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Estimated Background Values of Some Harmful Metals in Stream Sediments of Santiago Island (Cape Verde)

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1. Introduction

The aim of geochemical mapping programmes is to obtain regional background information for mineral exploration, planning and also to discriminate between anthropogenic pollution and geogenic sources. Resulting databases are multi-purpose basic tools with application in different areas, such as in environmental studies, agriculture, geomedicine, etc. (Darnley & Garret, 1990; Appleton & Ridgway, 1993; Darnley et al., 1995; Tarvained, 1996; Xie Xuejing et al., 1997; Plant et al., 2001; Albanese et al., 2007; Inácio, 2008) and national geochemical surveys became a priority for many countries.

In Santiago Island, Cape Verde, a total of 337 stream sediments samples were collected at a density of approximately 1 sample per 3 km² to compile an environmental geochemical atlas. The estimation of the background values is very important in countries like Cape Verde, where intervention limits for soils and stream sediments were not yet established.

There are two major methods used for assessing background concentrations (Matschullat et al., 2000): (1) direct (geochemical) and (2) indirect (statistical). The first method, also known as empirical method, consists of sampling locations not affected by industrial activities or relatively pristine sites, and usually use the mean or median to estimate the background concentrations. The indirect methods use more advanced statistical procedures to estimate the background concentrations. There are also other methods, the so called integrated methods, which combines both direct and indirect methodologies. Here we used a direct method and we will use the term Estimated Background Value (EBV) to refer to the estimates of the background concentrations. Our EBV is sometimes called Baseline Value by other authors. Note that "Baseline Value" is not a synonym of

"Background Value", but a synonym of "Estimated Background Value". The EBV or Baseline Value is an estimator of the real and unknown Background Value (Cabral Pinto et al., 2011).

In this work we present EBV maps of some harmful metals of stream sediments from Santiago Island and study their relationships with the defined geological formations. The geochemical survey was conducted, following the guidelines of the International Project IGCP 259 at the sampling stage, sample preparation, analysis, data treatment and mapping (Darnley & Garrett, 1990; Darnley et al., 1995). Levels were determined, in the fraction <2mm. Each sample was digested in aqua regia and analysed by ICP-MS.

Clear relationships between the EBV spatial distribution and the defined geological formations is difficult, since the chemical composition of each sample represents the chemical composition of the entire area upstream, covering different geological formations. However, we seek these relationships using the mineralogical composition of the stream sediments and the results of Principal Component Analysis (PCA).

The layout of this chapter is as follows: in section 2 we describe a brief presentation of the location and geology of Santiago Island. The methodologies used are presented in section 3 and the results and discussion can be found in section 4. Finally, the major conclusions are summarized in section 5.

2. Location and geology of Santiago Island

2.1 Location of Santiago Island

The archipelago of Cape Verde is located at the eastern shore of the Atlantic Ocean, 500 km west from Senegal's Cape Verde, in the African Western Shore. It is composed by 10 islands (Figure 1), with land areas that vary from 35 km² to 991 km² (Santiago Island). The Cape Verde Islands are located in the Macaronesia region, that spreads between the 39°45' and 14°49' latitude and the 31°17' and 13°20' West longitude, within an area of 14 473 km², that holds, beside Cape Verde (4033 km²), the Canary Islands (7542 km²), the Azores Islands (2344 km²) and Madeira Islands (4 km²) (Lousada-Lima 1987-88). The Santiago island is located in the southern part of the archipelago, between the 15°20'N and 14°50' N parallels and the 23°50'W and 23°20'W meridians. It is the biggest island in the Archipelago, representing 25% of the entire land area; it's elongated in the NNW – SSE direction, with a maximum length of 54.9 km and a maximum width of 29 km. This Island has a maximum altitude of 1.394 m. It has 215 km² of arable area, and an average precipitation of 321 mm.

2.2 Geological setting of the Santiago Island

The geological cartography of Santiago Island (Figure 2) was published by Serralheiro (1976) and, along with the works developed by Matos Alves et al. (1979), helped to establish the volcano-stratigraphic sequence of the island. It is possible to identify the periods of intense volcanic activity which caused the growth of the island, separated by erosion and sedimentation periods, recorded by sedimentary formations intercalated between the main volcanic episodes. After the initial phase of submarine volcanism the volcanic building emerged and the volcanism became subaereal.

Below we provide a brief description of the lithostratigraphic formations in Santiago, named as: Ancient Internal Eruptive Complex (CA), Flamengos (FL), Orgãos (CB), Eruptive Complex of Pico da Antónia (PA), Assomada (AS), Monte das Vacas (MV) and Quaternary (CC). A more detailed description was presented at Cabral Pinto et al. (2011).
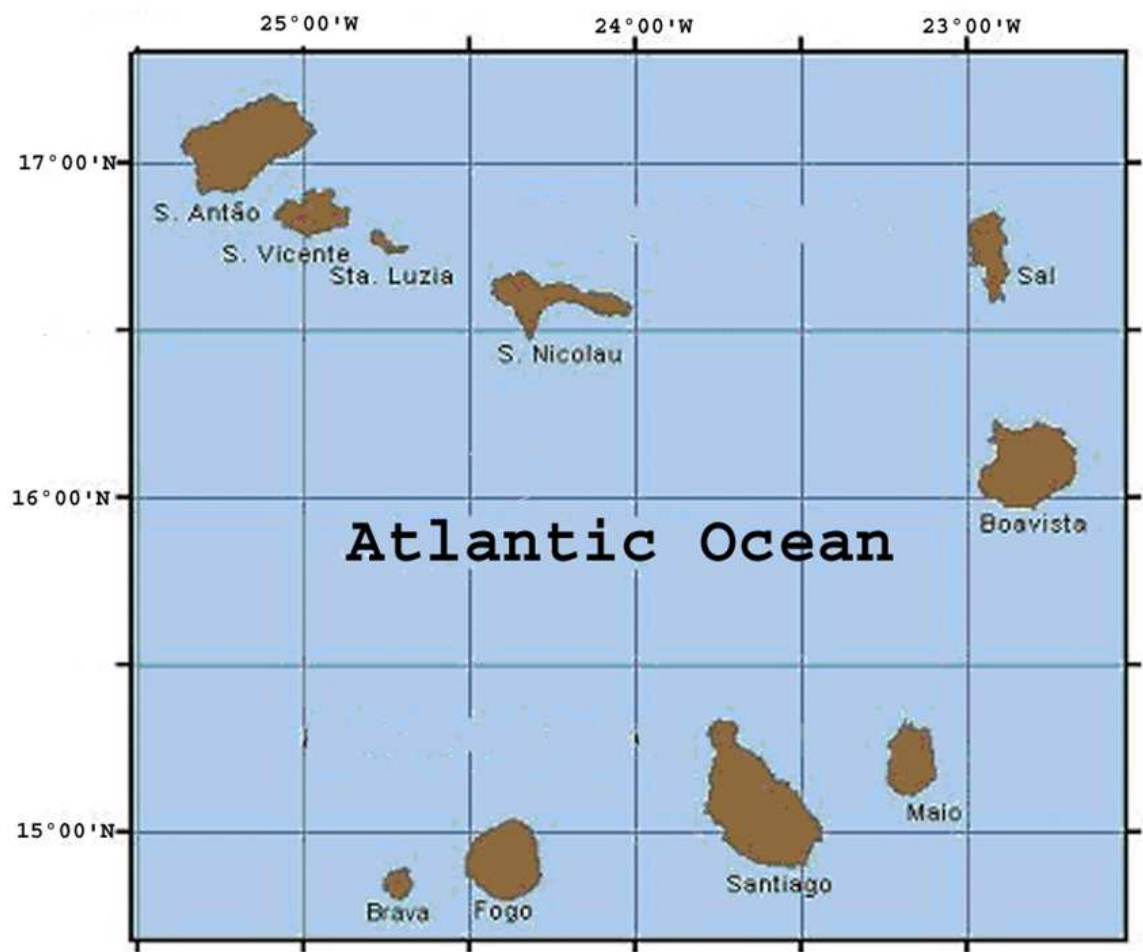

Fig. 1. Location of the Cape Verde Archipelago

2.2.1 Ancient Internal Eruptive Complex (CA)

There are a wide range of rock types in the Ancient Internal Eruptive Complex (CA), but they occupy small areas of the Santiago Island (Figure 2) and are always highly weathered.

The CA is essentially a dense, highly altered, dyke complex (Figure 3a) of basanite, ancaratrites and limburgites (Serralheiro, 1976; Matos Alves et al., 1979). The rocks are fractured and display light colors due to intense alteration (Figure 3 a, b), with zeolites and carbonates filling the fissures. There are also some foid gabbroic and alkaline sienitic rocks, intravolcanic breccias (Figure 3 c), phonolite, trachytic trachytes (Figure 3 d), carbonatites, piroxenites, and ijolites-melteijites (Silva & Figueiredo, 1976; Serralheiro, 1976; Matos Alves et al., 1979; Silva, 1979). Carbonatite is extremely altered, with intense dissolution (Figure 3 b) and occurs as dykes and masses.
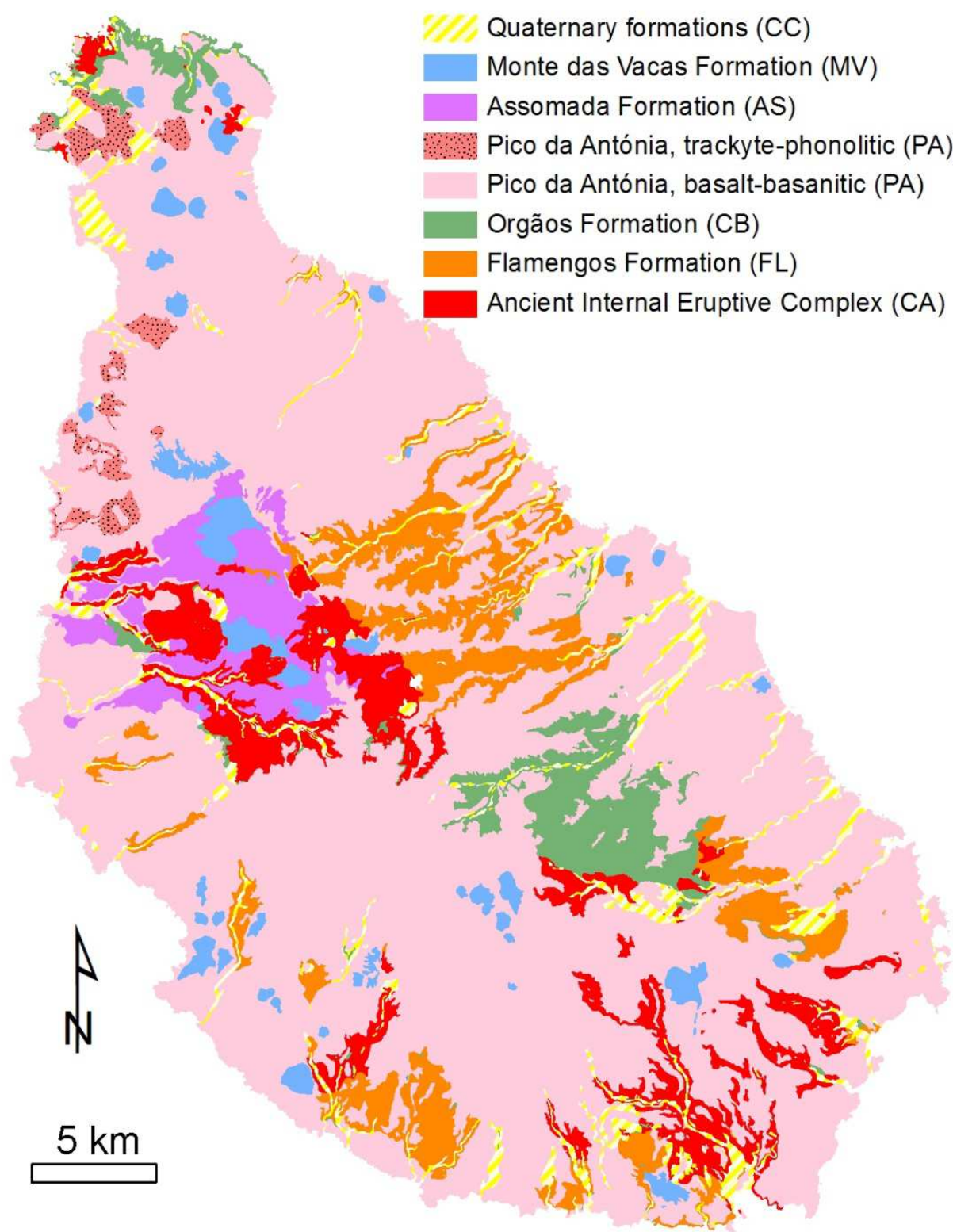
Fig. 2. Geological cartography of Santiago Island, Cape Verde, modified from Serralheiro (1976)
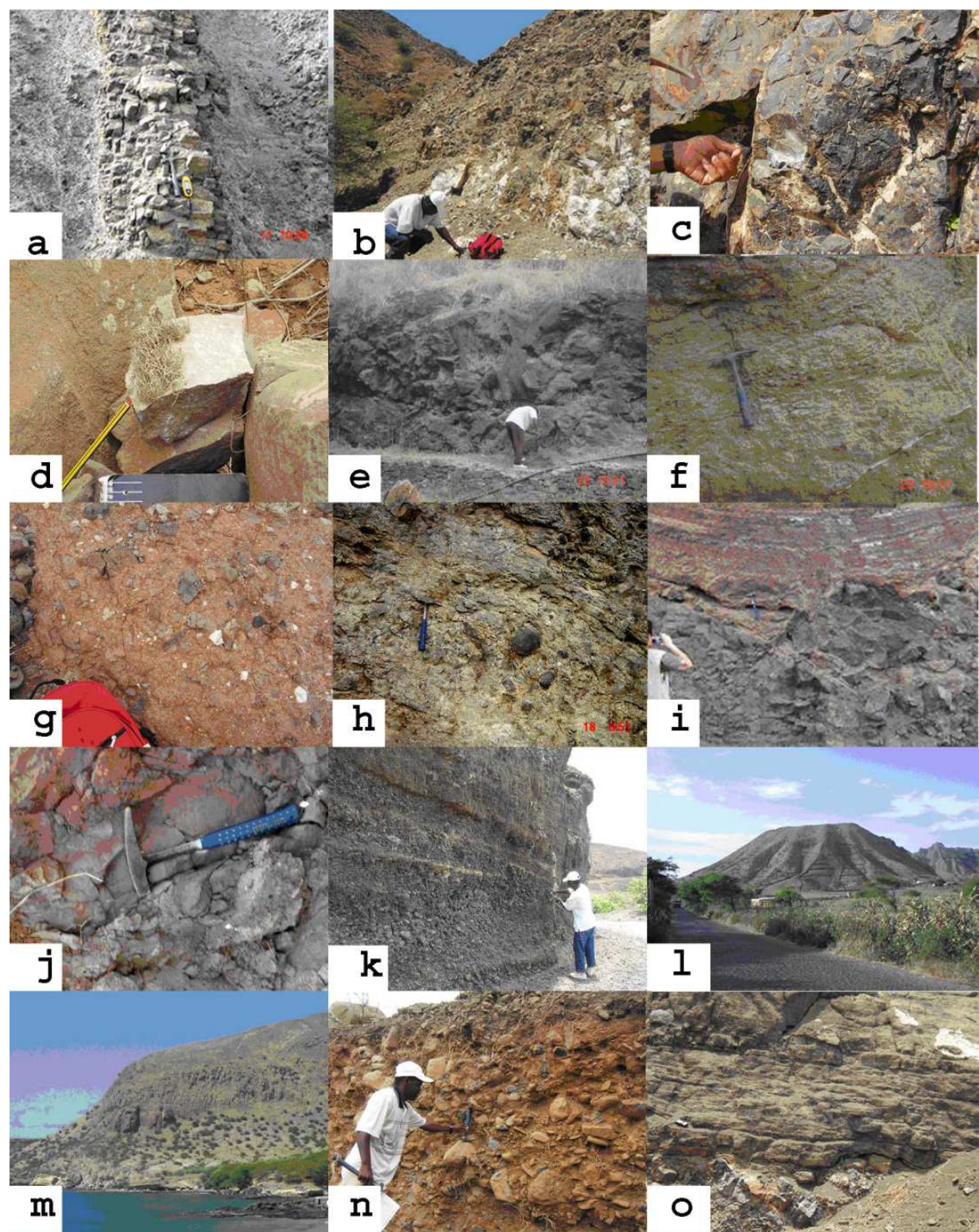
Fig. 3. Different geological formations

2.2.2 Flamengos Formation (FL)

The Flamengos Formation (FL) occurs essentially in the centre and south of the island, mainly at the northeast slope (Figure 2). It is of submarine nature and is constituted by

extended basaltic mantles, formed by the stacking of pillow-lavas (Figure 3 e), with subordinated breccias (Figure 3 e) and intercalated tuffs (Figure 3 f), which form compact deposits and are very altered. The rocks are limburgites, basanites and basanitoides, which are intensely altered into zeolites and carbonates.

2.2.3 Orgãos Formation (CB)

The Formation of Orgãos (CB) occurs mainly in the region of S. Lourenço dos Orgãos (Figure 2). The Formation of Orgãos (CB) is essentially a volcano-sedimentary unit, formed by a breccia/conglomerate with a sandstone matrix and may correspond to lahars. This formation is characterized by the high heterogeneity of materials (Figure 3 g, 3 h) and is generally weathered. The clasts are mostly of basalt, but also of phonolite and, not often, are of granular rocks derived from CA. The cement contains carbonated and zeolitic material. Beside the continental facies there are also marine and estuarine, fossiliferous deposits.

2.2.4 Eruptive Complex of Pico da Antónia (PA)

The PA is the geological formation more developed on the Santiago Island (Figure 2) and it is responsible for the high altitudes and the main structural platforms seen on the island. This unit is essentially formed by thick sequences of basaltic lava flows, intercalated by pyroclastic material (Figure 3i). The petrographic types are basanites, ancaratrites and limburgites and also nephelinites and olivine-melilitite (Matos Alves et al., 1979). PA also contains phonolites, trackytes and tuff-breccias. The phonolitic and trackytic rocks form dikes, chimneys, endogenous domes and pyroclastic formations. The PA Formation is constituted in its upper part by thick levels of pyroclasts, some lava flows and vertical dikes, which in certain cases have a glassy texture.

2.2.5 Assomada Formation (AS)

The Assomada Formation (AS) occupies a large depression, between the two largest elevations of the island, Pico da Antónia (1392 m) and Serra da Malagueta (1063m), (Figure 2). The Assomada Formation is constituted by basaltic mantles and some basaltic pyroclastes, originated exclusively from sub-aerial volcanic activity. The wide lavas flows, almost horizontal have reached the shore, flowing to west (Figure 2) and forming the plateau of Assomada. The rocks are essentially basanites, which are weathered in some places, presenting greyish and reddish colors (Figure 3 j).

2.2.6 Monte das Vacas Formation (MV)

The formation Monte das Vacas (MV) is the last volcanic episode in Santiago Island and it is represented by 50 cinder cones (Figures 2 and 3 k, 3 l) and small subordinated flows. The constituting materials are loosely aggregated (Figure 3 k) and are exploited for construction, originating gullies and landslides on the flanks due to erosive action of the water during intense rainfalls (Figure 3 l).

2.2.7 Quaternary Formations (CC)

The Quaternary Formations have a small spatial representation, occupying an area of 8.5% of the area of the Santiago Island above water (Figure 2). These sedimentary formations are

ancient and modern alluvium, torrent deposits, sand dunes and marine beaches (Figure 3 m, 3 n, 3 o). The terraces reach altitudes of about 100m and are formed by materials with dimensions ranging from clay to big blocks that reach 2 meters.

3. Methods

3.1 Sample collection and treatment

Sampling, sample preparation and analytical programme were performed according to the recommendations of the IGCP (International Geological Correlation Programme) Project 259 "International geochemical mapping" (Darnley et al. 1995). So, the sampling sites for stream sediments were randomly selected to represent small drainage basins and are evenly distributed within the study area. Composite samples of stream sediments were collected in 337 sites, representing stream sediments developed from all the geological formations in Santiago Island, at a density of approximately 0.3 site/km². To establish the sampling sites the guidelines of the IGCP 259 project were followed, which state that the stream sediments of these sites must be as pristine as possible. On each site the composite sample (~1kg) was obtained in collecting five points, spaced approximately 50 m along the water line. The sampling sites were selected to represent pristine sediments, therefore locations affected by pollution (near factories or heavy traffic roads) and arable soils were avoided. Duplicates samples were taken every 10 sites. The samples were dried at 35-40 °C, sieved to <2 mm through a plastic sieve, homogenized and quartered. Sub-samples of 50g each were obtained and crushed to < 75 μm for analysis.

3.2 Analysis and analytical quality control

The chemical analysis was performed in the ACME Analytical Laboratories, Ltd, Vancouver, Canada. Each sample was digested in aqua regia and analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U, and V. All the sub-samples were randomly numbered prior to analysis in order to remove any systematic relationship between the analysis order and geographic location. The data resulting from the chemical analysis of the elements was subjected to several data quality tests in order to determine which elements have reliable data to be analysed. The criteria used to select an element to subsequent statistical analysis were: (i) at least of 80% of the observations with a content greater than the detection limit; (ii) accuracy and precision (quantified by analytical duplicates) lower than 10%; and (iii) geochemical variance significantly representative (0.01 significance level) of the total observed variance (quantified by an Analysis of Variance using field duplicates). All above mentioned elements passed these quality tests. Table 1 shows the standard deviations (SD), asymmetry (Asy), curtosys (Kurt), coefficient of variation percent (CV%), minimum (Min), maximum (Max) and range of the concentrations of the elements analysed.

The mineralogical composition of the < 2mm fraction of 83 selected stream sediments samples, representing all geological formations of the island, was studied by X-ray diffraction (XRD). The XRD was performed at the Department of Geosciences, University of Aveiro. It was used the method of crystalline dust, and graphic mode register (post diffractometry technique). It was used a Philips X´Pert diffractometer, with a PW3050 goniometer, a PW 3040/60 microprocessor and a CuKμ radiation with a Ni filter. The

operation conditions were 30 mA, 50 kV, between 2º-60º, a step size of 0.02 (2t) and a scan step time of 1.05 s and a JCPDS software.

	SD	Asy	Kurt	CV	Min	Median	Max	Range concentrations			Average
Co	13.86	1.21	10.65	0.31	3.1	44.70	139.9	3.1	-	139.9	45.1
Cr	68.03	1.48	7.39	0.55	8.0	114.00	463.1	8.0	-	463.1	123.7
Cu	17.99	0.51	5.33	0.37	3.2	48.80	141.6	3.2	-	141.6	48.6
Fe	1.65	0.35	4.09	0.24	1.61	6.64	13.53	1.61	-	13.5	6.8
Mn	441.65	2.06	11.72	0.35	197.00	1191.00	4210.0	197.0	-	4210.0	1259.9
Ni	76.02	0.50	4.10	0.47	0.0	155.20	0.4	0.0	-	0.4	160.5
Pb	6.61	7.50	72.21	1.26	1.2	3.90	25.8	1.2	-	25.8	5.2
Th	1.45	2.72	17.49	0.35	0.0	3.90	1.4	0.0	-	1.4	4.2
U	0.24	1.83	10.21	0.35	0.2	0.6	2.3	0.2	-	2.3	0.7
V	45.68	0.64	5.51	0.28	24.0	160.0	372.0	24.0	-	372.0	170.0

Table 1. Statistical parameters of the metals Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U and V, analyzed from the stream sediments of Santiago Island (n=337). Contents of metals in mg kg⁻¹ except for Fe (%). Min: minimum; Max: maximun, SD: standard deviation, Ass: asymmetry, Kurt: kurtosis, CV: coefficient of variation

3.3 Estimated background value for selected harmful elements

Policy makers usually prefer a single value representative of an entire country or region, although the background value of an element may present a considerable spatial variability, and, thus, are presented by distribution maps. So, we determined an EBV representative of the entire Santiago Island (EBV-S), and one EBV representative of each one of its geological formations (EBV-xx, where xx are the initials of a particular geological formation). The EBV-S was calculated as the median of the data set limited by the Tukey Range or also referred to as the Non-Anomalous Range (Tukey, 1977):]P25-1.5*(P75-P25), P75+1.5*(P75-P25)[. The Tukey Range filters out the outliers or the anomalous data. The EBV-xx were calculated as the EBV-S, with the difference that the data set used in the calculations consists of those sampling points that belong to the xx geological formation.

The degree of depletion or enrichment of each element in the stream sediments of Santiago in relation to the value for the upper crust (Rudnick & Gao, 1995), using the EBV-S of each element, was also quantified.

3.4 Statistical analysis and mapping

The spatial distribution of the content of a geochemical element sampled in stream sediment points (spatial locations) is not a spatially continuous field. The content of a particular point is representative of that point only, although it has also the contribution of the points located upstream of the stream sediment line. Since the field is not continuous (or is only along each stream sediment line) it makes no sense to perform a spatial interpolation between two points lying on two different stream sediment lines. Because of this, the spatial distribution of each element is mapped using dot points and not contour lines (isolines).

Spatial distributions of Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U, and V content were mapped using 337 samples of stream sediments, following the recommendations of Darnley et al. (1995). All the calculations and data visualization were made using Matlab which is a well-known and widely used general purpose programming language (http://www.mathworks.com). The size of the dot increases with increasing class levels. The diameter of the symbols were classified in 8 classes defined by the following intervals: [minimum -P10[; [P10-P25[; [P25-P50[; [P50-P75[;[P75-P90[;[P90-P95[;[P95-P97.5[; [P97.5-maximum], where Px is the xth percentile value. In each figure, it is also shown the histogram (blue bars) and corresponding empirical Cumulative Distribution Function (CDF) (red dots), because they provide an estimate of the probability distribution of the data. The histogram was constructed using the same classes of dot distribution maps. The boxplot, calculated according to Tukey (1977), is also included.

A Principal Component Analysis (PCA) was also performed, using the correlation matrix, and the first three Principal Components (PCs) are mapped using the same methodology used to map the content of selected harmful elements. The number of PCs to retain was objectively determined using the scree plot.

4. Results and discussion

4.1 Relative proportions of minerals in the stream sediments of the Santiago Island

The mineralogical composition of the stream sediments is primarily governed by the mineralogy of the bedrock, climatic conditions (precipitation, temperature, wind direction) and topography. Chemical weathering is not intense in Santiago, due to the semi-arid climatic conditions and the vigorous relief. The chemical alteration of rocks leads to the formation of phyllosilicate, hematite, calcite and quartz, that, together with the primary minerals, desegregated by physical alteration of the rock, are eroded and will form the stream sediments. Figure 4 shows the relative proportions of the various minerals identified in stream sediments in the different geological formations of Santiago Island.
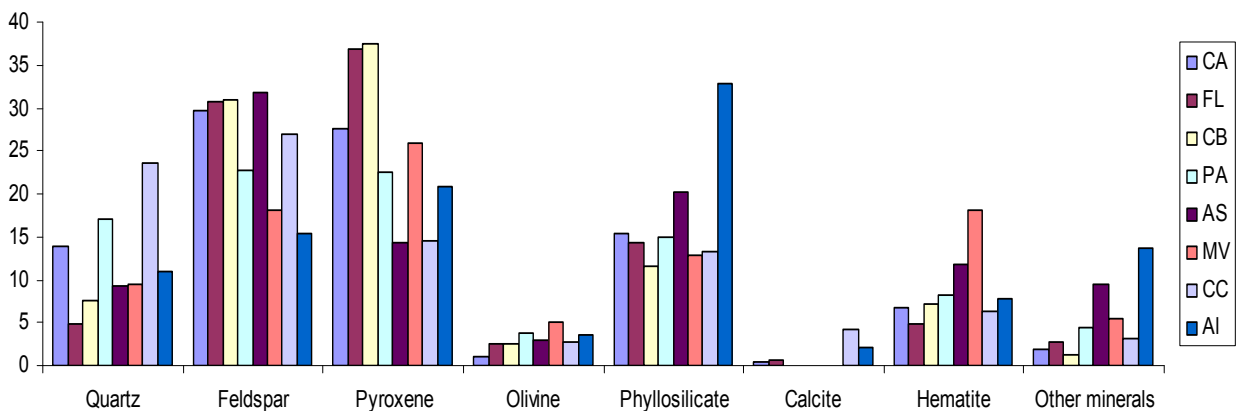

Fig. 4. Relative proportions, in percentage, of minerals in the stream sediments of Santiago Island. Geological formations: CA – Ancient Internal Eruptive Complex (n=5), FL– Flamengos Formation (n=23), CB– Órgãos Formation (n=13), PA – Pico da Antónia Formation (n=14), AS – Assomada Formation (n=5), MV – Monte das Vacas Formation (n=4), CC – Calcários e Cascalheiras Formation (n=4), Al: Alluvium (n=15)

The stream sediments associated with the CA Formation are composed mainly (in descending order of relative proportion) by plagioclase and K-feldspar (30.4%), pyroxene (28.3%), phyllosilicate (15.8%) (smectite, mica / illite), quartz (14.1%), hematite (6.8%), "other minerals" (1.8%) (such as larnite, siderite, leucite, apatite, magnetite, aragonite), olivine (1.1%) and calcite (0.4%) (Figure 4).

The stream sediments occurring in the FL, CB and PA formations consist mainly of pyroxene (36.8%, 37.4% and 23.9%, respectively), plagioclase and K-feldspar (30.8%, 30.9% and 24.0%, respectively), and phyllosilicate (14.3%, 11.6% and 15.9%, respectively). They differ by the proportions of different phyllosilicate and by the relative proportions of the other minerals identified. In descending order, in stream sediments of the FL it occurs (smectite+ interstratified, mica / illite), quartz (4.8%), hematite (4.9%), olivine (2.6%) and "other minerals" (2.8%) (magnetite, chromite, larnite, siderite, leucite, apatite, aragonite, opal, barite, halite); in stream sediments of CB formation it occurs (smectite and traces of mica / illite and kaolinite), quartz (7.5%), hematite (7.2%), olivine (2.4%), and "other minerals" (1.2%) (chromite, larnite, siderite, garnet, opal, barite, dolomite), and in the stream sediments of PA Formation it occurs (kaolinite, mica, illite and smectite), quartz (18.0%), hematite (8.7%), "other minerals" (4.7%) (larnite, siderite, zeolite, dolomite, garnet) and olivine (4.0%) (Figure 4).

The stream sediments associated with the AS Formation consist of plagioclase and K-feldspar (31.7%), phyllosilicate (20.3%) (mica / illite and smectite), pyroxene (14.3%), hematite (11.9%), "other minerals" (9.5%) (magnetite, zeolite, larnite, siderite), quartz (9.4%) and olivine (3.0%). These stream sediments have the highest proportion of phyllosilicate (with the exception of the alluvium) because the rocks of this formation are very weathered.

The stream sediments that occur on the MV Formation are composed by pyroxene (27.1%), plagioclase and K-feldspar (18.9%), hematite (18.8%), phyllosilicate (13.5%) (mainly kaolinite), quartz (9.9%), "other minerals" (5.6%) (magnetite, chromite, larnite, siderite) and olivine (5.3%). The stream sediments that occur on the CC Formation have plagioclase and K-feldspar (28.5%), quartz (24.8%), phyllosilicate (13.0%) (kaolinite, smectite), pyroxene (15.2%), and in lesser proportions calcite (4.3%), hematite (6.6%), olivine (3.9%) and "other minerals" (3.3%) (magnetite, larnite, siderite). The alluvium is distinct from the other stream sediments because it is richer in phyllosilicate (13.6%), "other minerals" (4.1%) (mainly magnetite, zeolite, siderite) and have very little feldspar (23.9%) (Figure 4).

The minerals that occur in higher proportions in the stream sediments are feldspars and pyroxene, which are the principal primary components of rocks forming the island and so they and were eroded from the volcanic rocks. So the mineralogy of stream sediments is essentially conditioned by the lithology and erosion, while the alluvium is conditioned by relief, as it is located in areas of flattened valleys, where the deposition of clay minerals occurs.

4.2 Estimated background values of Santiago Island and of its geological formations

Although the background value of an element may present a considerable spatial variability, and, thus, is presented by distribution maps, policy makers usually prefer a single value representative of an entire country or region. The chemical background of an element has been estimated in different statistical ways in the literature, either by interval

estimation or by point estimation. Table 2 presents four interval estimators (Observed Range, P_5-P_{95} Range, Tukey Range and Expected Range) and one point estimator (Estimated Background Value for Santiago stream sediments, EBV-S).

	Min	-	Max	P_5	-	P_{95}	Tukey Range			Dudka Range			EBV-S
Co	3.1	-	139.9	26.4	-	66.1	15.8	-	73.4	20.5	-	89.0	44.7
Cr	8.0	-	463.1	20.0	-	251.5	8.0	-	264.0	26.8	-	401.2	111.0
Cu	3.2	-	141.6	17.6	-	77.8	9.4	-	87.6	17.3	-	114.5	48.7
Fe	1.61	-	13.53	4.47	-	9.64	2.65	-	10.70	3.87	-	11.13	6.60
Mn	0.2	-	4.2	0.3	-	1.3	0.1	-	1.5	0.3	-	1.7	0.6
Ni	0.0	-	0.4	0.1	-	0.3	0.0	-	0.3	0.1	-	0.4	0.16
Pb	1.2	-	25.8	3.7	-	15.3	1.2	-	16.4	3.3	-	18.3	7.7
Th	0.0	-	1.4	0.3	-	0.9	0.0	-	1.0	0.2	-	1.2	0.5
U	0.2	-	2.3	0.4	-	1.1	0.5	-	1.25	0.3	-	1.2	0.6
V	24.0	-	372.0	92.4	-	237.3	50.5	-	262.5	81.6	-	290.7	159.0

Table 2. Background concentrations of metals from the stream sediments of Santiago Island estimated by five different estimators. Contents of metals in mg kg^{-1} except for Fe and Mn (%)

The difficulty of establishing a single value of background level is well illustrated in Table 2, given the ranges of variation in their natural concentrations. The range values contained between P5 and P95 is, in most cases, narrower than that obtained in the Non-Anomalous Range, calculated by the Tukey method (Tukey, 1977). The range values calculated by the Expected Range (Dudka, 1995), presents, usually, higher upper limits, while the Tukey Range (Tukey 1977) comprises lower bottom limits.

The EBV-S of the studied metals in Santiago stream sediments are compared with the values estimated for the upper crust (UC, Rudnick & Gao, 1995) in Figure 5, where the Tukey Range is also shown. Figure 6 shows the enrichment or impoverishment in metal content of Santiago stream sediments relative to the values of the upper crust (Holland & Turekian, 2005 in Rudnick & Gao, 1995).
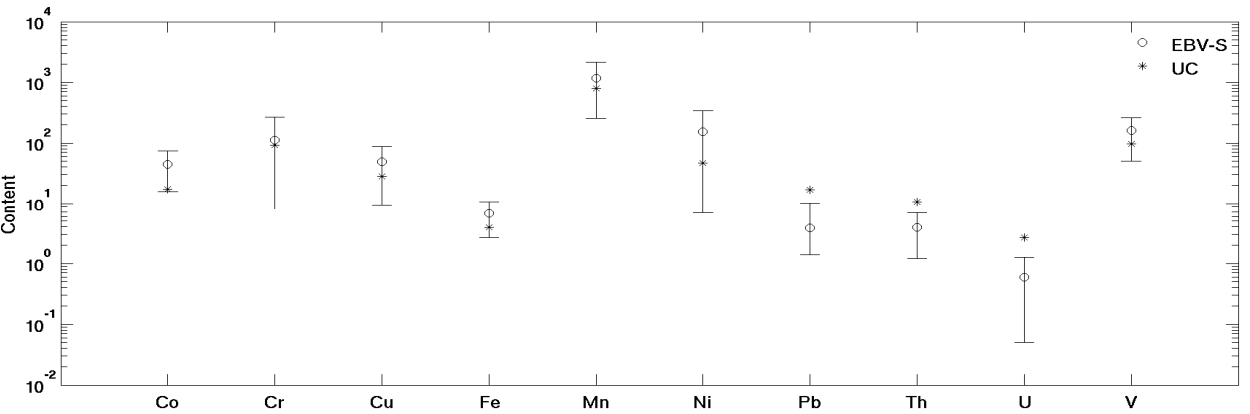

Fig. 5. EBV-S (circles) and Tukey Range of metals in Santiago stream sediments, and upper crust reference values (UC, asterisks), according to Rudnick & Gao, 1995
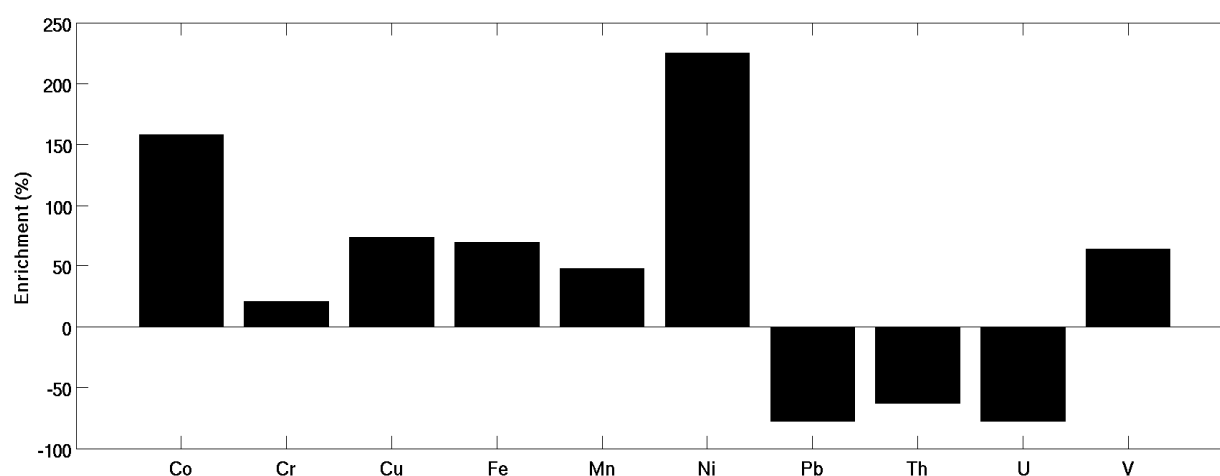
Fig. 6. Enrichment (%) in metal content of Santiago stream sediments relatively to the upper crust reference values (UC, Holland & Turekian, 2005 in Rudnick & Gao, 1995), determined by 100(EBV-UC)/UC

Stream sediments of Santiago Island have higher contents in Co, Cr, Cu, Fe, Mn, Ni and V than those on the upper crust (UC) (Figures 5 and 6). Volcanic rocks of Santiago Island, which occupy the majority of the area of the Island, are mainly basanites, alkaline basalt and trachytic-phonolitic rocks, rich in siderophile elements (Fe, Mn, Co, Cr, Ni). This agreement suggests that the metal composition of the stream sediments is controlled by the chemical composition of the parent rock. The results shows also that the stream sediments of Santiago are impoverished in Pb, Th, and U. Furthermore, the UC values of these metals are higher than the upper limit of the Tukey range (Figure 5). This is due to the fact that the upper crust has a granodioritic composition, and is therefore rich in these elements.

In order to further explore the relationship of the spatial distributions of the EPVs and the geological formations, we show in Table 3 the estimated background values (EBV-xx) of the studied metals in the stream sediments collected from the different geological formations of the Island. Stream sediments derived from Ancient Complex (CA) have high Cr and V. Stream sediments from Flamengos formation (FL) have low Pb and high Cu. Órgãos formation (CB) have stream sediments with high Cu, and low Fe, Mn, Th and U. Stream sediments derived from Pico da Antónia (PA) formation have high Co, Cr, Fe, Ni and V. Stream sediments derived from Assomada (AS) and Monte das Vacas (MV) formations have high Fe, Mn (as sediments from CA formation) and Pb, and low Co, Cr, Cu and Ni. Stream sediments samples collected in MV formation distinguish from the other sediments samples by its high Th and low V contents. Finally, stream sediments from CC formation have low Th and U.

4.3 Maps of estimated background values

Figure 7 presents the dot distribution maps of studied harmful metals. Is also presented for each element the boxplot, calculated according to Tukey (1977), the histogram (blue bars) and the corresponding empirical CDF (red dots).

	EBV-CA	EBV-FL	EBV-CB	EBV-PA	EBV-AS	EBV-MV	EBV-CC	EBV-AL
Cd	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.1
Co	43.6	41.3	40.3	48.8	35.8	42.6	42.2	44.9
Cr	116.0	112.5	99.0	122.5	20.5	76.0	93.5	119.3
Cu	53.8	57.6	56.7	46.6	26.4	34.2	47.4	48.9
Fe	7.04	6.12	5.99	7.03	8.12	6.90	5.97	6.54
Mn	1199.0	1035.5	980.0	1328.0	1612.0	1423.0	1026.5	1157.0
Ni	126.7	139.1	145.1	168.1	20.1	104.1	148.9	164.1
Pb	3.6	2.5	3.3	4.7	6.6	6.0	4.1	3.4
Th	4.0	3.6	3.4	3.9	4.0	4.1	3.7	3.8
U	0.7	0.7	0.5	0.6	0.7	0.7	0.5	0.7
V	166.0	157.5	148.0	167.0	153.0	131.0	147.0	156.0

Table 3. Comparison of the Estimated Background Values (EBVs) between the different geological formations of the stream sediments of Santiago Island, Cape Verde. Concentration of Fe expressed in % and Co, Cr, Cu, Mn, Ni, Pb, Th, U and V in mg kg^{-1}

The comparison of the Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U and V dot maps with the geological map shows that a clear chemical characterization of stream sediments in different geological formations is difficult, since the chemical composition of each sample represents the chemical composition of the entire area upstream, covering different geological formations. However, it seems that same associations between the geological formation and stream sediments composition can be identified.

Lead, Mn, U and Th appear to be highly correlated to phonolitic-trachytics rocks of Pico Antónia (PA) and Ancient Internal Eruptive Complex (CA), and also with pyroclastic deposits of Monte das Vacas and Assomada formations. Contrarily, the Órgãos and Flamengos formations are depleted in these metals. Assomada and Monte das Vacas formations are depleted in Ni, Co, Cr, Cu, and Flamengos and Órgãos formations are depleted in Fe. Stream sediments derived from CC formation is depleted in V and Fe. Cobalt, Cr, Ni, and V appear to be highly correlated to basaltic-basanite rocks of Pico Antónia formation.

In order to try to establish the association between the Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U, and V, spatial distribution and the geology, a correlation-based PCA was conducted. Using the scree plot it was decided to retain three Principal Components (PCs - Figure 8).
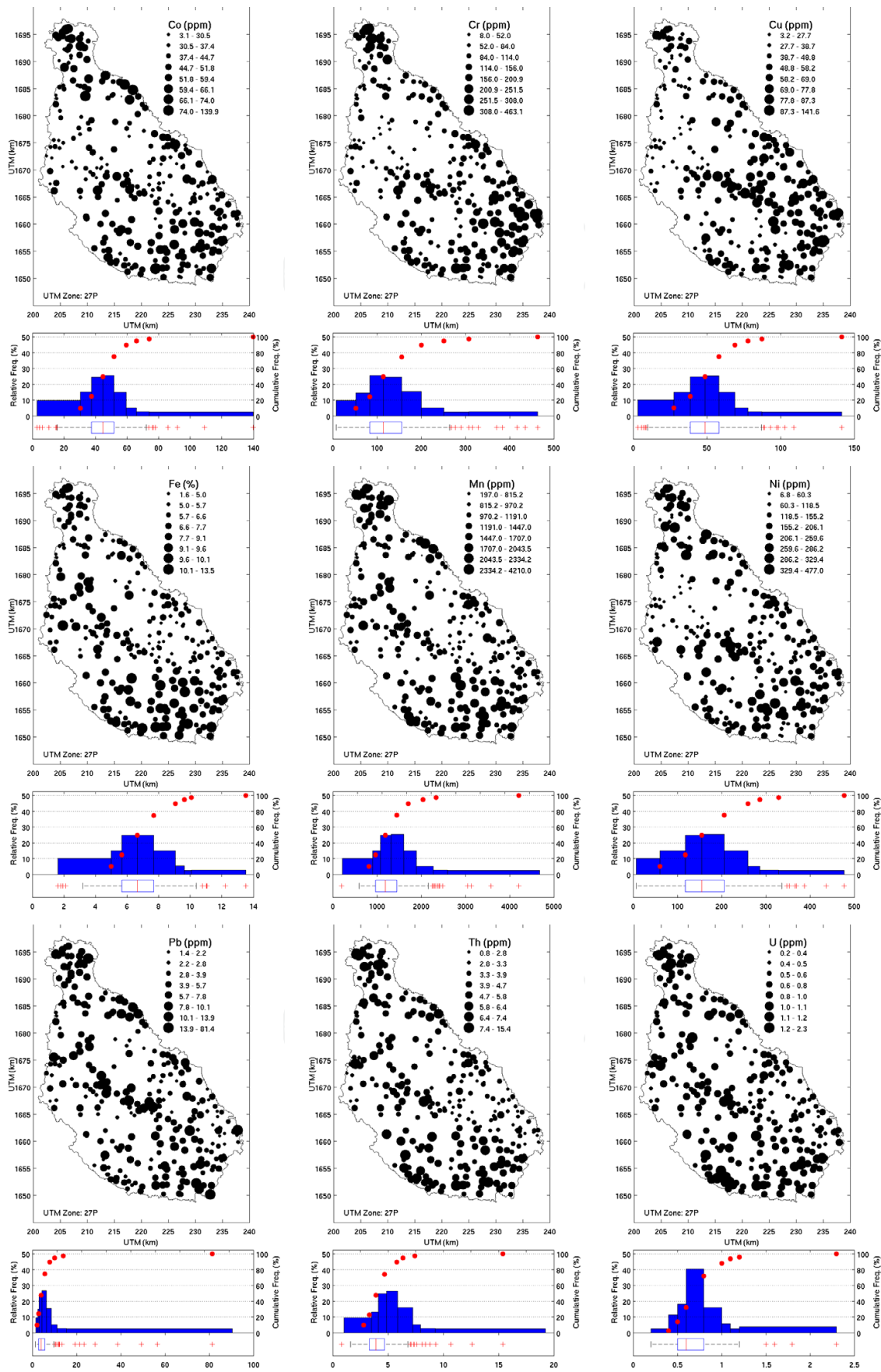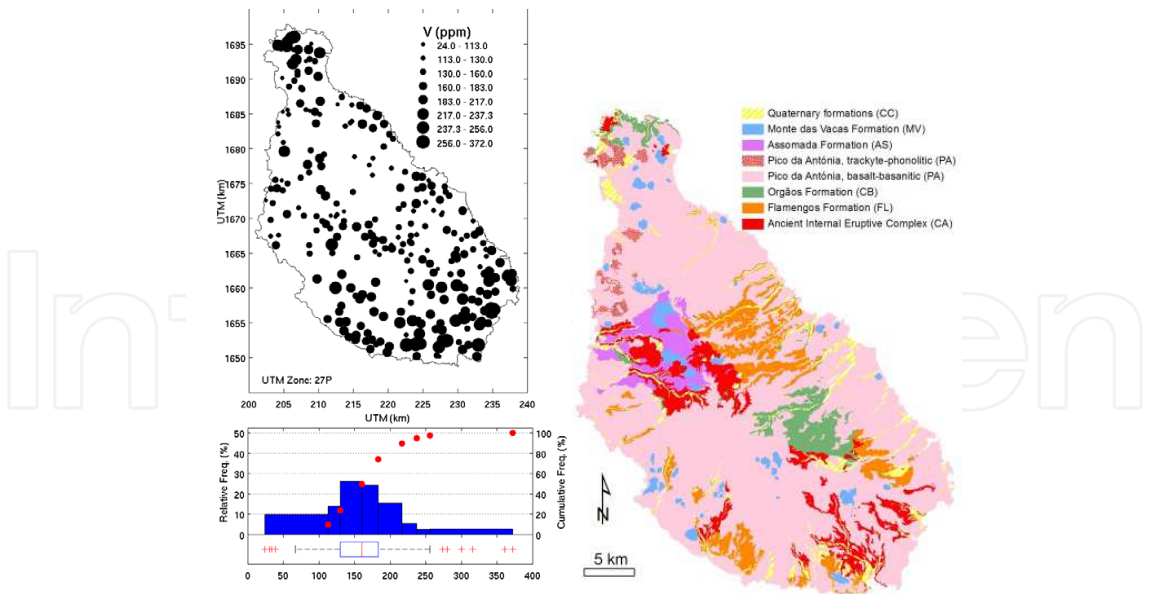
Fig. 7. Spatial distribution, histogram and associated empirical CDF, and boxplot of the EBV of Co, Cr, Cu, Fe, Mn, Ni, Pb, Th, U and V. Geological map is presented for comparison
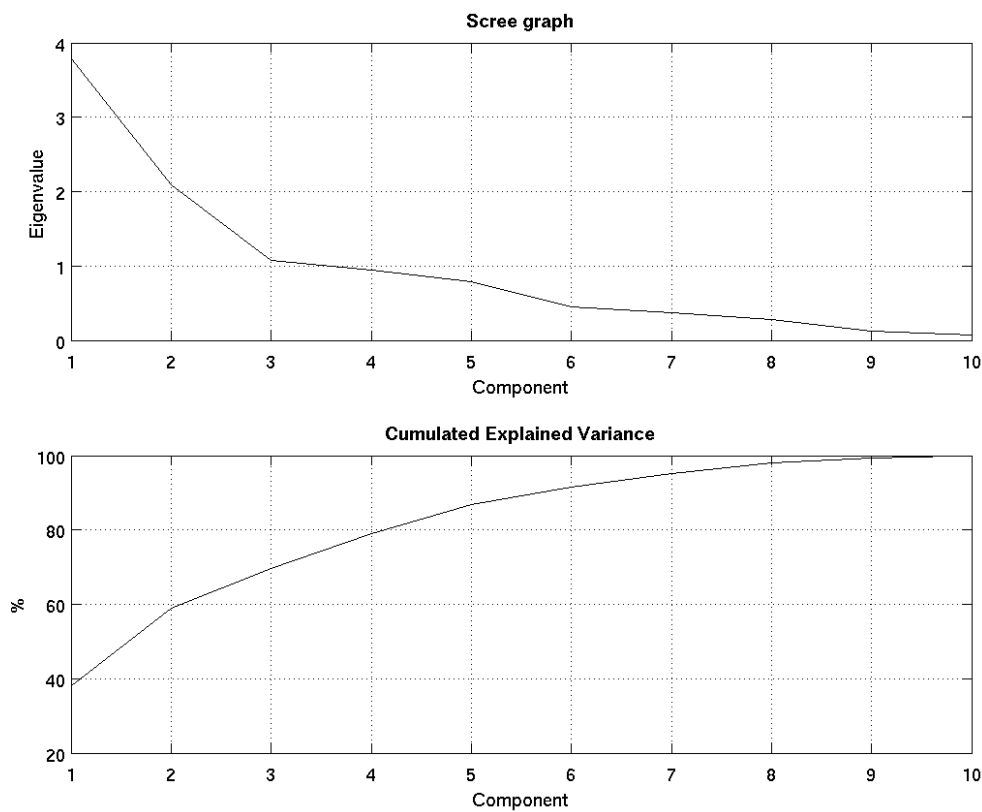

Fig. 8. Eigenvalue (upper panel) and Cumulative Explained Variance (lower panel) of the first ten PCA mode

The first three PCs represent 69.6% of total variability (37.96% + 20.87% + 0.77%). The loadings of these PCs are shown in the plots of PV1 vs PV2 and PV1 vs PV3 (Figure 9).
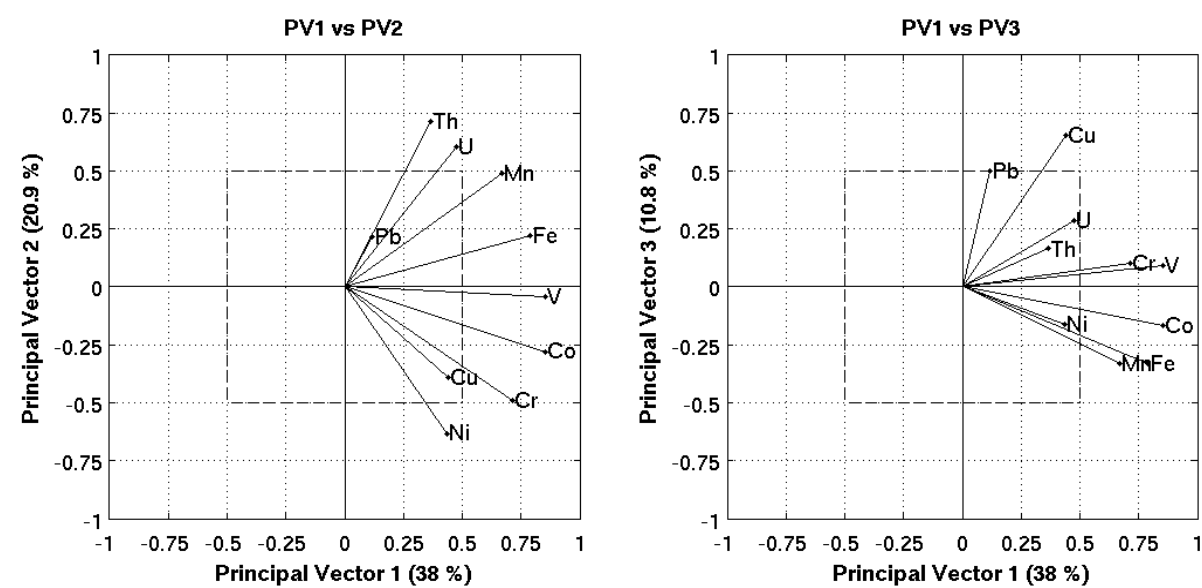
Fig. 9. PV1 versus PV2 (left) and PV1 versus PV3 (right)

The elements whose loadings in each PC have an absolute value greater than 0.5 are:

- PC1: Co, Cr, Fe, Mn and V
- PC2: Th and U oppose in sign to Ni
- PC3: Cu and Pb.

The association in PC1 clearly shows the influence of a rich lithology in siderofile elements (Co, Cr, Fe), typical of basic rocks and the presence of minerals such pyroxene (Fe, V), amphibole, olivine and magnetite (Fe), serpentine (Co, Cr, Ni). The metal association in PC2 represent crustal elements, typical of acid rocks, and show the presence of zircon (U, Th), oppose in sign to Ni, which enters in the structure of minerals typical of basaltic rocks, such as serpentine (Co, Cr, Ni). The PC scores are presented in Figure 10.
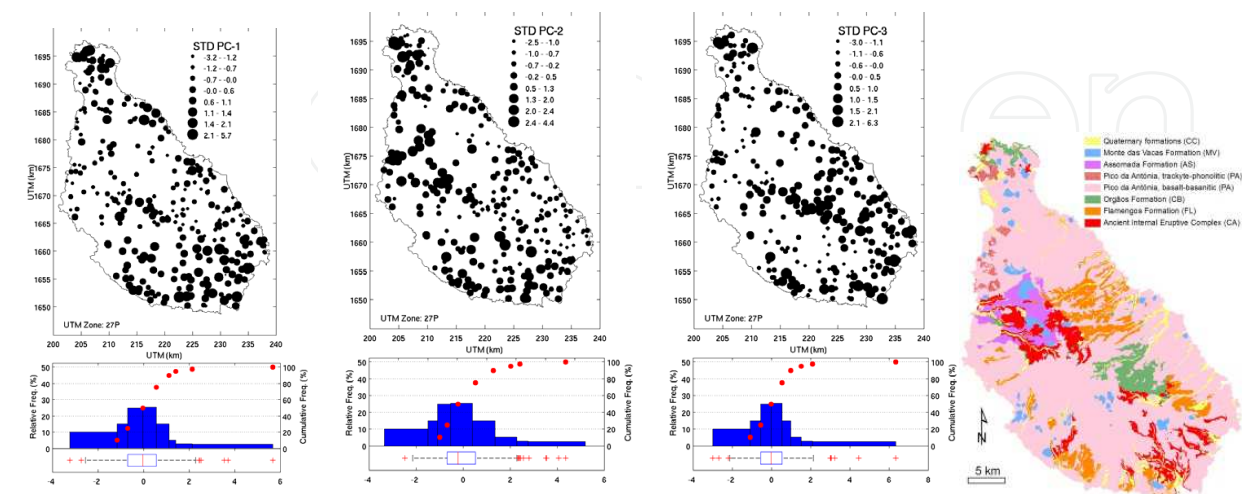
Fig. 10. Spatial distribution, histogram and associated empirical CDF, and boxplot of PC1, PC2 and PC3. Geological map is presented for comparison

When comparing the spatial distribution of the PCs (Figure 10) with the geological formations, it not clear a relationship between them. For example, PC1 is associated with basaltic-basanite rocks of the PA formation, contrarily to the Flamengos formation (FL); however, the AS formation is depleted in Co, Cr, but is the richest in Fe and Mn; PC2 is associated to phonolitic-trachytics rocks of Pico Antónia (PA), Assomada (AS) and Monte das Vacas (MV). PC3 is associated probably to anthropogenic origin.

5. Conclusions

A clear chemical characterization of the stream sediments in different geological formations is difficult, since the chemical composition of each sampling point represents the chemical composition of the entire area upstream, covering different geological formations. Despite this constraint, the results of PCA distinguished three associations of key variables. The first (Co, Cr, Fe, Mn, V) consists of elements enriched in basic rocks, and compatible elements. These elements are related to pyroxene, amphibole, and olivine minerals. The second association of variables, Th and U, as opposed to variable Ni, appears to be strongly controlled by the composition of alkaline volcanic rocks and pyroclastic rocks. The K-feldspar, zircon, pyroxene, amphibole, olivine are examples of minerals that are causing this association. The third association (Cu and Pb) consists of elements of anthropogenic origin.

The minerals present in stream sediments from Santiago Island are a combination of minerals inherited from the original lithology, minerals resulting from alteration of these primary minerals, and probably also wind-transported, largely from the Sahara desert (quartz and phyllossilicates).

The mineralogical composition of stream sediments of Santiago are dominated by primary silicate minerals, such as feldspar, pyroxene and olivine, and also quartz. The main secondary minerals are phyllosilicates (smectite, kaolinite, mica / illite), calcite and hematite. Thus the stream sediments have a high relative proportion of primary minerals, reflecting the mineralogical signature of the igneous rocks that support the island. In the "other minerals" group were identified leucite, apatite, nepheline, magnetite, titanomagnetite, ilmenite, chromite, garnet, zeolites, siderite, opal, barite, sphene, zircon, halite, aragonite, dolomite, brucite and chlorite, most of them are primary. The existence of quartz must result fundamentally of wind-transported from Saara desert, but also from the weathered of rocks;

The mineralogical composition of the stream sediments results mainly from the composition of the rocks upstream;

In terms of the relation between stream sediments composition and geological formation we can be concluded that:

a. the stream sediments that occur on the PA formation have the highest background values for the variables Co, Cr, Ni, V, which explains the enrichment seen in association Co-Cr-Fe-Mn, which is consistent with mineralogical analysis. They consist mainly of pyroxene, plagioclase, potassium feldspar, and phyllosilicates, and may also experience other minerals such as hematite, olivine, magnetite, chromite, larnite, siderite, leucite, apatite, garnet, aragonite, brucite, opal, barite, halite;

b. the stream sediments collected associated with the CB formation show depletion in Th-U and Mn, which is consistent with the results obtained for the analysis of rocks (Cabral Pinto et al. 2011a). The sediments associated with this formation are composed mainly of pyroxene, plagioclase, potassium feldspar, and phyllosilicates (smectite, mica / illite), hematite, quartz, olivine and chromite, larnite, sidereite, opal, barite, and garnet, dolomite, brucite;

c. the majority of the samples of stream sediments that occur associated with the AS formation is enriched in Th-U and in the elements Fe, V, Mn and impoverished in Co-Cr-Cu-Ni association, probably because this geological formation is significantly weathered and consequently impoverished in primary minerals such as pyroxene and olivine, and enriched in weathered minerals, such as hematite, phyllosilicates, serpentine and zeolite. Chemical analysis of this formation the rocks show higher levels of Fe (Cabral Pinto et al. 2011a).

d. the stream sediments associated with the Monte das Vacas formation are impoverished in Co-Cr-Ni-V. They consist of pyroxene, hematite, plagioclase and potassium feldspar, phyllosilicates, quartz, magnetite, chromite, barite, larnite, siderite and olivine;

e. the alluvium samples are distinguished from other stream sediments because they are rich in phyllosilicates, other minerals, and are poor in feldspar. Its mineralogical composition is conditioned by weathering and relief, as the alluvium is located in areas of flattened valleys were the deposition of clay minerals occurs;

The spatial distribution of the selected elements allowed to establish relationships between the concentrations and the geological formations. These relationships were confirmed by the results of PCA. Firstly, the metals with higher loadings in PC1 clearly show the influence of a rich lithology in siderofile elements (Co, Cr, Fe), typical of basic rocks and the presence of minerals such pyroxene (Fe, V), amphibole, olivine and magnetite (Fe), serpentine (Co, Cr, Ni) and opaque minerals (Cu). Secondly, the metals with higher loadings in PC2 represent crustal elements, typical of acid rocks, and show the presence of zircon (U, Th). Furthermore, the spatial distribution of the first two PCs also allowed us to distinguish associations between chemical elements, essentially of geogenic origin.

The determination of a single EBV for the entire Santiago Island (EBV-S) showed that, in general, stream sediments from this Island have higher contents in Co, Cr, Cu, Fe, Mn, Ni and V than those of the upper crust. Stream sediments from Santiago are impoverished in Pb, Th, and U, relatively to the upper crust.

Finally, the determination of an EBV for each geological formation (EBV-xx) gave us even more confidence on the dependence of the spatial distribution of the EPVs from the geological formations.

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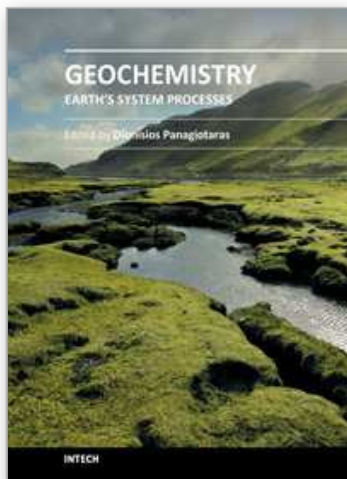
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