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Influence of particle-size on geochemical distribution of stream sediments in the Lese river catchment, southern Italy

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This study was carried out in a river catchment in southern Italy to determine some possible relationships between the distribution of chemical elements and size fractions in stream sediments. Through the presence of variations in concentration of some elements in each size fraction, it was possible to examine the influence of particle-size on geochemical distribution of stream sediments. From this point of view, it is very useful to study the Lese river catchment because it is representative of the whole Mediterranean area given its characteristics, which are common to other similar areas. Sediment samples were collected from 13 stations in the catchment area. The chemical compositions of bulk samples coupled with those of some selected particle size fractions were analyzed for 25 elements by using X-ray fluorescence spectrometry and for their sedimentological characteristics. Particle-size analysis was focused on trying to understand how samples from the same site showed different geochemical distribution in the different size fractions. Stream sediments in the study area consist mostly of sand particles. Chemical analyses were performed to determine to what extent the stream sediments retain the geochemical signature of their parent rocks. Some size fractions, and not only the recommended $< 150\ \mu$m, allowed testing of the validity of FOREGS procedures, which considers the $< 150\ \mu$m to be the optimum fraction for chemical analysis. The elemental values were analyzed according to the various thresholds imposed by Italian legislative Decree No. 152/2006. This study suggests that the geochemistry of stream sediments also needs to be characterized in order to evaluate the potential chemical pollution of an area.
Keywords. Sediment, particle size, geochemistry, pollution, environment, Italy.

Influence de la dimension des particules sur la distribution géochimique des sédiments fluviaux dans le bassin du fleuve Lese, sud de l'Italie. Cette étude a été effectuée dans un bassin du Sud de l'Italie afin de déterminer les relations possibles entre la distribution des éléments chimiques et les fractions granulométriques dans les sédiments fluviaux. En conséquence, on a pu examiner, à travers la présence de variations de certains éléments dans chaque fraction, l'influence de la granulométrie sur la distribution géochimique des sédiments fluviaux. De ce point de vue, l'étude du bassin du fleuve Lese a été très utile, car représentative de l'ensemble de la zone méditerranéenne, pour ses caractéristiques communes à d'autres zones similaires. Les échantillons de sédiments ont été recueillis dans 13 sites à l'intérieur du bassin. La composition chimique de la totalité de ces échantillons, avec celle de certaines fractions granulométriques sélectionnées, ont été analysées pour 25 éléments par la méthode de la fluorescence-X et pour leurs caractéristiques sédimentologiques. L'analyse granulométrique s'est concentrée sur la détermination des conditions dans lesquelles les échantillons du même site ont démontré différentes distributions géochimiques dans plusieurs fractions. Les sédiments fluviaux de la zone étudiée sont principalement constitués de particules de sable. Les analyses chimiques ont été effectuées afin de déterminer dans quelle mesure les sédiments fluviaux gardent la signature géochimique des roches mères. Dans certaines fractions granulométriques, le standard $< 150\ \mu$m a permis de vérifier des procédures imposées par le FOREGS, qui considère la fraction $< 150\ \mu$m comme la fraction optimale pour l'analyse selon les limites imposées par le Décret Italien n°152/2006. Cette étude suggère la nécessité de caractériser aussi la géochimie des sédiments fluviaux, afin d'évaluer l'éventuelle pollution chimique d'une zone.
Mots-clés. Sédiment, grosseur des particules, géochimie, pollution, environnement, Italie.

1. INTRODUCTION

Stream sediments are commonly used as an exploration tool for regional geochemical surveys (Cohen et al., 1999; Cannon et al., 2004). Active stream sediments represent the fine – to medium — grained solid material (clayey-silty-sandy), which consists of fragments that are derived from the erosion of weathered rocks and soil by stream or river water and, depending on their particle size and stream water velocity, are transported in suspension, by saltation or by creeping along the stream bed. Thus they represent the source catchment area of the stream drainage network (Ranasinghe et al., 2008).

The mineralogy, particle-size and geochemistry of stream sediment in rivers have commonly been explained as reflecting the composition of source rocks, mechanical and chemical weathering, hydrological and morphological features of the basin, winnowing and sorting, and climate, as well as several other, possibly less important, factors (Pratt et al., 2007; Grunsky et al., 2009; Ranasinghe et al., 2009; Singh, 2010). Identifying the impact of natural factors may contribute to the identification of the impact of human activities, *e.g.*, agriculture, mining, and industry, on stream sediment geochemistry (Piper et al., 2006).

It is important to consider the influence of geochemical and mineralogical controls on particle-size distribution of stream sediments (Ranasinghe et al., 2002).

Many research results reveal that the chemical composition of sediment varies with grain size due to:

- multiple sources contributing mineralogically and texturally distinct grain sizes;
- mechanical weathering of rock fragments into finer components;
- chemical weathering of weak grains into products of alteration.

The study of the size fractions in a stream sediment sample provides the best opportunity for recognizing different geological processes. They can have a strong influence on how the geochemistry of an area may be interpreted (Grunsky et al., 2009). Indeed, some elements have a strong affinity for particles, and their subsequent fate is strongly influenced by fluvial processes.

Studies of the distribution of trace elements in relation to the size fraction of stream sediments generally show that several elements, including Mo, Cu, Zn, Mn and Fe, are concentrated in the finest fractions of the sediment (Horowitz et al., 1987; Moore et al., 1989; Stone et al., 1996; Singh et al., 1999). Therefore the majority of stream sediment surveys have been based on the collection of < 200 µm material.

The FOREGS (Forum of European Geological Survey) standard sieve mesh is < 150 µm: this is not only fine enough to include the very fine sand, silt, clay and colloidal fractions, but it is also coarse enough to yield sufficient fine material in the majority of situations (Salminen et al., 1998).

Therefore the < 150 µm size fraction is particularly useful for regional geochemistry sampling. However, in this survey, other size fractions were also measured to test the possibility that some elements of interest may be tendentially bound to coarser ones.

It is also important to understand the distribution and variability of elements within fluvial systems in order to evaluate risk and potential environmental remediation options (Reneau et al., 2004). Indeed particle size plays a significant role in the accumulation of heavy metals and other potentially harmful elements, and managing the territory rationally means determining these toxic elements. Moreover, heavy metal accumulation can influence the impact that environmental pollution can have on man, animals and vegetation. For this reason, in recent years, the interest the geochemical mapping of stream sediments holds for the international scientific community has increased considerably. Based on the above considerations, we decided to carry out this study in a catchment, which is suitable for the study of these phenomena. In fact the Lese river catchment can be considered representative of the whole Calabrian territory, as well as Mediterranean zones in general, because of its geological, geomorphological, climatic, and human pressure characteristics that are common to these areas and make the Lese catchment of southern Italy an area of scientific interest. The purposes of this paper were:

- to compare the geochemistry of stream sediments with local parent rocks in the Lese river catchment (southern Italy), in order to investigate the influence of particle size and the lithological features of the source area on the concentration of chemical elements;
- to quantify potentially harmful element concentrations in different particle size fractions in relation to Italian legislative Decree No. 152 of 03/04/2006 by approximating the sediments to the soils. This was because the Italian government established intervention values for some selected toxic elements in soil, stream water and marine sediments, but not for stream sediments;
- to show that the particle size fraction < 150 µm, as imposed by FOREGS, is effective in representing the entire stream sediment in terms of geochemical composition.

2. MATERIALS AND METHODS

2.1. Geological and geomorphological setting

The Lese river catchment is located in the Sila Massif in the central-eastern sector of Calabria and is included in the Crotone sedimentary basin. The Crotone basin is considered to be a member of the Ionian Forearc Basin (Amodio-Morelli et al., 1976), located along the southern border of the Calabrian Arc (Zecchin et al., 2004). It is bounded by two NW-SE fault zones, Rossano-San Nicola to the north and Petilia-Sosti to the south (Tortorici, 1982; Meulenkamp et al., 1986; Van Dijk, 1990; Van Dijk, 1991; Van Dijk et al., 1991; Van Dijk et al., 2000).

The study area consists of middle-high- to low-grade metamorphic rocks, Palaeozoic plutonic rocks and a sedimentary turbiditic succession that occurred between the Miocene and the Pleistocene (Messina et al., 1991; Messina et al., 1994) (**Figure 1a**).

Lithological outcrops in the study area are mainly formed of a complex of intrusive acid rocks of varying composition (quartz-diorite, quartz-monzonite, granodiorites, granite) and low- to medium-grade metamorphites (shale, clayey-schist, phyllite) affected by cleavage (Lorenzoni et al., 1983). These rocks include elements relating to oceanic and continental alpine units and are generally affected by very intense cleavage and fractures. In addition, sedimentary detritic terrains, mainly pelitic with subordinate evaporite intervals, occur widely in the southernmost part of the catchment. These include upper Miocene deposits, with both evaporitic and detritic facies, and Pliocene sandy, clayey and marly deposits (Sorriso-Valvo et al., 1996). The most elevated portion of the catchment is the result of tectonic uplift, which occurred at the beginning of the Pleistocene, and is characterized by a widespread regolith, which has not yet been eroded and often reaches a thickness of several tens of meters (Le Pera et al., 2001). A thick mantle of altered products (regolith + soil) covers the crystalline bedrock of the Lese basin. The different stages of weathering of the basement rocks that initiated in the lower Cenozoic-Quaternary, are characterized by different colors, mineralogical alteration and textural change (Le Pera et al., 2000). The weathering profile usually consists of organic soil horizons on thicker layers of grus, which have been completely removed by erosion in places leaving fresh bedrock outcrops.

The Lese river drainage basin is a left tributary of the Neto river. The Neto river basin covers an area of 1,073.29 km^2 and, along its length, the principal channel gradually flows across plutonic, metamorphic and sedimentary rocks. Numerous streams within the catchment tend to emplace alluvial fans toward the lowest reaches of the Sila Massif, producing different natural (wild and suggestive) landscapes.

2.2. Sampling and chemical analyses

As was recommended by FOREGS, the Forum of the European Geological Survey (Plant et al., 1997), the active stream sediments were collected from the small, second order, drainage basin at a suitable site above the point of its confluence with the main, third order, channel of the large drainage basin.

Thirteen stream sediment samples were collected from the study area (**Figure 1b**) and sample locations were marked on compilation maps and digitized. Each

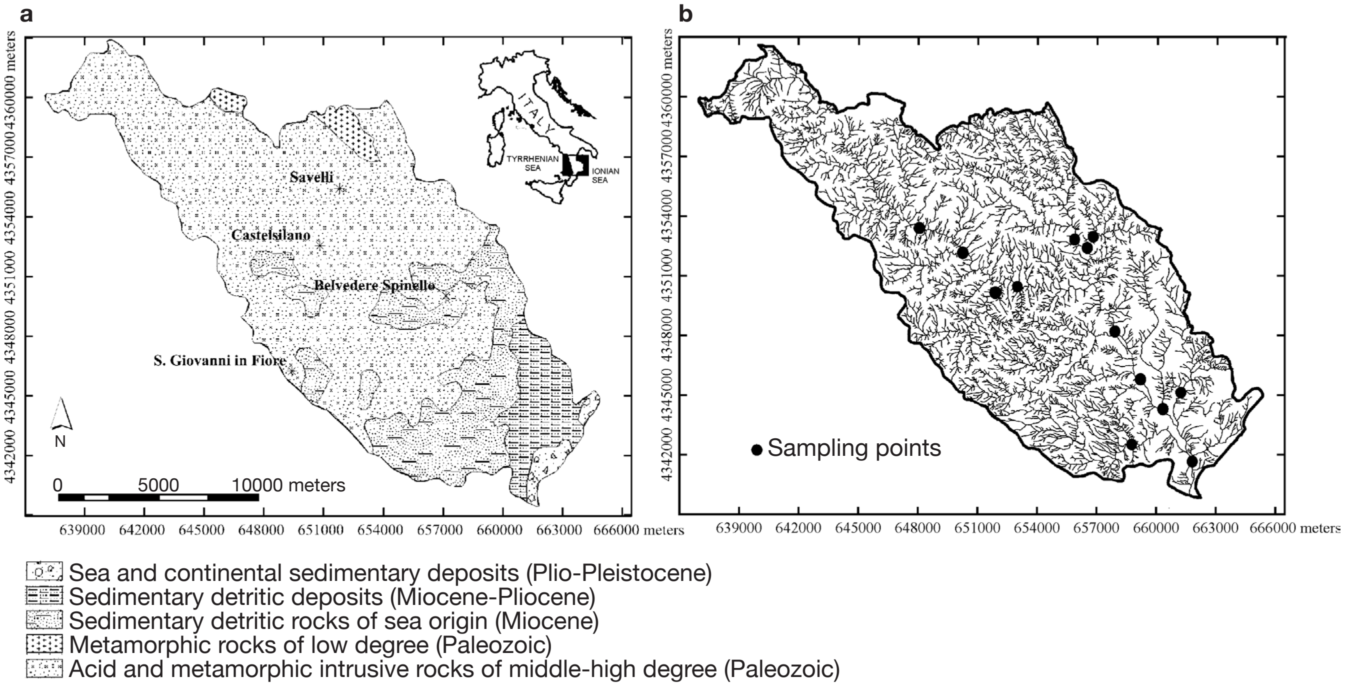

Figure 1. a: Geological sketch map of Lese river catchment that consists of metamorphic rocks and a sedimentary turbiditic succession — *Schéma géologique du bassin du fleuve Lese qui est constitué de roches métamorphosiques et de roches sédimentaires torbiditique en série*; **b:** Sampling map of study area with the indications of the 13 investigated sites — *Plan de l'échantillonnage de la zone d'étude avec l'indication des 13 sites étudiés.*

stream sediment sample includes material collected from 5-10 points over a stream segment of 250-500 m. The entire set of samples were collected with a plastic spatula and kept in PVC packages. Then, following FOREGS procedures, part of these samples was initially sieved *in situ* to a grain size of < 2,000 µm so as to remove coarse sand and after through a 150 µm sieve to pick up mud, clay and colloidal particles. Metal free nylon sieve-mesh housed in inert wood was used.

All the samples were moved onto a sheet of filter paper in the laboratory and placed into an oven at 50 °C for a varying period of three to five days on the basis of the greater or lesser presence of water in the sediments.

The bulk stream sediment samples were sieved through an unified series of sieves from > 2,000 µm to < 63 µm (ASTM codes) by using mechanical sieves. Quantitative assessment of the percentage of different grain size in stream sediments was performed and the distribution of different size fractions was determined by weighing the contents of each sieve.

Each size fraction in the samples was ground up into powder within a mechanical agate mortar and boric-acid backed pellets were prepared with the powder for X-ray fluorescence spectrometry (XRF).

Elemental analyses for major and some trace elements were obtained by Philips PW 1480 X-ray fluorescence spectrometry in the X-ray laboratory of the University of Calabria (Italy).

Ten oxides of major elements (NaO, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3) and fifteen trace elements (Ni, Cr, V, La, Ce, Co, Ba, As, Pb, Zn, Nb, Zr, Y, Sr, Rb) were determined on bulk sample, on seven size fractions (> 2,000 µm, 2,000-500 µm, 500-250 µm, 250-125 µm, 125-63 µm, < 63 µm) and particularly on the size fraction < 150 µm. Total loss on ignition (L.O.I.) was determined after heating the samples for 3 h at 900 °C.

To understand the significance of the geochemical composition of stream sediments, five samples of the main rocks present in the study area (evaporites, clays, schists, quartzites and granodiorites) were collected on outcrops. Portions of the rock samples were ground to fine particles, using a mechanical agate grinder, before being analyzed. The analyses of the rock samples, on pressed powder disks, were also carried out at the X-ray laboratory of the University of Calabria (Italy) by using the same X-ray fluorescence spectrometry utilized for stream sediment samples.

Accuracy of the data was determined as < 3% through analysis of the U.S. Geological Survey standards AGV-1, BCR-1, BR, DR-N, GA, GSP-1, and NIM-G, at the rate of 1 per each batch of 10 samples. The precision (< 5%) was determined by analysis of duplicate samples. During the analyses, tested methodologies of quality guarantee were applied for a good level of data reliability.

3. RESULTS AND DISCUSSION

3.1. Grain-size distribution

The study of the pattern of grain-size distribution in river-transported sediments is important because it is a source-rock-specific primary feature.

The curves of cumulative frequency for almost all of the samples show a high degree of homogeneity: indeed the sandy fraction, with about 83% of total percentages in weight of all samples on average, was most present, while the others, gravelly and silty-clayey fractions, showed lower percentages in weight. These results are displayed in **table 1**.

3.2. Geochemistry

Comparison of major and trace element concentrations in the different size fractions of stream sediments in the studied river catchment is shown in **table 2**. The stream sediment composition is strongly affected by the rock chemistry of the area.

It is useful to examine the available data through some binary diagrams in which the bulk compositions of the 13 samples are compared with the average compositions of local evaporites, clays, schists, quartzites and granodiorites. The trends identified include variations that almost always lie within the compositional ranges (mean values) of outcropping lithologies as well as some rare anomalies of some elements that are outside these ranges.

In the diagrams for these trends, silica was selected as a reference variable because it is one of the largest components of all rock types in the study area, although there are strong differences between evaporites (6,55% in weight), granodiorites (70,85%) and quartzites (75,35%). Almost all samples fall within the compositional field defined by the average contents of local clays, granodiorities and quartzites suggesting that stream sediments are strongly influenced by local geology. In **figure 2** some representative elements are shown.

The influence of local rock chemistry was also confirmed in some diagrams, shown in **figure 3**, on the particle size fraction > 2,000 µm, where two populations of samples can be easily separated, in comparison to the considered elements.

Table 1. Particle size distribution of Lese sediments — *Distribution granulométrique des sédiments du fleuve Lese.*

	Min (%)	**Max** (%)	**Mean** (%)	**St. Dev.**
Gravel	0	29.93	13.14	9.59
Sand	65.85	97.47	83.51	9.70
Silt-clayey	0.70	10.55	3.34	2.92

An initial group, including the samples C2, C7, C9, C10, C11 and C12, is characterized by low values of FME (Fe_2O_3, Ni, Cr, Co) and TiO_2, suggesting a derivation of the sediments by lithological intrusive acid outcrops. A second group, less homogeneous than the first one, includes the samples C1, C3, C4, CZ, LE1, C8.1 and C8.2 that showed a wider range in values of all the considered elements, although they are always higher than those relating to the first group. The origin of the sediment, in this case, can probably be ascribed to schists and gneiss.

Due to their common origin, geochemically similar sediments would be expected to have the same behavior, but there are two different main populations due to source variations or physical and/or chemical processes that systematically modify sediment composition.

From an environmental perspective, trends represent elemental natural background behavior.

The study of the chemical composition of the stream sediments allowed us not only to assess how it is influenced by the geological substrate, but also to evaluate the chemical effects due to hydraulic sorting. In fact these effects, together with the particle-size of the stream sands, notably influence the chemical composition of samples according to parent rock mineralogy.

The compositional changes among just three particle-size fractions, > 2,000 µm, 500-250 µm and < 63 µm, were represented by using spider diagrams normalized to the bulk composition of each sample so that rates higher or lower than 1 indicate element enrichment or depletion, respectively, in the considered

Table 2. Statistical analysis and comparison of major and trace element concentrations in the different size fractions of Lese sediments — *Analyse statistique et comparaison des concentrations en éléments majeurs et en eléments traces dans les différentes fractions granulométriques des sédiments du fleuve Lese.*

	Unit	**> 2,000 μm**				**2,000-500 μm**				**500-250 μm**			
		Min	**Max**	**Mean**	**St. Dev.**	**Min**	**Max**	**Mean**	**St. Dev.**	**Min**	**Max**	**Mean**	**St. Dev.**
NaO	% wt	0.7	3.5	2.4	0.9	1.0	2.4	2.0	0.5	0.8	2.4	2.0	0.5
MgO	% wt	1.2	3.8	1.7	0.7	0.7	3.1	2.1	0.8	0.7	3.8	2.1	0.9
Al_2O_3	% wt	5.9	15.9	13.3	3.5	5.6	15.3	12.7	3.2	5.9	16.0	12.6	3.2
SiO_2	% wt	36.4	72.2	64.7	11.6	46.2	74.5	67.2	6.9	40.3	74.1	67.0	8.4
P_2O_5	% wt	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0
K_2O	% wt	1.2	4.2	3.2	0.9	1.8	4.4	3.7	0.8	1.5	4.2	3.6	0.8
CaO	% wt	0.8	27.3	5.3	8.8	1.0	20.0	3.9	6.0	0.9	23.6	4.2	6.6
TiO_2	% wt	0.2	0.5	0.3	0.1	0.1	0.7	0.4	0.2	0.1	0.8	0.4	0.2
MnO	% wt	0.0	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.1	0.0
Fe_2O_3	% wt	2.0	4.1	2.9	0.8	1.2	5.0	3.3	1.1	1.2	5.2	3.4	1.1
Ni	ppm	5.0	36.0	15.2	9.6	5.0	39.0	11.7	8.9	5.0	56.0	13.2	13.3
Cr	ppm	11.0	51.0	29.0	15.3	12.0	31.0	19.0	6.6	13.0	39.0	21.4	7.9
V	ppm	27.0	80.0	47.0	14.7	14.0	84.0	51.7	22.4	14.0	93.0	52.5	22.3
La	ppm	18.0	31.0	22.5	4.7	6.0	32.0	19.2	8.2	10.0	42.0	24.0	8.8
Ce	ppm	30.0	58.0	42.5	10.2	13.0	60.0	31.2	12.6	15.0	72.0	44.2	15.9
Co	ppm	5.0	11.0	7.5	2.3	4.0	12.0	8.2	2.2	4.0	14.0	8.6	2.6
Ba	ppm	502.0	990.0	728.8	132.1	541.0	1265.0	801.5	159.8	484.0	2390.0	853.6	478.5
As	ppm	2.0	10.0	5.1	2.7	2.0	9.0	5.8	2.2	3.0	12.0	6.7	3.3
Pb	ppm	8.0	54.0	17.8	12.7	10.0	26.0	19.1	4.1	7.0	35.0	19.2	6.2
Zn	ppm	24.0	86.0	45.5	21.7	8.0	101.0	50.3	24.3	5.0	86.0	53.2	23.4
Nb	ppm	4.0	12.0	7.1	3.0	0.0	16.0	8.0	4.8	0.0	13.0	8.1	4.3
Zr	ppm	87.0	176.0	125.5	29.4	72.0	215.0	120.2	37.5	64.0	237.0	117.6	41.7
Y	ppm	2.0	25.0	14.8	7.4	0.0	17.0	11.1	6.1	1.0	17.0	11.7	5.4
Sr	ppm	100.0	5319.0	754.8	1461.8	125.0	6641.0	778.7	1856.6	118.0	7323.0	768.9	1976.5
Rb	ppm	52.0	147.0	110.8	27.1	62.0	142.0	116.3	24.5	58.0	133.0	112.6	20.8

Table 2 (continued). Statistical analysis and comparison of major and trace element concentrations in the different size fractions of Lese sediments — *Analyse statistique et comparaison des concentrations en éléments majeurs et en eléments trace dans les différentes fractions granulométriques des sédiments du fleuve Lese.*

	Unit	**250-125 μm**				**125-63 μm**				**<63 μm**			
		Min	**Max**	**Mean**	**St. Dev.**	**Min**	Max	Mean	St. Dev.	Min	Max	Mean	St. Dev.
NaO	% wt	0.8	2.7	2.1	0.5	0.6	2.5	1.7	0.5	0.6	2.5	1.5	0.5
MgO	% wt	0.9	2.9	1.9	0.6	1.9	4.4	2.8	0.7	2.5	5.0	3.3	0.8
Al_2O_3	% wt	5.9	14.8	12.3	2.9	8.6	17.7	14.1	2.8	8.8	18.6	15.2	3.4
SiO_2	% wt	36.3	72.2	65.5	9.4	38.4	67.1	59.3	8.3	37.2	61.0	53.6	6.6
P_2O_5	% wt	0.1	0.2	0.1	0.0	0.1	0.2	0.2	0.0	0.2	0.4	0.2	0.1
K_2O	% wt	1.3	3.8	3.2	0.7	1.5	3.4	2.9	0.6	1.4	3.6	2.7	0.6
CaO	% wt	0.9	25.2	5.0	7.0	1.4	21.8	6.6	6.6	1.9	19.9	6.9	6.0
TiO_2	% wt	0.2	0.6	0.4	0.1	0.4	0.9	0.6	0.2	0.4	1.0	0.7	0.2
MnO	% wt	0.0	0.2	0.1	0.0	0.1	0.2	0.1	0.0	0.1	0.1	0.1	0.0
Fe_2O_3	% wt	1.5	6.0	3.7	1.1	3.0	5.9	4.4	0.7	3.9	6.7	5.1	0.8
Ni	ppm	4.0	68.0	16.4	16.8	8.0	58.0	21.5	13.8	12.0	61.0	34.2	14.8
Cr	ppm	16.0	44.0	26.4	7.7	26.0	69.0	45.3	12.6	38.0	135.0	79.7	25.8
V	ppm	21.0	117.0	59.8	24.1	57.0	103.0	76.8	13.5	81.0	125.0	96.2	13.3
La	ppm	14.0	48.0	32.2	10.9	25.0	53.0	36.6	9.5	24.0	73.0	46.9	16.1
Ce	ppm	14.0	100.0	64.4	24.1	31.0	114.0	67.8	23.9	53.0	140.0	94.1	30.8
Co	ppm	6.0	17.0	10.2	3.1	9.0	18.0	11.2	2.6	13.0	18.0	14.7	1.7
Ba	ppm	441.0	1993.0	820.2	408.3	372.0	848.0	625.6	118.3	360.0	695.0	590.8	95.8
As	ppm	3.0	19.0	8.6	5.0	3.0	27.0	9.8	7.2	5.0	24.0	10.7	6.9
Pb	ppm	12.0	38.0	21.4	7.0	9.0	39.0	24.1	8.4	12.0	49.0	27.4	10.0
Zn	ppm	14.0	107.0	59.7	25.3	29.0	137.0	70.6	32.1	54.0	147.0	96.2	28.8
Nb	ppm	1.0	11.0	8.2	3.3	5.0	14.0	10.9	3.1	6.0	18.0	13.0	3.4
Zr	ppm	72.0	179.0	129.0	30.8	167.0	662.0	339.9	167.9	258.0	1454.0	754.3	459.6
Y	ppm	3.0	24.0	16.9	6.2	8.0	50.0	30.8	12.6	12.0	86.0	50.8	24.0
Sr	ppm	118.0	5335.0	627.8	1423.1	122.0	4902.0	665.4	1297.4	127.0	6123.0	819.6	1630.4
Rb	ppm	54.0	120.0	105.0	18.6	65.0	137.0	107.6	18.0	67.0	141.0	114.1	22.6

fraction. In these representations, it was observed that the particle-size fraction that was compositionally most different from the bulk composition was that of < 63 µm (**Figure 4**).

The effects of particle-size and grain shape are responsible for the concentration of clay minerals in concomitance with a decrease of quartz and feldspar in the finest fraction. In the < 63 µm particle-size, this produces a decrease in SiO_2 and a corresponding increase in the content of other elements, such as Al_2O_3, K_2O and TiO_2, and many trace elements that are probably related to clay minerals and/or iron oxides. In particular, these elements may enter the crystal lattice of these mineral phases or be adsorbed on their charged surfaces as a consequence of pedogenetic processes (Nesbitt, 1979; Patino et al., 2003; Caspari et al., 2006). Argast et al. (1987) suggest that, in the silty-clayey fraction (< 63 µm), potassium is transported in the form of detrital or neogenic illite in which the principal inter-layer cation is potassium. The positive correlation between Al_2O_3 and K_2O existing in the < 63 µm fraction confirmed that the finest fraction contains the most detrital or neogenic illite and that, in contrast, the coarse fraction (> 2,000 µm) contained the most quartz. If the siliciclastic component is considered to be the source of quartz in the bed sediment, the regression for SiO_2 *versus* Al_2O_3 can be interpreted as tracing the change in composition of this two-component system as the Al-silicate minerals are selectively removed by sediment winnowing or chemical leaching.

Fe_2O_3, Co and Cr show higher values of concentration in the silty-clayey fractions than in

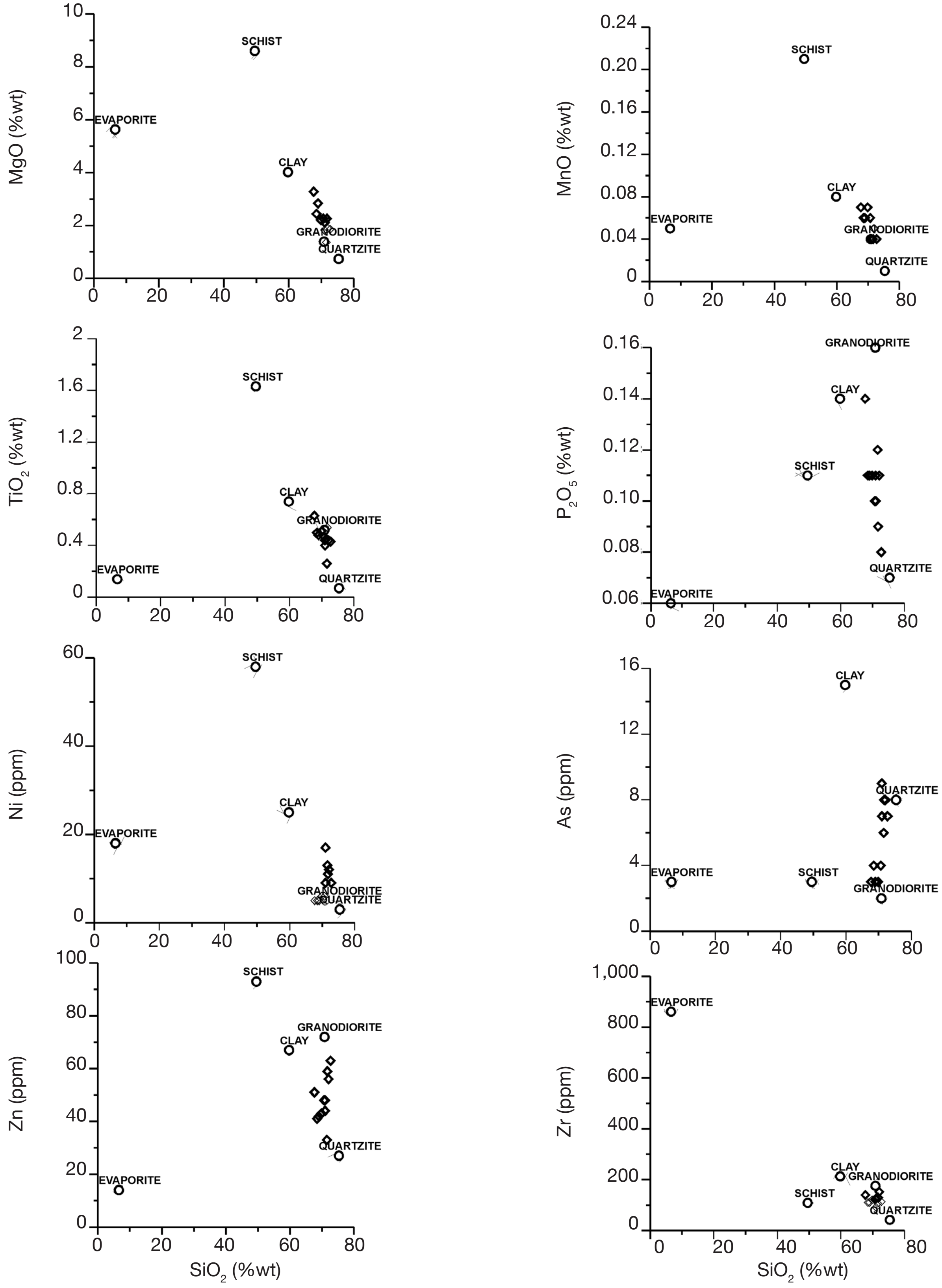

Figure 2. Correlation diagrams — *Diagrammes de corrélation.*

Bulk compositions of samples are compared with the local average compositions of local rock types for some representative elements — *Les compositions de la masse des échantillons sont comparées avec les compositions moyennes des roches locales pour certains éléments représentatifs.* ○: lithological outcrops composition — *composition lithologique des affleurements;* ◇: stream sediments composition — *composition des sédiments fluviaux.*

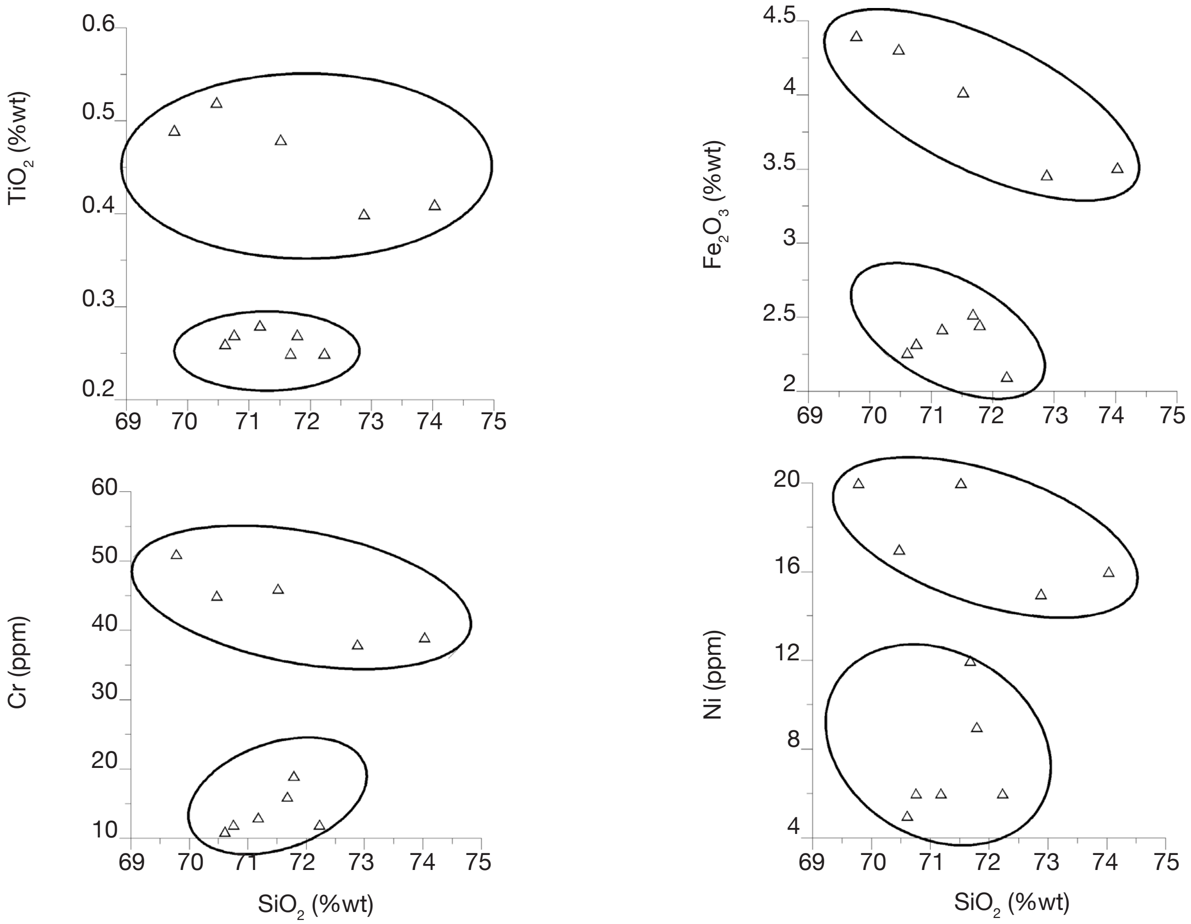

Figure 3. Elemental concentration in the particle size fraction > 2,000 µm — *Concentration des éléments de la fraction granulométrique > 2 000 µm.*

Two populations of samples can be easily separated, such as represented with ellipses — *Les deux populations d'échantillons peuvent être facilement séparées, comme représenté par les ellipses.*

the coarse ones (**Figure 4**). This may be related to a greater concentration of biotite, chlorite, and magnetite crystals in the silty-clayey fraction of the sediment (Cullers, 1988).

Data on the study area show correlations between these elements and certain minerals. These associations are described by some authors, such as Deer et al. (1992) who reported that sphene, zircon and rutile are associated with magnetite and probably account for the strong relations between magnetite and Fe, Co and Cr. This is also true for Lese sediments where, furthermore, Ca, Mg, Ti and V are associated too.

In the silty-clayey fractions, more elevated concentrations of Zr and Y were found. The positive correlation ($R^2 = 0.851$) between these two elements (**Figure 5**) suggests the presence of zircon crystals. Indeed, zircon is an accessory residual mineral that is common in many sediments, in which it is often resistant to more than one cycle of alteration (Wu et al., 2004). Thus grain-size effects may contribute to a high zircon concentration in the < 63 *µ*m fraction.

The positive correlation between Fe_2O_3 and V ($R^2 = 0.665$) (**Figure 5**) clearly suggests that their abundance is related to the presence of iron-rich chlorite in the finest fractions. Indeed, chlorite often occurs in clay minerals in fine iron-rich sediments, because the deficit of negative charge left in it by aluminium is balanced by the Fe^{3+} ion (Le Pera et al., 2000).

The contents of some trace elements, such as La, Ce, Zr and Y, were very low in the sandy fraction, due to its being particularly depleted in transition elements, in comparison with the other fractions and the bulk sample. The transition elements are located in the octahedral layers and/or adsorbed on to negatively charged surfaces of clay minerals. In the < 63 µm fraction, an enrichment of these elements was noticed together with an increase of Al_2O_3, which indicates a dominant influence on element fractionation by weathering and pedogenetic processes (Mongelli, 1993; Laveuf et al., 2009; Scarciglia et al., 2011).

For the bulk composition, the lack of any significant relationship between SiO_2 and Sr was noticed together

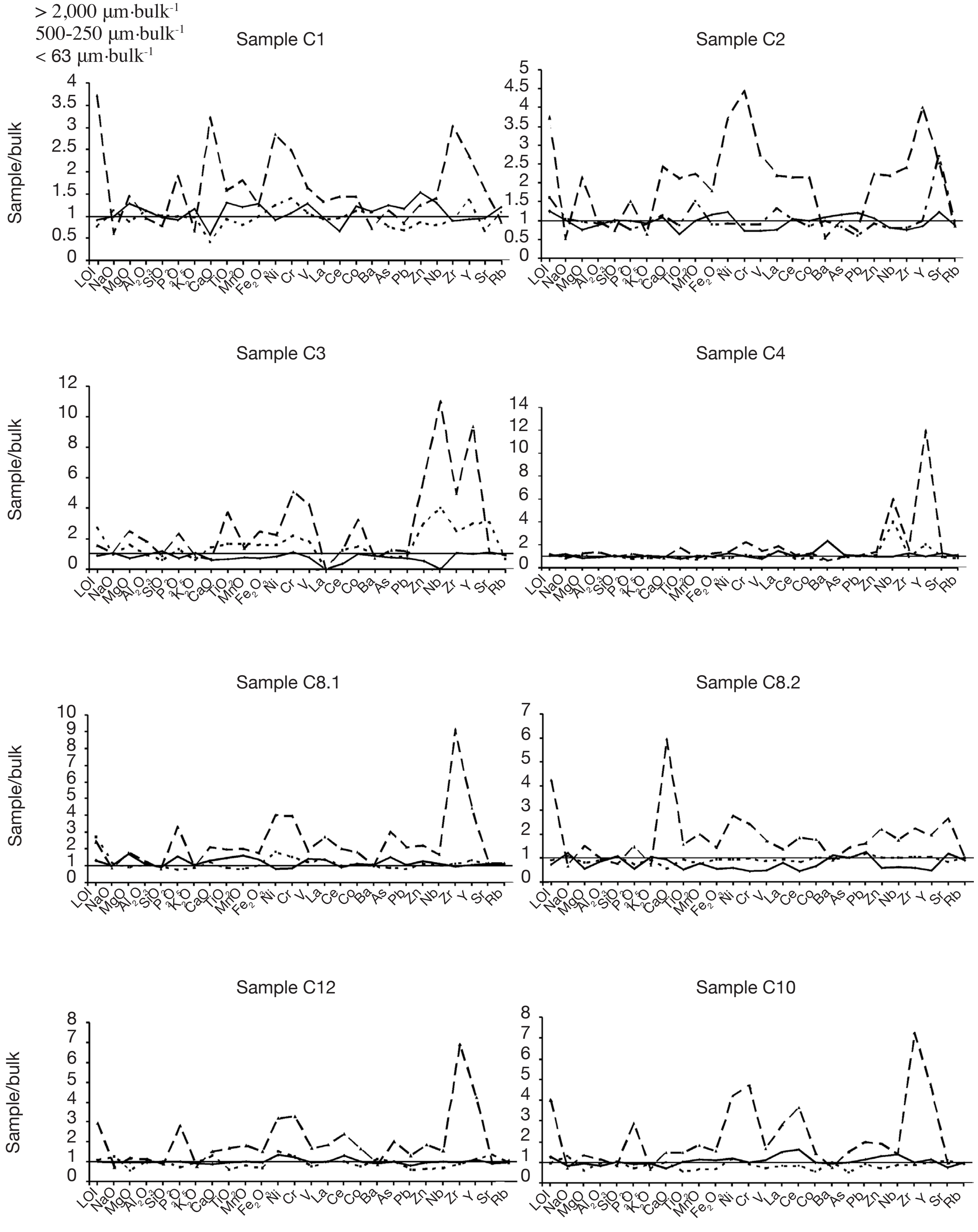

Figure 4. Bulk normalized plots of data from three size fractions (> 2,000 µm, 500-250 µm and <63 µm) of the same samples — *Diagrammes normalisés à la totalité des échantillons de trois des fractions granulométriques (> 2 000 µm, 500-250 µm et < 63 µm) des mêmes échantillons.*

The compositional changes are represented with spider diagrams normalized to the bulk composition of each sample — *Les changements de composition sont représentés par des diagrammes spider normalisés à la composition totale de chaque échantillon.*

with a high correlation ($R^2 = 0.867$) between Sr and CaO: this behavior suggests that strontium may replace calcium in calcite or aragonite (Reimann et al., 2003).

3.3. Is < 150 µm the optimum fraction for chemical analysis?

Recommendations in the FOREGS Geochemical Mapping Field Manual (Salminen et al., 1998) regarding the optimum fraction indicate < 150 µm as being the most appropriate fraction for chemical analysis, because it is not only fine enough to include the very fine sand, silt, clay and colloidal fractions, but it is also coarse enough to yield sufficient fine material in the majority of situations. In this study, we tested this assumption by comparing seven particle-size fractions, as well as the < 150 µm, in order to corroborate or contradict the recommendations of FOREGS. The main results of this comparison are displayed in some binary diagrams (**Figure 6**), which show that the < 150 µm fraction encapsulates the entire stream sediment well and reproduces its dominant geochemical behavior. This confirms the validity of the FOREGS assumption that considers the < 150 µm fraction to be the optimum fraction for chemical analysis.

3.4. Evaluation of the regulatory thresholds of element contamination

The Italian government has established intervention values for some selected toxic elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V and Zn) in soil and stream water (Ministero dell'Ambiente, 2006), but not for stream sediment. By adopting the same thresholds for sediments as for soils, it was noticed that two elements exceeded the regulatory thresholds which are considered acceptable in sites destined for public, private and residential green use (Limit A of Italian Legislative Decree No. 152 of 03/04/2006).

More precisely, arsenic exceeded the regulatory threshold (20 ppm) of concentration for 18% of the analyzed sediments in the < 150 µm fraction of

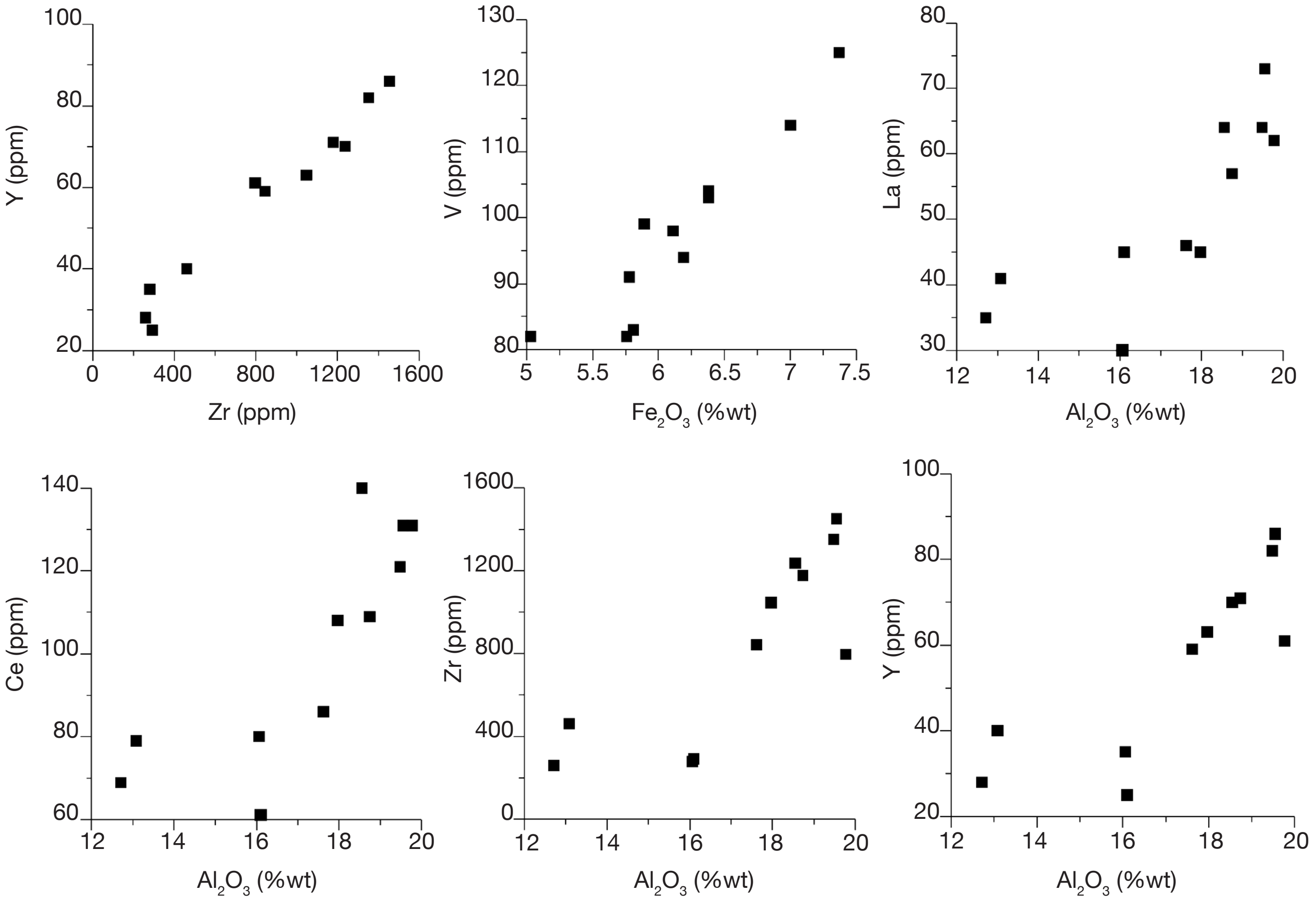

Figure 5. Elemental concentration in the particle size fraction < 63 µm — *Concentration des éléments dans la fraction granulométrique < 63 µm.*

In these graphs are showed the positive correlations between the considered elements — C*es graphiques montrent les relations positives entre les éléments étudiés.*

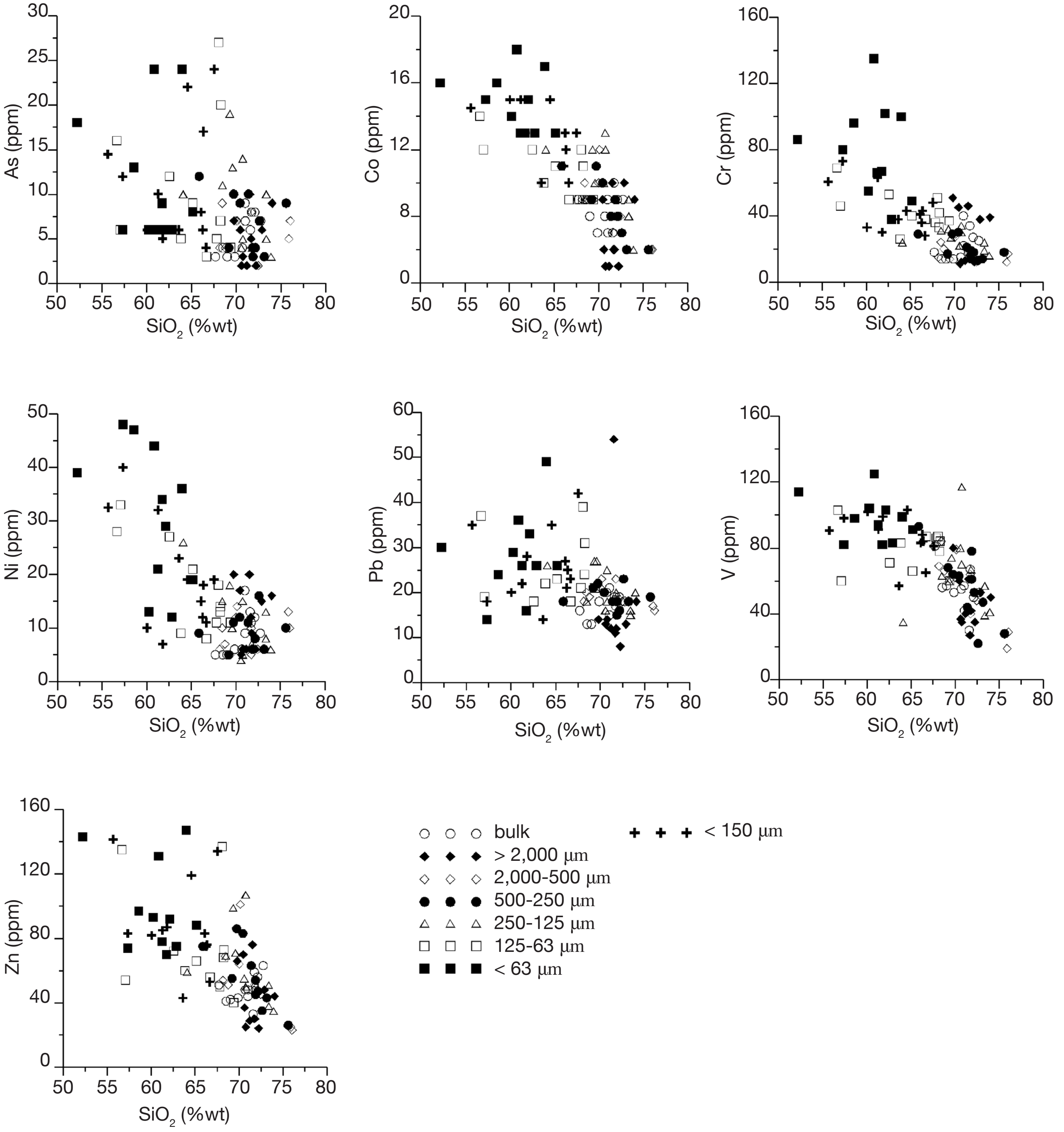

Figure 6. Comparison of elemental concentration in all size fractions and in < 150 µm — *Comparaison de la concentration des éléments dans chaque fraction granulométrique et dans la fraction < 150 µm.*

In these graphs it is clearly displayed that the < 150 µm fraction is well able to represent the whole stream sediment such as indicated in FOREGS — *Ces graphiques montrent clairement que la fraction < 150 µm est parfaitement capable de représenter la totalité des sédiments fluviaux, comme le FOREGS l'indique.*

the CZ and C8.1 samples. Vanadium exceeded the regulatory threshold (90 ppm) in 50% of the analyzed samples, particularly in the < 150 µm fraction of the C1, C4, LE1, C8.1, C8.2, C9 and C10 samples. In all the analyzed samples, the values of cobalt, chrome, nickel, lead and zinc concentration fell below Limit A and were, therefore, within the limits of acceptability imposed by the Decree.

4. CONCLUSION

The elemental distribution in different grain size fractions of stream sediments is a very important aspect that needs special emphasis in geochemical exploration.

The Lese catchment provided an excellent opportunity for evaluating how particle-size influences the geochemical distribution of stream sediments and for formulating some considerations on their relationships with mineralogical assemblages of parent rocks. This study proved that element concentration levels vary significantly with grain size.

All the stream sediment samples analyzed displayed one prevailing particle size fraction, *i.e.* the sand-grained fraction, which is far more evident than both the finer and coarser fractions.

Analysis of element concentrations in the bulk compositions suggests that local lithologies are the main factor in their distributions. The chemical analyses of some major and trace elements showed a clear geochemical imprint that allowed the possible mineralogical composition to be hypothesized.

The comparison of the patterns relating to the three fractions, chosen as representatives of the whole set of samples, underlined the behavior of some elements within the fractions. Among other things, the decrease in SiO_2 and the corresponding increase in the content of other elements, such as Al_2O_3, K_2O, TiO_2 and most trace elements, suggest that they are probably bound in the clay mineral or iron oxide crystal lattices or adsorbed on their charged surfaces, in the < 63 µm fraction. Due to their size and morphology, as well as mechanical sorting or pedogenesis, the phyllosilicates usually dominate the finest sedimentary fraction, while quartz and feldspar dominate the coarsest.

The study of all the particle size fractions, and not only the < 150 µm fraction used in standard procedure, allowed better detailing of the concentration behavior within the sampled sediments. Indeed, thanks to this more detailed analysis, it was possible to get results on element distributions, within single samples, in terms of their particle size distribution and the presumed mineralogy of their parent rocks.

Although the < 150 µm fraction appears to capture the entire stream sediment composition well, only the complete set of particle size fractions permits the tracing and correct interpretation of their specific geochemical distribution and behavior.

Therefore, this paper allows optimization of the analytical procedure for the determination of the chemical elements in stream sediments.

In addition, it emerged from the chemical analysis that two elements, arsenic and vanadium, exceeded the threshold imposed by Italian Legislative Decree No. 152/2006. This result suggests that, given that it represents an important tool to preserve human health, the geochemistry of stream sediments also needs to be characterized in order to evaluate potential chemical pollution of an area.

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