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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 thisconceptwe need to establishwhatis the thresholdvaluethatidentifies the anomaly and whatis the matrix / depth of exploration to whichreferenceisbeing made. The presentdocumentidentifiesas positive anomalies the areascharacterized by soilswhoseunderlyingvalueexceeds the thresholdvalues for the public and residential green areas ofItalian Legislative Decree 152/06, distinguishingbetweenpedo-geochemicalcontentand background content. In thisperspectivechromium and nickel mapsproduced 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 in-depth studies [1].

The cartographyproducedisbased on analytical data of 770 sampling points which are alsosoilobservationsrelated to soiltypes, and describes the arealdistribution of the concentrationof metalswithin 150 cm of depth.

The appliedmethodologyis 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 contentmapshavebeendrafted, for tin and arsenicthere are currentlyonlybackground maps [2].

3. Pedo-Geochemicalmaps

Assumingthat the metals are always naturallypresent in the soil, the units of the pedo-geochemicalmaps aresoilgroups with geochemicalaffinities (Genetical Functional Units -GFU, **Table 1**) identified on the basis of the sameprovenance (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 characterizationhasbeen added, whichidentifiesboth the environmental complexes (macro-environments such as delta, alluvialplain, etc.) and the depositionalenvironments 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**	**Depositionalenvironment**
A1	Medium to fine-textured, high degree of weathering	Mixed (from Apenninic sources with extremely variable ophiolitic contribution)	Alluvial fan, interfluve, fluvialterrace (indifferentiated)
	StagnicLuvisols, VerticCambisols		
A2	Fine-textured, low to moderate degree of weathering	Apenninic sources, with no ophiolitic contribution	Alluvial plain
	VerticCambisols, HyposalicVertisols, CalcicVertisols		Floodplaindeposits
A3	Fine-textured, low to moderate degree of weathering	Mixed Po-Apenninic sources, with moderate to high ophiolitic contribution	Alluvial plain
	VerticCambisols, CalcicVertisols, EutricVertisols		Floodplaindeposits
A4	Fine-textured, low to moderate degree of weathering	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	Apenninic sources, with no ophiolitic contribution	Alluvial plain and alluvial fan
	Haplic Cambisols, Haplic Calcisols		Channel-levee and crevasse deposits
B2	Moderately fine-textured to moderately coarse-textured, with rare gravels, low to moderate degree of weathering	Mixed (mostly from Apenninic sources, with moderate ophiolitic contribution: Enza, Baganza and Tresinaro rivers)	Alluvial plain and alluvial fan
	HaplicCambisols, HaplicCalcisols		Channel-levee and crevasse deposits
B3	Moderately fine-grained to moderately 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
B4	Medium to moderately 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
B6	Medium to moderately 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
	EndogleyicArenosols		Beach-ridge deposits
C2	Coarse-textured, low degree of weathering	Po River	Delta (delta front)
	EndogleyicArenosols		Beach-ridge deposits
D1	With organic horizon	Po River	Delta (delta plain)
	Thionic Histosols, Thionic Fluvisols		Interdistributarybaydeposits

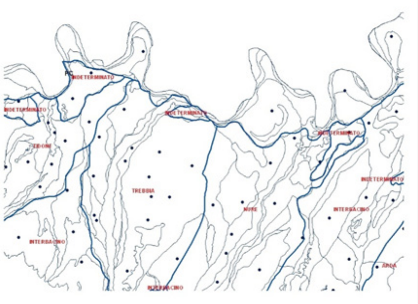

Figure 2: Identification of soilgroups with geochemical affinity.

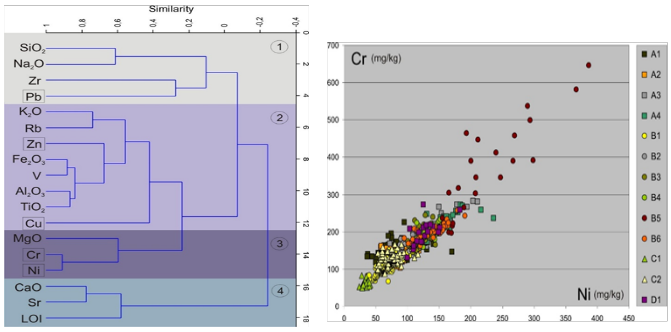

Figure 3: Identification of geneticallyrelatedgroups of data through R-mode cluster analysis and check throughgeochemical markers.

Eachunit (GFU) has a range of content for the variousmetals and ischaracterized by its "pedo-geochemicalvalue" corresponding to the 95th percentile of its data population, after elimination of outliers.

The map representation hasbeendrafted by attributing the polygons 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 pedo-geochemical 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**).

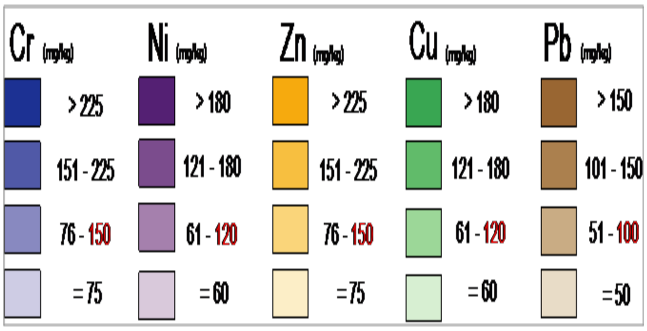

Figure 4: Legend of the five Maps of the Geochemical Content (see text). The red numbers indicate the maximum permitted levels according to the Italian legislation.

4. Chromium and Nickel

The map of the hydrologicalbasinsidentifies the sedimentprovenance for eachriverbed: crossing it with the geologicalmapcan be identified the formation of eachbasin and subsequently, with the geochemicalanalysison soils, the relationshipsbetween 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 sepetrographiccompositionisrevealing the origin from an ancient area-source typeophiolite. For eachbasin the area extensions of the ophioliteunitswerecalculated (**Figures 4, and 5**) and related to the ophioliticcontent of the Genetical Functional Units [5,6].

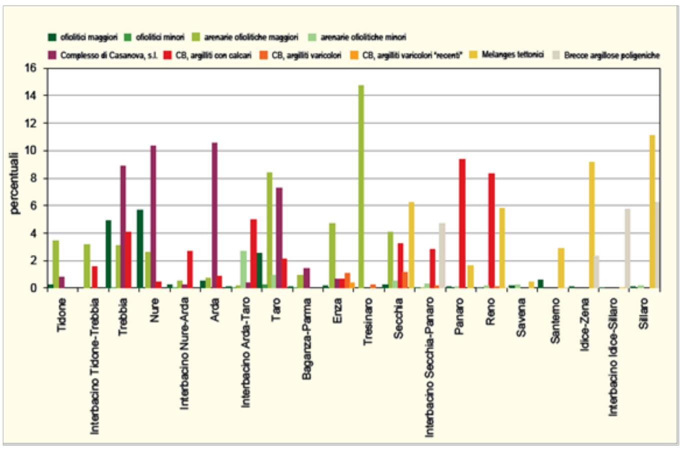

Figure 5: Percentages of the formation with ophiolits with respect to the area of eachriverbasin.

In the Emilia-Romagna there are alsoareas of Po riverpertinence, which are located in the alluvialplainat the boundary with LombardyRegionand in the area of the Poancient delta;they can be consideredas a medium to high-level ophiolitebasinthat in the portion of the alpine archwhichconstitutesPo Riverhydrographicbasinthere are severalextensiveophiolithiccomplexes (**Figure 8**).

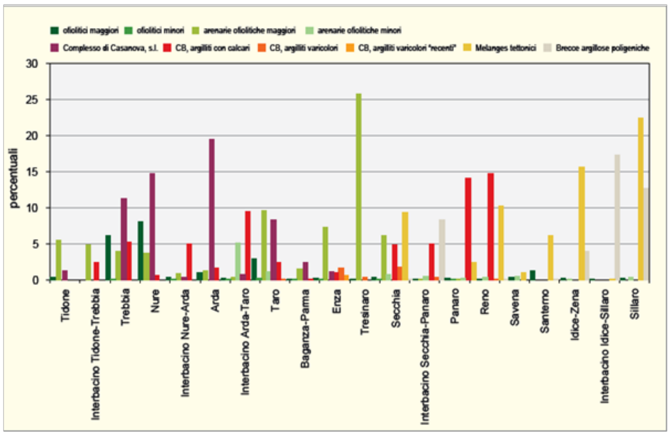

Figure 6: Percentages of the formation with ophiolits with respect to the mountain area of eachriverbasin.

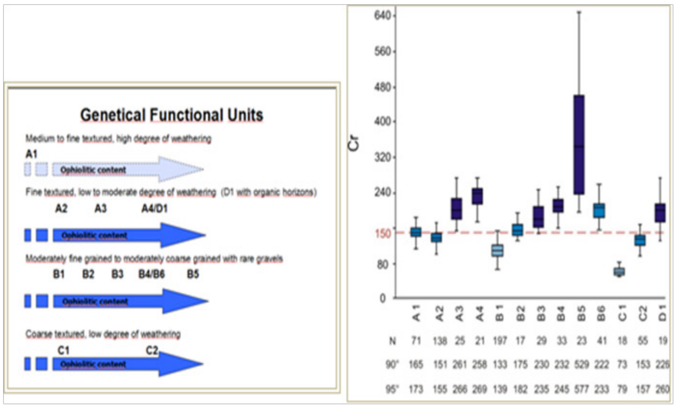

Figure7: Scheme of Units (GFU) in relation to the ophiolitic content with relative chromium content expressed in mg/kgss.

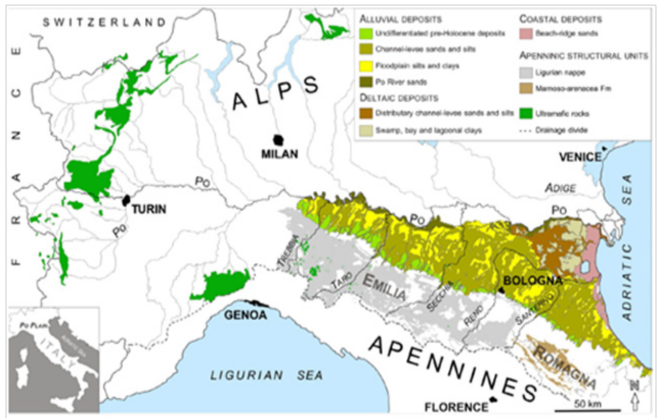

Figure 8: Simplifiedgeologicalmap of the Emilia-Romagnaplain (modifiedfrom RegioneEmilia-Romagna, 1999).

The geochemical provinces of chromiumcan be identified both through the Pedo-geochemicalmapat 1: 250.000 scale (Figure 9), and through the hydrographicbasins and relevant interbacinal areas classified according to their ophiolitic contentat a scale of about 1: 100.000 .000 (Figure10): 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 anomaliesfor chromiumare (in according to **Table 1**) A3, B2, B3, B4, B5 for the Apenninespertinence; A4, B6, D1 in the plain of the ancient delta of the Po and C2 on the coast. The basins that constitute a positive anomalycompared to thresholdvalues of environmental Decree 152/2006 are those of: F.Trebbia, T. Nure, T.Arda, F.Taro, T Baganza, T.Enza, T.Tresinaro in order of decreasingcontent [9].

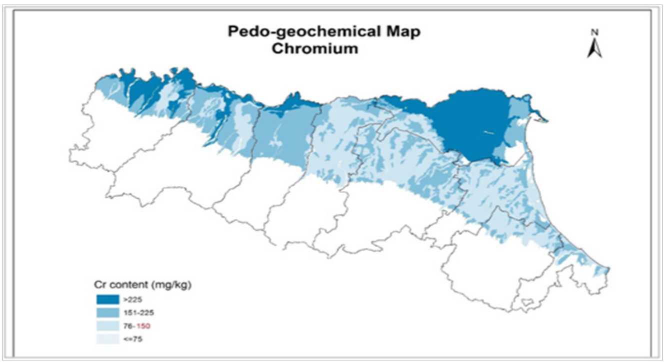

Figure 9: Chromiumgeochemicalprovincesaccording to pedo-geochemicalmap.

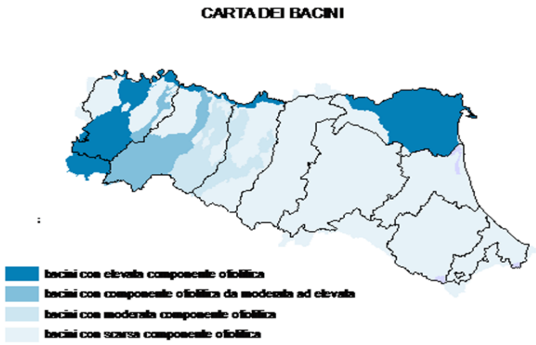

Figure 10: Chromium geochemical provinces according to the map of hydrological basins classified by ophiolitic content. Scale 1: 1000,000 (ed.2012).

The analogy between the are aldistribution of the chromiumcontent 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 atmosphericfall 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**).

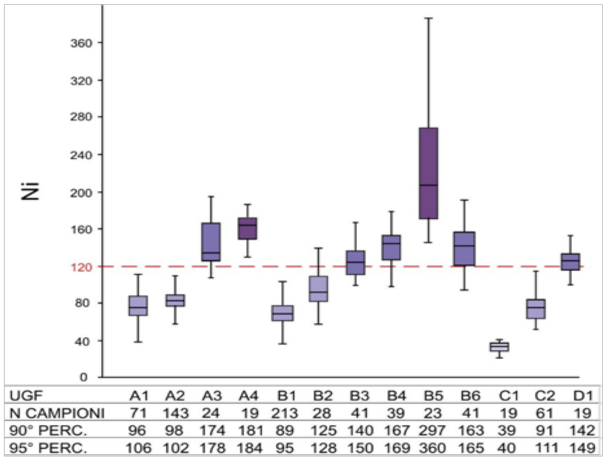

Figure 11: Nickel content of GeneticalFunctionUnitsexpressed in mg/kgss.

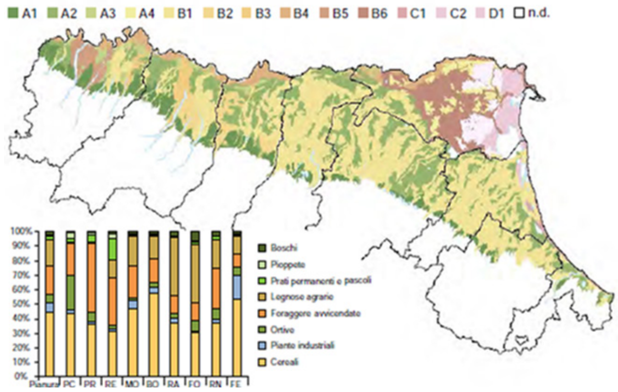

Figure 11: Geografical distribution of GFU and of agricultural districts.

Values are determined by the direct water extraction method associated with the ICP-Mass reading (UNI 13346 + EPA 6020) and expressed in mg /kgss; thisanalitical methodunlike the XRF method, represent the pseudo totalcontent and thereforegives 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 simulatedis 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 classi fied on the basis of the Threshold Value for the residentialareas 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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