

THE PEDOGEOCHEMICAL MAP

of the

Emilia-Romagna Plain

1:250,000 scale

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Explanatory Notes
2012

Cr

Ni

Zn

Cu

Pb

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1. INTRODUCTION

The aim of the Pedogeochemical Map of the Emilia-Romagna plain at 1:250,000 scale is to start up a process of basic knowledge of natural metal contents in soils. This issue is of paramount importance for the reliable estimate of soil contamination and to develop policies of environmental protection.

According to the Thematic Strategy for Soil Protection (COM 2006/231), soil is regarded as non-renewable resource. In an environmental perspective, D.lgs 152/06 considers soils as environmental matrix, like air and water. Soil also has several different functions and represents an essential support to human activities and to ecosystem survival.

The Pedogeochemical Map of the Emilia-Romagna plain, edited during a five-year period (2009-2012), represents the extension to the whole Emilia-Romagna region of the pilot study carried out between 2004-2006 in the area of Sheet 181 (Parma), as a collaborative project between the Department of Earth Science of Bologna University (today Department of Biology, Earth and Environmental Sciences), the Geological, Seismic and Soil Survey, and the Department for Agriculture of Regione Emilia-Romagna.

Soil characterization on a geochemical basis led to the building up of a new type of geochemical map, namely Pedogeochemical Map, following the definition of standard ISO/DIS 19258, 2005 - *Guidance on the determination of background values* -. The Pedogeochemical Map of the Emilia-Romagna plain is emphasized here as (i) a possible efficient alternative to the conventional approach to geochemical analysis and mapping based on statistical interpolation methods alone, and (ii) a powerful tool to identification and quantification of the anthropogenic influence on soil.

1.1. Definition

The “Pedogeochemical Map of the Emilia-Romagna plain (1:250,000 scale)” depicts the subsoil (90-140 cm) spatial distribution of five potentially toxic metals – Chromium [Cr], Nickel [Ni], Zinc [Zn], Copper [Cu] and Lead [Pb] - in soils for agricultural use. This depth is regarded as representative of the pedogeochemical content of metals (see standard ISO/DIS 19258), and is generally considered free from anthropogenic contribution in soils subject to common agricultural practices.

2. MATERIALS AND METHODS

For the redaction of the Pedogeochemical Map of the Emilia-Romagna plain, we followed the recommendations of standard ISO/DIS 19258, 2005, from sample collection to the statistical treatment of data. Particularly, we used the 95th percentile as a good approximation for the pedogeochemical content.

The designation of soil status with reference to its metal content (Chromium, Nickel, Zinc, Copper and Lead) was carried out through the following phases:

- Grouping of soil units into Genetical-Functional Units (GFUs)
- Soil sampling
- Laboratory analyses
- Statistical analysis
- Map processing

Reference data for the Pedogeochemical Map of the Emilia-Romagna plain are: the Soil Map at 1:50,000 scale (Regione Emilia-Romagna, 2010), the Map of Drainage Basins, modified (Regione Emilia-Romagna, 2009), the Geological Map of the Po Plain at 1:250,000 scale, and the Geological Map of Regione Emilia-Romagna (Apenninic foothills portion) at 1:10,000 scale. Additional data were taken from the Soil Use Map (Regione Emilia-Romagna, 1976-2008) and aerial photographs (1954-2008), with the aim of establishing precise relationships between sampling sites and present (and past) soil use.

2.1. Genetical-Functional Units (GFUs)

Soils were grouped into Genetical-Functional Units (*GFUs*) on the basis of two major parameters (Table 1):

- soil texture
- degree of soil weathering

Additional features for the *GFUs* classification include the identification of sediment provenance and the depositional environment. Each of the 13 *GFUs* recognized in the Emilia-Romagna plain is fingerprinted by a unique combination of the above parameters (Table 1).

On the basis of soil texture, soils were grouped into three major classes: fine-textured soils, moderately fine to moderately coarse-textured soils, and coarse-textured soils. Concerning soil weathering, a major distinction was carried out between soils with low *versus* moderate degree of weathering. Soils with high degree of weathering (ex. Luvisols), cropping out exclusively at the basin margin, were grouped into a separate unit (*GFU A1*), irrespective of texture.

As widely documented in the scientific literature, the natural spatial distribution of metals in soils is strongly influenced by the composition of rocks cropping out in the different drainage basins. In the specific case of the Emilia-Romagna plain, which represents a characteristic example of multi-sourced system fed by the Apenninic rivers to the south and by Po River (and its Alpine and NW Apenninic tributaries) along W-E direction, differences in lithology observed in the individual drainage basins result in significant differences in the geochemical composition of the detritus delivered to the plain.

Of particular interest for the Pedogeochemical Map is the presence of ultramafic (ophiolitic) complexes in the Po drainage basin, as well as in the river catchments of selected Apenninic (Emilia) rivers. These lithological units supply an abundance of metals as part of specific minerals, such as spinels, chlorites and serpentine. Ophiolitic rocks in the Apenninic chain are intimately related to a complex structural units (the Ligurian Sheet), cropping out more or less continuously along the basin margin, W of Sillaro Line. East of this tectonic line, in the Romagna Apennines, the major outcropping unit is the thick Miocene turbidite Marnoso-arenacea Formation; as a result, river catchments are virtually ophiolite-free in the Romagna Apennines.

It should be noted, however, that the general distinction between Emilia (ophiolite-rich) and Romagna (ophiolite-free) Apennines cannot be taken as a rule. For example, a few rivers draining the Emilia Apennines have no ophiolites in their drainage basin. On the other hand, Ligurian units are discontinuously present in Romagna, as in the case of the S. Piero-S. Sofia syncline and the Val Marecchia *nappe*.

Finally, from a sedimentological perspective the Emilia-Romagna deposits can be grouped into four distinct depositional systems (alluvial fan, alluvial plain, coastal plain and delta - see Table 1). These depositional systems, in turn, include a variety of depositional facies, corresponding to distinct depositional environments.

In the *GFUs* classification scheme of Table 1, the initial "A" is used to identify four groups of fine-textured soils, corresponding to floodplain (A2 and A3) or interdistributary deposits of the upper delta plain (A4). These *GFUs* are characterized by lack (A2), moderate presence (A3) or abundance (A4) of ophiolitic rocks in the drainage basin, respectively. *GFU A1* includes soils with high degree of weathering, cropping out at the Apenninic margin. This *GFU* has ambiguous palaeoenvironmental interpretation.

The initial "B" characterizes six *GFUs*, with moderately fine to moderately coarse-textured soils. The degree of soil weathering varies from low to moderate, while the depositional environments encompass fluvial-channel, levee and crevasse deposits, formed within alluvial fan or alluvial plain environments (Table 1).

GFUs B1-B5 are differentiated on the basis of lack (B1), moderate presence (B2 and B3) or abundance (B5) of ophiolitic rocks in the related Apenninic river catchments. *GFUs B4 e B6* represent channel-levee and crevasse deposits related to the Po River activity, in alluvial plain (B4) or deltaic (B6) sub-environments.

The two *GFUs* characterized by the initial "C" are referred to coarse-textured soils, with low degree of weathering. These units are inferred to represent beach-ridge deposits (Table 1), more specifically related to coastal plain (C1) or deltaic (C2) sub-environments. As far as sediment provenance is concerned, C1 was fed by the Romagna Apenninic rivers (with no ophiolites in their drainage basin), while C2 is a delta front deposit fed by the southernmost branches (distributary channels) of an ancient Po River Delta.

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Unit	Diagnostic features		Environmental features
Code	Soil	Sediment provenance	Depositional environment
A1	Medium to fine-textured, high degree of weathering <i>Stagnic Luvisols, Vertic Cambisols</i>	Mixed (from Apenninic sources with extremely variable ophiolitic contribution)	Alluvial fan, interfluvial terrace (indifferentiated)
A2	Fine-textured, low to moderate degree of weathering <i>Vertic Cambisols, Hyposalic Vertisols, Calcic Vertisols</i>	Apenninic sources, with no ophiolitic contribution	Alluvial plain Floodplain deposits
A3	Fine-textured, low to moderate degree of weathering <i>Vertic Cambisols, Calcic Vertisols, Eutric Vertisols</i>	Mixed Po-Apenninic sources, with moderate to high ophiolitic contribution	Alluvial plain Floodplain deposits
A4	Fine-textured, low to moderate degree of weathering <i>Vertic Cambisols, Calcic Vertisols, Hyposalic Vertisols</i>	Po River	Delta (delta plain) Interdistributary area deposits
B1	Moderately fine-textured to moderately coarse-textured, with rare gravels, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Apenninic sources, with no ophiolitic contribution	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B2	Moderately fine-textured to moderately coarse-textured, with rare gravels, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Mixed (mostly from Apenninic sources, with moderate ophiolitic contribution: Enza, Baganza and Tresinaro rivers)	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B3	Moderately fine-grained to moderately coarse-grained, with rare gravels, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Apenninic sources, with moderate to high ophiolitic contribution (Arda and Taro rivers)	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B4	Medium to moderately coarse-textured, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Po River	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B5	Moderately fine-grained to moderately coarse-textured, with abundant gravels, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Apenninic sources, with high ophiolitic contribution (Trebbia and Nure rivers)	Alluvial plain and alluvial fan Channel-levee and crevasse deposits
B6	Medium to moderately coarse-textured, low to moderate degree of weathering <i>Haplic Cambisols, Haplic Calcisols</i>	Po River	Delta (delta plain) Distributary channel-levee and crevasse deposits
C1	Coarse-textured, low degree of weathering <i>Endogleyic Arenosols</i>	Apenninic sources, with no ophiolitic contribution	Coastal plain Beach-ridge deposits
C2	Coarse-textured, low degree of weathering <i>Endogleyic Arenosols</i>	Po River	Delta (delta front) Beach-ridge deposits

D1	With organic horizon <i>Thionic Histosols, Thionic Fluvisols</i>	Po River	Delta (delta plain) Interdistributary bay deposits
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Table 1 – Pedological and geological features of the Genetical-Functional units (GFUs) that form the Pedogeochemical Map of the Emilia-Romagna plain (WRB, 2006).

Finally, GFU D1 includes soils with high organic component, and locally low pH values. Soils in this unit are fine-grained to moderately fine-grained, and were formed at the margin of a brackish environment (marsh, lagoon or interdistributary bay).

2.2 Sampling

For the evaluation of the pedogeochemical contents, soil samples were collected by hand drilling at 90-140 cm depth (60-80 cm in gravelly soils), using Eijkelkamp Agrisearch equipment (01.11.SO hand auger set for heterogeneous soils).

Sampling did not follow regular grids, but was set up taking into account the spatial distribution of the various GFUs, *i.e.*, the pedological and geological characteristics of the study area. General information at each sampling station include: location, elevation, soil slope, soil use, stratigraphic unit (with reference to the Regione Emilia-Romagna Geological Map at 1:10,000 scale). Core descriptions include: grain size, colour, reaction to hydrochloric acid, pH (in soils with high OC content), plant fragments, wood, fossils, carbonate nodules, etc.. All data were stored in the Emilia-Romagna Soil Database.

In addition, topsoil samples at 20-30 cm depth were collected at each sampling site. These samples were used to detect the geochemical anomalies, through comparison with pedogeochemical contents.

2.3. Analytical methods

2.3.1. XRF analyses

Among the analytical methods for the determination of metals in the soil and / or sediment was used X-ray fluorescence spectrometry (XRF). Contrary to the majority of the extraction methods, this procedure determines the absolute abundance of the metal, irrespective of the mineralogical phase to which the metal is linked. Using the XRF method, it is possible to perform quantitative analysis of a wide range of elements. XRF is a non-destructive technique, suitable for solid, liquid and powdered samples that can measure metal concentrations of up to 100%. In this study, we focused on five metals (Cr, Ni, Cu, Zn and Pb), although XRF analyses gave information on 26 elements (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, LOI, Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb).

Soil samples were analyzed at the Department of Biology, Earth and Environmental Sciences of Bologna University. Soil samples, pressed into tablets, were analyzed for major and trace elements in a Phillips PW1480 spectrometry with Rh tube, using the matrix correction methods of Franzini et al. (1972; 1975), Leoni and Saitta (1976) and Leoni et al. (1982). Reference samples, such as samples BR, BCR-1, W1, TB, NIM-P, DR-N, KH e AGV-1 (Govindarajiu, 1989), 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, 10-30% for Pb and elements with concentrations lower than 10 ppm).

Although this method is not standardized according ISO standards, it is regarded by ISO/DIS 19258 as suitable for the determination of total concentrations, along with extractions with hydrofluoric acid. According to D.lgs. 152/06, XRF analysis is admissible for metals whose limit values is 10 times higher than the detection limit.

2.3.2 ICP-MS analyses

In order to make the results of this study comparable with most environmental data available on the Italian territory, topsoil samples collected at 20-30 cm depth were also analyzed by aqua-regia extraction and inductive coupled plasma mass spectrometry (ICP-MS) determination. This procedure of “pseudo-total” digestion, especially at high temperatures, is able to mobilize metals associated to oxides, sulfates and several silicates. This technique, although *not* representative of total metal contents in soils, is one of the most employed extraction techniques in environmental studies. It is harmonized with several International Standards (for example: ISO, EPA 3051, UNIEN 13346), and officially used as a protocol in most European countries. ICP-MS analyses following aqua regia extraction are, however, loosely related to the bioavailable fraction and provide an estimate of the long-term release of metals from soils. ICP-MS analyses were performed at ARPA laboratories, in Ravenna, following UNIEN 13346 standard method. The analyzed metal are as follows: V, Cr, Ni, Cu, Zn, As, Cd, Sn, Sb and Pb.

The proportion of metal extracted by aqua regia is largely variable as a function of the element considered. Incomplete digestion for aqua regia extractions, especially for Chromium, is not a new issue (see Sartori et al., 2004; Amorosi & Sammartino, 2011), and it is well established that ICP-MS analyses result invariably in lower metal concentrations than those obtained by XRF on the same samples. In the study samples of the Emilia-Romagna soils, the following mean percentages of metal were extracted following aqua regia digestion: Cr 69%, Ni 72%, Zn 82%, Cu 83%, and Pb 108%. It should be noted that XRF analyses on Pb are commonly affected by analytical errors.

2.4. Statistical analysis

In order to examine the distribution of geochemical data and identify potential outliers, a set of statistical analyses was undertaken on the 13 GFUs described in the previous sections. Statistical analyses are of crucial importance to a correct quantification of pedogeochemical contents. All GFUs are represented by a minimum number of 10 samples. This sample size is considered large enough to provide adequate statistical information.

Frequency histograms and related cumulative frequency curves were constructed for each dataset (Fig. 1). The type of distribution was then evaluated through the Kolmogorov-Smirnov test (Kolmogorov, 1933; Smirnov 1939).

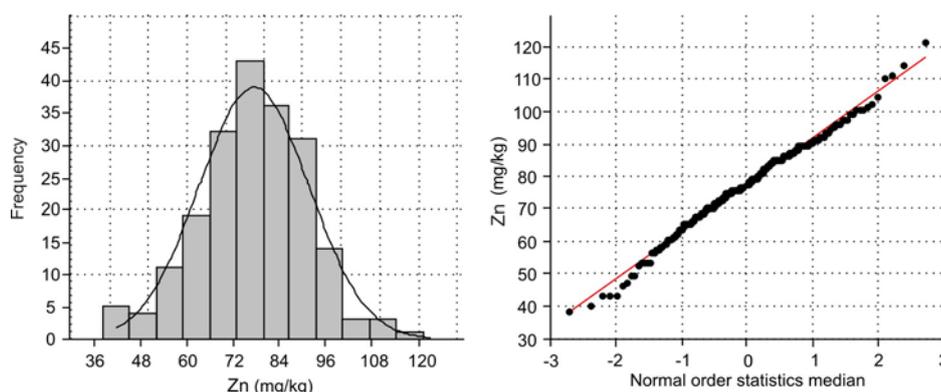


Fig. 1 – Example of frequency histogram and normal cumulative distribution of Zn in GFU B1.

The Kolmogorov-Smirnov (K-S) test, applied to a specific dataset, can be used to verify if a cumulative distribution can be modeled as a standard normal or log-normal distribution. The K-S test is likely the most common non-parametrical test, and is typically applied to continuous distributions, through comparison of theoretical *versus* observed cumulative distributions. In particular, this test quantifies the distance (or maximum difference) D between the empirical distribution function of the sample and the cumulative distribution function of the reference. The null hypothesis H_0 that is used as a basis for this test (this

hypothesis is accepted if the data distribution is consistent with a standard distribution), is the equivalence between the observed and expected distributions. In contrast, the alternative hypothesis H_1 is based on the complementary condition that the two distributions are divergent, and it needs to be rejected to get a normal or log-normal cumulative distribution. For large D values, the null hypothesis is rejected, whereas for small values is accepted. D values are used to calculate the P-values, *i.e.*, the probability that the null hypothesis is true. In practice, D-values are compared automatically to critical values that vary as a function of sample size.

The P-values of 13 GFUs, calculated through the K-S test for each metal, are shown in Table 2. The statistical significance commonly used for this test is 0.05. As a result, all P-values below this threshold led to the rejection of the null hypothesis, indicating that the cumulative distribution for that metal-GFU combination is divergent compared to the standard distribution. Six P-values, highlighted by asterisks, fall below the statistical significance (Table 2): these values correspond to GFUs B1 (Cr, Ni and Cu), C2 (Cu and Zn) and A2 (Cu). For all other 59 combinations, P-values are larger than 0.05. In these instances, the null hypothesis is confirmed and the cumulative distributions can be considered as standard (normal or log-normal) distributions. For these datasets, it was possible to proceed to the identification of potential outliers.

	A1	A2	A3	A4	B1	B2	B3	B4	B5	B6	C1	C2	D1
Cr	0,49	0,27	0,84	0,68	0,01*	0,23	0,31	0,25	0,94	0,81	0,60	0,33	0,24
Ni	0,11	0,37	0,68	0,52	0,00*	0,32	0,87	0,24	0,39	0,63	0,95	0,63	0,37
Cu	0,23	0,00*	0,97	0,73	0,00*	0,97	0,44	0,74	0,47	0,20	0,94	0,03*	0,35
Zn	0,62	0,07	0,64	0,50	0,45	0,98	0,97	0,53	0,91	0,46	0,93	0,00*	0,36
Pb	0,43	0,06	0,19	0,55	0,46	0,66	0,56	0,52	0,66	0,60	0,34	0,49	0,56

Table 2 – P-values obtained for the 13 GFUs and 5 metals, following the K-S test.

To the six datasets (asterisks in Table 2) inconsistent with a standard cumulative distribution (see Fig. 2, as an example), we applied the Box-Cox transformation (Box and Cox, 1964). This technique leads to a dataset for which the normality assumption is reasonable. The Box-Cox normality plot is a plot of correlation coefficients for various values of the λ parameter. The value of λ corresponding to the maximum correlation on the plot is the optimal choice for λ (Fig. 2B).

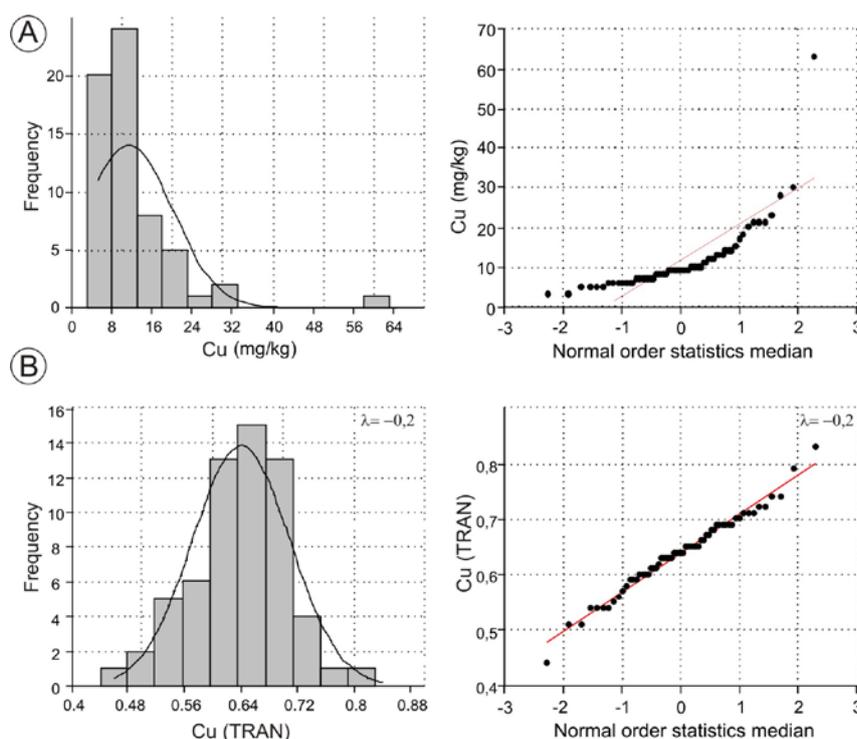


Fig. 2 – Example of frequency histogram and related cumulative distribution for Cu in GFU C2, before (A) and after (B) the Box-Cox transformation. The Box-Cox normality plot shows that the maximum value of the correlation coefficient is at $\lambda = -0.2$.

In order to test the efficiency of the Box-Cox transformations, a second K-S test was carried out onto the six transformed datasets (Table 3). From the comparison with the P-values obtained before the Box-Cox transformations (see asterisks in Table 2), it can be observed that, after the transformations, all datasets are consistent with a normal or *log*-normal distribution. This implies the possibility of moving to the next step: the identification of potential outliers.

Met.	GF	P-value
Cr	B1	0,25
Ni	B1	0,15
Cu	A2	0,18
	B1	0,20
	C2	0,56
Zn	C2	0,46

Tab. 3 – P-values obtained for the six GFU databases transformed with the Box-Cox technique, following a second K-S test.

The identification of potential outliers was performed through box-and-whiskers plots (Fig. 3). These plots highlight values that exceed by 1.5 times the interquartile distance between the 25th and 75th percentiles of the distribution. On the six datasets subject to the Box-Cox transformation, two groups of outliers were calculated, on both transformed and reconverted data (Table 4).

Metal	N. OUT K-S	GFU	N. OUT B-C	GFU	N. OUT B-C*
Cr	26	A1, A2, B4, C1, C2, D1	4	B1	5
Ni	27	A1, A2, A3, A4, B2, B4, C2, D1	2	B1	5
Cu	49	A1, A3, B3, B4, B5, B6, C1, C2, D1	11	A2 B1 C2	3
Zn	21	A2, A3, A4, B1, B4, C2, D1	2	C2	
Pb	53	A1, A2, A3, A4, B1, B4, B5, B6, C1, C2, D1			

Tab. 4 –Number of outliers identified following the Kolmogorov-Smirnov (K-S) test. The number of outliers in the six “anomalous” datasets, after the Box Cox transformation (B-C) and after a new dataset reconversion (B-C*) is shown to the right.

The outliers were then eliminated from the following statistical analysis and excluded from calculation of the pedogeochemical contents.

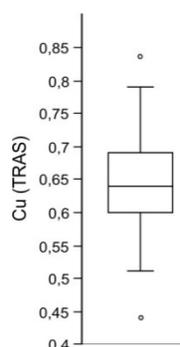


Fig. 3 – Outlier identification (white circles) for Cu in GFU B1, based on box-and-whiskers plot, following Box-Cox transformation (Fig. 2B).

Following outlier removal, descriptive statistics was carried out for each metal, leading to GFUs characterization in terms of: minimum value, maximum value, sum, mean, standard error, variance, standard deviation, median, skewness, kurtosis and geometric mean (Table 5).

CHROMIUM	A1	A2	A3	A4	B1	B2	B3	B4	B5	B6	C1	C2	D1
N	71	138	25	21	197	17	29	33	23	41	18	55	19
Min	113	99	152	173	66	130	145	159	196	156	50	96	130
Max	184	169	272	273	151	192	244	250	646	256	82	167	273
Sum	10525	18636	5118	4854	21411	2637	5363	6841	8352	8179	1101	7242	3769
Mean	148.2	135.0	204.7	231.1	108.7	155.1	184.9	207.3	363.1	199.5	61.2	131.7	198.4
Std. error	1.8	1.3	6.9	5.5	1.3	4.2	5.4	3.8	27.0	3.4	2.2	2.2	7.8
Variance	231.1	226.0	1194.3	644.6	326.1	300.0	860.7	469.7	16732.8	473.8	89.1	257.3	1168.1
Stand. dev	15.2	15.0	34.6	25.4	18.1	17.3	29.3	21.7	129.4	21.8	9.4	16.0	34.2
Median	148.0	137.0	197.0	237.0	108.0	153.0	180.0	209.0	345.0	203.0	60.0	132.0	199.0
Skewness	0.1	-0.4	0.5	-0.4	0.0	0.4	0.5	-0.1	0.4	0.2	0.7	0.0	0.2
Kurtosis	0.0	-0.4	-0.9	-0.6	-0.2	-0.9	-1.1	-0.4	-0.9	-0.2	-0.5	-0.4	-0.1
Geom. mean	147.5	134.2	202.0	229.8	107.1	154.2	182.8	206.2	341.2	198.3	60.5	130.7	195.5

Tab. 5 – Descriptive statistics for Chromium, with reference to the 13 GFUs analyzed in this work.

In order to define the pedogeochemical contents of Cr, Ni, Zn, Cu and Pb, following recommendations from ISO 19258 and APAT 2006 protocol we calculated the 90th percentile in 13 different GFUs. At the same time, we also calculated the 95th percentile. This value has recently been considered as representative of the pedogeochemical contents by ARPAV (2011).

2.5. Cluster analysis

In order to obtain additional information on the relationships between metal contents and provenance of soil parent material, we performed an R-mode cluster analysis on the XRF data from the subsoil samples (90-140 cm depth), by selecting a series of major and trace elements (SiO₂, Al₂O₃, TiO₂, Fe₂O₃, MgO, CaO, Na₂O, K₂O, LOI, V, Cr, Ni, Cu, Zn, Rb, Sr, Zr and Pb). Through this technique, it is possible to maximize similarities between soil units, leading to the identification of possible genetical relationships between elements and GFU.

Careful inspection of the dendrogram shows the presence of four clusters exhibiting distinct compositional affinities (Fig. 4). Group 1 includes elements typically associated to the sand fraction (SiO₂, Na₂O, Zr). Pb is part of this group, though with very low correlation index. Group 2, instead, includes elements typically associated to the fine-grained size fraction (K₂O, Rb, Fe₂O₃, V, Al₂O₃, TiO₂). Zn and Cu display affinity for this group. Group 3 is representative of the ultramafic (ophiolitic) contribution. The presence of Cr and Ni within this group supports the classification of the GFUs based on the amount of ophiolitic detritus (see Table 1). Finally, Group 4 is represented by a cluster of variables typical of the carbonate fraction (CaO, Sr, LOI).

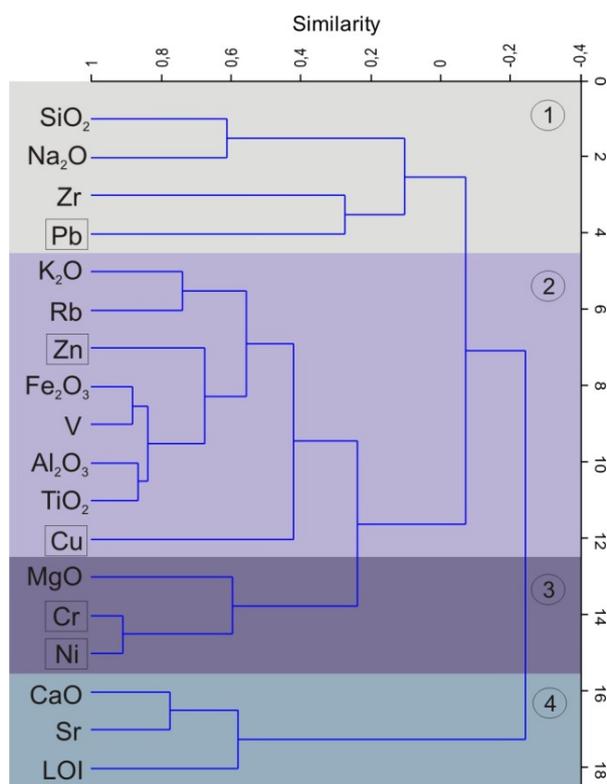


Fig. 4 – Dendrogram showing the relationships between the five metals investigated in this study (boxed) and four clusters reflecting distinct geochemical compositions (XRF analyses on samples at 90-140 cm depth).

2.6. Identification of the geochemical anomalies

In order to obtain reliable estimates of anthropogenic influence, the natural pedogeochemical content from subsoil samples at 90-140 cm depth was matched against metal concentrations of topsoil samples (20-30 cm depth), collected at the same sites. To allow comparison with the data representative of the natural background, chemical analyses on topsoil samples were conducted using the same analytical procedure (XRF) used for subsoil samples. The pollution status of a soil can efficiently be evaluated through comparison between topsoil metal concentrations and natural pedogeochemical contents. In this respect, the two (interchangeable) parameters that are most commonly calculated are:

the Index of geoaccumulation, Igeo (Müller, 1979; Förstner and Müller, 1981), defined as

$$I_{geo} = \log_2 C_n / (1.5 \cdot B_n), \text{ and}$$

the Enrichment Factor, EF (Rubio et al., 2000), defined as

$$EF = (B_n - C_n) / C_n$$

where:

C_n is metal concentration in topsoil samples (at 20-30 cm depth)

B_n is the pedogeochemical content of the same metal (calculated on the basis of subsoil geochemistry, at 90-140 cm depth).

On the basis of distinct Igeo values, the pollution status of a soil can be differentiated into six classes (Müller, 1981; Banat et al., 2005; Sainz and Ruiz, 2006), according to the following classification scheme (Table 6):

CLASS	I GEO VALUE	POLLUTION STATUS OF SOIL
0	≤ 0	unpolluted
1	0-1	unpolluted to moderately polluted
2	1-2	moderately polluted
3	2-3	moderately to strongly polluted
4	3-4	strongly polluted
5	4-5	strongly to extremely polluted
6	>5	extremely polluted

Table 6 – Pollution status of soils based upon values of the Geoaccumulation Index.

2.7. Map Processing

Map of the Pedogeochemical content

The Pedogeochemical Map of the Emilia-Romagna plain at 1:250,000 scale is made up of two distinct products for each out of the five investigated metals: (i) Map of the Pedogeochemical Content, and (ii) Map of Geochemical Anomalies.

The Map of the Pedogeochemical Content of Cr, Ni, Zn, Cu e Pb is based on the pedogeochemical characterization of the GFUs. Consequently, on the attribution of soil units of the Soil Map of the Emilia-Romagna plain (1:50,000 scale) to specific classes of natural metal concentration (v. § 3). One of the objectives of this map is to provide a readily understandable picture of natural metal distribution in the study area, to be compared with the threshold values established by the Italian legislation.

In the Map of the Pedogeochemical Content, for each metal the legend is centered on the threshold value (x) related to the use of soil for parks and residential areas (see D.lgs 152, 2006 – red number in Fig. 5). 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 (Fig. 5). Darker shades of the same colour indicate progressively higher metal concentrations. 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 (Fig. 6).

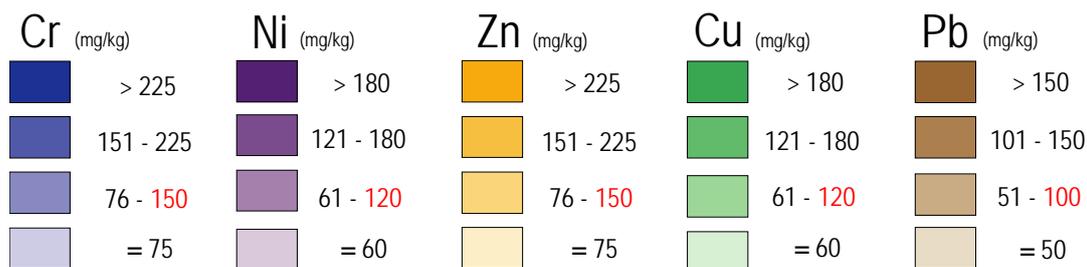


Fig. 5 – Legend of the five Maps of the Geochemical Content (see text). The red numbers indicate the maximum permitted levels according to the Italian legislation.

On the website http://www.regione.emiliaromagna.it/wcm/geologia/canali/suoli/carta_pedogeochemica/01_introduzione.htm, the Map of the Pedogeochemical Content can be consulted by single polygon, and the following information is retrieved: GFU attribution, class on map (i.e., natural metal content), and 50th, 90th and 95th percentiles values. The 95th percentile corresponds to the pedogeochemical content of the metal and is used as reference value for mapping the class, as indicated by the Guidelines of Italian EPA. In order to provide the reader with an “average” value of reference, the 50th percentile is also indicated.

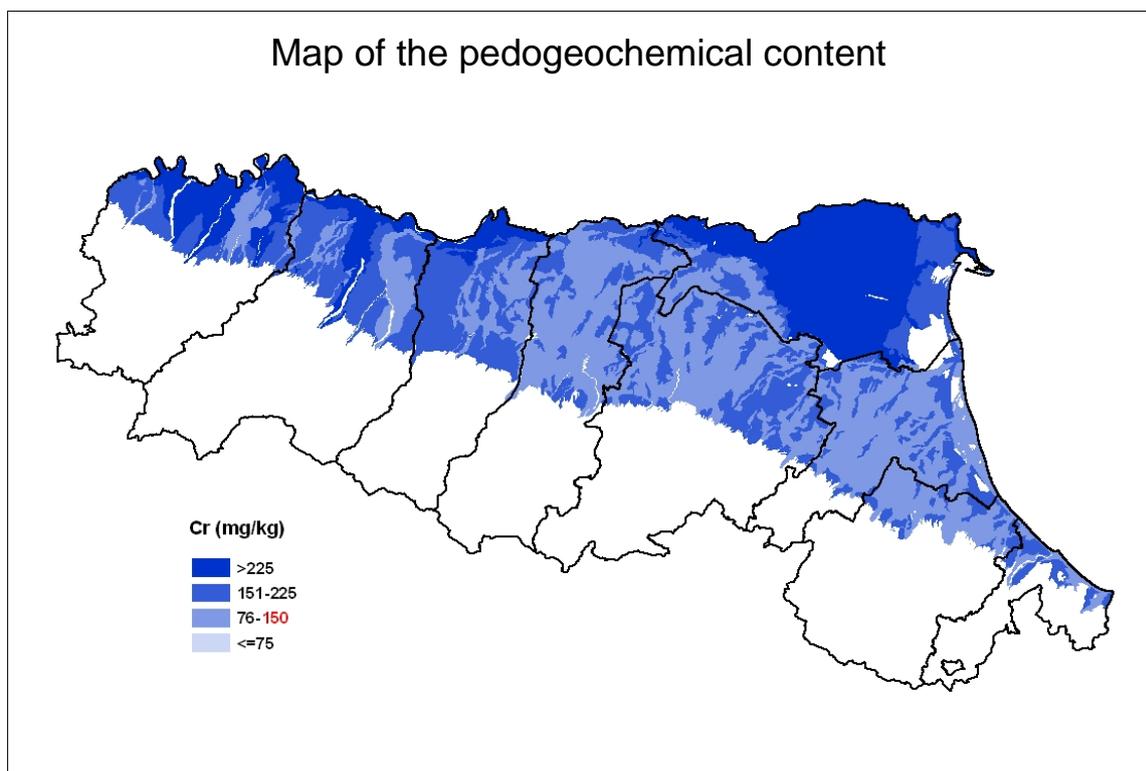


Fig. 6 – Map of the Pedogeochemical Content of Cr (for legend explanation, see Fig. 5 and text).

Map of Geochemical Anomalies

The Map of Geochemical Anomalies is obtained comparing the pedogeochemical content of a metal (from subsoil samples at 90-140 cm depth) with metal concentrations measured in the same sites at 20-30 cm depth (both analyses performed by XRF). The Map of Geochemical Anomalies is a dot density map, built on a simplified topographic map, where the Geoaccumulation Index values, I_{geo} (Müller, 1979; Förstner & Müller, 1981 - § 2.6), obtained at each sampling site are plotted. The pollution status of soils, which may vary from “unpolluted” to “extremely polluted”, is depicted by different circle colours (Fig. 7), each corresponding to a different class in the classification scheme of Müller (1981) (v. Tab. 6). Unpolluted soils have green colour, unpolluted to moderately polluted soils are shown in yellow, whereas moderately polluted soils have orange colour. Moderately to strongly polluted soils exhibit red colour, and so forth.

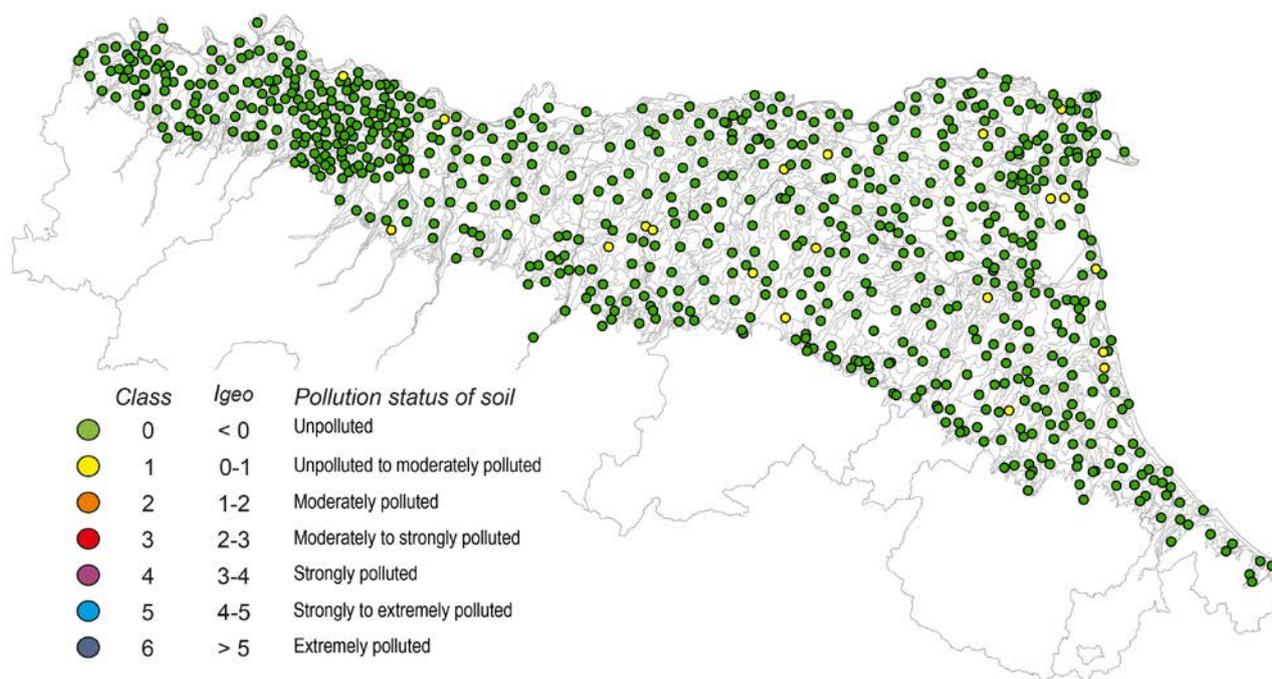


Fig. 7 – Map of Geochemical Anomalies for Cr (for legend explanation, see Table 6 and text).

3. METAL CONTENTS IN SOILS OF THE EMILIA-ROMAGNA PLAIN

The pedogeochemical content of potentially toxic metals in soils of the Emilia-Romagna plain is a function of three major controlling factors: (i) provenance of parent material, (ii) soil texture, (iii) degree of soil weathering. The specific influence of such factors on sediment composition (see preliminary studies by Bini et al., 1986; Bianchini et al., 2002) has been already documented across a significant portion of the Emilia-Romagna plain (Amorosi & Sammartino, 2007; Amorosi, 2012) as part of a collaborative research project between Regione Emilia-Romagna and Bologna University.

The following sections document to what extent the different factors may influence the spatial distribution of Cr, Ni, Zn, Cu and Pb in the study area. A comparison of the 13 different GFUs is shown with the aid of scatterplot diagrams and box-and-whiskers plots.

3.1. Chromium [Cr] e Nickel [Ni]

The representation of geochemical data through scatterplot diagrams (Figs. 8-10) and box-plots (Figs. 11-12) shows that pedogeochemical contents of Chromium and Nickel in the Emilia-Romagna soils are primarily influenced by the composition of parent material (*i.e.*, the amount of ultramafic detritus - § 2.1), though soil texture and the degree of soil weathering also play a significant role in controlling natural metal distribution. The lowest concentrations of Cr and Ni are observed within GFUs A2, B1 and C1. These units reflect provenance from Apenninic sediment sources in which river catchments are ophiolite-free (Figs. 8-9). A relative enrichment in Cr e Ni is recorded in fine-textured soils (floodplain deposits - A2), whereas the lowest values are characteristic of coarse-textured soils, such as those formed on beach-ridge sands (C1). Soils with intermediate texture characteristics (B1) exhibit intermediate values for these two metals.

GFU A1, consisting of soils with high degree of weathering, exhibits relatively higher metal values than the above GFUs, though lower than the GFUs with an important ultramafic component. This is because the high degree of weathering leads to a loss of the provenance signal of the parent material, and only the portion of the metals linked to the residual minerals is left.

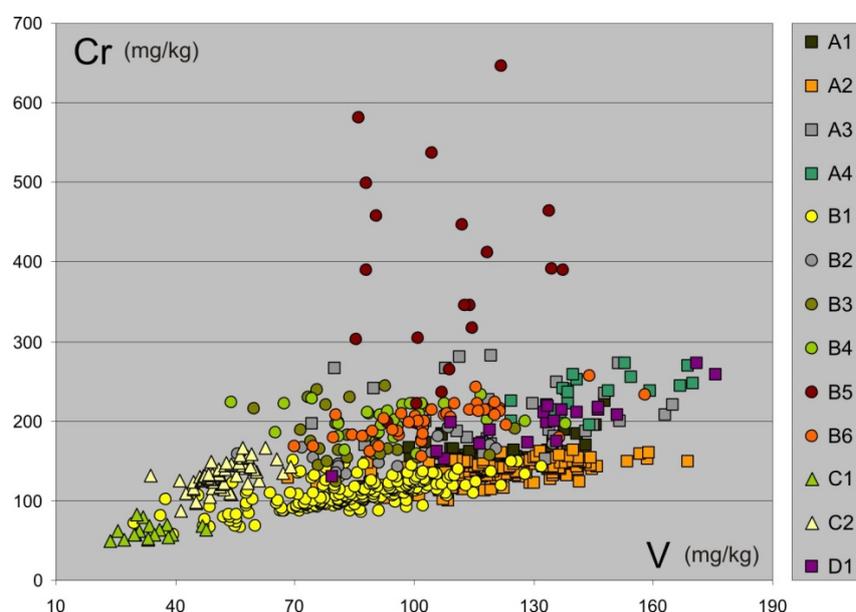


Fig. 8 – Scatterplot diagram Cr-V.

A similar behaviour, though with general shifts toward higher Cr e Ni values, is observed for the GFUs supplied by abundant ophiolitic detritus (C2, B3-B6, D1 and A4, in Figs. 8-9). In particular, relatively higher metal concentrations are invariably associated to finer-textured soils (*i.e.*, interdistributary area and bay clays – GFUs A4 e D1). The lowest values are observed within coarse sand soils (beach-ridge deposits – C2).

In general, when plotted against V, Cr and Ni values from soils supplied by compositionally different parent materials (ophiolitic *versus* non-ophiolitic) draw two distinct regression lines (Figs. 8 and 9). An obvious anomaly is represented by GFU B5, including soils from the Apenninic margin, close to Piacenza, where a clear relative enrichment in Cr and Ni can be observed (Figs. 8 and 9).

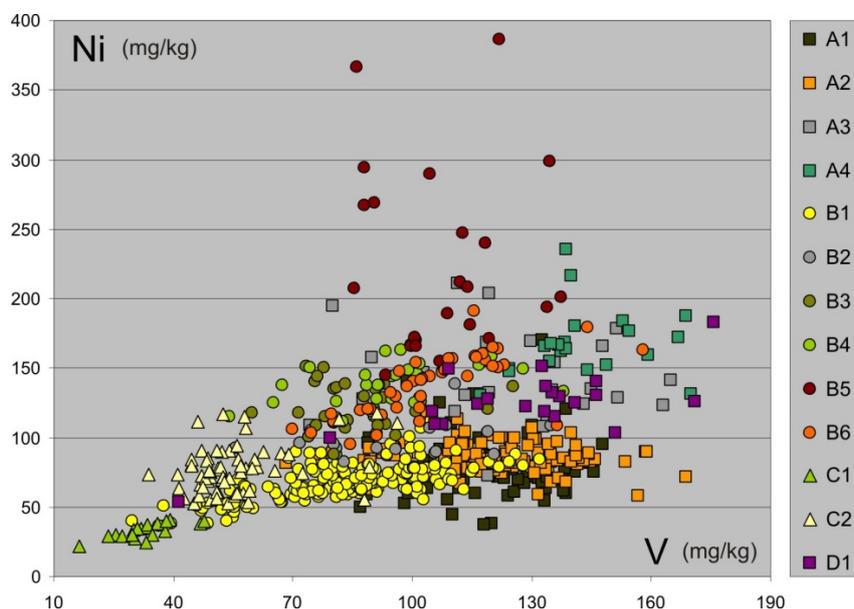


Fig. 9 – Scatterplot diagram Ni-V.

Distribution of Cr and Ni plots along a single regression line in the Cr-V scatterplot diagram (Fig. 10) indicates that these two metals are associated within the same ultramafic complexes. Specifically, the relatively high Cr contents in the clay fraction are interpreted to reflect high concentration of chromium chlorites (kämmererite) within peridotitic rocks belonging to the ophiolitic complexes of the Western Alps (Bianchini et al., 2002). A similar provenance is hypothesized for Ni, which is typically associated to Cr within serpentine (Amorosi et al., 2002). Chromium spinels (chromite) and/or serpentinite rock fragments are inferred to represent the major carriers of Cr in the sand fraction. This is the case of the very high Cr and Ni values observed within GFU B5 (Fig. 10). Detailed sedimentological analysis of hand-drilled cores has shown that these soils were formed on alluvial fan deposits made up almost entirely of highly altered pebbly material, including abundant serpentinite lithic fragments. Despite generally lower contents, Cr and Ni display distinctive concentrations also in sands, thus allowing differentiation of Apenninic from Po-derived sediment sources (Figs. 9-10).

The box-plot representation of Cr and Ni values as a function of the different GFUs (Figs. 11 e 12) enables comprehensive visualization of the relative influence of parent material, soil texture, and degree of soil weathering on natural metal distribution. Comparison of the 95th percentiles calculated for each box-plot with threshold levels of Italian legislation (see legends of Fig. 5) results in the automatic attribution of the various GFUs to specific classes of the Pedogeochemical Map. From this comparison, it is evident the difference between threshold levels and natural contents. In particular: soil groups formed, in part at least, of detritus supplied by the erosion of ophiolitic complexes exhibit 95th-percentile values largely higher (up to 577 mg/kg for Chromium and 360 mg/kg for Nickel) than the threshold levels for unpolluted soils (150 mg/kg for Cr and 120 mg/kg for Ni; D.lgs.152, 2006). The highest concentrations are recorded in soils developed on the alluvial fans of Trebbia and Nure rivers, where highly altered serpentinite rock fragments are a common constituent of the parent material (B5). Pedogeochemical contents of Cr and Ni close to the limits admitted by the law are observed, instead, within floodplain soils of non-ophiolitic provenance (A2), as effect of preferential metal accumulation within the fine-grained fraction.

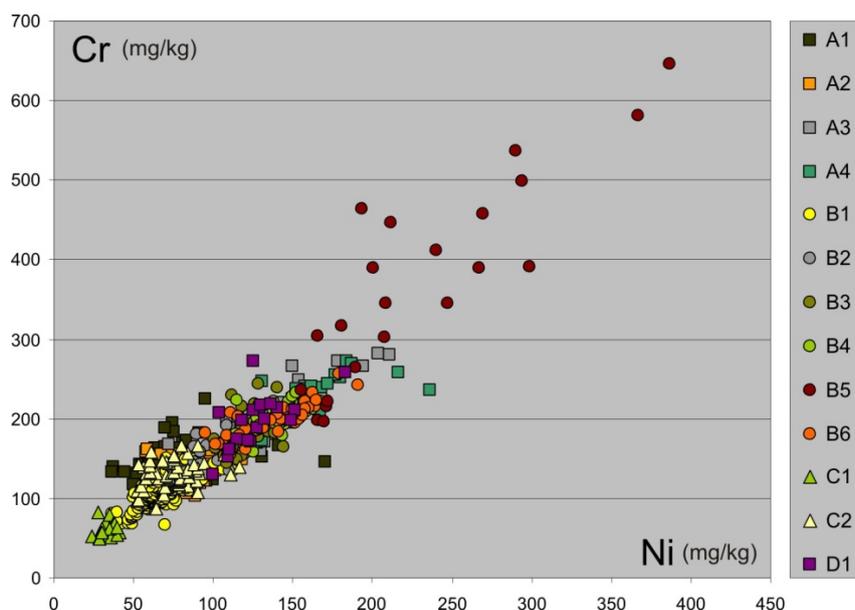


Fig. 10 – Scatterplot diagram Cr-Ni.

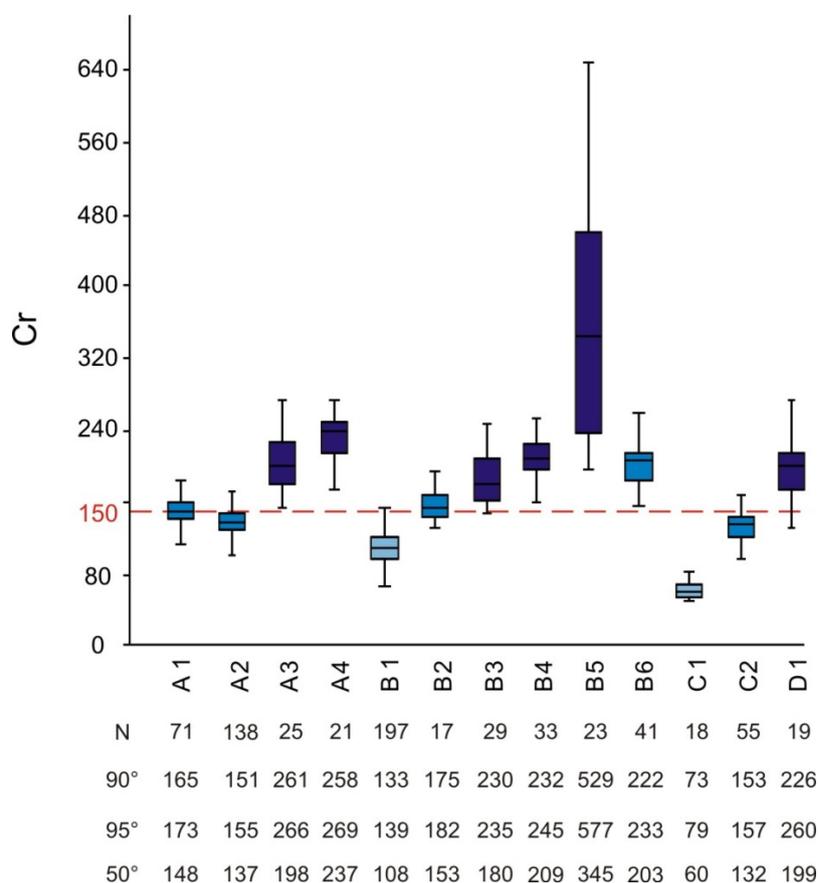


Fig. 11 – Natural distribution of Cr in the studied GFUs, with indication (in mg/kg) of the 90th, 95th and 50th percentile values.

Natural concentrations of Cr higher than the threshold values are also recorded in soils of the Apenninic margin, with high degree of weathering (A1), and along river courses that drain moderately ophiolitic areas, such as Enza, Baganza and Tresinaro drainage basins (B2).

In contrast, where the drainage basin is ophiolite-free, natural concentrations of Cr e Ni in coarse-grained soils (GFUs B1 and C2) are well below the maximum permitted levels, with very low values in beach-ridge sands supplied by the Apenninic rivers (C1).

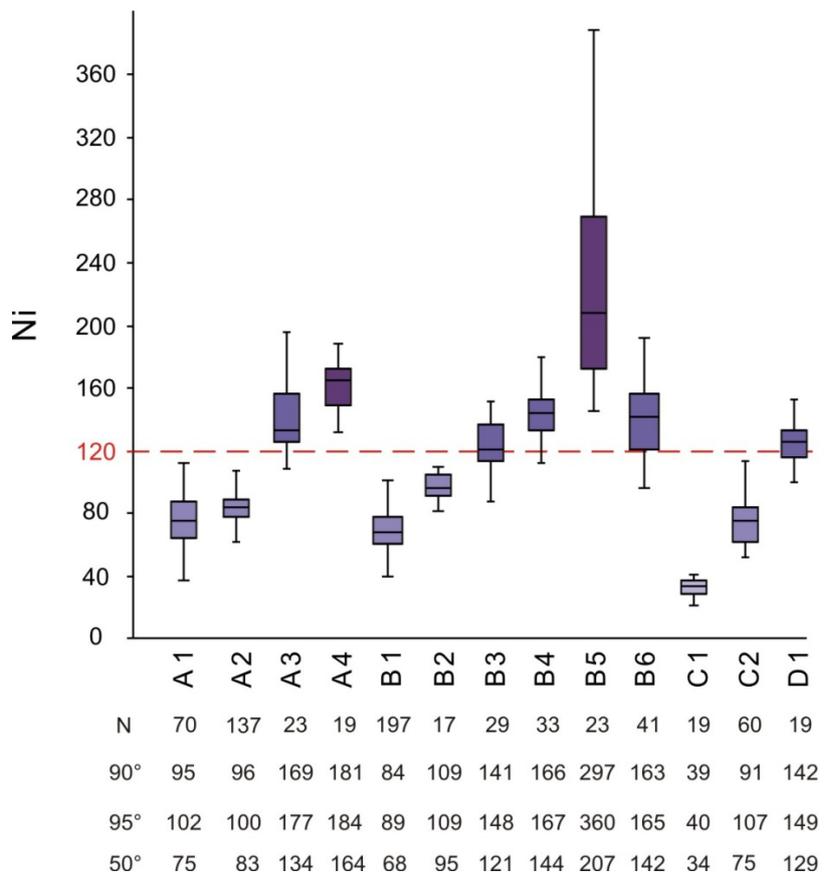


Fig. 12 – Natural distribution of Ni in the studied GFUs, with indication (in mg/kg) of the 90th, 95th and 50th percentile values.

3.2. Zinc [Zn]

The pedogeochemical content of Zn in soils of the Emilia-Romagna alluvial plain is primarily controlled by soil texture, with only subordinate influence of parent material composition. With the exception of GFU A1 (soils with high degree of weathering), all GFUs plot along a single regression line in the Zn-V scatterplot (Fig. 13). The positive correlation between Zinc and Vanadium (similar results, however, are obtained between Zn and Al_2O_3) indicates affinity of Zn for the aluminosilicate sediment fraction (Fig. 4), thus implying its preferential accumulation in silt and clay deposits. This interpretation is consistent with the relatively high Zn and V concentrations observed in fine to moderately fine textured soils developed on floodplains (A2, A3 and A4). Zn and V decrease progressively with increasing sand proportion (*i.e.*, soils developed on channel-levee and crevasse splay complexes (B1-B6), the lowest values being recorded within soils formed on beach-ridge sands (C1-C2). In soils with relatively higher degree of weathering (A1), Zn exhibits lower values if compared to all other GFUs (Fig. 13). This fact is likely related to a certain mobility of Zn in response to pedogenic processes.

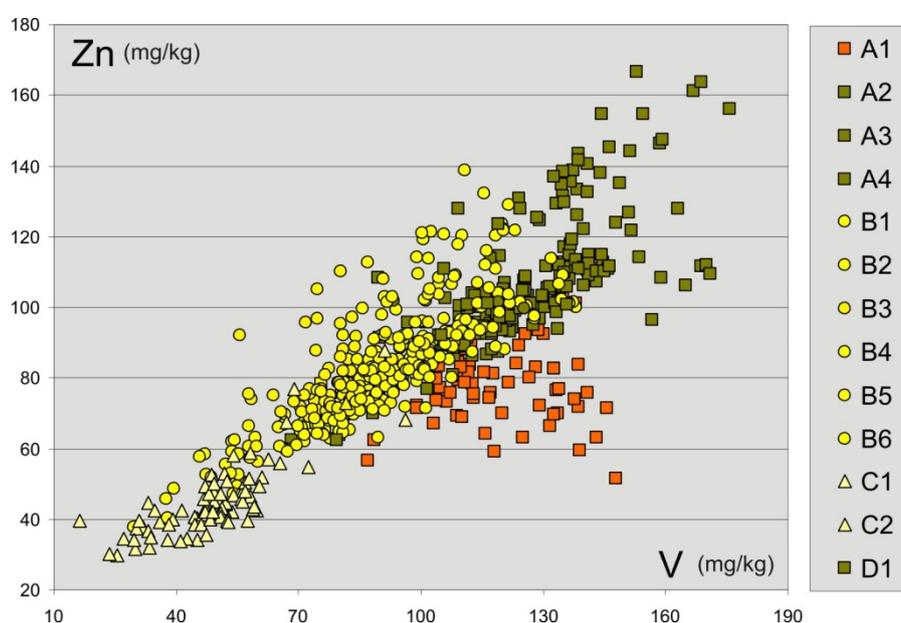


Fig. 13 – Scatterplot diagram Zn-V.

Matching the natural Zn concentrations of individual GFUs in the study area (see box-plots in Fig. 14) against the threshold values (see legend of Fig. 9) results in natural Zn contents invariably lower than the maximum permitted level of 150 mg/kg. Unique exception is GFU A4 (soils developed on interdistributary area clays of the abandoned Po Delta), where the 95th percentile is 164 mg/kg. Relative Zn enrichments are also observed in soils rich in organic material, formed in interdistributary bays (D1 - 146 mg/kg). The slight increase in Zn within sediments supplied by Po River (B6) is likely related to metal concentration in Zn-clorite, a typical component of peridotites, which is abundant in ophiolitic rocks.

In all other fine textured GFUs, the 95th percentile values range between 114 and 124 mg/kg (see soils on floodplain clays and silts - A2, A3). These values contrast markedly with those (99-106 mg/kg) recorded from channel-levee and crevasse soils (B1-B5). Finally, coarse textured soils formed on beach-ridge sands display 95th percentile values well below the maximum permitted levels (< 60 mg/kg in Fig. 14).

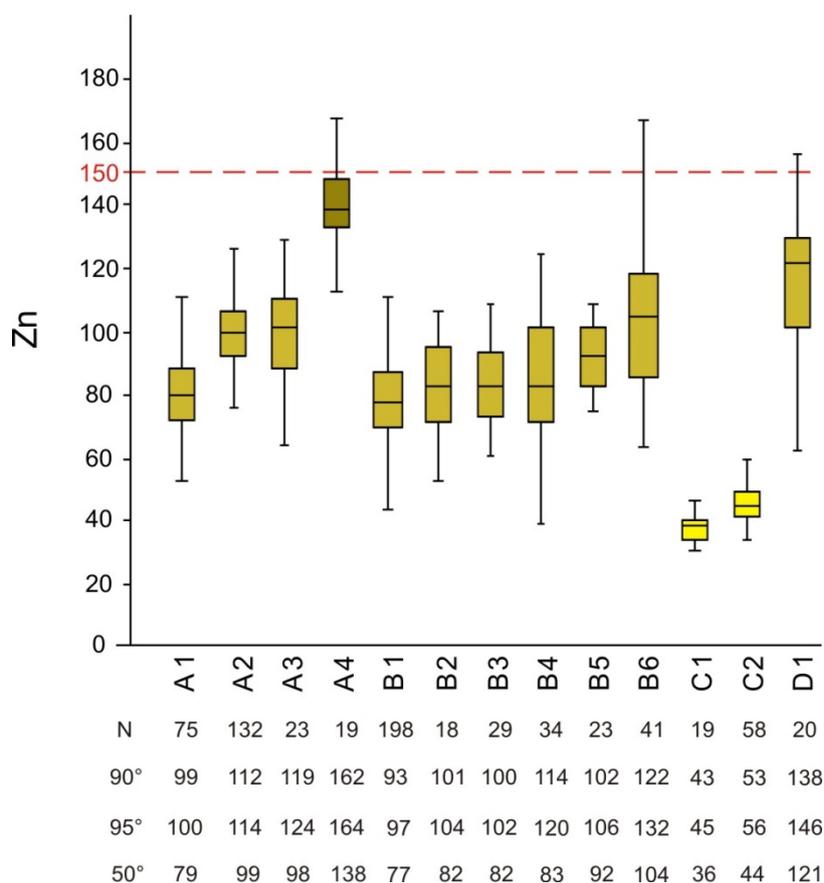


Fig. 14 – Natural distribution of Zn in the studied GFUs, with indication (in mg/kg) of the 90th, 95th and 50th percentile values.

3.3. Copper [Cu]

In general, Copper behaves as Zn in the Map of the Pedogeochemical Content, though with some peculiarities. As for Zn, the natural spatial distribution of Cu appears to be related primarily to changes in soil texture (Fig. 15). Soils on both floodplain clays/silts and swamp clays (GFUs A2, A3, A4 and D1) display higher Cu and TiO₂ contents than soils formed on silty sands and sandy silts (channel-levee and crevasse deposits - GFUs B1-B6). Likewise, soils developed on coarse sands (beach-ridge deposits: GFUs C1-C2) show the lowest Cu concentrations. Unlike Zn, however, Cu and TiO₂ have significantly lower correlation, as documented by their high dispersion on the scatterplot diagram.

GFU A1, which includes relatively more weathered soils developed at the Apenninic margin, displays a distinctive geochemical signature (compare with Fig. 13), being Cu-depleted and relatively Ti-enriched (Fig. 15). This geochemical behavior is consistent with the higher degree of soil weathering. Particularly, the decrease in Cu concentration within these soils is due, as for Ca, to weathering and eluviation processes. This suggests that Cu is linked to mineral phases poorly resistant to pedogenesis, while Ti is concentrated within the residual fraction.

The box-plot representation of Cu values in soils with low to moderate degree of weathering, subdivided by depositional environment (Fig. 16), shows a subtle distinction in metal concentration. Moving away from the fluvial-channel axes, floodplain soils display higher values than their channel-levee sandy-silty counterparts. Soils with higher degree of weathering (A1) plot in a distinct field of the diagram, with generally lower Cu contents. Finally, soils developed on coastal sands (C1-C2) exhibit the lowest metal values.

Despite the remarkable difference in terms of mean Cu concentrations between sandy soils (95th percentile: 10-20 mg/kg) and fine textured to moderately coarse textured soils (95th percentile: 40-50 mg/kg), all GFUs in the Emilia-Romagna plain fall into a single class of the Map of the Pedogeochemical Content. This

is due to the threshold level for Cu (120 mg/kg) on which the map legend is built, which causes a sort of “flattening” of the values ranging from low to moderate.

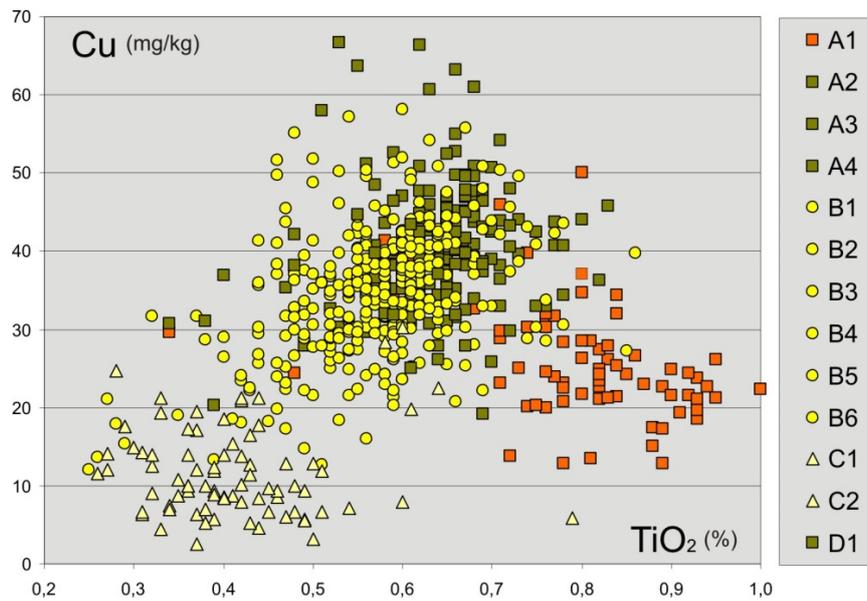


Fig. 15 – Scatterplot diagram Cu-TiO₂.

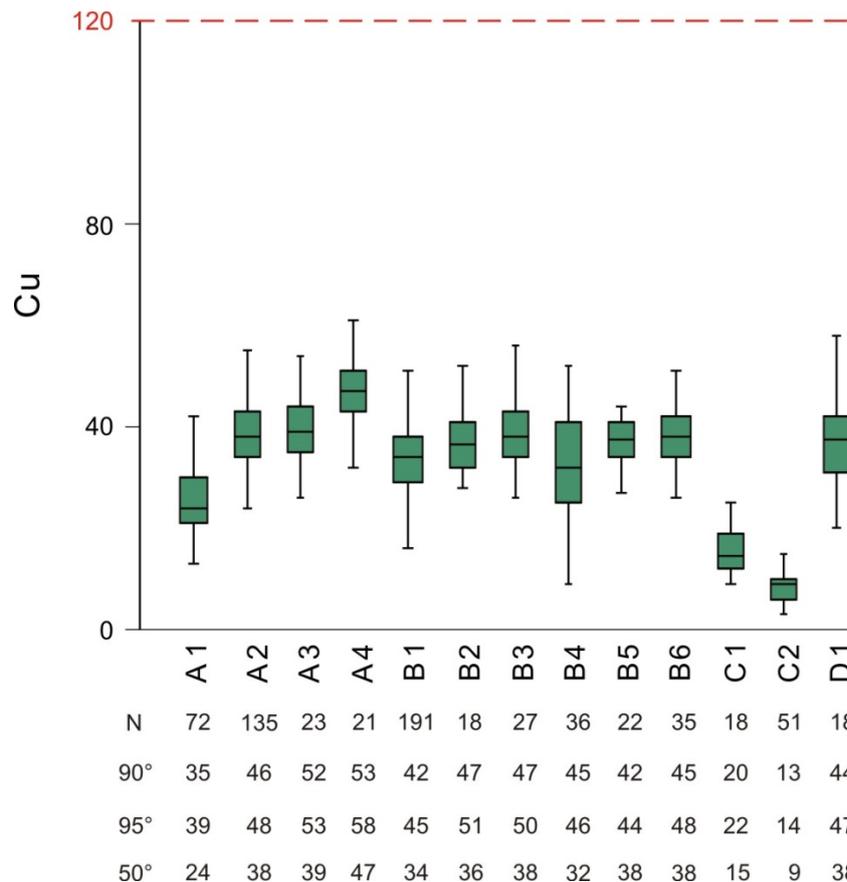


Fig. 16 – Natural distribution of Cu in the studied GFUs, with indication (in mg/kg) of the 90th, 95th and 50th percentile values.

3.4. Lead [Pb]

The identification of the factors that may influence natural Lead distribution in soils of the Emilia-Romagna plain is a difficult task. This is due primarily to the very low difference in metal values recorded for the different GFUs, but also to the fact that such low metal contents are commonly close to the detection limits of the analytical (XRF) technique. Owing to lack of important natural sources of Pb in the river catchments, changes in parent material do not represent a major controlling factor. However, neither texture nor the degree of soil weathering appear to play an important role in controlling the natural spatial distribution of Pb. This is clearly shown in Figure 17, where the scatterplot diagram between Pb and Al₂O₃, an oxide representative at the same time of clay minerals proportion and soil weathering, does not show any difference between the GFUs in terms of Pb contents.

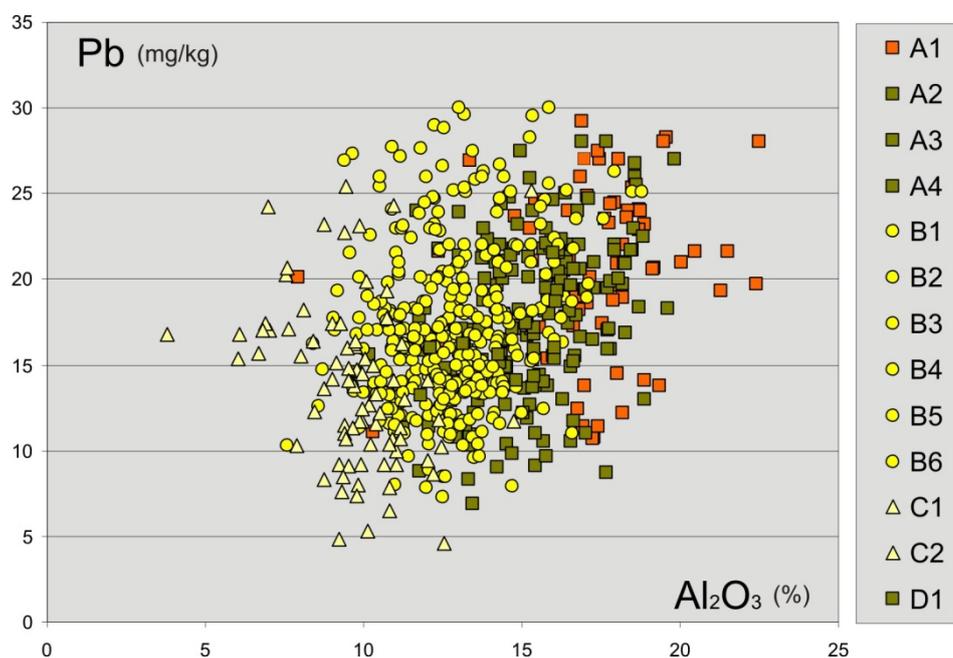


Fig. 17 – Scatterplot diagram Pb - Al₂O₃.

The overall compositional homogeneity of all GFUs is clearly documented by the box-plot representation of Pb concentrations (Fig. 18). In particular, there appear to be very small differences, not statistically significant, between the 13 groups of soils, with very subtle changes in the 95th percentile values (min: 18 mg/kg; max: 30 mg/kg).

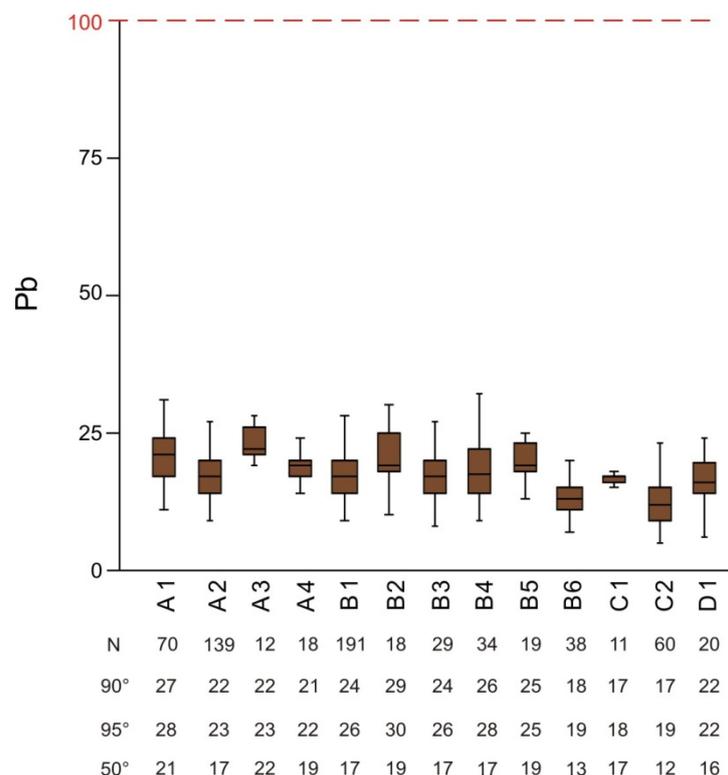


Fig. 18 – Natural distribution of Pb in the studied GFUs, with indication (in mg/kg) of the 90th, 95th and 50th percentile values.

3.5. Geochemical anomalies

The accurate determination of the pedogeochemical content across the study area provides the basis for a realistic estimate of the anthropogenic contribution. Specifically, its comparison with metal concentrations in topsoil samples leads to quantification of the Geoaccumulation Index, providing important information about the pollution state of soil. It should be kept in mind, however, that point information obtained from individual study sites cannot be extrapolated outside such small areas, and that specific, local studies should be undertaken in order to detect precisely the sources of anthropogenic contamination.

The diagrams of Figure 19, which show the relative abundance of the various Igeo-classes for the five studied metals, summarize the data shown extensively by the Map of Geochemical Anomalies.

For Cr and Ni, Igeo exhibits negative values (= unpolluted soil) for > 98% of the > 700 samples examined. This fact confirms that high metal concentrations, even greater than threshold levels, are not *per se* an indication of anthropogenic pollution. Nor the Emilia-Romagna soils display important contamination by Zn (93% negative values of Igeo). Pb and Cu offer, instead, a different picture: unpolluted soils decrease to 72% for Pb, and to less than 60% for Copper. For this latter metal, the spatial distribution of geochemical anomalies suggests that soil use exerted a major role on anthropogenic metal concentration. The superficial enrichment in Cu observed in the Reggio Emilia, Modena and Ravenna countryside is likely due to the use of pesticides for viticulture, and to the vast quantities of manure.

It is important to remark, however, that not all that may appear a geochemical anomaly based on the Geoaccumulation Index, is really representative of anthropogenic contribution. Since Igeo is a function of metal concentrations detected in subsoil and topsoil samples, a simple vertical change, along the soil profile, of textural characteristics or sediment composition may generate false positives, of geogenic or pedogenic (and not anthropogenic) origin. Another common possibility, especially where the pedogeochemical content is very low, is that the supposed geochemical anomaly simply be the result of an instrumental error.

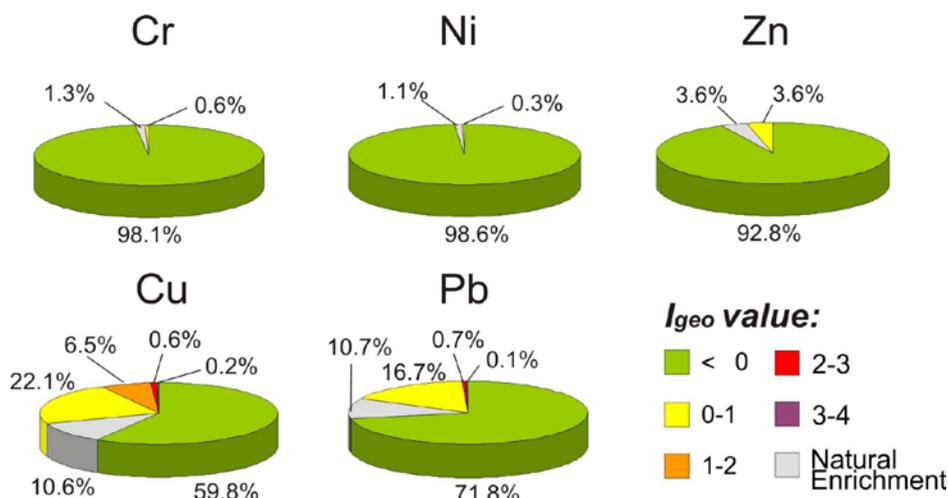


Fig. 19 – Pollution state of soils of the Emilia-Romagna plain, as revealed by the Geoaccumulation Index from about 700 sampling sites (for classification of Igeo values, see Table 6).

The distinction between actual geochemical anomalies (yellow, orange and red colours in Fig. 19) and natural enrichments (in grey) is possible plotting samples with Igeo > 0 onto the same scatterplot diagrams (Cr-Ni, Zn-V, Cu-TiO₂ and Pb-Al₂O₃ in Fig. 20) used for the geochemical characterization of subsoil samples (in green). Samples that plot significantly off the regression line are interpreted as anomalies, and are thus likely to represent anthropogenic contamination. In contrast, samples that plot along the same regression line as the green samples (see grey samples in Fig. 20), simply with higher metal values, are interpreted as false positives, and their relatively higher metal contents as due to either (i) change in sediment provenance, (ii) decrease in grain size, or (iii) abundance of carbonates or organic matter in the deep sample, which generates an underestimation of the other elements.

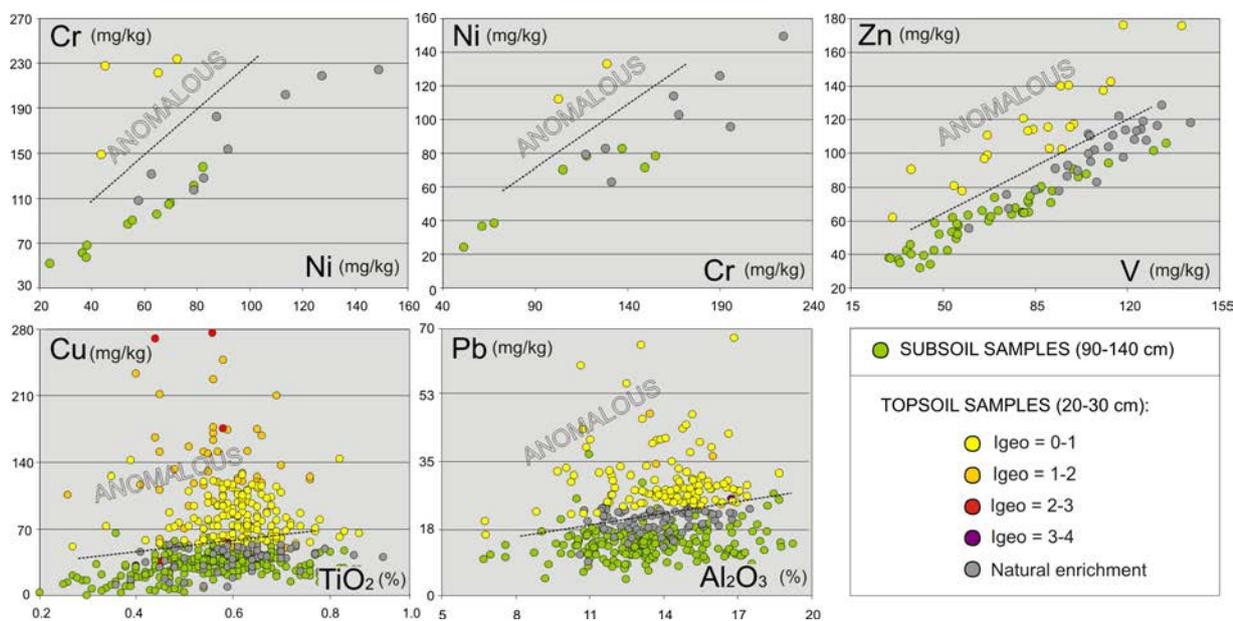


Fig. 20 – Detecting soil contamination with the aid of scatterplot diagrams. The green dots are representative of the pedogeochemical content. Coloured dots are inferred to represent metal contamination. The grey dots are interpreted as false positives (see text).

The above corrections proved to be effective for Cr, Ni, and Zn. In contrast, ambiguous interpretations persist locally for Pb and Cu (20% and 30% of the anomalies, respectively - see Fig. 20). This fact further suggests that the Map of Geochemical Anomalies should not be used as a template, but as a guide to specific, and more detailed investigations, to be undertaken, necessarily, on a local basis.

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