Alma Mater Studiorum – Università di Bologna

DOTTORATO DI RICERCA IN

Scienze ambientali: tutela e gestione delle risorse naturali

Ciclo XXVI

Settore Concorsuale di afferenza: 04/A1

Settore Scientifico disciplinare: GEO 08

Stream sediments analysis for geochemical mapping of Romagna Apennines (Northern Italy): monitoring and management tool of environmental resources at various scales

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Esame finale anno 2014

«Soyez régulier et ordonné dans votre vie comme un bourgeois,
ainsi vous pourrez être emporté et original dans votre œuvre.»

(Gustave Flaubert)

ABSTRACT

Geochemical mapping is a valuable tool for the control of territory that can be used not only in the identification of mineral resources and geological, agricultural and forestry studies but also in the monitoring of natural resources by giving solutions to important environmental and economic problems. The mapping of the elements is needed to understand the geochemical processes from global- to local-scale, detect geochemical backgrounds and their changes in a defined time, identify and document the human impact on the distribution of the elements, manage the plans regarding the land use and many other policy decisions. Stream sediments are widely used in the sampling campaigns carried out by the world's governments and research groups for their characteristics of broad representativeness of rocks and soils, for ease of sampling and for the possibility to conduct very detailed sampling

In this context, the environmental role of stream sediments provides a good basis for the implementation of environmental management measures, in fact the composition of river sediments is an important factor in understanding the complex dynamics that develop within catchment basins therefore they represent a critical environmental compartment: they can persistently incorporate pollutants after a process of contamination and release into the biosphere if the environmental conditions change. It is essential to determine whether the concentrations of certain elements, in particular heavy metals, can be the result of natural erosion of rocks containing high concentrations of specific elements or are generated as residues of human activities related to a certain study area. The determination of the natural background may be an important product of this analysis as this information could have management implications useful as a reference point in the investigation of a possible alteration and environmental contamination.

This PhD thesis aims to extract from an extensive database on stream sediments of the Romagna rivers the widest spectrum of informations. The study involved low and high order stream in the mountain and hilly area, but also the sediments of the floodplain area, where intensive agriculture is active. The geochemical signals recorded by the stream sediments will be interpreted in order to reconstruct the natural variability related to bedrock and soil contribution, the effects of the river dynamics, the anomalous sites, and with the calculation of background values be able to evaluate their level of degradation and predict the environmental risk.

RIASSUNTO

La cartografia geochimica costituisce un valido strumento di controllo del territorio che può essere utilizzato non solo nell'identificazione di risorse minerarie e in studi a carattere geologico, agricolo e forestale ma anche nel monitoraggio delle risorse naturali dando risposte importanti a problemi ambientali ed economici. La mappatura degli elementi è necessaria per comprendere i processi geochimici a larga e piccola scala, documentare i background geochimici e le variazioni in un tempo definito, identificare e documentare l'impatto umano sulla distribuzione degli elementi, pianificare l'uso del suolo e molte altre decisioni politiche. I sedimenti fluviali sono da decenni tra i materiali più utilizzati nelle campagne di campionamento realizzate dai governi mondiali e dai centri di ricerca di tutto il mondo per le caratteristiche di ampia rappresentatività di rocce e suoli, per la facilità di campionamento e per la possibilità di effettuare ricerche dettagliate con sforzi e risorse più contenute in termini economici e temporali.

In questo contesto il ruolo ambientale dei sedimenti fluviali costituisce una valida base per l'implementazione di misure di gestione ambientale, infatti la composizione dei sedimenti fluviali è un importante fattore nella comprensione delle complesse dinamiche che si sviluppano all'interno dei bacini idrografici in quanto rappresentano un comparto ambientale critico: essi possono incorporare sostanze inquinanti persistentemente dopo un processo di contaminazione e rilasciarle nella biosfera se cambiano le condizioni ambientali. È essenziale determinare se le concentrazioni di certi elementi, in particolare dei metalli pesanti, può essere il risultato di erosione naturale delle rocce contenenti alte concentrazioni di specifici elementi o sono generati come residui delle attività umane legate ad una certa area di studio. La determinazione del valore naturale dei tenori di fondo può essere un importante prodotto di questa analisi poiché tale informazione potrebbe avere implicazioni gestionali utili come punto di riferimento nell'investigazione di una possibile alterazione e contaminazione ambientale.

Questa tesi di dottorato è finalizzata ad estrarre da un vasto database dei sedimenti fluviali dei fiumi della Romagna il più ampio spettro di informazioni. Lo studio riguarda aste fluviali di vario ordine che si sviluppano tra montagna e pianura dove sono presenti aree urbanizzate, attività agricole e industriali. I segnali geochimici registrati dai sedimenti fluviali sono stati interpretati allo scopo di ricostruire la variabilità naturale relativa ai contributi del suoli e delle rocce, studiare gli effetti delle dinamiche fluviali e, con il calcolo dei valori dei tenori di fondo, valutare ed indentificare i siti anomali, il loro livello di degradazione e predire il rischio ambientale.

CONTENTS

CHAPTER 1

Introduction and summary

1.1 Geochemical mapping projects in environmental monitoring at various scales

Geochemical mapping is a powerful method to assess environmental status, background concentration and provide a basis for monitoring changes in the levels of chemical elements at the Earth's surface. Geochemical maps have traditionally been valuable in addressing a whole range of environmental problems, geological, agricultural and forestry studies, in addition to probably the original application of geochemical mapping, that is for mineral prospection. Several decades of geochemical mapping by national geological surveys and related organisations throughout the world, have resulted in a wealth of valuable information (Thornton and Plant, 1980; Bolviken et al., 1990; Darnley, 1990; Reid, 1993; Simpson et al., 1993; Davenport et al., 1993; Birke and Rauch, 1993; Darnley et al., 1995; Cocker, 1996a, b, 1998a, b; Moon, 1999) available at local, regional, national scale.

Geochemical mapping projects have been carried out in some little countries since the late 1960s (Garrett and Nichol, 1967; Armour-Brown and Nichol, 1970; Redman and Gould, 1970) and in continental countries during the late 1970s in China (Xie 1979) and early 1980s in USA (Shacklette and Boerngen, 1984). These countries were mapped conducting low-density geochemical survey with sample densities ranging from 1 site per 200 km^2 to 1 site per 18000 km^2. Sampling densities were a direct reflection of the purpose of the survey and the scale at which they were conducted, indeed as the area to be mapped becomes larger, the task becomes economically and logistically difficult (Smith and Reimann, 2008). In the same years were carried out high density geochemical survey at regional-scale in European countries: England and Wales (1 site per 3.1 km^2; Webb et al. 1978), Germany (1 site per 3 km^2; Fauth et al., 1985) and Austria (1 site per 1.4 km^2; Thalmann et al., 1989).

In the early 1990s, Darnley (1990) began to promote the realization of the International Geochemical Mapping project (IGM) and suggested the use of the global geochemical reference network (GRN) promoting guidelines in multi-media approach (stream sediments, surface waters, soils, floodplain sediments) for multi-scale projects (Darnley et al., 1995). During the last twenty years, these documents and the early mapping projects have led to the proliferation of global-, continental-, regional-, local- and detailed-scale geochemical mapping projects in each continent (Tab.1). This has resulted in the use of new sampling densities, different sample types and various analytical techniques. According with Reimann et al. (2010), the following definitions of scale are used:

- global scale: >50 million km^2 – suggested sample density < 1 site/5000 km^2;
- continental scale: 0.5–50 million km^2 – sample density between 1 site/5000 km^2 and 1 site/500 km^2;
- regional scale: 500–500,000 km^2 – sample density between 1 site/500 km^2 and 1 site/km^2;
- local scale: 0.5–500 km^2 – sample density between 1 site/ km^2 and > 100 sites/km^2;
- detailed scale: <0.5 km^2 – sample density usually >100 sites/ km^2 or detailed scientific investigations on some few samples.

Projects	Sampling density (km^2/site)	Area(km^2)	Scale	Sample type	Mapping technique	References
China	18000 - 1	9.572.900	Continental	Foodplain sediment, stream sediment Lag materials,rockdebris	Interpolation	Xie & Cheng (1997,2001)
Australia	10000 – 1000	7.617.930	Continental	Foodplain sediment at 2 dephts	EDA	Caritat & Cooper (2011)
USA	6000	9.372.614	Continental	Soil	Interpolation[1]	Gustavsson et al. (2001)
FOREGS	5000	4.450.000	Continental	Foodplain sediment, humus, sub soil, top soil, stream sediment, stream water	Interpolation[1]	Salminen et al. (2005)
GEMAS	2500	5.600.000	Continental	Arable soils and grazing soils	Interpolation	Reimann et al. (2009)
Baltic Soil Survey	2500	1.800.000	Continental	Agricultural top and botsoils	Interpolation[2]	Reimann et al. (2003)
North America	1600	21.329.304	Continental	Soil	Interpolation	Smith et al. (2005,2006)
Barents Project	1000	1.550.000	Continental	terrestrial mosses, organic topsoil, C-horizon, and stream water	Interpolation	Salminen et al. (2004)
Germany	380	357.124	Regional	Stream sediment, surface water	Interpolation	Birke et al (2009)
Finland	300 – 5	338.424	Regional	glacial till, organic stream sediments, groundwater, surface water	Interpolation[1]	Siewers (1992)
Kola Project	300	188	Local	Top and subsoil	Grid	Reimann et al. (1998)
Parana (Brazil)	220	199.727	Regional	Overbank sediment,stream sediments, stream water	Interpolation	Licht (2005)
Portugal	135	89000	Regional	Topsoil(A),organic horizons(humus, O)	Interpolation[2]	Inácio et al. (2007)
Holland	70	41.526	Regional	Topsoil, parent material	EDA	Veer et al. (2006)
Croatia	25	56.542	Regional	Soil	Interpolation[3]	Halamić et al. (2012)
Aquitania (France)	16	41.309	Regional	Soil (30 cm)	Administrative boundaries	El Hadri et al. (2012)
India	5 – 1	3.268.090	Continental	sediment	Interpolation	Geological Survey of India (2012)
Campania (Italy)	5	13600	Regional	Stream sediment, topsoil	Interpolation[4]	De Vivo et al. (2003)
Emilia Romagna plain (Italy)	5	10.507	Regional	Topsoil (60-80cm), subsoil (90-140cm)	Pedology	Amorosi et al. (2011)
Muravera (Italy)	5	690	Local	Stream sediments, soil	Catchment basins	Valera P (2008)
South Africa	1	1.219.090	Continental	Stream sediment, soil	Interpolation	Lombard et al. (1999)
UK	1	152.195	Regional	Topsoil,subsoil,stream sediments, water	Interpolation[3]	Rawlins et al (2012)
Aaroy district (Philippines)	1	101	Local	Stream sediments	Interpolation[4], Catchment basins	Carranza (2010)

[1] MWM (Moving Weighted Median), [2] Kriging, [3] IDW: Inverse Distance Weighting, [4] MIDW: Multifractal Inverse Distance Weighting

Tab. 1 Table of some geochemical mapping projects carried out in the world. For each project specified: sampling density (km^2/site), area (km^2), scale (continental, regional, local), sample type, mapping technique and references.

1.2 Density sampling and scale of representation

At continental scale, there have been some initiatives in China (Xie and Cheng, 1997, 2001) providing very low-density floodplain sampling (1 per 18000 km^2) collected as part of the EGMON project and very high density stream sediment sampling of RGNR Project (Xie et al., 1989, 1997; Xie and Ren, 1997) (Fig.1 a). In United States (Fig.1 b) , it has been confirmed the low-density soil sampling (1 per 6000 km^2) collected for the conterminous USA (Gustavsson et al., 2001); in fact studies by Smith et al. (2005, 2006) allow additional tests of the robustness of the maps generated from the low-density soil data. Another very low-density sampling (1 per 10000 km^2) has been carried out in Australia (Caritat and Cooper, 2011) using catchment outlet sediments sampled at two depths (Fig.1 c). In Europe, some countries as Germany (Fig.2 a), Finland (Fig.2 b), Portugal (Fig.2 c), Holland (Fig.2 d) and Croatia (Fig.2 e) have produced national atlases (Birke et al., 2009; Siewers, 1992; Inácio et al., 2007; Veer et al., 2006; Halamić et al., 2012) with a low-density sampling ranging from 1 site per 300 km^2 to 1 site per 25 km^2.

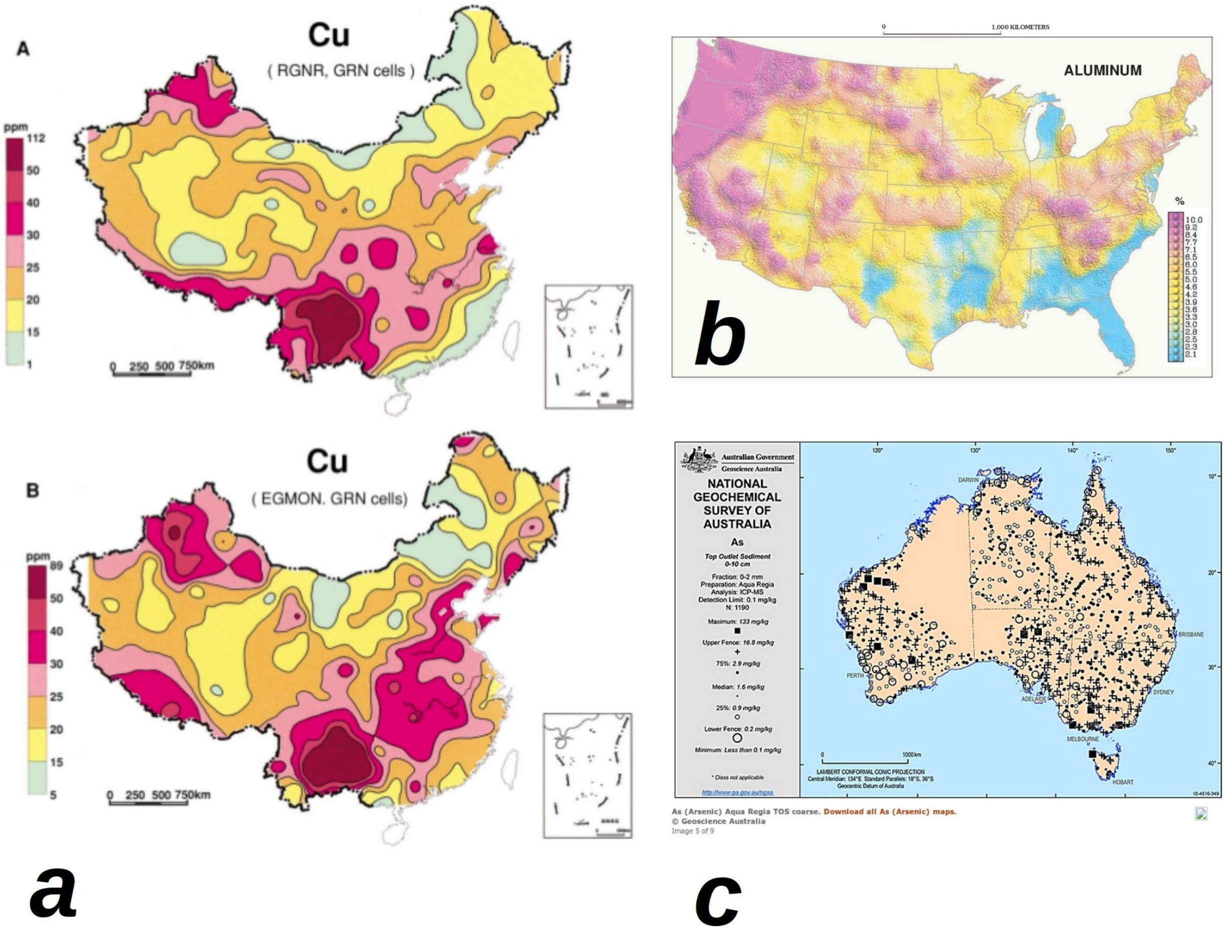

Fig.1 Geochemical maps of China (a), United States (b) and Australia (c).

Also continental european projects have been mapped in various projects at different low-density sampling: Kola project (1 site per 300 km^2; Reimann et al., 1998) (Fig.3 a); Barents Project (1 site per 1000 km^2; Salminen et al., 2004) (Fig.3 b); Baltic Soil Survey (1 site per 2500 km^2; Reimann et al., 2003) (Fig.3 c); GEMAS Project (1 site per 2500 km^2; Reimann et al., 2009) (Fig.3 d); FOREGS (1 site per 5000 km^2; Salminen et al., 2005) (Fig.3 e).

At regional-, local- and urban-scale, occurred different choices in the sampling density therefore the determining factor in the preservation of patterns is the original magnitude of the geochemical variation and size of the geological features (Ridgway et al., 1991). Surveys can be carried out at density which are compatible with the local scale of geological and geochemical features, the purpose of the geochemical survey and its logistical and funding constraints. Moreover higher density sampling would be appropriate in areas where social and environmental factors are more important (Fordyce et al., 1993). Geochemical mapping projects at regional- and a more local-scale have been much more common (El Hadri et al., 2012, Fig.4 a; De Vivo et al., 2003, Fig.4 b; Carranza, 2010, Fig.4 c; Amorosi et al., 2011, Fig.4 d; Valera, 2008, Fig.4 e). Chiprés et al. (2008) recognize various factors: the easier logistical considerations, the smaller budgets required and the need to obtain more precise informations. Further, Ohta et al. (2011) point out that high density mapping in an urban region is an effective tool for risk assessment for human health. The importance of this survey's scale is confirmed by various projects regarding urban geochemical mapping (Urban Geochemistry project of major European cities; 2012 Annual report for the international union of geological science). These projects were carried out at very high-density sampling (4-8 samples per 1 km^2) (Guillén et al., 2011, Fig.5 a; Flight et al., 2011, Fig.5 b).

Some exceptions are represented by national geochemical mapping projects of India (Fig.6 a), England and Wales (Fig.6 b), South Africa (Fig.6 c) (Geological Survey of India, 2012; Rawlins et al., 2012; Lombard et al., 1999) in which correlations between area and sampling density is not respected. Although the areas have a national-scale, atlases were carried out at high-density sampling (1 site per km^2).

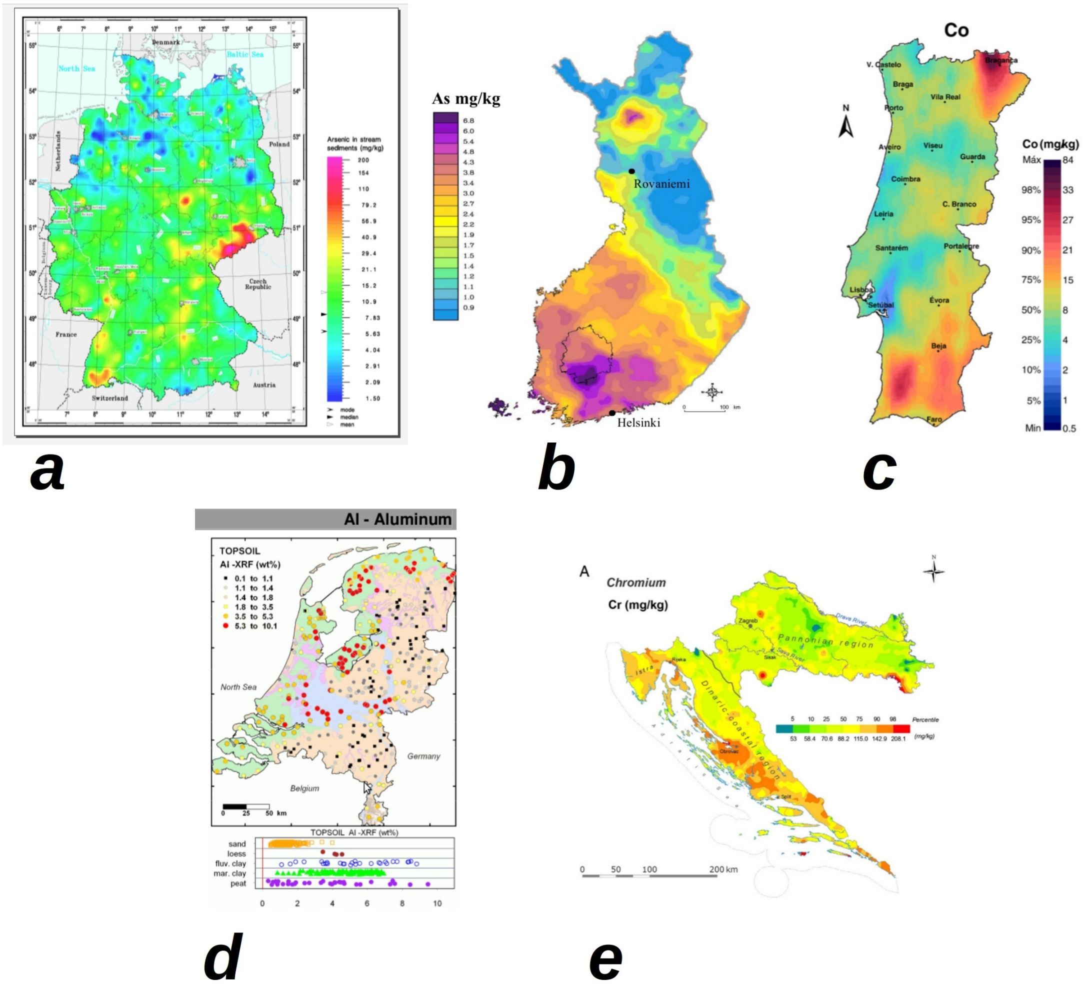

Fig.2 Geochemical maps of Germany (a), Finland (b), Portugal (c), Holland (d) and Croatia (e).

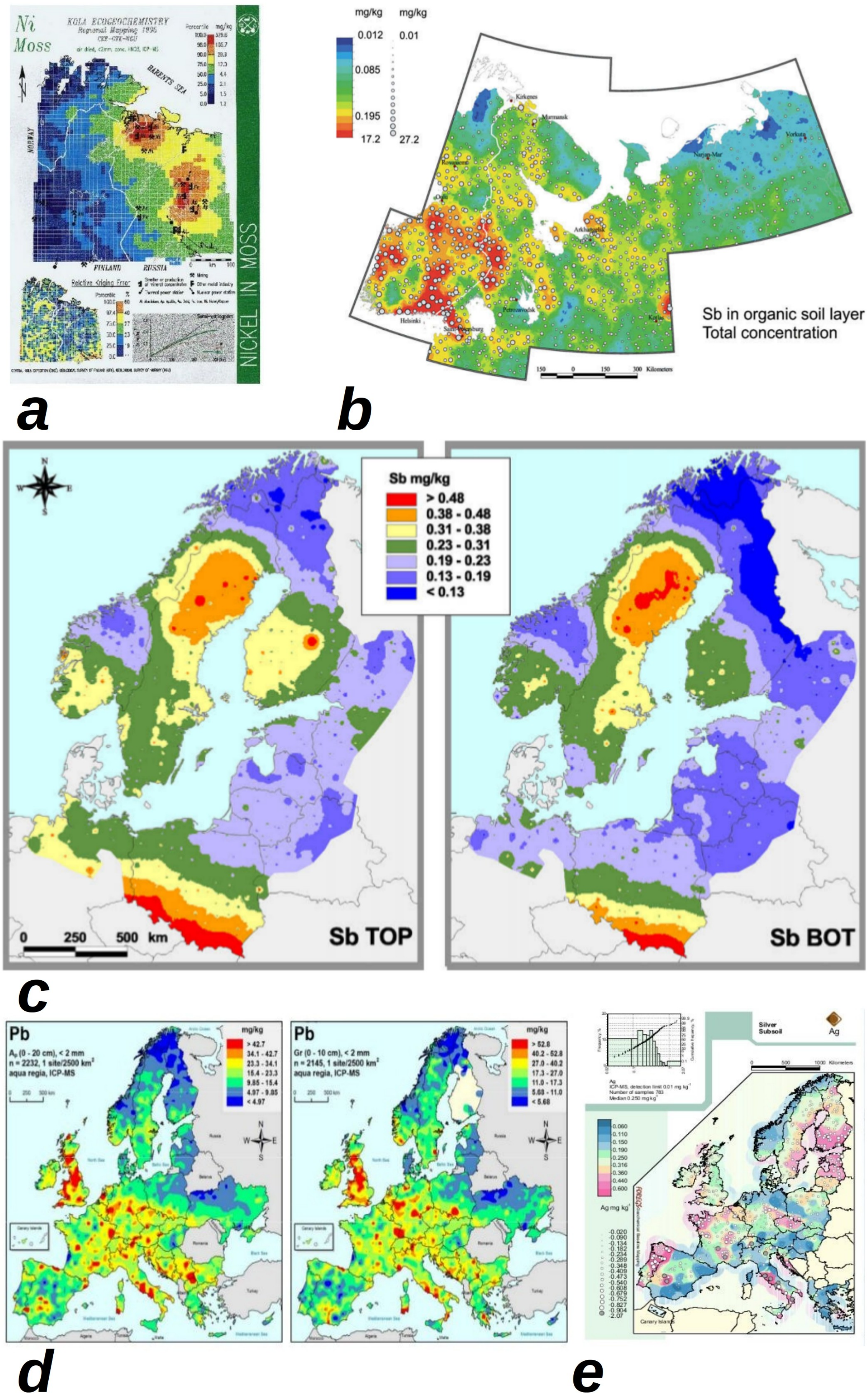

Fig.3 Geochemica maps of Kola project (a), Barents project (b), Baltic Soil Survey (c), GEMAS project (d) and FOREGS (e).

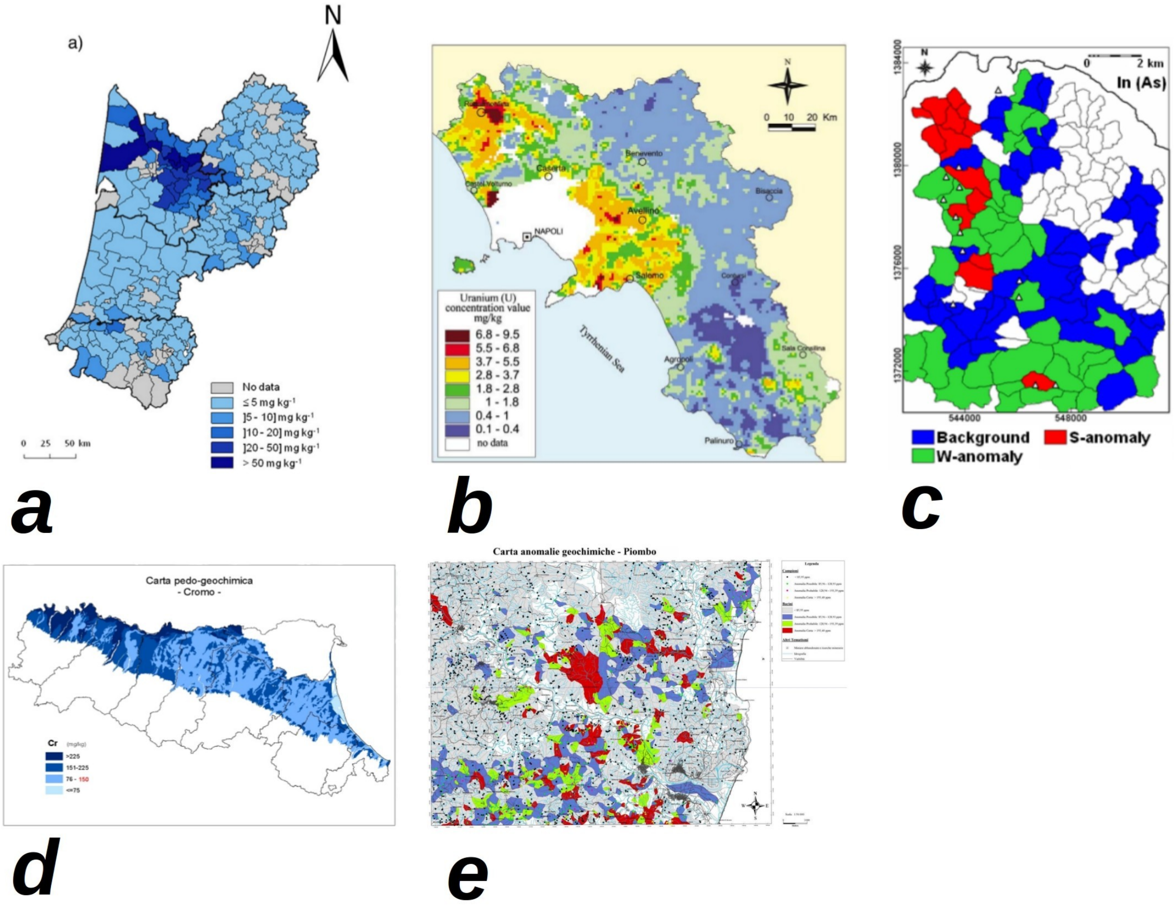

Fig.4 Geochemical maps of Aquitaine region in France (a), Campania region in Italy (b), Aaroy district in Phylippines (c), plain of Emilia Romagna region in Italy (d) and Muravera area in Sardegna-Italy (e).

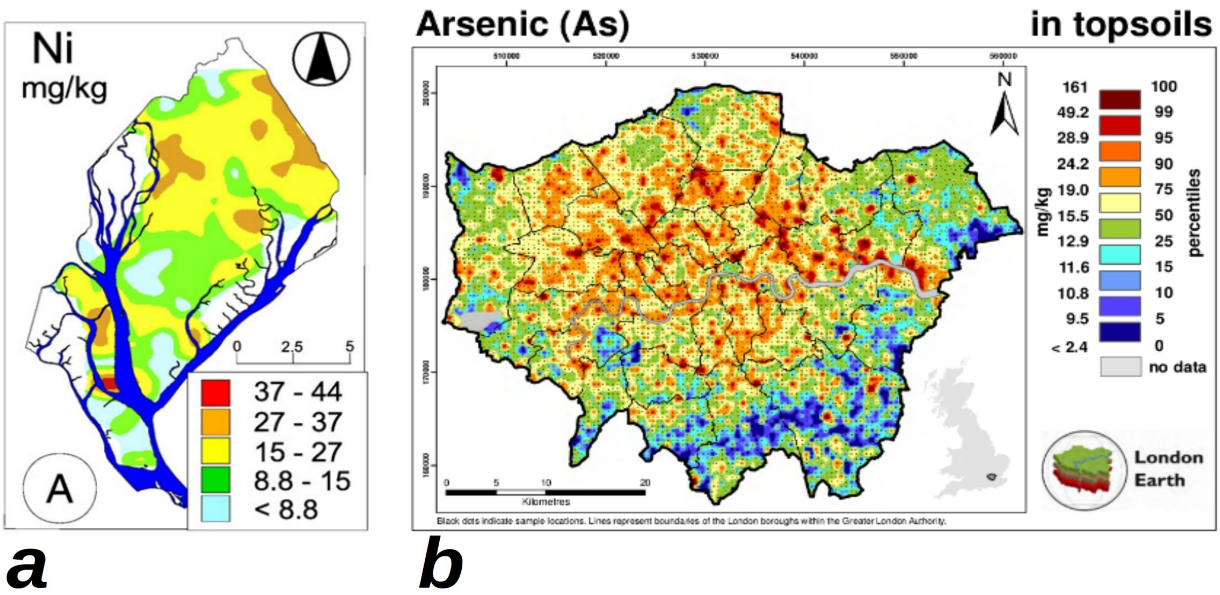

Fig.5 Urban geochemical maps of Huelva municipality in Spain (a) and London in UK (b).

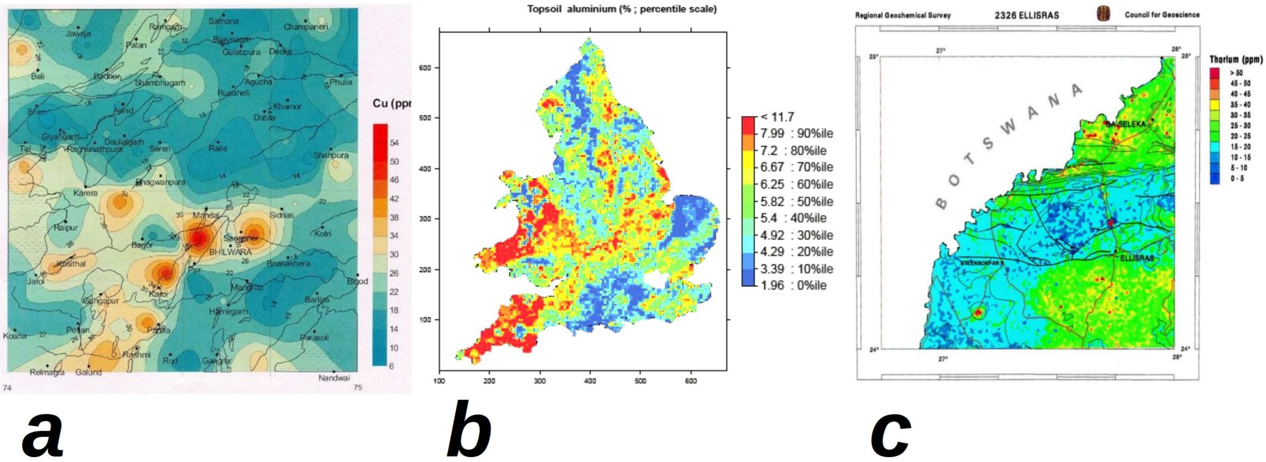

Fig.6 Some extracts from the geochemical maps of India (a), England and Wales (b) and South Africa (c).

1.3 Mapping techniques

An informative geochemical map and a visible data structure are the goals of each geochemical survey's group. The task is not simple because its realization requires the application of certain graphics (histogram, density trace, one-dimensional scattergram, boxplot and cumulative probability plot) to investigate the data structure, trends, relation among variables and identify anomalies. Another critical point regards the data elaboration for map production: the choice between point maps and interpolated maps, and application of gridding algorithm for interpolation (IDW, MWM, Kriging, Spline) but also some aspects of art. In fact the choice of colour scales or symbols are not secondary details (Reimann, 2005) for a powerful representation of the information. If we look at many geochemical maps produced in the last years, we notice that sampling density and sample type have influenced the use of certain mapping techniques. Dividing mapping techniques in two groups, statistics and non statistics, defined and discussed in the following section. In general, we can notice that there is a widespread implementation of statistical techniques (interpolation, EDA) and a restricted use of non statistics techniques in geochemical maps carried out at high-density sampling (Table 1, Fig. 7).

1.3.1 Statistical techniques

Interpolation techniques have become a “routine” tool in geochemical mapping, especially with development of powerful multifractal models that identify geochemical anomalies (Cheng et al., 1994, 2000; Li et al., 2003; Cheng, 2008; Azfal et al., 2011) and determine geochemical baselines (Cicchella et al., 2005; Lima et al., 2003, 2008). At national and continental scale this technique is very useful because the extension of point data covers areas that were not sampled reducing analytical costs (Fig.8). For this reason pattern data of large countries (China, USA, India, South

Africa, Germany) and continental projects (FOREGS, GEMAS, Baltic Soil Survey, Barents Project) were processed using interpolation techniques. Otherwise at regional and local scale, multifractal models (Concentration-Area model, Spectrum-Area model, Concentration-Distance model, Concentration-Volume model) associated to interpolation have proven very effective in mineral exploration and environmental assessment (De Vivo et al., 2003, Carranza, 2010). Also EDA has proved to be a robust technique in defining threshold data (Kürzl, 1988; O'Connor et al., 1988; Reimann et al., 1988; Bounessah and Atkin, 2002) and we notice that some countries (Holland and Australia) have adopted this technique for respectives geochemical atlases (Veer et al., 2006; Caritat and Cooper, 2011) at low-density sampling.

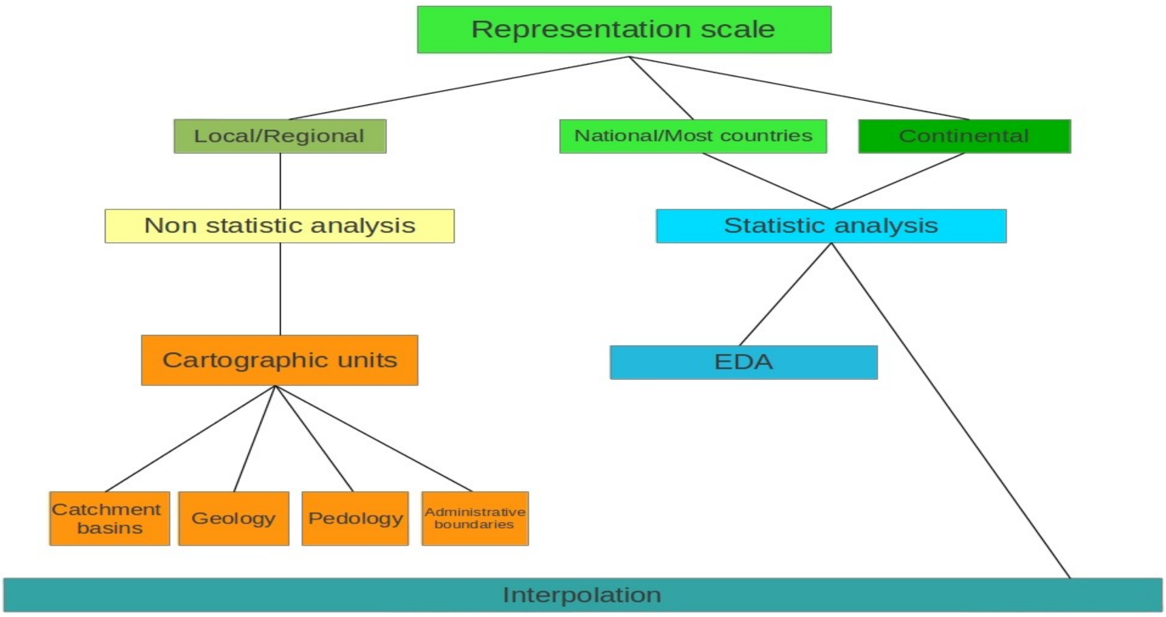

Fig.7 Diagram of statistical and non statistical technique applied in geochemical mapping projects (up). The techniques of representation are also ordered according to sampling density (bottom).

1.3.2 Non statistical techniques

In the group of non-statistical techniques are grouped methods of representation that use cartographic units as catchment basins, pedologic units, administratives boundaries and cell grid (Fig. 8). The use of catchment basins is not recent and positive results of its application are known since the late 1980s (Bonham-Carter et al., 1987; Carranza and Hale; 1997; Moon, 1999; Seoane and Barros Silva, 1999; Spadoni et al., 2004; Spadoni, 2005) while pedogeochemical mapping, a model using pedologic landscape, has been developed in recent years (Amorosi et al., 2011). Also the application of administrative boundaries by El Hadri et al. (2012) is a new example of geochemical mapping. These projects were carried out at regional- (Amorosi et al., 2011; El Hadri et al., 2012) and local-scale (Carranza, 2010; Valera, 2008) because the application of these techniques requires an high-density sampling (1 samples per 1-5 km^2). An exception is represented by cell grid in fact this technique has been applied in the continental Kola project.

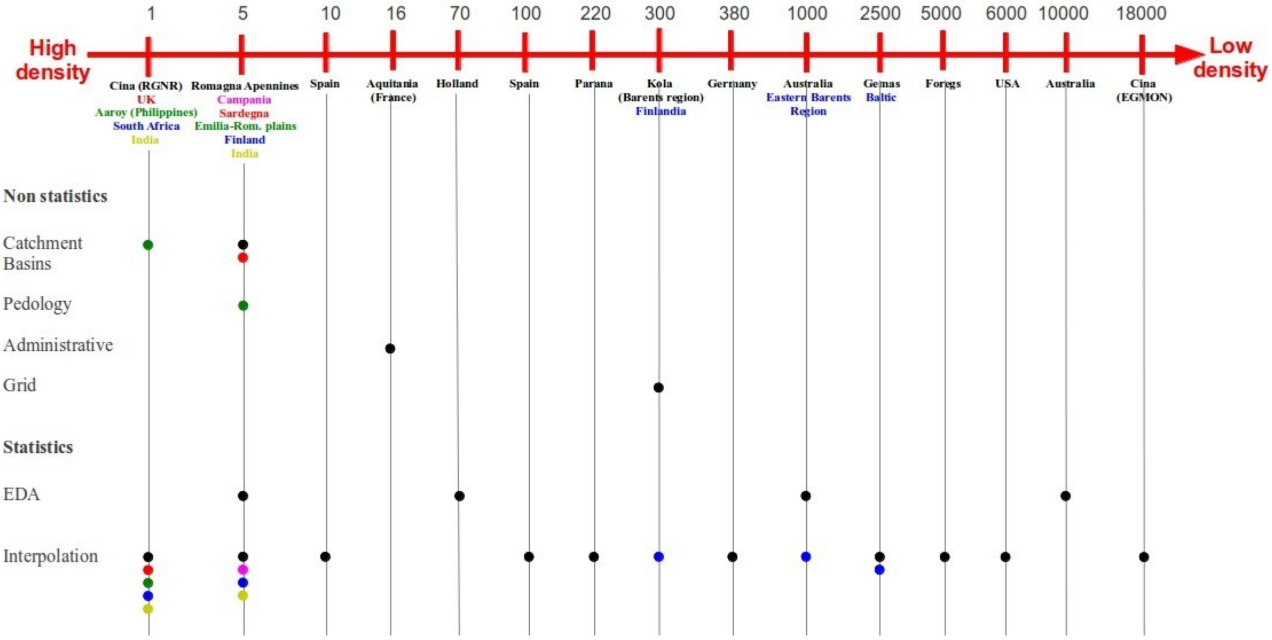

Fig.8 Frequency of statistical and non-statistica techniques in geochemical mapping projects according to sampling density.

1.4 Sample type

The selection of appropriate sampling media and procedures has been identified as the most crucial decision-area in the context of international geochemical mapping, and therefore it has received the most attention. In order to benefit from standardization at later stages in the mapping process, it is necessary that the various sample media collected conform to accepted specifications. Since 1990s, Darnley et al. (1995) have suggested materials with a broad significance for certain environments and scales. Indeed Ottesen et al. (1989) showed how overbank sediments have turned out to be an important medium for the construction of maps of geochemical elements in large regions (Fig. 9). These samples are used in geochemical mapping of China, Australia, Europe and in the pilot project for a global geochemical mapping in the brazilian area of Paraná (Licht, 2005).

Soils have been used largely in a lot of projects from continental- to local-scale mapping (Fig. 9) (Reimann et al., 1998; De Vivo et al., 2003; Reimann et al., 2003; Salminen et al., 2005; Smith et al., 2005, 2006; Inácio et al., 2007; Veer et al., 2006; Halamić et al., 2012; Reimann et al., 2009; Amorosi et al., 2011; Gustavsson et al., 2011; Lombard et al., 2012; Rawlins et al., 2012) therefore reflect variations in the geogenic composition of the uppermost layers of the Earth's crust but are also important in regional surveys to avoid soil sampling at locations that have visible or known contamination (Salminen, 2008). Other sampling media such as till, surface water and terrestrial mosses were tested and became more commonly used in geochemical surveys (Siewers, 1992; Lahermo et al., 1990, 1996; Ruhling, 1994; Reimann et al., 1998; Salminen et al., 2005). These samples have been exploited mainly as a sampling material on national- and regional-scale (Finland, Norway and Kola project) (Fig. 9).

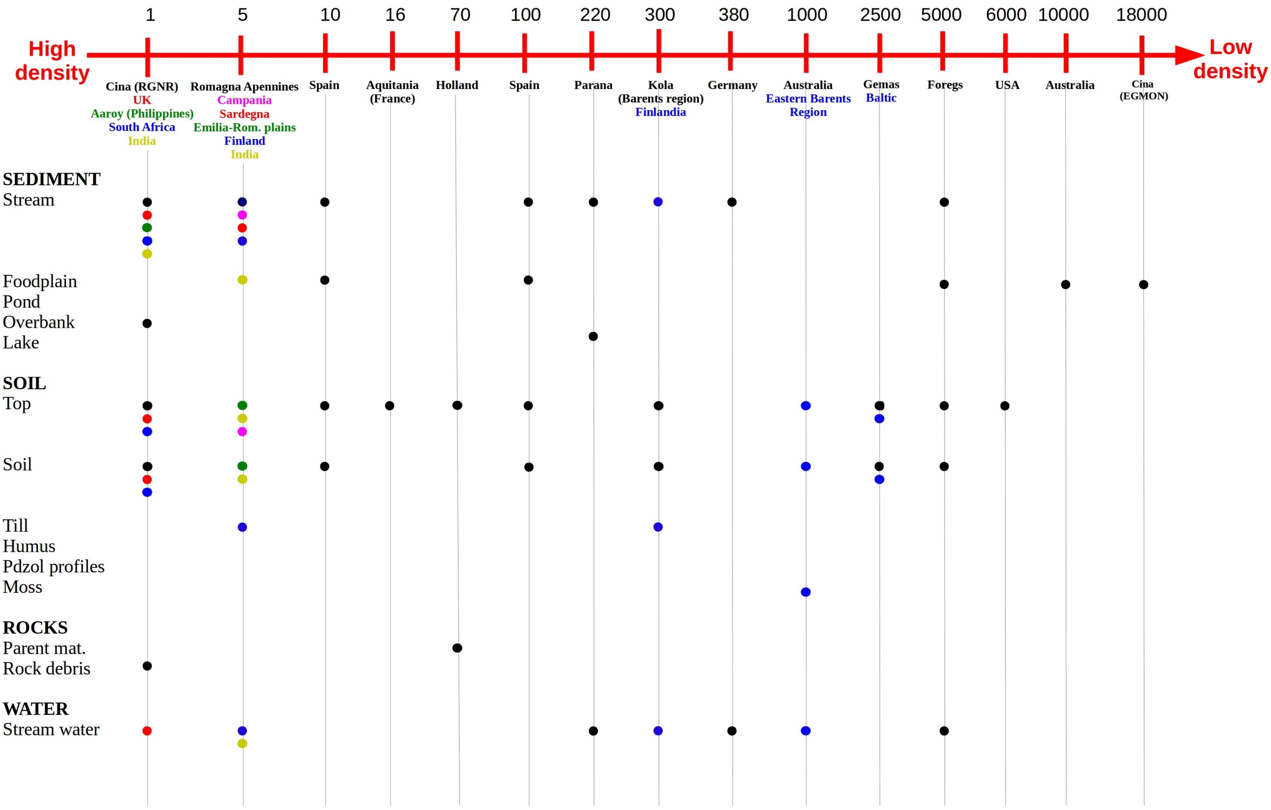

Fig.9 Frequency of sample types used in geochemical mapping projects according to sampling density.

1.5 Stream sediments as medium samples in environmental monitoring

Wherever the landscape permits, stream sediments have been the preferred sampling medium for reconnaissance geochemical surveys concerned with mineral exploration. According to the definition given by the Forum of the European Geological Surveys (FOREGS), these are represented by the fine and medium size fraction of sediments (< 0.150 μm) carried and settled by second order streams (Salminen et al., 2005). The samples, if properly collected, represent a composite of materials from the drainage basin upstream of the collection site (Darnley et al., 1995) therefore can be genetically considered as a mixing between grains and particles of different nature originated from erosive processes within a catchment basin (Spadoni, 2005) (Fig. 10).

However, sediment yield and the geochemistry of river sediments are controlled not only by the physical and chemical weathering of parent rocks, but also by factors such as climatic, hydrological and morphological features of the basin. Incongruent and congruent dissolution, which takes place in the presence of aqueous solutions during penetration through soils and rocks, can result in differences between the chemical composition of a parent rock and its resulting weathering product (Nahon, 1991). Similarly, channel bed morphology and bank slope can strongly influence the transportation and sorting of minerals. Sufficiently intense rainfall can initiate bed load transport, bringing the − 100 μm fraction into suspension (Fletcher, 1996). The energy slope of the channel bed also positively contributes to the initiation of bedload transport. This will result in a downslope variation in the composition of lag deposits, with deposits that are rich in heavy minerals and coarse materials located in areas with steeper slopes and deposits that contain finer or lighter materials located in flatter areas (Fig. 10).

Government-sponsored reconnaissance surveys covering, for example, large parts of China, Germany, South Africa, UK, USA (Rawlins et al., 2012; Lombard et al., 1999; Geological Survey of India, 2012; Xie and Cheng, 2001) have been based on stream sediments and for regional geochemical surveys is the most widely used sample material throughout the world (Salminen, 2008). In this regard various projects have been developed considering a high-density sampling at local-(Carranza, 2010, Valera, 2008) and regional- (De Vivo et al., 2003; Spadoni, 2005) scale (Fig.9). Stream sediments have some characteristics that provide a lot of advantages in the realization of geochemical mapping:

- they have a good sensitivity for many heavy metal trace elements;
- they reflect the rock and soil composition of wide areas that permits to avoid high-density sampling; consequently, the geochemical characteristics of each sample can be considered as a function of the composition of different geological materials and sediments of anthropogenic origin transported along the hydrographical network (Bolviken et al., 1990; Webb et al., 1978; Lahermo et al., 1996);
- the sampling is more facilitated by the accessibility of sites because the best place is the closing section of catchment basin;
- the chemical composition is relatively stable;
- during the deposition the selection of a certain type of material occur, allowing for greater uniformity in the fraction sampled for analysis.

The complex nature of stream sediments and their capacity to incorporate different sources of geochemical imput have fundamental importance in environmental geochemistry, especially when investigating the background concentrations, the presence of natural and anthropic anomalies (Spadoni, 2005) and the identification of local enrichments of geochemical concentrations

(Rantitsch, 2000). Geochemical landscapes have been modelled as continuous fields by interpolating stream sediment geochemical data with sampling density sufficiently high and spatial autocorrelation (De Vivo et al., 2003; Lombard et al., 1999; Rawlins et al., 2012; Carranza, 2010; Birke et al., 2009) and alternatively as discrete fields by attributing stream sediment data to their sample catchment basins (e.g. Bonham-Carter et al., 1987; Carranza and Hale, 1997; Spadoni et al., 2004). These studies have shown that the appropriateness of these techniques using stream sediment depend largely on the mapping scale of exploration and/or environmental geochemical surveys: continuous field modelling of geochemical landscapes based on stream sediment is an advantageous in regional-scale geochemical surveys, in which the objective is to delimit broad anomalous areas for further investigations at higher scales. In regional-scale geochemical surveys over large areas (say, western Europe; see Lima et al., 2008), discrete field (e.g.: catchment basin) modelling of geochemical landscapes based on stream sediment is not totally inappropriate but, because of variations in sizes of sample catchment basins due variations in sampling density and sample distribution, could be both tedious and impractical with respect to the scale(s) of output map(s) (e.g. 1:100 000 or smaller). On the other hand, discrete field modelling of geochemical landscapes based on stream sediment is arguably advantageous in many cases of district-scale to local-scale environmental and/or exploration geochemical surveys, in which the objective is to establish precisely sources of contamination and/or significant anomalies in individual catchment basins (e.g.: Goodyear et al. 1996; Ódor et al., 1998; Moon, 1999).

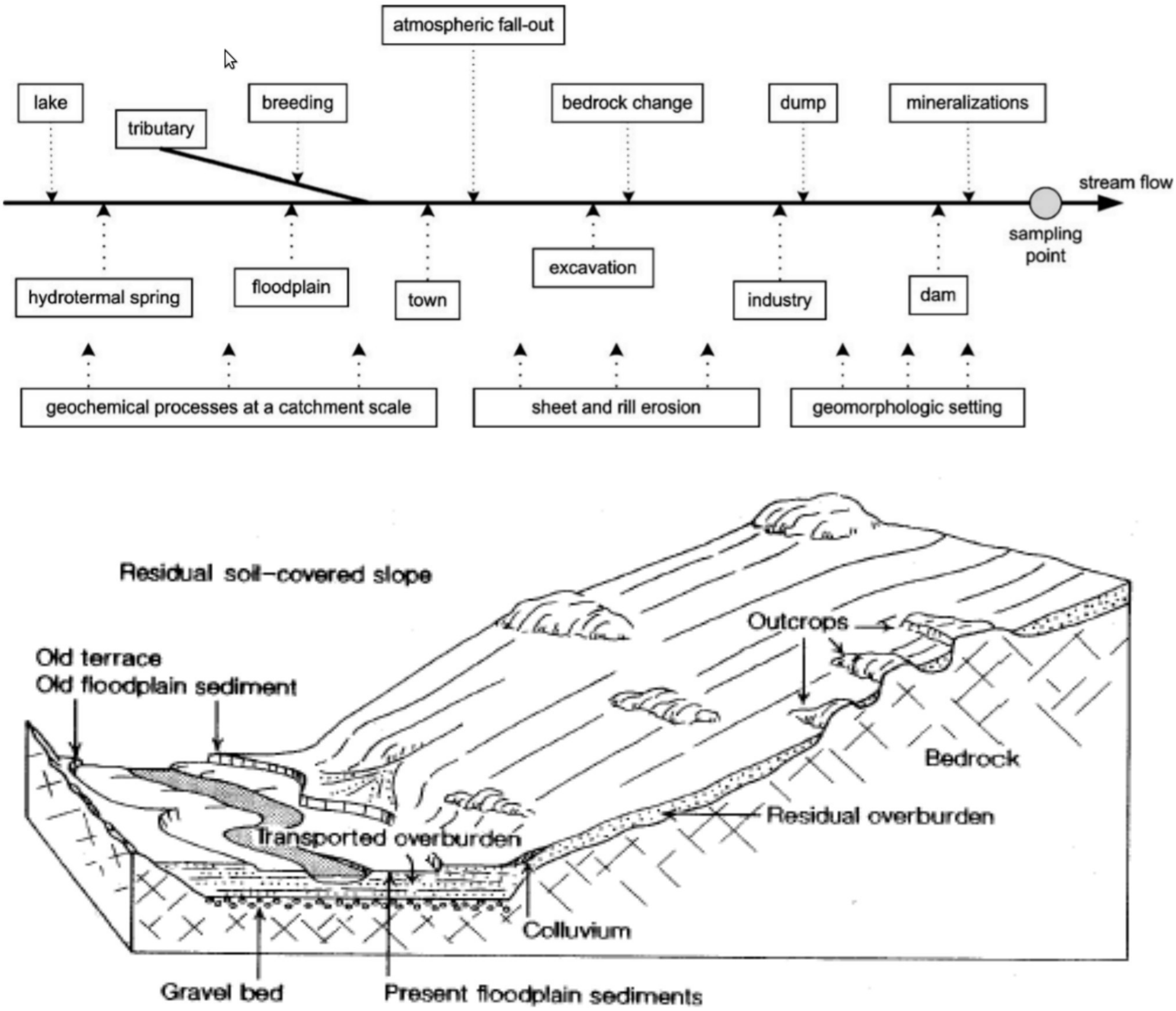

Fig. 10 Some of the most important factors affecting the composition of stream sediments. From a practical point of view, tributaries can be also considered as sources of geochemical inputs (Spadoni et al., 2006). Below is reprented the geomorphology of a typical catchment basin (Strahler, 1969).

1.6 The aims of the doctorate and the environmental role of stream sediments

The purpose of the doctorate is to develop innovative methods for data analysis and elaboration concerning stream sediment. These approaches will increase the knowledge, identify natural sources for chemical elements as well as compromised sites, provide useful information in terms of land management.

In this context the environmental role of stream sediment constitutes a valid base for the implementation of environmental management measures: in fact the composition of stream sediments is an important factor, although sometimes neglected, in the comprehension of the complex dynamics that occur within catchment basins. They can be affected by fluvial processes and climate, they are strongly influenced by bedrock lithology and soil composition, they collect anthropogenic products that can modify their quality. In general, stream sediments represent a critical environmental compartment because they can persistently incorporate contaminants, even after an episode of contamination and eventually release if environmental conditions change (Baudo et al., 1990). In particular the section of fine particle size of the sediment represents the geochemically more active component since it can adsorb large quantities of contaminants (Sodergen, 1997) and transport away from the initial source. The sediments play a fundamental role in the processes of deposition, accumulation and transport of contaminants in aquatic environments because they could move with the sediment and may interact with various components of the biosphere (Karickhoff et al., 1979; Santiago et al., 1994). On the other hand their composition can be useful to trace their source, since the presence of heavy metals and minerals in different concentrations allows us to determine the origin of the sediments in fact each tributary has its own characteristics of sedimentation that give it a unique and recognizable geochemical signal (Lake et al., 1990). It is essential to determine whether the concentrations of certain elements, and in particular some heavy metals may be the result of natural erosion of rocks containing elements or are generated as residues of human activities that are carried out in a given study area.

Determination of the natural background, thus, can be an important product of such an analysis. The data from small catchment can be considered to be affected by anthropogenic alteration only to a limited degree and thus could be helpful in the determination of the natural background of any element analysed. This information could have great management implication since could be used as a reference point to investigate possible alteration.

This PhD thesis aims to extract from an extensive database on stream sediments of the Romagna rivers the widest spectrum of information. The study involved low and high order stream in the mountain and hilly area, but also the sediments of the floodplain area, where intensive agriculture is active. The geochemical signals recorded by the stream sediments will be interpreted in order to reconstruct the natural variability related to bedrock and soil contribution, the effects of the river dynamics, the anomalous sites, and with the calculation of background values be able to evaluate their level of degradation and predict the environmental risk.

1.7 Chapter summary

Chapter 2 discusses various geochemical representation techniques of a regional-scale area characterized by complex geology and multiple factors. The investigation of stream sediment geochemistry of the Romagna Apennines point out the importance in different approaches that can evidence peculiarities otherwise concealed by a standardized technique. Firstly a reasoned elaboration of dataset and the classification with adequate statistical techniques such as growing dot maps and cumulative probability plots can evidence clear differences in the spatial distribution of chemical composition of stream sediments derived from geology. In addition the choice of certain symbols and class division in the exploration of dataset can draw attention to particular anomalous areas that are not evident in overall representations. Finally the use of mapping techniques based on IDW interpolation and SBC techniques highlight the potential of stream sediments and high-density sampling in the identification of probable contamination sources.

Chapter 3 presents a geochemical mapping technique based on geological units of the turbiditic Marnoso-arenacea Formation. This local-scale area is derived from the regional-scale area studied in *Chapter 2* therefore the aim is to assess the potential resulting from an increase in stream sediment sampling density and the presence of a more detailed scale. The results of this study show that a geochemical map based on geological units could be a valid tool supporting the geology reconstruction of a complex area and providing additional data for interpretation: in fact, the recognition of a time-dependent evolutionary trend of geological members of the Marnoso-arenacea formation characterized by Apenninic and Alpine inputs is consistent with the available petrographical, mineralogical and geochemical literature.

Chapter 4 broadens the scope of the thesis in several ways. The analysis of stream sediments moves to a more local-scale deepening the study of heavy metals content in the catchment basins of the Romagna rivers. The upper threshold level of background for every single catchment is evaluated following the ISO/DIS 19258 recommendation and these data are applied to show the environmental status of the major rivers working either on the elemental concentration and on nromalized values. So the analysis of stream sediment becomes not only a means for establishing thresholds that identify the geological background of the area but also a powerful tool for identifying sources of pollution. In this ways are detected with a major precision the samples contaminated according with the study of land use and geochemical index (Igeo).

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CHAPTER 2

Regional geochemical mapping at high density sampling: various criteria in representation of Romagna Apennines, Northern Italy[1]

Abstract

Geochemical mapping is a fundamental tool in environmental monitoring and land management. For this reason, regional-, national- and global-scale geochemical mapping projects have been carried out in some countries since the late 1960s. In the Romagna Apennines (Northern Italy) has been conducted an high density stream sediment geochemical survey (1 sample per 5 km^2): 770 samples were collected in a regional-scale area (4125 km^2) and analysed for 30 elements by X-ray fluorescence spectrometry on the fraction < 180 µm. The area has a complex geology dominated by sedimentary rocks and characterized by different geological units that belong to specific palaegeographic domains: Ligurian, Tosco-Umbrian and Padano-Adriatic. In the area industrial settlements and largest towns are in the plains, agricultural areas in the hills and a wooded mountainous area is common in the upper reaches of the major streams.

In data interpretation different mapping techniques were applied: growing dots, EDA symbols, IDW interpolation and Sample Catchment Basin (SCB) mapping approach. Growing dot maps associated with cumulative probability plots are effective tools for an indicative framework of the area in fact is evidenced the lithological control of geological units. EDA symbols based on quantiles demonstrate that some informations could be more evident considering relevant symbols and class divisions: moreover subdivision of a total dataset in separate populations related to a specific grouping variable highlights anomalous areas that are not evident in an overall representation. Finally the comparison of mapping techniques based on IDW interpolation and SCB approach show different methods in the identification of anomalous distribution of chemical elements and in particular SCB approach indicate the source of the possibile signal.

This study shows how in an area characterized by multiple factors, chemical elements cannot be represented properly with a standardized mapping technique. Indeed, the use of different mapping techniques point out peculiarities useful for interpretation of the effect of geology or of the human impact.

Keywords: Geochemical mapping; Stream sediments; Sample Catchment Basin (SCB) approach; IDW interpolation, Geostatistics

1 This chapter consists of a paper by Lancianese V. and Dinelli E. submitted at Journal of Geochemical Exploration.

2.1 Introduction

During the last forty years, geochemical mapping projects have been carried out in many places of the world playing an important role both in mineral exploration and environmental studies (Darnley et al, 1995; Grunsky et al., 2009). The spatial distribution of chemical elements presented as geochemical maps allows a better visualization of the geochemical processes active in a study area, facilitating for example the decision-making process in land management and assessment (De Vivo et al., 1998). According to available literature some important criteria were considered when creating geochemical maps. The representation scale has influenced the choice of density sampling because at continental- and national-scale some countries were mapped conducting low-density geochemical survey with sample densities ranging from 1 site per 25 km^2 to 1 site per 18000 km^2 whereas at regional- and local-scale prevailed high-density sampling ranging from 1 site per 1 km^2 to 1 site per 5 km^2. The same sampling density influenced also the sample type, in fact low-density surveys have been conducted searching materials with a broad significance (Darnley et al., 1995). Ottesen et al. (1989) showed how overbank sediments can be a representative medium for the construction of maps of geochemical elements over large areas. Also Smith et al. (2005, 2006) allow additional tests of the robustness of maps generated from the low-density soil data although a soil sample is only considered to be representative of the point on the Earth's surface where it was collected (Smith and Reimann, 2008). However this peculiarity has been exploited in a lot of high-density projects because is useful in avoiding locations that have visible or known contamination (Salminen, 2008). Other authors (e.g.: Lahermo et al., 1990; Ruhling, 1994; Salminen et al., 2005; Siewers, 1992) suggested other low-density sampling media such as till, surface water and terrestrial mosses as other matrices to be used in geochemical surveys.

At regional scale, stream sediment is the most widely used sample material in high-density geochemical surveys throughout the world (Salminen, 2008) and, as the overbank sediment samples, represents a composite of materials from the drainage basin upstream of the collection site (Darnley et al., 1995). The stream sediment composition is closely linked to different factors such as geological setting, history, slope, vegetation, pedogenesis and industrial activities (Spadoni et al., 2005). This complex nature of stream sediments can be exploited in environmental and exploration geochemistry and the resulting maps can be useful in defining background values and localizing geochemical anomalies (Spadoni, 2006). Studies undertaken at higher density can investigate the local effects of anthropogenic influence and the relationships between the chemical composition of stream sediments and bedrock geology (Yamamoto et al., 2007). The abundance of spatial informations in stream sediment data should be appropriately investigated and supported by various statistical and cartographic techniques. The goal is to obtain an informative geochemical map and a visible data structure but the task is not simple because its realization requires the choice of certain statistical graphics as histogram, density trace, boxplot and cumulative probability plot, the use of specific gridding algorithm for interpolation but also some aspects of art that involve the employment of effective colour scales, class selection and explicative symbols (Reimann, 2005).

Geochemical data structure often follow a log-normal distribution due to outliers or are poly-populational, related to the geochemically distinct bedrock lithologies or anthropogenic contamination (Reimann, 2005). For these reasons, operating a class selection for colour map or choosing symbols for black and white map is very difficult and requires several tests. Percentiles, boxplot, cumulative probability plot, QQ-plot are widespread univariate tools for data exploration and representation and, since interpolation techniques have become a “routine” tool in geochemical mapping, have been developed also other techniques of class selection, especially powerful multifractal models that identify geochemical anomalies (Cheng et al. 1994, 2000; Li et al. 2003; Cheng, 2007; Azfal et al. 2011) and determine geochemical baselines (Cicchella et al., 2005; Lima et al., 2003, 2008).

In other cases, different approaches have been applied, especially common are those based on map units. The use of sample catchment basins (SCB) in building geochemical maps based on stream sediment data is not recent and positive results of its application at regional scale are known since the late 1980s (Bonham-Carter et al., 1987; Carranza and Hale; 1997; Spadoni et al., 2004; Spadoni et al., 2005; Spadoni, 2005). Geochemical maps based on soil samples produced pedogeochemical maps using a pedologic landscape approach (Amorosi et al., 2011) which follows an approach similar to the SCB, but based on pedologic maps. Other maps were produced using administrative boundaries (El Hadri et al., 2012) as a base for representation. These techniques show advantages and disadvantages: SCB avoid “mathematical interference” between neighbouring samples (Spadoni, 2005) and establish precisely sources of contamination or significant anomalies in individual catchment basins (Carranza, 2010), but are suitable for morphological contexts characterized by mountainous or hilly areas (Spadoni et al., 2004) and not for large plain areas.

In most cases, research groups conduct regional-scale sampling focusing on a single representation technique and ignoring the possibility to explore the results obtained by different techniques, specially in areas influenced by geology, mineral exploration and human impact. Nevertheless some authors (Reimann, 2005; Carranza, 2010) aims to reflect about realization process and consider land morphology, sample type and the purpose of analysis as parts of the decision-making.

This paper presents the results of a regional-scale stream sediment survey to which various statistical and cartographic techniques have been applied. Maps based on symbols, chosen with different criteria and with secondary subdivision have been produced and compared with other maps produced by interpolation algorithm and sample catchment basins extrapolation. The objective is to critically investigate a spatially distributed dataset in order to identify optimal data treatment and visualization to highlight natural phenomena and eventual human impacts.

2.2 Study area

The study area, extending over 4125 km^2, includes the whole Romagna Apennines (northern Italy) which includes the catchment basin of eleven rivers: Idice, Sillaro, Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello and Marecchia (Tab. 1 and Fig. 1). Industrial activities are developed mostly around the main cities located at the closing of the mountain section of several rivers (Imola, Faenza, Forlì, Cesena and Rimini), whereas in the hills and mountains agricultural activities prevail. The geology of the area is dominated by sedimentary rocks and include different geological units attributed to different palaeogeographic domains and structural units (Vai, 2001): Ligurian, Tosco-Umbrian and Padano-Adriatic (Fig. 2). The Ligurian domain, including also the sedimentary successions deposited in satellite basin (Epiligurian deposits), is located in the north-western and south-eastern part of the area and is dominated by chaotic clays, argillaceous sheet, turbiditic units (limestone/clay alternations) and sandstones. The Tosco-Umbrian domain (more correctly Romagna Umbria) crops out along the central part of the study area and is composed exclusively by the Marnoso-arenaceo Formation. Finally the Padano-Adriatic domain lies parallel to the Tosco-Umbrian domain and includes evaporitic, clastic and clayey sediments and alluvial deposits (AA.VV., 1987; Regione Emilia-Romagna., 1996).

Basins	Number of samples	Area basin (km^2)	Lenght (km)
Idice	53	323	37,5
Sillaro	49	223	37,7
Santerno	50	468	50,7
Senio	67	271	42,2
Lamone	58	293	43,4
Acerreta-Tramazzo	53	254	36,6
Montone	51	225	39,6
Rabbi	23	240	46,6
Bidente	75	570	50,5
Savio-Borello	147	648	61,6
Marecchia	144	610	56,7

Tab. 1 Catchment basins of rivers included in Romagna Apennines. Number of samples, Area basin (km^2) and Lenght (km) are specified for each catchment basin.

2.3 Methods

2.3.1 Sampling and analytical methods

The Department of Biologic, Geologic and Environmental Sciences of Bologna has conducted an high density regional-scale sampling (1 sample per 5 km^2) during five years collecting 770 stream sediment samples for environmental geochemistry studies. The survey has been carried out sampling one stream sediment sample for each catchment basin previously extracted by DEM, considering that a sampling site is presumed to express the average chemical concentration in a drainage basin (Howarth and Thornton 1983). In the field, sediment collected in a range of 200 m within the stream channel was combined and directly sieved in the field to < 180μm with local running water and stored in PET 1.5l bottles. In the laboratory samples sediments were dried, homogenized and pulverized with an agate mill. Pressed powder pellets were prepared for analysis of major and trace element (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S) by X-ray fluorescence spectrometry. Analyses were performed with a Philips PW1480 automated spectrometer at the BiGeA X-Ray Fluorescence Lab, following the methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976) and Leoni et al.

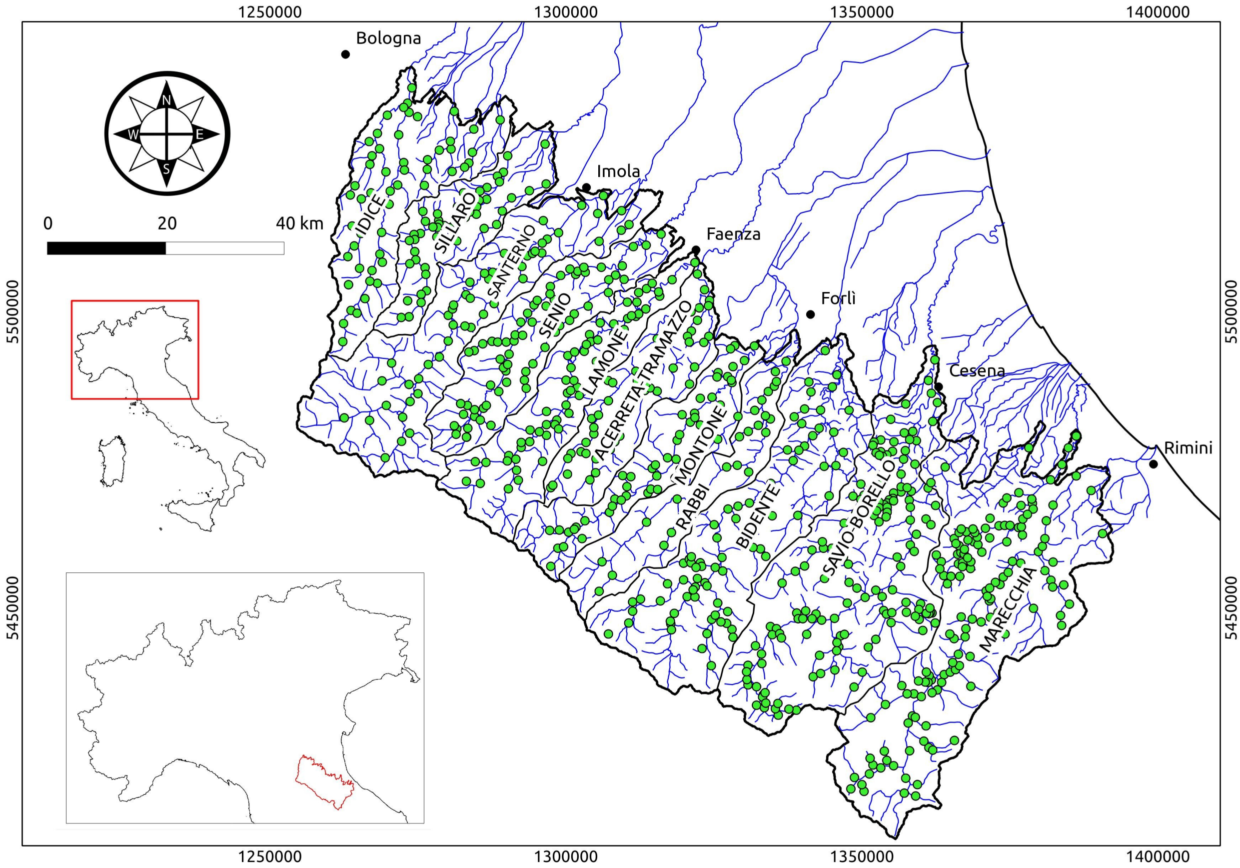

Fig. 1. Schematic map of the study area at a scale of 1:400000. Points indicate sampling locations, solid lines show rivers drainage basins.

(1982) for matrix corrections. Long term reproducibility for major elements was generally better than 7%, whereas for trace elements, it was on average better than 10%. Absolute accuracy relative to certified values of International Reference Material was generally within the reproducibility range. Analytical homogeneity between batches was checked by duplicate analysis of selected samples and found to be better than 5%. Loss on ignition (LOI) was estimated after overnight heating at 950° in a muffle furnace.

2.3.2 Cartographic and statistical techniques

Geochemical maps have been produced using Quantum GIS, a Geographic information system software downloadable at http://www.qgis.org/. Regarding Sample Catchment Basin (SCB) mapping approach, the watershed stream network was calculated from a SRTM 30m DEM's provided by the USGS web site and were taking into account basins greater than 100 m^2. Considering a continuous field model, the elemental concentration of each cell (300 m x 300 m) was calculated using the Inverse Distance Weighted (IDW) method (Watson and Philip, 1985).

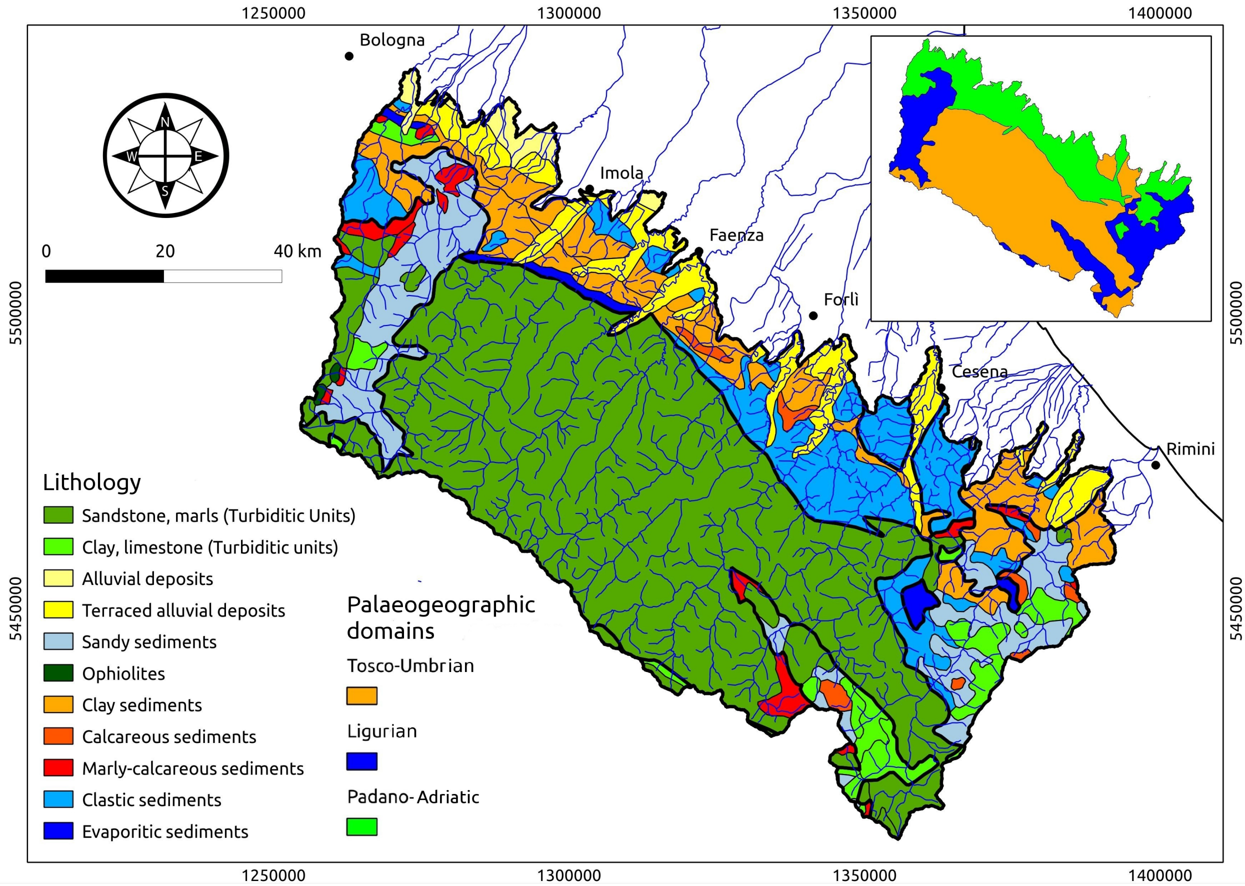

Fig. 2. Lithological map of Romagna Apennines (Northern Italy). The upper right insert represent the map of the palaeogeographical domains.

Data analysis have been carried out in R, an open source software which can be freely downloaded from CRAN server at http://cran.r-project.org. For producing analytical results, non-parametric test and graphics has been used the DASplusR package, downloadable at http://www.statistik.tuwien.ac.at/StatDA/DASplusR/. Analytical results are characterized by computation of mean, median, Standard Deviation, Median Absolute Deviation, minimum, maximum, 2th, 5th, 10th, 25th (lower quartile), 50th (median), 75th (upper quartile), 90th, 95th, and 98th percentile. To display the underlying data structure in a map, class selection of chemical element concentration has been carried out using percentiles (2, 5, 10, 25, 50, 75, 90, 95, and 98%) in growing dot maps and boxplot (1st quartile, median, 3rd quartile and 95%) in maps represented with EDA symbols, IDW interpolation and SCB mapping approach.

Elements	unit	Min	2°le	5°le	10°le	25°le	Median	Mean	75°le	90°le	95°le	98°le	Max	SD	MAD
Al_2O_3	wt. %	1.5	6.38	7.65	8.61	9.74	10.8	11.1	12.4	14.1	14.8	15.9	18.4	2.21	1.9
CaO	wt. %	1.5	6.63	8.8	10.3	13.5	17.1	17.6	21	25.3	29.5	33	40.7	6.2	5.54
Fe_2O_3	wt. %	1.09	2.57	2.99	3.36	3.85	4.31	4.36	4.89	5.51	5.78	6.12	6.93	0.847	0.771
K_2O	wt. %	0.86	1.08	1.26	1.39	1.58	1.77	1.78	1.97	2.2	2.36	2.5	2.84	0.323	0.282
MgO	wt. %	0.61	2.06	2.32	2.48	2.8	3.2	3.25	3.66	4.07	4.4	4.65	5.84	0.648	0.63
MnO	wt. %	0.03	0.0838	0.09	0.1	0.11	0.12	0.13	0.13	0.15	0.17	0.216	1.5	0.0753	0.0148
Na_2O	wt. %	0.05	0.214	0.29	0.4	0.53	0.72	0.77	0.96	1.23	1.42	1.68	2.39	0.346	0.311
P_2O_5	wt. %	0.01	0.03	0.06	0.07	0.09	0.12	0.15	0.15	0.18	0.22	1.09	1.5	0.202	0.0445
SiO_2	wt. %	16.7	21.6	27.5	31.1	36.4	41.2	40.8	45.5	49.7	52.7	57.8	76.2	7.84	6.72
TiO_2	wt. %	0.22	0.32	0.37	0.4	0.45	0.51	0.51	0.56	0.61	0.66	0.74	1.29	0.103	0.089
As	mg kg^{-1}	1	1	1.5	1.5	1.5	3	4.8	7	11.7	14	16.3	26.6	4.4	2.22
Ba	mg kg^{-1}	1.5	221	241	260	289	322	352	377	449	555	699	2210	142	57.8
Ce	mg kg^{-1}	1.5	25.4	30	34.6	42	50.3	50.4	58	66	71.9	80.8	117	13.2	11.9
Co	mg kg^{-1}	1	1.5	3	5	7.6	10	10.5	13	16.1	19	21.6	31	4.65	4.45
Cr	mg kg^{-1}	1.5	50.5	65.1	74	86.9	99	101	111	129	142	168	517	31.5	17.9
Cu	mg kg^{-1}	1.5	9.38	15	18.3	25	30	30.7	36	42.9	48.4	57	119	11.3	8.82
Ga	mg kg^{-1}	1.5	1.5	1.5	1.5	1.5	1.5	6.6	13	16.7	18.2	21	27	6.66	0
La	mg kg^{-1}	1.5	8.68	13.7	16.7	20	24.7	24.6	29	33	35.2	40.8	62	7.2	6.38
Nb	mg kg^{-1}	1.5	4.74	5	6	7	9	9.7	12	14	16	18	97	4.71	3.04
Ni	mg kg^{-1}	1.5	35	42	47	53.9	61.5	61.4	68	77.1	82.6	88.1	160	13.8	11.1
Pb	mg kg^{-1}	1.5	1.5	3	5.6	9.22	14	13.6	18	20	22	24.2	58	6.13	5.93
Rb	mg kg^{-1}	1.5	47.6	56.8	64	74	86	87.2	101	112	122	134	158	21.2	19.3
S	mg kg^{-1}	1.5	1.5	1.5	348	590	910	1220	1410	2240	2880	5170	18000	1340	563
Sc	mg kg^{-1}	1.5	1.5	1.5	1.5	5.32	17	15.4	22.7	28	33.2	36.4	49	10.4	11.9
Sr	mg kg^{-1}	1.5	179	215	248	306	394	440	509	617	734	1200	3260	255	145
Th	mg kg^{-1}	1	1.5	3	4	8	11	17.2	21.2	42.9	49	58	102	15.5	7.41
V	mg kg^{-1}	1.5	42.4	48	55.3	67	76.3	78.4	89	104	115	127	152	20.1	16.8
Y	mg kg^{-1}	1.5	7.29	9.35	13	17	20	19.9	23	25	27	30	58	5.89	4.45
Zn	mg kg^{-1}	1.5	45	53	57.2	67	81	84.7	96.4	112	121	134	956	39.8	22
Zr	mg kg^{-1}	1.5	1.5	22.2	53.8	90.3	117	124	146	187	223	317	688	72.4	40.3

Table 2 Summary statistics for the geochemistry of stream sediments in Romagna Apennines. Have been reported the 2°, 5°, 10°, 25°, 75°, 90°, 95° and 98° percentile, median and mean value, Min (Minimum), Max (Maximum), SD (Stamdard Deviation) and MAD (Median Absolute Deviation).

2.4 Results and discussion*s*

2.4.1 Distribution data pattern: a first view using dot maps

Table 2 presents a summary statistics for the stream sediment data, including percentiles, median, mean, SD (Standard Deviation) and MAD (Median Absolute Deviation) for compositional data. Some major elements show significant variation (e.g. CaO (1.5-40.7 wt.%), MgO (0.61-5.84 wt.%), MnO (0.03-1.5 wt.%), Na_2O (0.05-2.39 wt.%), P_2O_5 (0.01-1.5 wt.%), Al_2O_3 (1.5-18.4 wt.%) TiO_2 (0.22-1.29 wt.%)) whereas for other is lower (e.g. Fe_2O_3 (1.09–6.93 wt.%), K_2O (0.86–2.84 wt.%), SiO_2 (16.7–76.2 wt.%). Also trace elements, As (1.5–26.6 ppm), Ba (1.5–2210 ppm), Ce (1.5–117 ppm), Co (1–31 ppm), Cr (1.5–517 ppm), Cu (1.5–119 ppm), Ga (1.5–27 ppm), La (1.5–62 ppm), Nb (1.5–97 ppm), Ni (1.5–160 ppm), Pb (1.5–58 ppm), Rb (1.5–158 ppm), S (1.5–18000 ppm), Sc (1.5–49 ppm), Sr (1.5–3260 ppm), Th (1–102 ppm), V (1.5–152 ppm), Y (1.5–58 ppm), Zn (1.5–956 ppm), Zr (1.5–688 ppm) identify remarkable differences. We will discuss only some selected and indicative elements (Al_2O_3, CaO, SiO_2, Sr, Cr and Pb), but all dot maps, cumulative probability plot, geochemical maps obtained by IDW interpolation and catchment basin approach of the complete dataset are included as supplementary material.

The first step was to produce dot maps (Fig. 3a-f), in order to provide a preliminary indication on the distribution of Al_2O_3, CaO, SiO_2, Sr, Cr and Pb. Ten classes, representing 2°, 5°, 10°, 25°, 50°, 75°, 90°, 95° and 98° percentiles were used to identify the symbols. As background information the boundaries of the three palaeogeographic domains are included in the figure. Calcium (Fig. 3a) shows high values in the Tosco-umbrian domain, in particular along Santerno, Senio, Lamone, Acerreta-Tramazzo and Savio valleys. In the other domains (Ligurian and Padano-adriatic) there are only three samples with CaO exceeding 33 wt.% respectively in the Marecchia valley and in the Acerreta-Tramazzo catchment near Faenza. On the contrary the Al_2O_3 dot map (Fig. 3b) shows higher values (> 15.9 wt.%) in the Ligurian domain, in particular along the Idice and Sillaro valleys. Also the samples from the Ligurian domain in the Marecchia valley shows relatively high concentration, while in Tosco-umbrian and Padano-adriatic domains have been clearly lower concentrations. The SiO_2 dot map (Fig. 3c) shows in general higher concentrations in the north-western sector of the studied area, with the highest concentrations in scattered locations within the Ligurian and Tosco-umbrian domains. Considering trace elements, the Sr dot map (Fig. 3d) evidences a concentration of higher values in the south-eastern part of the area within Ligurian and the Padano-adriatic domains, but also relatively high concentrations occur in the Tuscan domain, showing an increasing trend to the East. The Cr dot map (Fig. 3e) shows values higher than 168 ppm in the north-western and south-eastern parts of the area respectively in the Padano-adriatic domain and between the Ligurian and the Padano-adriatic domain. In the Tosco-umbrian domain

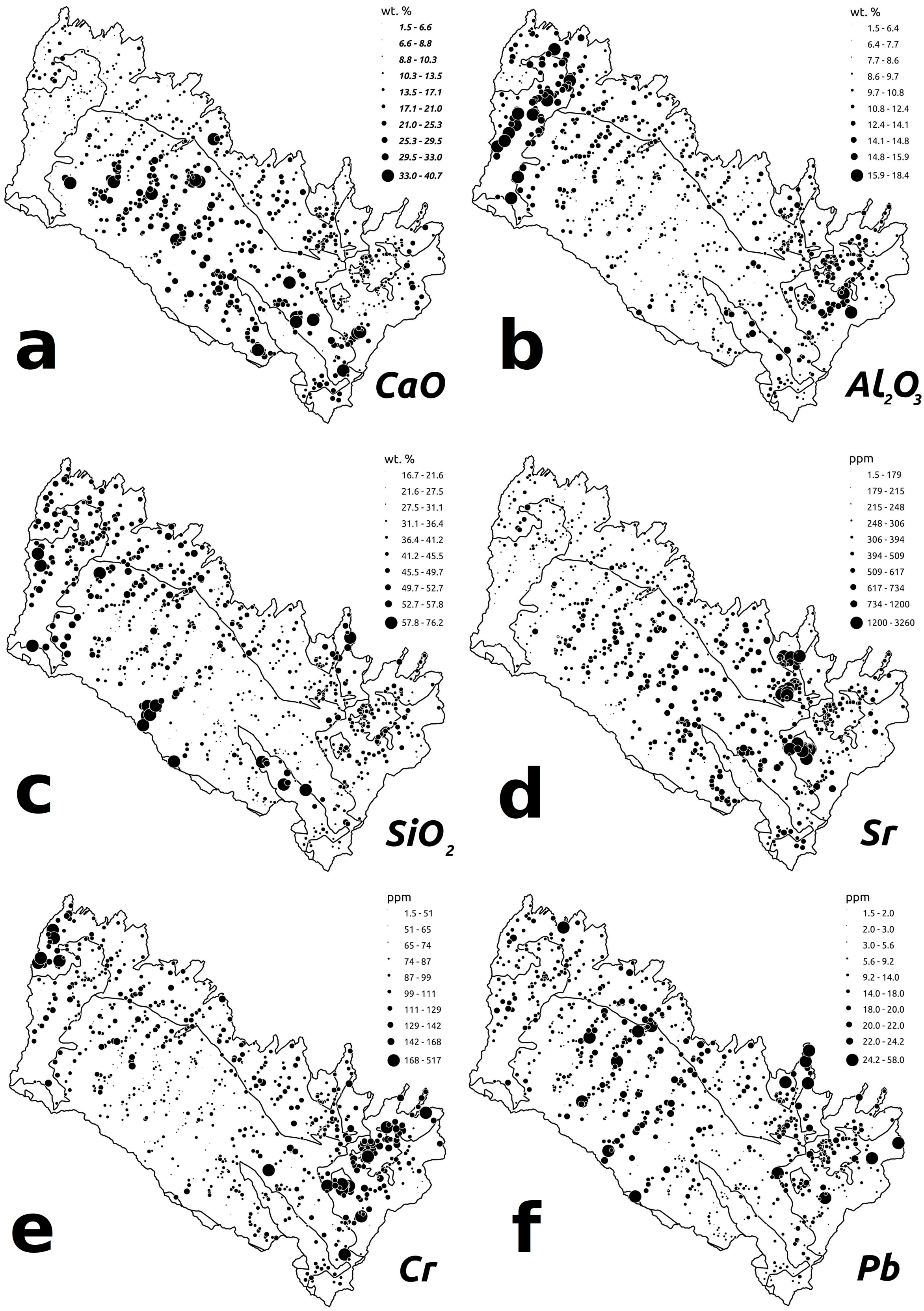

Fig. 3 Geochemical dot maps of CaO (a), Al_2O_3 (b), SiO2 (c), Sr (d), Cr (e) and Pb (f).

the Cr concentrations are generally much lower, except for a high value in the Savio-Borello valley. The Pb dot map (Fig. 3f) shows higher values (> 24.2 ppm) in the Tosco-umbrian domain, in particular along the Senio, Lamone, Rabbi and Bidente valleys, and in the south-wastern Ligurian and Padano-adriatic domains, respectively along Marecchia valley and near Cesena. These are scattered points, generally located along the major rivers, were urban settlements are more common.

2.4.2 Pattern related to palaeogeographic domains: a secondary screening by inference of cumulative probability plots.

As suggested by the dot maps, there are distinct regional patterns that coincide with major palaeogeographical domains, mostly related to major lithological differences at least for the major elements, as confirmed by the cumulative probability plots in Fig. 4 a-c. There is only partial overlap for SiO_2 (Fig. 4c) but for the other elements the three palaeogeographic domains are clearly differentiated. Calcium is much higher in the Tosco-umbrian which is characterized by the Marnoso-arenacea Formation, a turbiditic unit with alternating sandstones and marls. In addition to a calcium contribution from the fine-grained lithologies there are sandstone beds enriched in carbonate (Gandolfi et al., 1983), and in general compared to other turbiditic sandstones of the northern Apennines, these rocks have higher CaO content (Dinelli et al., 1999). The Ligurian domain records the highest values of Al_2O_3 (Fig. 4b) which is directly related to the clay rich nature of the tectonic mélange that outcrop in both zones of the Ligurian domain area (Pini, 1999; Vannucchi and Bettelli, 2010) as well as from feldspar-rich sandstones occurring in the area as scattered blocks (Valloni and Zuffa, 1984). The lower values observed in the other domains basically reflect a dilution related to the different carbonate content.

The three curves of SiO_2 (Fig. 4c) cross at the 90 percentile, corresponding with the presence of greater dot in all domains. In general the Ligurian and the Padano-adriatic distribution are higher compared to the Tuscan-umbrian and overlapping up to the 90^{th} percentile, where the Ligurian curve bend to higher values. Occurrence of quartz rich sandstones in the Ligurian domain is known (Valloni and Zuffa, 1984; Cibin et al., 2011) in the north western area south of Bologna and is likely reflected by some samples. The high SiO_2 values in the Tuscan-Umbrian domain occur in the north-eastern part, where during the Tortonian stage sediment supply was related to an Alpine provenance (Gandolfi et al., 1983), with an high arenite/pelite ratios (Martelli et al., 1994), producing a clear geochemical signal within the Marnoso-arenacea formation (Lancianese and Dinelli, submitted). Other high values observed in this unit occur in the upper reaches of the Montone valley, possibly reflecting, older (Langhian-Serravallian), quartz-rich sediments.

CP plot of Sr (Fig. 4e) displays only minor differences up to the 90^{th} percentile, with the Ligurian

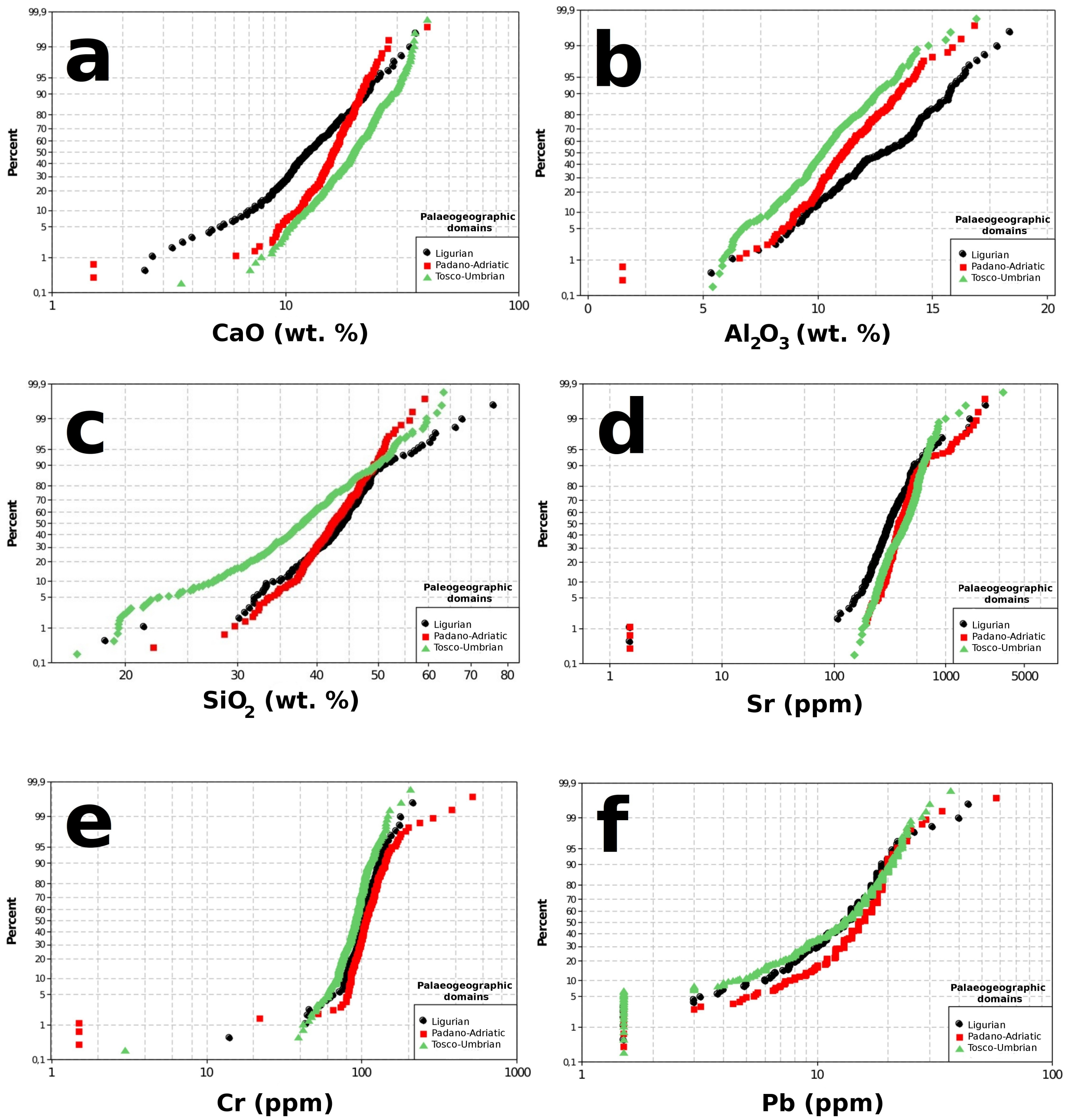

Fig. 4. Cumulative probability plots of CaO(a), Al2O3 (b), SiO2 (c), Sr (d), Cr (e) and Pb (f). Three curves represent palaegeographical domains: Ligurian domain (black), Padano-adriatic domain (red) and Tosco-umbrian domain (green).

domain having the lower concentration. In the upper distribution there is a sharp increase in concentrations in the Padano-Adriatic and few high-concentration samples from the Ligurian domain. Being Sr a substitute of Ca, we expected high values in Tuscan-umbrian domain, especially in the south-eastern part of the area, but the highest values were observed downstream of evaporitic units of the Padano-adriatic domain that crossed also the other geological units occurring douwnstream of the sources. Strontium substitutes Calcium also in gypsum but the strong enrichment in some scattered areas is located to the occurrence of mine wastes associated to former sulphur mines strongly enriched in Sr (Dinelli, 1995).

The curves of Cr plot (Fig.4e) indicate three distinct curves however with very small differences and only few anomalous samples observed in the Padano-adriatic population in the Idice and Marecchia Valley, in association with calcareous sandstones of Pliocene age. These deposits formed in a shallow marine environment (Amorosi et al., 2002) receiving sediments from the growing apenninic mountain belt which included also ophiolitic rocks. A similar source, an enrichment in chromium-rich heavy minerals or less likely an anthropogenic source could be the origin for these high values.

The Cp plot of Pb (Fig.4f) shows slightly higher concentrations of Pb in the Padano-adriatic domain, but after the 80th percentile (20 ppm Pb) the three curves overlap. The reason for the slight difference could be related to the geological nature of this unit, being characterized by fine-grained sediments, but the fact that it located at closer to the Po River Plain and with higher anthopogenic pressure possibly suggest the occurrence of diffuse pollution. High concentrations occur in all the three population, suggesting that there are localized sources of anomaly within the study area.

2.4.3 Total dataset vs. pattern divided for palaegeographical domains: a third step to investigate background and anomalous values with the support of EDA symbols

We have seen that the dot maps of chemical elements (Fig. 3) and the cumulative probability plots according to palaeogeographical domains (Fig. 4) gave interesting results for interpretation. Dot maps provide a primary indication regarding the spatial distribution of chemical elements, while the cumulative probability plots strengthen the importance of lithological control and point out some inferences for human impact. To go deeper in the interpretation we applied a combined approach to better point out the geochemical features of the study area. To the sample populations belonging to the three palaeogeographic domains we applied an EDA graphic approach. The use of EDA symbols and boxplots constitute a valid tool in displaying a data distribution (Tukey, 1977; Velleman and Hoaglin, 1981) giving an optical graphical weight to higher and lower values using respectively crosses and circles. Furthermore, a class division characterized by boxplot quantiles (25th, 50th, 75th percentile) with the addition of a discretionary upper percentile (in this paper has been used the 95th percentile) could discriminate between background and anomalous values among the entire population (Fig. 5a-c). The same approach as been applied to the three separate sub-population referring to the palaeogeographic domains (Fig.5b-d). We present this kind of elaboration to two elements CaO and Pb, that better then others are representative of lithology (CaO) and can be influenced by anthropogenic activities (Pb).

The map of CaO shown in Fig. 5a is a good example of EDA symbols utility because the appearance and interpretation of data are facilitated. Compared to the growing dot map (Fig. 3a) the high and low areas are even more evident respect to growing dot symbols, and once again the Ligurian domain clearly stands out for its low content, either to the north-west and the south-east. There is also a heterogeneous within the Tosco-umbrian domain with higher values in the central and southern portion of this domain. If the dataset is splitted more details come out (Fig. 5b) that can be attributed to specific geological features. For example, in the Padano-adriatic domain high concentration (filled circles and crosses) occur in the central area between the Bidente and the Savio-Borello catchment where Pliocene sandstones and biocalcarenite are common (Benini et al., 2009) and also in the north-eastern sector south of Bologna where calcareous sandstones belonging the Pliocene Intra-Apenninic Basin outcrop (Panini et al., 2002).

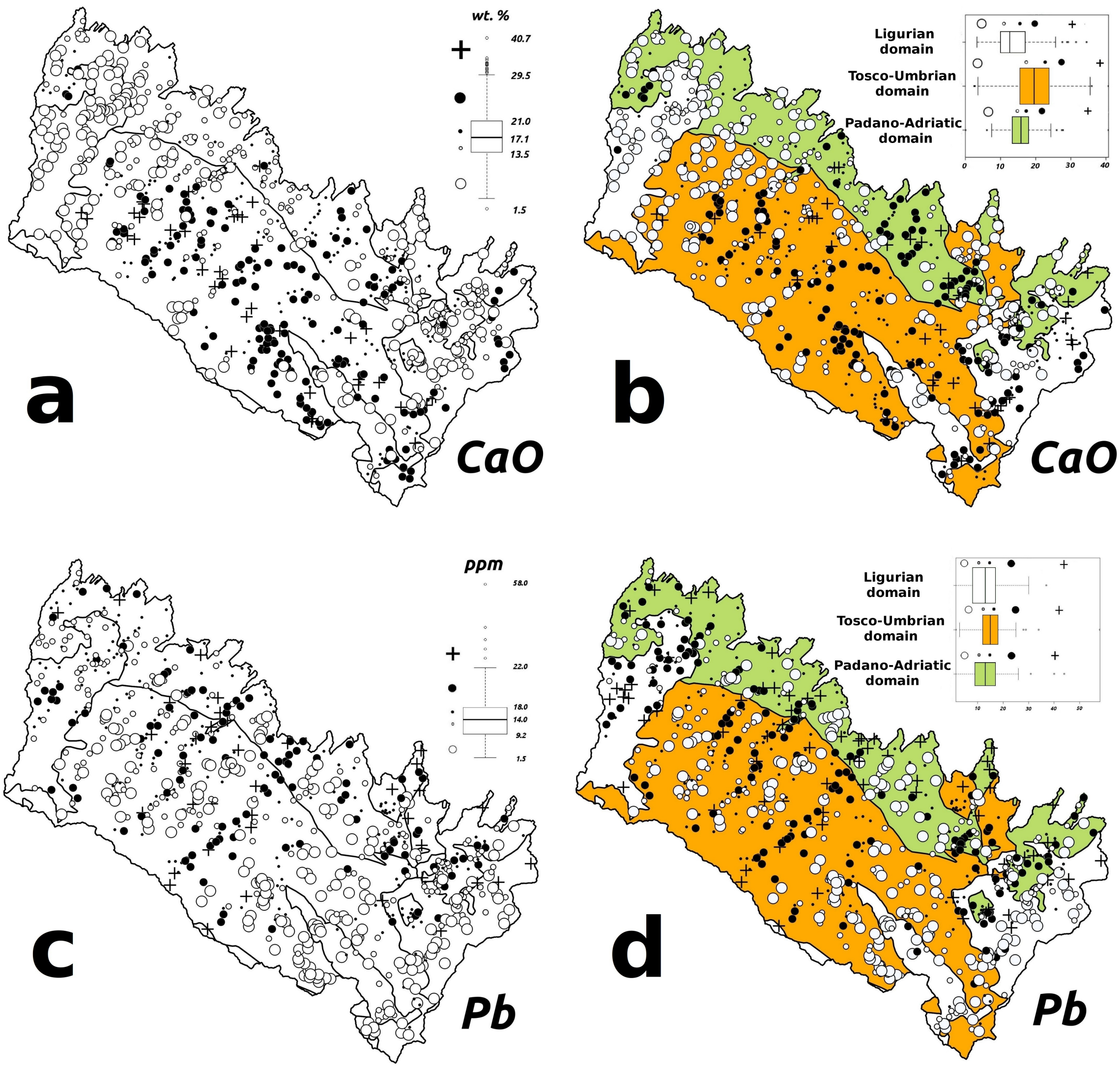

Fig. 5. Geological maps of CaO and Pb are represented using EDA symbols applied to total data pattern (a,c) and divided for palaegeographical domains (b,d).

A more complicated picture comes out for the Ligurian unit in the Marecchia valley where scattered limestone and calcareous arenites Cornamusini et al., 2009) strongly influence the stream sediment composition. Given the higher values in the Tosco-umbrian population this treatment compresses the original data clearly point out section of the unit with remarkably different composition, better discussed in Lancianese and Dinelli (submitted).

For an element like Pb, which can be strongly influenced by anthropogenic sources, the EDA symbols clearly locate the points with localized anomaly (Fig. 5c) which are not “domain-dependent”, and clusters of high rank data (filled circles and crosses) are concentrated along the main course as in the Lamone and Montone case, irrespective of the palaeogeographic domain boundary. Considering the Pb map based on singular palaegeographic domains (Fig. 5d) there is a sort of normalization and even local deviation from the general trend of the sub-population can be outlined. Eventual lithological effects can be reduced and minimal alteration compared to background can be pointed out. For example filled circles and crosses appears in the north-western area of the Ligurian domain, in an area with diffuse anthropization. Similar considerations can be made also for the south-eastern sector of the Ligurian domain, where local anomalies along the Marecchia river in connection with urban areas become more evident. Instead the comparison of Tusco-umbrian and Padano-adriatic domains between Fig. 5c and Fig. 5d don't reveals significative differences.

2.4.4 Interpolation vs sample catchment basin approach

Geochemical maps based on interpolation and sample catchment basin (SCB) approach constitute a further tool of data presentation and analysis that can be applied to could provide additional information about the factors controlling element distribution. The use of interpolation techniques represent a common tool for environmental geochemistry, geochemical prospecting and geochemical mapping, as outlined in the introduction. Care in application and interpretation should be given for sampling density, since interpolation with low density data can lead to unrealistic responses. Less common is the application of the SCB approach, that however if sampling density is adequate can provide interesting information.

The interpolated geochemical maps of CaO and Pb (Fig.6 a-c) based on IDW interpolation and the maps based on the SCB approach (Fig.6 b-d) have been compared to each other and with maps of the other paragraphs. Geochemical maps drawn by means of mathematical interpolators do not take into consideration the geomorphologic contraint of the watersheds and the functional relationship, in term of transport and deposition processes, between sampling points along the stream network (Spadoni, 2005). The interpolated map for CaO clearly identifies the low values in the north-western Ligurian domain and the high belt in the central area of the Tosco-umbrian domain (Fig. 6a) which is confirmed also in the “catchment basin” map (Fig. 6b). Some of the observed encroachments depends on the extension of the catchment that do not follow the geological boundaries. For a major element like CaO the difference between the two maps can be minimal and still the association to bedrock geology is present. For an element like Pb the interpolated map produces an “hot-spot” appearance (Fig. 6c) related to the occurrence of spot anomalies, that have however also the same effect concerning the low values. The SCB map (Fig. 6d) provides direct information about the location of the anomaly, at least within the size of the catchment basin although the patchy appearance could not appear as elegant as the interpolated one. It highlights, for example, the occurrence of high concentrations in the closing section of the rivers, often in the suburbs of large towns. It also clearly localizes other anomalies in mountain stretches of the rivers, that generally include small towns and industrial settlements. This approach clearly permits a more precise identification of the location of the anomaly and guide the location for additional studies if needed, without the uncertainty related to spatial interpolation. Furthermore the application of IDW to derive the continuous geochemical surfaces could not be optimal in this case, particularly because stream sediments do not represent continuous geo-object (Carranza, 2010) as soil samples.

Compared to growing dot maps (Fig. 3a and f) and EDA symbol maps (Fig. 5a and c) there is a less clear visualization of the linkages between element concentration, lithology and anthropogenic factors because the colours representing specific range classes are extended over the boundaries of the palaeogeographic domains. Neverthless the use of mapping techniques based on IDW interpolation and SBC approach add further informations that may be useful in identifying anomalous concentrations of chemical elements.

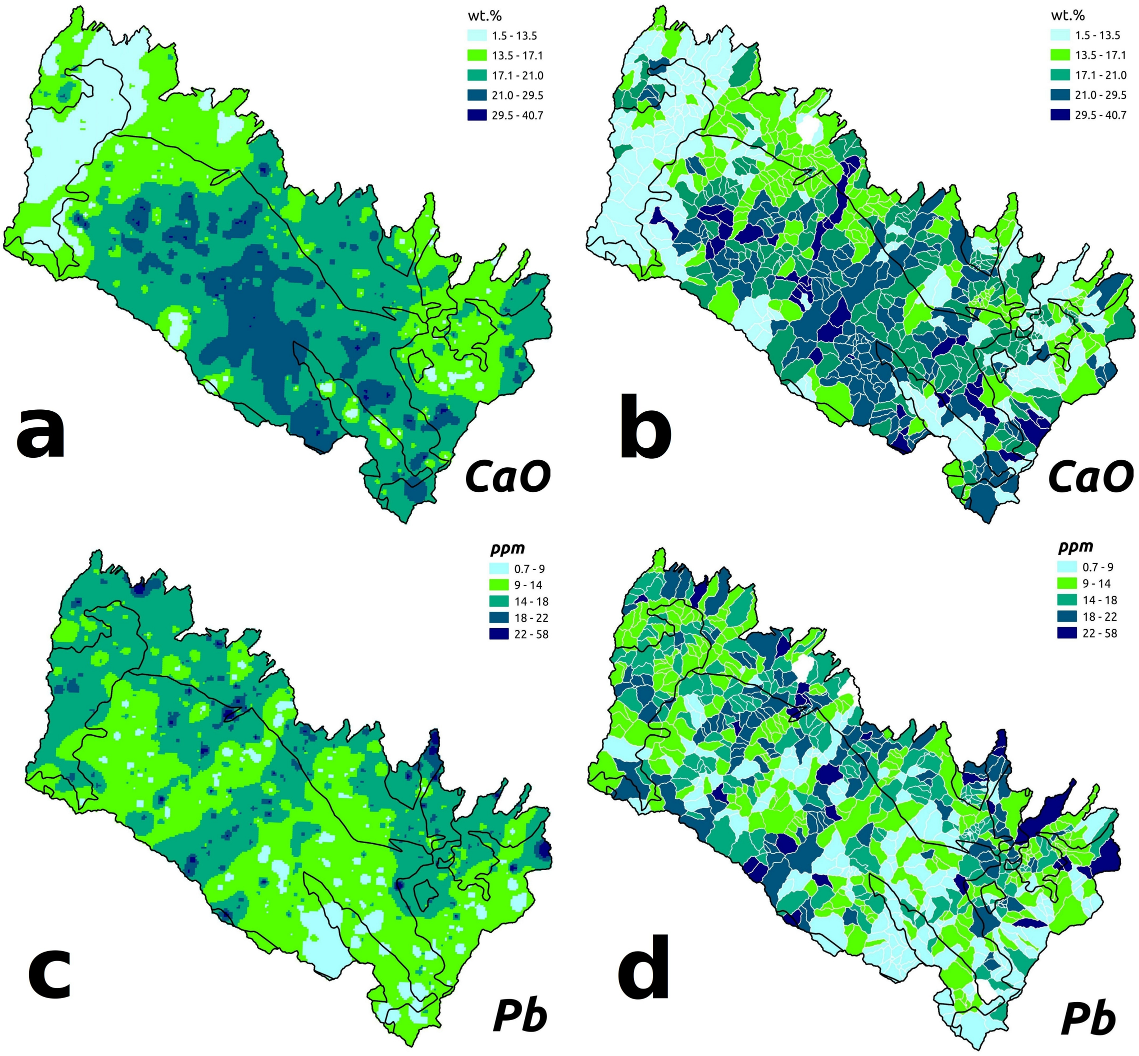

Fig. 6. Geological maps of CaO and Pb are represented using IDW interpolation (a,c) and SCB approach (b,d). In the maps are visibles the boundaries of palaegeographical domains.

2.5 Conclusions

Various representation techniques have been used to investigate stream sediment geochemistry of Romagna Apennines (Northern Italy). The comparison between growing dots, EDA symbols, IDW interpolation and Sample Catchment Basin (SCB) techniques, combined with statistical analyses, produced different considerations:

1) the distribution of chemical elements in an area characterized by complex geology and multiple factors cannot be represented properly with a standardized mapping technique because different approaches point out peculiarities useful for interpretation of the effect of

geology or human impact;

2) growing dot maps and cumulative probability plots are effective tools for an indicative framework of the area: in this case the visualization of linkages between chemical distribution and geology is stressed, since there are clear differences in the chemical composition of stream sediments derived from the three major geological units based on palaeogeographic considerations (Ligurian, Tosco-umbrian and Padano-adriatic domains);
3) the choice of symbols and class division are fundamental in exploring a data population: growing dot represented 10 classes and EDA symbols based on quantiles demonstrate that some informations could be more evident considering relevant symbols and class divisions: the EDA approach for example stress the tails of the distribution and draw attention to anomalous areas and zone possibly affected by deficiency.
4) the subdivision of a total dataset in separate populations related to a specific grouping variable, in this case the palaegeographic domains, highlights anomalous areas that are not evident in an overall representation, taking indirectly into account possible differences in background values related to natural factors;
5) the use of mapping techniques based on IDW interpolation and SBC techniques should be related to certain criteria: for this study the type of sample, the sampling density and the land physiography are adapted to a SBC technique because it directly indicate the source of the possible signal and permits possible detailed studies

Nowadays geochemical mapping it is no more an issue of data handling, since specific softwares allows the quick production of very beautiful geochemical maps. But also other tools for spatial analysis and accessible supporting background information of easy implementation in appropriate softwares enable other ways of data classification and elaboration more appropriate to the data studied. Dot maps or similar clearly represent the true results, but their interpretation is not easy even for a well trained eyes. For stream sediments samples, when appropriate sampling density is used, the SCB represent a very powerful tool which can be easily read also by not trained people and is very useful for management issues.

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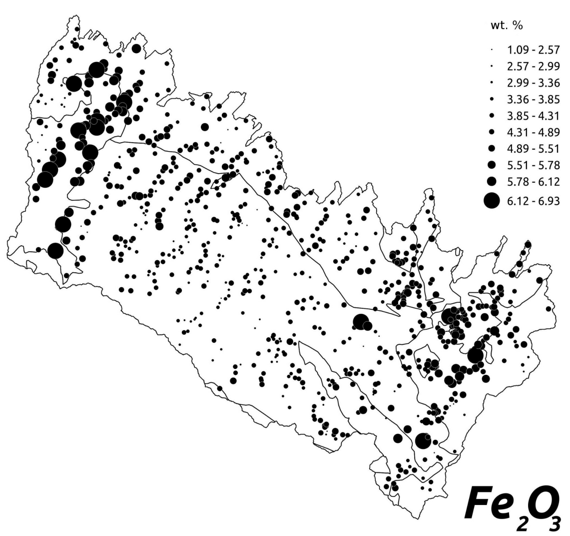
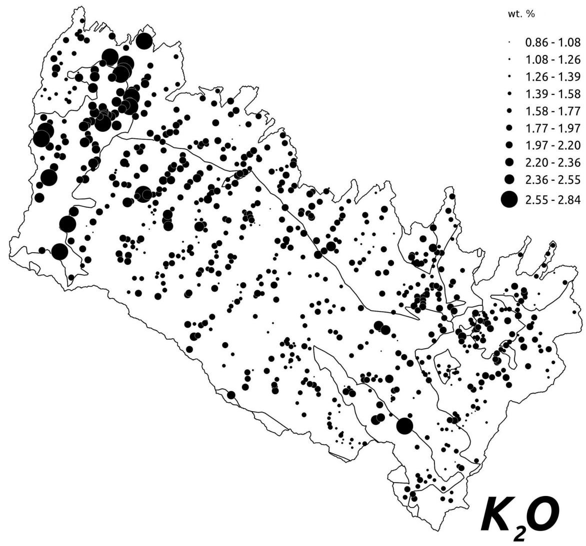
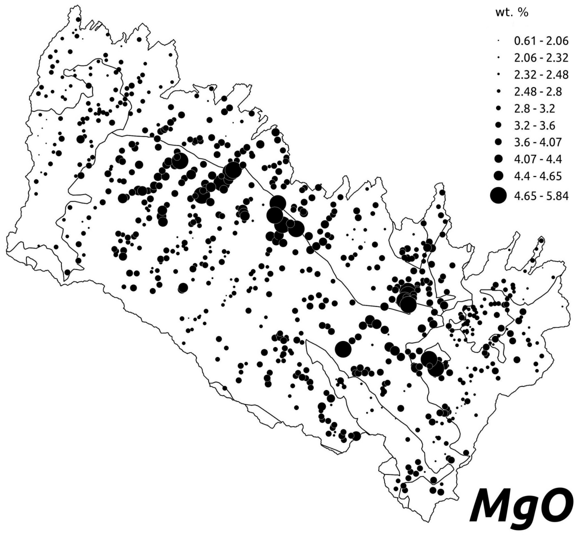
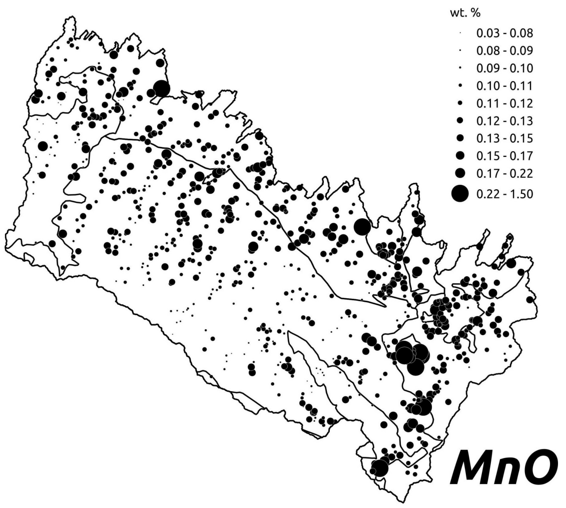
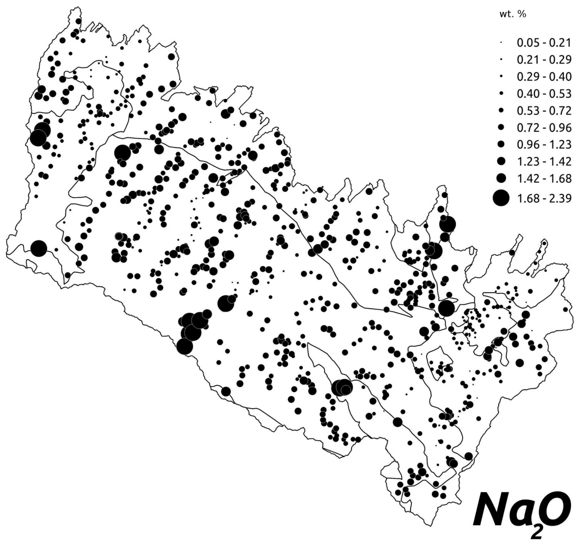
Supplementary material

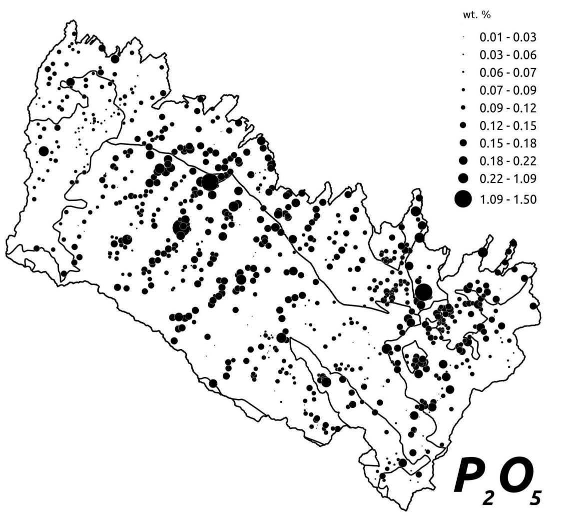


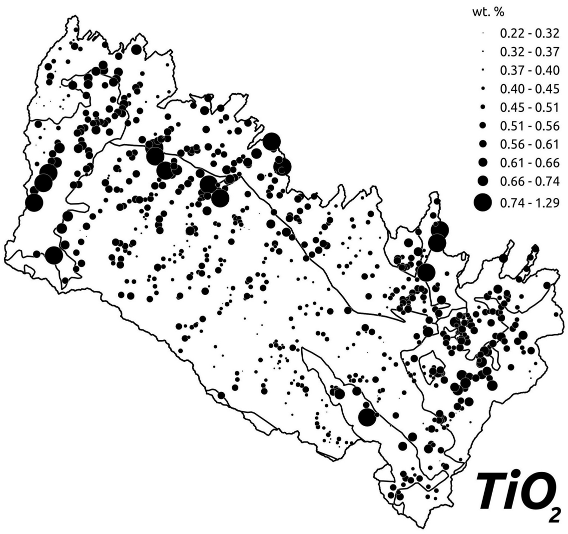








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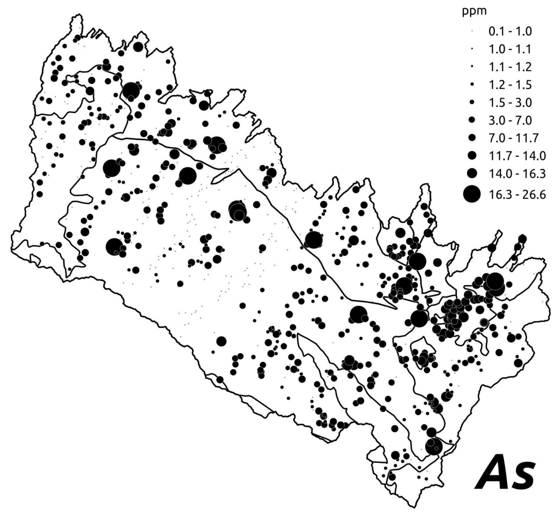
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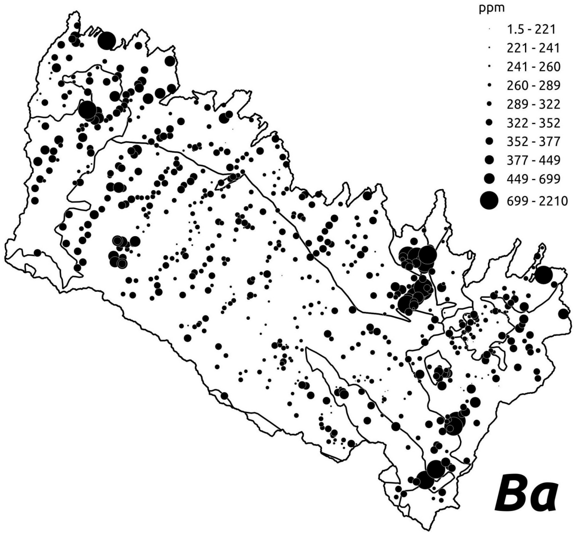
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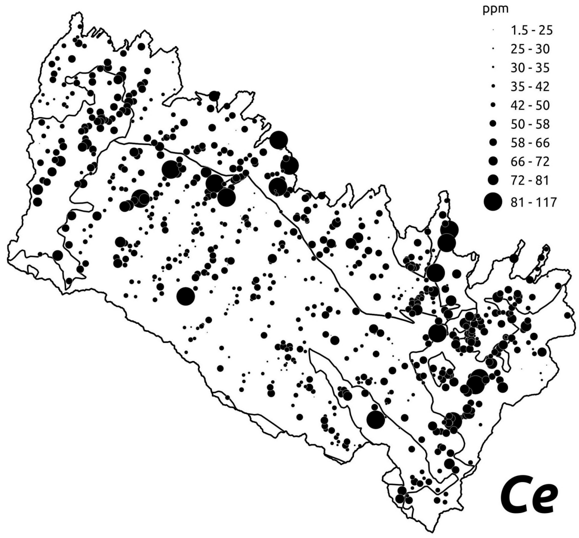
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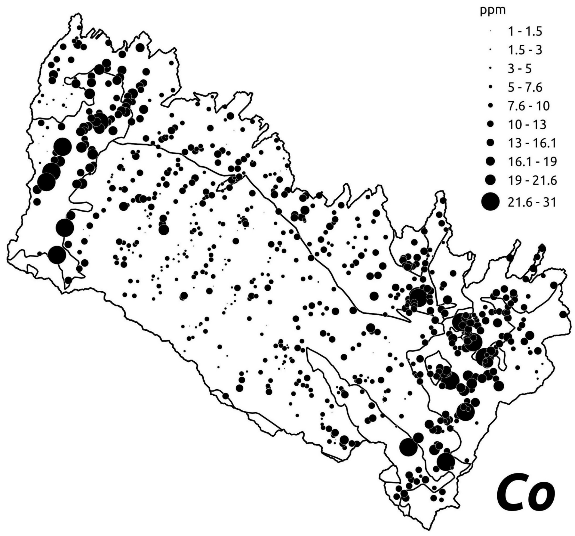
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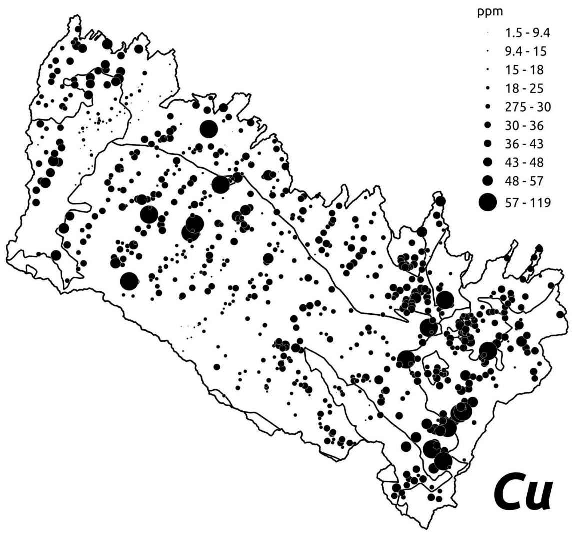
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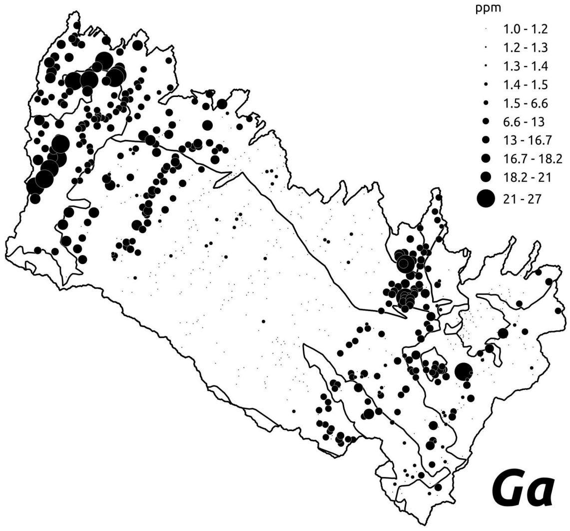
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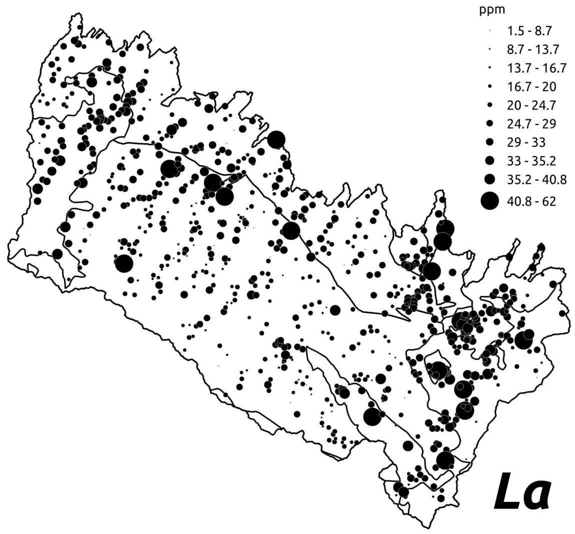
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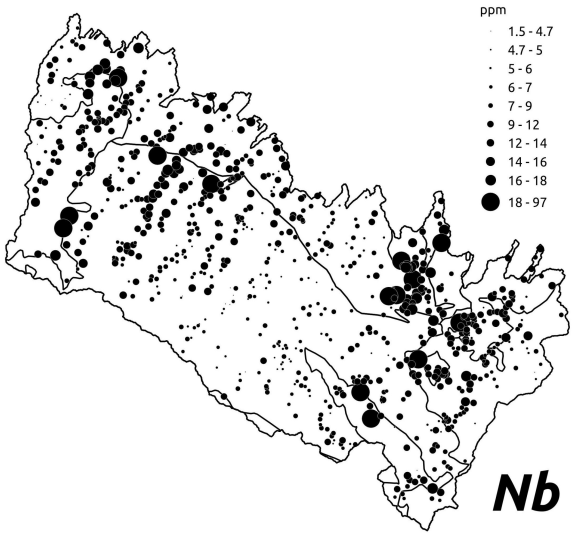
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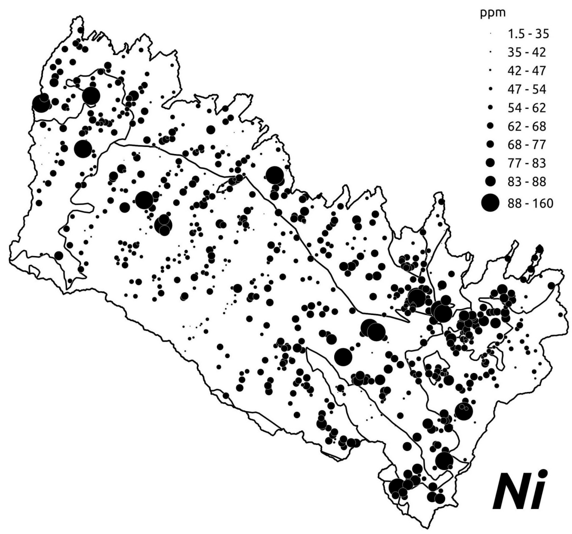
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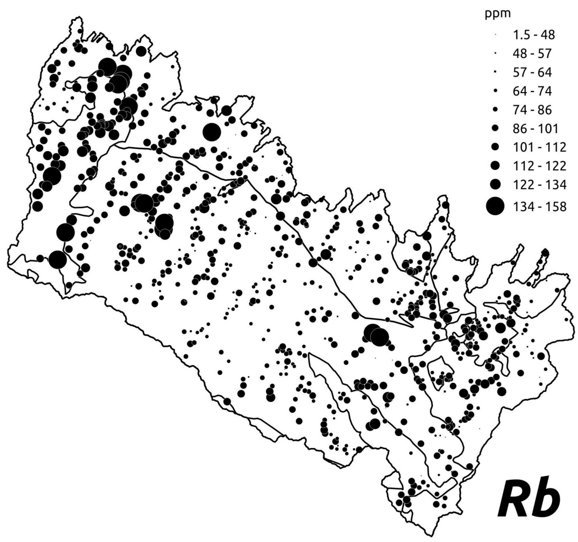
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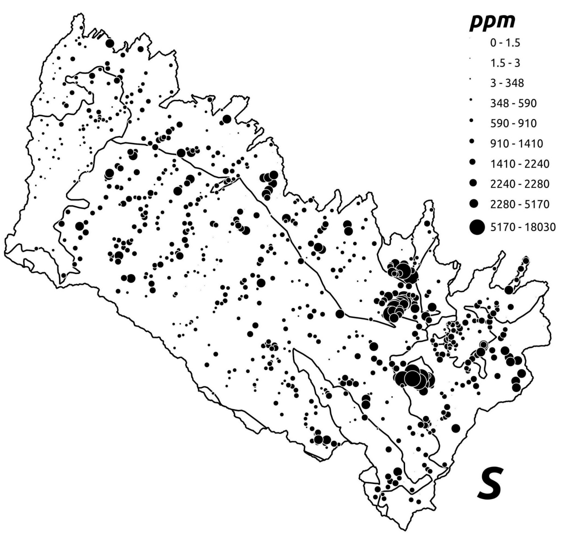
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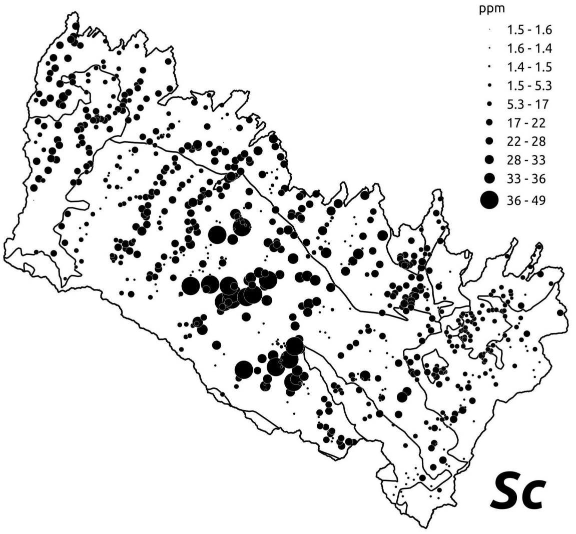
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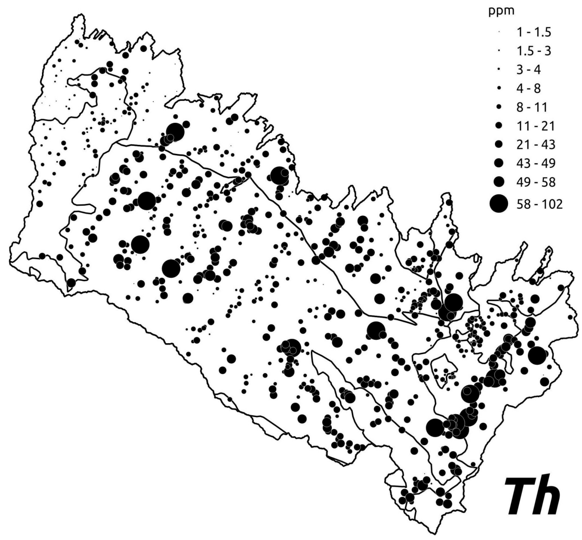
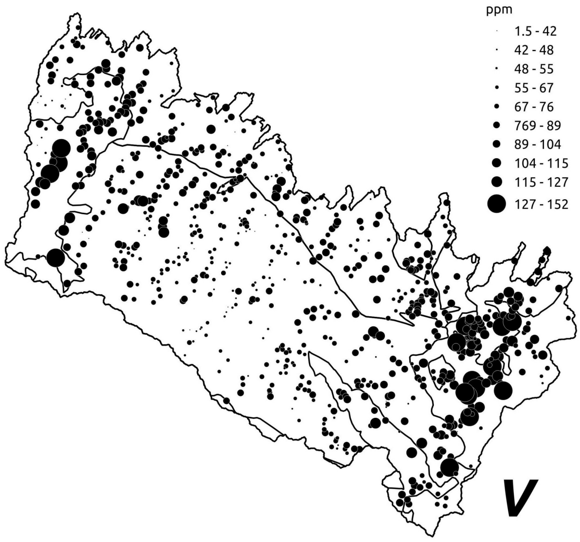
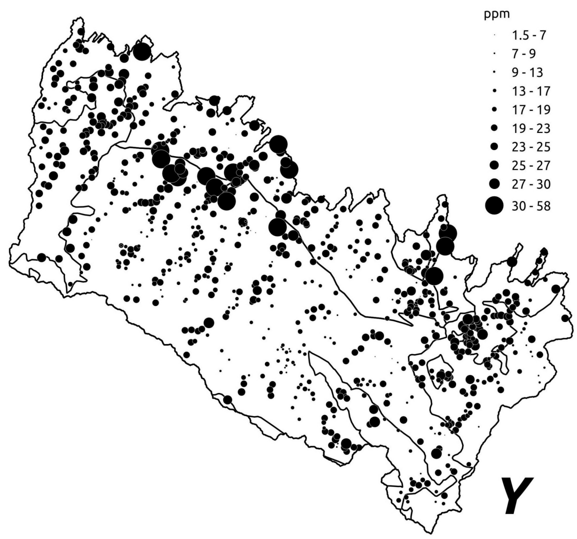

ppm
1 - 1.5
1.5 - 3
3 - 4
4 - 8
8 - 11
11 - 21
21 - 43
43 - 49
49 - 58
58 - 102
Th


ppm
1.5 - 42
42 - 48
48 - 55
55 - 67
67 - 76
769 - 89
89 - 104
104 - 115
115 - 127
127 - 152
V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1.5 - 7
7 - 9
9 - 13
13 - 17
17 - 19
19 - 23
23 - 25
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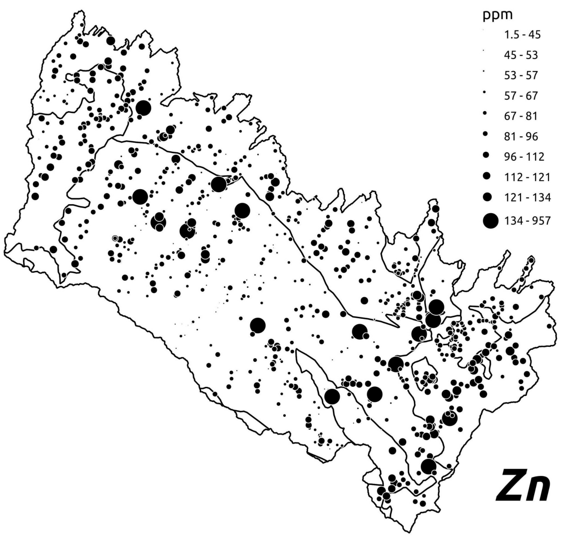
27 - 30
30 - 58
Y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1.5 - 45
45 - 53
53 - 57
57 - 67
67 - 81
81 - 96
96 - 112
112 - 121
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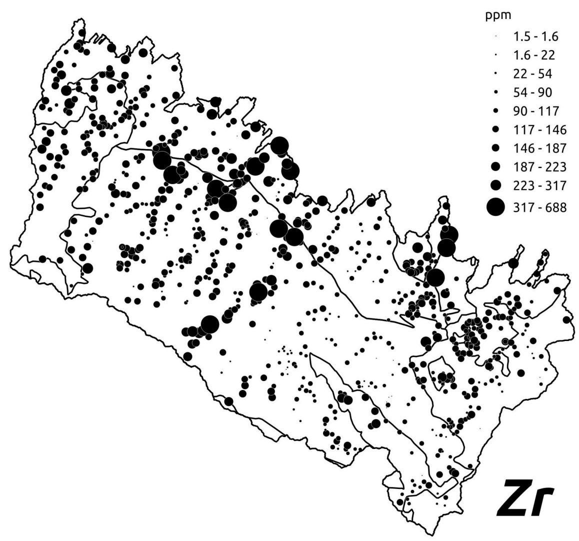
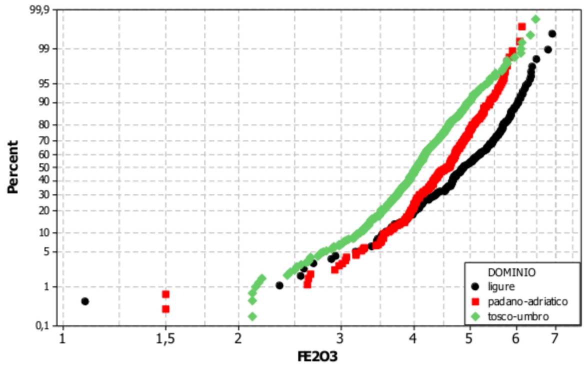
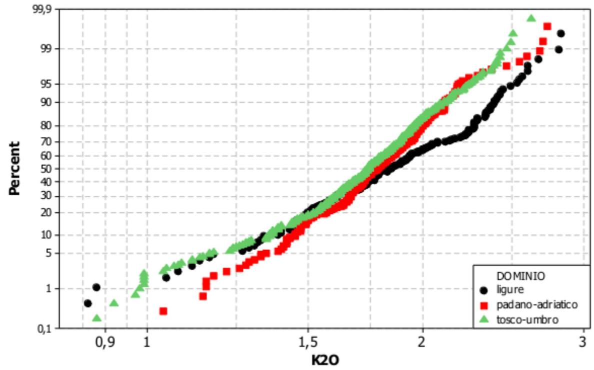
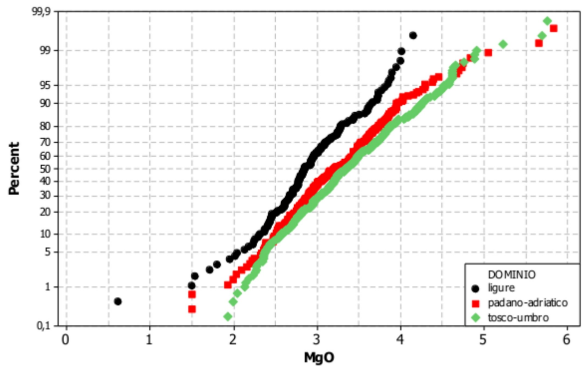
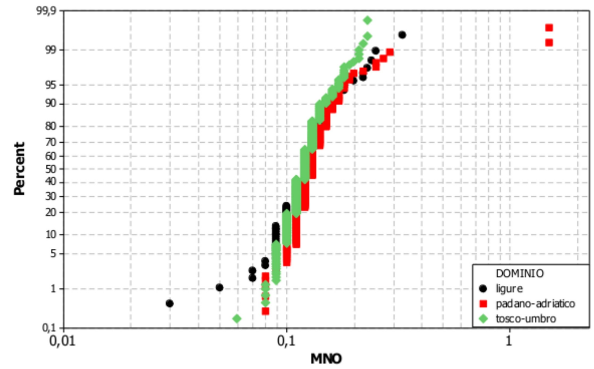
134 - 957
Zn


ppm
1.5 - 1.6
1.6 - 22
22 - 54
54 - 90
90 - 117
117 - 146
146 - 187
187 - 223
223 - 317
317 - 688
Zr


Percent
FE2O3
DOMINIO
ligure
padano-adriatico
tosco-umbro


Percent
K2O
DOMINIO
ligure
padano-adriatico
tosco-umbro


Percent
MgO
DOMINIO
ligure
padano-adriatico
tosco-umbro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MNO
DOMINIO
ligure
padano-adriatico
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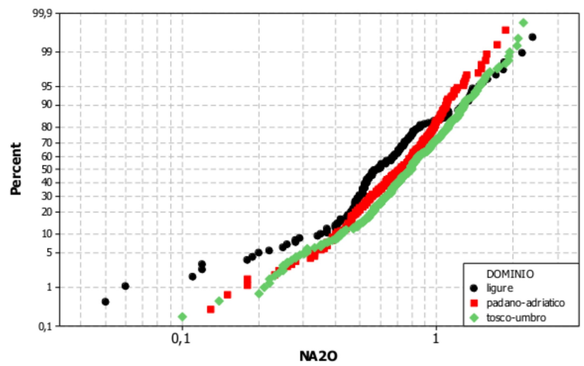
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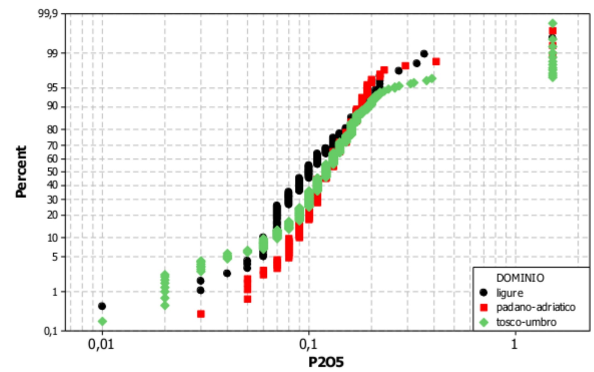
NA2O
DOMINIO
ligure
padano-adriatico
tosco-umbro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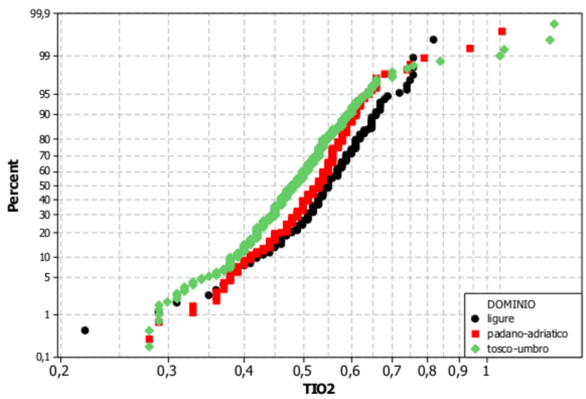
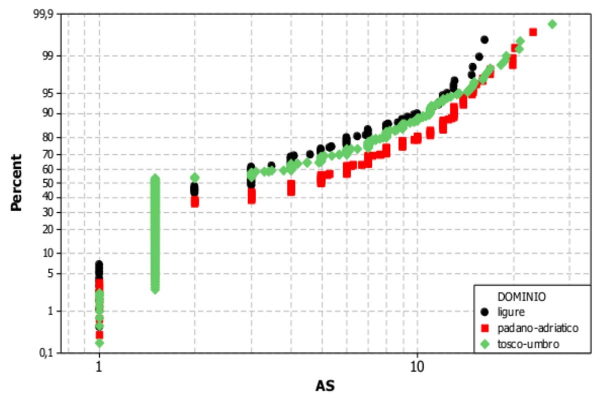
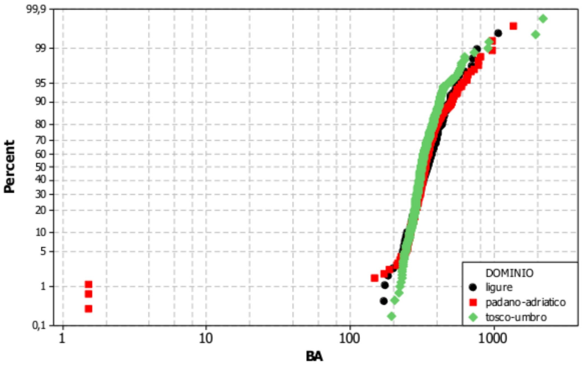
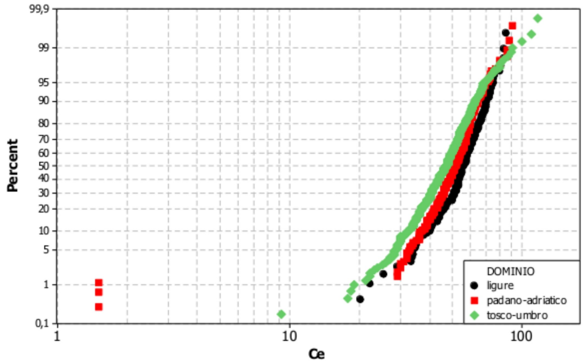
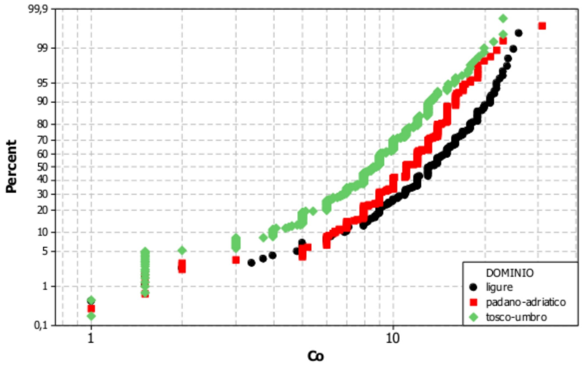
P2O5
DOMINIO
ligure
padano-adriatico
tosco-umbro

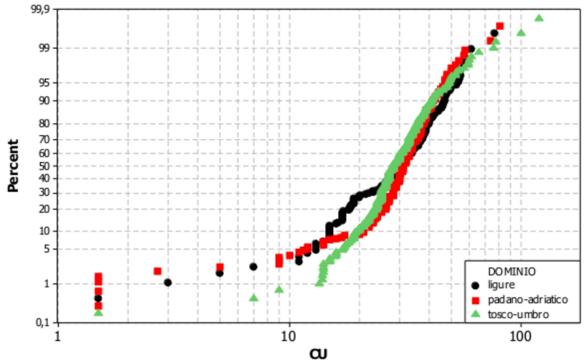

Percent
TIO2
DOMINIO
ligure
padano-adriatico
tosco-umbro

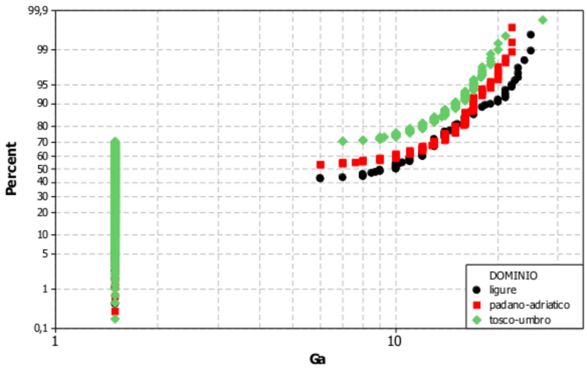

Percent
AS
DOMINIO
ligure
padano-adriatico
tosco-umbro

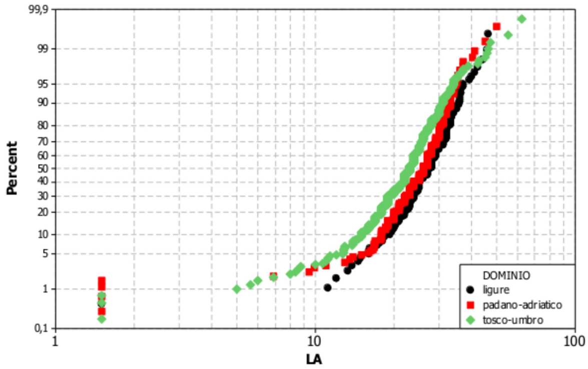

Percent
BA
DOMINIO
ligure
padano-adriatico
tosco-umbro

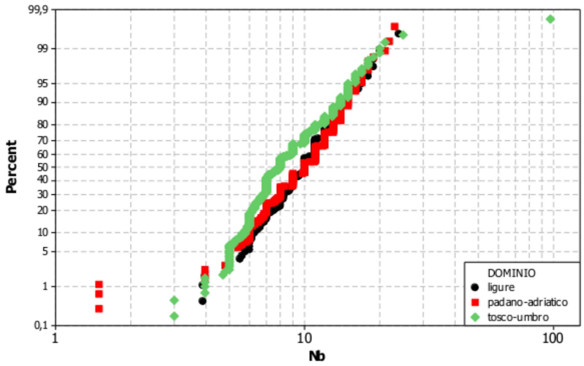

Percent
Ce
DOMINIO
ligure
padano-adriatico
tosco-umbro

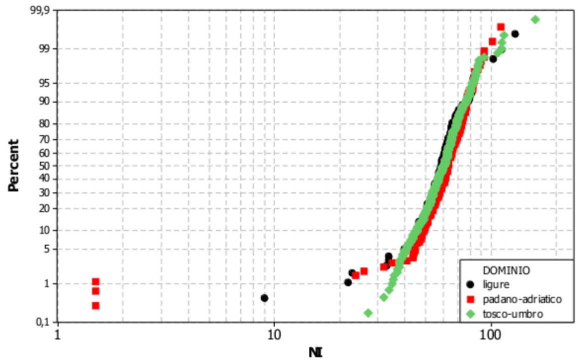

Percent
Co
DOMINIO
ligure
padano-adriatico
tosco-umbro

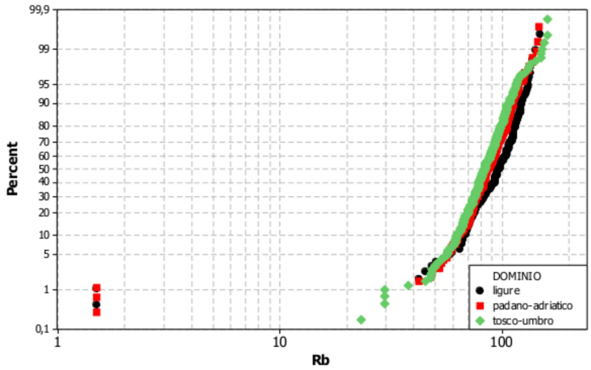

Percent
CU
DOMINIO
ligure
padano-adriatico
tosco-umbro

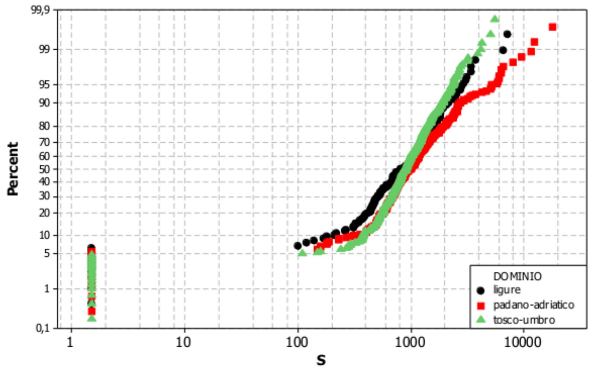

Percent
Ga
DOMINIO
ligure
padano-adriatico
tosco-umbro

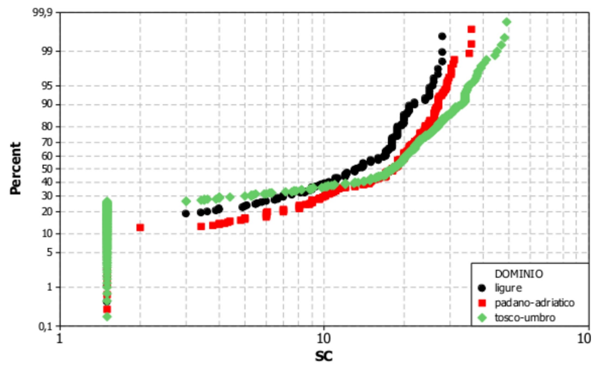

Percent
LA
DOMINIO
ligure
padano-adriatico
tosco-umbro

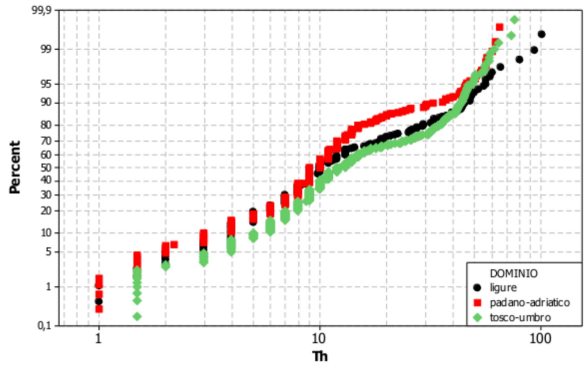

Percent
Nb
DOMINIO
ligure
padano-adriatico
tosco-umbro

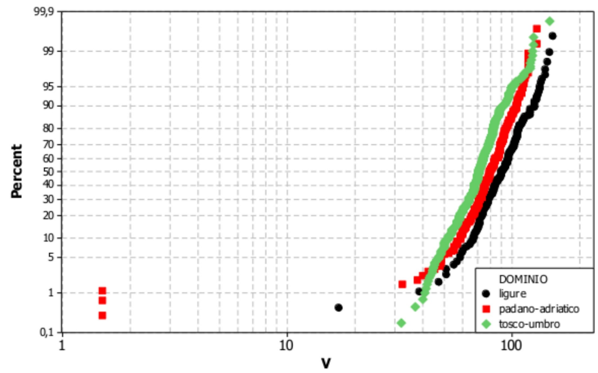

Percent
NI
DOMINIO
ligure
padano-adriatico
tosco-umbro

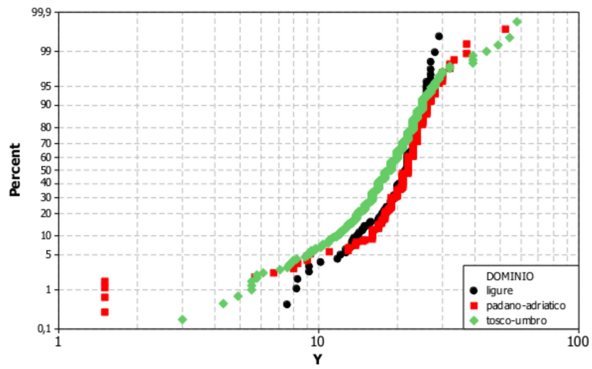

Percent
Rb
DOMINIO
ligure
padano-adriatico
tosco-umbro

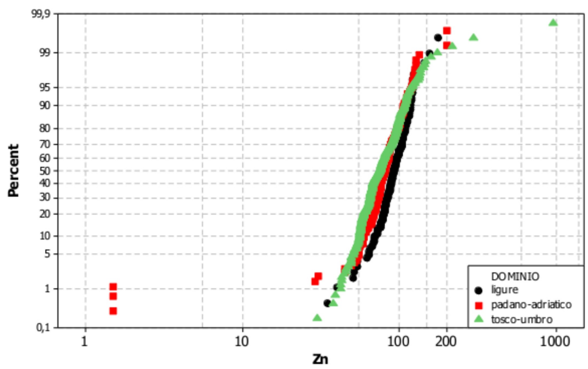

Percent
S
DOMINIO
ligure
padano-adriatico
tosco-umbro

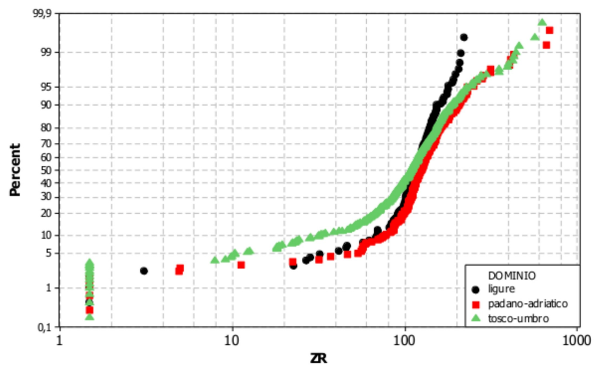

Percent
SC
DOMINIO
ligure
padano-adriatico
tosco-umbro

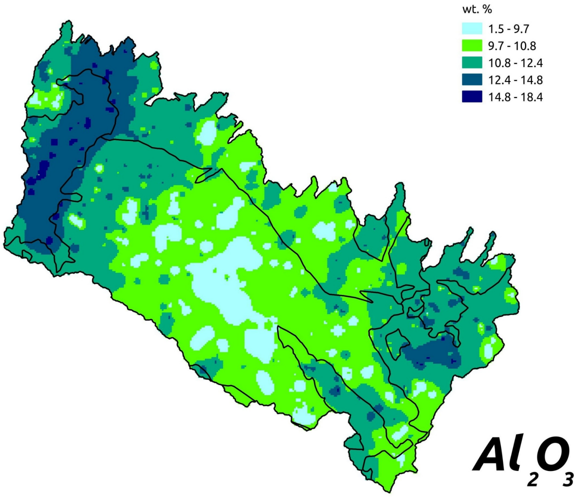

Percent
Th
DOMINIO
ligure
padano-adriatico
tosco-umbro

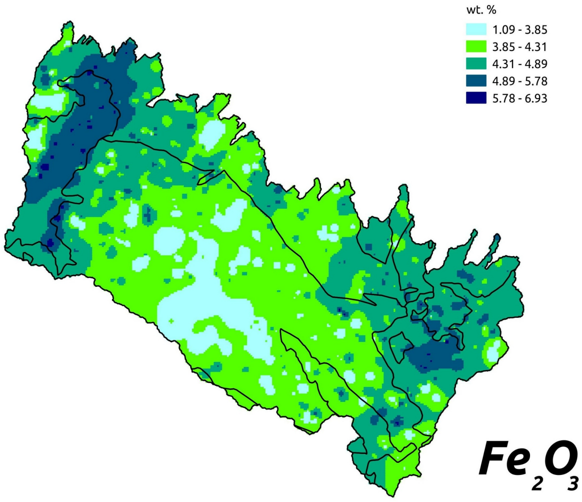

Percent
V
DOMINIO
ligure
padano-adriatico
tosco-umbro

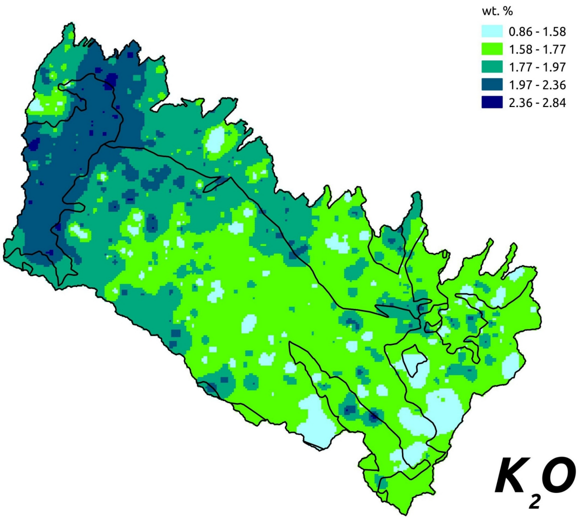

Percent
Y
DOMINIO
ligure
padano-adriatico
tosco-umbro

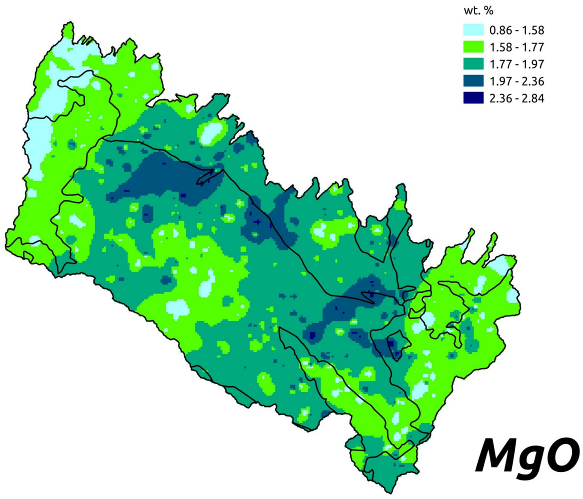

Percent
Zn
DOMINIO
ligure
padano-adriatico
tosco-umbro

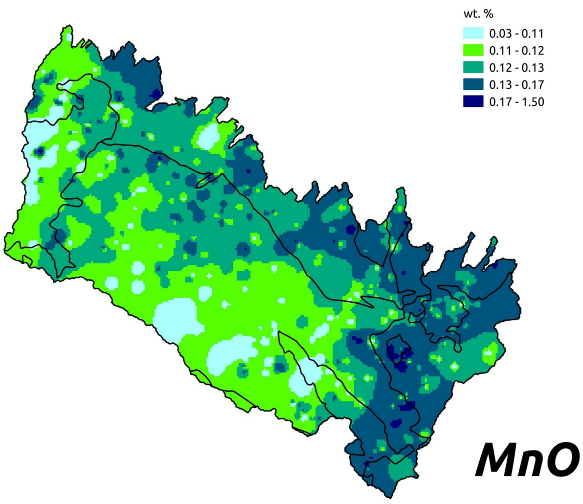

Percent
ZR
DOMINIO
ligure
padano-adriatico
tosco-umbro

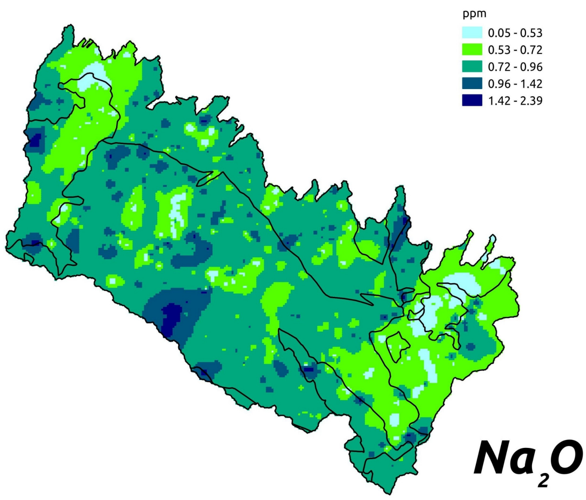

wt. %
1.5 - 9.7
9.7 - 10.8
10.8 - 12.4
12.4 - 14.8
14.8 - 18.4
Al_2O_3

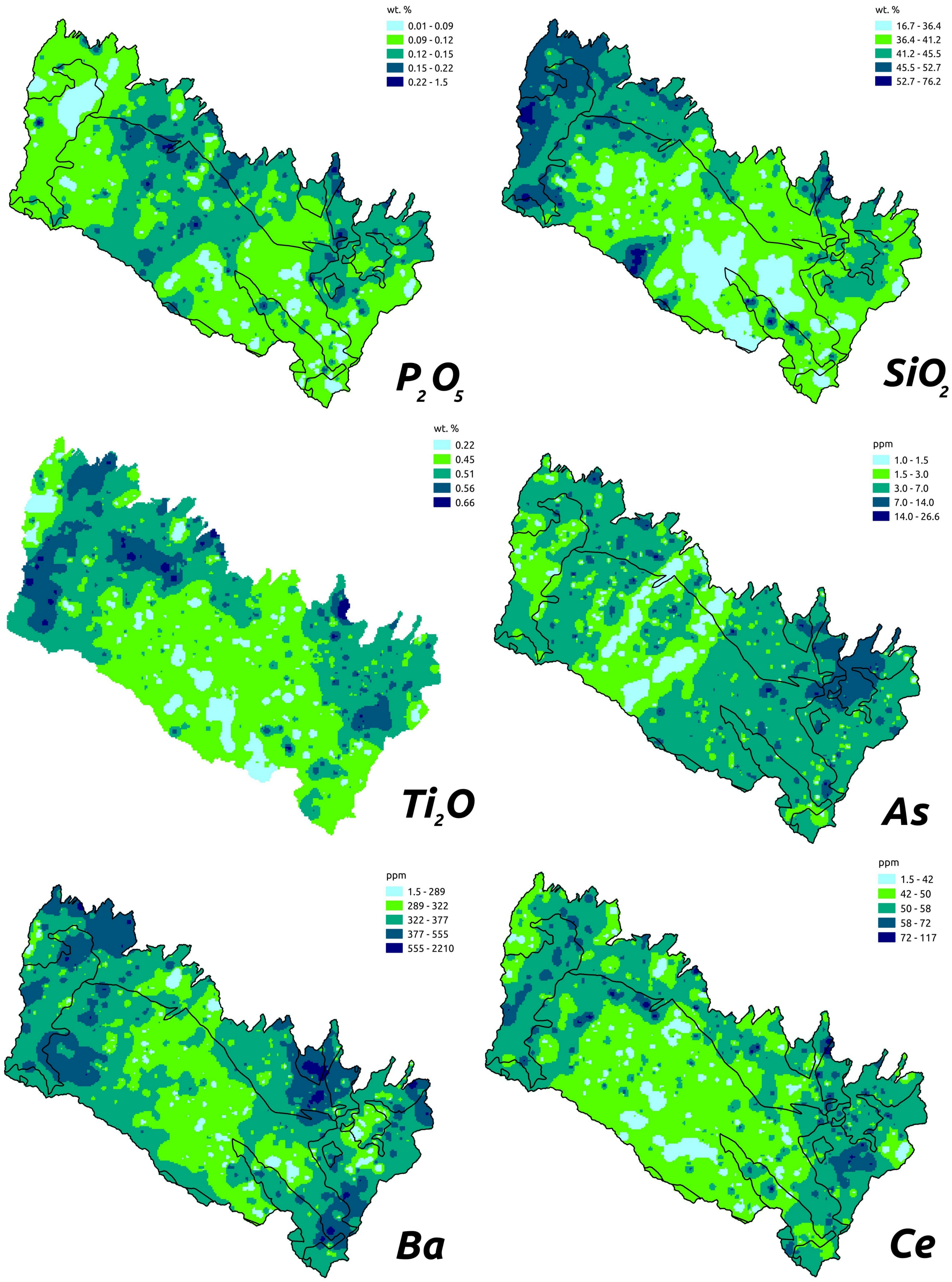

wt. %
1.09 - 3.85
3.85 - 4.31
4.31 - 4.89
4.89 - 5.78
5.78 - 6.93
Fe_2O_3

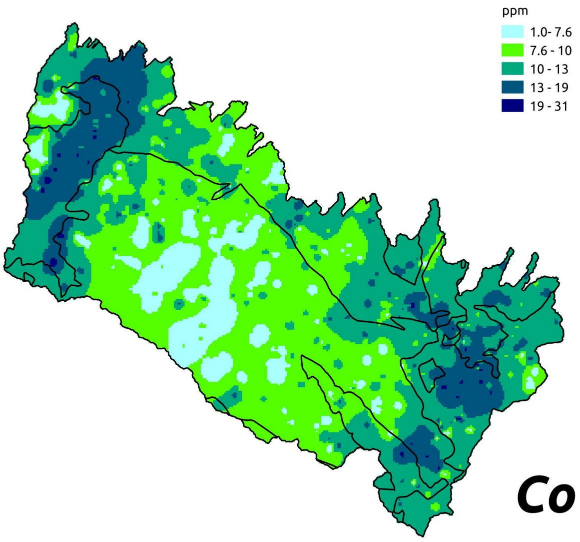

wt. %
0.86 - 1.58
1.58 - 1.77
1.77 - 1.97
1.97 - 2.36
2.36 - 2.84
K_2O

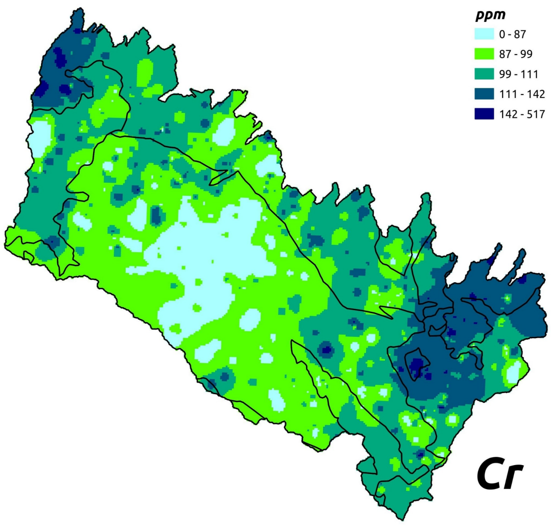

wt. %
0.86 - 1.58
1.58 - 1.77
1.77 - 1.97
1.97 - 2.36
2.36 - 2.84
MgO

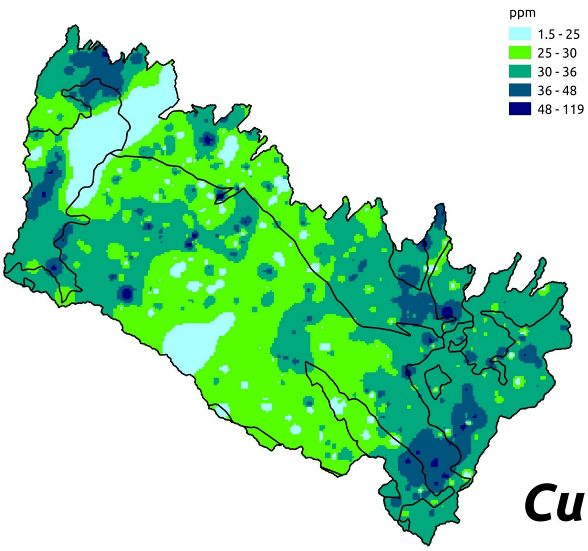

wt. %
0.03 - 0.11
0.11 - 0.12
0.12 - 0.13
0.13 - 0.17
0.17 - 1.50
MnO

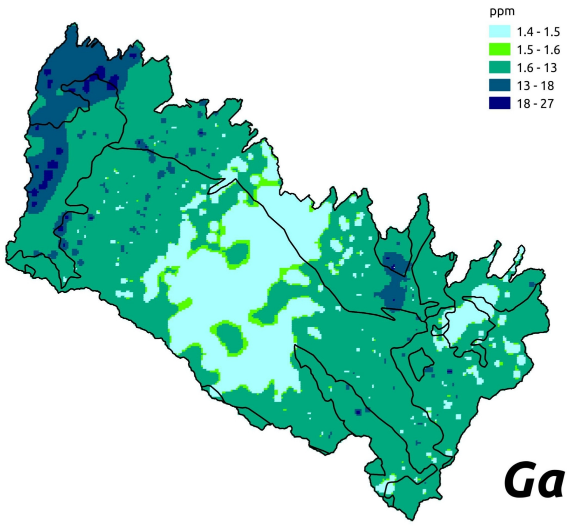

ppm
0.05 - 0.53
0.53 - 0.72
0.72 - 0.96
0.96 - 1.42
1.42 - 2.39
Na_2O

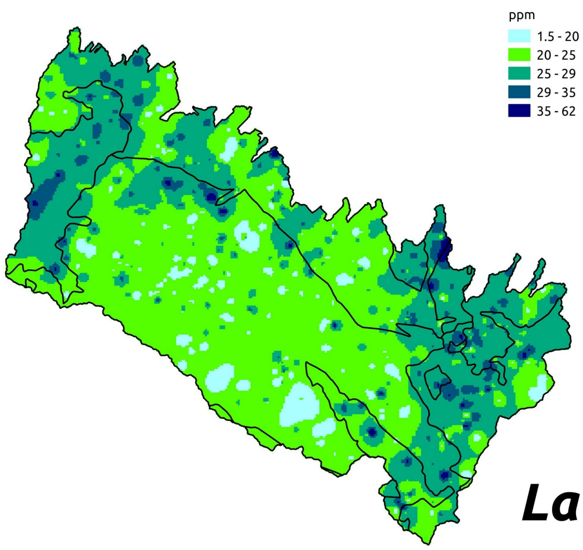

wt. %
0.01 - 0.09
0.09 - 0.12
0.12 - 0.15
0.15 - 0.22
0.22 - 1.5
P2O5
wt. %
16.7 - 36.4
36.4 - 41.2
41.2 - 45.5
45.5 - 52.7
52.7 - 76.2
SiO2
wt. %
0.22
0.45
0.51
0.56
0.66
Ti2O
ppm
1.0 - 1.5
1.5 - 3.0
3.0 - 7.0
7.0 - 14.0
14.0 - 26.6
As
ppm
1.5 - 289
289 - 322
322 - 377
377 - 555
555 - 2210
Ba
ppm
1.5 - 42
42 - 50
50 - 58
58 - 72
72 - 117
Ce

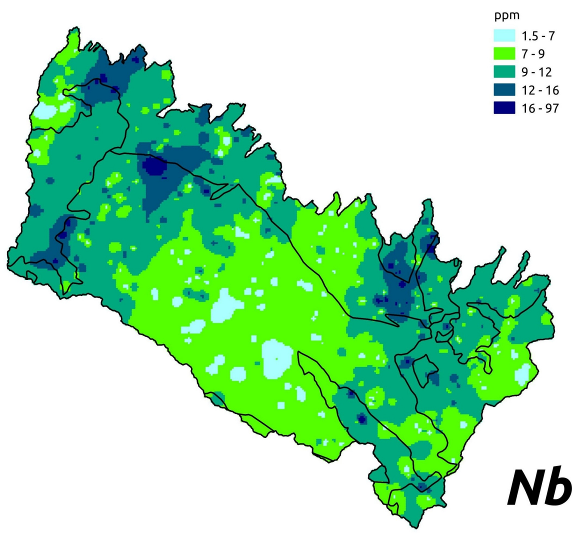

ppm
1.0- 7.6
7.6 - 10
10 - 13
13 - 19
19 - 31
Co

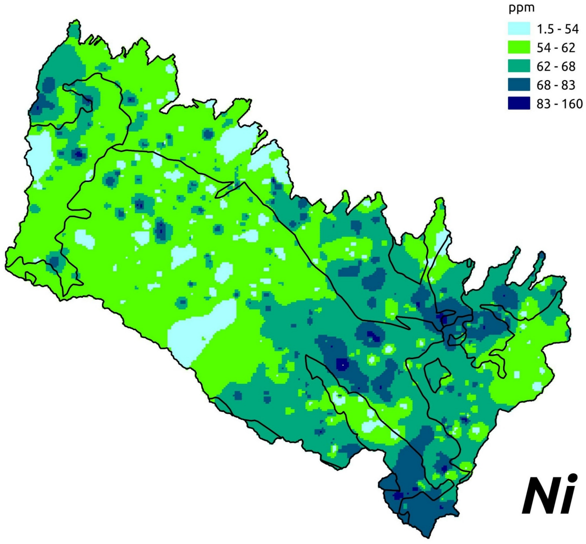

ppm
0 - 87
87 - 99
99 - 111
111 - 142
142 - 517
Cr

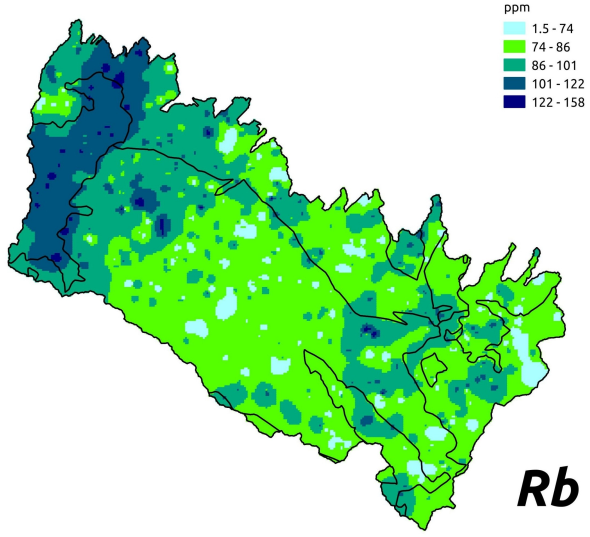

ppm
1.5 - 25
25 - 30
30 - 36
36 - 48
48 - 119
Cu

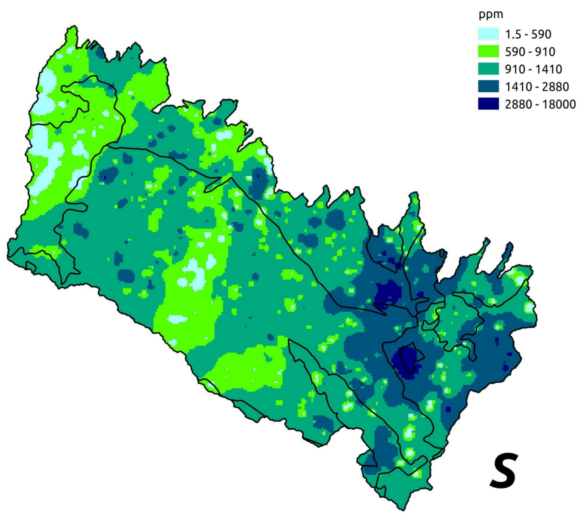

ppm
1.4 - 1.5
1.5 - 1.6
1.6 - 13
13 - 18
18 - 27
Ga

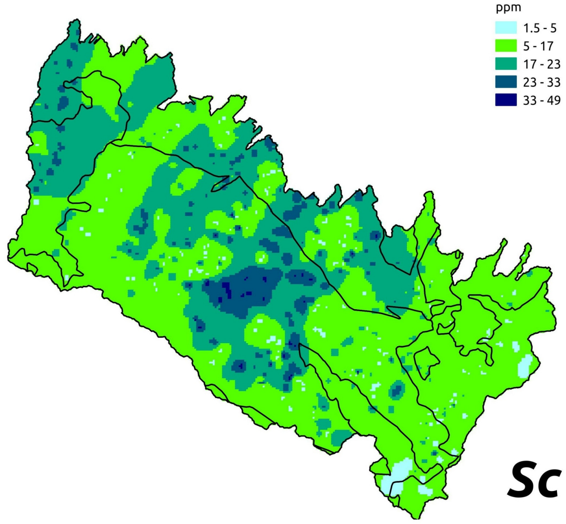

ppm
1.5 - 20
20 - 25
25 - 29
29 - 35
35 - 62
La

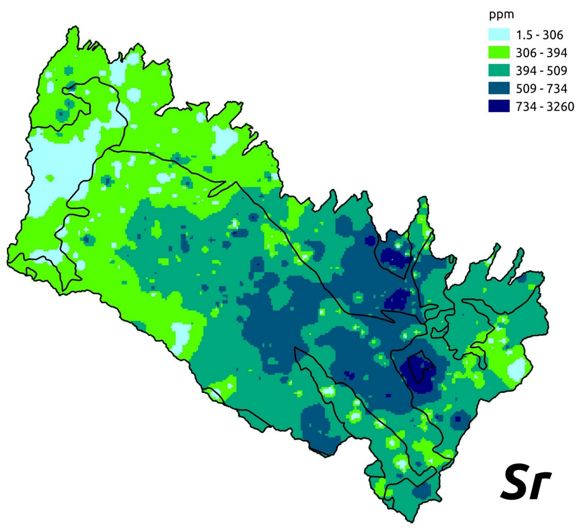

ppm
1.5 - 7
7 - 9
9 - 12
12 - 16
16 - 97
Nb

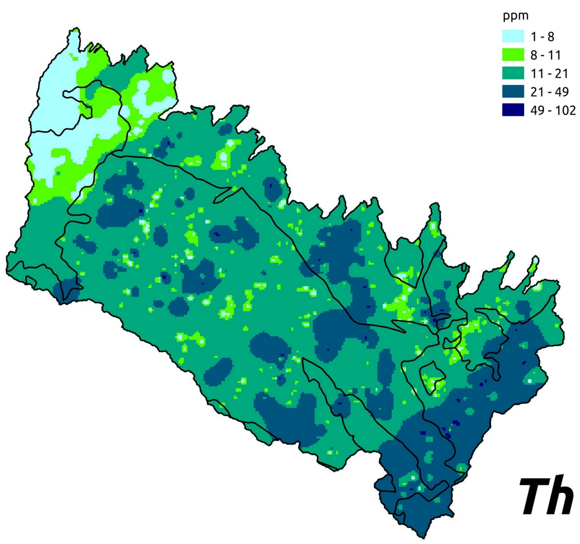

ppm
1.5 - 54
54 - 62
62 - 68
68 - 83
83 - 160
Ni

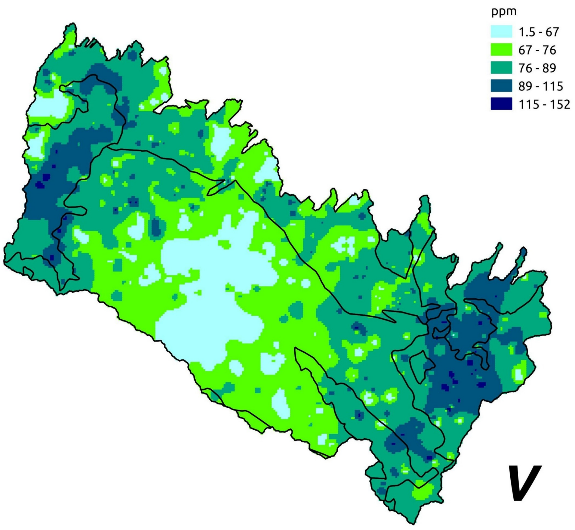

ppm
1.5 - 74
74 - 86
86 - 101
101 - 122
122 - 158
Rb

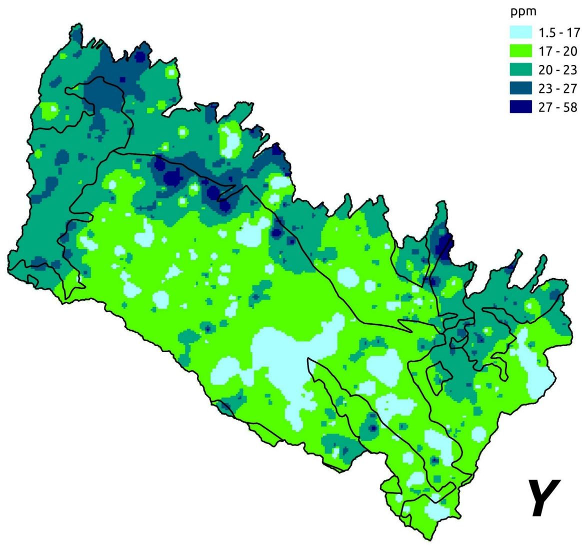

ppm
1.5 - 590
590 - 910
910 - 1410
1410 - 2880
2880 - 18000
S

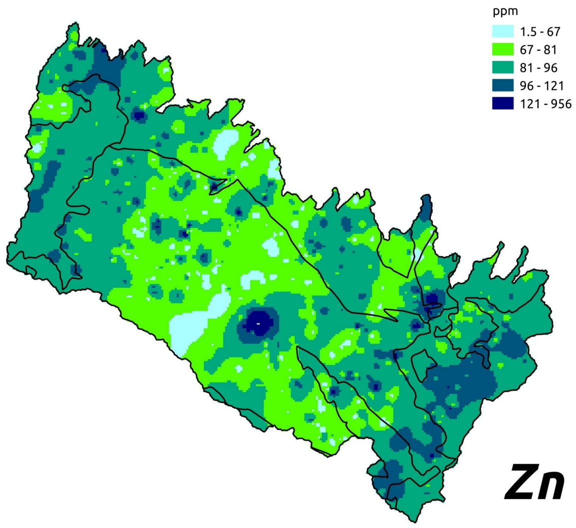

ppm
1.5 - 5
5 - 17
17 - 23
23 - 33
33 - 49
Sc

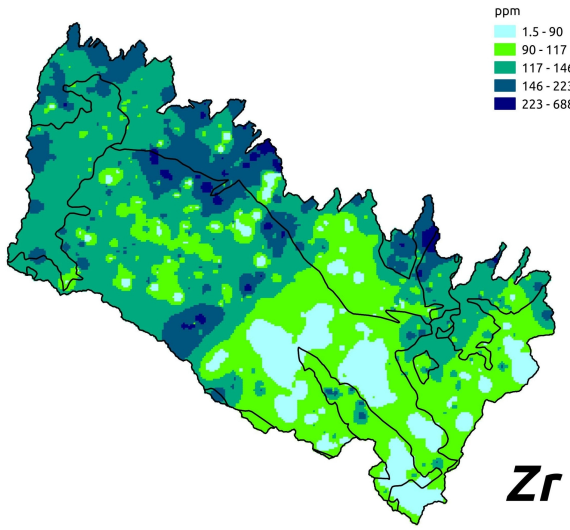

ppm
1.5 - 306
306 - 394
394 - 509
509 - 734
734 - 3260
Sr

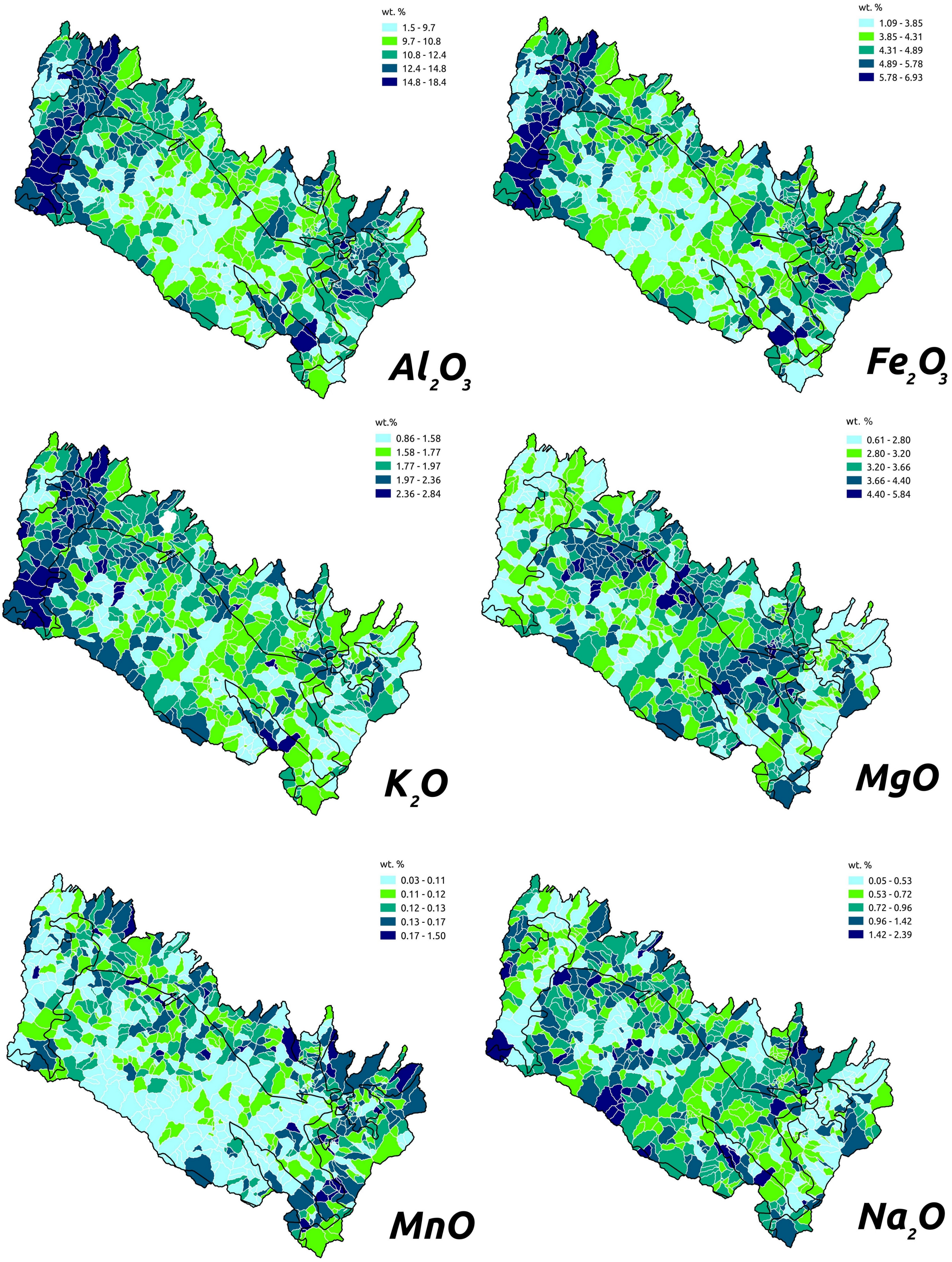

ppm
1 - 8
8 - 11
11 - 21
21 - 49
49 - 102
Th

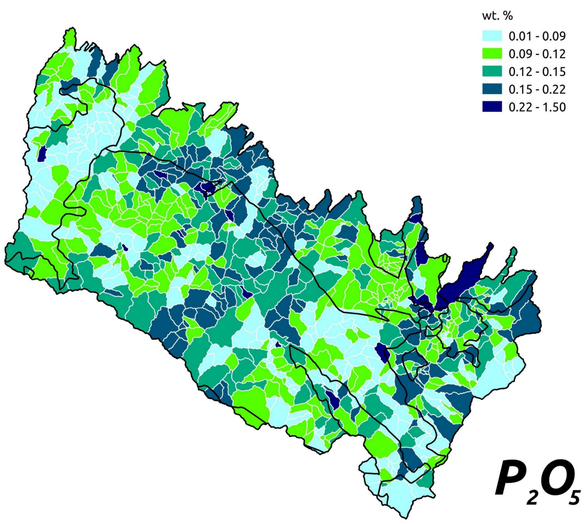

ppm
1.5 - 67
67 - 76
76 - 89
89 - 115
115 - 152
V

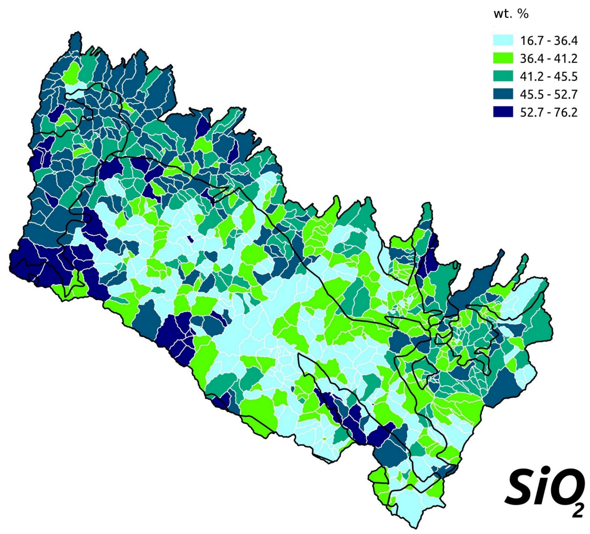

ppm
1.5 - 17
17 - 20
20 - 23
23 - 27
27 - 58
Y

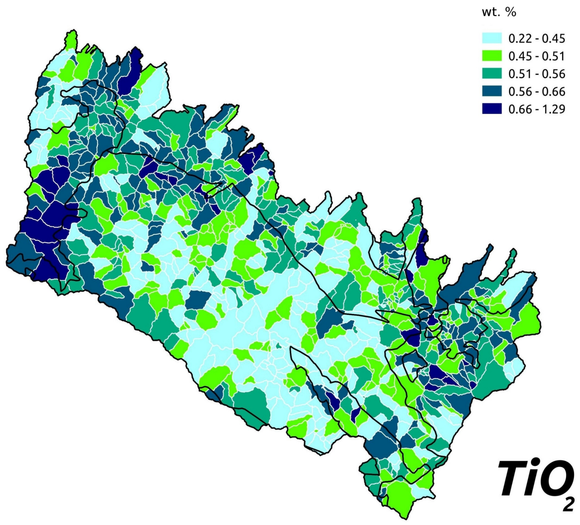

ppm
1.5 - 67
67 - 81
81 - 96
96 - 121
121 - 956
Zn

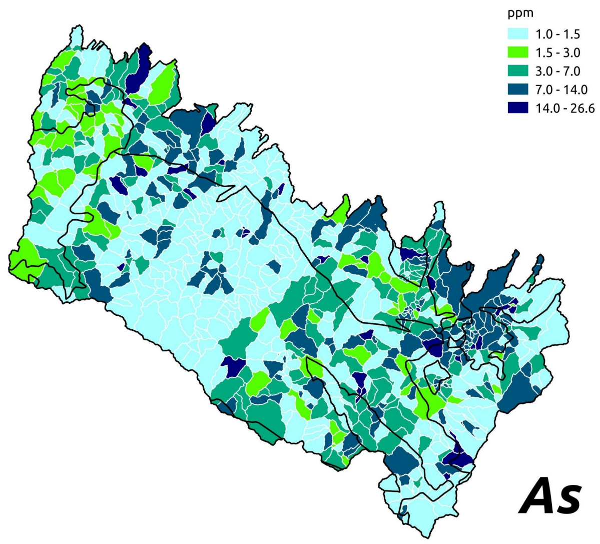

ppm
1.5 - 90
90 - 117
117 - 146
146 - 223
223 - 688
Zr

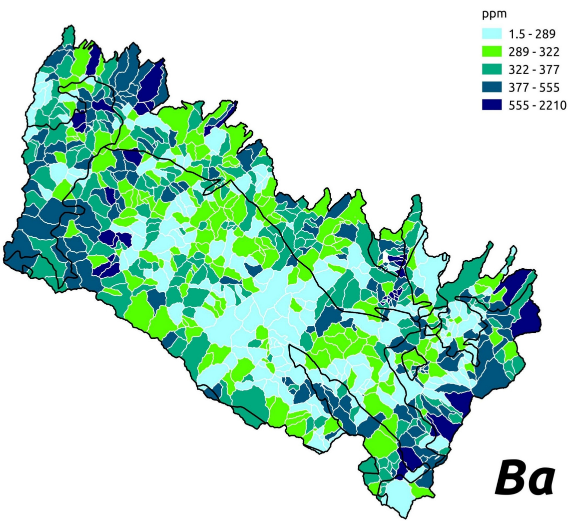

wt. %
1.5 - 9.7
9.7 - 10.8
10.8 - 12.4
12.4 - 14.8
14.8 - 18.4
Al_2O_3
wt. %
1.09 - 3.85
3.85 - 4.31
4.31 - 4.89
4.89 - 5.78
5.78 - 6.93
Fe_2O_3
wt.%
0.86 - 1.58
1.58 - 1.77
1.77 - 1.97
1.97 - 2.36
2.36 - 2.84
K_2O
wt. %
0.61 - 2.80
2.80 - 3.20
3.20 - 3.66
3.66 - 4.40
4.40 - 5.84
MgO
wt. %
0.03 - 0.11
0.11 - 0.12
0.12 - 0.13
0.13 - 0.17
0.17 - 1.50
MnO
wt. %
0.05 - 0.53
0.53 - 0.72
0.72 - 0.96
0.96 - 1.42
1.42 - 2.39
Na_2O

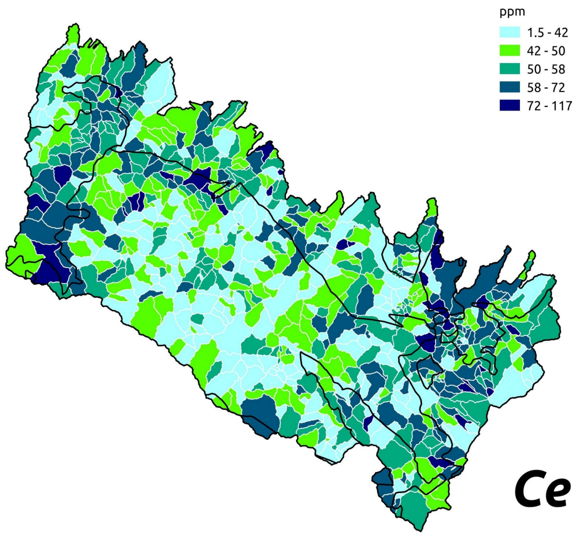

wt. %
0.01 - 0.09
0.09 - 0.12
0.12 - 0.15
0.15 - 0.22
0.22 - 1.50
P_2O_5

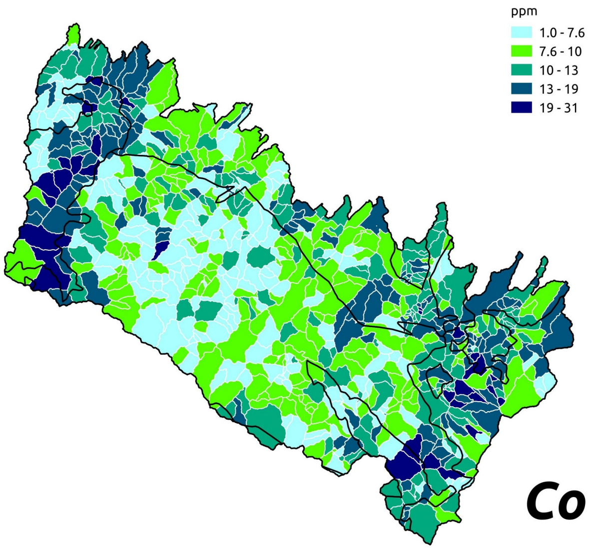

wt. %
16.7 - 36.4
36.4 - 41.2
41.2 - 45.5
45.5 - 52.7
52.7 - 76.2
SiO_2

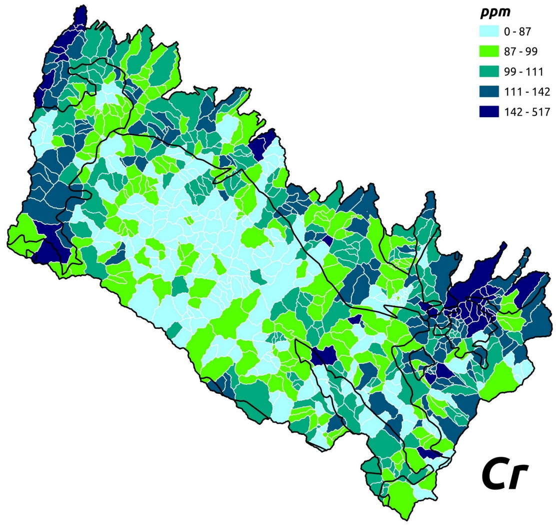

wt. %
0.22 - 0.45
0.45 - 0.51
0.51 - 0.56
0.56 - 0.66
0.66 - 1.29
TiO_2

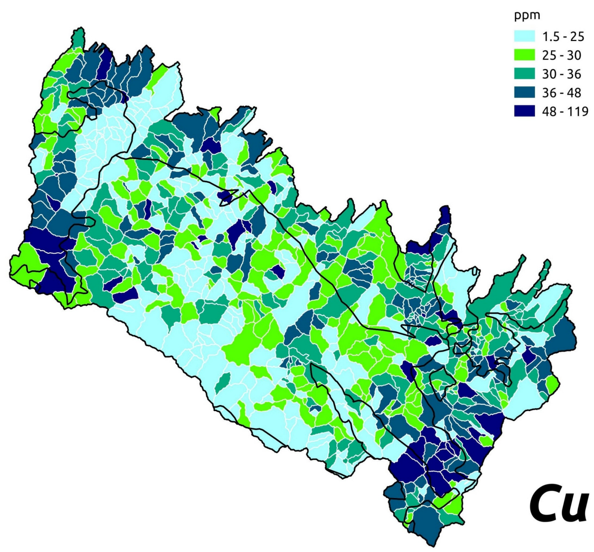

ppm
1.0 - 1.5
1.5 - 3.0
3.0 - 7.0
7.0 - 14.0
14.0 - 26.6
As

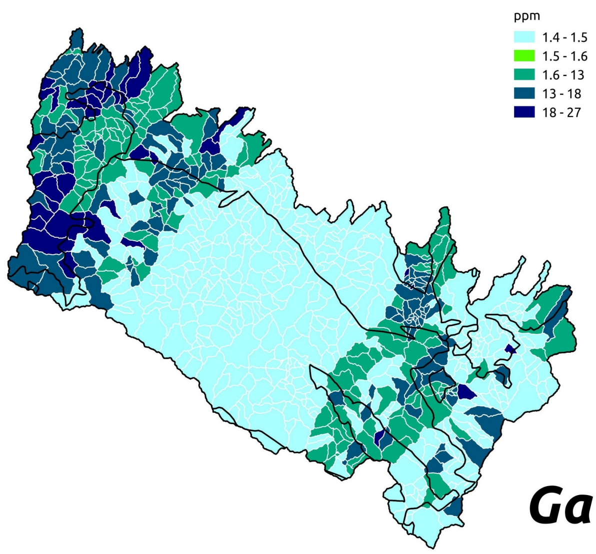

ppm
1.5 - 289
289 - 322
322 - 377
377 - 555
555 - 2210
Ba

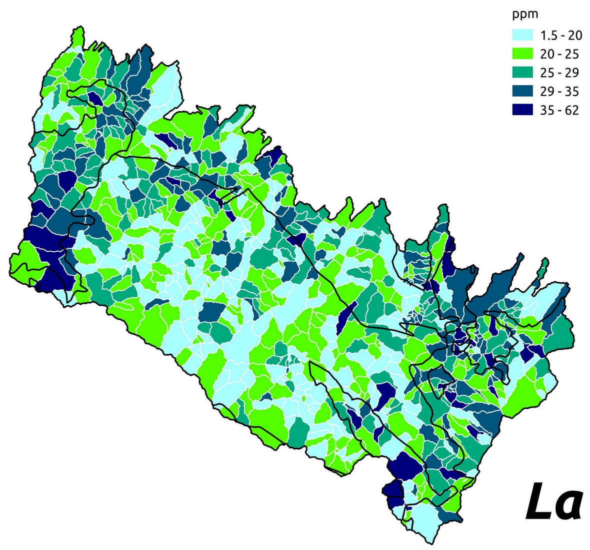

ppm
1.5 - 42
42 - 50
50 - 58
58 - 72
72 - 117
Ce

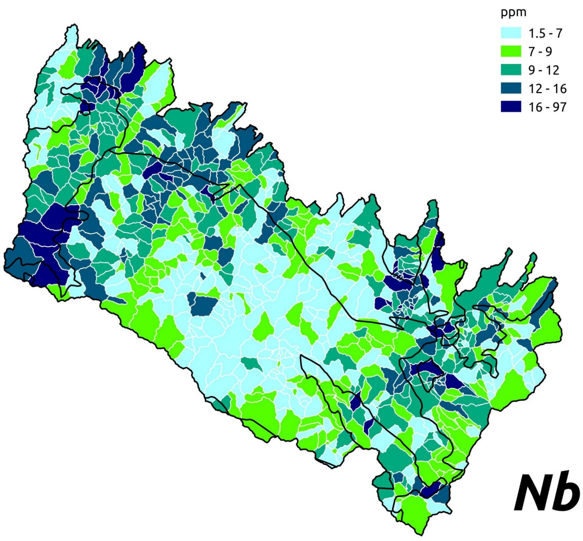

ppm
1.0 - 7.6
7.6 - 10
10 - 13
13 - 19
19 - 31
Co

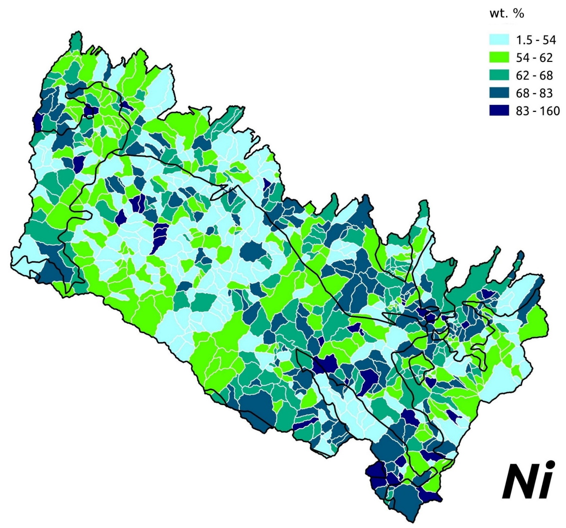

ppm
0 - 87
87 - 99
99 - 111
111 - 142
142 - 517
Cr

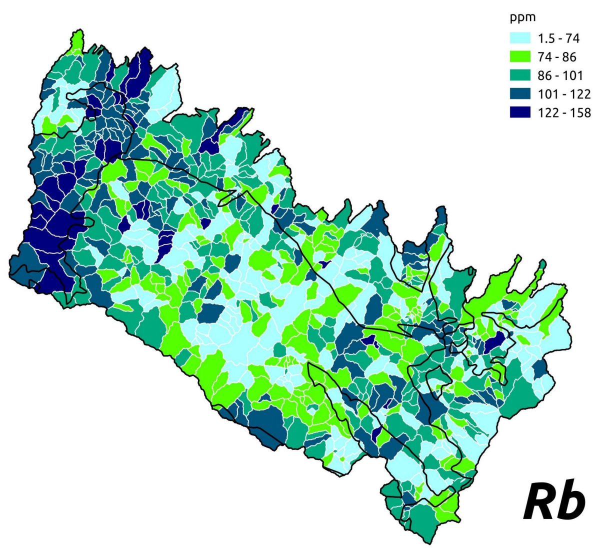

ppm
1.5 - 25
25 - 30
30 - 36
36 - 48
48 - 119
Cu

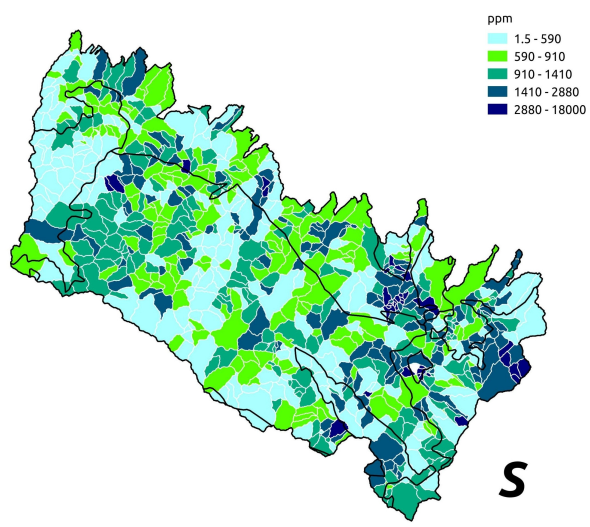

ppm
1.4 - 1.5
1.5 - 1.6
1.6 - 13
13 - 18
18 - 27
Ga

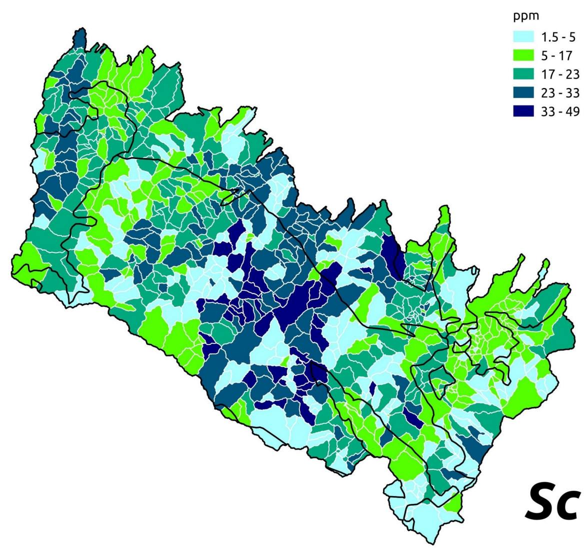

ppm
1.5 - 20
20 - 25
25 - 29
29 - 35
35 - 62
La

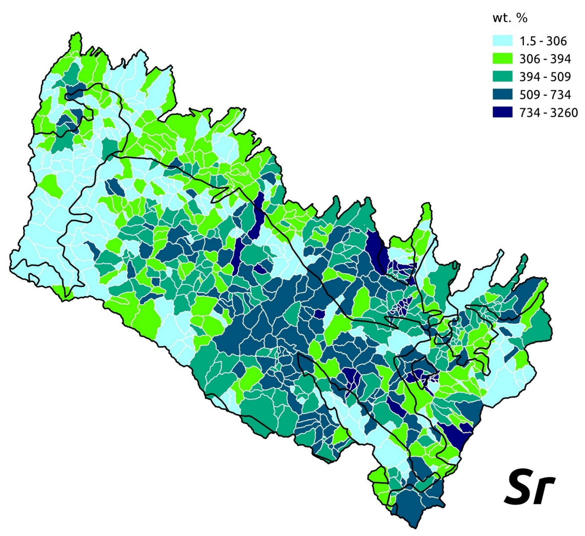

ppm
1.5 - 7
7 - 9
9 - 12
12 - 16
16 - 97
Nb

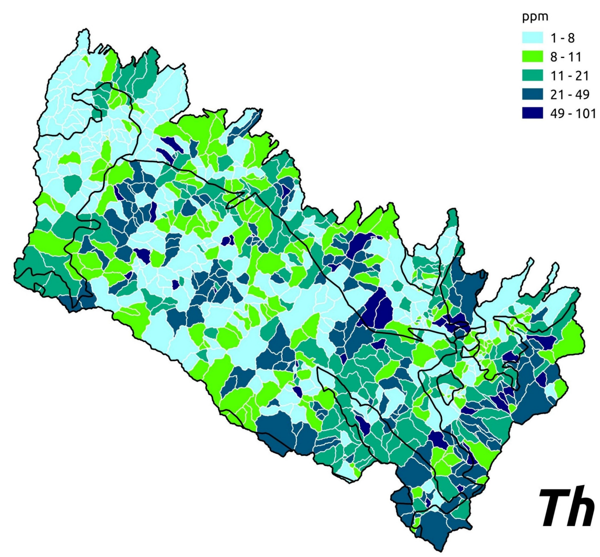

wt. %
1.5 - 54
54 - 62
62 - 68
68 - 83
83 - 160
Ni

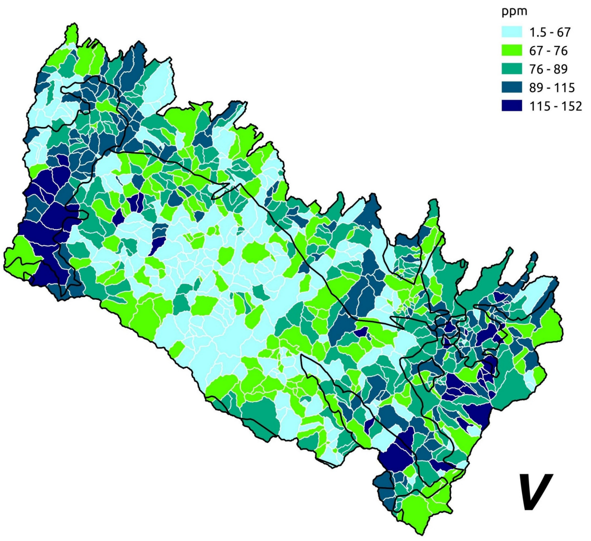

ppm
1.5 - 74
74 - 86
86 - 101
101 - 122
122 - 158
Rb

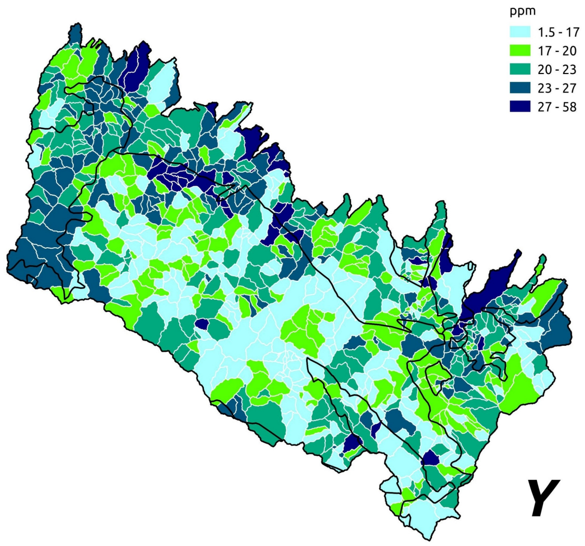

ppm
1.5 - 590
590 - 910
910 - 1410
1410 - 2880
2880 - 18000
S

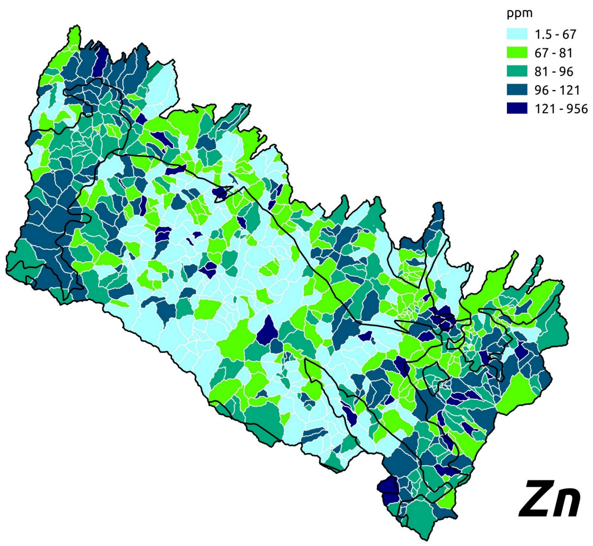

ppm
1.5 - 5
5 - 17
17 - 23
23 - 33
33 - 49
Sc

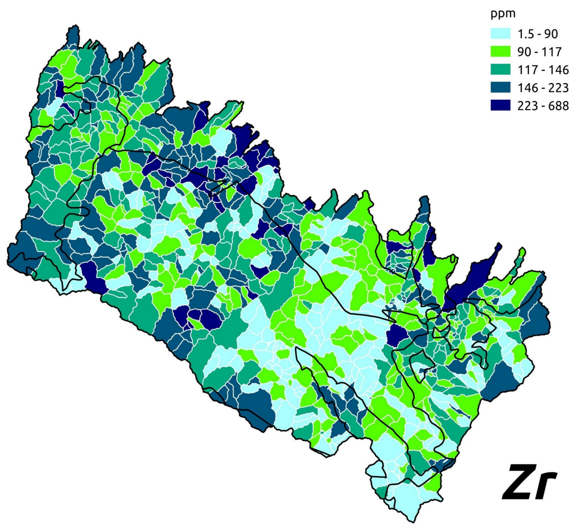

wt. %
1.5 - 306
306 - 394
394 - 509
509 - 734
734 - 3260
Sr


ppm
1 - 8
8 - 11
11 - 21
21 - 49
49 - 101
Th


ppm
1.5 - 67
67 - 76
76 - 89
89 - 115
115 - 152
V


ppm
1.5 - 17
17 - 20
20 - 23
23 - 27
27 - 58
Y


ppm
1.5 - 67
67 - 81
81 - 96
96 - 121
121 - 956
Zn


ppm
1.5 - 90
90 - 117
117 - 146
146 - 223
223 - 688
Zr

CHAPTER 3

Geochemical mapping based on geological units: a case study from the Marnoso-arenacea Formation (Northern Apennines, Italy)[2]

Abstract

Geochemical maps can provide lot of information about geology, earth surface processes, anthropogenic pressures and represent valuable tools for ore prospecting and land management. Stream sediment collected from the active channels were considered in this study and they represent an integral of the various possible sources of sediments upstream of the sampling point. Of course there can be multiple sources of signal, but in general the one related to bedrock geology should be the prevailing one. In this paper we investigated their potential application to integrate geological interpretation and produce a geologically-oriented geochemical map. Among the samples (770) collected for a regional geochemical mapping program, we selected a number of them (149) whose catchment basin included only one of the members recognized within the Marnoso-Arenacea formation. This Middle-Upper Miocene (Langhian-Tortonian) turbiditic unit forms the backbone of the Romagna Apennines and has been subdivided in 14 members according to age and lithostratigraphic criteria. The results indicate that there are marked differences in the composition of the members of the Marnoso Arenecea formation that reflect the provenance of the sediment and the palaeogeographic evolution of the units. Based on univariate and multivariate analysis (Factor analysis) two principal types sediment compositions can be idenfied: Tortonian members are characterized by sialic coarse grain-sediments while the Langhian-Serravallian members are richer in carbonate fraction, slightly enriched in a mafic contribution. This work elaborated the geochemical data with attention to geology, integrating the literature information available to spatially extend the interpretation based on limited site observation as the petrographic ones. In general the geochemical map based on geological unit could be a valid tool supporting the geology recostruction of a complex area.

Keywords: Geochemical mapping, Geochemistry, Stream sediments, Provenance, R-mode factor analysis, Marnoso-arenacea formation, Geological members, Sediment composition, Source rock weathering, Apennines

2 This chapter consists of a paper by Lancianese V. and Dinelli E. submitted at “Chemie der Erde/Geochemistry”

3.1 Introduction

Since the early 1980's, the geochemistry of clastic (Bhatia, 1983, 1985a,b; McLennan et al., 1983, 1993; Taylor and McLennan et al, 1985; Roser and Korsch, 1986, 1988; Condie et al., 1992; Condie, 1993), lake (Krishnamurthy et al., 1986; Fontes et al., 1993; Mullins, 1998; Willemse and Tornqvist, 1999; Last and Smol, 2001; Jin et al., 2001, 2003; Laird et al., 2003; Rose et al., 2004) and stream sediments (Swennen and Sluys, 1998; Cannon et al., 2004; Ortiz and Roser, 2006 a, b; Ranasinghe et al., 2008, 2009; Singh, 2010; Bhuiyan et al., 2011) has been used for the evaluation of tectonic setting and provenance studies because the original signature of the source still remains preserved in the sediments. Chemical compositions of sediments have been examined in different ways: some trace elements as Sc, Th, Zr, Cr, Ni, Co and REEs generally remain immobile during several processes of sediment production and are useful indicator of source region composition (Singh, 2010); SiO_2/Al_2O_3 ratio, CaO, Na_2O and Sr suggest clay matrix control, grain size and residence in feldspars (Bhuiyan et al., 2011); some geochemical indices of sandstones (Th/Sc, La Sc, Co/Th, Cr/Th, Cr/V and V/Ni ratios) and shales (La/Sc and La/Cr ratios), based on low mobility elements, were used to reconstruct the source area characteristics (Taylor and McLennan, 1985; McLennan et al., 1993; Condie, 1993).

Stream sediments are composite samples of the outcropping rocks and surface material upstream of the sampling point (Levinson, 1974; Rose et al., 1979; Darnley, 1990; Hale and Plant, 1994) a key feature for exploration, mapping and management and are useful for background concentrations (Bölkiven et al., 1990) therefore stream sediment is one of the best medium in provenance studies and evalutation of tectonic setting (Carranza and Martin, 1997; Chandrajith et al., 2000; Ohta et al., 2004; Cannon et al., 2004; Singh, 2010; Tripathy et al., 2013). The chosen grain-size fraction can have an important influence on the analytical results for stream sediment samples, since many metals tend to be enriched in the fine grain-size fractions (Förstner and Müller, 1974).

If there is an adequate sample density it is possible to highlight the litological effect of specific geological units (Cocker, 1999; Lima et al., 2003; Ohta, 2005; Albanese et al., 2007; Breward, 2007) based on the differences that characterize several rock types (e.g.: ultramafic, granitoid and sedimentary). The present study takes advantage of an high-density stream sediment sampling and a detailed geological map to investigate the geochemical evolution within each single geological unit providing strong connection between geological evolution and geochemical composition. In this way, the geological information is considered as a key of representation in geochemical mapping approach that follows a particular criterion of attribution of geochemical data. The resulting geochemical map based on geological unit could be a valid tool supporting the geology recostruction of a complex area.

3.2 Study area

3.2.1 Geologic and stratigraphic setting

The Marnoso-arenacea Formation (MAF) is a turbiditic unit, deposited in the Tuscan-Umbrian portion of the Inner Periadriatic basin during the Miocene (Cipriani and Malesani, 1963 a, b, c; Ricci Lucchi, 1978; Ricci Lucchi and Valmori, 1980; Gandolfi et al., 1983). This basin was elongated in a NW-SE direction in front of the growing Northern Apennines orogenic wedge (Ricci Lucchi, 1978, 1981, 1986). In the Romagna Apennines it forms a belt 90 km long and 40 km wide, and reaches a thickness of up 3500 m. It is limited to the north-west and to the south-east by two allocthonous units of the Sillaro valley and of the Marecchia valley (Fig. 1).

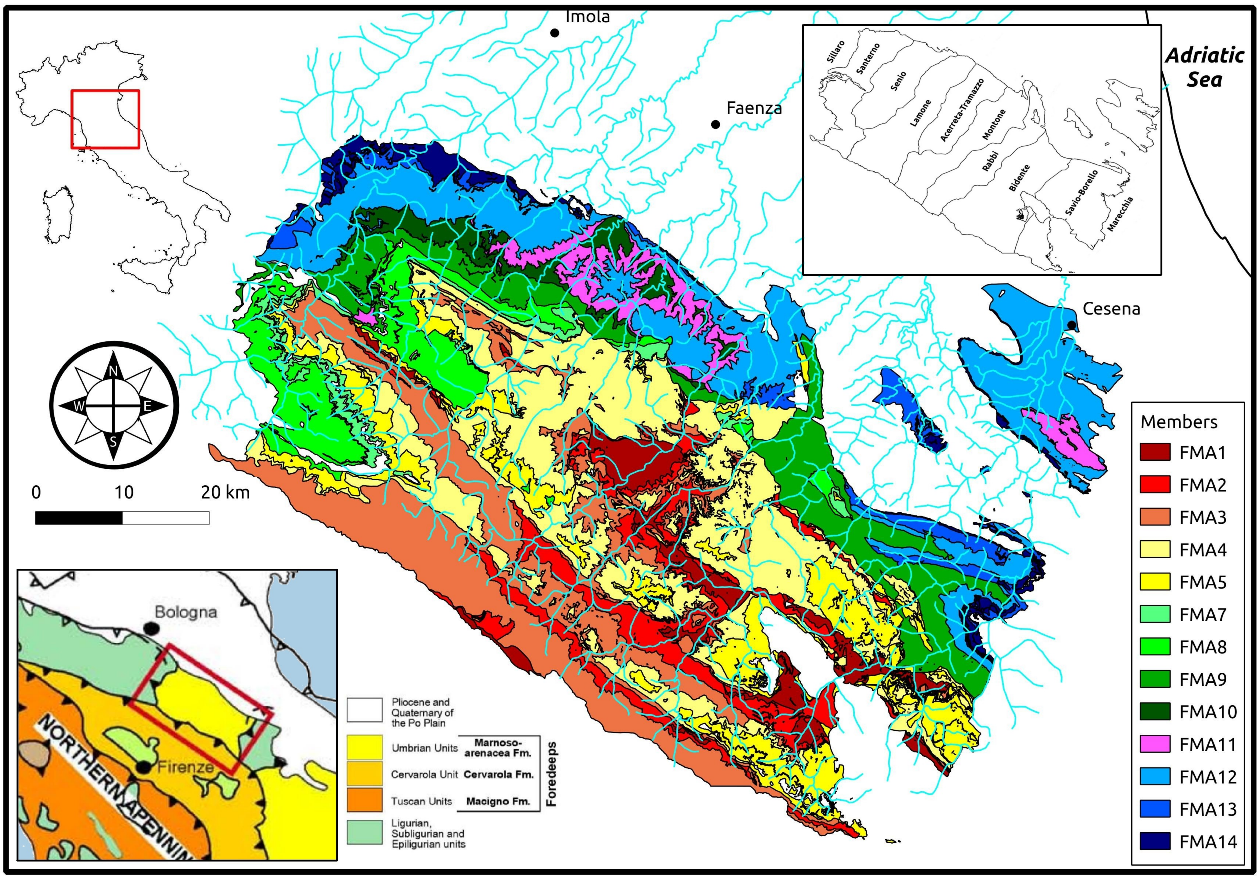


Fig. 1. Geological map of MAF modified from the source available at Servizio Geologico, Sismico e dei Suoli Regione Emilia Romagna showing the 13 members recognized by Martelli et al. (1994). The area is part of the catchment of nine rivers (upper right insert): Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello. It is limited to the north-west and to the south-east by two allocthonous units of Sillaro valley and Marecchia valley. The MAF (lower left insert) is part of the Umbrian Units between Ligurian, Subligurian, Epiligurian units at north-west and south-east, the Pliocene and Quaternary unit at north-east and Cervarola unit at south-west (from Muzzi Magalhaes and Tinterri, 2010).

The MAF has been subdivided in 14 members for cartographic purposes (Tab. 1 and Fig. 1), based on litostratigraphic criteria such as arenite/pelite ratio, average thickness of arenaceous levels, composition of arenites and stratigraphic position (Martelli et al., 1994). These members can be correlated with those proposed by Mutti et al. (2002) and Ricci Lucchi (1981). Based on Ricci Lucchi's work, the sedimentary evolution involves two stages or basins: an older inner stage (Langhian to Serravallian) and a younger outer stage (Tortonian), as a result of the basin depocenter shifting through time toward the NE and the progressive closure of the MAF foredeep. According to Ricci Lucchi (1981) the change from inner to outer stage is marked by an increase in the sand/mud ratio and a decrease in clastic carbonate input. Moreover Ricci Lucchi (1986) adds that MAF deposits can be subdivided into four depositional sequences, LS (Langhian-Serravallian) and S (Serravallian) characterizing the inner stage, and T1 (Tortonian 1) and T2 (Tortonian 2) characterizing the outer stage, each recording the shift towards the foreland (E-NE) of the main depocenter (Fig 2). Recent studies (Argnani and Ricci Lucchi, 2001; Conti, 2001; Mutti et al., 2002a; Roveri et al., 2002; Lucente, 2004; Muzzi Magalhaes and Tinterri, 2010; Tinterri and Muzzi Magalhaes, 2011) shown that the MAF depositional setting was complicated by a structural deformation and sedimentary/tectonic load that exerted control over basin geometry and facies distribution. These considerations have produced a further sedimentary evolution characterized by three stages: a Langhian/Serravallian inner basin, an upper Serravallian phase recording the transition between inner and outer basin and a Tortonian outer basin.

Geologic Member	Name	Arenite/Pelite ratio	Age
FMA14	Membro di Borgo Tossignano	3 – 20	Tortonian
FMA13	Membro di Fontanelice	3 – 20	Tortonian
FMA12	Membro di Castel del Rio	0.66-6	Tortonian
FMA11	Membro di Modigliana	0.2 – 0.5	Tortonian
FMA10	Membro di Dovadola	0.5 – 2	Tortonian
FMA9	Membro di Civitella di Romagna	0.2 – 0.5	Serravallia-Tortonian
FMA8	Membro di Nespoli	0.33 – 1	Serravallian-Tortonian
FMA7	Membro di Monte Bassana	<1	Serravallian
FMA6	Membro di Monte Coronaro	<0.2	Serravallian
FMA5	Membro di Collina	0.2 – 0.33	Langhian-Serravallian
FMA4	Membro di Galeata	0.33 – 0.5	Langhian-Serravallian
FMA3	Membro di Premilicuore	1 – 2	Langhian-Serravallian
FMA2	Membro di Corniolo	0.33 - 0.5	Langhian-Serravallian
FMA1	Membro di Bisemo	0.2 – 0.33	Langhian-Serravallian

Tab. 1. Subdivision of MAF on the basis of litostratigraphic criteria and age as proposed by Ricci Lucchi (1981), Martelli et al. (1994), Mutti et al. (2002). FMA 6 and FMA7 are not included because there are no avaibles stream sediment samples within these geological members.

3.2.2 Sediment petrographic composition

Sediment compositional variations within the MAF basin are derived by three main detrital inputs (Fig. 2) (Ricci Lucchi and Valmori, 1980; Gandolfi et al., 1983; Ricci Lucchi and Ori, 1985; Capozzi et al., 1991; Roveri et al., 2002; Mutti et al., 2003; Zattin and Zuffa, 2004; Muzzi Magalhaes and Tinterri, 2010): a prevalently Alpine input (siliciclastic) is associated to NW-to-SE flowing turbidity currents; other important inputs derived from southwestern area, from the growing apenninic mountain belt, and minor inputs are located in the southern and southeastern margins of the basin which produced carbonate ("Colombine") and hybrid siliciclastic/carbonatoclastic ("Contessa-like") turbidity currents flowing in the opposite direction towards the NW. Gandolfi et al. (1983) associated these provenances with five petrofacies (Alpine I and II, Apenninic I, II and III): among the main distinctive petrographic features of Alpine I and II petrofacies there is K-feldspar < plagioclase, the presence of dolomite, serpentine schist and volcanic lithics and a distinctive heavy mineral association (epidote, glaucophane, kyanite). In contrast Apennine II and III sandstones are characterized by K-feldspar > plagioclase, the presence of limestone and siliciclastic sedimentary rock fragments and a different heavy mineral association (picotite, monazite + xenotime, zircon). Finally Apennine I presents K-feldspar < plagioclase, fragments of granite and aplite and an epidote-glaucophane-kyanite heavy mineral association.

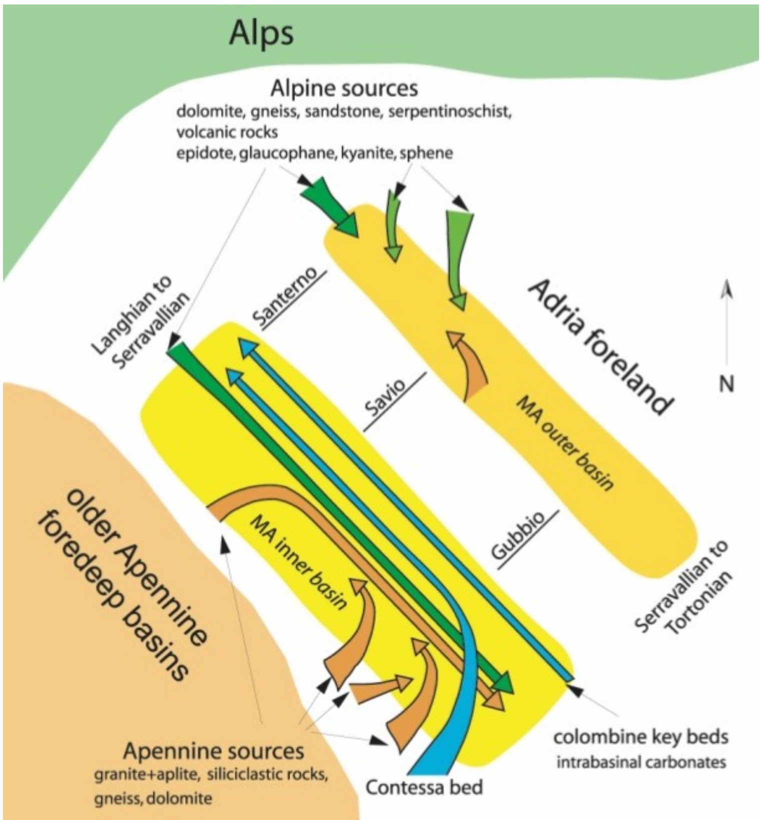


Fig. 2. Scheme of the main sediment inputs in the MAF basin (redrawn from Gandolfi et al., 1983; Roveri et al., 2002).

3.3 Methods

3.3.1 Sampling methodology and analysis

Stream sediments were collected from the active channel, at adequate distance from the banks, to minimize the influence of very local contribution. Sediment collected in different points within the site was sieved in the field using a stainless steel with running water. The fraction < 180µm was separated and collected in 1,5 l bottle. settling the bottle was emptied, cut and the solid material oven dried at 40°C, until dryness. 30 grams were homogenized and milled in an agate mortar, and powder pellets were prepared for XRF analysis. The concentration of 30 major and trace element analyses (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S) were perfomed by X-ray fluorescence spectrometry at the XRF laboratory of the Department of Biological, Geological and Environmental Sciences of the University of Bologna. Matrix corrections were applied in the analytical work (Franzini et al., 1972, 1975; Leoni and Saitta, 1976; Leoni et al., 1986). Based on the analysis of international reference material, the estimated precision and accuracy for trace element determination was better than 5%, except for those elements at 10 ppm or lower (10–15%). Total loss on ignition (LOI) was estimated after overnight heating at 950° in a muffle furnace.

3.3.2 Data selection and treatment

Starting from an extensive database resulting from a stream sediment geochemical survey (Dinelli and Lucchini, 2004) subsequently integrated by additional sampling, to reach a total of 770 samples, and discussed in a separate paper (Lancianese and Dinelli, submitted), samples were selected to be the most representative of the bedrock signal. Among the 390 collected with the MAF boundaries, further selection involved the removal of samples from high stream order (Fig. 3a) and samples whose upstream catchment included different geological members (Fig. 3b). In addition were excluded from further analysis also those samples were anthropogenic disturbances were clear. According to these criteria, 149 samples were selected and subsequently assigned to a specific member of the MAF. It was not possible to assign any samples to member 6 and 7 which were thus excluded from the following elaboration.

The computation of median and median absolute deviation (MAD) have been carried out in R, a free software environment (http://cran.r-project.org), using the DASplusR package (http://www.statistik.tuwien.ac.at/StatDA/DASplusR/), as well as the elaboration of Factor Analysis (FA) to describe the data in terms of correlation structures that fit a predefined number of components (factors) and in the processing of notched boxplot of chemical elements. Binary diagrams of elemental ratios were constructed with GCDkit package (Janoušek et al., 2006).

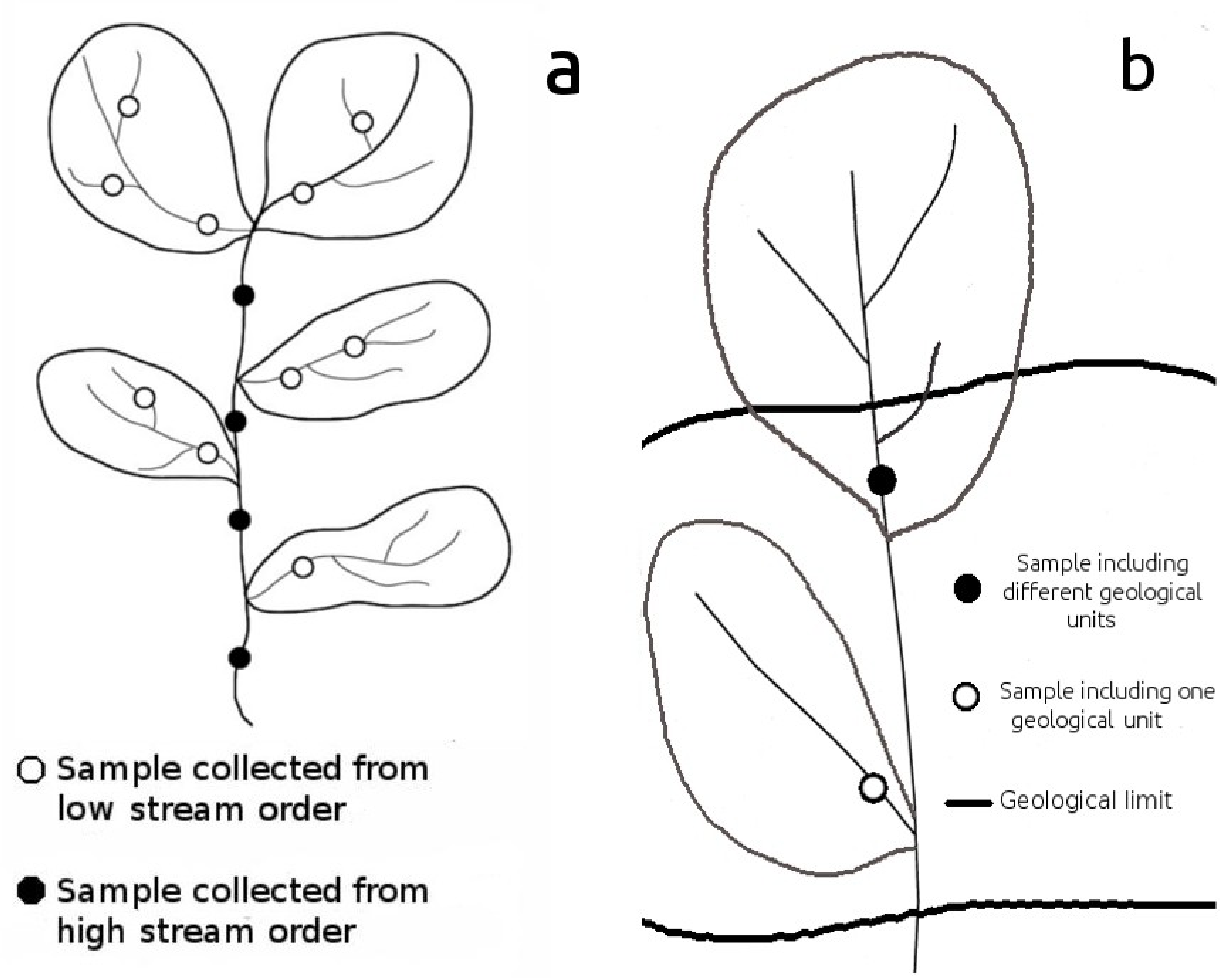


Fig. 3. Stream sediments were collected with specific criteria in order to avoid contamination sources: (a) samples collected from high stream order (black dots) have been deleted because are located near sites characterized by human activities and influenced by multiple sources; (b) samples collected in catchment including different geological members (black dots) are deleted because contaminated by different geochemical signals.

3.3.3 Methodology for the elaboration of geochemical maps

We have discussed in a separate paper (Lancianese and Dinelli, submitted) about the need of various techniques in the comprehension of geochemical phenomena focusing on the representation of spatial distribution of chemical elements. The choice of geochemical mapping techniques is greatly influenced by representation scale, sample density and sample type. At a regional scale geochemical maps based on certain landscape units (Carranza and Hale; 1997; Spadoni et al., 2004; Amorosi et al., 2011; El Hadri et al., 2012) proved to be very effective compared to other representation techniques in presenting for example, the effect of geology especially for areas influenced by natural and anthopogenic factors. In this paper, we consider a local-scale area with a complex geology but supported by an high-density sampling and detailed geological landscape units. Based on the availability of a detailed geological map of the area at a scale 1:10000 from

Servizio Geologico, Sismico e dei suoli Regione Emilia Romagna providing a background of suitable resolution, we realized the geochemical maps using the geological members of MAF as landscape units. Figure 4 summarizes the next steps in data analysis: to each member was assigned the median value of stream sediments collected within the unit. Following, the median values of the geological members, represented in a summary boxplot (Fig. 4a), have been subdivided for mapping purposes according to the 25th, 50th, 75th and 90th percentile (Fig. 4 a) then the same filling was applied to the whole member area (Fig. 4 b). Geochemical maps have been produced using Quantum GIS, a Geographic information system software available at http://www.qgis.org/.

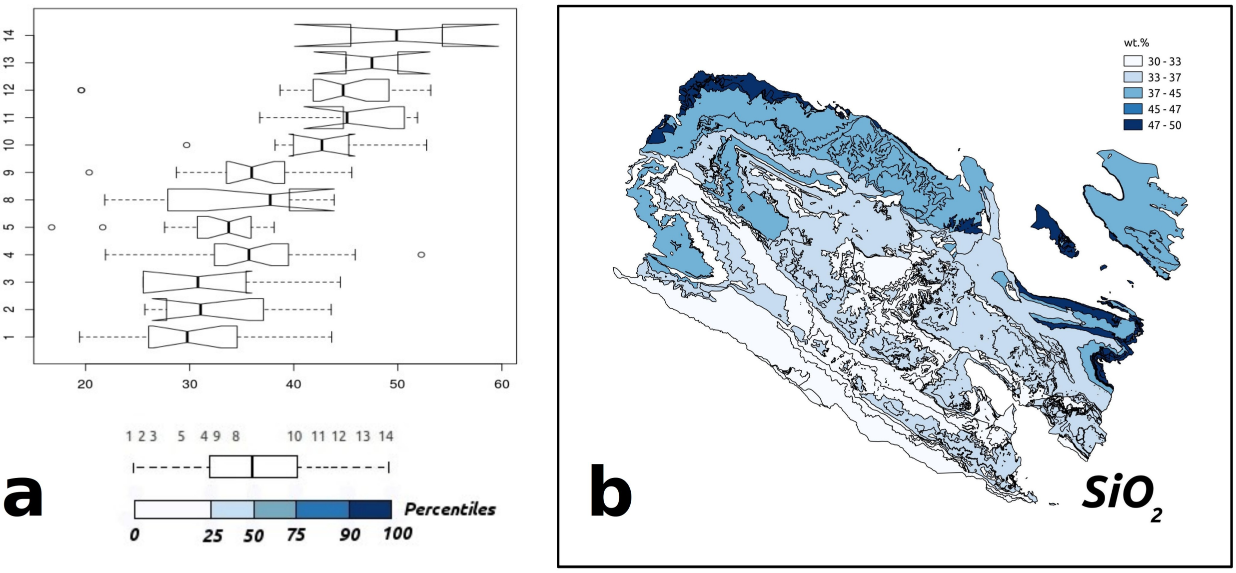


Fig. 4. Geochemical maps of chemical elements have been carried out in two steps: (a) the median values of geological members of MAF have been extracted and calculated in a class division based on 25°, 50°, 75° and 90° percentile; (b) median values have been assigned to each geological members considered such as landscape units.

3.4. Results and discussions

3.4.1 Stream sediment composition

Table 2 reports statistical parameters (median and Median Absolute Deviation (MAD)) for the members of the MAF. Selected major and trace element variations, as well as geochemical ratios are presented as box-plots in Fig. 5.

Considering the major elements (Fig. 5), the median content of Al_2O_3 increases from MAF1 (9.5 ± 1.87 wt. %) to MAF14 (11.1 ± 0.45 wt. %) while the concentration of CaO decreases from Langhian-Serravallian (25 ± 5.7 wt.%) to Tortonian members (13 ± 2.5 wt.%). MgO, Na_2O, and SiO_2 values are higher in Tortonian members: in particular the median content of SiO_2 increases constantly from MAF1 (30 ± 7.1 wt.%) to MAF14 (50 ± 6.5 wt.%) whereas MgO and Na_2O present discontinuous values. Fe_2O_3/Al_2O_3 and MgO/Al_2O_3 ratios display also significant differences:

Fe_2O_3/Al_2O_3 ratio presents lower values in Tortonian members (0.33-0.39) compared to Langhian-Serravallian members (0.40-0.42) while MgO/Al_2O_3 ratio is lower in Langhian-Serravallian members (0.35-0.36) than Tortonian members (0.37-0.39) with some exceptions (MAF8, MAF13, MAF14). Trace elements concentrations present similar trends (Fig. 5): fundamentally Nb, Rb, V, Zr, Y and Ce increase from MAF1 to MAF14. Sr follows the same evolution of CaO, therefore decreases from MAF1 (608 ± 121 ppm) to MAF14 (305 ± 66 ppm).

Generally, the results show a lithologic control that can be referred to major provenance inputs and to grain-size balance between sandstones and marl, which is a discriminating member attribution. The high SiO_2 values of Tortonian reflect the relative importance of sandstones against finer grained material and could be indicator of an Alpine provenance, as suggested by the studies of Ricci Lucchi and Valmori (1980), Gandolfi et al. (1983), Ricci Lucchi and Ori (1985), Capozzi et al. (1991) and Roveri et al. (2002).

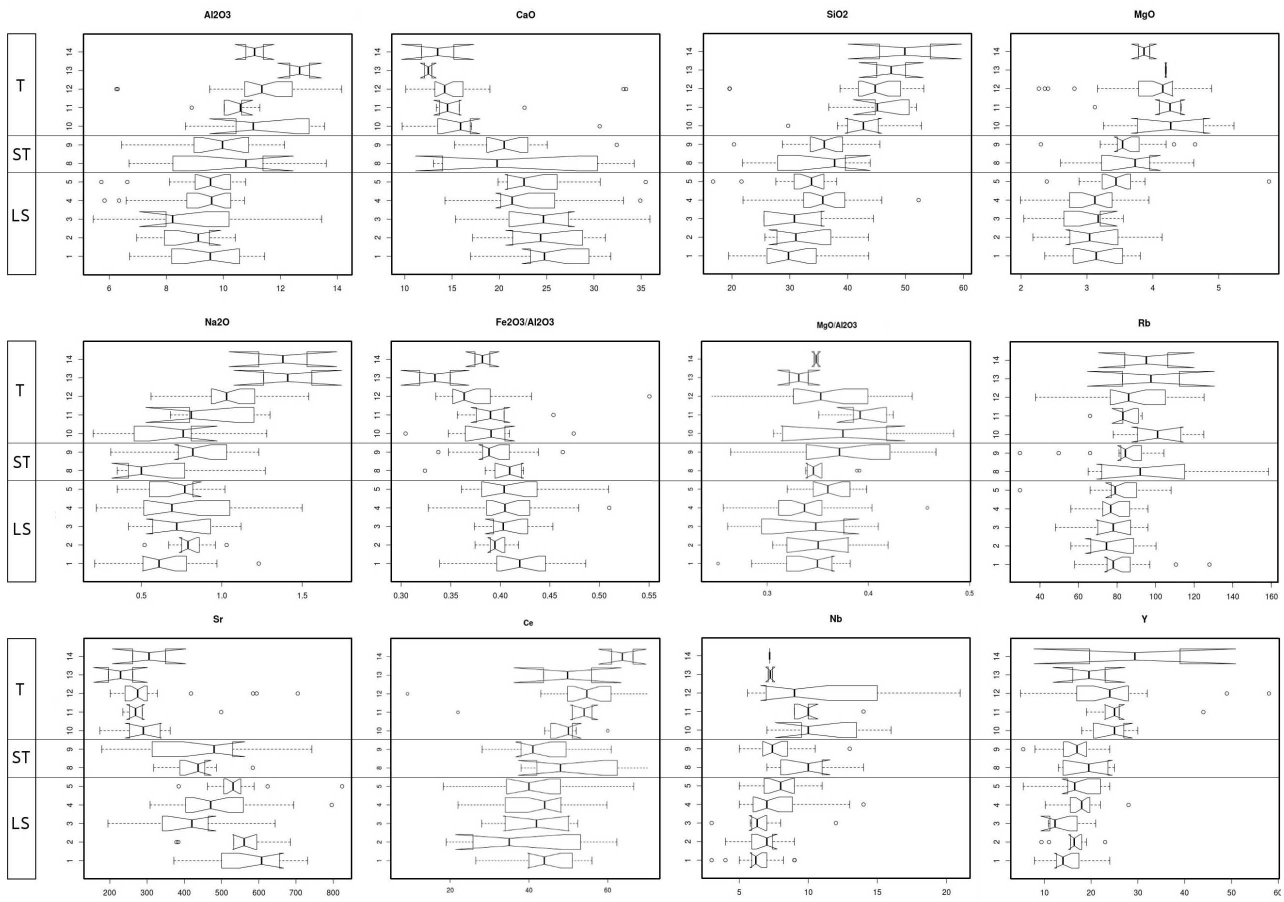


Fig. 5. Box-plots showing the variations of selected major elements (Al2O3, CaO, SiO2, MgO), geochemical ratios (Fe2O3/ Al2O3, MgO/Al2O3) and selected trace elements (Rb, Sr, Ce, Nb, Y) in geological members of MAF. The numbers in Y axis (from 1 to 14) indicate geological members from MAF1 to MAF14 (excluding MAF6 and MAF7). The values in X axis are expressed in wt.% for major elements and ppm for trace elements. The box-plots have been subdivided in three chronostratigraphic periods (LS=Langhian-Serravallian; ST=Serravallian-Tortonian; T=Tortonian) based on division shown in Tab.1, in order to highlight differences in the evolutionary trend of MAF.

The same arguments might explain also the high Na_2O and Rb results in these members, being related to the higher proportions of plagioclase and feldspar, which are known to be abundant in this section of the MAF (Gandolfi et al., 1983; Cavazza and Gandolfi, 1992; Gandolfi et al., 2007). The high CaO and Sr values in Langhian-Serravallian members could reflect the major importance of limestone clastic inputs whose provenance has been attributed to Apenninic sources (Ricci Lucchi and Pialli, 1973; Ricci Lucchi and Valmori, 1980; Zuffa, 1980; Gandolfi et al., 1983; Martelli et al., 1994). Given the sample type considered, we are aware that these elements could be influenced by several other possible sources, such as carbonate cement within sandstones, carbonate fraction in marls, and even direct travertine formation locally observed close to springs or in riffles, but their signal is consistent with the petrographic information available. The high MgO values in North-eastern members (from MAF10 to MAF14) indicate the importance and extension of a dolomitic contribution which has been recognised in the upper portion of the FMA formation (Gandolfi et al., 1983) and attributed to a Southern Alpine source. Also the MgO/Al_2O_3 ratio, although with restricted range, point out an increase in Tortonian members. The decreasing Fe_2O_3/Al_2O_3 ratio value from MAF1 to MAF14 reflect changes in provenance (e.g.: sources from acidic rocks?) as well as changes in the sandstone/pelite ratio, that if the sandstone is arkosic could maintain high Al_2O_3. Zr, Y, Ce, in sandstones are basically associated to relatively common heavy minerals (e.g. monazite, xenotime, zircon, garnet) in the FMA (Gandolfi et al., 1983) and could be useful additional provenance indicators. Their interpretation however cannot be straightforward because sorting effects could affect their occurrence in alluvial environment where enrichment can reflect high energy environment and not source area characters (Vital and Statteger, 2000; Dypvik and Harris, 2001; Fralick and Kronberg, 1997. Garcia et al., 2004; Dinelli et al., 2007) as could happen if some highly sloping stream-bed are eventually sampled.

Geochemical maps of MAF based on geologic members as cartographic units can be powerful tools for the comprehension of geological history of the area. From the geochemical maps of Fig. 6 we observe some clear relation between chemical element contents and geological stages. For example Fig.6 (a, c) indicate higher content of Al_2O_3 and SiO_2 along the north-eastern part of the area corresponding to Tortonian stage while Fig.6 (b) highlights higher median concentration of CaO along the south-western part corresponding to Langhian-Serravallian members. These maps reflect the nature of the provenance of turbidity currents deposited in the FMA foredeep: the sialic coarse-grained turbidity current derived from the north-eastern Alpine area and the carbonate-rich fine-grained turbidity currents originating from Apenninic sources. Fig.6 d shows the major content of MgO in the Tortonian members that testify the dolomitic contribution of this stage but also in the Apenninic supply that characterize the Langhian-Serravallian stage. Fig.6 e show clearly the higher content of Na_2O in geological members of the Tortonian stage suggesting the great influence of minerals such as plagioclase. Considering element ratios, we note that Fig.6 f shows the highest Fe_2O_3/Al_2O_3 values in high-carbonate members of Langhian-Serravallian stage suggesting the possible presence of a slightly higher mafic supply in sediments deposited in this period or the presence of iron-rich clay minerals. In Fig.6 g the MgO/Al_2O_3 ratio indicates the higher values in the central area, possibly reflecting a less evident, but present, dolomite contribution recognized also in other provenances (Gandolfi et al., 1983). The Tortonian members that does not appear in this diagram for the high Al_2O_3 related to plagioclase content.

Also the trace elements give some important graphical results: Rb and Sr have opposite distributions being elements related respectively to sialic and carbonatic components of the sediment (Fig. 6 h, i). In these Figures the sialic composition of Tortonian members characterized by higher content of Rb and the carbonate composition of Langhian-Serravallian members characterized by major contents of Sr are clear. The distribution of Ce, Nb and Y (Fig. 6 l, m, n) highlight higher values in the Tortonian members whose turbidity currents were richer in heavy minerals (Gandolfi et al., 1983).

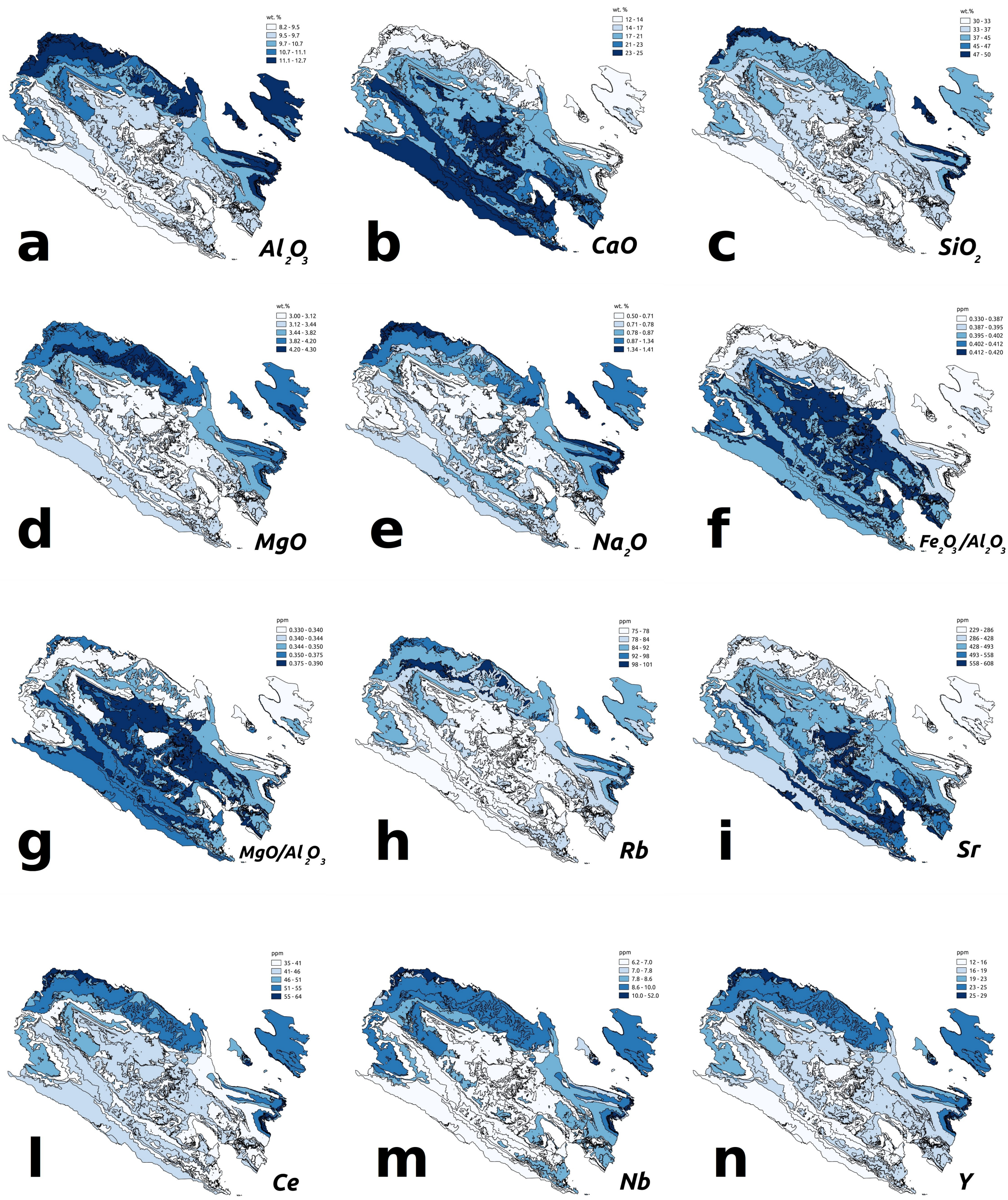


Fig. 6. Geochemical maps of Al2O3 (a), CaO (b), SiO2 (c), MgO (d), Na2O (e), Fe2O3/Al2O3 (f), MgO/Al2O3 (g), Rb (h), Sr (i), Ce (l), Nb (m), Y (n).

Element	Unit	FMA1		FMA2		FMA3		FMA4		FMA5		FMA8		FMA9		FMA10		FMA11		FMA12		FMA13		FMA14	
		Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD	Median	MAD
Al_2O_3	wt.%	9.5	1.87	9.1	1	8.2	0.61	9.6	1.01	9.6	0.83	11	3.8	10.0	1.48	11	2.18	10.6	0.85	11	1.3	13	0.51	11	0.45
CaO	wt.%	25	5.7	24	4.8	25	5.4	21	4.3	23	3.2	20	9.8	21	3.7	16	1.73	15	1.76	14	2.06	12	0.56	13	2.54
Fe_2O_3	wt.%	3.9	0.71	3.6	0.35	3.4	0.25	3.8	0.4	4.0	0.34	4.2	1.16	4.1	0.58	4.2	0.13	4	0.59	4.3	0.58	4.2	0.46	4.2	0.30
K_2O	wt.%	1.66	0.34	1.56	0.13	1.5	0.24	1.71	0.16	1.62	0.19	1.85	0.59	1.75	0.16	2.05	0.31	1.96	0.16	1.95	0.24	2.2	0.06	1.91	0.10
MgO	wt.%	3.1	0.55	3.0	0.53	3.2	0.53	3.1	0.43	3.4	0.33	3.7	0.76	3.5	0.37	4.3	0.95	4.3	0.24	4.2	0.25	4.2	0.01	3.9	0.13
MnO	wt.%	0.12	0.01	0.11	0.01	0.11	0.01	0.12	0.01	0.11	0.01	0.11	0.01	0.11	0.01	0.12	0.01	0.12	0.01	0.13	0.01	0.16	0.02	0.14	0.01
Na_2O	wt.%	0.61	0.25	0.79	0.08	0.72	0.31	0.69	0.415	0.77	0.21	0.5	0.13	0.82	0.22	0.76	0.13	0.81	0.19	1.03	0.22	1.41	0.22	1.38	0.22
P_2O_5	wt.%	0.1	0.07	0.11	0.04	0.08	0.07	0.12	0.03	0.1	0.03	0.11	0.05	0.1	0.03	0.12	0.03	0.16	0.01	0.14	0.07	0.1	0.01	0.16	0.06
SiO_2	wt.%	30	7.1	31	7.0	31	7.8	36	4.9	34	4.1	38	5.0	36	4.7	43	5.4	45	8.2	45	5.9	48	3.7	50	6.5
TiO_2	wt.%	0.48	0.06	0.42	0.04	0.4	0.04	0.46	0.04	0.42	0.04	0.51	0.13	0.46	0.04	0.55	0.74	0.54	0.06	0.56	0.07	0.56	0.01	0.66	0.16
Ba	ppm	271	58	289	40	309	37	290	34	300	42	306	21	305	45	319	45	304	7.4	334	42	375	39	338	79
Ce	ppm	44	10.2	35	14	42	12	44	12	40	12	48	12	41	10	50	5.9	54	4.5	55	8.8	50	9.0	64	4
Co	ppm	7.8	4.2	5.7	2.97	6.1	2.97	7.3	2.5	9	2.97	8	4.5	8	2.97	9	2.97	9	0.07	10	2.97	10	2.52	8.9	1.33
Cr	ppm	90	19	87	13	75	18	81	15	94	8.9	88	22	91	8.2	97	8.9	92	19	99	18	104	8.4	97	12.1
Cu	ppm	31	6.1	25	5.2	26	5.3	27	4.5	27	5.9	35	5.9	27	2.97	29	5.9	24	5.9	29	7.4	18	9.0	26	3.3
La	ppm	25	5.0	19	5.2	15	9.5	22	4.5	21	4.7	24	2.22	23	5.8	25	4.5	26	1.48	28	6.4	26	11	29	2.89
Nb	ppm	6.2	1.19	7	1.19	6.3	0.74	7	1.48	8	1.78	10	2.97	7.4	1.48	10	4.5	10	1.48	9	4.5	7.3	0.22	52	67
Ni	ppm	63	11.9	61	5.4	59	4.2	55	8.9	65	7.4	51	12	62	7.7	65	7.4	51	8.9	57	14	6.7	13	49	13
Pb	ppm	7.9	5.8	11	5.8	7.6	3.3	13	3.1	8	3.0	12	5.3	8.1	4.6	17	2.97	20	1.48	15	7.3	11	1.19	16	1.04
Rb	ppm	78	12	75	16	78	13	77	12	79	15	92	31	84	11	101	25	83	12	86	22	98	22	95	17
S	ppm	931	458	770	111	1150	312	770	362	690	400	1000	104	1110	382	630	297	530	222	870	769	840	901	1213	835
Sr	ppm	608	121	561	47	420	101	471	128	531	37	437	73	480	200	290	76	269	27	275	41	229	48	305	66
Th	ppm	11	10	13	13	27	27	9	7.4	15	10	8	5.9	32	18	10	4.5	13	1.48	19	15	33	20	24	15
V	ppm	71	11	64	9.0	64	12	61	9.3	68	5.9	69	17	74	7.1	72	5.9	71	8.9	79	11	84	8.1	69	1.63
Y	ppm	14	3.0	16	1.78	12	2.1	18	3.0	17	6.7	20	7.9	17	3.7	25	4.5	25	3.0	24	7.4	20	5.1	29	14
Zn	ppm	82	28	61	11	78	13	65	10	65	13	68	13	96	19	72	8.9	67	12	76	25	75	25	81	25
Zr	ppm	72	59	83	54	68	54	106	26	87	31	100	30	95	41	158	15	170	43	179	106	126	5.1	232	177

Tab. 2. Median composition and Median Absolute Deviation (MAD) of 30 chemical elements in MAF geological members.

3.4.2 Geochemical signatures

A more general indication can be obtained through application of factor analysis to the selected data set. The analyses included 28 elements listed in Table 2, excluding As and Ga because many samples are below the detection limit. The results of factor analysis indicate 5 factors with eigenvalue > 1, accounting for 77 % of the total variance, that are discussed in detail and shown in Fig. 7.

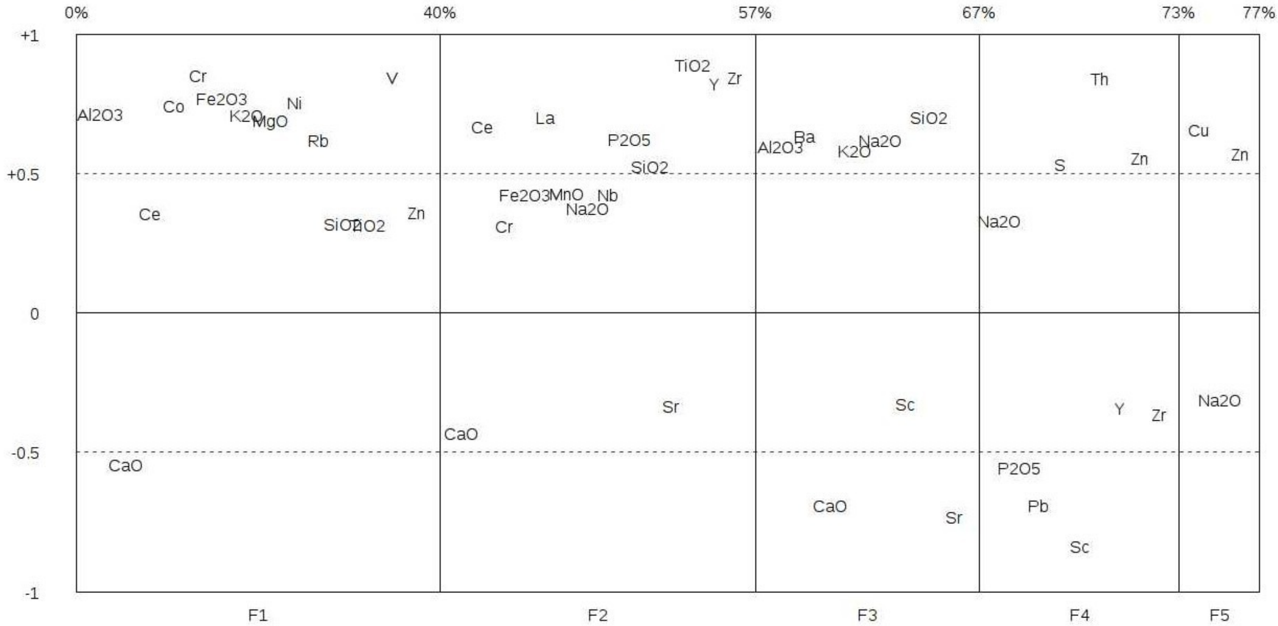


Fig.7. Factor loading plot for five factor scores applied to MAF stream sediment data. The factors can be referred to: F1 = clayey components; F2 = heavy metal components; F3 = sandy components; F4 = unclear; F5 = unclear.

The first factor (positive Al_2O_3, Co, Cr, Fe_2O_3, MgO, K_2O, Ni, Rb, V; negative CaO) explaining 40 % of the total variance (Fig. 7), can be referred mainly to the clayey fraction of the sediment, which is opposed to a carbonate fraction. The clay mineral fraction is important in the type of samples studied, based on a relatively fine-grained fraction. The stratigraphic distribution outlined by factor scores (Fig. 8) indicate an increase in higher median values from Serravallian to Tortonian members. Information on the mineralogy of the fine-grained fraction of the MAF is rare (Tilling et al., 2007) and indicate that the mudstones originating northwestern sources (Alpine) are enriched in illite and mica and to a lower degree in dolomite, whereas those beds originating from the southeast and to the southwest (Apenninic) have a distinct higher carbonate content and slightly higher quartz content. The geochemical map of first factor (Fig. 9a) identifies an increasing content of the clayley component in Tortonian members but also high contents in Langhian-Serravallian members, especially FMA5 and FMA8.

The second factor, explaining 17 % of the total variance, is characterized by high positive loadings for Ce, La, Nb, P_2O_5, SiO_2, TiO_2, Y, Zr and negative loading for CaO (Fig. 7). The elements with positive loadings could be associated to a suite of heavy minerals that are present in the sediment and derive from the outcropping rocks. The presence of SiO_2 could reflect quartz occurrence and suggest association with a fine-sand coarse silt sediment fraction (Dinelli et al., 2006) eventually enriched in steep sloping channels. As already mentioned, a similar geochemical association have been observed in sediments and sedimentary rocks from high-energy environments (Fralick and Kronberg, 1997; Dypvik and Harris, 2001; Garcia et al., 2004). The stratigraphic pattern outlined by factor scores (Fig. 8) indicate a shift towards higher median values from older FMA members towards the younger one, and is reflected in the geochemical map (Fig. 9b). These youngest members outcrop in the closing section of the Santerno and Savio rivers (Fig. 1), areas with lower topographic gradient compared to other sampling sites in the upper reaches where older members occur. Of course localized situations favourable to heavy mineral accumulation can occur, but this consideration would likely support an interpretation more related to the bedrock composition instead of a sorting effect.

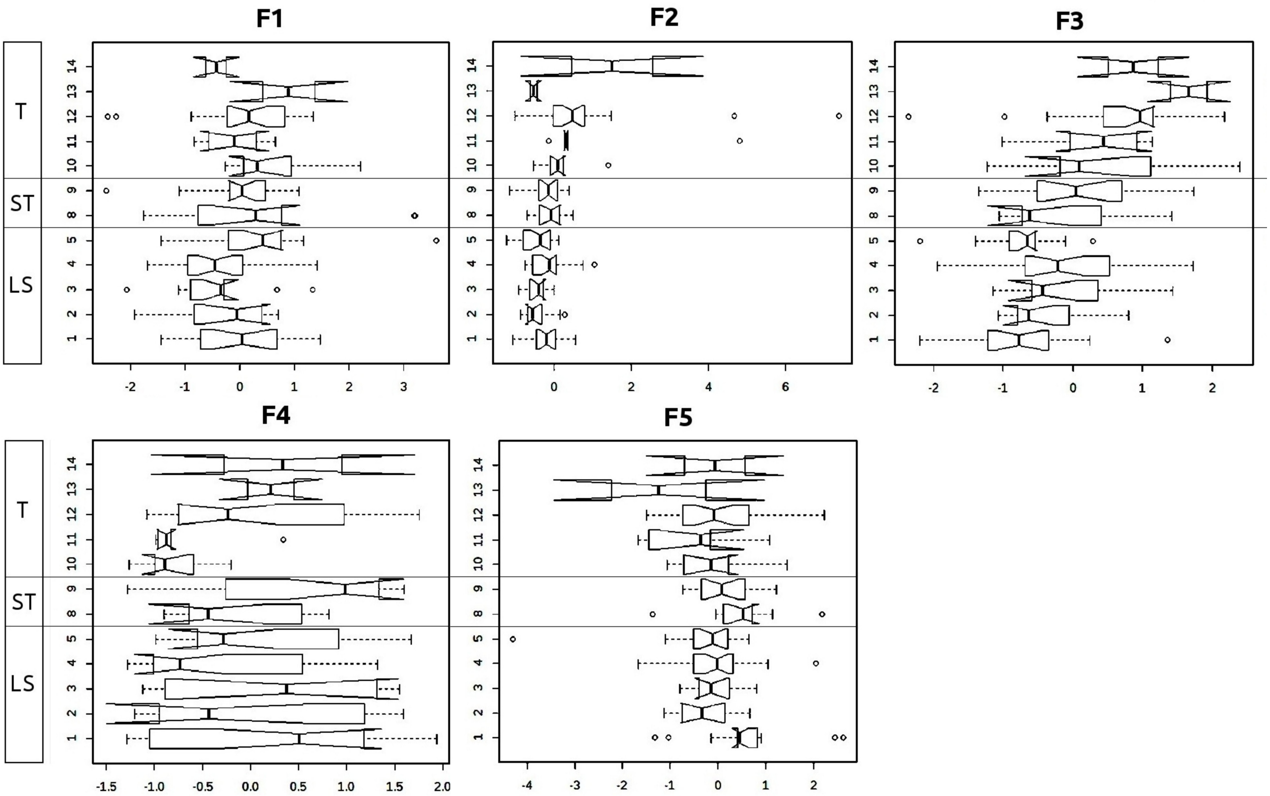


Fig. 8. Box-plots showing the variations of factor scores (F1, F2, F3, F4, F5) in geological members of MAF. The numbers in Y axis (from 1 to 14) indicate geological members from MAF1 to MAF14 (excluding MAF6 and MAF7). The box-plot have been subdivided in three chronostratigraphic periods (LS=Langhian-Serravallian; ST=Serravallian-Tortonian; T=Tortonian) based on division shown in Tab1, in order to highlight differences in the evolutionary trend of MAF.

The third factor explains 10 % of the total variance and includes the positive Al_2O_3, Ba, Na_2O, K_2O, Si_2O and the negative CaO (Fig.7) that can be referred to a relatively coarse-grained fraction dominated by feldspars and plagioclase which is opposed to a carbonate fraction, possibly also associated to a coarse-grained fraction. The stratigraphic distribution outlined by the factor scores (Fig. 8) indicates an increase in higher median values from Langhian-Serravallian to Tortonian members that confirms the arenite/pelite ratio trend shown in Table 1. The geochemical map of the third factor (Fig. 9c) shows very well that the plagioclase component increases in Tortonian members testifying how Alpine turbidites deposited in the foredeep after Langhian-Serravallian have been important in determining the sediment composition of these geological members.

The fourth factor explains 6 % of total variance. It includes Th-Zn-S-Na_2O and the negative P_2O_5-Y-Zr-Pb-Sc (Fig. 7). The stratigraphic plot (Fig. 8) shows very large variations, testifying for heterogeneity. Only FMA10 and FMA11 have the lowest values and restricted spread reinforcing the role of heavy minerals. The elemental association of the positive side is rather strange and likely supports a non natural sources, possibly related to agricultural practices and eventually to effects of sulphur mining (Savio-Borello catchment, northeastern part of Marecchia and Bidente valleys) (Fig. 9d). The fifth factor support 4 % of total variance including Cu-Zn and negative Na_2O (Fig. 7). as for the preceding factor, there is not great difference among the members (Fig. 8) so a lithologic control can be ruled out. The positive elements likely reflect a signal of diffuse pollution that has not been completely removed during the selection step.

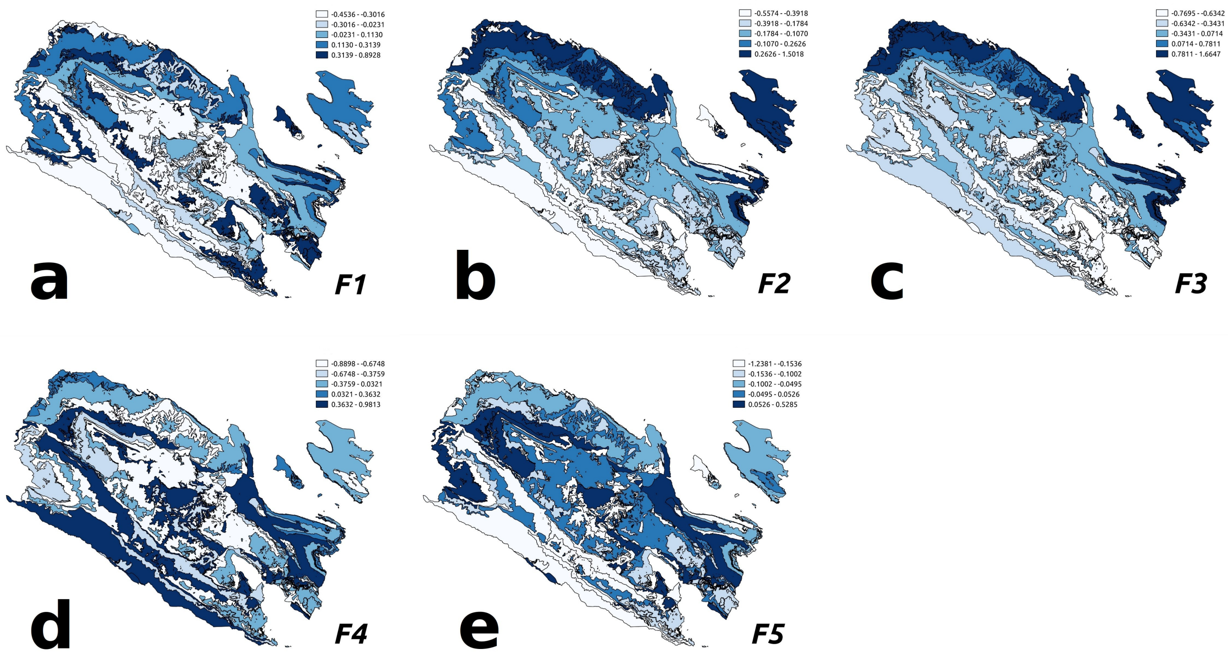


Fig. 9. Geochemical maps of F1 (a), F2 (b), F3 (c), F4 (d), F5 (e).

3.4.3 Different supplies of material: the evolutionary trend of MAF

The components highlighted in factor scores can be investigated using variations of element ratios in binary plots. Given the presence of a sialic, carbonatic, mafic and heavy minerals component, a division of MAF members related to their provenance and composition may be inferred. With the purpose of discriminating possible inputs, in Figs. 10-11 have been included as references average data representing important rock types and local sources.

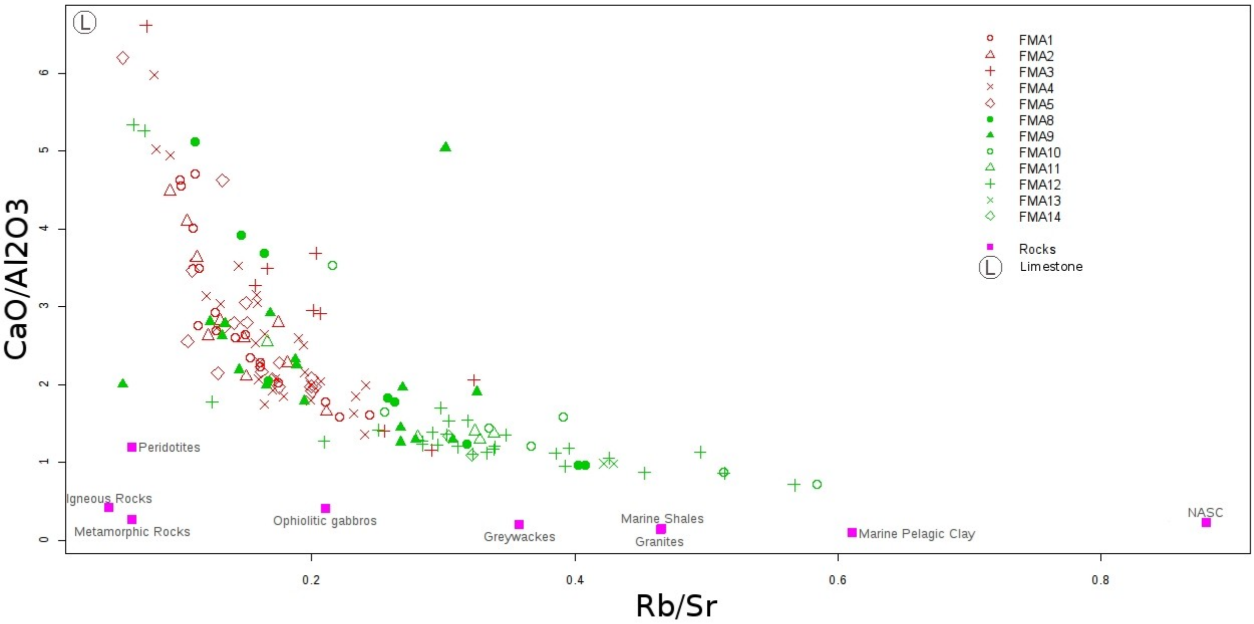


Fig. 10. Binary plot of CaO/Al2O3 vs. Rb/Sr showing the distribution of MAF geological members. The sources for the reference rocks: ultramafic rocks (Turekian and Wedephol, 1961; Puchelt, 1992), metamorphic rocks (Wedepohl, 1995), igneous rocks (Morgan et al., 1978) greywackes (Wedepohl, 1995), marine shales (Li, 1991), granites (Le Maitre, 1976), marine pelagic clay (Li, 1991), North American Shale Composite (NASC) (Morgan et al., 1978; Li, 1991), peridotites (Le Maitre, 1976), ophiolitic gabbros (McDonough, 1991), Northern Apennines sandstones (Macigno Formation, Modino sandstones, Cervarola Sandstones, Marnoso-arenacea Formation, from Dinelli et al., 1999) and limestones (Reimann and Caritat, 1998).

To evaluate the silicate and carbonate supplies has been used a Rb/Sr vs. CaO/Al_2O_3 diagram (Fig. 10) considering these elements as rough indicators of the changes in siliclastic/carbonate ratios. The predominant siliciclastic source inputs has high Rb/Sr and low CaO/Al_2O_3 ratios while carbonatic inputs have low Rb/Sr and high CaO/Al_2O_3 ratios. The differentiation in geological members of MAF describe a wide variation through time in the two types of contribution: the carbonate inputs characterize the Langhian-Serravallian stage while siliciclastic inputs influence the Tortonian stage. In fact considering the references and the results already presented, it is apparent an evolutionary trend showing a decrease in carbonate inputs from Langhian-Serravallian members to Tortonian members. Moreover the members deposited in Upper Serravallian-Lower Tortonian (MAF8, MAF9) show geochemical features belonging to both Tortonian and Langhian Serravallian members: this dispersion could be related to the contemporary deposition of siliciclastic and carbonate detritus input occurred during this period.

The mafic and felsic supply has been identified using a Y/Ni vs. Cr/V diagram (Hiscott, 1984). In Fig. 11 the Langhian-Serravallian members (MAF1-MAF5) stend to have a slightly higher Cr/V compared to the majority of the samples, whereas the Tortonian members (MAF-10-14) have a clearly higher Y/Ni ratios which is indicative of a sialic supply. Also in this graphic the members deposited in Serravallian sup.-Tortonian inf. (MAF8, MAF9) are positioned between Tortonian and Langhian Serravallian members testifying for a mixed supply. Compared to the similar graph presented in Dinelli et al. (1999) which was relative only to sandstone samples, there is a shift towards lower Y/Ni values which reflect and increasing influence of fine-grained grained sediments, as suggested by the position of reference data.

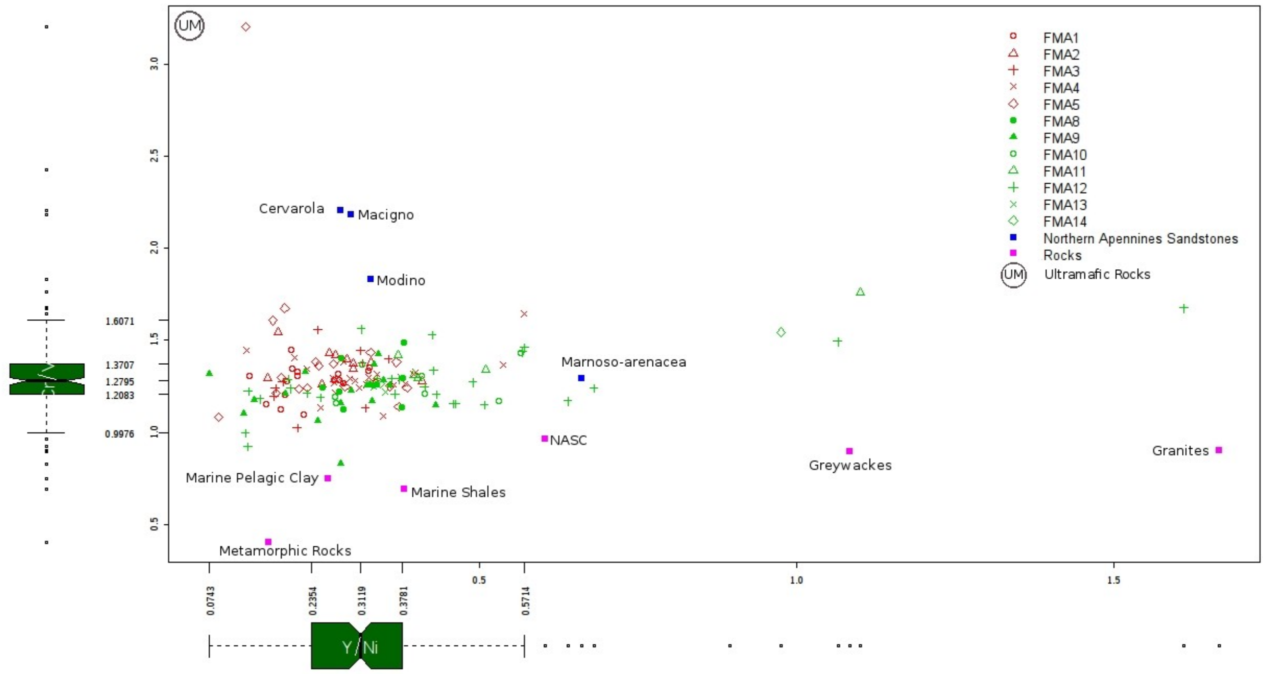


Fig. 11. Binary plot of Cr/V vs. Y/Ni (Hiscott, 1984) showing the distribution of MAF geological members. Element contents of rocks used as references (metamorphic rocks, greywackes, marine shales, granites, marine pelagic clay) are from Morgan et al., 1978; Wedepohl, 1995 and Li, 1991. Element contents of Northern Apennines sandstones (Cervarola, Macigno, Modino and Marnoso-arenacea Formation) and ultramafic rocks are from Turekian and Wedephol (1961) and Puchelt (1992).

3.5 Conclusions

The results of this study show that the distribution pattern of chemical elements is greatly influenced by geological members, suggesting that it can provide useful additional data for interpretation. After accurate selection of samples representative of a single geological member, according to cartographic information, these data can be used to extend the interpretation over a wide (basin) area. Based on the data analyses and on the geochemical maps produced and considering the time-dependent evolutionary trend of geological members from Langhian to Tortonian stage, we can put forward some conclusions:

6) In the Langhian-Serravallian inner stage, southeastern geological members (from MAF1 to MAF5) are characterized by prevailing carbonate, fine-grained sediments derived from southern Apenninic supply.
7) In the Serravallian-Tortonian stage, considered as a transition phase between inner and outer stage, geological members as MAF8 and MAF9 have hybrid geochemical features because they are influenced by both Appenninic and Alpinic turbidity currents characterized by a decrease in the carbonate signal and an increase in the siliciclastic contribution.
8) In the Tortonian outer stage, the northwestern geological members (from MAF10 to MAF14) are characterized by sialic, siliciclastic (either enriched in plagioclase and mica) with high MgO related to important dolomite inputs derived from Alpine supply.

These considerations are consistent with the available petrographical, mineralogical and geochemical literature. One major difference is that those reconstructions were based on point observation whereas these data cover a large part of the outcrop area on the FMA, so that a large overview can be obtained. The data selection and the availability of high quality supporting information has enabled the clear indication of a chronologic evolutionary trend in the deposits of MAF and the geologically oriented geochemical maps clearly display the distribution.

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CHAPTER 4

Geochemical Backgrounds of the Romagna river basins: the effect of geology, normalization and land use on heavy metal content of stream sediments[3]

Abstract

The identification of geochemical background levels plays a fundamental role in the quantitative assessment of heavy metal contamination in the sediments but it is not sufficient to obtain an objective and definitive overview of a study area therefore the effect of contaminating factors of the geochemical signal can affect the quality of results. The computation of the upper limit of background can be combined with normalization procedures to minimize the effect of geology and weathering and with techniques that associate anomalous values to land use types.

In the Romagna area, 784 stream sediment samples has been collected in twelve river basins that cross different geological units and land use types from the mountains to the plain. The spatial distribution of heavy metal elemental content (Cr, Cu, Ni, Pb and Zn) is different in each river basins and greatly influenced by the occurrence of calcareous or clays. For this reason we calculated a background value based on Low Stream Order rivers for each catchment, a procedure that minimize the chance of missing anomaly. The upper limit of background, calculated according to the ISO 19258 guidelines, varies over wide ranges, suggesting the importance of a similar approach and the presence of differences also in the normalized to Al_2O_3 results that evidence the importance of different provenance and the role of dilution on stream sediment geochemistry.

The calculated background thresholds were applied to the results of the High Stream Order samples, identifying anomalous sites. The probable contamination sources were evaluated taking into account also the association to land use types. In this way anomalous values of Cr and Ni are principally related to geology and elemental enrichment caused by sorting effect while Cu, Pb and Zn are principally related to anthropogenic impact characterized by agricultural and industrial activities.

Keywords: background, normalization, heavy metals, stream sediments

3 This chapter consists of a paper by Lancianese V. and Dinelli E. submitted at “Journal of Soils and Sediments”.

4.1 Introduction

The quantitative assessment of heavy metals contamination in the rivers is a very sensitive issue that has been addressed in European Union since the introduction of the European Water Framework Directive (WFD, 2000) with the aim to achieve a good status of all European waters by the year 2015. Afterwards the necessity of an environmental monitoring for sediments with precises quality objectives has been stressed in successive documents (WFD, 2010) and sediment quality guidelines (OSPAR commission, Guidance Document No:25) that have highlighted the importance of reference levels of heavy metals. There are many factors that control the reference levels of any chemical element, and these include the geochemical variation in bedrock geology, the influence of soil-forming processes, and erosion-transport effects, but it also can include more localized disturbing factors such as the occurrence of mineralization or other various types of anthropogenic influences (Salminen and Gregorauskiene, 2000). Not secondary is the reference to the analytical method followed, since for certain elements the value can change significantly for example if different digestion protocols are followed (e.g.: Salminen and Gregorauskiene, 2000) uences.When dealing with surface material (e.g.: stream sediments, soils). The knowledge of this information has great importance in environmental legislation, that indicates limits for selected elements in soil, contaminated land and other surface materials, that could be exceed simply for natural reasons, such as the presence of a particular rock type with peculiar geochemical features (e.g.: Cr and Ni in ultramafic rocks) and its effecto on soil and even on transported material (e.g.: Amorosi and Sammartino, 2007; Amorosi, 2012).

In fact the identification of background thresholds, although there is confusion in its definition (Reimann and Garrett, 2005), is a fundamental tool in recognition of contamination sources therefore allows to compare anomalous values to more representative regional values respect to average shale contents or crust contents shown in literature (Bowen, 1979; Wedepohl, 1995). In this regard, some authors have applied robust techniques (Matschullat et al., 2000; Fukue et al., 2006, Kalender et al., 2013; Mil-Homens et al. 2007) that are referred to specific databases and that reflect the characteristics of the study area. In these cases another factor is considered: the normalization. Heavy metals are influenced by grainsize and mineralogical effects derived from anthropogenic activities and geochemical processes (UNEP, 1995; Summers et al., 1996; Grant and Middleton, 1998) that determine enrichment and accumulation in the sediments and then difficulties in the identification of the kind of source. Some authors (Covelli and Fontolan, 1997; Ho et al., 2012). discuss the potential of this approach considering aluminum (Al) or alumina (Al_2O_3) as normalizers , being one of the most important constituents of the aluminosilicate mineral fraction. These factors prove that is complicated to determine reliable background values, especially in areas influenced by contrasting geology, where other factors as as land use can produce significant changes in the concentration value of heavy metals (Reimann and Garrett, 2005; Fok et al., 2013; Hao et al., 2014).

This study shows the results of a sampling campaign carried out on stream sediments on several river basins of an extensive regional area in northern Italy, characterized by contrasting lithology, dominated by sedimentary rocks, different land use and with possible localized sources of anomaly. We evaluated the upper threshold level of background for every single catchment, following the ISO/DIS 19258 recommendation, based on the low stream order dataset. We applied this data to evaluate the environmental status of the major rivers, and used it for the calculation of Igeop, working either on the elemental concentration and on nromalized values.

4.2 Study area

The study area, extending over 6856 km^2, includes the whole Romagna Apennines and the Romagna plain and include the catchment basins of twelve rivers: Idice, Sillaro, Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello, Uso and Marecchia (Fig. 1).

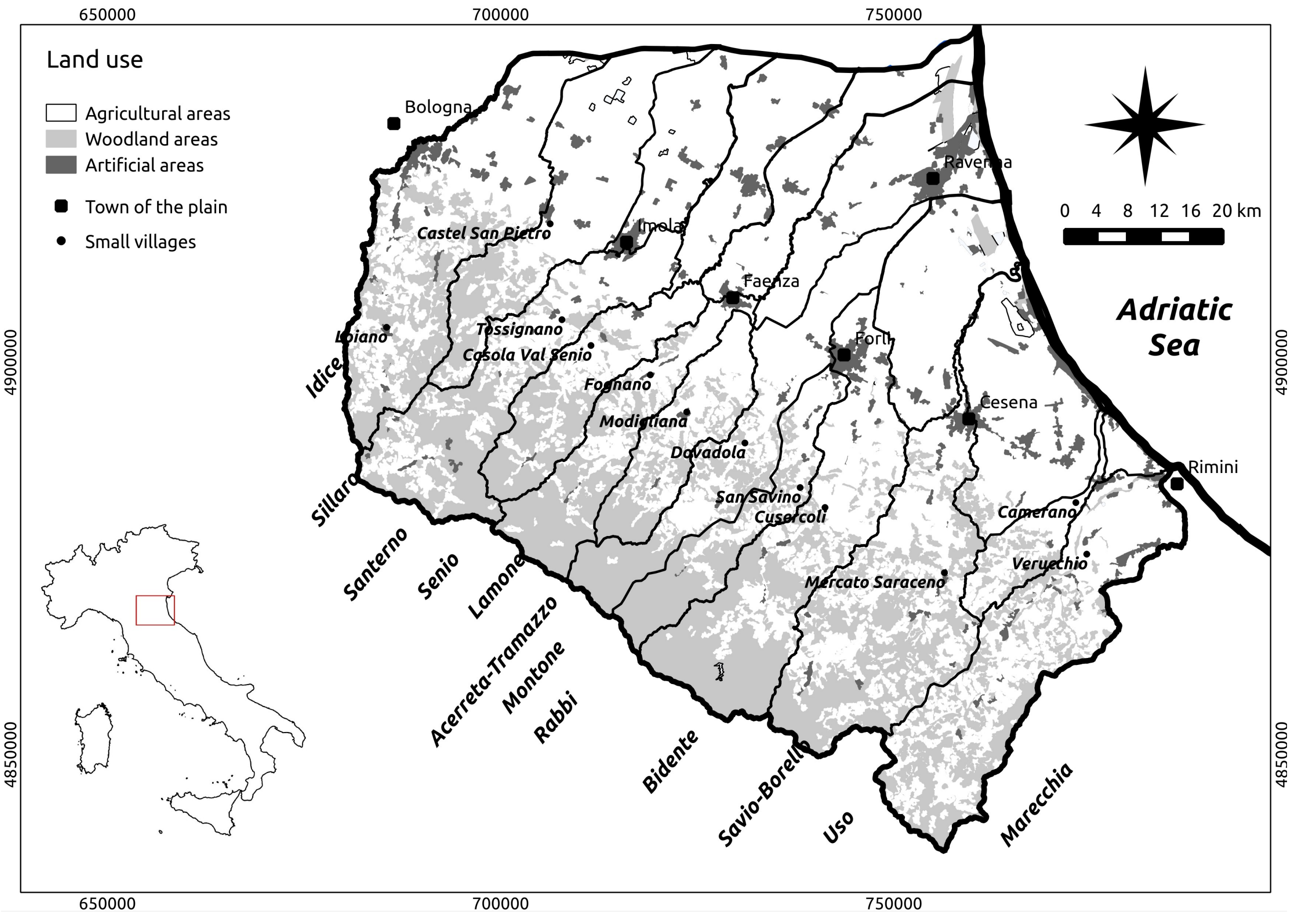

Fig.1 Distribution of land uses in the study area. The classification of the map (download at http://www.eea.europa.eu/) is organized according with the level 1 of Corine Land Cover.

The main land use type (64% of total area) include agricultural activities widespread in the plain section and in the valley bottoms. The industrial activities and urbanarea (4% of the total area) are developed mostly in the Romagna plain around the main cities located at the closing of the mountain section of several rivers (Imola, Faenza, Forlì, Cesena and Rimini) and in several minor urban centers along the main valley. In the hill and mountain area of the Romagna Apennines human activities are almost absent, wooded areas prevail (31% of total area).

The geology of the area (Fig.2) is dominated by sedimentary rocks formed during different periods: in the northern and southern part of Romagna Apennines, the Cretaceous-Miocene Ligurian and Epiligurian domains are characterized by the presence of ophiolites, chaotic clays, argillaceous sheet, turbiditic units (limestone/clay alternations) and sandstones. The central part of the Romagna Apennines is composed exclusively by the sandstones and marls of the turbiditic Marnoso-arenacea Formation (Langhian-Serravallian). Along the mountain range border outcrop the messinian evaporites of the Gessoso-Solfifera formation, the Plio-pleistocene clay and clastic sediments of the Padano-Adriatic domain (AA.VV., 1987; Regione Emilia-Romagna., 1996). In the plain area Quaternary alluvial deposits occur.

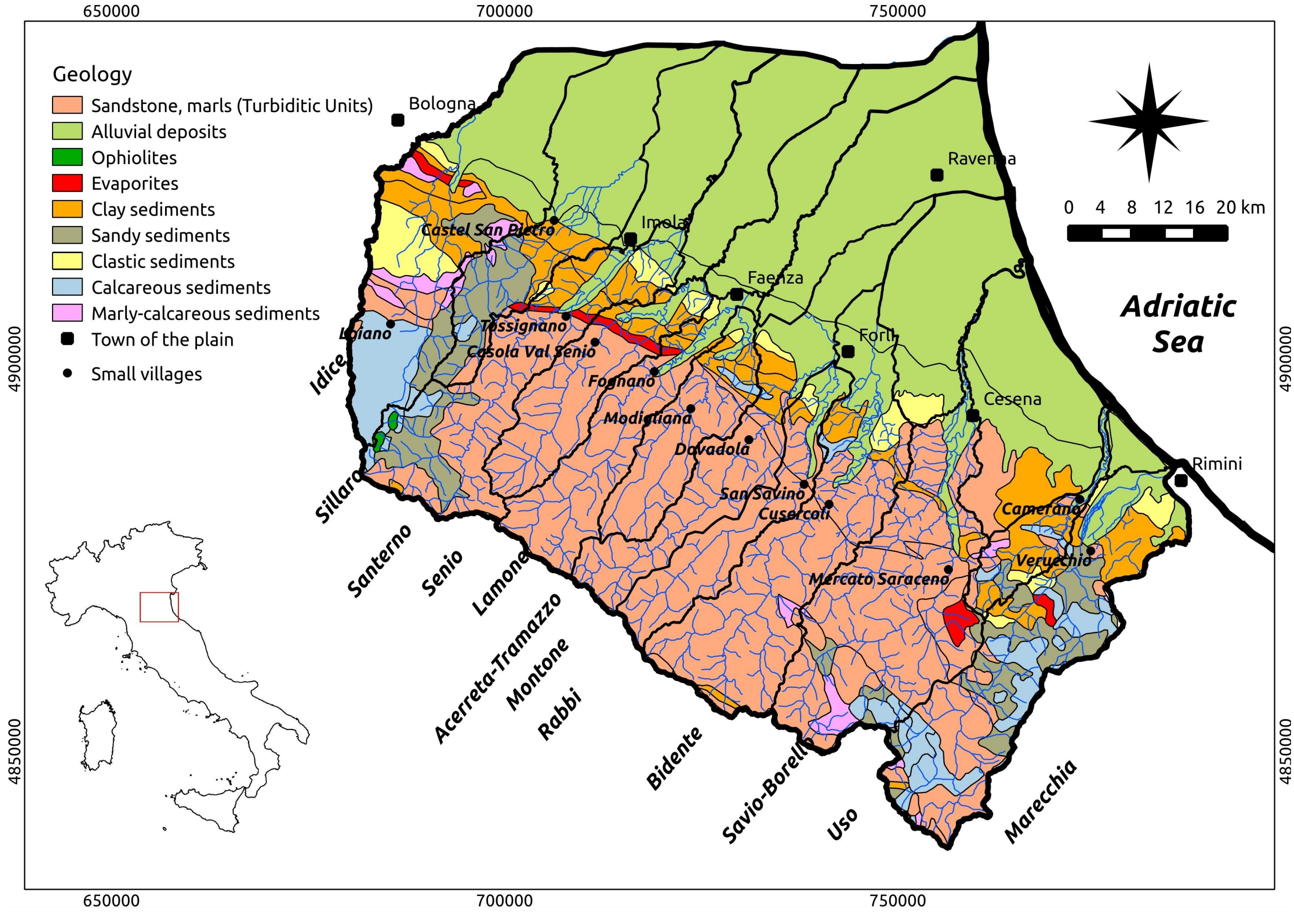

Fig.2 Simplified geology of the study area. The maps indicates also few localities close to changes in the geological units, and cited in the text as geographic reference. Some will be recalled also in the data discussion.

4.3 Methodology

4.3.1 Sampling and analytical methods

The Department of Biological, Geological and Environmental Sciences of Bologna has conducted a sampling campaign during five years collecting 753 stream sediment samples for environmental geochemistry studies (Fig. 3). The survey has been carried out sampling one stream sediment sample for each catchment basin previously extracted by DEM, considering that a sampling site is presumed to express the average chemical concentration of geologic material upstream (Howarth and Thornton, 1983). The total 753 samples have been divided in two categories: stream sediments collected from high stream order (HSO sediments; n=254) and stream sediments collected from low stream order (LSO sediments; n=499). Subsequently this database has been integrated by additional samples (n=31) collected in the Romagna plain over the highway line, to reach a total of 784 samples.

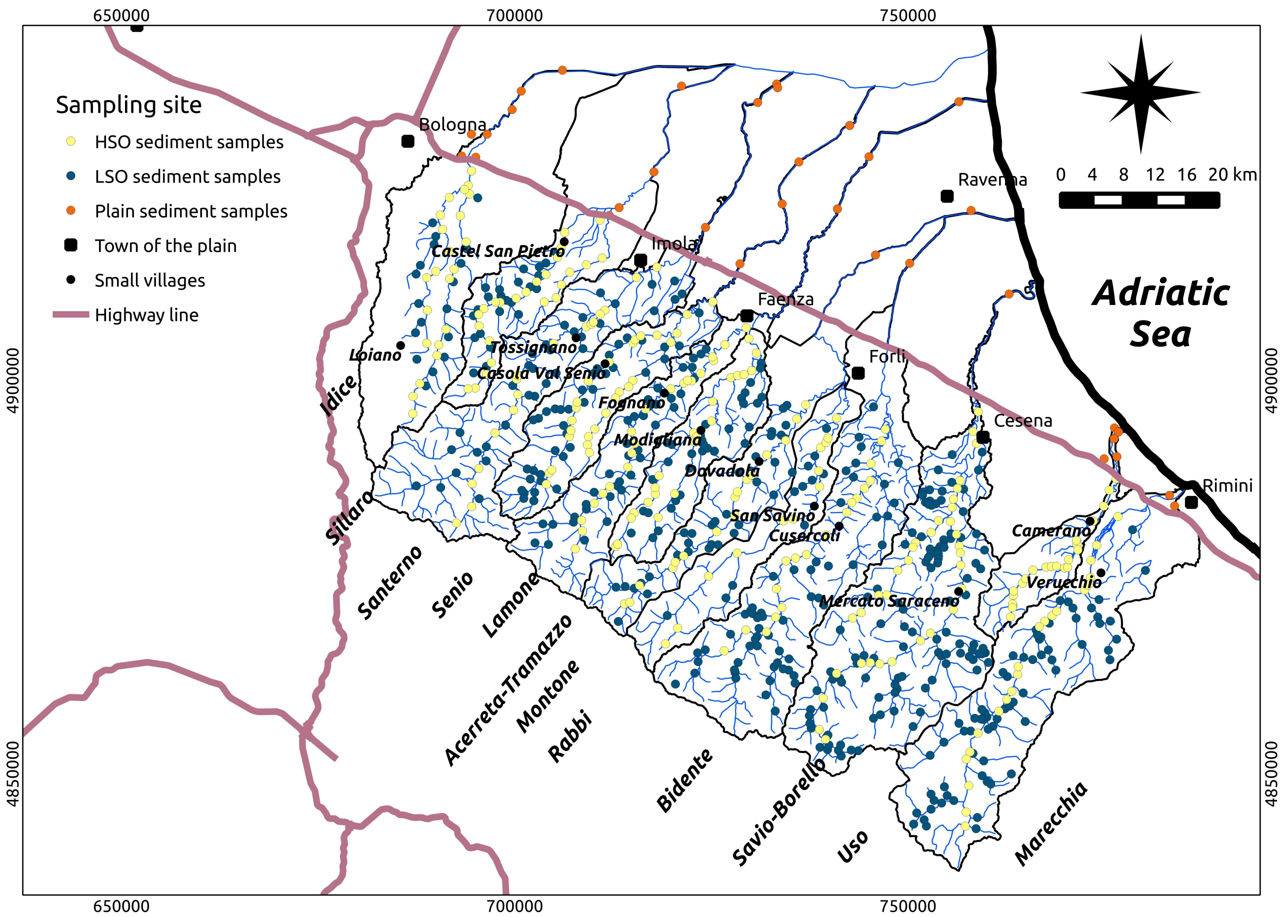

Fig. 3 Location of stream sediment samples of high stream order (HSO) and low stream order (LSO). The Plain sediment samples are located over the highway line.

Stream sediments were collected from the active channel, at adequate distance from the banks, to minimize the influence of very local contribution. Sediment collected in different points within the site was sieved in the field using a stainless steel with running water. In the field, sediment collected in a range of 200 m within the stream channel was combined and directly sieved in the field to < 180µm with local running water and stored in PET 1.5 l bottles. In the laboratory samples sediments were dried, homogenized and pulverized with an agate mill. Pressed powder pellets were prepared for analysis of major and trace element (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S) by X-ray fluorescence spectrometry. Analyses were performed with a Philips PW1480 automated spectrometer at the BiGeA X-Ray Fluorescence Lab, following the methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976) and Leoni et al. (1982) for matrix corrections. Long term reproducibility for major elements was generally better than 7%, whereas for trace elements, it was on average better than 10%. Absolute accuracy relative to certified values of International Reference Material was generally within the reproducibility range. Analytical homogeneity between batches was checked by duplicate analysis of selected samples and found to be better than 5%. Loss on ignition (LOI) was estimated after overnight heating at 950° in a muffle furnace.

4.3.2 Statistical analysis and graphic elaborations

Data analysis have been carried out in R, an open source software which can be freely downloaded from CRAN server at http://cran.r-project.org. For producing analytical results (median, standard deviation, minimum maximum and 95°le), Shapiro-Wilk normality test, non-parametric tests (Levene's test and Kruskal-Wallis test) and graphics (boxplot and profiles) have been used the DASplusR package (http://www.statistik.tuwien.ac.at/StatDA/DASplusR/) and GCDkit package (Janoušek et al., 2006) downloadable at http://www.gcdkit.org/. The maps of the study area have been produced using Quantum GIS, a Geographic information system software available at http://www.qgis.org/.

4.4 Results and discussions

4.4.1 Elaboration of data

For the elaboration of the dataset, HSO sediments, LSO sediments and Plain sediments have been used for different aims: HSO sediments and Plain sediments have been used for the construction of profiles representing the variation along the major rivers (Idice, Sillaro, Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello, Uso and Marecchia). Instead LSO sediments have been used for the computation of background limit, considering these sites as less influenced by the anthropogenic activities. The cumulative distribution function (CDF) of HSO and LSO sediments for Cr, Cu, Ni, Pb and Zn are reported in Fig. 4. For a proper comparison of the data some outlier were censored: for Cr the values greater than 200 ppm in the LSO sediment population (max = 517 ppm), for Ni the concentrations greater than 100 ppm in the LSO sediment population (max = 160 ppm) and for Zn the concentrations greater than 200 ppm in the LSO sediment population (max = 957 ppm). The curves are comparable, with overlaps, with slightly higher values for LSO population. This slight difference can be related to the greater integration capacity of the major rivers that mixes sediments from different sources while LSO could be influenced by the localized occurrence of peculiar rock types.

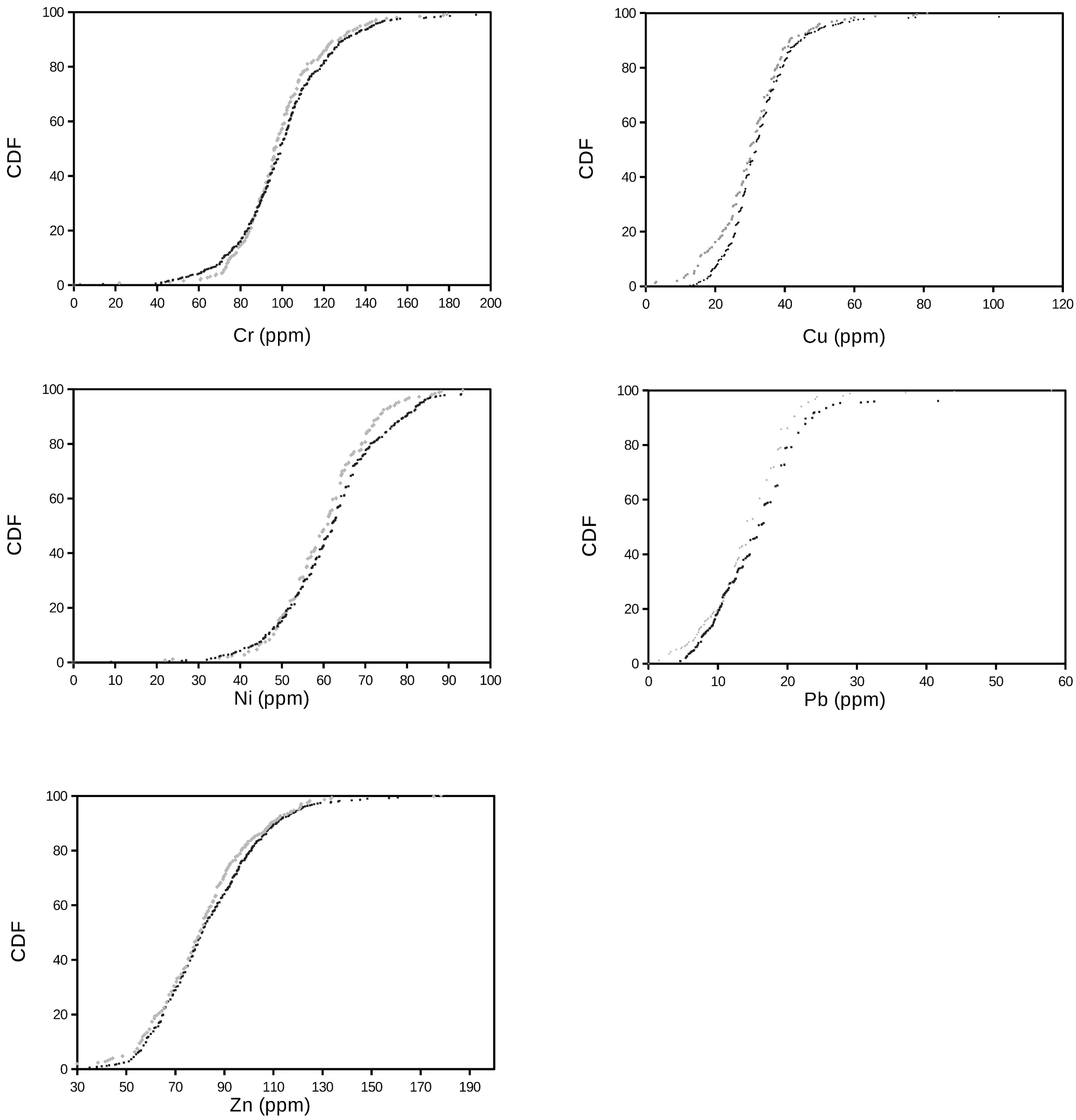

Fig. 4 Cumulative distribution function (CDF) of elemental concentration in the HSO (grey points) and LSO (black points) stream sediments for Cr, Cu, Ni, Pb and Zn.

4.4.2 Normalization

When discussing heavy metals data it is often applied a normalization procedure for the compensation of grain-size and mineralogical effects (UNEP, 1995; Summers et al., 1996; Covelli and Fontolan, 1997; Grant and Middleton, 1998; Aloupi and Angelidis, 2001; Ho et al., 2012). We have considered Aluminum (as Al_2O_3) as potential normalizer, It displays a marked spatial distribution (Fig. 5) with higher concentrations in northern and southern rivers (respectively Idice, Sillaro and Uso, Marecchia) compared to central rivers (Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente and Savio-Borello). This clearly indicates a specific lithological control on stream sediment composition, more clayey in the Bologna and Rimini territories compared to the others which are more rich in carbonates, as already outlined in a more general work (Lancianese and Dinelli, submitted). The central rivers on the other hand are those with the highest CaO content (Fig. 5), due to the important contribution of the Marnoso-arenacea Formation. This is important since the carbonate component can have a dilution effect on the concentration of the discussed elements.

In the heavy metal boxplots we have censored some values for a proper comparison of the data, in particular in Cr boxplot 2 outliers up 300 ppm, in Cr/Al_2O_3 boxplot 1 sample up 25, in Zn boxplot 2 outliers up 300 ppm, in Zr/Al_2O_3 boxplot 1 sample up 120. The Chromium has a spatial distribution in which central basins (in particular Acerreta-Tramazzo, Montone and Lamone) show lower values respect to basins that are situated in the northern (Idice, Sillaro and Santerno) and in the southern part (Uso, Savio and Marecchia) of the area, reflecting a carbonate dilution effect. However some of the differences disappear considering the Cr/Al_2O_3 indicating values around 10 as a possible reference. Similar values have been observed in borehole samples from the Lamone and Montone (Amorosi et al., 2002) and are consistent with the value of 11.5 considered by Amorosi and Sammartino (2007) and Amorosi (2012) as representative for sediments of Apenninic source. The lower values observed in the northern rivers, Sillaro in particular, are consistent with data from boreholes (Amorosi et al., 2002) and testify a slightly different provenance signal.

Copper has a spatial distribution similar to Cr: median values of Cu in the central basins (in particular Lamone, Montone and Rabbi) are lower respect to values of northern (Idice, Santerno) and southern (Marecchia, Uso, Savio-Borello) basins. On the contrary Cu/Al_2O_3 ratio doesn't show a particular differences, except for the Sillaro basin, and have similar median values.

Ni doesn't have a clear spatial distribution although the median values of central basin (Acerreta-Tramazzo, Montone, Lamone and Senio) are lower than northern (Idice, Sillaro) and southern (Uso, Bidente) basins. On the contrary Ni/Al_2O_3 ratio evidences a more clear spatial distribution influenced by lithological composition of study area in which central basins (Bidente, Montone, Lamone and Acerreta-Tramazzo) have higher median values compared to northern (Sillaro, Santerno) and southern (Marecchia, Uso) basins.

Also for Pb there is not evidence of a spatial distribution of the elemental content. We note also that some northern basins (Idice and Sillaro) have median values that are higher respect to some southern (Marecchia and Bidente) and central (Rabbi and Acerreta-Tramazzo) basins while Pb/Al_2O_3 ratio presents a spatial distribution similar to Pb. Zn spatial distribution indicates lower median values for some central basins (Montone, Lamone and Acerreta-Tramazzo) respect to northern (Idice, Sillaro, Santerno) and southern (Marecchia, Uso, Savio-Borello and Bidente) basins. Zn/Al_2O_3 ratio has a different distribution in which some northern rivers (Sillaro and Idice) have lower median values respect to southern ones (Marecchia, Savio-Borello and Bidente).

As expected the normalized plots tend to minimize the differences but still indicate peculiarities that can be related to geological features of each catchment.

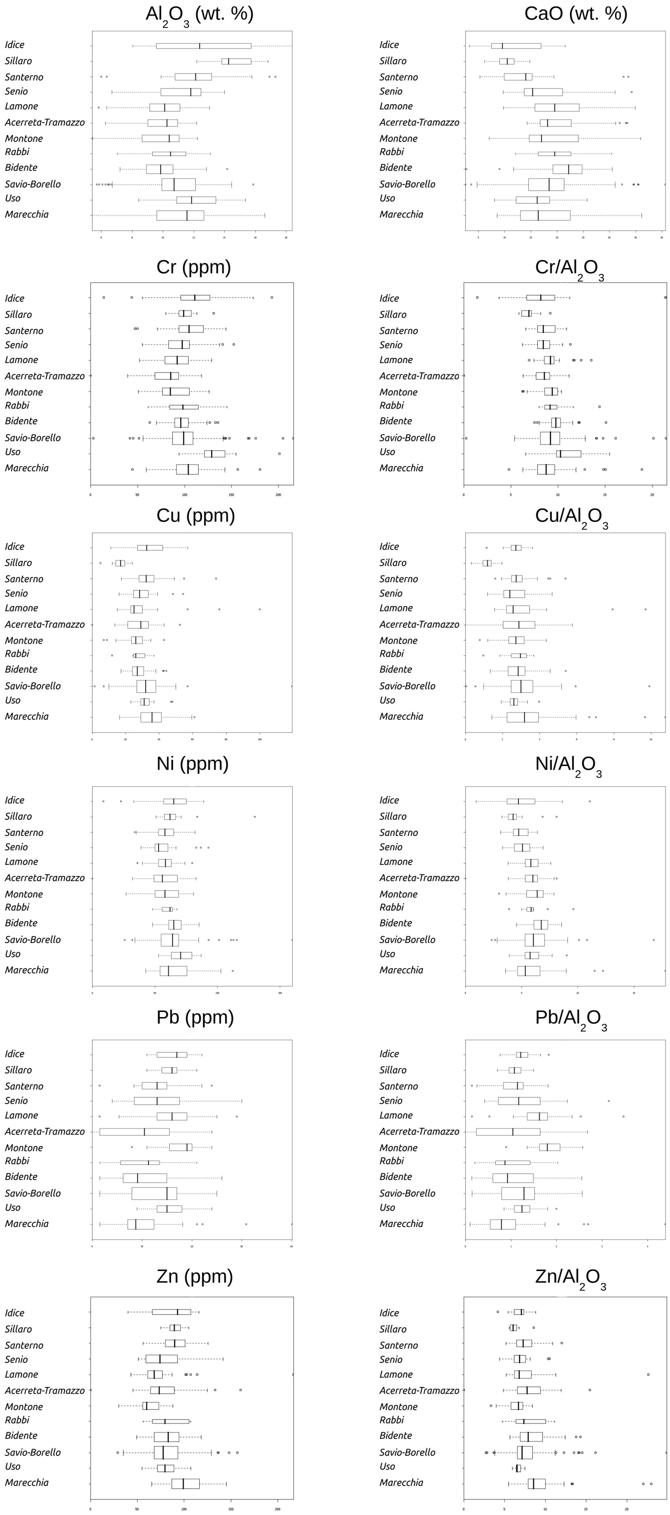

Fig. 5 Boxplots of the elemental concentrations (Al2O3, CaO, Cr, Cu, Ni, Pb and Zn) and normalized values (Cr/Al2O3, Cu/Al2O3, Ni/Al2O3, Pb/Al2O3, Zn/Al2O3) in the Romagna rivers, subdivided according to catchment.

4.4.3 Background level for each catchment

The evaluation of a background level in the content of heavy metals is the major aim of this paper. Various techniques have been used by many authors (e.g.: Matschullat et al., 2000; Fukue et al., 2006; Mil-Homens et al., 2007; Kalender and Cicek Uçar, 2013; Liu et al., 2013) based on the number of observations considered for its evaluation and on the approach followed. For the evaluation of the background values we followed the ISO 19258 guidelines (ISO/DIN 19258, 2005), that consider the upper limit of background to be represented by the 95th percentile of a dataset previously cleaned by outliers. We performed this calculation either for the entire LSO population and for any single catchment already discussed (e.g.: Fig. 4), and calculated the upper limit of background both on total concentrations and on normalized data.

The first step of the statistical analysis is to study the distribution (normal or lognormal) of the measured variables to choose the data for the elaborations. Shapiro-Wilk normality test has been applied on LSO population and the results indicated that the dataset follows a normal distribution. The second step consists in the removal of outliers identified by the concentration distribution histograms and boxplots relative to the elements (Cr, Cu. Ni, Pb, Zn) and normalized data (Cr/Al_2O_3, Cu/Al_2O_3, Ni/Al_2O_3, Pb/Al_2O_3, Zn/Al_2O_3), this for the entire database and for any single catchment.

The third step consists in calculating the 95th percentile for the total dataset of LSO sediments and for the single catchment basin dataset. These results are reported in Tab. 1. We stress the wide range of variation of the calculated upper limit of background for the singular catchment, either for the total concentrations and for the normalized values. The difference is very large for example for Cu (23-49.8 ppm) or Zn (86-123 ppm) in any case greater than 20% compared to the relative maximum for the elements, which means that the differences in bedrock geology greatly influence these values.

Another important consideration can be made from the comparison of the limits calculated with the entire population with those of the single catchment. The overall limit is close to the higher values calculated for the single catchments, and thus quite different from those calculated in many singular catchment. This has clear environmental drawbacks, since considering a general regional value as reference as could be reasonably argued to be a logical condition at a regional scale, could lead to the missing of anomalous situation in many catchments, that for geological reasons have a different natural concentration.

	Cr	Cu	Ni	Pb	Zn	Cr/Al_2O_3	Cu/Al_2O_3	Ni/Al_2O_3	Pb/Al_2O_3	Zn/Al_2O_3
Total dataset	135	43	82	22	119	11.34	4.26	8.03	1.96	10.43
Idice	133	45.5	74	20	112	9.32	3.50	6.18	1.64	8.74
Sillaro	112	23	67	18.8	101	8.11	1.67	6.61	1.45	6.76
Santerno	129	43.5	77	20.7	108	10.60	3.41	5.79	1.71	7.52
Senio	123	37.7	66	23	112	10.10	4.58	6.39	1.95	8.28
Lamone	119	37.1	68	24	86	10.50	3.83	6.76	2.11	9.85
Acerreta-Tramazzo	108	38.5	71.6	16.8	97	9.89	5.26	7.96	2.18	12.30
Montone	122	33.7	80.2	23.2	87	10.30	3.81	7.84	2.39	7.65
Rabbi	134	31.8	66.5	20.8	102	10.90	3.19	6.06	1.45	9.96
Bidente	119	36	79.4	20.2	113	10.60	4.11	8.32	1.90	11.60
Savio-Borello	121	43	79.3	21.5	111	11.70	4.50	8.10	1.94	10.60
Uso	139	35	76.6	22.6	101	13.40	3.79	6.80	1.66	7.32
Marecchia	134	49.8	83.5	17	123	11.40	4.46	8.91	1.56	11.20
Range	108-139	23-49.8	66-83.5	16-24	86-123	8.11-13.4	3.19-5.26	5.79-8.91	1.45-2.39	6.76-12.3

Tab. 1 Background thresholds of Cr, Cu, Ni, Pb, Zn, Cr/Al2O3, Cu/Al2O3, Ni/Al2O3, Pb/Al2O3, Zn/Al2O3 calculated for total LSO stream sediment dataset and for LSO stream sediment dataset of each Romagna river (Idice, Sillaro, Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello, uso and Marecchia). In the bottom row we reported the range between the min and max background threshold calculated in the rivers of Romagna.

4.4.4 Calculation of the Geochemical Index (Igeo)

Having defined the upper limit of background provides a key reference value that can be applied for the evaluation of sediment quality. Among the several index suggested and applied in the literature, the Geoaccumulation Index (Igeo), originally defined by Muller (1969) in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels. The index has the advantage of providing also a descriptive definition of the quality of the sediment (Table 2) thus making easier the communication with non expert people.

The Igeo is calculated as follows:

$$Igeo=Log2(Cn/1.5* Bn)$$

where, Cn is the concentration of metals examined in sediment, and Bn geochemical background concentration of element (n). The Factor 1.5 should account for heterogeneity in the background values but sometimes can lead to underestimation of pollution (Covelli and Fontolan, 1997; Dung et al., 2013)

In the calculation of the Igeo we used the calculated upper limit of background (Table 1) as Bn, applying the specific catchment value. The results will be pointed commented in section 4.6 when discussing single elements in detail. In general the overall quality is good, with only 11 uncontaminated to moderately contaminated samples including 2 for Cr, 9 for Cu, 5 for Zn and 4 for

Pb. Considering the normalized elements there is an increase in the number of sample therefore are detected 43 uncontaminated to moderately contaminated samples including 27 for Cr/Al_2O_3, 16 for Cu/Al_2O_3, 10 for Ni/Al_2O_3, 22 for Pb/Al_2O_3 and 25 for Zn/Al_2O_3, and 7 moderately contaminated samples including 3 for Cr/Al_2O_3, 3 for Cu/Al_2O_3 and 1 for Zn/Al_2O_3. Apart some single anomalies, it is important to note that in some cases there are sites with poor sediment quality for multiple element, which suggest a non natural origin and situations to be further considered.

I_{geo}	I_{geo} class	Description of sediment quality
>5	6	Extremely contaminated
4–5	5	Strongly to extremely strongly contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

Tab. 2 Description of sediment quality Igeo classification (Muller, 1969).

4.4.5 Analysis of HSO samples: elemental content along the Romagna rivers and association to land use

The background limits for total dataset and singular dataset for each catchment basin are reported on profiles (Figs. 7-11) that represent the spatial distribution of elemental contents in the HSO sediments samples along the rivers from wooded and agricultural zones (hill and mountain) to industrial and populated zones (plain). This subdivision is graphically presented by the two boxes for each element and parameter. The left box describes the mountain course, whereas the right one represents the results of sampling in the plain section of each river. The separation represents the highway line (see Fig. 1) took as reference. The figures include in mountain-hilly section as geographic reference (vertical dashed lines) the location of some localities close to changes in the geological units to facilitate the observation of heavy metals and normalized elements profiles that are presented in the following paragraphs.

An additional step that we integrated to the investigation of HSO sediment samples is the evaluation of possible relations with the land use of study area. A specific land use could be a source of contamination: for example the presence of industrial activities is often related to the use of pollutants or extensive agricultural activities are interested by the use of pesticides that affect the concentration of heavy metal in the sediments (Schintu and Degetto, 1999; Santana-Perez et al., 2007; N'guessan et al., 2009; Vega et al., 2009; Oyarzun et al., 2011; Albanese et al., 2013). HSO sediment samples are located precisely near the critical points of the rivers that cross these types of areas therefore could be interesting to verify an association between anomalous values and critical land uses.

Based on Level 3 of Corine Land Cover classification have been considered three categories:

9) natural areas (NA), that include wooded and grazing lands;
10) semianthropic areas (SA), that include agricultural lands, orchards, vineyards and permanent cultivation systems;

- anthropic areas (AA), that include mining sites, road and rail networks, continuous and discontinuous urban areas.

The classification was elaborated associating a buffer of 500 m around each HSO sediment sample to estimate which category has the most influence on the nature of the sediment. In this case the most extensive land use within the area of the buffer has been associated to HSO sediment sample. Secondly, HSO sediment population has been divided in two datasets: a background dataset, related to all values below the background limit and an anomalous dataset in which are included all the values that are greater than the background limit.

For each dataset was calculated the number of HSO sediment samples grouped according to land uses (NA, SA, AA) and represented in boxplots (Fig.6). There is great similarity among the boxplots of the Background dataset, while there are differences according to land use within the Anomalous dataset. In particular for Cr the Anomalous dataset shows higher median in AA and SA compared to NA. On the contrary the Cu and Pb Anomalous dataset have higher median in AA than SA and NA. Ni Anomalous distribution evidences that NA has median values major than SA and AA. Finally Zn Anomalous dataset evidence that SA has median values major than NA and AA

Fig.6 shows some results that are coherent with a major association of anomalous heavy metal concentration to SA or AA categories while in other cases the results evidence a major influence of natural areas on the anomalous elemental content. Certainly these results are not sufficient to define the anomalous or background value of a stream sediment but if associated to profile of the next paragraphs may be useful in integrating considerations on specific contaminated sites.

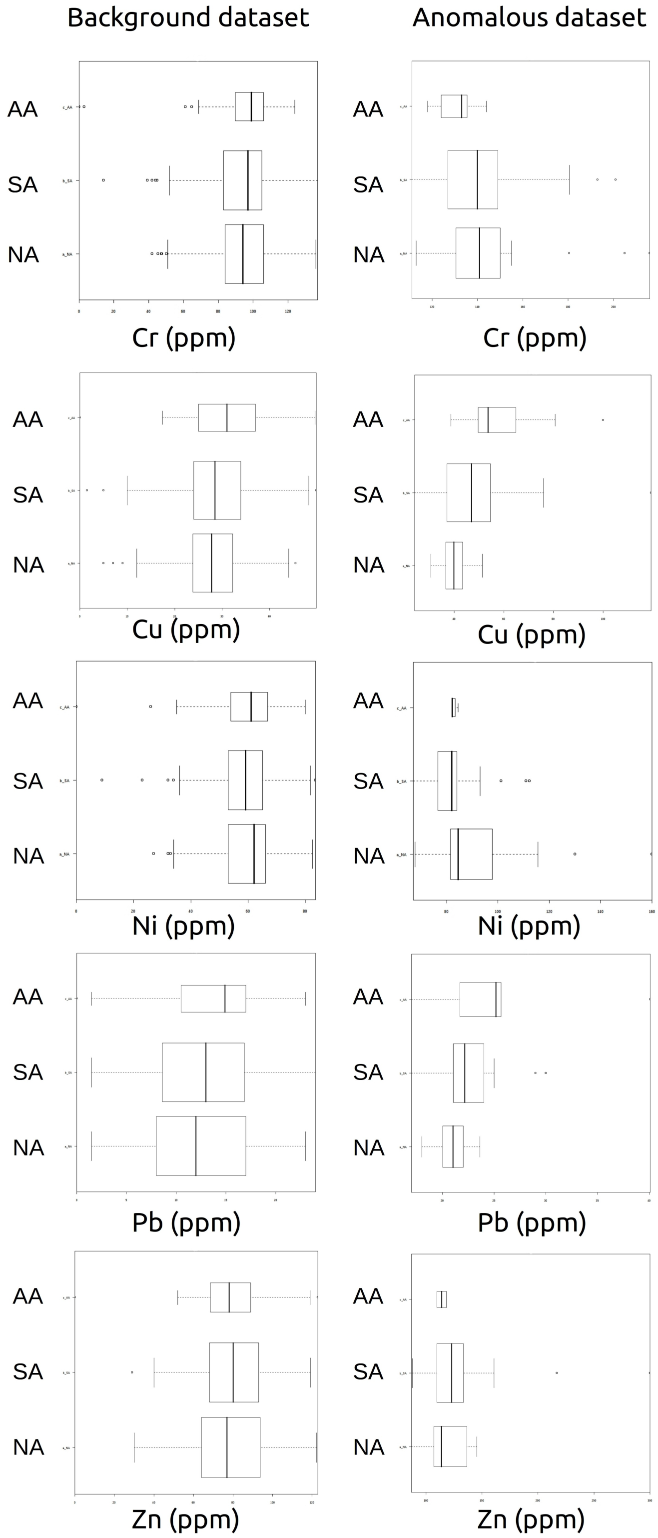

Fig. 6 Boxplots for Background and Anomalous dataset of Cr, Cu, Ni, Pb and Zn: the dataset are divided in anthropic areas (AA), semianthropic areas (SA) and natural areas (NA).

4.4.5.1 Cr and Cr/Al_2O_3

The profile of Cr (Fig. 7a) shows three trends: in Idice, Santerno, Lamone, Montone, Rabbi, Bidente and Uso rivers, the content tends to increase from mountain to plain although presenting some peaks up to 100 ppm in the central hilly areas. In Sillaro, Savio-Borello and Marecchia rivers the content remains roughly uniform although in the samples over the starting point the values are higher. In Senio and Acerreta-Tramazzo rivers the content tends to decrease. Considering the background level of total database (solid line), the samples that exceed the threshold of 135 ppm are 14 whereas considering the diversified thresholds the number increases to 23. The Cr/Al_2O_3 profile (Fig. 7b) shows various differences respect to the Cr profile: in Idice, Bidente and Savio-Borello rivers the profiles point out some peaks up to 12 that are strongly dependent on the lithology of the area. However, the most remarkable difference concerns the Sillaro river because the profile tend to regularly increase from mountain to plain. The number of samples that exceed the threshold of 11 (solid line) are 20 whereas considering the diversified thresholds the number increases to 42. In particular the major remarkable differences are detected in Idice, Sillaro, Lamone and Rabbi rivers.

The spatial distribution of boxplots in Fig. 4 shows that Cr is influenced by the geology and the dilution effect since a major concentration in the catchment basins of the northern (Sillaro Idice) and southern part (Uso) of the study area is revealed. In the northern catchment basins, mafic and ultramafic rocks of Ligurian domain and clay and sandy sediments of Padano-adriatic domain have an important role in the high content of Cr, while in the Uso basin the high content is characterized by the presence of clay sediments. Instead in the central catchment basins, especially Senio, Lamone, Acerreta-Tramazzo and Montone, the Cr low content is strongly influenced by a dilution effect from calcareous sediments of the marls of Marnoso-arenacea Formation.

In the profiles of Cr and Cr/Al_2O_3 (Fig. 7 a, b) the local effects of geology on the elemental content are clearly evidenced: in the Idice river, we note the effect of calcareous sediments on the low content of Cr upstream of Loiano village and the effect of clastic and clay sediments on the high content of Cr downstream of Loiano village. In particular, upstream of Loiano village, the effect of dilution is evidenced by the Cr/Al_2O_3 profile because the role of $CaCO_3$ is minimized. In this part of the area the concentrations above the threshold values are due to natural factors not only for the effect of dilution but also for the geological characteristics of this catchment basin receiving sediments by ophiolitic rocks (Amorosi et al., 2002). Nevertheless certain anomalous samples could be moderately contaminated by the effect of anthropogenic activities as evidenced by Igeo that detect values ranging 0,13 and 1,33. In particular these samples are located near Loiano village and upstream of the Plain.

In Sillaro, Savio-Borello and Rabbi rivers the regular trend of profiles reflect the homogeneous sandy and marly composition of these catchment basins. In the other basins, the differences in the end sections of the river are probably due to an increase in clay sediments and alluvial deposits (Lamone, Montone, Rabbi e Bidente) and a decrease in the elemental content characterized by the presence of evaporites (Acerreta-Tramazzo, Montone, Santerno, Senio).

In the plain are revealed some anomalous values, especially in Idice, Sillaro, Lamone, Montone, Savio-Borello and Marecchia, that are probably influenced by anthropogenic activities as confirmed by Igeo that detect samples moderately contaminated with values ranging between 0,16 and 1,14.

The major influence of geology respect to anthropogenic factor is confirmed by the graphs of landuse (Fig. 6) in which remarkable differences between land uses not occur. Nevertheless the anomalous values influenced by anthropogenic activities are present, especially in the Plain area.

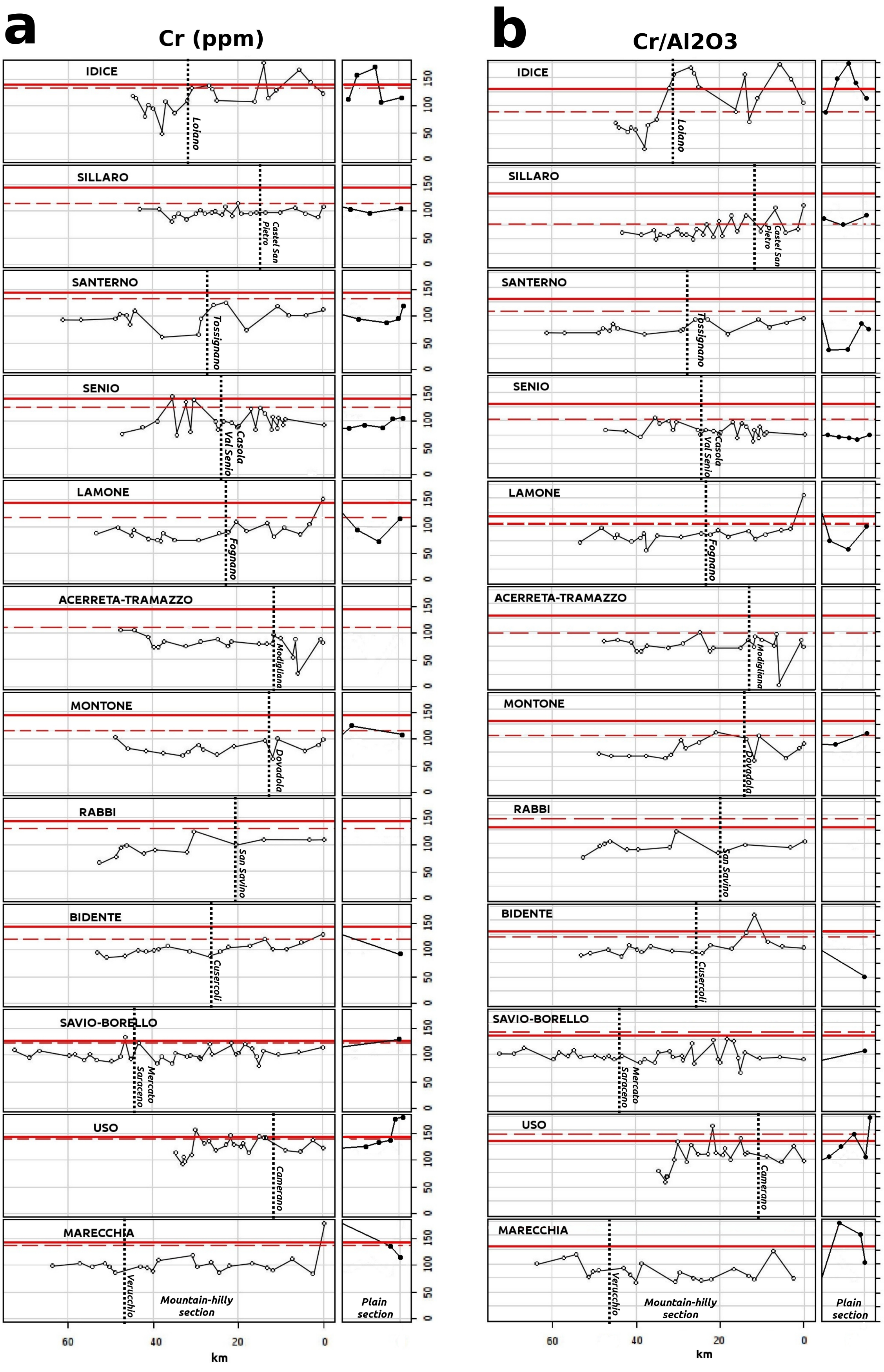

Fig. 7 Longitudinal trends of Cr content expressed in ppm (a) and Cr/Al2O3 ratio (b) of HSO stream sediment samples along the rivers of Romagna from mountain/hill (left box) to the plain (right box). The solid horizontal lines represent the background threshold of total database while the dashed horizontal lines show the diversified local background thresholds for each river.

4.4.5.2 Cu and Cu/Al_2O_3

The profile of Cu (Fig. 8a) shows three trends: in Sillaro and Savio-Borello rivers, the content tends to increase from mountain to plain although presenting some peaks in the central hilly areas. In Idice, Santerno, Senio, Lamone, Acerreta-Tramazzo, Rabbi, Bidente and Uso rivers the content remains roughly uniform although some spikes occur, especially in Lamone and Senio rivers up to 60 ppm. In the Marecchia river the content tends to decrease while in the Montone river the values increase in the central area. Considering the background level of total database (solid line), the samples that exceed the threshold of 43 ppm are 28 whereas considering the diversified thresholds the number increases to 42. In particular the most remarkable differences are shown in Bidente and Acerreta-Tramazzo rivers. Also Cu/Al_2O_3 profile (Fig. 8b) shows various trends: in Idice, Sillaro and Acerreta-Tramazzo rivers the profiles tend to increase from mountain to plain while in the Marecchia river the content of Cu/Al_2O_3 tends to decrease from mountain to plain. In Santerno, Senio, Lamone, Rabbi, Savio-Borello and Uso rivers the content remains roughly uniform although there are some peaks, especially in Lamone , Bidente and Savio-Borello . In the Montone river the profile evidence higher values in the central area. The number of samples that exceed the threshold of 4.26 (solid line) are 15 whereas considering the diversified thresholds the number increases to 31. The most remarkable differences are present in Idice and Sillaro rivers.

The spatial distribution of Cu and Cu/Al_2O_3 of Fig. 5 evidences the influence of geology and dilution: the central catchment basins (in particular Montone) that have lower content in Cu, are affected by the presence of the dominant sandy and marly composition of Marnoso-arenacea formation while in the external basins (Idice and Marecchia) the higher Cu content is influenced by the clay and clastic sediments. The lower values observed in the Sillaro catchment basin are due to the prevailing sandy composition of the basin.

The Cu and Cu/Al_2O_3 profiles (Fig. 8 a, b) show a local variability along the high stream order that in certain sites reflect the geology of the area while in other zones detect anomalous values. In Sillaro river the Cu content reflect the geology of the area because the values are lower upstream of Castel San Pietro town for the presence of sandy sediments while these values are higher downstream of Castel San Pietro village. In the end section of Sillaro river the values that exceed the local threshold value of 23 could be influenced not only by the presence of clay sediments and alluvial deposits of Padano-adriatic domain in the Plain sediment samples but also for the presence in the zone of various intensive agricultural activities as confirmed by Igeo that evidences samples moderately contaminated (0,68-1,16). The central rivers (from Santerno to Bidente) don't reflect the homogeneous sandy-marly composition of the catchment basins in fact are detected some peaks upstream of Casola Val Senio, Fognano, Modigliana and Dovadola villages. Downstream of these villages the profiles have an irregular trend probably due to the heterogeneous geological composition of the end section of the rivers but also to the presence of settlements in the plain that could affect certain values that exceed the threshold values up to 40 ppm as confirmed by Igeo (0,3-0,4). In the Santerno river the negative peak overlaps with the evaporites, suggesting a lithological influence, while the positive peaks of Lamone, Acerreta-Tramazzo and Savio-Borello rivers overlap with the sandy sediments and the alluvial deposits that are located respectively dowstream of Fognano, Modigliana and Mercato Saraceno villages. In these sites the presence of extended industrial activities could affect the elemental content of samples that exceed the local threshold as confirmed by Igeo that detect samples moderately contaminated in the hilly area (0.3-0.7) and in the Plain (0,2-0,7). The profiles of Marecchia and Uso rivers have the trend that are coherent with the geology of study area: Uso river is characterized by an homogeneous clayey lithology, except for the plain area where alluvial deposits are present, while Marecchia river has an irregular profile that reflect the heterogeneous lithological composition of the area characterized by calcareous and clay sediments.

Comparing these observations with the land use (Fig. 6) the higher association of stream sediment samples to anthropic areas (AA) is coherent with the little relation between anomalous values of Cu and geology, especially in the mountain and hilly sections of the rivers. Therefore the values that exceed the background threshold have an anthropic origin, probably due to agricultural and industrial activities.

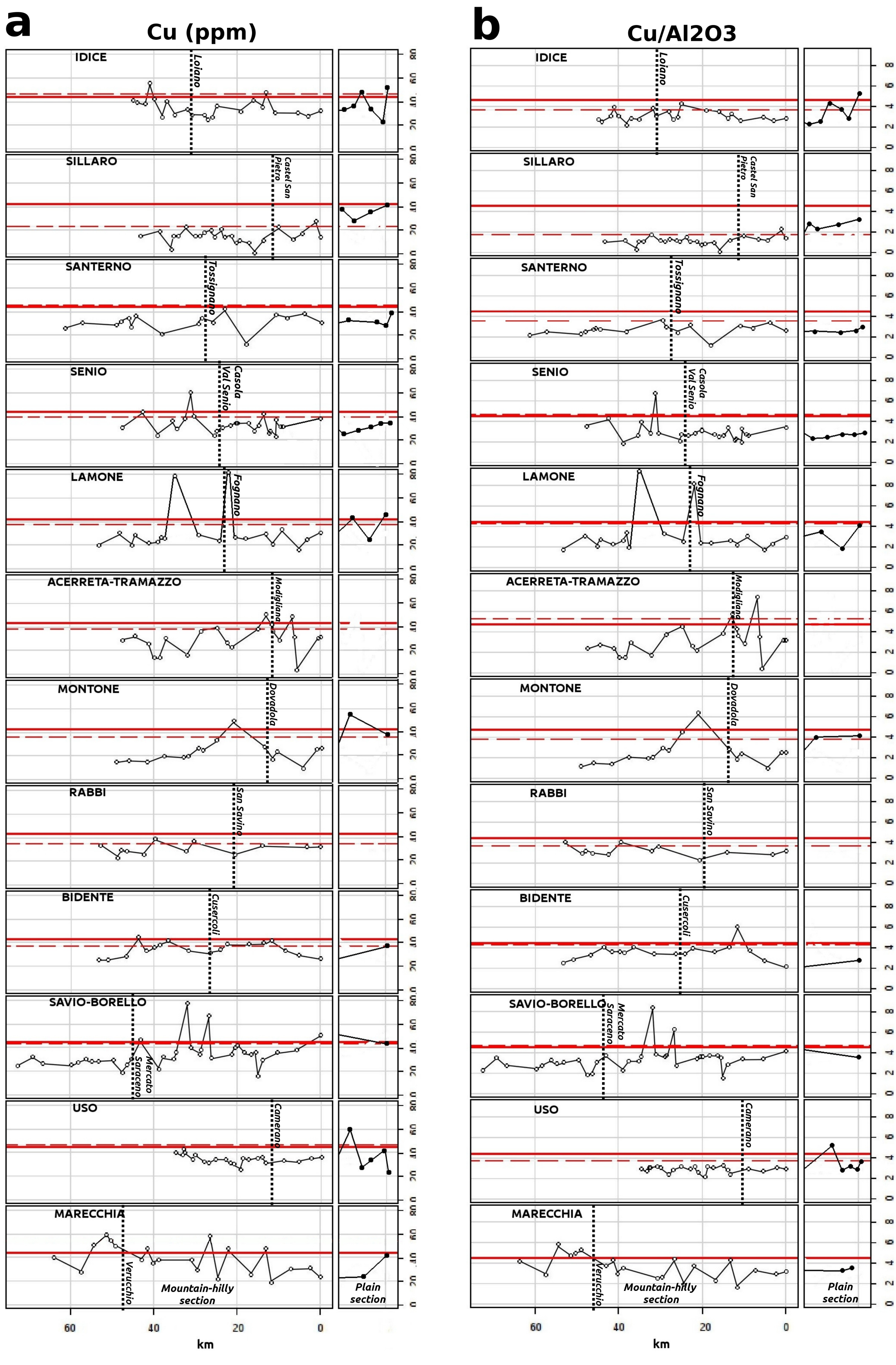

Fig. 8 Longitudinal trends of Cu content expressed in ppm (a) and Cu/Al2O3 ratio (b) of HSO stream sediment samples along the rivers of Romagna from mountain/hill (left box) to the plain (right box). The solid horizontal lines represent the background threshold of total database while the dashed horizontal lines show the diversified local background thresholds for each river.

4.4.5.3 Ni and Ni/Al_2O_3

The Ni profile (Fig. 9a) shows different trends: in Acerreta-Tramazzo and Marecchia rivers the elemental content tends to decrease from mountain to plain although there is one peak in the Acerreta-Tramazzo river up to 80 ppm. In Idice, Sillaro, Santerno, Lamone, Montone, Rabbi, Savio-Borello and Uso rivers the elemental content remains roughly the same although presenting some peaks, especially in Montone river (1) and Savio-Borello river (1). In Senio and Bidente rivers the profiles evidence higher Ni values in the central hilly areas. Considering the background level of total database, the samples that exceed the threshold of 82 ppm (solid line) are 8 whereas considering the diversified thresholds (dashed line) the number increases to 25. The most remarkable differences are present in Senio and Savio-Borello rivers. Also the Ni/Al_2O_3 profile (Fig. 9b) shows different trend: in Idice, Santerno and Montone rivers the profiles point out higher values in the central area while in Lamone, Acerreta-Tramazzo, Rabbi, Bidente, Savio-Borello, Uso and Marecchia river the profiles are constant although are some peaks, especially in Acerreta-Tramazzo , Savio-Borello and Marecchia . In Sillaro river the elemental content tends to increase from mountain to plain while in Senio river the profile tend to decrease from mountain to plain. The samples that exceed the threshold of 8 (solid line) are 13 whereas considering the diversified thresholds (dashed line) the number increases to 29. The most remarkable differences are present in Idice and Rabbi rivers.

The spatial distribution of Ni (Fig. 5) doesn't evidence a particular correlation with geology of the area differently by Ni/Al_2O_3 that reflect a probable effect of dilution and possibly different sediment provenance: in fact central catchment basins (especially Savio-Borello, Bidente and Rabbi) have higher median values respect to northern (Sillaro) and southern (Marecchia and Uso) catchment basins. This is reflected in the differences of Ni and Ni/Al_2O_3 profiles of Fig. 9 although certain sections of the profile point out a concentration related to lithology. In particular, upstream of Loiano village and downstream Verucchio village the low values of Ni are coherent with the dominant calcareous composition of these zones and increase in the clayey lithology. In catchment basins that are geologically homogeneous, the profiles are regular (Uso, Montone, Rabbi and Sillaro) with values below the background threshold. In the other catchment basins (Santerno, Senio, Lamone, Acerreta-Tramazzo e Bidente) the profile are less regular in the hilly/plain sections of the rivers in which the lithologies are heterogeneous (evaporites, calstic sediments, sandy sediments, clay sediments and alluvial deposits). Despite this in certain zones, upstream Tossignano, Casola Val Senio, Modigliana and Rabbi villages are detected elemental concentrations above the threshold value that are likely not natural. In these cases the normalization has an important role in determining the effect of dilution on the elemental concentration therefore upstream of Tossignano there are high ratios on carbonaceous lithologies and lower ratios on clay sediments downstream of Tossignano village. In this site the Igeo detect the presence of samples moderately contaminated with values ranging between 0,2 and 0,5. Also in the mountain section of Senio river upstream of Casola Val Senio village the high values of Ni in marl of Marnoso-arenacea formation are minimized in the Ni/Al_2O_3 profile presenting the ratio values below the threshold value. Considering the Plain samples only in Uso river is evidenced the presence of a sample moderately contaminated as confirmed by Igeo (0,4):

The landuse of anomalous values (Fig. 6) is coherent with the elemental content of Ni in the profiles therefore the effect of geology is confirmed by the major association of anomalous values with natural areas although few samples are moderately contaminated.

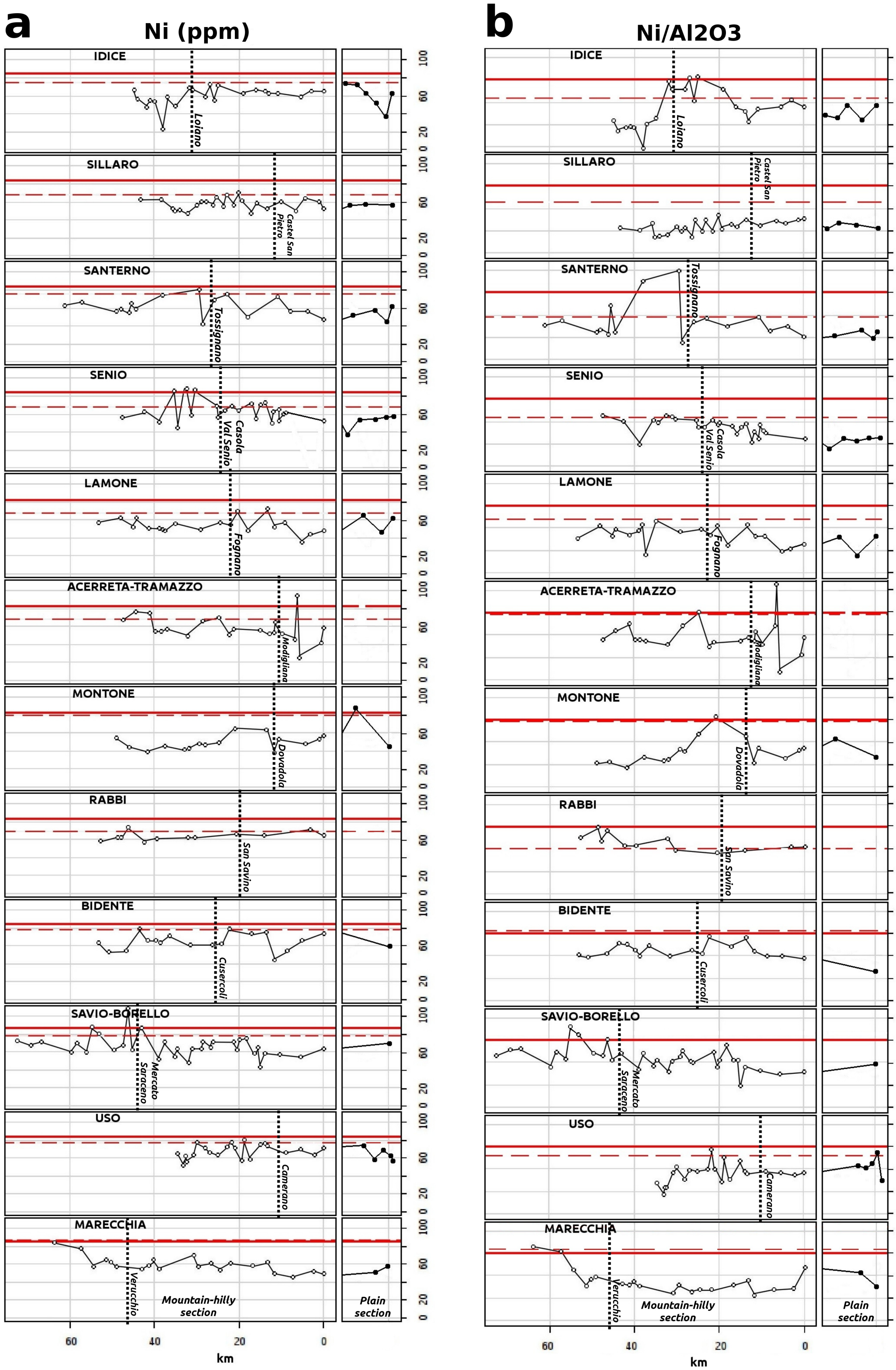

Fig. 9 Longitudinal trends of Ni content expressed in ppm (a) and Ni/Al2O3 ratio (b) of HSO stream sediment samples along the rivers of Romagna from mountain/hill (left box) to the plain (right box). The solid horizontal lines represent the background threshold of total database while the dashed horizontal lines show the diversified local background thresholds for each river.

4.4.5.4 Pb and Pb/Al_2O_3

The Pb profile (Fig. 10a) shows a trend in which the rivers have roughly uniform elemental contents with some peaks up to 20 ppm in Lamone, Acerreta-Tramazzo and Savio-Borello rivers. Considering the background level of total database (solid line), the samples that exceed the limit of 22 ppm are 27 whereas considering the diversified thresholds (dashed line) the number increases to 30. The most remarkable differences are present in Sillaro and Acerreta-Tramazzo rivers. Also Pb/Al_2O_3 profile (Fig. 10b) shows uniform trends in the rivers but respect to Cr is evidenced an increase in some peaks up to 2, especially in Idice, Lamone, Acerreta-Tramazzo, Rabbi, Bidente and Savio-Borello. Considering the background level of total database (solid line), the samples that exceed the threshold of 1.96 are 40 whereas considering the diversified thresholds (dashed line) the number increases to 41. The most remarkable differences are present in Sillaro river.

The elemental content of Pb doesn't reflect a particular spatial distribution (Fig. 5) and an association with the geology of the area therefore the central catchment basins, especially Lamone, Acerreta-Tramazzo, Montone and Rabbi, have different medians although the lithologic composition is similar and dominated by the sandstones and marls of Marnoso-arenacea formation. Also in Idice and Sillaro catchment basins, the higher content of Pb respect to other basins could be coherent with the presence of clastic and clay sediments. Instead the geological heterogeneity of Savio and Marecchia catchment basins characterized by calcareous and clay sediments reflect the wide range of boxplots. We could aspect that these values reflect a real concentration in the sediments therefore the Al_2O_3 normalization doesn't point out remarkable differences between Pb and Pb/Al_2O_3.

These results are evident in the profiles of Pb and Pb/Al_2O_3 (Fig. 10 a, b) in which the peaks detected above the background threshold are similar in these profiles, in particular some samples of Lamone river near the Fognano village, Acerreta-Tramazzo river upstream of Modigliana village, Bidente river downstream of Cusercoli village and Savio-Borello river downstream of Mercato Saraceno village. These anomalous values could be associated to the proximity to urbanized areas and the presence of agricultural and industrial activities as confirmed by Igeo that identifies samples moderately contaminated with values ranging between 0,16 and 0,97. In Idice and Sillaro rivers the elemental concentration reflect the prevailing clay and clastic sediments of mountain/hilly section while the anomalous concentrations in the alluvial deposits of the plain could be an anthopic origin as confirmed by Igeo with values ranging between 0,45 and 0,82. In Senio, Acerreta-Tramazzo, Montone and Bidente rivers, the negative peaks of Pb are probably due to the evaporites and calcareous sediments downstream of Casola Val Senio, Fognano, Dovadola and Cusercoli villages. In Marecchia catchment basin the irregular profile of Pb reflects the geological heterogeneity due at the presence of calcareous and clay sediments while the Savio-Borello profile evidence an increase in the Pb content probably influenced by the presence of clastic, clay sediments and alluvial deposits downstream of Verucchio village. Uso, Montone and Lamone rivers reflect the geology but present some values above the local threshold that could be associated to anthropic activities as evidenced by Igeo with samples moderately contaminated (0,2-0,54). Although some Pb profiles reflect the geology of the area, other profiles evidence anomalous values, confirmed by the Pb/Al_2O_3 profile, that could be due to anthropic activities, as suggested by the major association of anomalous values to anthropic areas and semianthropic areas (Fig. 6).

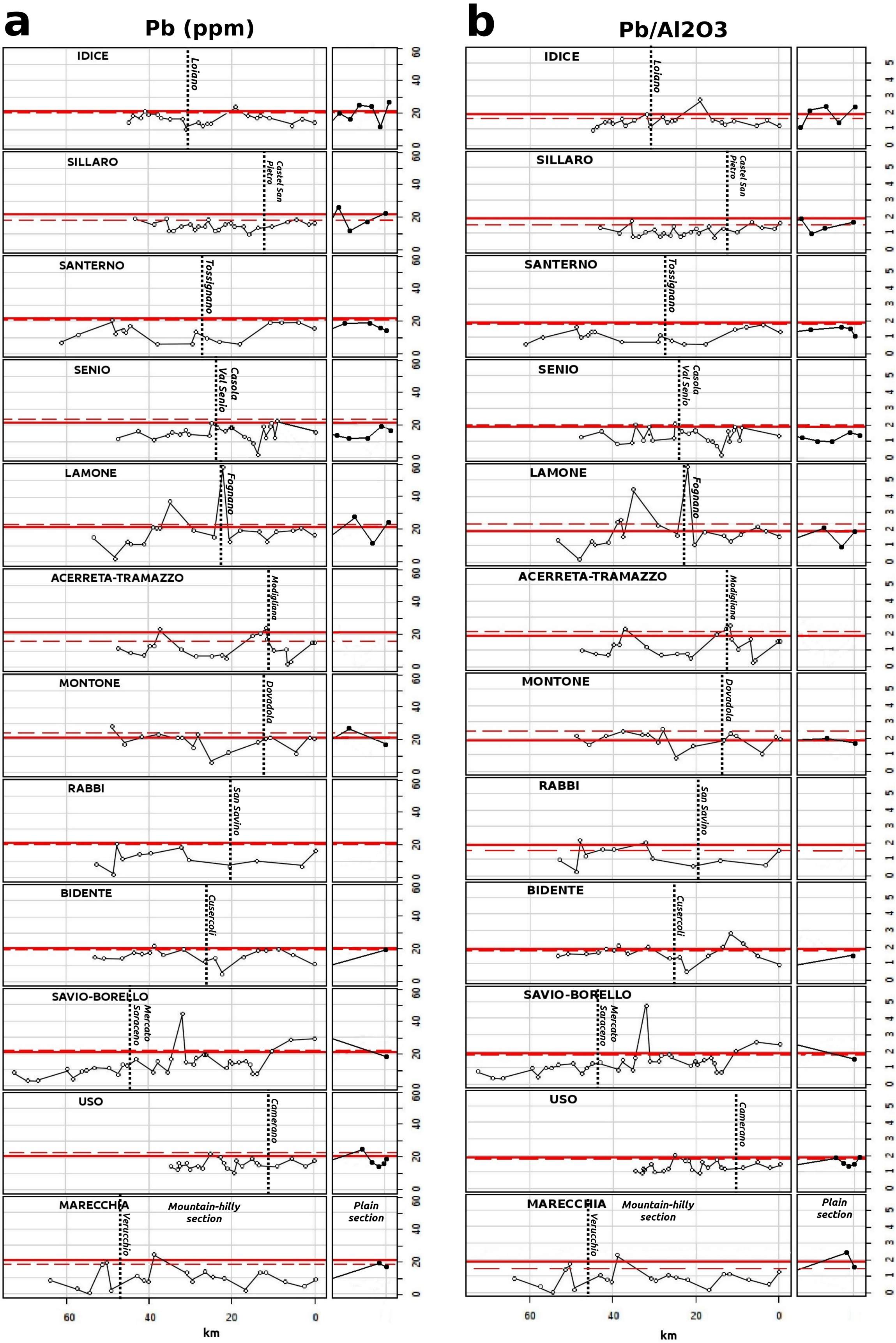

Fig. 10 Longitudinal trends of Pb content expressed in ppm (a) and Pb/Al2O3 ratio (b) of HSO stream sediment samples along the rivers of Romagna from mountain/hill (left box) to the plain (right box). The solid horizontal lines represent the background threshold of total database while the dashed horizontal lines show the diversified local background thresholds for each river.

4.4.5.5 Zn and Zn/Al_2O_3

The Zn profile (Fig. 11a) shows different trends: in Sillaro, Santerno, Rabbi, Uso and Marecchia rivers the elemental content tends to remain constant along the river although are present some peaks, particularly strong the one in Sillaro, up to 150 ppm. In Senio, Lamone, Acerreta-Tramazzo and Savio-Borello rivers the elemental content is higher in the central hilly areas, with a spike up to 200 ppm in the Lamone river. In Idice, Montone and Bidente rivers the elemental content tend to increase from mountain to plain. Considering the background level of total database (solid line), the samples that exceed the threshold of 119 ppm are 26 whereas considering the diversified thresholds (dashed line) the number increases to 42. The most remarkable differences are present in Acerreta-Tramazzo river. Zn/Al_2O_3 profiles (Fig. 12b) show uniform trends with some peacks up to 10, especially in Idice, Sillaro, Lamone, Acerreta-Tramazzo, Bidente and Savio-Borello rivers. The samples that exceed the threshold of 10.43 (solid line) are 20 whereas considering the diversified thresholds (dashed line) the number increases to 45. The most remarkable differences are present in Acerreta-Tramazzo river.

The spatial distribution of Zn (Fig. 5) shows an influence of geology on the elemental content of Zn: in the northern (Sillaro and Santerno) and southern (Marecchia) catchment basins the higher content of Zn reflect the presence of clastic, clay and sandy sediments while some central catchment basins (Senio, Lamone, Acerreta-Tramazzo and Montone) evidence lower contents of Zn probably due to the calcareous and marly composition of the Marnoso-arenacea formation. The Al_2O_3 normalization point out a dilution effect in Zn/Al_2O_3 reducing the effect of $CaCO_3$ in the central catchment basins, especially Senio, Lamone, Acerreta-Tramazzo and Montone. Instead in the northern (Idice, Sillaro and Santerno) and southern (Bidente, Savio-Borello, Uso and Marecchia) catchment basins the normalization have not a significant influence.

Zn and Zn/Al_2O_3 profiles (Fig. 11 a,b) show elemental contents of Zn and values of Zn/Al_2O_3 ratio that are coherent with the geology of the area: in Sillaro, Montone and Bidente the values of Zn reflect the low concentration below the background threshold in calcareous sediments and marls of Marnoso-arenacea formation while Uso river. Other rivers (Santerno, Savio-Borello and Marecchia) show complex trends that could be related to the heterogeneous geological composition of these catchment basis in which are present evaporites, calcareous sediments, sandstone and marls.

The Zn and Zn/Al_2O_3 profiles evidence some peaks that have a different significance: in the Idice river downstream of Loiano river, in Senio river upstream of Casola Val Senio river, in Acerreta-Tramazzo river upstream of Modigliana village and in Bidente river upstream Cusercoli village, the differences between Zn and Zn/Al_2O_3 profiles are due to the effect of dilution played $CaCO_3$ for Senio, Lamone and Acerreta-Tramazzo and clay sediments for Idice and Bidente. In Sillaro river near Castel San Pietro village, in Lamone river downstream of Fognano village and in Savio-Borello river downstream of Mercato Saraceno village the peaks of Zn and Zn/Al_2O_3 profiles are similar therefore the anomalous values can be considered as real. In these case the anomalous values are probably due to anthropogenic factor as confirmed by Igeo that reveal sample moderately contaminated with value ranging between 0,28 and 0,60. Also in the closing section of the rivers the Zn contents above the background threshold could be related to anthropogenic activities for the presence of extensive urbanized, industrial and agricultural areas. The Igeo detect sample moderately contaminated with values that ranging between 0,14 and 1,07.

The boxplots of land use shown in Fig. 6, reflect the important role of geology dilution effect in determining the anomalous values of some samples: however is likely that certain samples in Santerno, Lamone and Savio-Borello rivers in central hilly areas and Idice, Sillaro, Santerno, Montone and Uso rivers in the Plain are influenced by anthropic factors.

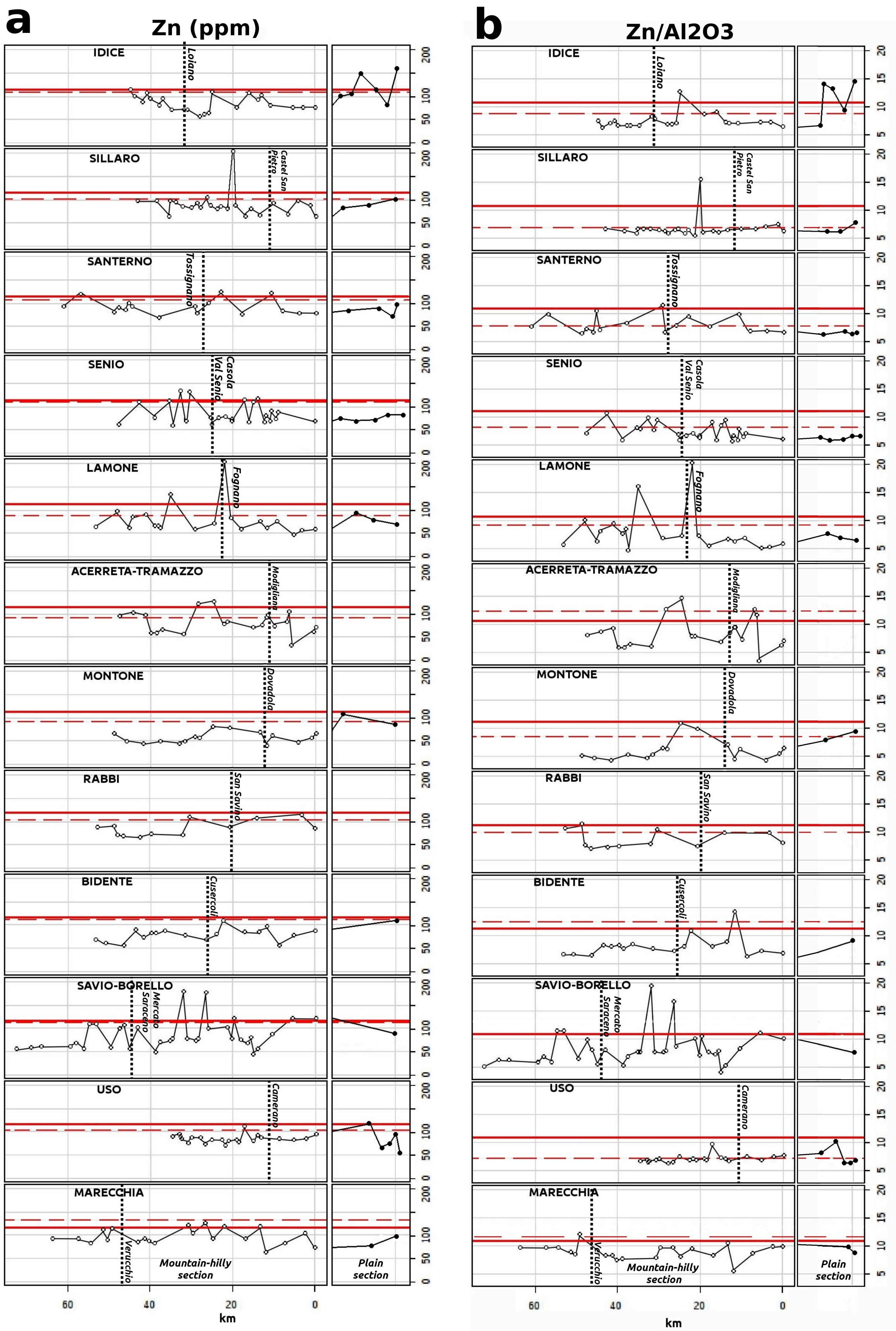

Fig. 11 Longitudinal trends of Zn content expressed in ppm (a) and Zn/Al2O3 ratio (b) of HSO stream sediment samples along the rivers of Romagna from mountain/hill (left box) to the plain (right box). The solid horizontal lines represent the background threshold of total database while the dashed horizontal lines show the diversified local background thresholds for each river.

4.5 Conclusions

The study area is greatly influenced by different geological units that overlap various catchment basins: these rivers (Idice, Sillaro, Santerno, Senio, Lamone, Acerreta-Tramazzo, Montone, Rabbi, Bidente, Savio-Borello, Uso and Marecchia), show a specific spatial distribution of chemical elements that evidences the characteristic lithology of the area. The major elements (Al_2O_3 and CaO) have opposite trends that point out the major clayley composition of northern (Idice, Sillaro) and southern (Marecchia and Uso) catchment basins and the calcareous and marly composition of central catchment basins (from Santerno to Savio-Borello). This distribution of major elements is reflected in the content of some heavy metals that are presented in this paper: Cr, Cu, Ni, Pb and Zn. Cr, Cu, Ni and Zn have similar geochemical behavior that show a spatial distribution influenced by the content of major elements: their concentration is lower in the catchment basins characterized by high content of limestone and is higher in the basins that reflect a more clayey composition. On the contrary Pb doesn't reflect a geologically-oriented distribution.

Considering the effect of enrichment of heavy metals in certain sediments, especially with a more clayey composition, has been required the Al_2O_3 normalization to investigate the probable effect of dilution and/or sorting in some catchment basins. The differences in normalized ratio, if extensive and not related to a singular point, can reflect local geochemical characteristics (e.g.: provenance) of the bedrock lithology. Spikes, sometimes reaching values very different from the rest of the data, can identify anomalies, in almost every case related to anthropogenic activities. A change, towards homogeneization reducing the differences between the other groups observed in absolute values can indicate a major effect of dilution, for example related to different amounts of CaCO3. Specifically the normalization has an effective role in the central catchment basins where the effect of dilution is associated principally to $CaCO_3$: this is evident in Cr, Cu, Zn and Ni where the ratios have a content similar to northern and southern catchment basins and the effect of these heavy metals is minimized.

Based on these considerations is applied a methodology for identifying the background values that consider also the effect of geology. The application of the ISO/DIS 19258 technique for total dataset and for singular catchment basins evidence a wide range of values in all the elements that confirms the influence of geology on background values. This consideration demonstrates that a fixed background values for the total dataset doesn't reflect a representative threshold: for example a fixed value of 135 ppm for Cr is not coherent with the calcareous and marly geological characteristics of central catchment basin that are dominated by the Marnoso-arenacea formation. Instead different background thresholds applied to singular basin take into account also the geological factor and could be more reliable in the identification of anomaly. This concept is evidenced by comparing the number of values above the total background (TB) threshold that is lower respect to the number of values above the background basin (BB) threshold for all heavy metals. It means that without a background level fixed for each catchment basins a lot of potential anomalous values are missed. From an environmental point of view, this approach can point out low-grade anomaly susceptible of further investigations that would be missed with a more generalistic approach, and provides clear evidence that background values are dependent on location and scale, as pointed out by Reimann and Garret (2005).

Whereas in an area characterized by agricultural and industrial activities the anthropic factor could be determinant in anomalous values, we have considered also the role of land use on the spatial distribution of elemental content. In this paper we note that some samples with anomalous values don't reflect the influence of geology or dilution effect whereby the association of certain values to land use could be determinant in the comprehension of the responsible factor. Cr, Ni and Zn values that exceed the local background threshold are equally distributed between anthropic, semianthropic and natural areas and the samples moderately contaminated, as confirmed by Igeo, are present mostly in the Plain and in few sites of mountain-hilly zones where urbanized areas and intensive agricultural and industrial activities occur. The only example of a diffuse area of contamination is along Idice river with anomalous values of Cr. Pb and Cu values exceeding the local background threshold show a major association of anomalous values to anthropic areas: in this case the samples moderately contaminated are present exclusively in the Plain for Cu while for Pb are detected also some sites of contamination in central hilly areas. Although anthropic activities are developed in the rivers from mountain to plain, the effect of human impact in the plain is more determinant in the contamination of stream sediment.

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General conclusions

The primary aim of this thesis was to explore the potential of stream sediment analysis applied to geochemical mapping of Romagna area (Northern Italy) in the monitoring and management of environmental resources. Stream sediments were selected for their wide application as sampling medium in geochemical surveys regarding mineral exploration, environmental problems, geological, agricultural and forestry studies from global- to local-scale area. In fact the great capacity of reflecting the rock and soil composition of wide areas as catchment basins, the facility of sampling and the good sensitivity for many chemical elements, especially for those implicated with environmental pollution have been good parameters for the success of this geochemical study applied to an area with a complex geology and environmental factors.

The first part of the study concerned the comparison of various geochemical representation techniques used to investigate stream sediment geochemistry of the regional scale-area of Romagna Apennines. In this paper, different aspects have been discusses: firstly the influence of geology on the spatial distribution of chemical elements and consequently the importance of manipulating datasets through the analysis of separate populations associated to geology. These elaborations have highlighted anomalous values that were not evident in an overall representation. Secondly, the use of mapping techniques based on IDW interpolation and Sample Basin Catchment techniques has shown the great potential of stream sediments in representing the geochemical signal of wide areas as catchment basins and detecting the extension of anomalous sources. The comparison of these techniques confirmed the importance of different approaches that can point out peculiarities usfeul for interpretation of the effect of geology.

In the second part a more local-scale approach was applied to the study of the Marnoso-arenacea Formation (MAF). Stream sediment analysis was exploited to evaluate the distribution pattern of geological members, the chronologic evolutionary trend in the deposition of sediments and the composition and origin of sediments. The richness of informations related to high density sampling and a more detailed scale have permitted to carry out a further tool supporting these considerations: a geochemical mapping based on geological units. Also this cartographic technique, as well as IDW interpolation and SBC technique, has evidenced the great capacity of stream sediments in reflecting the rock and soil composition of wide areas: the Alpine and Apenninic supplies composing the geological members of MAF are recognized throughout the representation of spatial distribution of certain chemical elements that point out the prevailing carbonate, fine-grained sediments deposited in the Langhian-Serravallian stage, the sialic, siliciclastic inputs deposited in Tortonian stage and the hybrid carbonate-siliciclastic contributions deposited in the Serravallian-Tortonian stage.

The third part of the study explored the stream sediment analysis applied to different local-scale areas represented by catchment basins of Romagna rivers. In this paper was indagated the influence of geology, normalization and land use on the background threshold of some heavy metals. The elemental content of major elements in stream sediment of rivers evidenced the clayey composition of northern and southern catchment basins and the calcareous and marly composition of central catchment basins: this geologically-oriented distribution and the effect of dilution and/or sorting in some catchment basins have inducted to consider diversified background thresholds for each river. The profiles of heavy metals representing the elemental content along Romagna rivers from mountain to plain have highlighted some contaminated sites exceeding the local background thresholds: these anomalous site compared to land use and a geochemical index (Igeo) of contamination confirmed the effect of human impact related to agricultural and industrial activities on the level of pollution in stream sediments.

Generally stream sediments proved to be a powerful sampling media at various scale-areas. Their great potential applied to the realization of geochemical mapping is an effective tool of monitoring that shows is efficiency not only in geochemical exploration, but also in geological recostruction of a complex area and in the management of environmental problems related to pollution and contamination of natural resources in anthropogenic areas.