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STORAGE AND ORIGIN OF METALS IN ACTIVE STREAM SEDIMENTS FROM MOUNTAINOUS RIVERS: A CASE STUDY IN THE RIVER DOURO BASIN (NORTH PORTUGAL)

Anabela Reis[1], Andrew Parker[2], Ana Alencoão[1]

1. Department of Geology, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal, Centre for Geophysics, University of Coimbra, Coimbra, Portugal, anarreis@utad.pt, **corresponding author**

1. Department of Geology, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal, Centre for Geophysics, University of Coimbra, Coimbra, Portugal, alencoao@utad.pt

2. Soil Research Group, School of Human and Environmental Sciences, University of Reading, UK, a.parker975@btinternet.com

Abstract

The study area is located in the transboundary River Douro basin (northern Portugal); it comprises the River Corgo fluvial network, which drains a meso-scale rural catchment with an area of 295 km^2, underlain by crystalline rocks, in a temperate climate. The results reported in this study derive from a geochemical survey of active fluvial sediments, with the aim of characterising the spatial and temporal distribution of the contents of Cd, Co, Cr, Ni, Cu, Zn, Pb, Fe and Mn, in a basin with mountainous features. To assess total contents of metals and their potential availability, as well as possible different origins of metals (natural vs. anthropogenic), a sequential chemical approach was used (modified BCR procedure). Multivariate data analysis (PCA) was used to assist the interpretation of datasets.

The results show that, on the one hand, the metal contents distribute among all the geochemical phases studied. For the most relative labile fractions the reducible fraction is the most significant. The element-partitioning among geochemical phases indicates: a) Co and Mn are transported in greater proportions in the most labile fraction, as exchangeable ions, as well as important proportions of Ni, Zn and Cu; b) Cd and Pb associate preferentially with the hydroxides of Fe and Mn; c) Cr and Cu are also transported by the organic phase; d) the residual phase transport important proportions of Cr, Ni, Zn, Cu, Fe and Pb. The higher concentrations of Cu, Zn and, in particular, Pb, in the most labile fractions, which are higher where the total contents are also higher (and not concomitant with a correspondent increase in the residual fraction), suggest an important contribution of anthropogenic activities to the total contents of these elements in the sediments. Chromium and Ni are the main metals from a lithological source, with relatively higher contents in the residual fraction, and the lowest in the most mobile fractions. On the other hand, the spatial distribution pattern of metal contents in the mobile and semi-mobile fractions (available + reducible + oxidisable), shows that, in general, higher contents of metals in the most mobile fractions occur along the main courses of the major tributaries, in particular in the flatter reaches. The patterns of seasonal occurrence and distribution of metals show, in general, that the relative contents associated with the potentially available fraction increase during the period of low flow, which extends from April to September.

1. Introduction

The concentration of human activities in urban environments has lead to an increase in levels and diversity of contaminants (organic and inorganic), mainly transported by runoff to aquatic systems. In agricultural lands, it is the application of substances to achieve higher yields, in addition to anthropogenic erosion of soils and irrigation, which affect the water quality. In a catchment context, the effective water-resources management should be based on recognition of these diffuse and point-pollution sources, regarding its combined effects. The knowledge of the source, fate and transport of contaminants is helpful to manage many water-quality degradation problems.

Studies of river pollution and the quality of stream sediments have increased over the last few decades. However, sediment-pollutant dynamics and related water quality in mountainous areas with a temperate climate, underlain by crystalline rocks, are still not well understood (Wohl, 2006; Symader *et al.*, 2007). Mountainous rivers have an important role in the transport of sediments: they have a lower water-storage capacity and a quicker response to short precipitation episodes, therefore transporting significant sedimentary loads, with associated pollutants, in short periods of time.

The results reported in this study derive from a geochemical survey of oxic active fluvial sediments in a basin with mountainous features – the River Corgo catchment in north-eastern Portugal. The main objective is to investigate the storage, availability and possible origin of sediment pollutants in mountainous rural rivers in a temperate climate. At the regional scale it is an important study, because as a consequence of the geological setting, most of the water used in human consumption comes from dammed reservoirs. There is also a recognised lack of knowledge of pollution at basin scale in the Douro Region – classified as UNESCO World Heritage, and about the amount of contaminants that are introduced in fluvial systems (SedNet, 2007).

2. Study Area

2.1 Locality

The River Corgo catchment is a meso-scale mountainous rural basin located in a temperate climate, in the Trás-os-Montes e Alto Douro province (northwest Portugal); the river is a tributary in the trans-boundary Douro river basin (Fig. 1), in the well-known Douro Region – a world heritage site classified by UNESCO. The River Corgo rises near the village of Vila Pouca de Aguiar, crosses Vila Real city, and the confluence with the River Douro is in the village of Peso da Régua.

2.2 Geological setting

In the southern part of the basin, Palaeozoic metasediments outcrop (Fig. 2). These are composed essentially of alternating phyllites and greywackes, dating from the Cambrian (Sousa, 1982), and a conglomerate overlain by alternating quartzites and phyllites, with iron-rich levels interlayered (Pereira, 1989), dating from the Ordovician. These were involved in mining activities until 1979, in the Vila Cova Mines (Neiva, 1946). In the northern part of the basin granitic rocks occur. In the Campeã Valley, mineralised quartz veins with Cu, Pb and Zn sulphides are dispersed in crystalline rocks; one of these was mined in the Facuca Mines (Neiva, 1951). In the northern part of the basin, granites intruded the older metamorphic rocks. The oldest ones are two-mica, fine to medium-grained (Pereira, 1989; Gomes, 1989; Matos, 1991; Neiva and Gomes, 1991); the most recent are biotitic granites (Pereira, 1989, Martins, 1998).

Locally the crystalline rocks are covered by sedimentary deposits from the Cenozoic, with major expression in the Campeã valley, in the southwest area, the Vila Pouca de Aguiar valley (Lourenço, 1997), in the northern area, and Vila Real basin (Baptista, 1998). These valleys have a plan basement; the deposition of these sediments was controlled mainly by the major tectonic structure Penacova-Régua-Verin fault (Gutiérrez Claverol *et al.*, 1987), which originated the Vila Real basin and the Telões basin in Vila Pouca de Aguiar, along this fault zone.

2.3 Catchment morphology and land use

The geomorphology of the Corgo valley is controlled mainly by the lithology and tectonics. The study area of 295 km^2 comprises the River Corgo catchment up to the gauge station Ermida; the altitudes vary between 130 m and 1400 m and the hillslopes are between 0 and 20%. There are two main tributaries of the River Corgo in the study area, both in the western margin. The River Cabril, flows from the north parallel to the Corgo, in the Vila Real basin to join the latter just south of Vila Real. The River Sordo, in the south-western part of the basin, flows from the west, draining upstream the Campeã valley, to join the Corgo at about 2 km south of Vila Real. The main river, drains in its more upstream reach, the large valley of the Vila Pouca de Aguiar basin. Downstream these large valleys, the channels became narrow and incised, alternating between steep riffles and quiet pools. The remainder of the basin is drained by a few smaller tributaries, mainly in the eastern margin. Frequently, the streambed is composed, of exposed bedrock, boulders and cobbles.

The shape and the slope of the drained valleys lead to a quick response to precipitation events. During the rainy season, in the lower reaches, the fluvial water-level can raise several metres (3.5 m) above its medium level; through these flood events the water velocity is high. In the valleys of Telões and Campeã the flooding is widespread over the banks in lower reaches, inundating large areas of land for several days.

The land is occupied mainly by forest and natural vegetation in the highlands, and agriculture, which predominates in the valleys (Fig.3). After Vila Real, the Corgo runs through the terrains of the vineyards of the Douro Region. Urban settlements are spread throughout the basin area. Industrial activity is scarce.

3. Methodology

3.1. Sampling and sampling preparation

A total of 107 stream sediment samples were collected in 2004 (sampling network is presented in Fig.3), during two sampling campaigns: one at the end of the wet period (WP) in April, and the other at the end of the dry period (DP) in October. The sampling was planned (Mudroch & Azcue, 1995; Parker *et al.*, 2007) to obtain a representative spectrum of the variability of the studied parameters in conditions of high and low flow. The year of 2004 was characterized by a rainy winter, followed by a very dry summer period, and the sampling campaign at the end of the Dry Period was done before the first autumn rain. A representative sample of each sampling site was taken manually (about 1 to 3 kg), and the finer and most recently deposited sediment was preferentially sampled – approximately the uppermost 2-3 cm below the interface water-sediment. The samples were stored in plastic bags, adequately sealed and identified, transported to the laboratory at low temperature in thermos boxes and stored at 4 °C, prior to analysis. Sediments were wet-sieved to separate the <63 µm fraction, to minimise the effects of variable grain size and report results on a size-normalised basis (Förstner, 2004). The samples were then oven-dried at 40°C, which is thought to not affect the results of contaminant contents (Kralik, 1999; Förstner, 2004).

3.2. Analyses

To assess the bioavailability of As and metals (Cd, Cr, Ni, Co, Cu, Pb, Zn, Fe, Mn), the modified BCR sequential extraction procedure (Rauret, 1999) was used. This method separates three chemical phases: (a) available – exchangeable metals and metals bound to carbonates (acetic acid, 0.11 mol/dm^3); (b) reducible – metals bound to Fe and Mn oxides (hydroxylamine hydrochloride, 0.5 mol/ dm^3); and (c) oxidisable – metals bound to organic matter and sulphides (hydrogen peroxide, 8.8 mol/ dm^3; ammonium acetate, 1 mol/ dm^3). The residual fraction was then decomposed with *aqua regia*. The elemental concentrations were obtained by ICP-AES.

In each analytical sequence, replicates were used to assess repeatability. To ensure accuracy, an in-house reference material was also used, and analyses of the decomposed total sample were performed. The recovery rates ranged from 84% e 99%, for Co, Cu, Ni, Pb, Zn, Fe and Mn; and from 75% to 115% for As and Cd. The precision of the measurements is about ±5%.

3.3. Chemometric analysis of the data

The multivariate data analysis (Principal Component Analysis – PCA method) was used to explore data structure and to assist the interpretation of geochemical datasets of the River Corgo sediments system. The Statistica 6.0 statistical software program was used to perform PCA of the data. Prior to PCA analysis the data were lognormalized. Variables having very few values above the detection limit were removed before multivariate analysis was applied.

4. Results and discussion

4.1. Partitioning of metals and As in the geochemical phases

The total concentrations of the studied elements (Table 1), considered as the sum of each element contents within the geochemical phases analysed, are relatively higher than the reference values of the stream sediments of unpolluted rivers (Salomons & Forstner, 1984), in particular As, Cd and Zn. The experimental results obtained in the sequential extraction analyses for each one of the studied elements are discussed in the following paragraphs. Fig.4 shows the box-plot diagrams of the variation range of As, Cd, Co, Cr, Cu, Ni, Pb and Zn contents in geochemical phases at the end of the dry period (this is considered to be representative of the metals distribution).

Arsenic and **Cd** show similar distribution patterns. These elements are largely concentrated in the reducible and available phases - bound to the Fe and Mn oxides and hydroxides and as exchangeable cations. The higher contents of As and Cd are observed in a few samples from the eastern tributaries (27, 28, 32, 33, 34, 36) and River Sordo (1, 13, 15); the samples collected along the River Corgo mainstream (38, 57, 58) and in the River Cabril (56) south of Vila Real also show higher contents of Cd. The higher ability of As, that reach of the fluvial system derived from weathering and soil leaching, to be bound to Fe and Mn oxides and hydroxides, is outlined by several authors (Datta & Subramanian, 1997; Ravenscroft *et al.*, 2005). The spatial incidence of higher contents of As suggest that the metamorphic units and the mineralized quartz veins with sulphides outcropping in the central-southern zone of the basin influence the contents of As in the sediments. In addition, the samples with higher contents also show relative higher proportion of these elements in the residual phase. The occurrence of As and Cd in the more available fractions (reducible and exchangeable) and concomitant non-occurrence in the residual fraction, in particular in the samplings from 2004, suggests an anthropogenic origin also, owing to the use of manure (As) and fertilizers with phosphate in agriculture and urban sewage. Most of these samples were collected in sites along the tributaries' main courses.

Cobalt occurs in all the analysed geochemical phases. The available and reducible phases are responsible for the fixation of most of the more labile proportion of Co in the sediments; the less-important phase in its retention is the organics. The contents of Co are higher in the River Sordo catchment, and the concentrations in the residual phase are also higher in the samples from this part of the basin. In the samples collected along the main course of River Corgo in the Vila Pouca de Aguiar valley the organic phase seems to play a more important role in the fixation of Co. The information available on the contents of Co in the rocks outcropping in the Corgo basin indicates that the granitoid rocks from the central part of the basin have higher contents than the schists. However, Co is commonly present in sulpharsenides and arsenides (Goldschmidt & Muir, 1954), which occur in the quartz veins identified in the Campeã valley. In the latter, Noronha *et al*. (2003) identified Co in the first stage of sulphide deposition. In the zone of the Vila Pouca de Aguiar valley there is information about Co contents only for the post-tectonic granites; the higher contents along the main course of the River Sordo might have some influence from urban wastewaters from the Vila Pouca de Aguiar urban settlement. Generally the variation of relative contents between the samples of the Wet Period and the Dry Period shows an irregular trend with small increases or decreases amongst the geochemical fractions depending on the sampling site.

Chromium and **Ni** are present essentially in the residual fraction. Chromium does not occur in the available phase and concentrates more in the organic phase than in the reducible phase. Nickel is distributed amongst the three first phases. The distribution pattern of contents is rather similar all over the basin and between the sampling campaigns.

Zinc and **Cu** exhibit a rather similar distribution pattern. Both metals are largely concentrated in the residual phase but with a significant percentage in the more labile fractions (Zn:

residual>reducible>available>oxidisable; Cu: residual>reducible>oxidisable>available). Zinc occurs in larger amounts in the available fraction when compared with Cu. The organic material is important in the retention of both metals, in a few samples, and apparently is more effective in the retention of Cu. The spatial pattern show as general trend a relative increase in contents from the Wet Period to the Dry Period, related to an increase in the available and reducible phases; in a few sampling sites a relative decrease is registered. The contents of these metals in the residual fraction are similar between the samplings from the Dry and Wet periods. Spatially the contents of Zn and Cu are slightly higher in the River Cabril sub-basin and Zn is also relatively higher in the Vila Pouca de Aguiar valley and in the eastern tributaries samples. These metals show a few anomalous values (Samples 11, 6, 24, 16, 17, 56, 28, 53, 48, 57, 58); some of which are common to the different sampling campaigns for Zn (6, 24, 17, 56, 53, 57, 58). We observe a markedly increase in the three most labile fractions in these samples. In the Stations 6 and 11 (Campeã valley) the peak contents of Cu and Zn are influenced by the mineralisations identified in the Facuca quartz vein. The anomalous contents registered in the River Cabril sub-basin occur in sites of the drainage network under the influence of urban settlements (Sites 22, 24 and 56) and agricultural zones (Sites 16, 17). The organic phase acquires relevance in the stations presenting peak values.

Lead almost does not occur in the available fraction (reducible>residual>oxidisible>>available). In a few samples it does not occur in the residual fraction (Dry Period sampling). This metal shows a strong affinity to the reducible phase, such as Fe and Mn oxides, being associated essentially with reducible>residual>oxidisable phases. Even in the sampling sites showing anomalous values the major proportion of Pb is concentrated in the reducible phase. These sampling sites are 11 and 6, where high contents are attributed to the mineralised quartz veins occurring upstream; the Sites 56, 51, 57 and 58 are under the influence of urban sewage effluents; the Sites 22, 25, 19, 17, 33 and 34 drain areas occupied by mixed urban settlements and small agricultural fields, which are located in the River Cabril catchment and in the Eastern tributaries. The pattern of spatial variation of Pb contents in the studied fractions is similar for both campaigns; the variation between sampling campaigns is irregular; in a few sites we observe a slight increase in contents in the Dry Period campaigns and in others sites a decrease.

Iron is present in the residual phase and is almost absent in the available fraction (residual>reducible>oxidisible>>available). The higher contents are registered in the River Sordo catchment, which are derived from the Ordovician lithologies rich in Fe that outcrop in the drained area. The content peaks in sampling Sites 10, 1, 13 and 14 are related to the mining activities in the Vila Cova mine (Site 10) and the abandoned ore-processing plant located in the vicinity of sampling Site 1. Sites 13 and 14 are located downstream of Site 1 and are influenced by this drained area. The pattern of distribution of Fe is similar for the sampling campaigns.

Manganese occurs essentially as a soluble ion; the percentage in the residual fraction is low (available>reducible>residual>oxidisible). In general the contents are relatively higher in the River Sordo and River Cabril sub-basins (peaks in the Sites 16 and 19), but it is along the River Corgo mainstream in the Vila Pouca de Aguiar valley (Sites 53, 52, 51) and southward Vila Real (Sites 57 and 58) that the highest contents are registered.

4.2. Environmental implications

Considering the assumed relation between bioavailability and mobility (Forstner & Wittmann, 1979; Salomons & Forstner, 1984), the elements can be classed, in general, by potential relative mobility: Co, Mn > As, Cd, Pb > Cu, Zn, Fe > Cr, Ni. Regarding its relative relevance, all the geochemical phases studied are important in the transport of the elements; from the most labile fractions the reducible fraction is the most significant. The observed affinity of the studied elements with the geochemical phases, as a whole, is summarised in the paragraphs below. The results show that Co and Mn are transported in greater proportions in the most labile fraction, as well as important proportions of Cd, Ni, Zn and Cu. The most labile fraction (**available phase**) is an indication of the metal contents that are weakly bound to the sediment. It is considered the most unstable phase and therefore an indication of the pollution potential of the metals linked with the sediments. Several authors attribute to this phase the more recent contamination (e.g. Forstner & Wittmann, 1979; Salomons & Forstner, 1984; Horowitz, 1985; Rauret, 1998). In this study Co and Mn are the metals which show relative higher contents in this phase; Cd, Ni, Zn and Cu are also present as exchangeable metals in the sediments. Relatively higher contents of Cd, in the available fraction, are observed in samples collected in network sites located in the vicinity of urban settlements, in particular in the River Cabril sub-basin and downstream Vila Real urban centre (42, 41, 40, 20, 22, 23, 24, 25, 16, 38, 57, 58). Cobalt (with the exception of the River Sordo sub-basin) and Mn also show some of the higher contents in this phase in some of these samples. Sampling sites 50, 51 and 52 (along the River Corgo main course in the Vila Pouca de Aguiar valley) also show relative increases of Co and Mn in the most available fraction. Hence the significant amounts of Cd, Co and Mn in the most labile fractions and in samples collected in sites under urban influence are attributed to the presence of anthropogenic material.

Arsenic, Cd and Pb associate preferentially to the hydroxides of Fe and Mn (reducible phase), and in relative minor proportions to other more labile fractions, also Co, Zn and Cd. Lead was the metal with the largest proportion in the reducible fraction. The higher proportions of metal contents in this phase occur in the zones of the basin where the total contents are higher.

The organic phase (**oxidisable phase**) is important in the transport of Cr and Cu in the sediments. Arsenic does not occur in this geochemical phase and Co, Zn, Pb and Ni occur in minor proportions. Spatially, the higher contents of Cu in this phase occur in the River Sordo and River Cabril sub-basins. The contents of Ni associated with the oxidisable fraction are higher in the Campeã valley; on the contrary Zn, Pb contents associated with the organics is relatively higher in the Vila Pouca de Aguiar valley and in the River Cabril sub-basin. Copper seems to be sensitive to the occurrence of urban effluent discharges: higher proportions of Cu in the oxidisable phase occur in the samples collected in the vicinity of urban settlements (6, 2, 22, 24, 25, 16, 53, 55, 56, 57, 58). Thus, the results suggest that Cu shows higher affinity to the organics when the organic content increases in the river water and sediments.

The **residual phas**e transport important proportions of Cr, Ni, and Zn, Cu, Fe and Pb. Cr and Ni showed the greatest contents, concentrating almost entirely in this phase. Hence these metals are less available to the fluvial water. The rest of the metals studied also show considerable amounts in the residual fraction, indicating that they also have a natural origin component in their contents, derived from the source rocks outcropping in the basin area.

4.3. Discussion of the results on the partitioning of metals and As in the geochemical phases of the sediments

The general metals distribution pattern, amid the studied geochemical phases of the sediments, is consistent with previous studies (e.g. several studies compiled by Forstner & Wittmann, 1979; Salomons & Forstner, 1984; Salomons *et al.*, 1995), although with some variability on partitioning patterns of metals between geochemical phases (Dawson & Macklin, 1998b, 1998a; Van Ryssen *et al.*, 1999; Song *et al.*, 1999; Birch *et al.*, 2001; Morillo *et al.*, 2002; Akcay *et al.*, 2003; Filgueiras *et al.*, 2004; Reis *et al.*, 2005; Segura *et al.*, 2006; Rath *et al.*, 2009; Passos *et al.*, 2010). The hydrous oxides of Fe and Mn are important as scavengers of all studied metals, as outlined in literature (Jenne, 1968; Whitney, 1975, Macklin & Dowsett, 1989; Hudson-Edwards *et al.*, 1996) followed by the organics.

The affinity of a specific metal for a specific geochemical phase has been outlined by several authors (e.g. Kinninburg *et al.*, 1976 and Jonasson, 1977, as cited by Stone & Droppo, 1996; Salomons & Forstner, 1984; Forstner & Wittmann, 1979; Baruah *et al.*, 1996), in particular, it has been found in several studies that Cd is characteristically enriched in the more mobile fractions and Cu, more than the other metals, shows a tendency to refer the organic phase. The reducible phase is usually an important sink for metals. The behaviour of Cd and Cu in this study, mainly associated with reducible phase, except Cu in the stations under influence of urban effluent discharge, is in contrast to the general trend and to several prior studies mentioned in the above paragraph.

As suggested by several authors, the retention of metals in the Fe-Mn oxides and hydroxides seems to be sensitive to the effects of the discharge of municipal sewage (Eisenreich *et al.*, 1980, Tessier *et al.*, 1980, as cited by Salomons & Förstner, 1984; Neumann *et al.*, 1998; Bhosale & Sahu, 1991; Gonçalves *et al.* (2004)); Filipek *et al.* (as cited by Chao, 1984) refer to the importance of the organic matter as a control in the retention of metals in fluvial sediments, even in systems with high concentrations of Fe-Mn oxides and hydroxides. In the Corgo fluvial system the generally relatively low contents of organic matter associated with the sediments might condition the behaviour of metals in relation to the oxidisable fraction, and thus relatively low contents of metals are retained in this fraction. However, as already mentioned, Cu associates with the oxidisable phase in those samples collected in river sites where the organic content is higher.

The results from studies available in the literature, cited above, suggest that the mentioned affinities and relative proportions of metals distributed amongst the phases will depend on the specific characteristics of the fluvial environment under study, like the geological and geomorphological background (not even mentioned in part of the studies), types of pollution sources and related form in which the metals enter the fluvial water (in dissolved form or bound to weathered or soil particles), as well as the intrinsic properties of the sediments generated through the basin. The hydrodynamics is also a controlling factor; for example, Dawson & Macklin (1998b) observed different distribution patterns in different stages of the flood hydrograph, which are related to the relative particle size of the sediments in transport. The contents of metals in the reducible phase are dependent on particle size, increasing in the finer fractions (e.g. Stone & Droppo, 1996; Song *et al.*, 1999). The results from the present study suggest that in mountainous fluvial systems where there is a permanent supply of detrital sediments, derived from soils and weathering products, to the basin, and the organic content is in general low, the oxides of Fe and Mn are the most important geochemical phase in the transport of metals. The results on the soil samples, collected in the ambit of this study (Reis, 2010), show similar distribution patterns of metals between the geochemical phases to the sediment samples.

4.4. The possible origin of the elements

The identification of the origin of the metals and As in the sediments, as well as their temporal and spatial distribution, and the relationships existing amongst the elements was interpreted with the aid of the PCA multivariate method. This method has been successfully applied to environmental data related to metal contents in freshwater sediments in other studies (e.g. Viganò *et al.*, 2003; Filgueiras *et al.*, 2004; Pardo *et al.*, 2004; Kartal *et al.*, 2006; Simeonov *et al.*, 2007; Passos *et al.*, 2010), always having as the base of interpretation the knowledge of the environmental system under study. Chemometric analysis was applied to the total contents (the sum of the most mobile phases and the residual phase). Major ions (Ca, K, Mg and Na) were included in the analysis since these elements can have both natural and anthropogenic origin.

For the different sets of data, four to six principal components show eigenvalues higher than 1, but the data structure is in general explained by four PCs, which explain 64-70% of the total variance. The variables loadings and the variance explained are presented in Table 2; the loadings of the variables higher than 0.5 were considered in the analysis.

4.4.1. The significance of the associations defined by PCA

The PC1, accounting for 29-35% of the total explained variance, is defined by the association Cr, Fe, Ni, Co, K, Mg and, partially, Cu. This component is interpreted as the lithological contribution; it groups the elements which are common in the outcropping lithologies of the basin and show higher contents in the residual fraction, and therefore interpreted as having a strong natural component in the contents of the samples. Potassium and Mg are the less-mobile major cations; K is incorporated in illite, and Mg mainly in expandable clays.

The PC2 explains 16-21% of the total variance in the data, and describes the general loading of sediments with Pb, Zn, Ca, Na and, partially, Cu; in the Wet Period campaign from 2004, Ca does not associate with this component, unlike Cd, which contributes to its formation. This PC is considered to represent the anthropogenic contribution of metals transported with the sediments. These metals may have different anthropogenic emission sources. The point-pollution sources (urban effluents) are indicated by the peak contents of these metals found in some samples. Wastewater can be a point-source for the high Pb values, but atmospheric deposition is considered another important source (from traffic, solid particles and toxic fumes) (Micó *et al.*, 2006). The traffic in the main road, as well as secondary roads with permanent local traffic, that cross the basin, would probably contribute to a Pb increase in the available fraction by surface runoff. However, a significant proportion of these metal contents in the sediments is probably owing to the application of commercial manures, cattle slurry, fertilisers and pesticides to the agricultural soils. The chemical analyses of samples from this material revealed relatively high contents of these metals, in particular, manures; as well as the results on the soil samples, collected in the course of this study, show similar distribution patterns of metals amid the geochemical phases to the ones in sediment samples (Reis, 2010). Phosphate fertilizers are an important source of heavy metals entering agricultural soils, especially Cd, Cu and Zn (N'Guessan *et al.*, 2009). The anthropogenic origin is also indicated by the relatively higher proportion of contents in the most labile fractions when compared with the contents in the residual fraction. The association between Pb, Zn, Cu and Ca seems to be particularly strong in the Dry Period samples. The association between Cu, Zn and Pb and their origin in the organic and inorganic fertilisers has been outlined by several authors in studies about trends of metals in soils (Micó *et al.*, 2006; Franco-Uría *et al.*, 2009) and also in sediments (Masson, 2007).

Copper associates with both PC1 and PC2, which can be attributed to a mixed source, both from lithogenic and from anthropogenic inputs, related in particular to the application of Cu insecticides in several periods through the hydrological year, as already mentioned.

The other components (PC3, PC4 and PC5) account for 7-11 % of the total variance. Cobalt and Mn are associated in PC3, which accounts for about 10% of the total variance. This association is linked to a similar origin, in particular in specific samples associated with point sources, probably anthropogenic in origin. Arsenic and Cd show higher loadings in the PC4, and also peak contents in the samples. This association is probably due to mixed origin: a natural one, owing to the weathering of schists and local quartz veins with sulphides, since the contents are higher in the central-southern zone of the basin (namely in River Cabril sub-basin, eastern tributaries and more southern reach of the River Corgo); and derived from fertilisers, in particular the NPK-fertilisers, As is used frequently in different kinds of fertilisers (Alloway & Ayres, 1997; Terrado *et al.*, 2006). The relatively low contents of Cd in sediments may be indicative of a high Cd retention by soil, probably in the organic matter (Franco-Uría *et al.*, 2009).

Manganese does not show a specific pattern in its association with the other elements. An association with Fe should be expected, indicative of the importance of Fe and Mn oxides/hydroxides as scavengers for trace metals in the mineral phase, but this is not observed, and the association of Fe with Cr, Ni, Co, K, Mg and Cu in the first component suggests that the Fe is associated with these metals in particular in the residual phase.

4.4.2. The contribution of the samples to the formation of the first two factor planes

The graphic presentation of variables and samples scores in the two first components, which explain the major proportion of the data variance, shown in Figure 5, synthesises the trends observed in element contents well. The graphs with the projection of the variables for the datasets of the Wet Period show higher dispersion in the two components projected, but the cluster formed by the metals with higher loadings in the first component is common to all the graphics (Cr, Ni, Co, Fe, K, Mg). In the graphs relative to the projection of variables from the Dry Period datasets, the clusters of variables are better individualised, in particular the other group formed by Cu, Zn, Pb and Ca. The projection of the coordinates of the samples shows a clear separation between the samples draining the schists from the samples draining the granites by the first component. The samples draining schists, and some of the samples draining both schist and granite lithologies, contribute to the formation of the clusters Cr, Ni, Co, Fe, K, Mg and Cu, Zn, Pb and Ca. Samples draining granites contribute, in general, more to the formation of the axis of As and Cd. The information available on the chemistry of the lithologies outcropping in the southwestern part of the basin, indicates that the zones of the schist are characterised, generally, by higher contents of metals, in particular Co, Cr and Ni. Apart from the more upstream zones where only the granite lithologies outcrop, the downstream areas are a mixture of lithologies and are influenced by the anthropogenic activities, hence the corresponding samples contribute to the formation of the mentioned first two clusters.

The metals association in the PCs is interpreted as a result of the hydrodynamic behaviour of the river: in the dataset from the end of the Wet Period, the projection of variables in the two factor planes show a more dispersed pattern; the projection of the variables from the dataset of the end of the Dry Period form relatively individualised clusters in the factor plane, in particular the cluster relative to the variables attributed to anthropogenic origin. Anyway, the samples collected in the downstream reaches of the tributaries, which are mixtures in terms of chemical and mineralogical composition of the sediments derived from corresponding drainage areas, have the most significant score contribution to the formation of the principal components resulting from the PCA analysis.

5. Concluding remarks

It is important to take into consideration the significant influence of the streamflow regime in this kind of geomorphological hydrographic basin. Every rainy season, the finer sediments are moved downstream in the drainage network, representing a considerable contribution of metals in the mainstream river Douro. We are looking at values from "fresh sediments", and not from accumulated sediments in the river bottom.

The results show that the pollutant dispersion and transport in mountainous fluvial environments is governed by multiple interrelated factors difficult to control over time, and predictive models still need better information about the processes governing the transport into and within the fluvial network. The regular monitoring of bed sediments in this kind of basins is important to give some insight into the micro-pollutant transport in small mountainous catchments with an impact on the quality of receiving waters.

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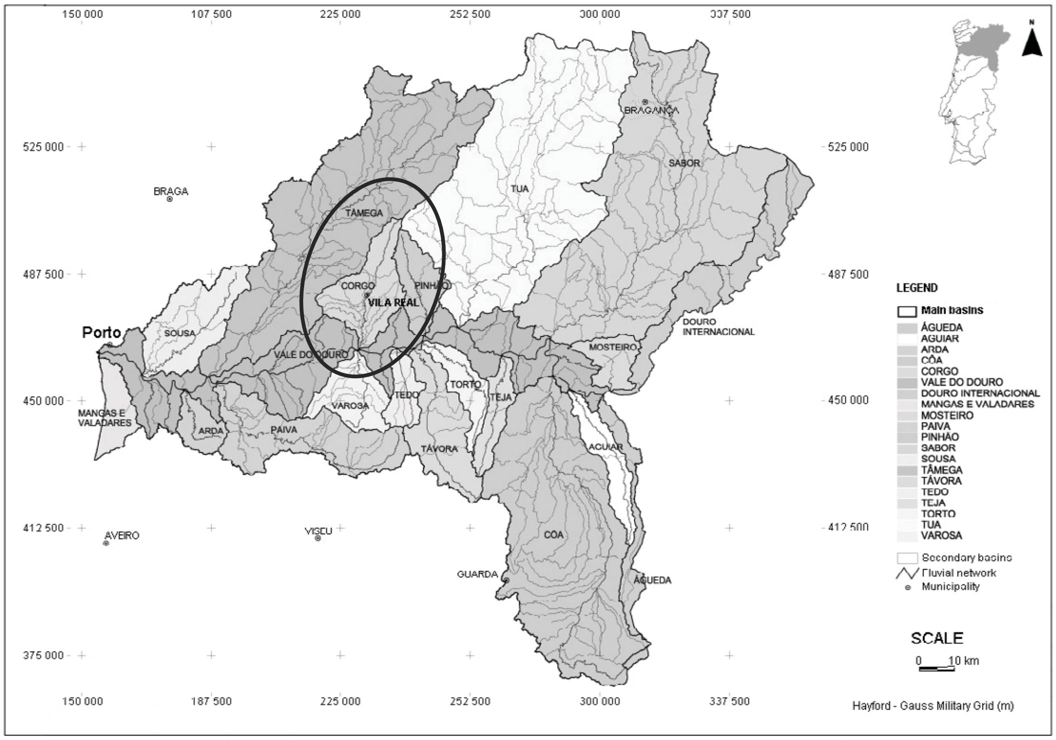


Fig. 1 – Locality of River Corgo catchment in the Douro Basin in Portugal (modified from Plano da Bacia Hidrográfica do Rio Douro (INAG - Instituto da Água, 2001, http://www.inag.pt)).

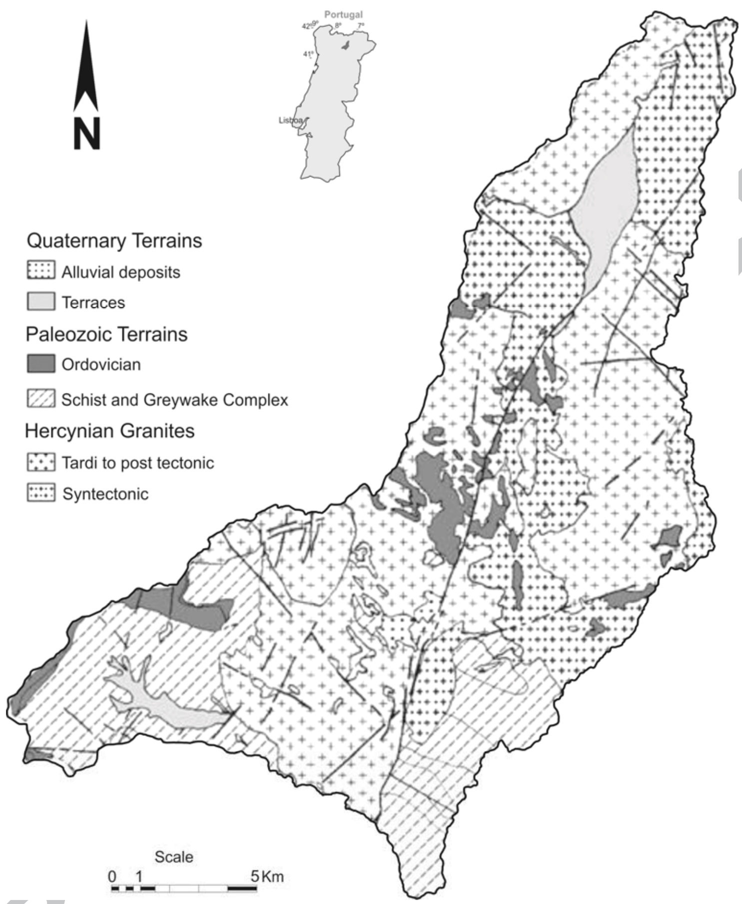


Fig. 2. Simplified geological map of Corgo River Basin (modified from Portuguese Geological Map at 1:200000 scale, Sheet 2 (modified from Pereira, 2000)).

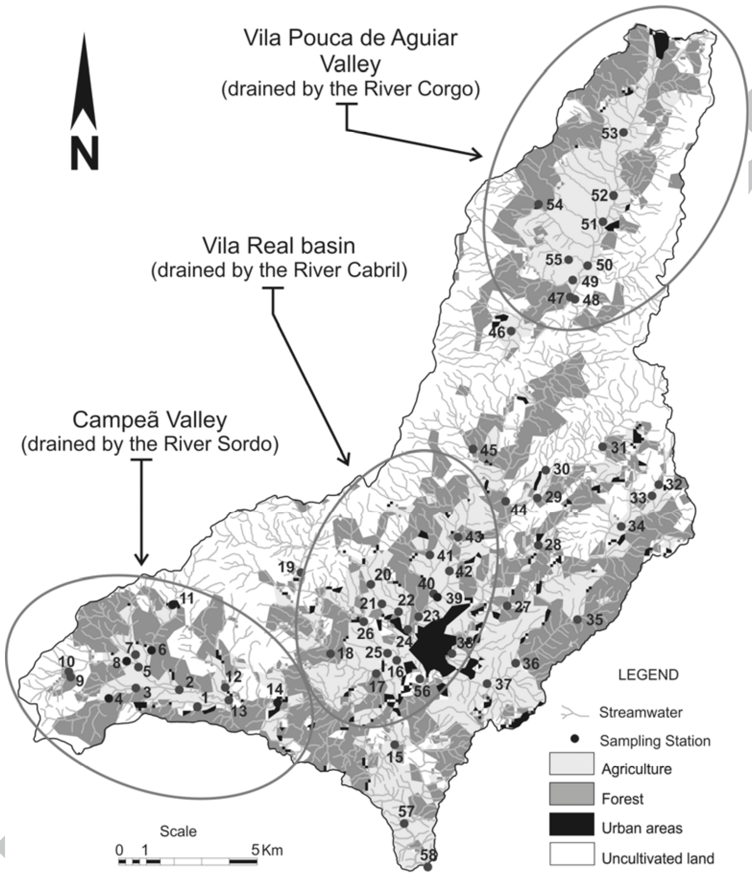
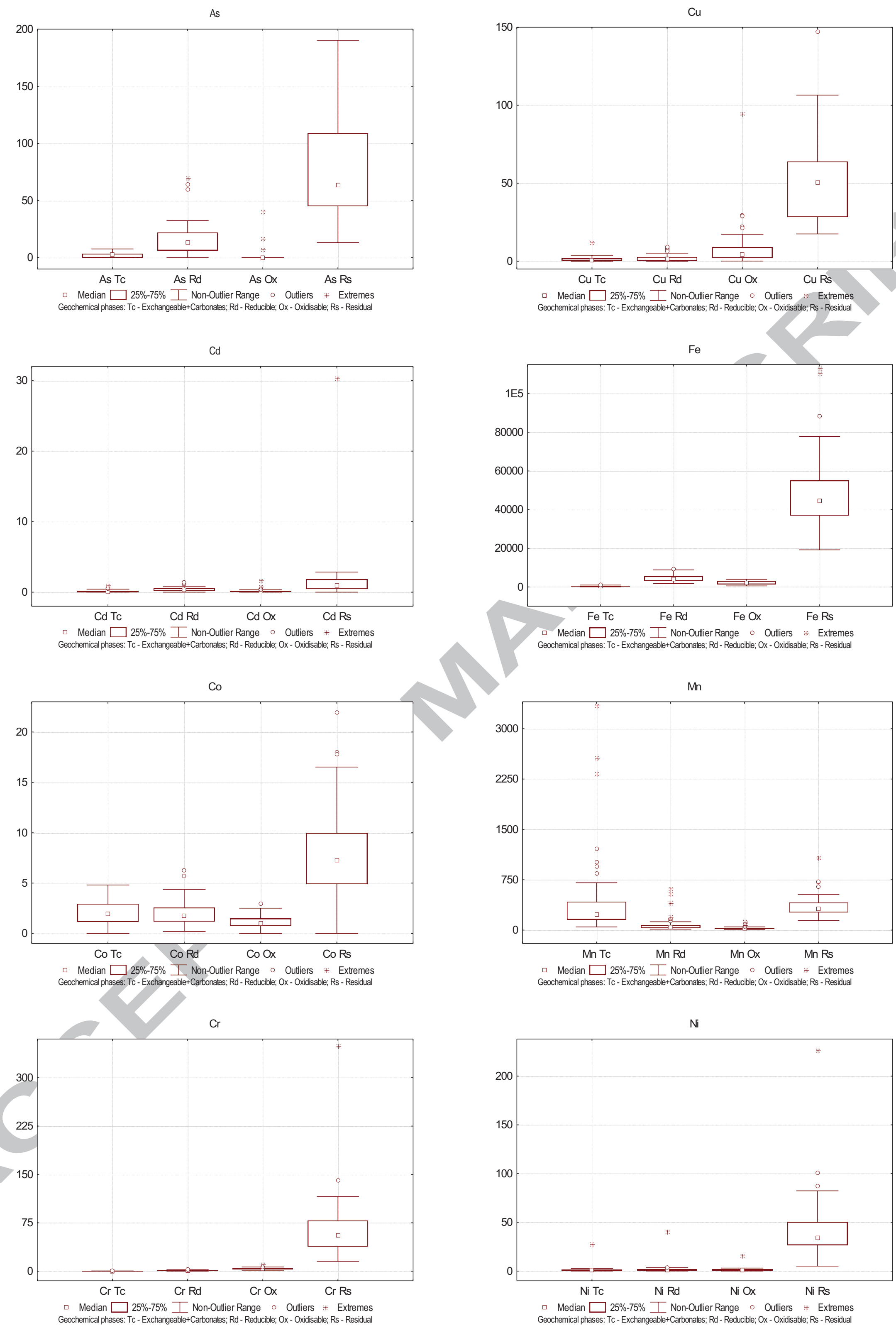


Fig. 3. Land-use map (modified from Alencoão *et al.*, 2006), with fluvial network and sampling stations represented. The zones pointed out in the figure correspond to the major valleys occurring in the basin: a) Campeã valley, drained by the River Sordo; b) Vila Real basin, drained by the River Cabril; c) Vila Pouca de Aguiar valley, drained by the River Corgo in its more upstream reach.


As
200
150
100
50
0
As Tc
As Rd
As Ox
As Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Cu
150
100
50
0
Cu Tc
Cu Rd
Cu Ox
Cu Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Cd
30
20
10
0
Cd Tc
Cd Rd
Cd Ox
Cd Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Fe
1E5
80000
60000
40000
20000
0
Fe Tc
Fe Rd
Fe Ox
Fe Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Co
20
15
10
5
0
Co Tc
Co Rd
Co Ox
Co Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Mn
3000
2250
1500
750
0
Mn Tc
Mn Rd
Mn Ox
Mn Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Cr
300
225
150
75
0
Cr Tc
Cr Rd
Cr Ox
Cr Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual
Ni
200
150
100
50
0
Ni Tc
Ni Rd
Ni Ox
Ni Rs
Median 25%-75% Non-Outlier Range Outliers Extremes
Geochemical phases: Tc - Exchangeable+Carbonates; Rd - Reducible; Ox - Oxidisable; Rs - Residual

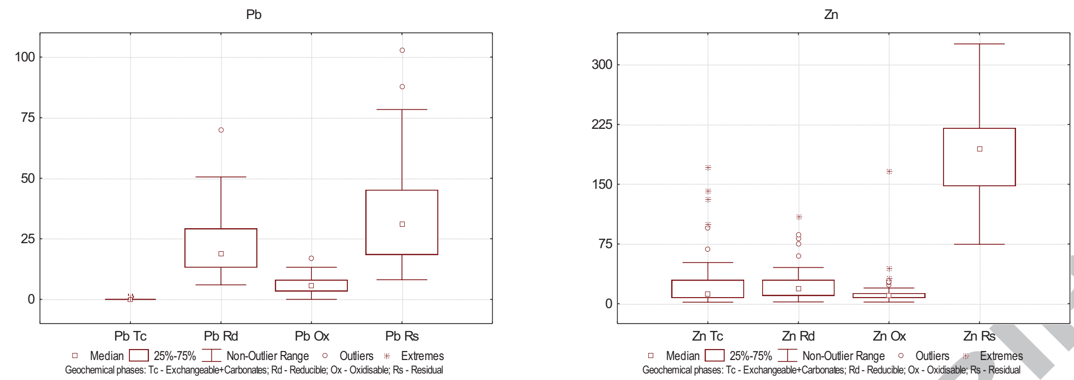


Fig. 4 – Box plots of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn showing outliers and extreme values, from River Corgo sediment samples collected at the end of the of the Dry Period (DP). Contents are in µg/g.

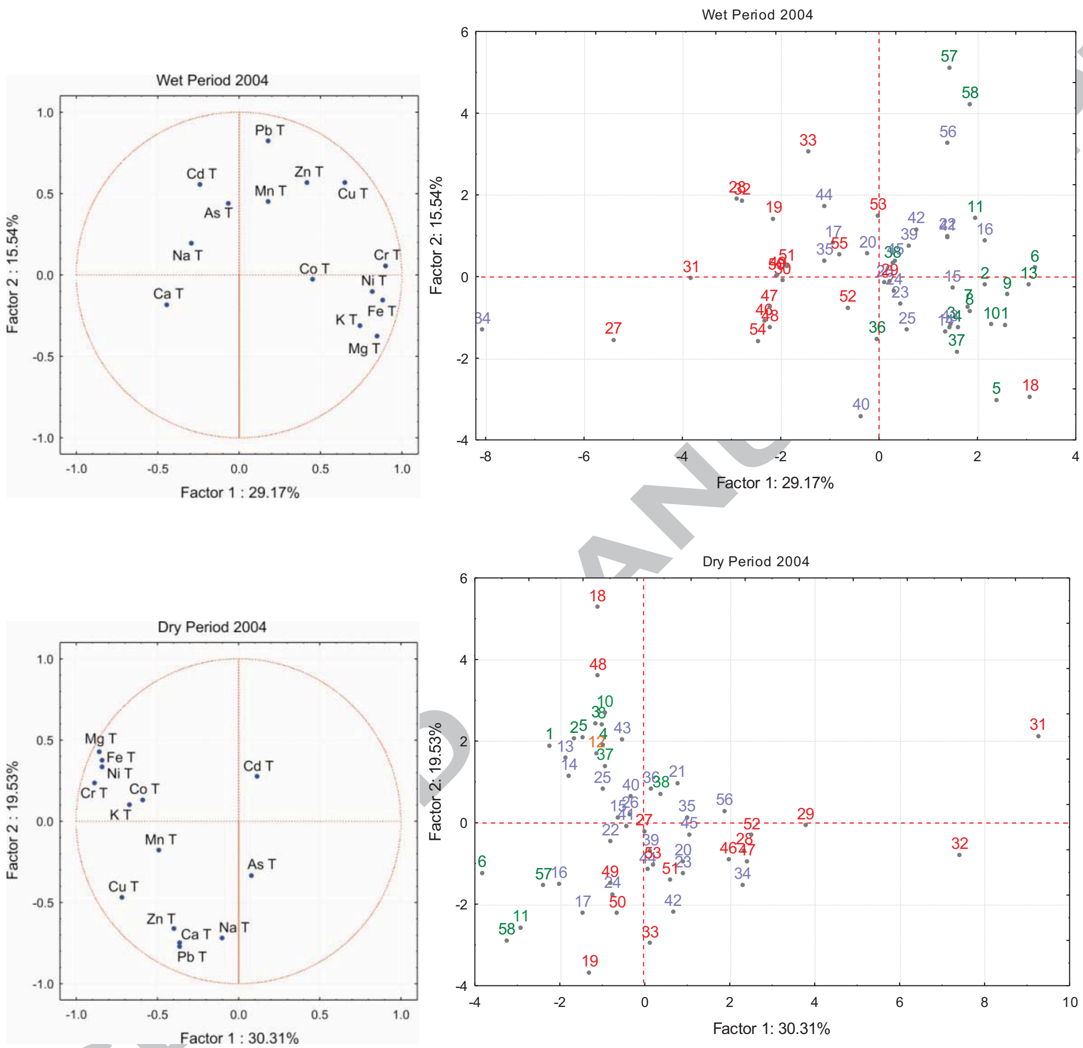


Fig. 5. Projection of the results of PCA (factor and case scores) of the metals in sediments from river Corgo onto the F1-F2 principal components. Sampling campaigns of Wet Period (WP) and Dry Period (DP). The different colours of sample numbers correspond to the lithologies of sites draining upstream: ■ granites; ■ schists; ■ granites/schists.

Table 1. Comparison of the concentrations ranges (µg/g) of metals and As in the bottom sediments from the River Corgo (fraction ≤ 63 µm) with the mean contents in average shale, shallow-water sediment and river-suspended sediment.

		As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Mn	Fe
Average shale [a]		13	0.22	19	90	45	68	20	95	850	47000
Shallow water sediment [b]		5	-	13	60	56	35	22	92	850	65000
River suspended sediments [c]		5	1	20	100	100	90	150	350	1150	48000
River Corgo sediments	**WP** 2004	0-146	0-8	0-21	9-58	10-68	2-37	15-121	49-246	188-5020	13692-85549
	DP 2004	0-100	0-2	0-22	1-60	1-99	0-37	5-154	29-448	119-1889	2585-66508

[a] Turekian and Wedepohl, *in* Salomons and Förstner (1984)
[b] Wedepohl, *in* Salomons and Förstner (1984)
[c] Martin and Meybeck, *in* Salomons and Förstner (1984)

Table 2. Loadings of the variables on significant principal components for the bottom sediments data of the River Corgo.

	Wet Period 2004						Dry Period 2004			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 1	Factor 2	Factor 3	Factor 4
As	-0.07	0.44	-0.16	0.11	0.65	0.12	0.08	-0.33	0.33	-0.52
Cd	-0.24	0.56	0.24	-0.09	0.38	0.31	0.11	0.28	-0.35	-0.30
Co	0.45	-0.02	0.76	-0.18	0.15	0.01	-0.59	0.14	0.58	-0.29
Cr	0.90	0.06	-0.07	-0.01	0.25	-0.11	-0.89	0.24	-0.08	0.07
Cu	0.65	0.57	-0.21	-0.09	-0.11	-0.20	-0.72	-0.46	-0.27	-0.07
Fe	0.88	-0.15	0.18	-0.10	0.17	0.01	-0.84	0.38	0.13	-0.02
Mn	0.18	0.45	0.49	-0.54	-0.30	0.17	-0.50	-0.18	0.54	0.35
Ni	0.81	-0.10	0.03	-0.11	0.01	-0.08	-0.84	0.34	-0.06	0.10
Pb	0.18	0.83	-0.12	-0.08	-0.10	-0.05	-0.37	-0.77	-0.01	-0.27
Zn	0.41	0.57	-0.39	0.04	-0.27	-0.22	-0.40	-0.66	-0.53	0.00
Ca	-0.45	-0.18	0.02	-0.75	-0.03	-0.17	-0.37	-0.74	-0.18	-0.07
K	0.74	-0.31	-0.31	0.11	-0.01	0.02	-0.67	0.11	-0.27	0.02
Mg	0.85	-0.37	0.01	-0.20	0.16	-0.12	-0.86	0.43	-0.09	-0.03
Na	-0.30	0.20	-0.53	-0.50	0.15	-0.08	-0.10	-0.71	0.06	0.22
Eigenvalue	4.96	2.64	1.83	1.47	1.26	1.08	5.15	3.32	1.77	1.61
% Total variance	29.17	15.54	10.79	8.66	7.42	6.37	30.31	19.53	10.39	9.44
Cumulative % variance	29.17	44.71	55.50	64.15	71.57	77.94	30.31	49.84	60.23	69.68

Highlights

- We examine the quality of oxic active fluvial sediments in mountainous rural catchments.
- We found considerable contribution of metals from the different sources: geogenic, urban and agriculture.
- The influence of the streamflow regime is significant: the sediments are constantly in transit.
- There is a considerable contribution of metals into the mainstream of river Douro.
- Quality of finer sediments influences the quality of the associated ecosystems.