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Review Article

The Chromium and Nickelgeochemical Provinces of Emilia-Romagna Region

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1. Abstract

The definition of geochemicalprovinces in literature coincide with that of "areas with positive anomalies" with respect to this conceptwe need to establish what is the threshold value that identifies the anomaly and what is the matrix / depth of exploration to which reference is being made. The present document identifies as positive anomalies the areas characterized by soils whose underlying value exceeds the threshold values for the public and residential green areas of Italian Legislative Decree 152/06, distinguishing between pedo-geochemical content and background content. In this perspective chromium and nickel maps produced by Emilia-Romagna Region are reinterpreted.

2. Introduction

From 2005 until today the Geologicalseismic and soilsurvey of Emilia-Romagna Regionhas started a process of knowledge on the content of some potentiallytoxicmetals in the soils of the alluvialplainwhich led to the publication of thirteenmaps on the scale 1: 250.000 with relative explanatorynotes and several indepth studies [1].

The cartographyproducedisbased on analytical data of 770 sampling points which are also soil observations related to soil types, and describes the areal distribution of the concentration of metals within 150 cm of depth.

The appliedmethodology is the ISO / DIN 19258: 2005 standard "Soilquality: guidance on the determination of background values"; forchromium, nickel, copper, lead, vanadium and zinc pedo-geochemical and background contentmaps have been drafted, for tin and arsenicthere are currently only background maps [2].

3. Pedo-Geochemicalmaps

Assumingthat the metals are always naturally present in the soil, the units of the pedo-geochemical maps are soil groups with geochemical affinities (Genetical Functional Units -GFU, **Table 1**) identified on the basis of the same provenance (of the parental material), texture and degree of weathering: (**Figures 2 and 3**). For the purpose of a better understanding of the pedological data, the environmental characterization has been added, which identifies both the environmental complexes (macro-environ-

ments such as delta, alluvialplain, etc.) and the depositional environments to which the UGF can be attributed [3].

Table 1: Pedological and geological features of the Genetical-Functional units (GFUs) that form the Pedogeochemical Map of the Emilia-Romagna plain (WRB, 2006).

Unit	Diagnostic features		Environmental features
Code	Soil	Sedimentprovenance	Depositionalenviron- ment
A1	Medium to fine-textured, high degree of weathering	Mixed (from Apenninic sources with extremely variable ophiolitic contribu- tion)	Alluvial fan, interfluve, fluvialterrace (indifferen- tiated)
	StagnicLuvisols, VerticCambisols		
A2	Fine-textured, low to moderate degree of weath- ering	Apenninic sources, with no ophiolitic contribution	Alluvial plain
	VerticCambisols, HyposalicVerti- sols, CalcicVer- tisols		Floodplaindeposits
А3	Fine-textured, low to moderate degree of weath- ering	Mixed Po-Apenninic sources, with moderate to high ophiolitic contribution	Alluvial plain
	VerticCambisols, CalcicVertisols, EutricVertisols		Floodplaindeposits
A4	Fine-textured, low to moderate degree of weath- ering	- Po River	Delta (delta plain)
	VerticCambisols, CalcicVertisols, HyposalicVertisols		Interdistributary area deposits

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B1	Moderately fine-textured to moderately coarse-textured, with rare gravels, low to moderate degree of weathering Haplic Cambisols, Haplic Calcisols	Apenninic sources, with no ophiolitic contribution	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B2	Moderately fine- textured to moder- ately coarse- textured, with rare gravels, low to moderate degree of weathering	Mixed (mostly from Apenninic sources, with moderate ophiolitic contri- bution: Enza, Baganza and Tresinaro rivers)	Alluvial plain and alluvial fan
	HaplicCambisols, HaplicCalcisols		Channel-levee and crevasse deposits
вз	Moderately fine- grained to moder- ately coarse- grained, with rare gravels, low to moderate degree of weathering	Apenninic sources, with moderate to high ophiolitic contribution (Arda and Taro rivers)	Alluvial plain and alluvial fan
	Haplic Cambisols, Haplic Calcisols		Channel-levee and crevasse deposits
В4	Medium to moder- ately coarse- textured, low to moderate degree of weathering	Po River	Alluvial plain and alluvial fan
	HaplicCambisols, HaplicCalcisols		Channel-levee and crevasse deposits
B5	Moderately fine-grained to moderately coarse-textured, with abundant gravels, low to moderate degree of weathering	Apenninic sources, with high ophiolitic contribution (Trebbia and Nure rivers)	Alluvial plain and alluvial fan
	HaplicCambisols, HaplicCalcisols		Channel-levee and crevasse deposits
В6	Medium to moder- ately coarse- textured, low to moderate degree of weathering	Po River	Delta (delta plain)
	HaplicCambisols, HaplicCalcisols		Distributary channel-levee and crevassedeposits
C1	Coarse-textured, low degree of weathering	Apenninic sources, with no ophiolitic contribution	Coastal plain
	EndogleyicAre- nosols		Beach-ridge deposits
C2	Coarse-textured, low degree of weathering	Po River	Delta (delta front)
	EndogleyicAre- nosols		Beach-ridge deposits

D1	With organic horizon	Po River	Delta (delta plain)
	Thionic Histosols, Thionic Fluvisols		Interdistributarybayde- posits

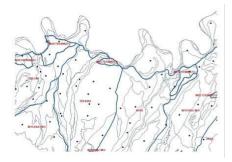


Figure 2: Identification of soilgroups with geochemical affinity.

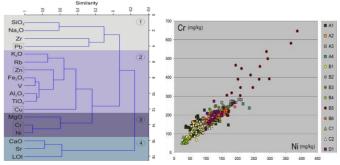


Figure 3: Identification of genetically related groups of data through R-mode cluster analysis and check through geochemical markers.

Eachunit (GFU) has a range of content for the various metals and is characterized by its "pedo-geochemical value" corresponding to the 95th percentile of its data population, after elimination of outliers.

The map representation hasbeendrafted by attributing the poligons of the soilmap to the GFU on the basis of dominantsoils, subsequentlyeachpoligonhasbeenclassedfor each metal the legend is centered on the threshold value (x) related to the use of soil for parks and residential areas (D.lgs 152, 2006). Each map consists of up to four classes: two classes are related to natural metal concentrations lower than the threshold value, while the other two correspond to natural metal concentrations higher than the permitted level. Darker shades of the same colour indicate progressively higher metal concentrations [4]. The lower two classes in each map are separated by metal content equal to x/2, while the upper two classes are separated by metal content equal to 3/2x. This simple structure makes the Map of the pedogeochemical content readily usable for legislation purposes. From lighter to darker shades, the four classes can indeed be referred to, respectively, as: "significantly below", "below", "above" and "significantly above" the threshold value (Figure 4).

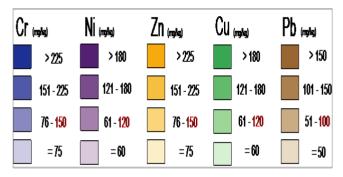


Figure 4: Legend of the five Maps of the Geochemical Content (see text). The red numbers indicate the maximum permitted levels according to the Italian legislation.

4. Chromium and Nickel

The map of the hydrologicalbasinsidentifies the sedimentprovenance for each riverbed: crossing it with the geological map can be identified the formation of each basin and subsequently, with the geochemical analysis on soils, the relationships between rock-types and metal content.

The cluster analysis reported above (**Figure 3**) showed that chromium and nickel are positively correlated in Group 3 whichrepresents the mineralogical associations referable to ultrafemicrocks and therefore in basins with ophiolitic rocks soil will have a high ercontent of chromium and nickel . With the term "ophiolitic rock" weintendboth the form ations that contain ophiolitic bodies and the arenaceous or conglomeratic for mations who sepetrographiccompositionis revealing the origin from an ancient area-source typeophiolite. For eachbasin the area extensions of the ophioliteunits were calculated (**Figures 4, and 5**) and related to the ophiolitic content of the Genetical Functional Units [5,6].

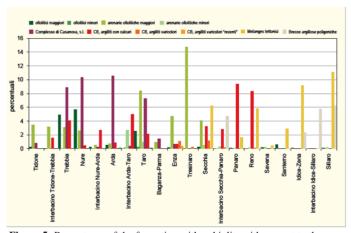


Figure 5: Percentages of the formation with ophiolits with respect to the area of each riverbasin.

In the Emilia-Romagna there are also areas of Po riverpertinence, which are located in the alluvialplainat the boundary with LombardyRegionand in the area of the Poancient delta; they can be considered as a medium to high-level ophiolite basinthat in the portion of the alpine archwhich constitutes Po Riverhydrographic basinthere are several extensive ophiolithic complexes (**Figure 8**).

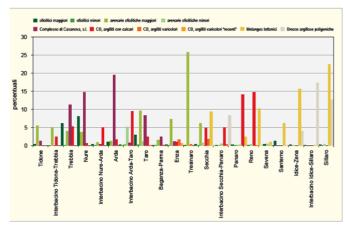


Figure 6: Percentages of the formation with ophiolits with respect to the mountain area of each riverbasin.

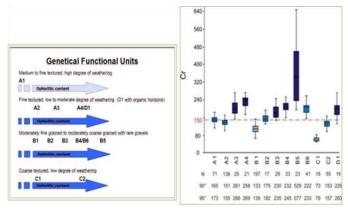


Figure7: Scheme of Units (GFU) in relation to the ophiolitic content with relative chromium content expressed in mg/kgss.



Figure 8: Simplifiedgeologicalmap of the Emilia-Romagnaplain (modifiedfrom RegioneEmilia-Romagna, 1999).

The geochemical provinces of chromiumcan be identified both through the Pedo-geochemicalmapat 1: 250.000 scale (Figure 9), and through the hydrographic basins and relevant interbacinal areas classified according to their ophiolitic contentat a scale of about 1: 100.000.000 (Figure 10): the concentration values in the individual basins will vary according to the unitspresent in the pedo-geochemical map [7,8].

The Genetical Functional Unitsthatrepresent positive anomalies for chromium (in according to **Table 1**) A3, B2, B3, B4, B5 for the Apennines pertinence; A4, B6, D1 in the plain of the ancient delta of the Po and C2 on the coast. The basins that constitute a positive anomaly compared to threshold values of en-

vironmental Decree 152/2006 are those of: F.Trebbia, T. Nure, T.Arda, F.Taro, T Baganza, T.Enza, T.Tresinaro in order of decreasing content [9].

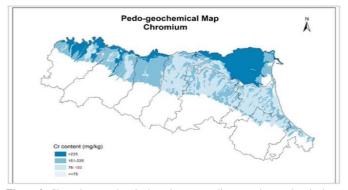


Figure 9: Chromiumgeochemicalprovinces according to pedo-geochemicalmap.

CARTA DEI BACINI



Figure 10: Chromium geochemical provinces according to the map of hydrological basins classified by ophiolitic content. Scale 1: 1000,000 (ed.2012).

The analogy between the are aldistribution of the chromium content and that of the nickel contentin soilisvery strong because, as already mentioned, they are affected by the same determining factor of origin and the twopedo-geochemical map of chromium and nickelhave a verysimilar pattern (Figure 10); the nickel contentalthough well correlated, in basins with moderate ophiolitic component loses visibility because it is not represented by the classes provided for by the map (**Figure 11**).

5. Background Maps

The background content of metals in soilsis relative to the top soil and there fore influenced not only from the intrinsic geochemical characteristics but even from atmosphericall out and agronomic management [10-13].

Geochemical provinces can also be found in the background map: in this case they are notonlydue to the natural content but to the antropogenic factors that have led to positive anomalies (ISO 19258: 2005).

The cartographic units are no longer just the Genetical Functional Unitsbut the UGF divided for Agricultural District and for each population of data the background values corresponding to 95 percentile after elimination of outliers (**Figure 12**).

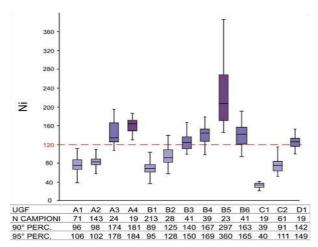


Figure 11: Nickel content of GeneticalFunctionUnitsexpressed in mg/kgss.

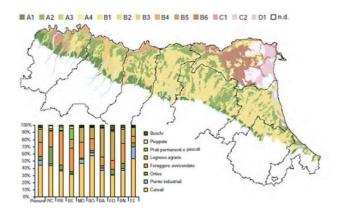


Figure 11: Geografical distribution of GFU and of agricultural districts.

Values are determined by the direct water extraction method associated with the ICP-Mass reading (UNI 13346 + EPA 6020) and expressed in mg /kgss; this analitical methodunlike the XRF method, represent the pseudo total content and therefore gives lower values.

To elaborate the data, simulation geostatistics were used on a 1Kmq using the data of the agricoltural census as proxy: the 95th percentile simulated assigned to the centroid of each Finished Square Element, which is then assigned to the relevant concentration class. Also in this case the values were classified on the basis of the Threshold Value for the residential areas of Chromium and nickel

The trend of the concentrations of the two metals in the topsoil is quite similar to that of the subsoil confirming that the most important factor determining the contentis the parent material provenance.

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