Occurrence and mobility of metals in sediments from mountainous catchments:
a case study in the River Douro basin (Northern Portugal)

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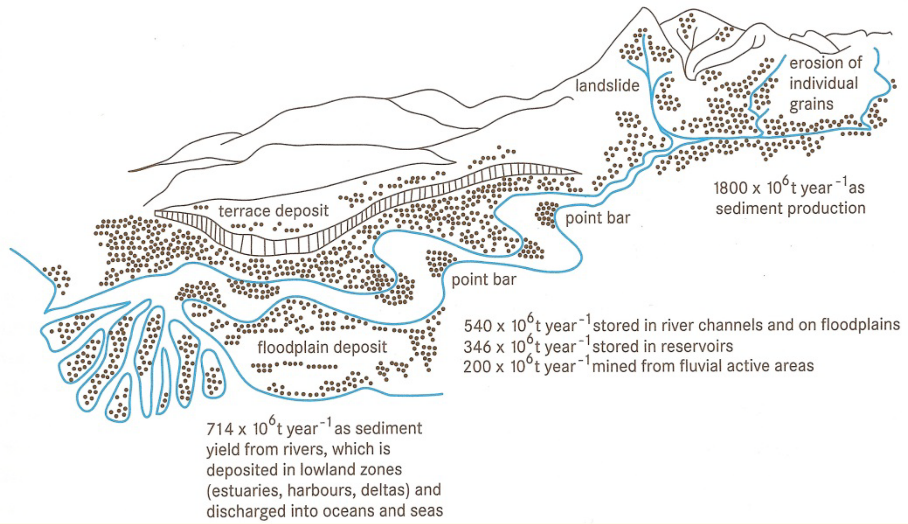
Introduction

In the context of the management of sediments-associated contaminants, concerning quality and quantity, in European Rivers, little attention has been given to mountainous rivers.

Mountainous rivers contribute with significant sedimentary loads, transported in short periods of time, in response to short precipitation episodes.

Estimated annual flux of fine-grained sediment to the ocean

- On a **world scale**, is of the order of **15-20 x 10^9 t year^{-1}** (Owens, 2008).
- In **Europe**, is of the order of **714 x 10^6 t year^{-1}** (Owens, 2005).



Conceptual model of the transport of sediments for Europe (Owens, 2005)

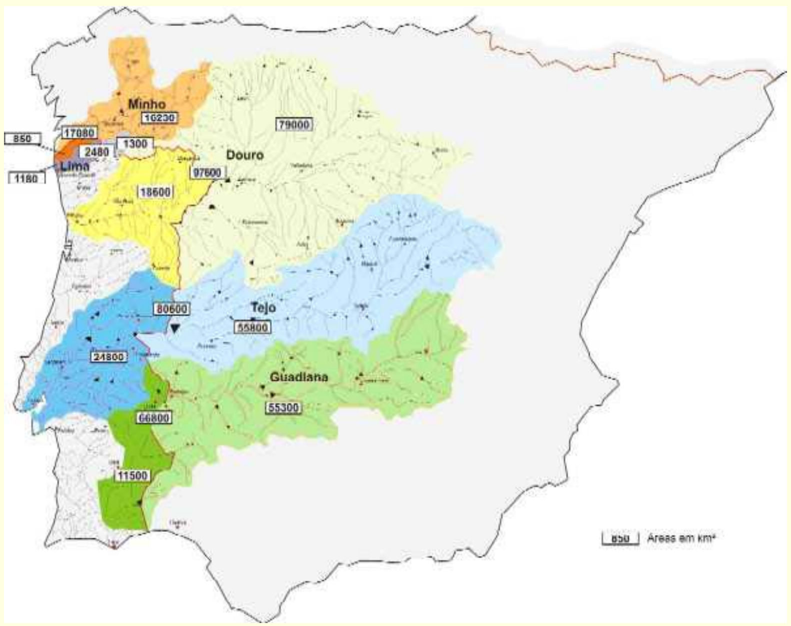
Introduction

Our contribution presents results of a research study developed in the River Corgo catchment, which is one of the tributaries of the Iberian trans-boundary River Douro basin.

River Corgo Catchment area: 295 km^2

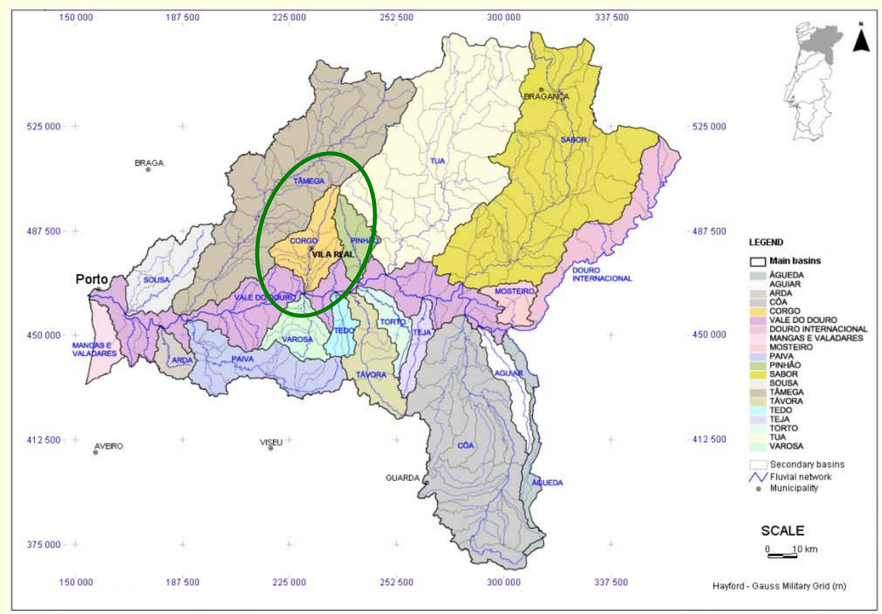
Annual rainfall: 1938 – 974 mm

Riverflow: 0.01 – 66.1 m^3/s



Douro basin area (Spain and Portugal): 97.603 km²

In Portugal: 18.643 km² (19,1%)

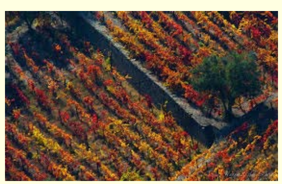


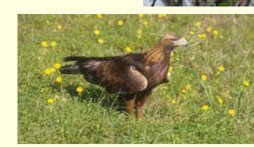
Modified from Plano da Bacia Hidrográfica do Rio Douro (INAG - Instituto da Água, 2001)

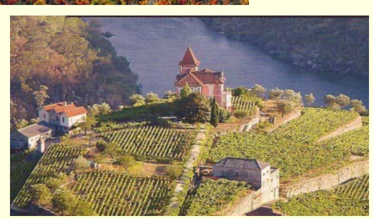
Introduction

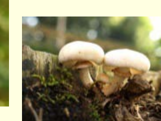
River Corgo catchment: is located in the West limit of the

Douro Region – classified as UNESCO World Heritage.









Aim of the study

The global objective is to investigate the dynamics and availability of sediment pollutants in mountainous rural rivers, in a temperate climate.

The retention and/or mobilisation of metals, derived from agricultural and urban activities, in oxic fluvial sediments was evaluated, as well as its variability in space and time overall the basin area.

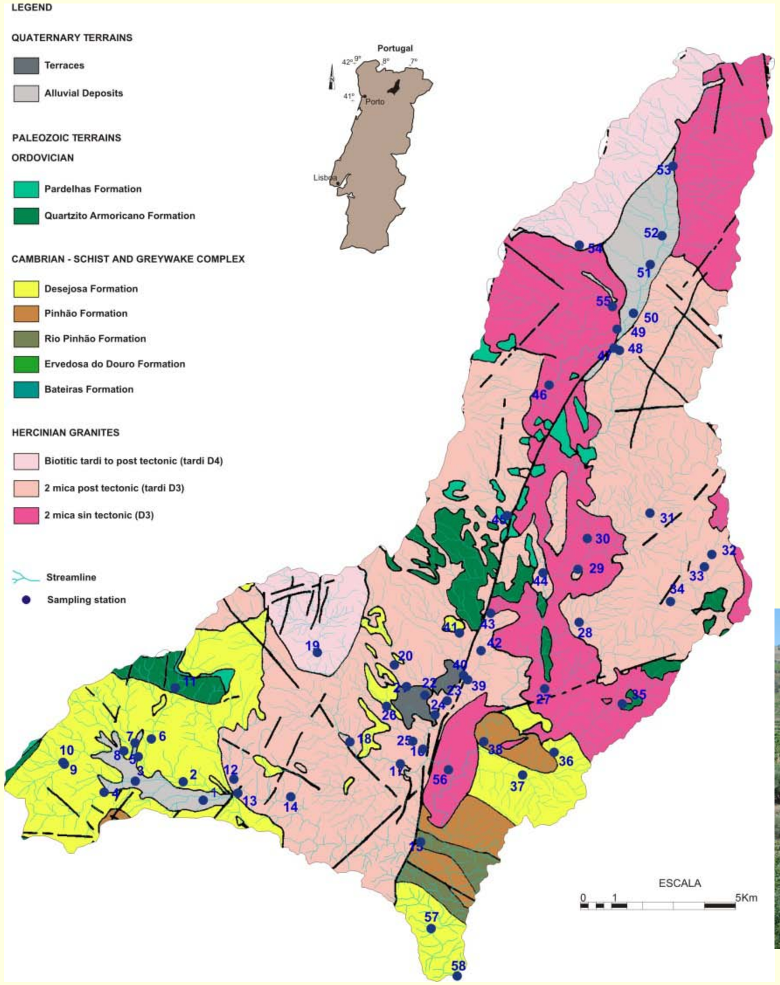
This study is considered to be relevant at the regional scale, because as a consequence of the geological setting, most of the water used in human consumption comes from dammed reservoirs.

There is also a lack of knowledge of levels of pollution at basin scale in the Douro Region, and about the amount of contaminants that are introduced in fluvial systems.

In the ambit of the SedNet meetings, several aspects related to the sediment management in the Portuguese part of the River Douro hydrographic basin were discussed (Reports on the SedNet Round Table Discussion, 2007 and 2009). Relative to the sediment quality, though this parameter is not a priority, is considered the necessity of assessment and monitoring sediment quality, in the context of a plan of sediment management.

The River Corgo catchment (NE Portugal)

- **Geology**



- In the southern part: Palaeozoic metasediments outcrop (schists, greywackes and quartzites);
- In the northern part: granites intruded the older metamorphic rocks.

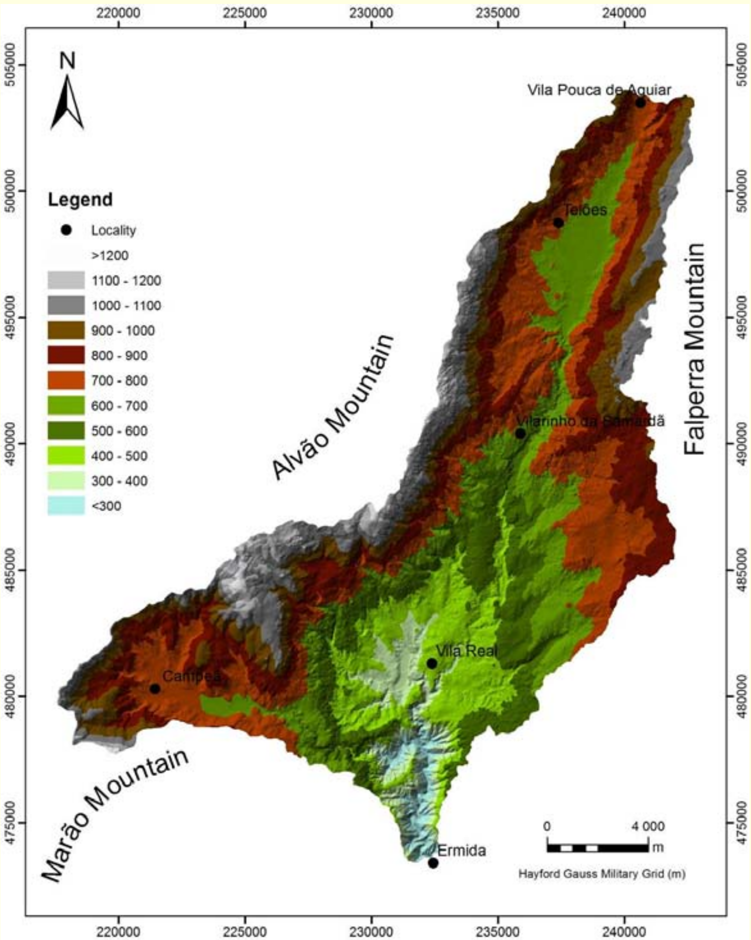
- Locally, Quaternary deposits, with major expression in two agricultural valleys:

  Campeã valley in the southwest area,

  Vila Pouca de Aguiar valley, in the northern area.

The River Corgo catchment (NE Portugal)

- **Catchment morphology**



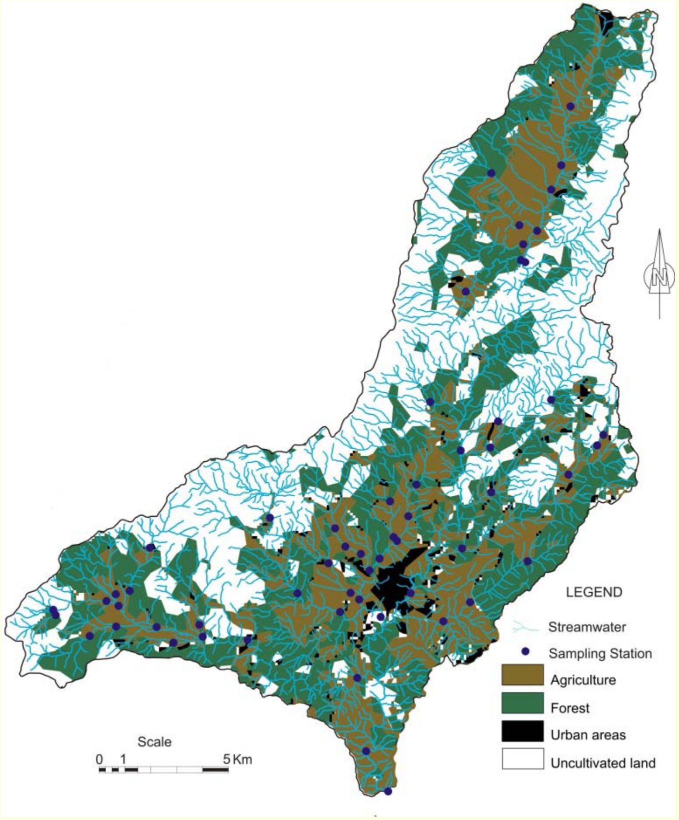
- The River Corgo rises at an altitude of 918m, and at the gauge station of Ermida the altitude is 130m. The river runs mostly along the Penacova−Régua−Verin major fault, with a length of approximately 43.3 km.

- The **altitudes** vary between **200-1400m**
- The **hillslopes** are between **0 and 20%**

The River Corgo catchment (NE Portugal)

- **Land use**

- Uncultivated land (33.7%)
- Forest (29.2%)
- Agriculture(32.8%), and Pastures (2.43%)
- Urban (1.6%) (total population of 50,000 inhab.)



Methodology

- The results reported in this study derive from a geochemical survey of active fluvial sediments
- Sampling campaigns were done at the end of the Wet Period (WP) in April, and at the end of the Dry Period (DP) in September-October
- wet-sieving of stream sediments to separate the fraction <63µm.
- the sediment fractions <63µm were analysed for:
    - bulk mineralogy and clay minerals,
    - grain size, surface area, cation exchange capacity, and organic carbon,
    - contents of As and the selected metals Cd, Co, Cr, Ni, Cu, Zn, Pb, Fe and Mn

Methodology

The contents of As, Cd, Co, Cr, Ni, Cu, Zn, Pb, Fe and Mn, in the sediments were determined by a sequential chemical approach (modified BCR procedure), in order to assess possible different origins of metals (natural vs. anthropogenic), and potential availability.

Extraction method	Geochemical phase released (operationally defined)
1. Single wash with 20 ml acetic acid (0,11 mol/dm^3), for 16 hours	**Exchangeable + carbonates**
2. Single wash with 20 ml of a solution of hydroxylammonium chloride (0,1 mol/ dm^3) at pH 2 with HNO_3 for 16 hours	**Fe and Mn oxides and hydroxides**
3. Single wash with 10 ml hydrogen peroxide (8,8 mol/ dm^3) in water bath at 85ºC, for 36 hours. Single wash with a solution of ammonium acetate (1 mol/ dm^3), for 16 hours, to remove the metal ions readsorbed	**Organics**
4. Single wash with HCl + HNO_3 + HF	**Residual**

The element concentrations were obtained by ICP-AES.

- In each analytical sequence, replicates were used to assess the analytical process.
- The precision of the measurements is about ±5%.
- The recovery rates ranged from 84% to 99%, for Co, Cu, Ni, Pb, Zn, Fe and Mn; and from 75% to 115% for As and Cd.

Metals and As in the sediments

Total element concentrations are relatively higher than the **reference values** of the stream sediments of unpolluted rivers, in particular **As, Cd and Zn** (Cu and Ni exhibit peaks).

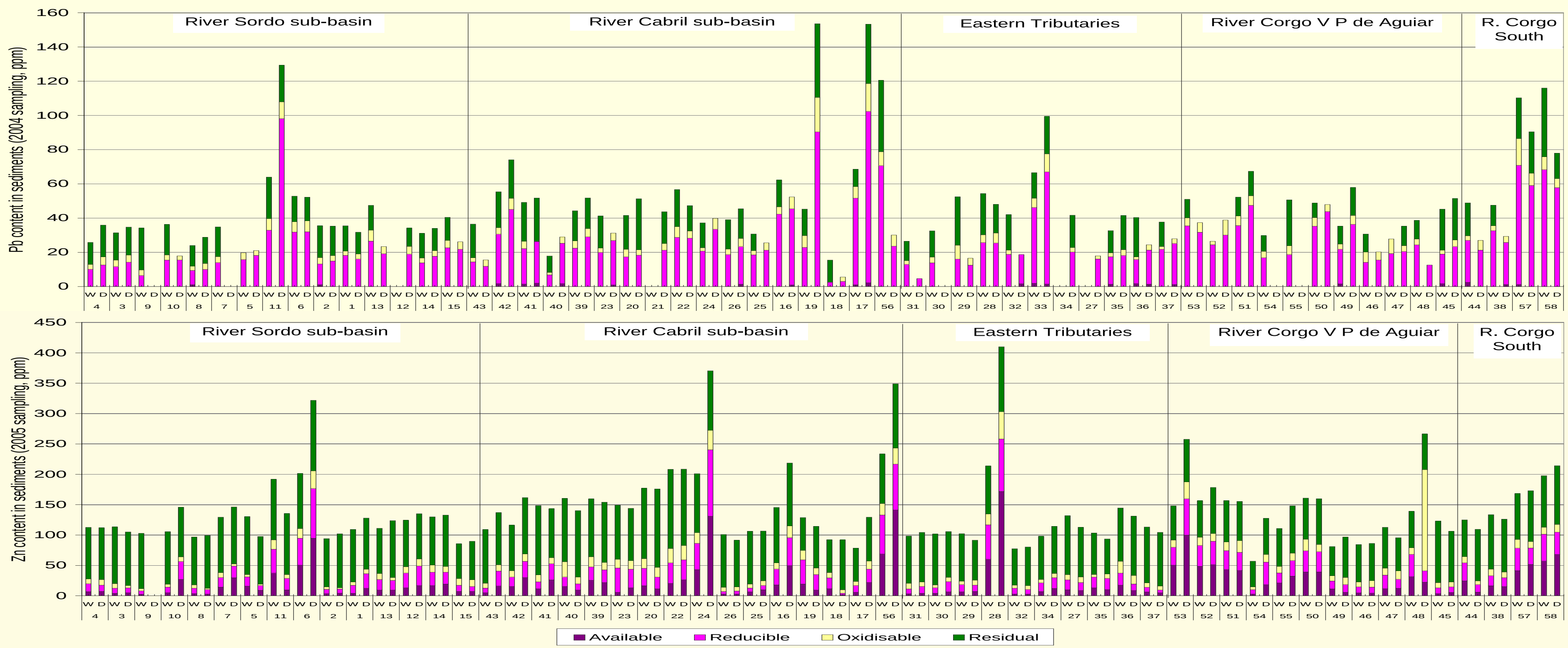
Comparison of the mean concentrations ranges (μg/g) of metals and As in the bottom sediments from the River Corgo (fraction • 63 μm) with the mean contents in average shale, shallow-water sediment and river-suspended sediment.

		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
	WP 2005	0-201	0-4	1-21	7-61	9-75	2-54	13-103	57-234	124-4800	14386-74331
	DP 2005	13-259	0-31	2-31	18-360	21-263	7-232	14-170	98-574	243-4324	27139-120623

[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)

Metals and As in the sediments

- All the geochemical phases studied are important in the transport of the metals, but the **reducible phase** is the most significant in the most labile fractions. The metals are transported mainly linked to Fe/Mn oxides (coatings and individual particles)
- The partitioning of contents in the geochemical phases of the sediments indicates that the elements can be ordered by their potential relative mobility, as follows: **Co, Mn > As, Cd, Pb > Cu, Zn, Fe > Cr, Ni**.



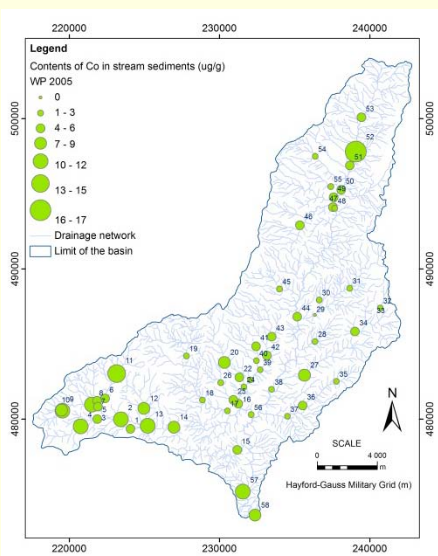
Metals and As in the sediments

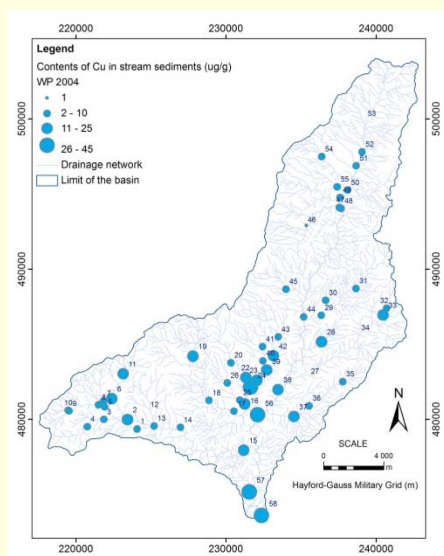
Variation of the relative proportions of contents in the **residual vs. most mobile fractions** suggest:

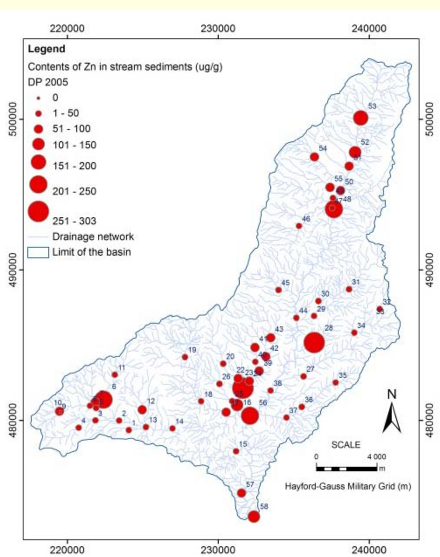
- an important **lithological contribution** to the contents of **As**, **Cd** and **Co**, and in particular **Cr** and **Ni**, which concentrate mainly in the residual fraction; significant proportions of As, Cd and Co occur in the most mobile fractions, which is indicative of a contribution from non natural sources.

- **Cu**, **Zn** and **Pb**, although present in higher total contents in the sediments, show **relative higher values in the most mobile fractions**, which suggests an important contribution of anthropogenic activities. The significant **association with Ca** suggest the influence of the agricultural activities in the quality of the river sediments.

- it is along the main courses of the major tributaries of the River Corgo that we observe the higher contents of metals in the most mobile fractions.







Concluding remarks

- The results obtained point towards a characteristic behaviour of more hydrodynamic fluvial systems.
- The sediments transported in the drainage system are essentially detrital in origin, derived from soils and weathering products. It seems that little mineralogical evolution towards more developed weathering products occurs during transport along the drainage network.
- The soil particles seem to be a significant pathway of transport and entrance of metals in the fluvial network by runoff, especially in the Wet Period, when the sediments are frequently remobilised.
- The morphology of the streambed exerts a major influence on the distribution of the sediment-associated metals in the fluvial environment.
- The influence of the point pollution sources in the basin, are reflected by a local increase of metal contents, indicating that even in more energetic streams the sediments control, to a significant extent, the levels of metals in the fluvial water.

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.

Aknowledgments

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Thank you for your attention!

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