Geochemical regional surveys: comparative analysis of data from soils and stream sediments

Virginia Pereira[A], Manuela Inácio[A], António Ferreira[A] and Manuel Pinto[A]

[A]Department of Geosciences, University of Aveiro, 3810-190 Aveiro, Portugal, Email vpereira@geo.ua.pt

Abstract
Geochemical maps based on soils and on stream sediments were compared. It was found that the natural background for elements in the two media is quite similar. The same applies to their spatial patterns, except for P. The ratio stream sediment/soil element concentrations increases with increasing soil acidity for Ca, Cu, K, Ba, and also for Mn, Sr and Zn, suggesting that element mobilization under low pH is an important process controlling sediment composition.

Key Words
Geochemical surveys, soils, stream sediments, Portugal.

Introduction
Multi- element geochemical mapping has been a priority for many countries since it provides basic information required to environmental research and legislation and to many other fields of investigation such as agriculture, forestry and human and animal health. The entire continental area of Portugal is covered by a geochemical survey (Ferreira et al. 2001; Inácio et al. 2008). Both topsoils and active stream sediments were collected and analysed according to standardized methods, in order to achieve a high quality and consistent database recording the present composition of the surface environment. Stream sediments generally represent a composite of the geological materials in upstream areas, whilst soil samples are considered point-source data, providing site-specific information. The main purpose of the present study was to compare (i) the natural background of 18 selected elements (Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, La, Mg, Mn, Ni, P, Pb, Sr, V and Zn) and (ii) their spatial variability in the two sampling media. Additionally, a relationship between topsoil pH and sediment composition was investigated.

Methods
Recommendations of the IGCP project 259 "International Geochemical Mapping" (Darnley and Garret, 1990; Darnley et al., 1995) were followed for sampling, sample preparation and analysis. A total of 652 sampling sites were obtained in this way, giving a sampling density of one site/135 km^2. At each site a composite sample of stream sediments was collected along a 200 m channel section, at a maximum depth of 30 cm; topsoil composite samples were collected in nearby upstream areas over an area of about 100 m^2, at a maximum depth of 25 cm.

The chemical analysis was performed in the ACME Analytical Laboratories (Vancouver, Canada). The samples were extracted with aqua regia and the extracts were analysed by ICP-AES for 31 elements: Ag, Al , Au, As, B, Ba, Bi, Ca, Cd, Co Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sr, Th, Ti, Tl, U, V, W and Zn. Soil pH was measured electrometrically in a soil:water suspension (1:2.5). The color maps for all elements, as well as for pH, were plotted by kriging. Dot maps were used to superimpose the spatial distribution of elements in topsoils on stream sediment color maps. The dot maps were obtained using the technique described in Björklund and Gustavsson (1987) and Gustavsson et al. (1997).

Results
Summary statistics
Summary statistics of 18 elements selected after analytical quality control are shown in Table 1. The mean, median, geometric mean, observed range and expected range for these elements in the two media are quite similar and they generally agree with the figures reported for world soils in Adriano (1986), Angeloni and Bini (1992) and Kabata-Pendias (2001).

Table 1.Summary statistics of the analytical data for 652 topsoils and stream sediments (M, median; GM, geometric mean; Observed Range, minimum-maximum; Expected Range, 5th- 95th percentile).

Element	Stream sediments				Soils			
	M	GM	Observed Range	Expected Range	M	GM	Observed Range	Expected Range
Al (%)	1.59	1.40	0.22-4.40	0.45-2.78	1.84	1.69	0.19-9.30	0.43-4.50
Ba (mg/kg)	68	68	8-492	27-178	53	51	6-422	16-154
Ca (%)	0.21	0.30	0.01-23.55	0.05-5.82	.10	.11	.01-23.24	0.01-4.08
Co (mg/kg)	9	8	1-155	2-23	8	7	1-84	1-27
Cr (mg/kg)	23	21	3-305	6-60	21	18	1-336	4-59
Cu (mg/kg)	22	20	1-817	5-69	16	14	1-245	3-53
Fe (%)	2.45	2.19	.39-7.64	0.75-4.80	2.74	2.26	.23-6.45	0.56-4.67
K (%)	0.14	0.15	0.01-1.63	0.05-0.53	0.15	0.16	0.02-1.52	0.05-.68
La (mg/kg)	23	23	2-100	10-50	25	24	1-155	9-60
Mg (%)	0.38	0.32	0.01-2.69	0.07-0.88	0.29	0.26	0.01-4.24	0.04-1.03
Mn (mg/kg)	411	444	32-19878	110-1798	394	357	13-4965	59-1857
Ni (mg/kg)	19	14	1-371	2-52	16	13	1-880	3-56
P (%)	0.046	0.047	0.006-0.281	0.015-0.148	0.038	0.036	0.004-0.610	0.010-0.136
Pb (mg/kg)	19	20	3-1378	8-65	21	21	3-585	8-51
Sr (mg/kg)	15	16	2-280	6-63	10	11	2-217	3-40
Th (mg/kg)	4	5	2-61	2-20	5	5	2-87	2-23
V (mg/kg)	26	25	3-143	8-69	27	25	3-192	7-75
Zn (mg/kg)	74	66	7-2365	14-203	55	46	5-738	10-113

Soil concentrations were correlated with the corresponding stream sediment data. Mono-element correlations (Spearman rank order) are significant (P< 0.00001) particularly for Al, Co, Cr, Fe, K, La, Mg, Mn, Ni and V. Soils are relatively enriched in Al, and present slightly higher concentrations in Fe, K, La and Pb. Stream sediments have higher median for Ca and Sr, followed by Ba, Cu, Mg, P and Zn.

Spatial patterns
Maps of spatial distribution of the elements in the two media, as assessed by visual inspection, are generally similar except for P. The composition of soils and stream sediments appears to be chiefly controlled by provenance from the same rock source but the patterns can also be related to anthropogenic factors as illustrated in Figure 1. The spatial pattern of V, presented in Figure 1a, is given as an example of lithological control. The highest V concentrations in soils and sediments are chiefly related to the mafic/ultramafic lithologies observed in Figure 1b.

The spatial distribution of Pb in soils and sediments (Figure 1c) is not related to the bedrock lithology shown in Figure 1b. The high concentrations in the littoral west, namely around the urban and industrial areas of Oporto, Lisbon, Setúbal and around the industrial complex of Sines, where mineral occurrences are not known, are likely to be anthropogenic. Some spots of high Pb concentrations in the interior can be related to old mines. High P contents in both soils and sediments (Figure 1d) are found in areas underlain by granitoids. High P concentrations only in stream sediments occur in an extensive agricultural area north of Lisbon and might be related to the use of phosphate fertilizers.

Point by point comparison of the two data sets
In order to examine more carefully the regional distribution patterns, the two data sets were compared point by point. For each element at each sampling site the ratio R = (concentration in topsoil)/ (concentration in sediment) was calculated. The maps prepared (not included due to lack of space) show that the stream sediments are impoverished in the residual elements Al and La and enriched in the mobile elements Ca and Sr throughout the country. The pattern for the remaining elements is more complex.

The influence of soil pH on stream sediment composition
Soil pH is a major parameter controlling the mobilization of many elements from soils. As soils become more acidic, their ability to retain Ca, Mg, K and many trace elements decreases. As a result, these elements are then more able to be exported by drainage water and flow into streams where they may precipitate or become adsorbed on bed load material.
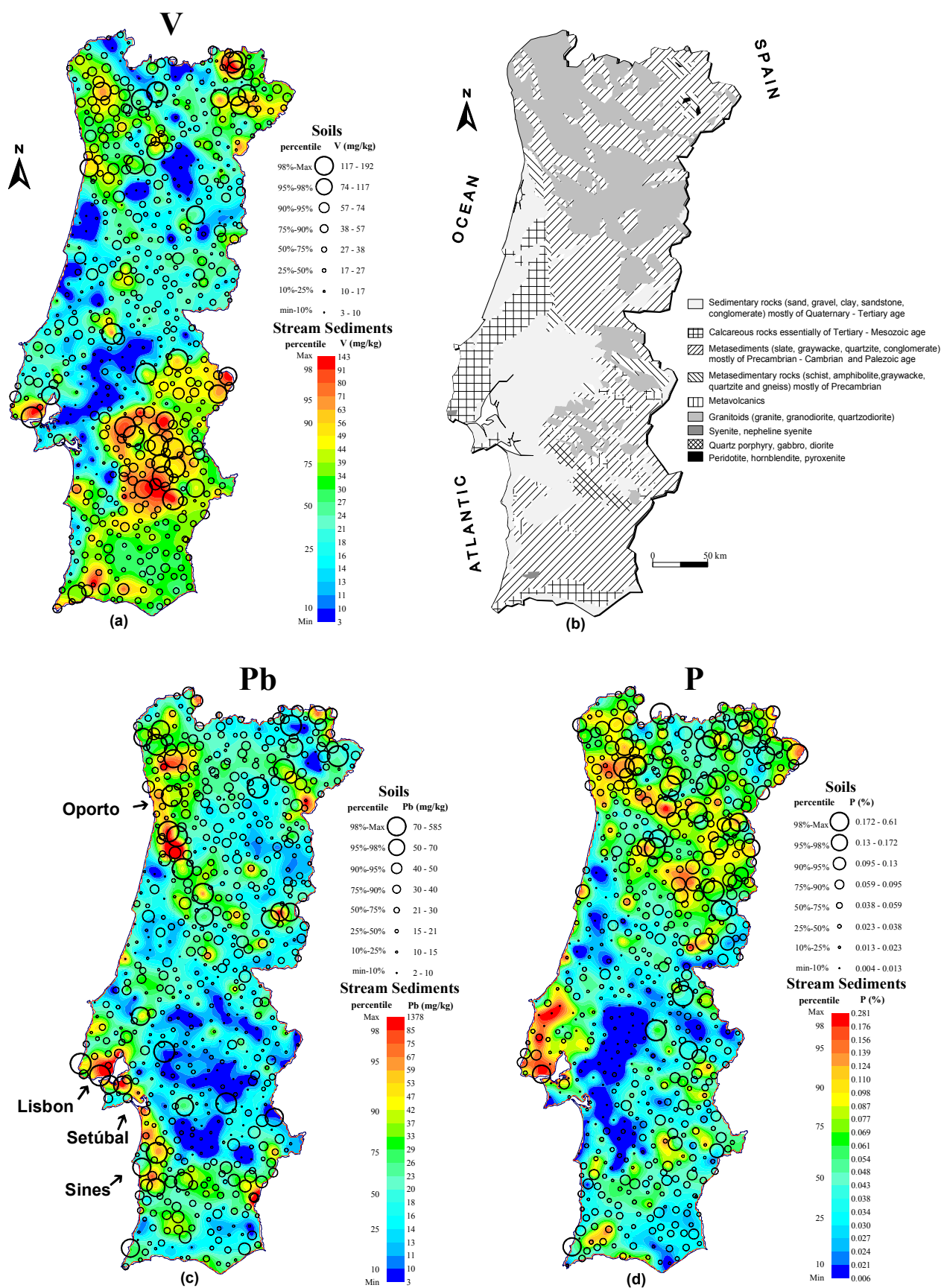
Figure 1. **(a) Spatial distribution of V, in stream sediments and topsoils; (b) Lithological map of Portugal (simplified from Atlas do Ambiente, 1992); (c) Spatial distribution of Pb in stream sediments and topsoils; (d) Spatial distribution of P in stream sediments and topsoils.**

The relationship between topsoil pH and sediment enrichment for the 18 elements was investigated adapting the procedure described in Hall et al. (2001) as follows. First, the R ratios (sediment/topsoil concentration) for each metal, calculated in the previous section, were grouped into three classes according to the pH of the topsoil: ≤4.50, 4.51-5.50 and ≥5.51. The three populations were then compared using the Kolmogorov-Smirnov test. The results showed that for Ca, Cu, K and Ba the median R ratio increases with decreasing pH. The same applies for Mn, Sr and Zn but the relationship with pH is weaker. This means that where the soils are more acid, the stream sediments are enriched in these 7 elements relative to topsoils. The R ratios for the remaining elements show non-significant correlation with top soil pH.

Conclusions

The two surveys give similar information on the background concentrations of 18 selected elements.
The composition of topsoils and stream sediments appears to be chiefly controlled by provenance from the same rock sources. The influence of anthropogenic factors such as mineral exploration, urban and industrial development and agricultural practices could also be detected as evidenced by the accumulation of Pb and P. The empirical relationships between the ratio stream sediment/topsoil element concentrations and topsoil pH suggest that mobilization of Ca, Cu, K, Ba, Mn, Sr and Zn from topsoils to stream sediments in acidic soils is a process not to be disregarded.

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