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Contaminated water, stream sediments and soils close to the abandoned Pinhal do Souto uranium mine, central Portugal

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A B S T R A C T

The Pinhal do Souto mine exploited a quartz vein containing uranium minerals, mainly autunite and torbernite. This vein intersects a two-mica granite containing 10 ppm U and uraninite. The mine was exploited underground and produced 93091 kg U_3O_8 between 1978 and 1989 and was then closed down. Two dumps were left in the mine area and these are partially covered by natural vegetation. Groundwater and surface water have a similar slightly acid-to-alkaline pH. The UO_2^{2+} is abundant and complexed with CO_3^{2-}, under neutral to alkaline pH. Metals and arsenic concentrations in the water increase during the dry season due to the evaporation. Uranium concentration in the water increases (up to 104.42 μg/l) in the wet season, because secondary uranium minerals are dissolved and uranium is released into the water. Soils tend to retain a higher concentration of several metals, including U (up to 336.79 mg/kg) than stream sediments (up to 35.68 mg/kg), because vermiculite from the former could adsorb it more easily than could kaolinite from the latter. The Fe-oxides precipitate retains the highest concentrations of several metals, including U and Th (up to 485.20 and 1053.12 mg/kg, respectively) and the metalloid As, because it is richer

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in oxyhydroxides and organic matter than stream sediments and soils. The median concentrations of Fe, As, Cd, Pb, Sb, Th, U, W and Zn in soils from this area are higher than in European soils of the FOREGS data. Waters from dry and wet seasons, stream sediments and soils are contaminated and must not be used. This area was compared with another Portuguese abandoned uranium mine area. The former mine caused a lower environmental impact attributable to it having lower sulfide concentration and mineral alteration than in the latter.

Keywords: Abandoned uranium mine; Water; Stream sediments; Soils; Contamination

1. Introduction

The extraction of uranium ore produces tailings, large volumes of contaminated waste rocks and heap-leach residues accumulated in dumps at the mine site. The sulfides present are oxidized, causing acidification of water and the release of metals. The erosion and weathering of dumps cause contamination of surface water and groundwater (e.g Gómez et al., 2006) leading to contamination of stream sediments and soils (e.g. Lottermoser and Ashley, 2005, 2006; Lottermoser et al., 2005; Kipp et al., 2009). Metals and metalloids are fixed by inorganic phases (e.g. Mulligan et al., 2001), as well as organic matter (e.g. Schaller et al., 2011). In the wet season and wet climates, acid mine drainage development and leaching of dumps are dominant pathways of contaminants into the surrounding environment. Recent rehabilitated uranium mine sites located in wet climates have been successfully remediated (e.g. Lottermoser and Ashley, 2006 and papers therein).

Portugal has about 58 uranium deposits that have been exploited and later abandoned, most of them without any remediation processes. Rare Portuguese studies on environmental pollution associated with uranium mines have been reported (e.g. Pinto et al., 2004; Antunes et al., 2011). This paper presents the investigation of environmental impacts caused by the Pinhal do Souto abandoned uranium mine, located in central

Portugal, focusing on water, stream sediments and soils. Such information reinforces the evidence of environmental and human health risks associated with old abandoned mining areas.

2. Geological setting and mineralized quartz vein

The Pinhal do Souto uranium mine is located at the western end of the village of Tragos, near Mangualde, ~ 120 km NE of Coimbra, in central Portugal (Fig. 1a, b) and, geologically it belongs to the Central Iberian Zone of the Iberian Massif. This area consists of two granites and is represented on the Fornos de Algodres Portuguese geological map (Gonçalves et al., 1990), where granites dominate. A coarse-grained porphyritic biotite granite partially surrounds a medium-grained two-mica granite (Fig. 1b). Both Variscan granites intruded the schist-greywacke complex.

The mine consists of a mineralized quartz vein trending N15-32º E, 65-77º ESE, up to 3 m thick at the surface and 18 m thick at depth, which intersects the two-mica granite. This vein is white in colour, locally smoked and reddish, but the last colour is due to Fe-oxides. It contains uranium minerals mainly autunite, $Ca(UO_2)_2(PO_4)_2.10\text{-}12H_2O$ and torbernite, $Cu(UO_2)_2(PO_4)_2.11H_2O$, but also uraninite, UO_2, meta-torbernite, $Cu(UO_2)_2(PO_4)_2.8H_2O$, sabugalite, $HAl(UO_2)_4(PO_4)_4.16H_2O$, parsonite, $Pb_2(UO_2)(PO_4)_2.2H_2O$, phosphuranylite, $Ca(UO_2)_4(PO_4)_2(OH)_4.7H_2O$ and black uranium oxides. The quartz vein is mainly accompanied by an altered lamprophyre. The host granite is altered showing some kaolinite, secondary muscovite and silicification close to fractures.

The uranium mine was exploited underground and had two levels and a gallery at the hillside. The mine produced 93091 kg U_3O_8, retained in ore minerals with 0.72 % U, from 1978 to 1989.

3. The mine site

The Pinhal do Souto uranium mine site is located in a steep, dipping N hillside with altitudes ranging from 650 to 550 m and a slope of about 13%, which is crossed by a NNE trending stream of torrential ephemeral regime. The surface drainage runs to N and W towards the valley of the Ludares stream, which has a very low water flux in the summer and belongs to the Dão river drainage basin.

The annual average temperature in the 1971-2000 period varied from 21.4ºC to 6.9ºC, reaching 40.5ºC in July-September and -7.3ºC to -5ºC in December-February. The rainfall dominates in the winter and the area receives about 1200-1400 mm/year. In 2009/2010 and 2010/2011, the temperature was lower and the precipitation was ~10 mm/month lower in February than in April and 80 mm/month higher in November than in February, although the temperature did not change significantly in these two months (SNIRH, 2012).

The mine gallery is closed and it is flooded in the rainy season. The mine has a vertical extraction shaft and a ventilation shaft. Some hydraulic backfill was also used with tailings from other uranium mines. Two mine waste heaps forming the dumps, were left, one with rock waste and another with low grade ore, and these are partially covered by natural vegetation. The stream sediments are mainly composed of weathered granite and quartz grains. Humic cambilsol holding low develop brown soil (Food and Agriculture Organization of the United Nations, 2006) occurs in the area. The area is almost covered by natural vegetation, consisting mostly of pines, some oaks and herbaceous species, but vineyards and orchards also occur in the valleys and there is also some pasture.

4. Analytical methods

Four wells, two springs, three streams and two mine galleries, all located close to the Pinhal do Souto abandoned uranium mine (Fig. 1c) made a total of eleven sampling points

that were chosen to collect water samples four times during a year in April and July 2010 during the dry season, and November 2010 and February 2011 during the wet season, obtaining a total of 44 water samples. Water from wells was collected 1-2 m below the water level and samples from springs, streams and mine galleries were collected ~ 20 cm below the surface. Temperature, pH, Eh, dissolved oxygen, electrical conductivity and alkalinity were measured in situ. The samples were filtered through 0.45 μm pore size membrane filters. They were acidified with HNO_3 at pH 2 for the determinations of cations by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a Horiba Jovin Yvon JY2000 2 spectrometer with a monochromator. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. The precision was mainly better than 5%, but only better than 15% for Na and Al. Duplicate blanks and a laboratory water standard were analysed for quality control. Total dissolved solids and total solids were determined, corresponding to the weight of material obtained by evaporating of 100 ml of filtered and unfiltered water through 0.45 μm filters, respectively. The analytical data show ion balance errors within ± 5% for most water samples.

A total of 15 samples of stream sediments were collected (Fig. 1c). They were from six places that receive surface drainage from the dumps and the mine gallery, five local streams and four places in the Ludares stream that receive some mine drainage, but at some distance from the mine. A sediment very rich in colloidal Fe-oxides, precipitated from a groundwater close to the old mine was also collected (sample 5; Fig. 1c). A total of 47 soil samples were collected inside or close to the mine area of influence, using a sampling grid of 0.5x0.6 km (Fig. 1d). The stream sediment and soil samples were collected at a depth of 20-30 cm, transported to the laboratory in polyethylene bags, dried

at 40º C, disaggregated with a rubber hammer and sieved through a 2 mm nylon sieve for the determinations of mineralogical, physico-chemical and chemical data. The pH of the samples was measured in a solid-water suspension (liquid/solid ratio of 2.5), whereas electrical conductivity (EC) was measured in a liquid/solid ratio of 1/5. Representative stream sediment (6) and soil (13) samples from the Pinhal do Souto area containing distinct Th and U concentrations were selected to determine organic matter (OM) and cation exchange capacity (CEC), while grain size and mineralogical identifications were also obtained in some of these representative stream sediments (4) and soil (9) samples. The grain size was determined by laser diffraction analysis of the < 2 mm fraction, using a Coulter LS 230 laser granulometer and the accuracy of the grain size analysis is up to 10%. The mineralogical identifications were carried out by X-ray diffraction, using a Philips PW 3710 X-ray diffractometer, with a Cu tube, at 40 kV and 20 nA. The mineralogical composition of the < 2 μm fraction was obtained in oriented samples before and after heating up to 550ºC and with ethylene glycol treatment. These determinations were carried out at the Department of Earth Sciences, University of Coimbra, Portugal. The cation exchange capacity (CEC) was determined as the sum of extractable bases and extractable acidity by the ammonium acetate solution (pH7) method (Thomas, 1982) with a precision of 2%. The organic carbon content was determined using an elemental analyser. After oxidation at 1100ºC, CO_2 was quantified by an NIRD (near infrared detector). The organic matter (OM) was calculated applying a factor of 1.724, on the assumption that OM contains 58% organic carbon (Nelson and Sommers, 1996), with a precision of 2% for stream sediment and 5% for soil. These two determinations were carried out at the Department of Edaphology, University of Trás-os-Montes and Alto Douro, Portugal.

Samples < 250 μm of stream sediments and soils were digested with aqua regia (3:1 HCl-HNO_3), filtered through a 2 μm filter and analysed by an ICP-OES to determine several metals and metalloids at the Department of Earth Sciences, University of Coimbra. An in-house reference soil, prepared for aqua regia analysis, was validated using the certified sewage sludge amended soil BCR 143 R. Duplicate blanks and a laboratory standard were included in each batch of 30 samples. The detection limits in mg/l for stream sediments and soils are 0.003 for Sr, 0.001 for Zn, 0.01 for Al, Fe and Pb, 0.02 for Cr and Mn, 0.03 for Co and Cu, 0.04 for Cd and Ni, 0.05 for As, Sb, Th and W and 0.135 for U. The precision for determinations in stream sediments is 4-12 %, with the highest value for Cu, and 1-16 % for soils with the 16% for Ni.

The spatial distribution of physico-chemical parameters, metals and metalloids of soils of the abandoned Pinhal do Souto uranium mine area is tested with a coupled methodology that performs geochemical distribution and geostatistical interpolation. A multivariate statistical analysis, using principal component analysis (PCA) is applied to the variables of waters and soils. In soils, a subsequent synthesis of the variables (PCA technique, Spearman) will reduce the outliers' weight. The results suggest spatial correlations between some variables and independence of others, which are characterized individually. Concentrations below the detection limits are considered zero. Samples without determined concentrations are not included in the PCA.

5. Results

5.1. Water samples

The physico-chemical parameters and chemical analyses of water samples from the Pinhal do Souto abandoned uranium mine area are shown in Table 1. The water sample from a spring (PS7) was collected upstream of the old mine area to represent the

background or natural levels (Fig. 1c). The PS5 water is from another spring that experiences some influence from the old mining activities, whereas PS9 and PS10 are groundwater samples from the mine gallery. The PS1, PS2, PS3 and PS8 are groundwater samples collected from wells and the PS4, PS6 and PS11 samples are from streams located inside the area of the Pinhal do Souto abandoned mine (Fig. 1c). According to the Piper classification, most water samples are of sodium-potassium type and chloride type or do not contain a dominant anion. However, those from springs and the mine gallery are of mixed cations, but of bicarbonate type.

The electrical conductivity ranges from 22 to 235 μS/cm and the total dissolved solids are within the range 14-131 mg/l, indicating that these waters are poorly mineralized. pH values range from 5.1 to 8.5 and increase in February (Table 1).

In general, As, Ba, B, Cd, Co, Cr, Cu, Li, Ni, Pb, Sr, Th and Zn show higher concentrations in April and July than in November and February due to the evaporation effect (Table 1, Fig. 2a,b, c). Uranium with concentrations ranging from 29.59 μg/l to 104.42 μg/l has a distinct behaviour as its concentration increases during rainfall periods (Fig. 2f). Furthermore, Na, Ca, Mg, HCO_3^- and NO_2^- show the highest concentrations in most water samples in July and November (Table 1, Fig. 2d) and in some groundwater samples (PS5, PS9 and PS10). These cations and anions are probably related to the weathering of the country two-mica granite (Fig. 1c), because they have higher concentrations in the spring water sample (PS5) and mine gallery water samples (PS9 and PS10) than in water samples from wells and streams, as those water samples show the highest electrical conductivity values (Table 1). The highest NO_2^- concentrations of these water samples are probably due to the fact that they have the lowest redox potential values (Eh). In general, surface water and groundwater have higher electrical conductivity in July

and November than in April and February, which is attributed to the higher concentrations of Na, Ca, Mg and HCO_3^- and NO_2^- in July and November. No significant distinction occurs in the physico-chemical parameters and chemical composition (e.g. Ba, Cd, Cr, Cu, Ni, Pb, Zn, Th and U concentrations) of groundwaters and surface waters (Table 1).

Samples PS1, PS3 and PS8 are from wells and PS4 and PS11 are from streams (Table 1) affected by fertilizers and therefore show the highest SO_4^{2-} (Fig. 2e) and NO_3^- concentrations.

Principal component analysis (PCA) was applied to 28 determinations (measured physico-chemical parameters and analysed anions and cations) in 44 water samples from the Pinhal do Souto uranium mine area (Table 2). The three first component axes (PC1, PC2 and PC3) explain most of the data variability (75% of the total variance). The first principal component axis PC1 shows the association of B, Ba, Cd, Co, Cr, Cu, Li, Ni, Pb, Sr, Zn, As and Th with its positive loading, whereas U is associated with negative loading in the PC1, supporting that finding the U has a distinct behaviour from the others, as its concentration increases in the wet season and the other concentrations increase in the dry season. NO_2^-, HCO_3^-, Na, Ca, Mg and Mn show a high loading in PC2 (Table 2), as they present the highest concentrations in most water samples in July and November (Table 1). The association of Cl^-, NO_3^-, SO_4^{2-} and K with the negative loading of PC3 (Table 2) is attributed to the water samples being affected by fertilizers, which have the highest SO_4^{2-} concentration.

5.2. Stream sediments

The textural characteristics, physico-chemical parameters and concentrations of metals and metalloids of stream sediments from the Pinhal do Souto abandoned uranium mine area are given in Table 3. They are dominated by sand (46.3-85.5 %) and have 12.8-47.5 % silt and 1.7-6.2 % clay. They consist of quartz, K-feldspar, plagioclase, muscovite, chlorite, kaolinite, illite and smectite. Of the clay minerals, kaolinite dominates (up to 46 %). The Fe-oxides precipitate (PS-SED5) has 19.8 % silt and 3.9 % of the < 2 μm fraction, which is amorphous. It has the highest organic matter content, cation exchange capacity and electrical conductivity (Table 3).

Organic matter in soils and recent sediments has a much higher CEC (up to 500 cmol/kg) than clay minerals or Al-Fe-oxides (up to 150 cmol/kg) (Mirsal, 2004). The sediment from the Ludares stream has the lowest organic matter content and cation exchange capacity (Table 3). The mine drainage stream sediment PS-SED20 with the highest silt (47.5 %) and clay (6.2 %) contents has the highest cation exchange capacity (4.53 cmol/kg), as shown in Table 3, but no correlation was found between these two parameters, because kaolinite is the most abundant clay mineral in stream sediments and has a low adsorption capacity.

There is no significant distinction between the average pH values of stream sediments that received the direct uranium mine drainage (4.8) and the local stream sediments (4.7), but a slightly higher value (5.2) appears in the Ludares stream sediments.

In general, stream sediments that received direct drainage from the abandoned uranium mine have the highest Fe, Mn, Cd, As, Zn, Pb, Cr and Th concentrations (Fig. 3). However, some of these sediment samples have similar As and Th contents to those of local stream sediments (Table 3, Fig. 3). Cobalt and Ni were only detected in some stream sediments that received the mine drainage and in the Fe-oxides precipitate. Uranium was

only detected in one sample from Ludares stream and in the Fe-oxides precipitate (Table 3). The Fe-oxides precipitate is the richest in organic matter (7.26%), electrical conductivity (200 μS/cm), As (3.71 g/kg), Cd (1.24 g/kg), Co (1.34 g/kg), Fe (278.9 g/kg), Th (1.05 g/kg), U (485 mg/kg), W (108 mg/kg) concentrations (Table 3). A correlation matrix was calculated for the data of the stream sediment samples (Table 4), but the Fe-oxides precipitate sample was not included in this calculation, because it has a different origin and higher concentrations of metals and metalloids when compared with the other samples. There are significant positive correlations ($r > 0.7$ at 95% level), between Fe concentration and As, Cd, Cr, Pb and Th concentrations. These correlations in stream sediments reflect the capacity of Fe-oxyhydroxides to adsorb metals and metalloids in the surface environment (e.g. Abdelouas, 2006; Grosbois et al., 2007; Root et al., 2007; Cabral Pinto et al., 2008; Carvalho et al., 2012) and indicate the influence of mine dumps, because the stream sediments receiving the direct drainage from these mine dumps have the highest concentrations of Fe, As, Cd, Cr, Pb and Th (Table 3).

5.3. Soils

The textural characteristics, physico-chemical parameters and concentrations of metals and metalloids of soils from the Pinhal do Souto uranium mine area are presented in Appendix A. Although the number of soil samples with determined textural characteristics is limited, they are dominated by sand (79.9-97.4 %) and the clay content is very low (0.3-1.8 %). The soil samples consist of quartz, K-feldspar, plagioclase, muscovite, kaolinite, illite, smectite and vermiculite. Of the clay minerals, kaolinite is generally the most abundant (up to 50 %), but vermiculite dominates (up to 46 %) in a few samples and smectite is only very rarely important (up to 55 %). The organic matter concentrations are very low ranging from 0.72 to 4.95 % (Appendix A). The cation exchange capacity is also

low 0.12-5.13 cmol/kg. The electrical conductivity values range from 10 to 103 μS/cm, suggesting low contamination. The pH values are acidic, as they range from 3.2 to 5.4, which is attributed to the influence of the granite background and in some soil samples is also due to mine tailings. The concentrations of metals and metalloids have a great range and most of them have two or more values below the detection limit, except for Fe and Zn (Appendix A).

Significant positive correlations ($r > 0.7$ at 95% level) occur between the concentrations of As and Al, Cu, Fe, Mn, Pb, Sb, Sr and W (Table 5). Tungsten is also positively correlated with Al and Sb, Ni with Co, and Sr with Pb. These correlations can be associated with the occurrence of these metals and metalloids in the U-mine and their similar geochemical behaviours.

Principal component analysis (PCA) was applied to these physico-chemical parameters and 14 metals and 2 metalloids determined in 47 soil samples collected from the Pinhal do Souto uranium mine area (Table 6). Most of the data variability is represented by the principal components (PCs), which can explain the behaviours of metals and metalloids and their absorption and retention according to soil properties. The first three factors (PC1, PC2 and PC3) explain most of the data variability (70% of the total variance). Most metals and metalloids, such as Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sr, Th, W and Zn are correlated, as confirmed by PC1 and space association (Table 6). The mobility of metals decreases as the pH approaches neutrality, which is correlated with EC, and confirmed by PC2 space association (Table 6). The independence of U is confirmed by PC3 factor (Table 6) and suggests a distinct behaviour relatively to other metals as it is probably mainly associated with the two-mica granite from Pinhal do Souto.

Concentrations of metals and metalloids were interpolated to the samples that are located in the nodes of the irregular grid used to collect soil samples in the study area,

using the multi-Gaussian Kriging implemented in SpaceSat v.2.2.17 (BioMedware, 2011). These concentrations were transformed into normal scores to attenuate the impact of extreme values on the computation of the variogram, and then interpolated using ordinary Kriging. The results (Kriging estimate and predicted variance) were back-transformed using the empirical procedure developed by Saito and Goovaerts (2000). Total metal and metalloid contents were grouped in four classes (minimum; median; median plus one standard deviation; median plus two standard deviations; higher values). Maps of Cr, Th and Zn total concentrations show patterns that define a coincident anomaly zone, inside the uranium mine area and close to the dumps. Chromium and Th are more widely dispersed and with lower values (Fig. 4). In the northern part of the area, the Zn anomaly (Zn > 258 mg/kg) is more widely dispersed than the U anomaly (167 mg/kg). Another U anomaly occurs in the southern part of the area. Both U anomalies are to close the mine dumps. Maps of Sb, Pb, Sr and W define coincident anomalies that are located to the west of the mine dumps (Fig. 4), but with different concentrations (Sb > 99 mg/kg; Pb > 404 mg/kg; Sr > 41 mg/kg; W > 56 mg/kg). There is another Pb anomaly which is related to the dump located to the north of the area. Two larger W anomalies with higher concentrations are defined (Fig. 4).

6. Discussion

6.1. Geochemistry of waters, stream sediments and soils

The pH values of groundwater samples from the gallery within the Pinhal do Souto uranium mine, when it was operating and autunite and torbernite were actively dissolved, ranged from 4.49 to 6.18 (Magalhães et al., 1985). After the mine was closed in 1989, primary minerals altered to secondary uranium minerals due to weathering. In general, secondary minerals are phosphates, carbonates, sulphates, oxyhydroxides and silicates

(Stefaniak et al., 2009). From April 2010 to February 2011 the pH values of groundwater range from 5.1 to 8.5 (Table 1) and are similar to those of surface water (5.1-8.3); they ranged from slightly acid to alkaline because sulphide oxidation is not enough to produce an acid pH and the formation of secondary minerals that retained the acidity, metals and metalloids until rainfall was favoured (Bigham and Nordstrom, 2000; Jambor et al., 2000; Jerz and Rimstidt, 2003). This neutral to alkaline pH is typical of waters close to uranium mines (e.g. Lottermoser et al., 2005; Gómez et al., 2006).

The water chemistry is mainly controlled by pH, Eh and the type of complexing agents present (Langmuir, 1997). Most samples collected in February 2011 do not contain Cd, Co, Cr, Cu, Fe, Li, Ni, Zn and Pb (Table 1), because they generally have the highest pH values (6.84-8.48, Table 1), which favours the formation of secondary minerals such as hydroxides and oxyhydroxides (Jambor, 1994). But in general, As, Ba, Cd, Co, Cr, Cu, Li, Ni, Pb, Sr, Th and Zn exhibit higher concentrations in summer than in winter (Table 1, Fig. 2a, b, c) due to the higher temperature, which causes water evaporation. In general, stream sediments that receive the direct mine drainage due to erosion and leaching of mine dumps have the highest concentrations of Fe, Mn, Cd, As, Zn, Pb, Cr and Th (Fig. 3, Table 3), which are adsorbed in organic matter and oxyhydroxides. In the stream sediments, Fe-oxides precipitate (PS-SED5) is the main carrier of Fe, As, Cd, Co, Sr, Th, U and W (Table 3), because it immobilizes metals and metalloids adsorbed onto the surfaces of Fe-oxyhydroxides (e.g. Frau and Ardau, 2004; Pinto et al., 2004; Grosbois et al., 2007; Cabral Pinto et al., 2008; Carvalho et al., 2012) and some is retained in organic matter. Variations in pH and Eh or a flood event can cause dissolution of these Fe-oxyhydroxides and thus release high amounts of toxic metals and metalloids into the environment (Siegel, 2002; Carvalho et al., 2012). The Fe-oxides precipitate (PS-SED5) is also the richest in organic matter (Table 3) which also retains metals and metalloids.

The Na, Ca, Mg and HCO_3^- concentrations of waters from the Pinhal do Souto uranium mine (Table 1) are related to Mn and those variables are dependent on the redox potential (Eh). The experimental studies indicate that Mn concentrations in waters have been attributed to the reductive dissolution of Mn oxyhydroxides that are mediated microbially and by the cation exchange (Petrunic et al., 2005; Loomer et al., 2011). The Mn^{2+} released by reduction reactions is important in the cation exchange reaction between the water and cations (Na^+, Mg^{2+} and Ca^{2+}) adsorbed on the solid phase. HCO_3^- is produced during the interaction of Mn oxides with dissolved organic matter in water. The Fe is not associated with these variables, because Fe-oxyhydroxides are hardly dissolved compared to Mn-oxyhydroxides (Alloway, 1995). The general decrease of water Eh in November 2010 (Table 1) caused the Mn oxyhydroxides dissolution and was the reason why most of the water has high values of the cations and also NO_2^-. However, in general they reach the highest concentrations in water in July because of the intense water evaporation. Their higher concentrations in water collected in July and November 2010 than in samples collected in April 2010 and February 2011 justify the higher electrical conductivity values in the first two than in the second two months (Table 1).

The U concentrations in water range from 29.59 μg/l to 104.42 μg/l (Table 1), which are typical of waters from uraniferous areas (e.g., Bernhard et al., 1996; Noller et al., 1997; Iwatsukí and Yoshida, 1999; Landa, 1999). U (VI) is much more soluble than U (IV) and occurs as UO_2^{2+} under neutral and alkaline conditions and forms complexes with carbonates, phosphates, vanadates, fluorides, sulphates and silicates (Langmuir, 1997). Uranyl carbonate and sulphate complexes, are the most stable complexes under water Eh-pH conditions (Lottermoser et al., 2005). The highest concentrations of U occur in surface water and groundwater from the Pinhal do Souto uranium mine area in the wet season

(November 2010 and February 2011) (Table 1, Fig. 2f), when the flow is high and leaching from the dumps and mineralized quartz vein takes place as is common in uranium mine areas (e.g. Pinto et al., 2004).

Of the stream sediments, only one sample from the Ludares stream and the Fe-oxides precipitate retain U up to 0.49 g/kg in the latter (Table 3), because U was adsorbed onto Fe-oxyhydroxides (Lottermoser and Ashley, 2006; Abdelouas, 2006) and probably retained in the organic matter, which is a main uranium binding (Idiz et al., 1986).

The low phosphate and sulphate concentrations in water samples from the Pinhal do Souto uranium mine area with high uranium concentration, in particular those related to the mine gallery (Table 1) suggest the occurrence of uranium as uranyl tricarbonate species, as these minerals are extremely stable and soluble (Clark et al., 1995; Stefaniak et al., 2009). Those samples from the spring (PS5) and mine gallery (PS9 and PS10) were selected for speciation, as they show the highest U concentrations (Table 1). The U speciation was obtained using the Visual Minteq version 3.0 (Gustafsson, 2010). The calculations predict that UO_2^{2+} is abundant and complexed with CO_3^{2-} in water samples PS5, PS9 and PS10 (Table 7). The formation of strong carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ is common under neutral to alkaline pH conditions (Grenthe et al., 1992), as in these three water samples from the Pinhal do Souto uranium mine (Tables 1, 7).

The high uranium concentration of up to 71.85 μg/l in the water sample (PS7) from upstream of the mine influence suggests that the country granite contains uranium. The Variscan two-mica granite from the Pinhal do Souto uranium mine, which is cut by the mineralized quartz vein, has a mean 10 ppm U concentration (Silva and Neiva, 2000) and contains uraninite (Cabral Pinto et al., 2008, 2009). This granite belongs to the Beira

batholith, which contains uranium minerals (Cotelo Neiva, 2003) and is an important source of uranium for surface water and groundwater (Porcelli et al., 1997).

In fluvial systems affected by the mine drainage, the contaminant concentrations in sediments tend to decrease downstream of the contaminant sources, due to hydrodynamic and chemical processes (Hudson-Edwards et al., 1996; Cidu et al., 2011). This attenuation is observed in Fig. 3, as there is a decrease in the concentrations of potential toxic metals and metalloids from the effluents that receive mine drainage for the Ludares stream, which flows a long away from the mine dumps and has a higher hydraulic flow than its effluents.

The metals Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sr, Th, W and Zn and the metalloids As and Sb continue to be released from the mine dumps, leaching through the mine area and are retained in soils (Appendix A, Fig. 4). These soils have an acid pH (3.2-5.4, Appendix A), which influences the adsorption capacity of metals and metalloids (Appendix A, Fig. 4), because these metals and metalloids are more mobile and more available in acid than neutral conditions (Alloway, 1995). Cr, Th, U, Zn and Pb anomalies of soils are related to the mine dumps (Fig. 4). The organic matter forms soluble and insoluble complexes with heavy metals causing their retention in soils (Kabata-Pendias and Mukherjee, 2009). But the organic matter concentration is very low in these soils, ranging from 0.72 to 4.95% (Appendix A), so it did not play a significant role. These soils are also poor in the clay fraction (content up to 1.8%), because they consist mainly of sand (up to 97.4%, Appendix A). Therefore, the clay minerals that are good to retain metals and metalloids could not have played an important effect. Metals and metalloids are probably mainly retained in the vermiculite and Fe-oxyhydroxides of soils (James and Barrow, 1981), which is also supported by the PC1 association (Table 6).

Although the number of solid samples analysed for texture is small, the stream sediment samples have a higher clay content (1.7 to 6.2 %) than the soil samples (0.3 to

1.8 %). The Al, As, Sr and Zn attain higher concentrations in a few stream sediment samples than in soil samples (Table 3, Appendix A). The Al content is a major constituent of kaolinite, which occurs in stream sediments. But kaolinite does not easily adsorb metals and metalloids, which explains that generally the stream sediments are not richer in them than soils. In general, soils tend to have higher Cu, Mn, Pb, Sb, U and W concentrations than stream sediments (Table 3, Appendix A), because soils contain vermiculite which adsorbs metals and metalloids. The Fe-oxides precipitate has higher As, Cd, Co, Fe, Sr, W, Th and U concentrations than the soils (Table 3, Appendix A), because its concentrations of iron-oxides and organic matter are higher than those in soils. Therefore, the Fe-oxides precipitate has a great capacity to adsorb metals and the metalloid As.

6.2. Contaminated waters, stream sediments and soils

In general, water from the Pinhal do Souto uranium mine area has higher NO_2^-, As, Cd, Cr, Cu, Fe, Ni and Pb concentrations than the acceptable levels for drinking water under Portuguese law (Decree, 2007), and higher U content than the level indicated by the World Health Organization (WHO, 2010) (Table 1, Fig. 2a, b, f). The sample PS5 also has a concentration of Co that is higher than permitted for agricultural use (Portuguese Decree, 1998).

To assess the contamination degree in stream sediments, the pollution index is given by the enrichment factor (EF), which was calculated for all metals and metalloids using the equation $EF = [(element_{sample}/Al_{sample})] / [(element_{baseline}/Al_{baseline})]$ (Sutherland, 2000; Andrews and Sutherland, 2004). EF has five categories: < 2 – no pollution; 2-5 – moderate pollution; 5-20 – significant pollution; 20-40 – very strong pollution; > 40 – extreme pollution. Geochemical normalization of trace elements to a conservative element, which has a uniform flux in the surface environment for a long period of time,

compensates for changes in the concentrations of trace elements (Sutherland, 2000). The Al content was used for normalization, as Al is almost immobile in the surface environment. The average of each element from the five regional stream sediment samples collected in the Pinhal do Souto uranium mine area (Table 3) was used as a baseline value, because background values depend on the scale and lithology and the use of background values obtained in large areas consisting of several lithological units can lead to spurious results (Reimann and Garrett, 2005). However, Co, Ni and U concentrations are below the detection limit in these five analysed samples. So, the concentrations of these elements (Co-9 ppm; Ni-19 ppm and U-0.5 ppm) given by Ferreira (2000) and Ferreira et al. (2001) for a low-density geochemical survey in Portugal were used.

The stream sediments that receive mine drainage (Table 3) are significantly to very strongly polluted in Cr (EF > 5, up to 38); moderately significantly to very strongly polluted in Mn (EF > 2, up to 23); moderately to significantly polluted in Pb (EF > 2, up to 6) and moderately polluted in Cd, Co, Fe, Th and Zn (EF > 2). The sediment from the Ludares stream that receives indirect contribution from the mine drainage is extremely polluted in U (EF = 97) and moderately polluted in Pb (EF = 3). The pollution found in streams that flow through the uranium mine area is greatly attenuated and disappears in the Ludares stream, except for one point, which receives a direct contribution from the mine drainage and has a very high U concentration (36 mg/kg, Table 3).

The level of contamination in soils from the Pinhal do Souto uranium mine area is defined by comparing the total concentrations in soils with the maximum accepted levels in soils according to Italian Legislation (Decreto Ministeriale, 1999), which are higher for industrial areas than for public, private green areas and residential sites. Most of the soils studied have high As, Cd and Sb concentrations that render them unfit for any use (Fig. 5). Some soil samples have higher Cu, Pb and Zn concentrations than the acceptable level for

public, private green areas and residential sites. This legislation does not provide values for some metals. The maximum contents of Fe, As, Cd, Co, Ni, Pb, Sb, U, W and Zn of these soils are higher than those of Portuguese soils from the FOREGS data (Table 8). The median values of Fe, As, Cd, Pb, Sb, Th, U, W and Zn of soils from this Portuguese area are higher than those of soils from European countries of the FOREGS data (Salminen et al., 2005). The concentrations of Cd, Pb, Sb, U and W of soils from this Portuguese area also attain higher maximum concentrations than those of soils from European countries (Table 8). Therefore, the soils from the Pinhal do Souto mine area are contaminated due to the dumps.

6.3. Comparison of the environmental impacts caused by two abandoned uranium mines in Portugal

The environmental impacts caused by the abandoned uranium mine from Pinhal do Souto (PS) are compared with those produced by another abandoned uranium mine located in Vale de Abrutiga (VA), central Portugal (Table 9). The PS mine was exploited for four years longer and produced more 3091 kg U_3O_8 than the VA mine, and both were closed down in 1989. However, the contamination of water in U, Pb and Cu is higher in the VA area than in the PS area, though the contamination with Th is higher in the PS area. The both the surface water and groundwater from the VA area have a higher electrical conductivity than those from the PS area, supporting the greater abundance of metals in waters from the VA area. The water from the VA area has an acid pH, whereas that from the PS area has a slightly acid to alkaline pH, because quartz veins from the VA area contain more sulfides than the quartz vein from the PS area which altered into oxides and SO_4^{2-} is formed and has a much higher value in waters from the VA area (Table 9). The open pit exploitation in the VA area favoured more alteration than the underground

exploitation in the PS area. Therefore, secondary uranium minerals should be more abundant in the VA quartz veins than in the PS quartz vein and dumps. Secondary minerals retain acidity and metals are liberated into water, particularly during the wet season (e.g. Jerz and Rimstidt, 2003). Water from the VA area is more contaminated with U, Pb and Cu than that from the PS area (Table 9). Water from the VA area is also contaminated with SO_4^{2-}, Fe, Mn and Ra and must not be used for drinking and irrigation (Pinto et al., 2004), whereas that from the PS area is also contaminated with NO_2^-, As, Cd, Cr and Ni and must not be used as drinking water (Portuguese Decree, 2007; WHO, 2010).

In both areas, stream sediments that receive drainage from the U mines were compared with sediments collected in local streams and found to be generally enriched in Fe, Co, Cu and Zn but those from the PS area are also generally enriched in Pb and Th. The contamination of these stream sediments in Cu, Zn, Co and Fe is higher in the VA area and the contamination in Th and Pb is higher in the sediments from the PS area. The stream sediments of the VA area are also contaminated in U. However, the Fe-oxides precipitate related to the PS mine has the highest U, Co, Fe and Th contents (Table 3), showing the importance of Fe-oxyhydroxides to adsorbing metals (e.g. Carvalho et al., 2012).

7. Conclusions

The Pinhal do Souto abandoned uranium mine caused contamination in several metals including Th and U and metalloids in water, stream sediments and soils, which must not be used. The OM content and precipitation of Mn, Fe oxyhydroxides in stream sediments due to the high pH values of water are the most important for the retention of metals and metalloids and some have higher concentrations than in soils. In general, stream sediments have a higher clay content than soils, but soils tend to show higher Cu, Mn, Pb, Sb, U and

W concentrations, which may be adsorbed by vermiculite, and a lower Fe content than stream sediments. The Fe-oxides precipitate is richer in As, Cd, Co, Fe, Sr, W, Th, U and organic matter than stream sediments and soils, as these metals and metalloid are retained in organic matter and oxyhydroxides. Specifically, the dumps must be rehabilitated.

Uranium concentrations in water from the Pinhal do Souto area are of particular concern because they are permanently above the human consumption limits, in both the wet and dry seasons, whereas metals and arsenic generally cause environmental concern in the dry season (April and July). In the wet season, secondary uranium minerals are dissolved and uranium is released into the solution. Metals and arsenic are released in lower concentrations than uranium, as sulphides occur in low amounts. In the dry season, their concentrations increase due to evaporation, whereas U is scavenged from the solution through the formation of secondary minerals.

This area was compared with the abandoned uranium mine area at Vale de Abrutiga. Although both mines were closed down in 1989 and the former was exploited for four years longer and produced ~3000 kg more U_3O_8, it caused less of an environment impact on the water and stream sediments than the latter. This is attributed to the fact that sulfides are less abundant and underground mineral alteration was less intense in the former, as shown by a lower SO_4^{2-} concentration in water than in the latter, which was exploited in an open pit. In the Pinhal do Souto uranium mine area, soils have higher median values of Fe, As, Cd, Pb, Sb, Th, U, W and Zn than soils from European countries of the FOREGS data (Salminen et al., 2005), because they are contaminated due to the dumps.

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Figure Captions

Fig. 1. Geological area containing the Pinhal do Souto uranium mine and the sample collection sites. a. Location of the Tragos area on the map of Portugal; b. Geological map of this area with the Ludares stream and its effluents and the area of detailed study; c.d. Simplified map showing the two mine dumps and location of water and stream sediment samples in c and soil samples in d., where the area used in the maps of soil anomalies (Fig. 4) is shown.

Fig. 2. Seasonal chemical variations in waters from the Pinhal do Souto uranium mine area. a) As, b) Pb, c) Th, d) Na, e) SO_4^{2-}, f) U. VMR - recommended values for agriculture; VMA - permitted values for agriculture; VP - permitted values for human consumption (Portuguese Decrees, 1998, 2007), except for U (WHO, 2010).

Fig. 3. Variation in concentrations of metals and a metalloid in stream sediments from the Pinhal do Souto uranium mine area.

Fig. 4. Location of soil samples and geochemical distribution of seven metals and one metalloid in the Pinhal do Souto uranium mine area.

Classes defined for Cr (0-3, 3-7, 7-12, >12 mg/kg); Th (0-23, 23-35, 35-47, >47 mg/kg); U (0-46, 46-106, 106-167, >167 mg/kg); Zn (3-112, 112-185, 185-258, >258 mg/kg); Sb (0-27, 27-63, 63-99, >99 mg/kg); Pb (0-98, 98-251, 251-404, >404 mg/kg); Sr (0-13, 13-27, 27-41, >41 mg/kg); W (0-21, 21-39, 39-56, >56 mg/kg).

Fig. 5. Selected concentrations of some metals and metalloids of soils from the Pinhal do Souto uranium mine area. Maximum levels for — public, private green areas and residential sites; - - - industrial areas (Decreto Ministeriale, 1999).

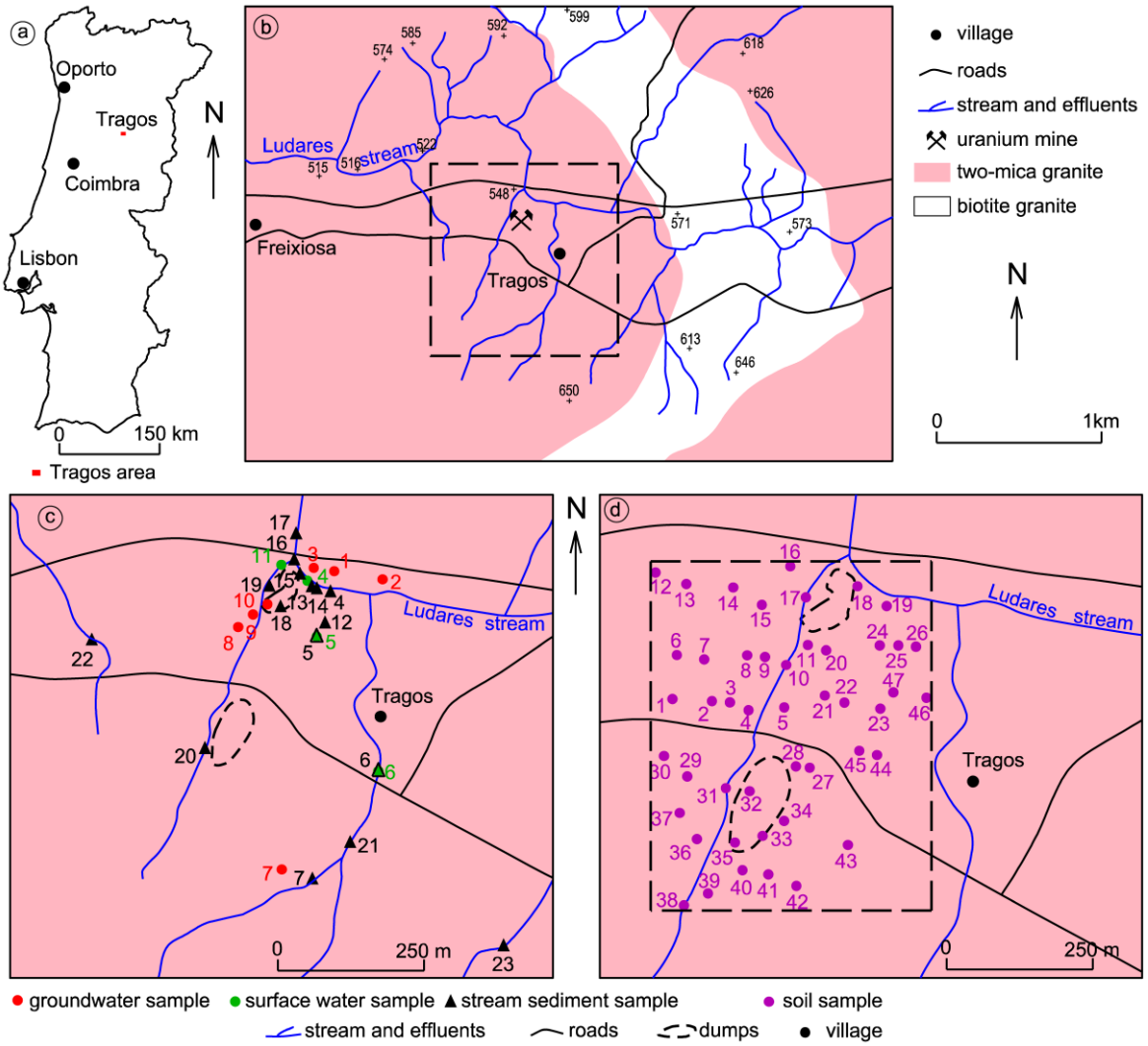

Fig 1

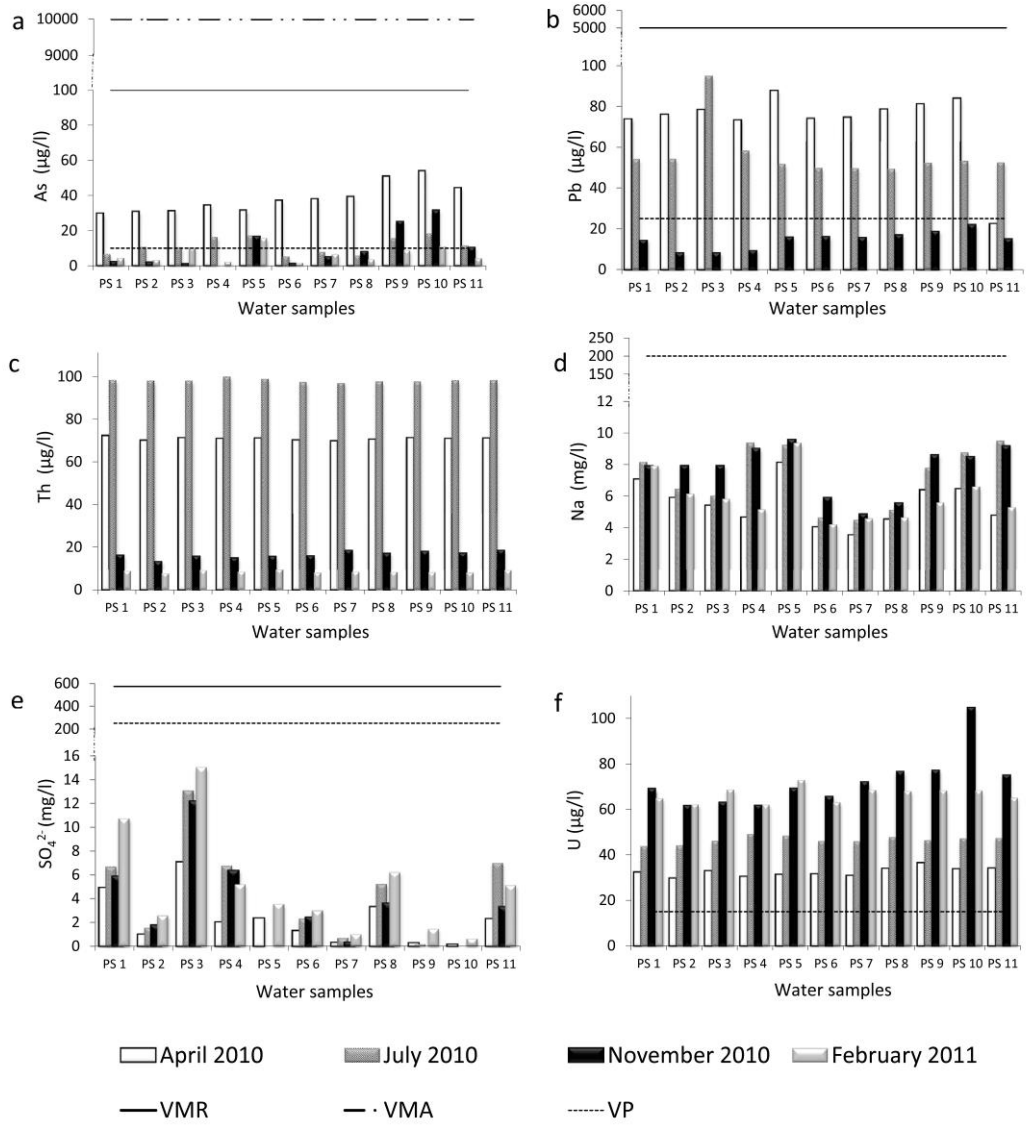

Fig 2

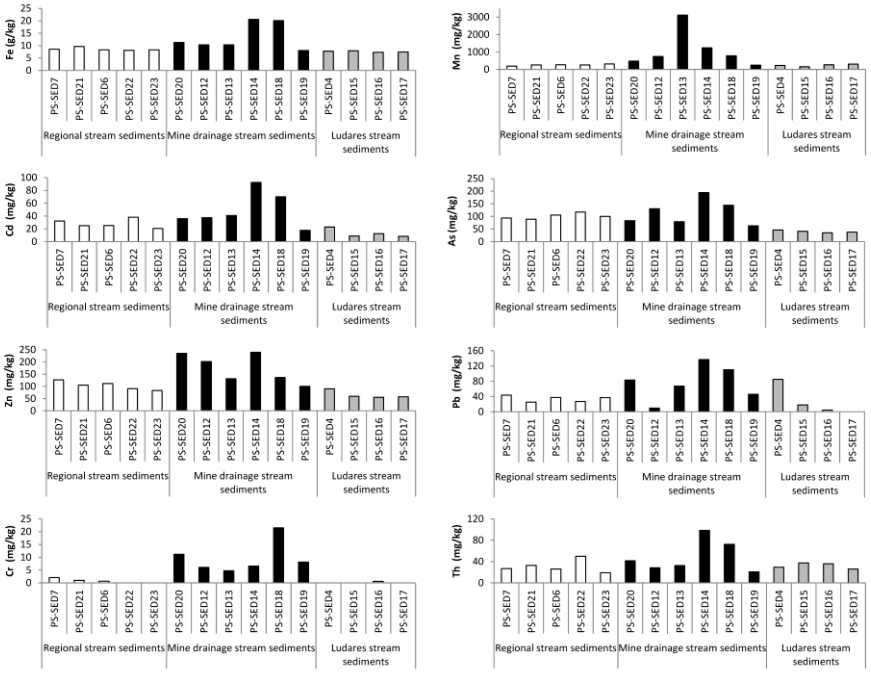

Fig 3

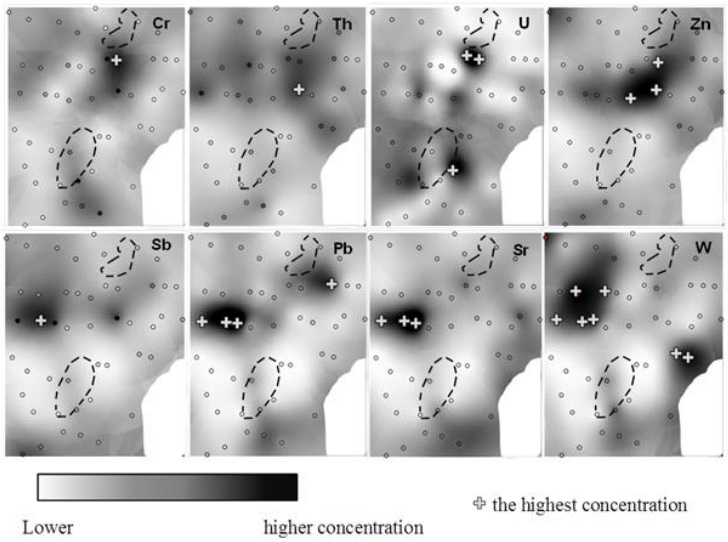

Fig 4

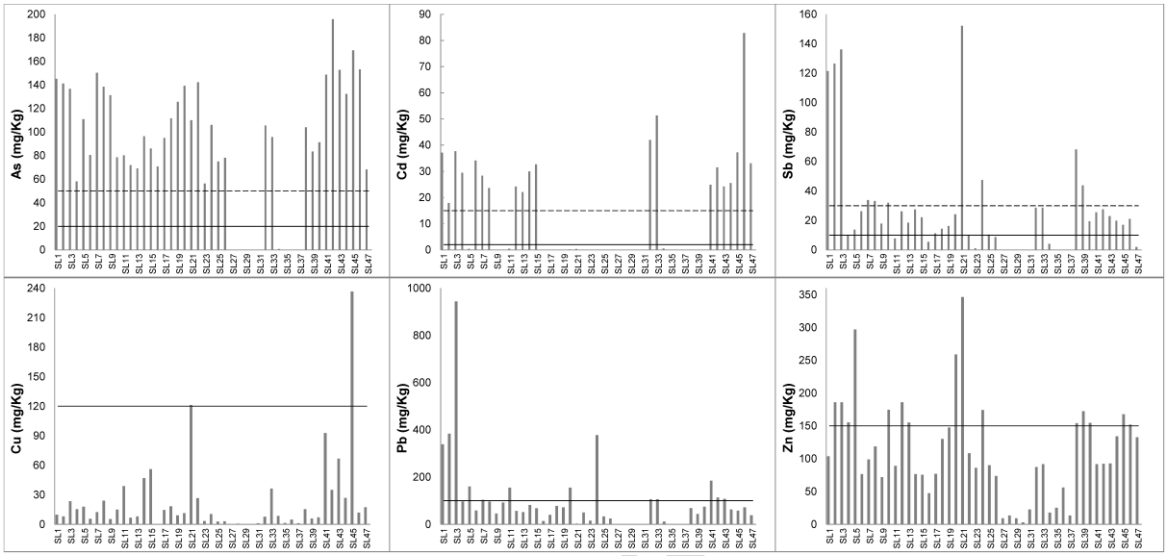

Fig 5

		Physico-chemical parameters					Anions (mg/l)							Major cations (mg/l)			
Sample		T (ºC)	pH	Eh (mV)	DO (mg/l)	EC (µS/cm)	HCO_3^-	SO_4^{2-}	PO_4^{2-}	NO_3^-	NO_2^-	Cl^-	F^-	Na	K	Ca	Mg
PS1 w	April 2010	13.9	5.12	333	7.29	96	9.31	4.91	0.09	17.04	0.38	14.51	0.09	7.05	4.03	3.90	3.01
	July 2010	15.6	6.03	51	5.65	94	10.80	6.66	0.09	14.88	0.76	14.61	0.04	8.14	3.85	3.28	3.46
	Nov. 2010	12.5	5.77	-134	3.75	80	10.20	5.85	0.21	10.88	0.65	12.25	0.06	7.88	3.09	3.59	1.95
	Feb. 2011	12.0	7.54	177	7.10	87	9.15	10.70	0.18	16.03	0.61	12.87	0.08	7.90	3.66	3.72	1.34
PS2 w	April 2010	11.0	6.23	59	1.92	53	14.45	1.01	< 0.006	0.10	0.86	11.78	0.13	5.88	1.55	2.07	2.00
	July 2010	14.4	6.52	-235	0.91	62	21.60	1.57	0.19	< 0.004	1.20	11.61	0.03	6.45	2.35	2.26	1.86
	Nov. 2010	8.3	6.47	-47	0	64	21.01	1.77	0.18	0.08	1.09	14.77	0.02	7.90	3.23	2.84	1.03
	Feb. 2011	6.3	8.11	-93	0	43	14.56	2.59	< 0.006	< 0.004	0.94	9.72	0.02	6.12	1.96	1.75	< 0.001
PS3 w	April 2010	12.1	7.96	91	2.93	83	17.82	7.04	< 0.006	4.33	0.83	10.95	0.11	5.40	1.47	7.04	3.16
	July 2010	17.6	6.87	-5	5.24	113	47.52	13.05	0.16	0.05	1.75	10.25	0.18	6.03	1.75	22.63	9.81
	Nov. 2010	12.8	5.87	-7	1.96	89	20.40	12.15	< 0.006	3.60	1.01	10.29	0.06	7.90	3.23	2.84	1.03
	Feb. 2011	9.0	8.07	133	2.01	89	24.96	14.99	0.21	10.19	1.14	11.12	0.10	5.80	1.94	11.5	2.61
PS4 st	April 2010	12.1	8.10	68	7.74	46	1.19	2.04	< 0.006	2.20	0.37	7.42	0.13	4.64	1.58	2.36	2.01
	July 2010	15.0	6.31	124	5.82	99	20.74	6.73	0.37	10.15	0.94	15.28	0.10	9.36	3.37	4.29	4.47
	Nov. 2010	10.2	6.53	-19	5.29	87	18.97	6.33	0.20	6.62	0.72	15.26	0.26	8.99	3.02	5.09	1.75
	Feb. 2011	10.1	8.11	134	9.59	49	12.06	5.19	0.06	3.82	0.52	8.35	0.12	5.14	2.22	2.82	< 0.001
PS5 sp	April 2010	13.7	7.14	56	3.17	134	101.38	2.37	< 0.006	0.18	8.62	9.10	0.30	8.11	2.62	11.52	5.57
	July 2010	14.2	7.55	-69	5.52	136	117.50	< 0.004	< 0.006	< 0.004	8.38	9.36	0.37	9.21	2.97	12.39	21.11
	Nov. 2010	14.3	7.17	-142	5.56	149	108.53	< 0.004	< 0.006	< 0.004	8.31	8.23	0.32	9.55	2.77	13.22	7.30
	Feb. 2011	13.7	8.30	52	6.19	141	100.26	3.54	< 0.006	< 0.004	6.65	8.42	0.28	9.33	2.93	13.27	7.47
PS6 st	April 2010	12.1	6.73	77	7.81	33	5.74	1.32	< 0.006	3.20	0.21	6.67	0.07	4.03	1.32	0.87	1.81
	July 2010	13.2	5.11	193	6.47	42	5.18	2.34	< 0.006	4.85	0.43	8.47	0.06	4.63	1.89	1.11	1.24
	Nov. 2010	11.4	5.86	12	6.96	49	5.10	2.44	< 0.006	8.05	0.40	9.43	0.06	5.89	2.06	1.80	0.90
	Feb. 2011	10.0	8.06	155	9.76	35	6.66	3.00	< 0.006	3.59	0.33	6.20	0.04	4.21	1.98	1.06	< 0.001
PS7 sp	April 2010	12.0	6.46	120	8.21	22	7.92	0.33	0.10	1.81	0.33	4.76	0.06	3.54	1.03	0.40	1.65
	July 2010	15.1	6.14	47	6.36	41	13.18	0.72	0.21	1.56	1.09	6.73	0.07	4.49	1.90	1.76	0.98
	Nov. 2010	14.1	5.30	72	7.25	41	14.08	0.34	0.20	1.73	1.17	6.18	0.06	4.84	1.81	1.88	0.49
	Feb. 2011	12.2	7.82	136	7.48	26	14.77	1.01	0.20	1.96	0.94	6.14	0.06	4.57	1.94	2.19	< 0.001
PS8 w	April 2010	11.5	6.35	64	5.78	38	6.14	3.31	0.06	2.85	0.25	9.81	0.08	4.52	1.20	0.80	1.88
	July 2010	13.5	6.03	36	6.80	44	5.40	5.23	0.12	3.96	0.52	7.05	0.06	5.12	1.85	1.03	1.42
	Nov. 2010	13.2	5.74	89	5.67	47	7.96	3.62	0.16	3.88	0.85	6.48	0.06	5.54	1.73	1.39	0.73
	Feb. 2011	11.1	7.46	238	7.37	37	4.58	6.20	0.09	2.45	0.48	5.86	0.06	4.62	1.82	0.84	< 0.001
PS9 mg	April 2010	14.9	6.57	35	5.02	120	70.29	0.30	< 0.006	0.17	1.82	9.26	0.20	6.37	2.19	7.01	4.09
	July 2010	17.2	6.50	-33	1.76	129	86.40	0.17	< 0.006	< 0.004	3.32	9.75	0.30	7.78	2.79	8.46	12.52
	Nov. 2010	12.0	6.40	10	0.22	107	57.12	< 0.004	< 0.006	< 0.004	8.41	8.77	0.24	8.58	2.75	10.48	5.49
	Feb. 2011	10.8	6.84	90	3.41	67	40.56	1.47	< 0.006	0.27	1.52	7.09	0.12	5.57	2.37	5.21	1.59
PS10 mg	April 2010	14.4	6.89	-30	3.50	109	60.39	0.16	< 0.006	< 0.004	2.09	9.38	0.21	6.44	2.15	7.33	4.15
	July 2010	19.7	7.70	-278	0.35	235	109.08	< 0.004	< 0.006	< 0.004	8.12	10.82	0.31	8.75	2.69	11.30	20.43
	Nov. 2010	9.5	6.95	-158	0.01	129	110.77	< 0.004	< 0.006	< 0.004	7.39	9.31	0.21	8.48	2.59	10.44	6.22
	Feb. 2011	9.2	8.48	11	0.72	84	57.20	0.63	< 0.006	0.07	2.31	8.01	0.06	6.58	2.44	6.91	3.37
PS11 st	April 2010	13.3	6.76	88	7.71	45	12.67	2.30	< 0.006	2.38	0.29	8.01	0.14	4.77	2.39	2.53	< 0.001
	July 2010	15.3	6.24	135	6.08	100	21.17	6.98	0.32	11.06	0.96	16.08	0.13	9.48	3.37	4.57	5.10
	Nov. 2010	10.0	6.85	43	5.72	86	17.75	3.31	0.11	4.60	0.55	11.10	0.11	9.15	2.94	5.26	1.78
	Feb. 2011	10.0	8.09	86	9.90	49	12.69	5.11	0.06	3.79	0.53	8.21	0.10	5.27	2.19	2.85	< 0.001
VMR							nd	575	nd	50	nd	70	1	nd	nd	nd	nd
VMA							nd	nd	nd	nd	nd	nd	15	nd	nd	nd	nd
VP							nd	250	nd	50	0.5	250	1.5	200	nd	nd	nd

Table 1- Physico–chemical and chemical results of waters from the Pinhal do Souto uranium mine area

T - temperature; Eh - relative to field pH electrode; DO - dissolved oxygen; EC - electrical conductivity. w- well; st- stream; sp - spring; mg - mine gallery; Nov.- November; Feb.- February; VMR - recommended value for agriculture use; VMA - permitted values for agriculture; VP - permitted values for human consumption (Portuguese Decrees 1998; 2007), except for U (WHO, 2010); TDS - total dissolved solids, TS - Total solids; nd - not defined. Analyst: A.C.T. Santos.

Table 1 (cont.) - Physico–chemical and chemical results of waters from the Pinhal do Souto uranium mine area

		Trace elements (µg/l)																		
Sample		Al	As	Ba	B	Cd	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Sr	Th	U	Zn	TDS (mg/l)	TS (mg/l)
PS1 w	April 2010	100.3	29.70	90.82	67.99	47.35	19.24	55.59	60.51	60.89	61.14	68.41	88.92	73.80	93.86	72.12	32.15	68.40	61	111
	July 2010	<1	6.54	62.50	59.91	46.92	3.90	46.43	55.47	105.40	45.50	51.54	46.41	54.03	80.52	98.10	43.55	60.67	57	123
	Nov. 2010	35.6	< 3	23.98	12.73	7.14	4.43	7.76	19.03	38.73	2.25	12.17	11.01	14.20	34.22	16.03	68.90	20.57	52	71
	Feb. 2011	9.0	4.29	17.83	10.97	< 1	<1	<1	< 1	< 1	2.00	5.15	< 1	< 6	34.33	8.51	64.75	< 2	58	108
PS2 w	April 2010	147.8	30.71	76.60	53.54	48.14	18.55	58.22	75.05	201.00	59.29	295	58.91	76.07	77.18	69.92	29.59	54.30	36	167
	July 2010	26.5	10.67	50.56	56.17	46.93	4.42	46.42	46.51	759.00	44.04	290	46.24	54.10	72.94	97.77	43.94	52.44	39	61
	Nov. 2010	61.0	< 3	13.93	13.92	6.51	3.65	5.67	2.64	980.00	0.39	334	4.17	8.07	30.53	12.98	61.50	8.64	47	83
	Feb. 2011	18.9	3.28	4.52	0.84	< 1	<1	<1	< 1	65.71	<1	288	< 1	< 6	22.09	7.51	61.97	< 2	33	66
PS3 w	April 2010	162.9	31.03	81.62	54.37	47.96	19.66	59.96	72.80	63.94	60.52	275	57.79	78.44	103.67	71.11	32.73	54.02	55	70
	July 2010	73.0	10.42	58.78	61.98	50.58	11.31	49.08	56.27	144.00	49.32	150	58.95	94.95	102.05	97.79	45.94	53.56	66	92
	Nov. 2010	61.0	< 3	13.93	13.92	6.51	3.65	5.67	2.64	980	0.39	334	4.17	8.07	30.53	15.50	62.88	8.64	58	64
	Feb. 2011	48.1	10.29	8.19	1.38	< 1	<1	<1	3.39	< 1	0.74	170	< 1	< 6	55.01	8.91	68.57	< 2	64	112
PS4 st	April 2010	144.5	34.25	73.98	53.19	47.04	18.47	55.35	79.69	84.52	59.82	65.88	56.93	73.29	74.61	70.75	30.25	51.35	43	30
	July 2010	6.4	16.21	51.61	68.11	47.00	4.01	47.90	48.55	82.23	46.56	65.58	45.89	58.15	76.77	99.71	48.96	54.65	93	61
	Nov. 2010	40.7	< 3	14.79	17.76	6.55	4.06	5.75	5.35	105.00	1.84	28.51	8.11	9.17	32.30	14.69	61.59	10.20	84	60
	Feb. 2011	16.3	< 3	2.84	1.58	< 1	<1	<1	20.05	10.29	0.29	8.02	< 1	< 6	22.20	8.23	61.90	< 2	50	34
PS5 sp	April 2010	129.3	31.42	122.19	56.88	48.71	82.25	60.66	68.14	51.76	101.20	2837	64.30	87.68	141.60	70.97	31.18	54.14	85	148
	July 2010	11.6	17.10	77.69	56.76	46.46	46.25	46.19	43.15	54.70	78.15	2141	48.45	51.58	118.51	98.70	48.21	49.63	85	260
	Nov. 2010	31.5	16.53	44.93	12.83	6.52	51.81	6.24	7.27	227.28	35.90	2494	9.45	15.79	78.08	15.46	69.01	7.73	94	153
	Feb. 2011	28.7	15.50	23.63	4.04	< 1	28.97	<1	1.82	< 1	37.22	2000	< 1	< 6	79.10	9.21	72.75	< 2	89	123
PS6 st	April 2010	138.0	37.01	75.00	47.29	46.98	19.28	57.35	56.67	48.69	59.15	55.49	58.02	74.07	69.94	70.03	31.44	49.81	22	67
	July 2010	20.1	5.30	48.68	50.16	46.35	3.63	46.23	47.44	40.07	43.34	47.74	45.70	49.68	66.38	97.12	45.79	49.92	27	54
	Nov. 2010	48.3	< 3	14.61	9.02	6.40	4.48	6.06	3.88	7.21	1.48	9.28	7.19	16.00	25.15	15.64	65.44	8.15	33	58
	Feb. 2011	17.6	< 3	2.30	<1	< 1	<1	<1	8.08	< 1	<1	< 1	< 1	< 6	17.68	7.83	62.87	< 2	24	47
PS7 sp	April 2010	128.4	37.81	72.63	42.79	47.06	19.17	57.61	56.51	49.10	59.30	54.44	58.39	74.64	66.39	69.62	30.72	49.36	14	35
	July 2010	<1	7.78	48.78	46.21	46.13	3.25	45.84	48.48	38.52	47.01	44.85	45.43	49.52	65.98	96.73	45.68	50.92	25	43
	Nov. 2010	8.6	5.02	12.75	3.72	6.28	4.60	6.51	13.35	4.41	4.49	3.79	5.58	15.50	21.31	18.21	71.85	13.15	26	43
	Feb. 2011	1.4	6.44	3.39	<1	< 1	<1	<1	24.50	< 1	3.79	< 1	< 1	< 6	18.98	8.14	68.36	< 2	17	61
PS8 w	April 2010	139.7	39.17	75.57	47.82	47.32	19.92	59.07	62.51	49.13	60.41	57.97	57.30	78.67	72.16	70.33	33.85	53.35	25	59
	July 2010	<1	5.81	48.13	50.83	46.13	3.92	45.97	48.13	40.07	45.97	48.28	45.70	49.19	67.72	97.38	47.53	52.96	28	50
	Nov. 2010	40.7	7.90	12.71	8.34	6.33	4.77	6.09	11.54	6.33	4.40	7.14	7.34	16.76	23.77	16.80	76.38	11.34	30	38
	Feb. 2011	12.4	3.66	2.01	<1	< 1	<1	<1	5.14	2.80	1.36	2.39	< 1	< 6	18.72	8.00	67.82	5.10	25	48
PS9 mg	April 2010	127.4	50.68	93.61	48.34	47.74	25.92	61.58	56.91	80.68	68.42	1277	61.29	81.17	108.91	71.11	36.23	54.77	74	106
	July 2010	4.5	15.53	62.24	52.95	46.06	8.39	46.29	43.62	58.63	64.52	1260	46.64	52.20	96.68	97.37	46.21	54.35	76	114
	Nov. 2010	66.7	24.88	33.03	10.18	6.44	12.01	6.22	14.05	12.96	23.99	1588	7.22	18.50	61.50	17.75	76.95	76.39	71	186
	Feb. 2011	7.2	8.75	13.94	<1	< 1	1.10	<1	18.50	69.49	9.61	648	< 1	< 6	34.33	7.94	68.16	6.82	46	101
PS10 mg	April 2010	128.3	53.71	89.67	47.74	47.57	24.28	60.13	72.83	316.00	66.83	945	59.53	83.91	109.02	70.72	33.63	53.34	68	132

	July 2010	12.6	18.09	66.48	51.46	46.27	7.40	46.66	43.23	70.75	55.25	1679	45.91	53.05	115.60	98.01	47.07	49.72	131	183
	Nov. 2010	31.9	31.14	30.65	8.98	9.08	10.41	6.49	3.50	12301.00	12.43	1455	8.47	21.63	62.93	16.91	104.42	12.83	91	148
	Feb. 2011	22.0	10.90	9.87	<1	< 1	<1	<1	8.09	424.00	6.48	370	< 1	< 6	43.72	7.73	68.14	1.05	60	96
PS11 st	April 2010	23.7	44.21	12.82	2.70	25.02	18.02	16.44	20.25	43.53	21.08	40.57	21.08	22.48	86.33	70.99	33.91	10.84	29	76
	July 2010	6.0	11.53	51.29	59.07	46.20	3.58	46.15	45.44	96.97	46.52	78.07	45.49	52.33	77.48	98.05	47.18	52.91	62	70
	Nov. 2010	38.6	10.28	15.27	14.73	6.43	4.75	6.21	14.45	96.87	2.38	34.58	7.53	14.88	32.56	18.22	74.83	11.57	60	94
	Feb. 2011	19.5	4.10	2.96	<1	<1	<1	<1	19.09	15.62	0.50	11.45	< 1	< 6	22.03	8.96	64.89	1.42	34	30
VMR		5000	100	1000	300	10	50	100	200	5000	2500	200	500	500	nd	nd	nd	2000		
VMA		20000	10000	-	3750	50	10000	20000	5000	nd	5800	10000	2000	20000	nd	nd	nd	10000		
VP		200	10	-	1000	5	nd	50	2	200	nd	50	20	25	nd	nd	15	nd		

Table 2
Results of principal component analysis for waters from the Pinhal do Souto uranium mine area

	PC1	PC2	PC3
pH	-0.209	0.328	0.364
Eh	-0.133	**-0.614**	-0.087
O_2	-0.130	**-0.537**	0.075
EC	0.394	**0.813**	-0.277
Cl-	0.166	0.106	**-0.861**
NO_2^-	0.292	**0.882**	0.169
NO_3^-	-0.126	-0.350	**-0.778**
SO_4^{2-}	-0.226	0.184	**-0.563**
HCO_3^-	0.349	**0.899**	0.162
Na	0.103	**0.736**	-0.573
K	-0.049	0.420	**-0.783**
Ca	0.303	**0.730**	-0.045
Mg	0.512	**0.672**	-0.100
B	**0.909**	-0.199	-0.287
Al	0.555	-0.262	0.325
Ba	**0.974**	-0.044	0.018
Cd	**0.935**	-0.261	-0.098
Co	**0.618**	0.363	0.285
Cr	**0.948**	-0.289	-0.029
Cu	**0.889**	-0.373	0.048
Fe	-0.068	0.371	0.086
Li	**0.978**	-0.004	0.080
Mn	0.392	**0.827**	0.228
Ni	**0.942**	-0.288	-0.081
Pb	**0.947**	-0.248	0.015
Sr	**0.930**	0.255	-0.025
Zn	**0.884**	-0.169	-0.154
As	**0.690**	-0.047	0.373

Th	**0.852**	-0.206	-0.201
U	**-0.783**	0.478	-0.022
Eingenvalue	12.29	6.76	3.45
Total	40.96	22.52	11.51
Cumulative	40.96	63.48	74.99

O_2 – dissolved oxygen; EC – electrical conductivity. Number of water samples (n = 44).

Table 3
Textural characteristics, organic matter (OM%), cation exchange capacity (CEC cmol/kg), electrical conductivity (EC μS/cm), pH, Al and Fe contents (g/kg) and concentrations of trace metals and metalloids (mg/kg) of stream sediments from the Pinhal do Souto uranium mine area

	Local stream sediments					Mine drainage stream sediments						Ludares stream sediments				Precip.
samples	PS-SED7	PS-SED21	PS-SED6	PS-SED22	PS-SED23	PS-SED20	PS-SED12	PS-SED13	PS-SED14	PS-SED18	PS-SED19	PS-SED4	PS-SED15	PS-SED16	PS-SED17	PS-SED5
% sand	—	—	—	—	—	46.3	85.5	—	—	—	83.1	—	—	—	—	76.3
% silt	—	—	—	—	—	47.5	12.8	—	—	—	14.8	—	—	—	—	19.8
% clay	—	—	—	—	—	6.2	1.7	—	—	—	2.1	—	—	—	—	3.9
OM	—	—	—	—	—	4.13	1.00	—	5.07	1.70	—	0.24	—	—	—	7.26
CEC	—	—	—	—	—	4.53	3.23	—	3.65	1.27	—	0.67	—	—	—	5.06
EC	16	18	20	46	49	59	34	57	115	22	46	26	33	21	15	200
pH	5.2	4.8	4.7	4.0	4.5	4.5	5.4	5.2	4.6	4.5	4.6	5.4	5.5	4.6	5.3	5.6
Al	13.66	17.98	12.26	14.27	18.90	16.46	16.17	8.01	10.05	11.63	13.28	11.34	9.73	9.41	9.49	8.07
Fe	8.55	9.63	8.30	8.09	8.31	11.27	10.33	10.32	20.54	20.08	8.05	7.78	7.91	7.34	7.44	278.94
As	93.37	89.09	105.82	117.62	100.25	82.83	130.31	79.17	194.27	144.49	62.43	46.14	40.96	35.29	37.80	3710.78
Cd	32.30	24.86	25.17	38.08	20.53	35.82	37.40	40.74	92.28	70.17	17.58	22.76	8.93	12.42	8.27	1241.37
Co	*	*	*	*	*	*	15.15	*	10.33	*	*	*	*	*	*	1337.19
Cr	2.09	*	*	*	*	11.18	6.05	4.74	6.57	21.47	8.11	*	*	*	*	9.25
Cu	5.91	5.6	11.84	3.19	11.36	12.50	8.79	*	20.81	4.29	1.98	5.67	*	2.28	*	10.26
Mn	190.35	253.87	267.73	263.10	311.98	475.90	741.45	3116.46	1242.92	784.66	250.25	229.70	156.57	269.32	302.42	1663.21
Ni	*	*	*	*	*	*	98.37	*	*	*	*	*	*	*	*	36.47
Pb	43.43	25.41	37.66	27.03	37.21	83.12	9.83	66.94	137.01	110.35	45.68	85.16	17.80	4.25	*	68.98
Sb	7.76	6.77	6.49	8.30	4.99	3.89	19.58	*	*	4.16	3.35	*	*	*	*	17.20
Sr	17.95	12.65	13.78	10.76	9.12	22.35	24.87	15.34	23.67	9.41	10.42	10.41	26.77	30.14	25.81	112.57
Th	26.70	32.64	25.80	49.72	19.05	41.59	28.38	32.45	98.35	72.27	20.53	29.40	37.28	35.95	26.00	1053.12
U	*	*	*	*	*	*	*	*	*	*	*	35.68	*	*	*	485.20
W	*	*	*	19.84	17.24	*	10.69	*	*	18.24	*	*	*	*	*	108.33
Zn	126.97	105.10	111.69	90.80	83.28	234.48	201.39	131.12	239.39	136.47	100.40	90.20	59.12	54.86	57.21	198.15

Precip. – Fe-oxides precipitate; * - below the detection limit; — not determined. Analyst: A.C.T. Santos.

Table 4
Correlation matrix in stream sediments from the Pinhal do Souto uranium mine area

	Al	As	Cd	Cr	Cu	Fe	Mn	Pb	Sb	Sr	Th	W	Zn	pH	EC
Al	1.0														
As	0.2	1.0													
Cd	-0.1	**0.9**	1.0												
Cr	0.0	0.5	0.6	1.0											
Ca	0.3	**0.7**	0.6	0.1	1.0										
Fe	-0.1	**0.8**	**0.9**	**0.7**	0.5	1.0									
Mn	-0.4	0.3	0.4	0.2	0.0	0.4	1.0								
Pb	-0.1	0.6	**0.8**	0.6	0.5	**0.8**	0.4	1.0							
Sb	0.6	0.4	0.1	0.1	0.2	-0.1	-0.2	-0.3	1.0						
Sn	-0.1	0.3	0.3	-0.2	0.4	0.1	0.4	0.3	0.1	1.0					
Th	-0.3	**0.7**	**0.9**	0.5	0.5	**0.9**	0.2	**0.7**	-0.2	0.1	1.0				
W	0.6	0.6	0.4	0.4	0.3	0.4	-0.1	0.2	0.5	-0.5	0.3	1.0			
Zn	0.2	**0.7**	**0.7**	0.5	**0.7**	0.6	0.3	0.6	0.3	0.1	0.5	0.2	1.0		
pH	-0.3	-0.4	-0.3	-0.3	-0.3	-0.2	0.1	-0.2	0.0	0.4	-0.3	**-0.7**	-0.1	1.0	
EC	-0.1	0.6	**0.7**	0.2	0.6	0.5	0.4	0.6	-0.2	0.1	0.6	0.1	0.6	-0.3	1.0

EC – electrical conductivity.

Table 5																			
Correlation matrix in soils from the Pinhal do Souto uranium mine area																			
	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sr	Th	U	W	Zn	Temp.	pH	EC
Al	1.0																		
As	**0.8**	1.0																	
Cd	**0.7**	0.5	1.0																
Co	0.4	0.2	0.6	1.0															
Cr	0.4	0.4	0.4	0.4	1.0														
Cu	0.6	**0.7**	0.6	0.3	0.5	1.0													
Fe	**0.8**	**0.7**	**0.7**	0.5	0.6	**0.7**	1.0												
Mn	0.4	**0.7**	0.3	0.1	0.4	**0.7**	0.6	1.0											
Ni	0.5	0.3	0.6	**0.8**	0.6	0.3	0.5	0.1	1.0										
Pb	0.6	**0.7**	0.6	0.4	0.6	0.6	**0.7**	0.6	0.6	1.0									
Sb	0.6	**0.7**	0.5	0.5	0.5	0.5	0.6	0.5	0.6	**0.7**	1.0								
Sr	0.6	**0.7**	0.6	0.2	0.3	**0.7**	**0.7**	**0.7**	0.3	**0.8**	0.6	1.0							
Th	0.5	0.5	0.5	0.4	0.5	0.6	**0.7**	0.5	0.5	0.5	0.5	0.6	1.0						
U	0.0	-0.2	0.2	-0.1	-0.1	-0.1	0.0	-0.4	0.1	-0.1	-0.3	-0.2	0.0	1.0					
W	**0.8**	**0.8**	**0.7**	0.5	0.5	0.6	**0.7**	0.5	0.6	**0.7**	**0.8**	0.6	0.6	-0.2	1.0				
Zn	0.4	0.6	0.3	0.3	0.4	0.5	0.5	0.5	0.3	0.6	**0.7**	0.6	0.6	-0.2	0.5	1.0			
Temp	0.2	-0.2	0.3	0.2	-0.3	-0.1	-0.1	-0.3	0.1	-0.4	-0.2	-0.2	-0.1	0.3	0.0	-0.3	1.0		
pH	0.2	0.1	0.2	0.0	-0.1	0.3	0.2	0.5	-0.1	0.2	0.2	0.4	0.1	-0.2	0.2	0.2	-0.2	1.0	

EC	0.0	0.0	-0.2	-0.2	-0.2	0.1	0.0	0.2	-0.2	0.0	-0.2	0.1	-0.2	-0.2	-0.1	-0.2	-0.2	0.4	1.0
Temp - temperature; EC - electrical conductivity.																			

Table 6
Results of principal component analysis for soils from the Pinhal do Souto uranium mine area

	PC1	PC2	PC3
pH	0.245	**0.669**	0.239
EC	-0.115	**0.628**	0.366
Al	**0.809**	-0.055	0.338
As	**0.824**	0.185	-0.005
Cd	**0.754**	-0.290	0.424
Co	**0.584**	-0.477	-0.077
Cr	**0.644**	-0.280	-0.257
Cu	**0.780**	0.257	0.167
Fe	**0.882**	-0.014	0.135
Mn	**0.665**	0.660	-0.141
Ni	**0.662**	-0.569	-0.008
Pb	**0.869**	0.036	-0.030
Sb	**0.832**	-0.080	-0.321
Sr	**0.816**	0.337	0.131
Th	**0.747**	-0.074	-0.093
U	-0.125	-0.527	**0.646**
W	**0.861**	-0.090	0.047
Zn	**0.695**	0.136	-0.358
Eingenvalues	8.91	2.45	1.30
Total	49.49	13.62	7.23
Cumulative	49.49	63.11	70.34

EC - electrical conductivity. Number of soil samples (n=47).

Table 7
Predicted U species in selected water samples from the Pinhal do Souto uranium mine area

	Unit	PS5	PS9	PS10
Uranium	μg/l	72.75	76.95	104.4
pH		8.30	6.40	6.95
Alkalinity	mg HCO_3^-/l	100.2	57.12	110.7
Redox potential	mV	52	10	-158
Sulphate	mg/l	3.54	<0.004	<0.004
Fluoride	mg/l	0.28	0.24	0.21
Phosphate	mg/l	<0.006	<0.006	<0.006
$UO_2CO_3(aq)$	% of U_{Tot}	0	73	25
$UO_2(CO_3)_2^{-2}$	% of U_{Tot}	12	24	50
$UO_2(CO_3)_3^{-4}$	% of U_{Tot}	88	1	25
$UO_2(OH)_3^-$	% of U_{Tot}	0	0	0
$UO_2(OH)_2(aq)$	% of U_{Tot}	0	0	0
UO_2^{+2}	% of U_{Tot}	0	0	0
UO_2OH^+	% of U_{Tot}	0	2	0

Table 8
Comparison of concentrations in mg/kg of metals and metalloids, except Fe in %, in soils from the Pinhal do Souto uranium mine area with those of soils of the FOREGS Geochemical Atlas of Europe

	Portuguese Pinhal do Souto area					Portugal		European countries				
	Median	Maximum	N	Methods		Range	N	Median	Range	N	Methods	
Fe	8.72	15.1	47	aqua regia	ICP-OES	0.35 - 3.49	19	1.96	0.070 - 15.2	837	aqua regia	ICP-AES
As	94.9	196	47	aqua regia	ICP-OES	5.00 - 31.00	19	6.00	< 5.00 - 220	837	aqua regia	ICP-AES
Cd	0.32	82.9	47	aqua regia	ICP-OES	0.03 - 0.10	19	0.140	0.010 - 14.1	840	total	ICP-MS
Co	0.00	52.9	47	aqua regia	ICP-OES	3.00 - 21.0	19	7.00	<1.00 - 260	837	aqua regia	ICP-AES
Cr	1.22	17.3	47	aqua regia	ICP-OES	8.00 - 28.0	19	22.0	1.00 - 2300	837	aqua regia	ICP-AES
Cu	10.4	237.0	47	aqua regia	ICP-OES	3.00 - 27.0	19	12.0	1.00 - 240	837	aqua regia	ICP-AES
Mn	214	6009	47	aqua regia	ICP-OES	250 - 6500	19	380	<10.0 - 6500	837	aqua regia	ICP-AES
Ni	0.00	46.1	47	aqua regia	ICP-OES	3.00 - 35.0	19	14.0	<2.00 - 2600	837	aqua regia	ICP-AES
Pb	62.2	944	47	aqua regia	ICP-OES	7.00 - 32.0	19	15.0	<3.00 - 890	837	aqua regia	ICP-AES
Sb	18.5	152	47	aqua regia	ICP-OES	0.280 - 3.06	19	0.600	0.020 - 31.1	840	total	ICP-MS
Sr	10.9	87.4	47	aqua regia	ICP-OES	30.0 - 3100	19	89.0	8.00 - 3100	848	total	ICP-MS
Th	26.2	47.2	47	aqua regia	ICP-OES	7.24 - 75.9	19	7.24	0.300 - 75.9	843	total	ICP-MS
U	25.1	337	47	aqua regia	ICP-OES	2.00 - 53.2	19	2.00	0.200 - 53.2	843	total	ICP-MS
W	19.1	57.2	47	aqua regia	ICP-OES	<5.00 - 14.0	19	<5.00	<5.00 - 14.0	848	total	ICP-MS
Zn	92.7	347	47	aqua regia	ICP-OES	13.0 - 85.0	19	48.0	4.00 - 2300	837	aqua regia	ICP-AES

N – Number of samples.

Table 9
Comparison of environmental impacts caused by two Portuguese abandoned uranium mines

	Pinhal do Souto (PS) area	Vale de Abrutiga (VA) area
Host rock of quartz veins	two-mica granite	schist-greywacke complex
U minerals from quartz veins	mainly autunite, torbernite, also uraninite, meta-torbernite, sabugalite, parsonite, phosphuranylite and black uranium oxides	saleeite, meta-saleeite, Fe-saleeite, coffinite
Exploitation way	underground	an open pit
Exploitation dates	1978-1989	1982-1989
Mine production	93091 kg U_3O_8	90000 kg U_3O_8
Surface water; groundwater		
pH	5.11-8.11; 5.12-8.48	2.25-6.65; 4.50-6.22
Electric conductivity μS/cm	33-100; 22-235	84-6660; 175-720
U μg/l	30.25-74.83; 29.59-104.42	⁎-18660; ⁎-1000
Th μg/l	7.83-99.71; 7.51-98.10	0.01-20.40; 0.03-0.11
Pb μg/l	⁎-74.07; ⁎-94.95	⁎-110.00; ⁎-170.00
Cu μg/l	3.88-79.69; ⁎-75.05	10.00-1470.00; 10.00-130.00
SO_4^{2-} mg/l	1.32-6.98; ⁎-14.99	⁎-6576; ⁎-284
Stream sediments with U mine drainage		
U mg/kg	⁎-35.68	27.80-301.00
Th mg/kg	20.53-98.35	3.30-10.80
Pb mg/kg	⁎-137.01	25.00-44.00
Cu mg/kg	⁎-20.81	18.10-66.50
Zn mg/kg	54.86-239.39	130.00-803.00
Co mg/kg	⁎-15.15	11.00-74.00
Fe g/kg	7.34-20.54	27.00-239.00
References	This article	Pinto et al. (2004), Cabral Pinto et al. (2008, 2009)

Waters and stream sediments samples are downstream the uranium mines and dumps. ⁎ – below the detection limit. In the Pinhal do Souto area, U was only detected in one stream sediment sample. The data on both areas were collected before rehabilitation. Only the VA area has been rehabilitated later.