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The Pedogeochemical Map of Parma alluvial plain: contribution of soil studies to geochemical mapping

Irene Sammartino¹, Alessandro Amorosi¹, Marina Guermandi² and Nazaria Marchi²

Abstract

The last decades have recorded a growing interest in geochemical mapping, and refined statistical techniques have been used in order to define the pedogeochemical content of potentially toxic metals in soils, following definition by ISO/DIS 19258. Advances in sedimentological and soil research provide today the opportunity to examine distribution of pedogeochemical contents of selected elements within a mixed pedological and sedimentological framework, through integration of geochemical data with detailed soil characterization.

Pedological and geochemical analyses of 200 soil samples from 100 sites of Parma alluvial plain (Sheet 181 of Soil Map to 1:50,000 scale), collected within depths of 20-30 cm and 90-100 cm, respectively, enable precise identification of the pedogeochemical content of selected geochemical elements as a function of soil maturity and sediment provenance. Increasing soil evolution invariably results in Ti, Zr, V, Fe₂O₃ and Al₂O₃ enrichment. In contrast, Ca is strongly depleted in highly mature soils, in response to leaching processes.

Similarly to what recently documented from the Po Delta area, sediment supplied by Po River to Parma alluvial plain is characterized by remarkably high natural concentrations of Cr and Ni, reflecting erosion of ultramafic complexes cropping out in the Po drainage basin. A striking similar composition is recorded within sediments supplied by Taro River, which also hosts ultramafic rocks in its drainage basin. In contrast, a markedly different composition, with significantly lower Cr and Ni values, is recorded within sediments supplied from other Apenninic (Stirone, Parma and Ongina) rivers. Soil distribution of other metals, such as Cu, Zn and Pb, does not reflect important differences in sediment provenance.

In order to obtain a realistic view of the pollution status of the study area, the pedogeochemical content, measured at 90-100 cm depth, was matched against metal content recorded in topsoil units (20-30 cm). Despite their locally very high concentrations, nickel and chromium do not show enrichments due to anthropogenic disturbance. In contrast, a diffuse (although moderate) soil contamination is observed for copper, lead and zinc.

The Pedogeochemical map illustrated here, including a Map of Pedogeochemical Content and a Map of Geochemical Anomalies, represents a novel approach to geochemical mapping. This map constitutes a powerful tool to assess the anthropogenic impact on alluvial plains, which can be of use for legislative purposes and for planning strategies for environmental protection.

Keywords: Pedogeochemical map, Heavy metals, Sediment Provenance, Geochemical anomalies, Po Plain

Introduction

In order to provide a reliable estimate of the pollution status of soils relative to its metal content, natural metal concentrations (pedogeochemical values) for different soil types should be established (ISO/DIS 19258). Once pedogeochemical content of metals is defined, geochemical anomalies can be assessed as deviations of measured metal content from the norm (Reimann and Garrett, 2005).

According to Italian legislation (D.lgs. 152/06), samples representative of background values for a study site are samples collected close to the investigated site, in which there is certainty of non-pollution in the same soil type". However, in presence of strong and widespread anthropogenic

influence, or a varied geologic framework, determination of pedogeochemical content strictly following this definition may provide highly unreliable results.

Lack of information about geochemical composition of local substrates has led in many instances to adoption of international reference values, instead of actual background concentrations (Rubio et al., 2000; Rapant and Kordik, 2003). These, however, may represent unreliable approximations of pedogeochemical values and lead, consequently, to incorrect estimates of geochemical anomalies. In other instances, geochemical mapping has been based upon interpolation of "baseline values" (Salminen et al., 1998; Plant et al., 2001; Albanese et al., 2007). The geochemical baseline, however, differs sub-

¹Dipartimento di Scienze della Terra e Geologico-Ambientali, Università di Bologna, Via Zamboni 67, 40127 Bologna, Italy. E-mail:irene.sammartino@unibo.it; alessan-dro.amorosi@.unibo.it

dro.amorosi@.unibo.tt ²Servizio Geologico, Sismico e dei Suoli, Regione Emilia-Romagna, Viale Silvani 4/3, 40122. Bologna, Italy.

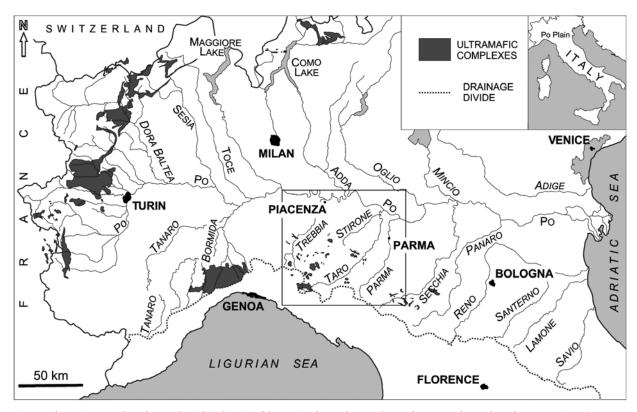


Fig. 1 - Schematic map of Northern Italy, with indication of the major ultramafic complexes of Western Alps and Northern Apennines (outcrops of ultramafic rocks after CNR, 1990). Figure 2 is shown in box.

stantially from the pedogeochemical content, in that it represents the total metal concentration measured in soils, irrespective of its natural *versus* anthropogenic contribution.

Recent studies (Darnley, 1997; Salminen and Tarvainen, 1997; Amorosi and Sammartino, 2005, 2007) have shown that the major factors controlling geochemical composition of sediments are: i) sediment provenance, which in turn is related to drainage-basin composition, and is a function of the geochemistry of the source material; ii) grain size, which depends on transport and selection processes taking place within different depositional environments.

The complex interaction between these factors allows for local yield of high natural concentrations of potentially toxic metals in soils, which may exceed the threshold limits designated for contaminated areas (Miller, 1997; Box and Wallis, 2000; Myers and Thorbjornsen, 2004). For instance, high natural Cr and Ni concentrations have been reported from core samples of Po River Basin, up to 200 m depth, within sediments supplied by Po River (Amorosi et al., 2002; 2007).

These high values have been attributed to erosion, by the Po river and its tributaries, of widespread chromium- and nickel-rich ultramafic complexes cropping out in several areas of the western Alps and the northern Apennines (Fig. 1).

Geochemical interpretation of core data is consistent with geochemical studies from stream sediments (Dinelli and Lucchini, 1999; Viganò et al., 2003), and has been recently supported by geochemical characterization of superficial sediments from the Romagna coastal plain, where a strong relationship between natural soil distribution of heavy metals and sedimentologic characteristics has been detected (Amorosi and Sammartino, 2007). Particularly, high natural pedogeochemical values of Cr and Ni, commonly exceeding the maximum values admitted for residential and park areas by D.lgs. 152/06, have been recorded within sediments of Po River provenance. In contrast, low Cr and Ni concentrations characterize sediments supplied by Romagna Apenninic rivers. Despite their high concentrations, chromium and nickel of geogenic origin are strongly linked to the mineral fraction

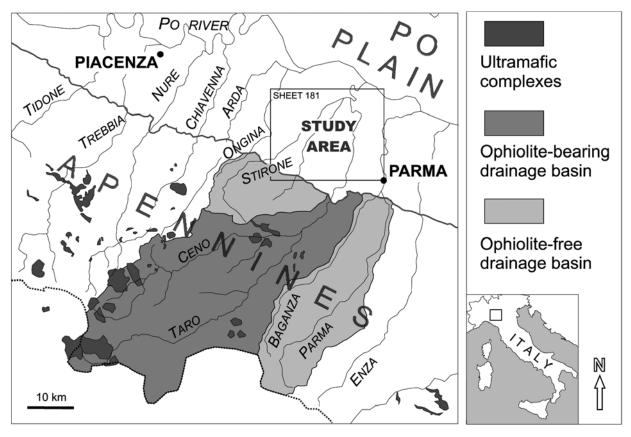


Fig. 2 - Close-up of Figure 1, with indication of the study area. Note ultramaphic rocks cropping out in Taro and Ceno drainage basins (dark grey), and lack of ophiolitic complexes in Ongina, Stirone, Baganza and Parma drainage basins (light grey).

and are not significantly bioavailable (Sammartino, 2004). This has led to the generation of a conceptually new type of geochemical map, in which natural metal distribution is depicted as a function of the sedimentological characteristics of the geological units (Amorosi and Sammartino, 2005).

Soil types developed on different substrates are also likely to be fingerprinted by distinctive geochemical compositions. In addition to sediment provenance and grain size, processes of soil formation and development may also play a fundamental role in determining the geochemical composition of soils, through selective element enrichment or depletion. These concepts, however, have been developed in few studies only (Facchinelli et al., 2001; Baize and Tercè, 2002; Sartori et al., 2004; Spadoni, 2006), and have not been taken into account within an official geochemical map, so far.

As part of a joint project between Regione Emilia-Romagna and University of Bologna

("Valutazione di caratteri del suolo in rapporto alla utilizzazione degli effluenti e alle modalità di conduzione dei terreni, e monitoraggio degli effetti e degli spandimenti protratti nel medio periodo"), financially supported by Servizio Sviluppo Agroalimentare and carried out in conjunction with Servizio Geologico, Sismico e dei Suoli, we investigated the natural pedogeochemical content of five metals (Cr, Ni, Pb, Cu and Zn) within soils of a pilot area.

The study area, located in SW Po Plain, between the Apenninic chain and Po River, corresponds to Sheet 181 ("Parma Nord") of Soil Map of Italy to 1:50,000 scale (Figs. 1 and 2). The primary aim of this study is the construction of a prototypal map, which is called here Pedogeochemical Map, aimed at defining a realistic representation of the natural content of heavy metals in soils, providing preliminary information about their pollution state. Specific goal is the definition of the major factors controlling elements distribution in different soil types. The five

metals considered in this study correspond to those included in Italian D.lgs. 99/92, which provides directives about the use of sewage sludge in agricultural soils.

Superficial geology and pedological setting of Sheet 181

Sheet 181 is located at the southern margin of the Po Plain, NW of the town of Parma. The area is not heavily urbanized, with the exception of its SE part, corresponding to Parma suburbs. The main soil use is for agricultural practice, while industrial activities are subordinate. A series of roughly parallel, SW-NE trending rivers, namely, from west to east, Ongina, Stirone, Taro and Parma, cross the study area, flowing into Po River. Drainage-basin composition of these rivers is varied, and its description is beyond the scope of this paper. Given, however, the important role of Ni and Cr as provenance indicators (Amorosi et al., 2002; 2007; Amorosi and Sammartino, 2005; 2007), we stress here the presence, in the northern Apennines, of ultramafic rocks cropping out extensively within the Taro River drainage basin, whereas Ongina, Stirone, and Parma drainage basins are virtually ophiolite-free (see Fig. 2).

The major geological features of the study area are: i) fluvial terrace and alluvial fan deposits of the Apennines foothills, cropping out in the SW portion of Sheet 181, close to the basin margin; ii) alluvial plain deposits of Apenninic provenance, representing the bulk of the study area; iii) fluvial deposits related to the Po River, which flows in the NE portion of Sheet 181.

Single terrace units are observed at distinct topographic heights, and generally include thin fining-upward fluvial sequences, capped by a variable thickness of colluvial material. Alluvial-fan deposits consist predominantly of thick successions of fluvial-channel gravels and sands, generally with fining-upward tendencies and upward transition to fine overbank and/or colluvial material.

The alluvial plain depositional system can be subdivided into two major facies associations: channel/levee and floodplain deposits, respectively. Channel deposits consist predominantly of medium to coarse sand, whereas crevasse and levee deposits are made up of sandy silt to fine sand. Floodplain deposits, corresponding to overbank fines, consist of silt and clay, with rare, thin sand intercalations.

The pedological framework for the study area is provided by the Geological Survey of Regione Emilia-Romagna Soil Map to 1:50,000 scale (Sheet 181), where 31 different soil units have been mapped. For purposes of geochemical characterization, soil units were assembled, on the basis of their different degree of soil weathering, into three major groups, which are shown in Figure 3:

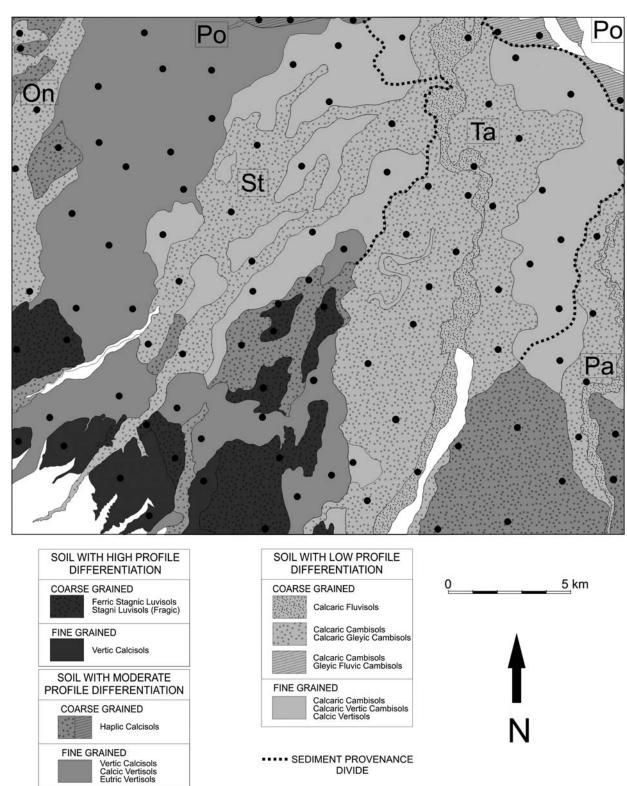
- i) Soils with high degree of weathering. These soils, which are restricted to the SW part of the study area, developed at top of comparatively old (pre-Holocene) substrates, corresponding to fluvial terrace deposits cropping out at the Apennines foothills.
- ii) Soils with moderate degree of weathering, developed on top of Holocene sediments of pre-Roman age. This group includes soils of both Apenninic and Po River provenance.
- iii) Soils with low degree of weathering, developed on alluvial plain sediments of post-Roman age. This group includes soils of both Apenninic and Po River provenance.

Methods

A total of 200 samples were collected in 100 selected sites by hand-drillings, using Eijkelkamp Agrisearch equipment. Two different sets of samples were collected at each site, within depths of 20-30 cm and 90-100 cm, respectively. Selection of sampling sites was not performed through regular grids, but finalized to cover the wide spectrum of individual soil units reported by the Soil Map, following the indications of ISO/DIS 19258.

Chemical analyses were conducted up to standard indications ISO/DIS 19528 on 90-100 cm deep samples, using X-ray fluorescence spectrometry (XRF), for determination of total pedogeochemical content. For the estimation of geochemical anomalies, analyses of samples collected within a depth of 20-30 cm were duplicated, using both XRF and inductively coupled plasma mass spectrometry (ICP-MS), with aqua regia digestion (Als Chemex Laboratories, Vancouver, Canada, code ME-MS41).

XRF analyses, including major and trace elements, were conducted at Dipartimento di Scienze della Terra e Geologico-Ambientali of Bologna University. Soil samples, pressed into tablets, were analyzed for major and trace elements



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Fig. 3 - Synthetic Soil Map of Sheet 181 ("Parma Nord"), showing location of sampling sites. Different provenance domains are distinguished uniquely for soils with low degree of weathering. On: Ongina River, Pa: St: Stirone River, Ta: Taro River, Po: Po River, Parma River.

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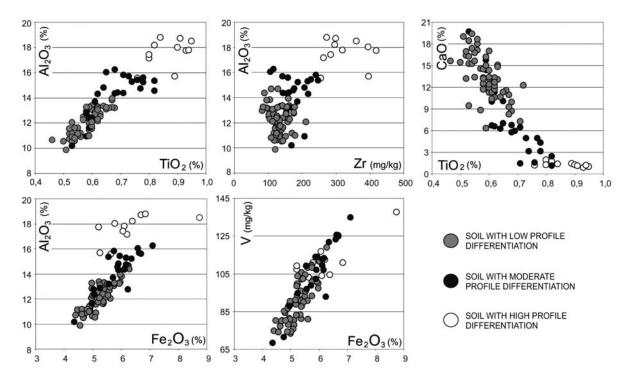


Fig. 4 - Scatterplot diagrams of selected geochemical indicators, showing changes in geochemical composition as a function of soil maturity.

in a Philips PW1480 spectrometry with a Rh tube, using matrix correction methods of Franzini et al. (1972), Leoni and Saitta (1976) and Leoni et al. (1982). Reference samples, such as sample JB-1A (GSJ reference sample, Imai et al., 1995) were also analyzed. The accuracy of determinations for trace-elements is 5% (<3% for Cr, <2% for Ni, about 2% for Cu, about 3% for Zn), except for elements with concentration of 10 ppm or lower, where the accuracy is 10-15%.

Geochemical characterization of soils

The following sections explore the major geochemical features of soils in the study area, through a selection of diagrams that summarize peculiar geochemical characteristics as a function of degree of weathering and sediment provenance.

Soil composition as a function of weathering

A set of scatterplot diagrams shows that soils with peculiar degree of weathering can be distinguished on the basis of distinctive geochemical attributes, with very few exceptions (Fig. 4). Specifically, soils with high degree of weathering invariably display the highest concentrations of Zr, V, TiO₂, Al₂O₃ and Fe₂O₃. These geochemical indicators are reciprocally characterized by strong positive correlation and show progressive decreasing values with decreasing soil maturity (Fig. 4). In contrast, soils with low degree of weathering display the highest CaO concentrations.

The abundance of Ti, Zr and V within high-maturity soils indicates that these elements are immobile within the soil profile and resistant to eluviation processes (Boyle, 2007). High Al₂O₃ and Fe₂O₃ values are likely to be due to accumulation of clays and Fe/Al hydrous oxides within illuvial deposits. The positive correlation between these geochemical indicators reflects their affiliation to the same mineral phases, and the tendency of selected minerals to concentrate as part of the same deposit. On the other hand, the inverse correlation between CaO values and soil maturity can be interpreted to reflect calcium loss due to leaching processes during pedogenesis.

The very scarce overlap between the three groups of soils documents the suitability of the scatterplots of Figure 4 to provide a geochemical

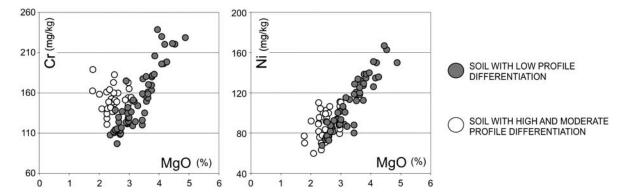


Fig. 5 - Scatterplot diagrams, showing increase in natural Cr and Ni concentrations as a function of increasing soil maturity.

characterization of soils as a function of soil maturity. In particular, soils with high degree of weathering have a marked tendency to plot into distinct fields of the scatterplot diagrams, while soils with moderate and low degree of weathering tend to coalesce. This is probably due to stronger pedologic differences between Pleistocene and Holocene soils, rather than between pre-Roman and post-Roman soils. Rare deviations from these trends (see a couple of black dots in Fig. 4) could reflect sampling inaccuracy (local sampling of colluvial material) or possible local errors in the soil map.

Metal distribution as a function of sediment provenance

Previous work on soil samples from the Po Plain has shown that chromium, nickel and magnesium, which reflect the ultramafic fraction of sediment, can be regarded as reliable provenance indicators for this area, providing an obvious distinction between a Po River-related (Cr, Ni and Mg-rich) province and an Apenninic (Cr, Ni and Mg-poor) province (Amorosi and Sammartino, 2005; 2007). These studies, however, dealt almost uniquely with deposits of post-Roman age (*i.e.*, soils with low degree of weathering).

In order to account for the relative effect of soil maturity and sediment provenance on natural Cr and Ni concentrations in the study area, we plotted first our data into two binary diagrams (Cr/MgO and Ni/MgO), with a subdivision into soils of post-Roman age and soils developed on older deposits (Fig. 5). It is apparent that Cr, Ni and Mg display clear positive relationships in samples from soils with low degree of weathering, whereas

relative metal enrichments are observed within higher-maturity soils. Particularly, remarkable Cr concentrations are observed within pre-Roman soils, which are invariably enriched in this metal with respect to their younger counterparts. This specific distribution suggests an affinity of Cr for mineral phases resistant to weathering processes, such as those belonging to the chromium-bearing spinel group (chromite) or the garnet group (uvarovite).

A set of boxplots (Fig. 6) can be used to depict geochemical attributes of soils with low degree of weathering, and thus emphasize the role played by sediment provenance on pedogeochemical content. As expected, Cr, Ni and MgO display remarkable differences as a function of the different sediment sources, and enable the identification, within the study area, of distinct provenance domains. Sediments supplied by Po River show the highest Cr, Ni and Mg contents. Among the Apenninic rivers, Taro River sediments are considerably enriched in Cr, Ni and Mg, although with slightly lower values than Po sediments. On the other hand, very low values of these geochemical indicators characterize Parma, Stirone and Ongina deposits.

Strontium mirrors the geochemical behaviour of Cr, Ni and Mg, showing the lowest value for Po River sediments, and increasing concentrations from Taro to Parma river sediments (Fig. 6).

Natural concentrations of other potentially toxic metals, such as Cu, Zn and Pb, exhibit a considerably different behaviour (Fig. 7). In these instances, except for relatively lower Cu values in sediments from Po River and higher Zn concentrations in sediments from Ongina River, the boxplots show substantial overlap, irrespective of



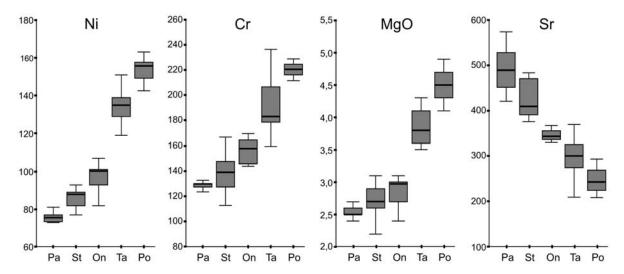


Fig. 6 - Boxplots of selected geochemical indicators from soils with low degree of weathering, showing the influence of sediment provenance on natural metal distribution. Each provenance domain is clearly fingerprinted by a peculiar geochemical composition (see text). The lower boundary of the box is the 25th percentile, the upper boundary is the 75th percentile, the bold line within the box corresponds to the median, the "whiskers" define the minimum and maximum values. Pa: Parma River, St: Stirone River, On: Ongina River, Ta: Taro River, Po: Po River.

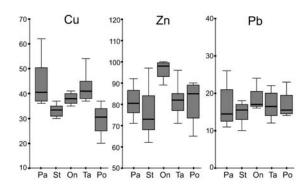


Fig. 7 - Boxplots of selected geochemical elements from soils with low degree of weathering, showing scarce (Cu, Zn) or no influence (Pb) of sediment provenance on natural metal distribution. Keys as in Fig. 5.

the different sediment sources. This can be especially seen for Pb.

This study confirms previous hypotheses about soil metal distribution in the Po Plain. The very high Cr, Ni and Mg contents observed in Po-derived sediments, combined with the slightly lower values observed in sediments from Taro River, support the interpretation of a natural provenance from ultramafic complexes (see distribution of ophiolitic rocks in Fig. 2). Chromium and nickel concentrations in Po River sediments average 217 and 151 ppm, respectively, while 192 and 134 ppm are recorded for sediments of Taro River. These values are significantly higher than maximum

concentrations admitted by Italian legislation for parks and residential areas (150 ppm for Cr and 120 ppm for Ni).

Higher CaO values of Parma and Stirone river sediments are interpreted to reflect the peculiar lithologic composition of the related drainage basins, which include abundant carbonate rocks. Similar contents of Cu, Zn and Pb indicate that sediment provenance did not exerted a significant control on spatial distribution of these metals across the study area.

The Pedogeochemical Map of Sheet 181

The Pedogeochemical Map of Sheet 181 is composed chiefly of two geochemical maps that summarize the results illustrated in the previous sections: i) Map of Pedogeochemical Content, and ii) Map of Geochemical Anomalies. Pedogeochemical maps of two selected metals (Ni and Cu), with opposite behaviour, are shown in Figures 8 and 9 for comparison.

Map of Pedogeochemical Content

This map (Fig. 8) results from the geochemical characterization of soils shown in the previous sections and is based on XRF data from 100 soil samples collected within a depth of 90-100 cm (black dots in Fig. 8). This map represents an in-

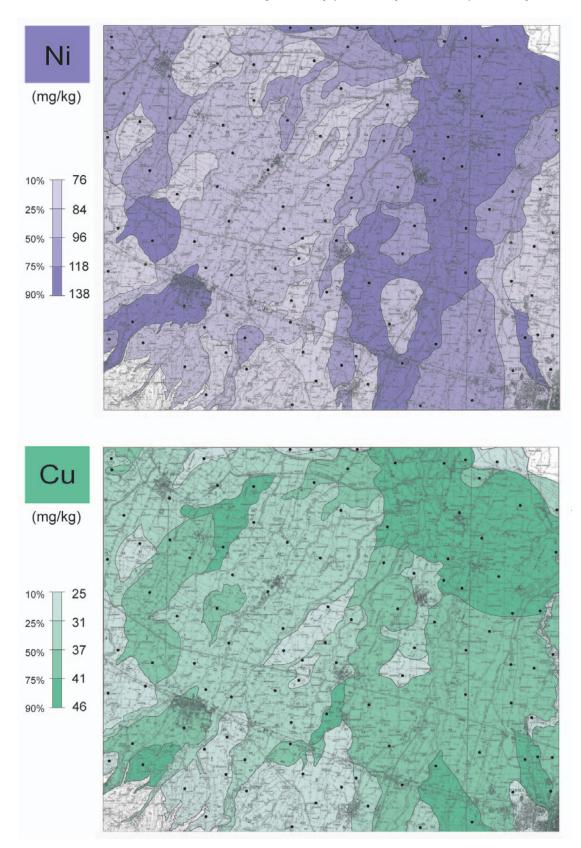


Fig. 8 - Map of Pedogeochemical Content of Ni and Cu, based upon metal contents at 90-100 cm depth.

I _{geo}	I _{geo} class	Designation of soil quality
< 0	0	Unpolluted
0-1	1	From polluted 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).

novative product in the field of geochemical mapping, combining soil and sedimentological features with traditional statistical interpolation methods, such as kriging (see discussion in Amorosi and Sammartino, 2005).

Different metal contents are indicated by tones of the same colour, darker shades corresponding to higher concentrations. Four classes are mapped for each metal, and boundaries between classes are calculated on a statistical basis on the whole data set (25th, 50th, 75th percentile concentrations, expressed as mg/kg), following recommendations of ISO/DIS 19258.

The geochemical characterization of soil units constitutes the guide to the construction of these maps. The boundaries for each class represent the lowest and the highest metal concentrations, respectively, which are expected for a specific soil type in a given site. As a consequence, metal concentrations higher than those predicted by the Map of Pedogeochemical Content are very likely to reflect an anthropogenic influence.

Comparison between the Map of Pedogeochemical Content and the soil map (see Fig. 3) allows prompt interpretation of metal distribution on a pedological basis, as a function of sediment provenance and soil weathering. In the case of Ni (Fig. 8a), the very good overlap observed between these two maps, with the highest Ni contents recorded in coincidence of alluvial sediments supplied by Po and Taro rivers, is fully consistent with interpretation of Ni provenance from the ultramafic complexes of the related drainage basins (Figs. 1 and 2). On the other hand, remarkably lower Ni values are observed for Ongina, Stirone and Parma rivers, whose drainage basins do not include ophiolites.

A totally different picture is observed where natural metal distribution does not appear to be controlled by sediment provenance. This is the case for Cu, Zn and Pb (see also the boxplots of Fig. 7), where Maps of Pedogeochemical Content do not show an important overlap with the soil map, and are traced mostly according to traditional statistical methods (Fig. 8b). Lead distribution, however, displays relative concentration within soils with higher degree of weathering.

Map of Geochemical Anomalies

For a reliable estimate of the anthropogenic disturbance, the natural pedogeochemical content resulting from samples at 90-100 cm depth was matched against metal concentrations observed within topsoil samples (20-30 cm depth) collected at the same sites. To this purpose, chemical analyses were conducted using the same analytical procedure (XRF), and metal pollution evaluated using the Index of geoaccumulation (I_{geo}) proposed by Müller (1979) and Förstner and Müller (1981):

$$I_{geo} = log_2 C_n / (1.5*B_n)$$

where C_n is the content of the element n at 20-30 cm depth and B_n is the pedogeochemical content of the same element at 90-100 cm depth.

On the basis of $I_{\rm geo}$, the pollution status of soils can be differentiated into seven classes (Table 1), from <0 to 6 (Müller, 1981; Banat et al., 2005; Sainz and Ruiz, 2006). The highest value of $I_{\rm geo}$ (6 in Table 1) reveals metal concentrations 100 times higher than background concentrations.

The index of geoaccumulation provides an obvious indication of the pollution status of the study sites, with reference to a specific metal (Fig. 9). Soil quality is indicated by dots, the colours of which reflect the classification scheme of Müller (1981). Green colours are indicative of non-contamination, while yellow and red dots correspond to slightly- to moderately polluted soils. Two values of metal concentration are reported for each sampling site: both are related to 20-30 cm deep samples, and expressed in mg/kg. Numbers in upper position reflect metal concentrations obtained by ICP-MS analysis, while values in lower position, are derived from XRF analysis.

When metal contents exceed maximum concentrations admitted by the law (D.M. 471/99 and D. lgs. 99/92), they are shown in red. Metal concentrations measured by XRF analysis are generally higher than those calculated on the same

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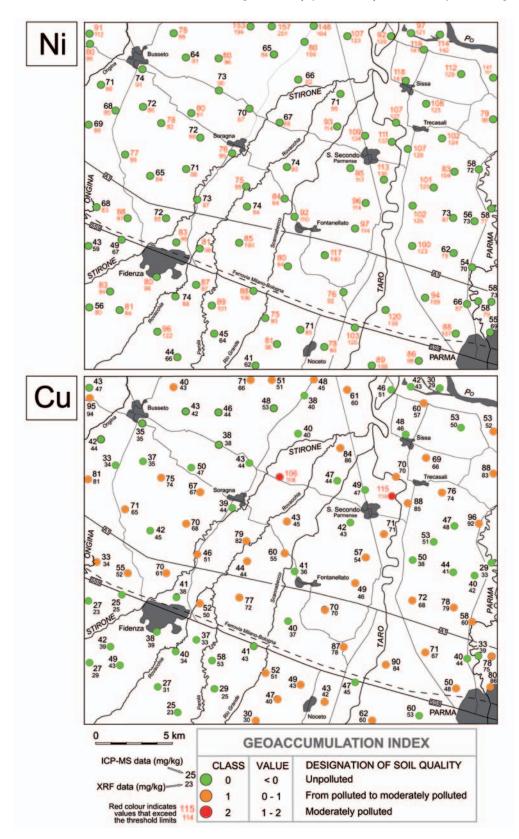


Fig. 9 - Map of Geochemical Anomalies of Ni and Cu, based upon metal contents at 20-30 cm depth versus 90-100 cm depth. Metal concentrations exceeding threshold limits (in red) may reflect either natural (Ni) or anthropogenic (Cu) origin.

samples by ICP-MS, which involves incomplete digestion (Rauret, 1998; Ianni et al., 2001), especially for Cr and Ni.

There is no indication of contamination from Ni (and Cr) in the study area (Fig. 9a), whereas a diffuse moderate contamination by Cu (Pb and Zn) can be observed, especially in areas subjected to agricultural practice (Fig. 9b). It should be kept in mind, however, that point information obtained from the 100 study sites can not be extrapolated outside these areas, and that specific, local studies should be undertaken in order to detect precisely sources of anthropogenic contamination.

Practical use of the Pedogeochemical Map

In summary, the Pedogeochemical Map represents a powerful tool which can be used pragmatically: i) to understand soil metal distribution as a function of soil maturity and sediment provenance; ii) to separate the anthropogenic contribution from pedogeochemical content, and thus delineate geochemical anomalies. Specifically, accurate intersection of the Map of Pedogeochemical Content with the Map of Geochemical Anomalies enables precise interpretation of metal distribution and may be of help in making sound environmental decisions.

The Map of Geochemical Anomalies of Ni and Cr (Fig. 9a) show uniform low $I_{\rm geo}$ values in all the study stations (green dots), which is a clear indication of unpolluted soils. The abundance of red

numbers, indicating Ni contents exceeding threshold limits, is not by itself diagnostic of soil contamination. Being coupled with green dots (which means that no metal enrichment is recorded in topsoil samples with respect to local pedogeochemical content), the red numbers indicate that the high Ni contents recorded in the Po and Taro river areas are not related to anthropogenic disturbance, but simply reflect high background concentrations of this metal in soils, owing to geogenic factors (see Fig. 8a). As documented by Sammartino (2004) in the Romagna coastal plain, high natural amounts of Cr and Ni, resulting from erosion of ultrafemic complexes, are not bioavailable, and thus not dangerous for human health.

Copper displays an opposite behaviour (Figs. 8b and 9b). Despite its relatively low concentrations, shown by black numbers on the Map of Geochemical Anomalies (indicating values below threshold limits for Cu), half of the study sites appear as slightly contaminated (yellow dots). In two cases (Soragna and San Secondo Parmense areas, respectively), soils are defined as "moderately polluted" (red dots) and Cu concentrations are beyond threshold limits. These areas require specific attention for environmental protection.

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