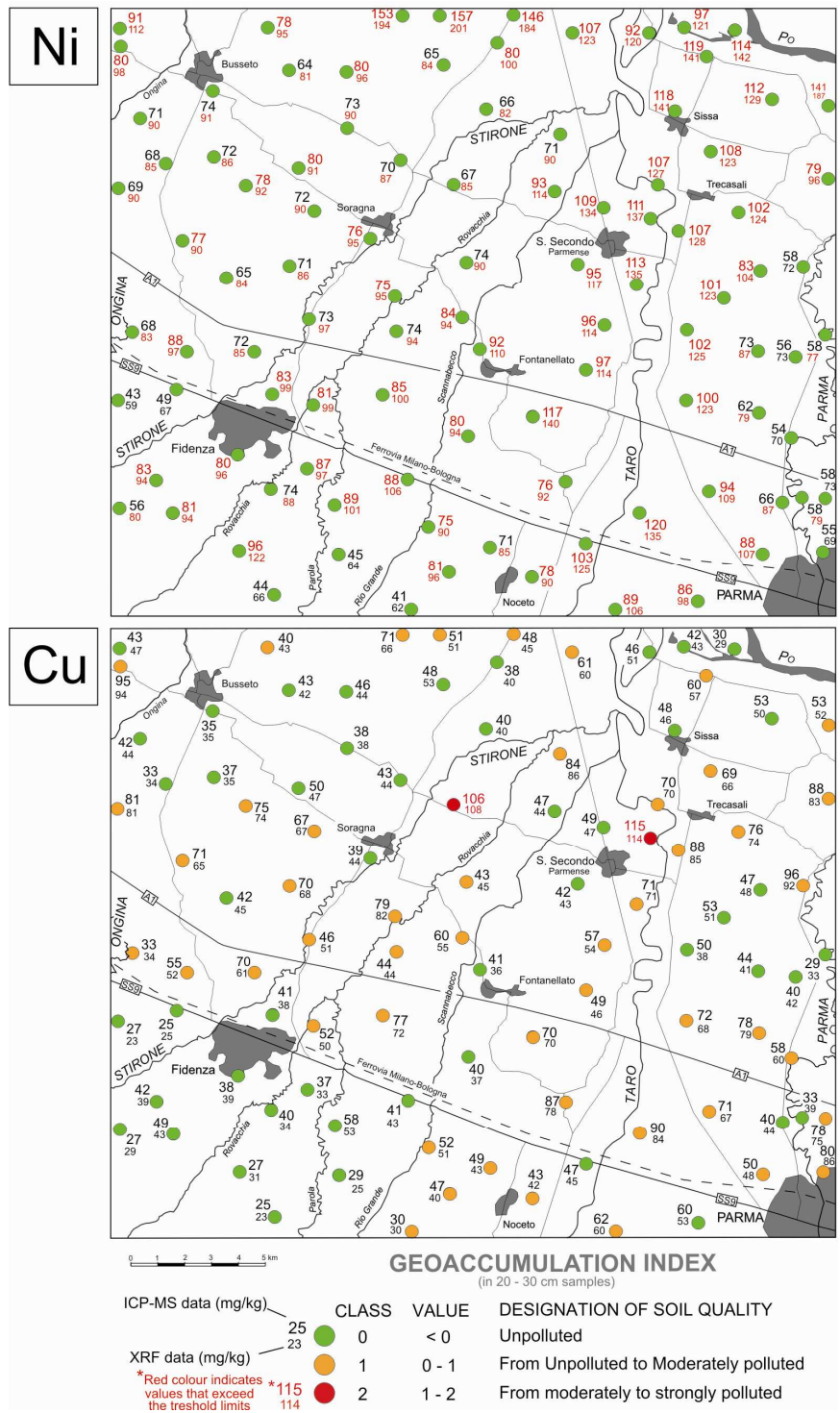


Figure 3: Example of Map of Geochemical Anomalies of Ni and Cu from Sheet 181 (Parma Nord).

4. CONCLUSIONS

A reliable determination of pedochemical values of potentially toxic metals has

important economic implications for soil management resulting in precise differentiation between contaminated and pollutant-free soils. Natural geological and pedological conditions may imply very high metal contents, that locally may exceed the threshold values admitted by law. Local geochemical characteristics of soils, as a function of sediment provenance, grain size and degree of soil alteration, should be taken into account by environmental legislation in the assessment of contamination. Despite locally very high abundance, Ni and Cr show uniform low geoaccumulation values in all the study stations, which is an obvious indication of generally unpolluted soils. Finally, in order to provide reliable information on the natural content of metals in soils or to quantify the anthropogenic contribution, a pedogeochemical mapping project should take into account the different metal concentrations that can be obtained on the basis of different analytical techniques.

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