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Spatial and temporal variability of surface water and groundwater before and after the remediation of a Portuguese uranium mine area

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ABSTRACT

The old Senhora das Fontes uranium mine, in central Portugal, consists of quartz veins which penetrated along fracture shear zones at the contact between graphite schist and orthogneiss. The mine was exploited underground until a depth of 90 m and was closed down in 1971. The ores from this mine and two others were treated in the mine area by the heap-leach process which ended in 1982. Seven dumps containing a total of about 33,800 m^3 of material and partially covered by natural vegetation were left in the mine area. A remediation process took place from May 2010 to January 2011. The material deposited in dumps was relocated and covered with erosion resisting covers. Surface water and groundwater were collected in the wet season just before the remediation, in the following season at the beginning of the remediation and also after the remediation in the following dry season. Before, at the beginning and after the remediation, surface water and groundwater have an acid-to-alkaline pH, which decreased with the remediation, whereas Eh increased. In general, before the remediation, uranium concentration was up to 83 μg/L in surface water and up to 116 μg/L in groundwater, whereas at the beginning of the remediation it increases up to 183 μg/L and 272 μg/L in the former and the latter, respectively, due to the remobilization of mine dumps and pyrite and chalcopyrite exposures, responsible for the pH decrease. In general, after the remediation, the U concentration decreased significantly in surface water and groundwater at the north part of the mine area, but increased in both, particularly in the latter up to 774 μg/L in the south and southwest parts of this area, attributed to the remobilization of sulphides that caused mobilization of metals and arsenic which migrated to the groundwater flow. Uranium is adsorbed in clay minerals, but also in goethite as indicated by the geochemical modelling. After the remediation, the saturation indices of oxyhydroxides decrease as pH decreases. The remediation also caused decrease in Cd, Co, Cr, Ni, Pb, Zn, Cu, As, Sr and Mn concentrations of surface water and groundwater, particularly in the north part of the mine area, which is supported by the speciation modelling that shows the decrease of most dissolved bivalent species. However, in general, after the remediation, Th, Cd, Al, Li, Pb, Sr and As concentrations increased in groundwater and surface water at south and southwest of the mine area. Before and after the remediation, surface water and groundwater are contaminated in U, Cd, Cr, Al, Mn, Ni, Pb, Cu and As. Remediation caused only some improvement at north of the mine area, because at south and southwest part, after the remediation, the groundwater is more contaminated than before the remediation.

1. Introduction

The discharges of uranium and associated radionuclides as well as heavy metals and metalloids from waste and tailing dumps in abandoned uranium mining and processing sites pose contamination risks to surface water and groundwater (Mkandawire, 2013; Skipperud et al., 2013).

In Portugal, there have been about 60 uranium mines exploited during the 20th century for radium and uranium production. These mining and milling activities originated about 13 million tonnes of solid wastes dumped at several sites in the centre-north of the country (Pinto and Silva, 2005; Carvalho et al., 2007). Uranium

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production in Portugal ceased in 2001 and was followed by the approval of an environmental remediation plan for the old and abandoned mine sites (Portuguese Law, 2001).

The effects of abandoned uranium mines on the Portuguese environment have rarely been studied (e.g., Pinto et al., 2004; Antunes et al., 2011; Neiva et al., 2014). Uranium as a heavy metal is chemically toxic and causes a health risk if incorporated in aqueous species (Schöner et al., 2009). The hazard potential of uranium depends on its species and its concentrations. In natural aquatic systems, uranium is stable as U(IV) or U(VI), but depends on redox conditions. U(VI) is more soluble than U(IV) and under neutral and alkaline conditions occurs as $(UO_2)^{2+}$, forming complexes with carbonates, phosphates, vanadates, fluorides, sulphates and silicates (Langmuir, 1997; Cabral Pinto et al., 2008, 2009; Arnold et al., 2011). U(VI) is much more soluble than U(IV) and may migrate as aqueous species in the environment (Arnold et al., 2011). The World Health Organization indicates 15 μg of uranium per litre for drinking water quality (WHO, 2010). Therefore, high concentrations of uranium in water cause a risk for the human health and environment.

Six decades of uranium exploration and mining milling in Europe has resulted in a considerable legacy of waste rock piles, below-grade ore heaps and milling residues disposal sites–Uranium Mine and Mill Tailings (UMMT) (Falck, 2008). The remediation of UMMT sites has two objectives: (1) to interrupt pathways to radiological and non-radiological exposures; (2) to mechanically stabilize the sites against environmental processes, such as erosion (Falck, 2008).

Several studies have shown that remediation processes are long. Many years after the initiation of remediation, metals and metalloids can be re-suspended in water, during hydrological phenomena, because they remain stored in sediments (Galán et al., 2002). In a mining area, recovery can become unpredictable, if high frequency and large spatial ranges are combined (O'Neil, 1998). However, none of the data are available for the effects of remediation in Portuguese mine areas.

The purpose of this study was to characterize the spatial and temporal variability of some chemical proprieties and trace element contents in surface and groundwater before, during and after the remediation of the abandoned Senhora das Fontes uranium mine. These results will allow assessing the impacts of the remediation process and could improve remediation in the study area and avoid similar problems in other mine areas.

2. Geology, mineralization and mine site

The old Senhora das Fontes uranium mine area is located in the Sorval village, Guarda County, in central Portugal (Fig. 1a). The Sorval village is at west and the Santa Eufémia village is at north and about 1 km from the mine area. The Póvoa díEl Rei village is located at 2.5 km SW of the mine area (Fig. 1b). Geologically, this area is located in the Central Iberian Zone (CIZ) of the Iberian Massif (Fig. 1a). The schist–greywacke complex (SGC) was intruded by two orthogneisses and a granite and contacts are sharp (Fig. 1b). The syn-F1 medium-grained muscovite-biotite orthogneiss of Senhora das Fontes–Sorval presents a N60–70°W, 80° ± 5S shear foliation given by the orientation of feldspar megacrystals and muscovite. It contains some torbernite and saleeite. This orthogneiss is cut by basic rock veins (Macedo, 1988). The syn-F1 fine-grained muscovite >biotite orthogneiss of Póvoa díEl Rei intruded the SGC and the orthogneiss of Senhora das Fontes–Sorval and the contacts are sharp. It is fine-grained, less deformed and contains more biotite than the other orthogneiss. Its shear foliation is N70W, 80°S and given by the micas orientation, mainly biotite. It is cut by granitic aplite and pegmatite dikes and quartz veins. The syn-F2 medium-grained muscovite granite from Santa Eufémia shows mainly a N75°E orientation of K-feldspar megacrystals, due to a shear deformation. This granite is cut by quartz veins and basic rock veins (Macedo, 1988).

The mine consists of divided quartz veins that penetrated along fractured shear zones, at the contact between graphite schists of the SGC and the Senhora das Fontes–Sorval orthogneiss. However, the mineralization only occurs in E–W fragmented quartz veins up to 1 m thick within the graphite schists. They contain tourmaline, some cassiterite, autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 10–12H_2O$, down to a depth of 40 m. But below, black uranium oxides, uraninite, UO_2, and Fe-saleeite, $(Fe,Mg)(UO_2)_2(PO_4)_2 \cdot 8H_2O$ occur in small veinlets or forming elongated nodules cutting the graphite schists of shear zones. The schists support the uranium mineralization, as indicated by radiometric values. The schists are also cut by N45°W, SW long basic rock veins (Fig. 1b) up to 27 m deep and 0.3–0.8 m thick, containing some secondary uranium minerals. This uranium deposit contains a mean of 0.4% U_3O_8, reaching 1–2% (Barros, 1966).

At the surface, the uranium deposit had a lense-shaped form of 190 × 10 m dimension (Barros, 1966). It was exploited underground and had three levels reaching the maximum depth of 90 m. The mine was closed down in 1971 and then a small open pit was made by removing the upper mineralized massif. The U was removed from the poor ores of the Senhora das Fontes by the heap-leach process, which consisted of crushing the ore and to add sulphuric acid to dissolve the ore and oxidize the U. This process has taken place in the open pit. The U enriched solution was collected inside the mine. The ores from other Portuguese uranium mines, such as Freixinho and Cótimos were also treated by heap-leach static threshing floors. Ionic exchange was carried out in the area. The heap-leach process ended in 1982.

In the area, there were a closed main well of 90 m depth connected to the three mine levels (Barros, 1966) and also seven main dumps (Fig. 1c). Two of them (A and C) consisted of mud from decantation and waste materials of large dimensions. Another (B) contained precipitates from dissolved wastes. Three others (D, E and F) consisted of waste materials left from the ore dissolution in the open pit. The dump G contained waste materials that came from the opening of the open pit. There was also a small dump associated with the main mine dump. The dumps were partially covered by vegetation.

A remediation took place approximately during one year from May of 2010 to January of 2011. Wells and chimneys were closed. The old structures and buildings were removed. The material deposited in dumps of about 33,800 m^3 volume was relocated to be together and covered with erosion resisting covers.

The Senhora das Fontes area is not mountainous, as the altitudes range between 605 m at west and 651 m at southeast of the old mine area. The climate is of maritime temperature. The annual precipitation was 466.8 mm in 2010 and 137.8 mm in 2011. Rainfall dominates during the wet season and was about 115.0 mm in November of 2009–February of 2010 and about 25 mm in the dry season, in May–June of 2010 and 2011, according to the data of the weather station from Pinhel, Guarda, northeast Portugal (SNIRH, 2012). The annual average temperatures ranged from 7 °C to 21 °C, but reached 40 °C in summers and −7 °C in winters. The area has rural characteristics, with dense vegetation, mainly of oaks and pinus and underbrush. Around the old mine, mainly downstream, there are rye fields and pastures. The surface drainage runs to the Massueime stream, which is a tributary in the left bank of the Côa river.

3. Water samples and analytical methods

A total of 21 water sampling points including seven streams, ten wells and four springs were chosen to collect water samples

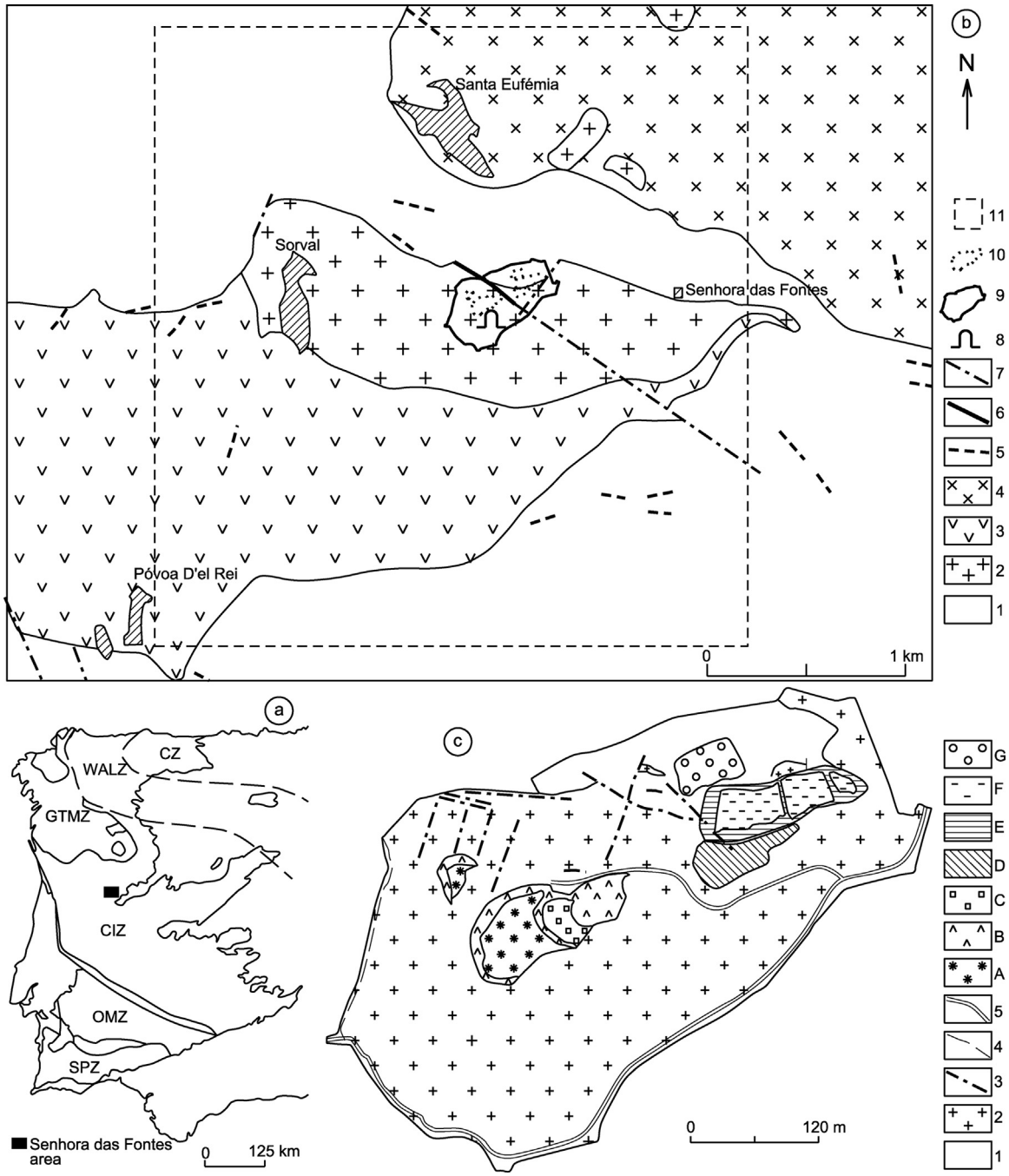

Fig. 1. Geological area containing the old Senhora das Fontes uranium mine. (a) Location of the area and tectonic zones in the Iberian Massif. CZ–Cantabrian Zone; WALZ–West Asturian Leonese Zone; GTMZ–Galicia-Trás-os-Montes Zone; CIZ–Central Iberian Zone; OMZ–Ossa-Morena Zone; SPZ–South Portuguese Zone (Julivert et al., 1974; Farias et al., 1987). (b) Geological map of this area, showing the studied area. 1 – schist–greywacke complex; 2 – Senhora das Fontes–Sorval orthogneiss; 3 – Póvoa dEl Rei orthogneiss; 4 – Santa Eufémia granite; 5 – quartz vein; 6 – basic rock vein; 7 – fault; 8 – uranium mine entrance; 9 – dumps area; 10 – dumps; 11 – the studied area. (c) Simplified map showing the mine dumps before the remediation. 1 – schist–greywacke complex; 2 – Senhora das Fontes–Sorval orthogneiss; 3 – fault; 4 – stream; 5 – road; A, B, C, D, E, F, G – dumps.

in the Senhora das Fontes mine area (Fig. 2). They were collected in a hydrological year, twice in the wet season, at November of 2009 and February of 2010, before the remediation and twice in the dry season, at May and June of 2010, at the beginning of the remediation. They were also collected after the remediation, at May and June of 2011, in the dry season. A total of 113 water samples was obtained, because occasionally some points were dry. Average values of the results of the water samples collected in the same sampling point, during the same season: (a) before remediation, (b) during remediation and (c) after remediation were used. Waters from streams and springs were collected about 20 cm below the surface of the water level and those from wells were collected below 1–2 m, or more, of the water level. Temperature (T), pH, electrical conductivity (EC), oxygen redox potential (ORP), dissolved oxygen (DO) and alkalinity (HCO_3^-) were measured in situ. The waters were filtered through 0.45 μm pore size membrane filters. They were acidified with HNO_3 at pH 2 and kept at 4 °C for cation determinations by an Inductively Coupled Plasma Optical

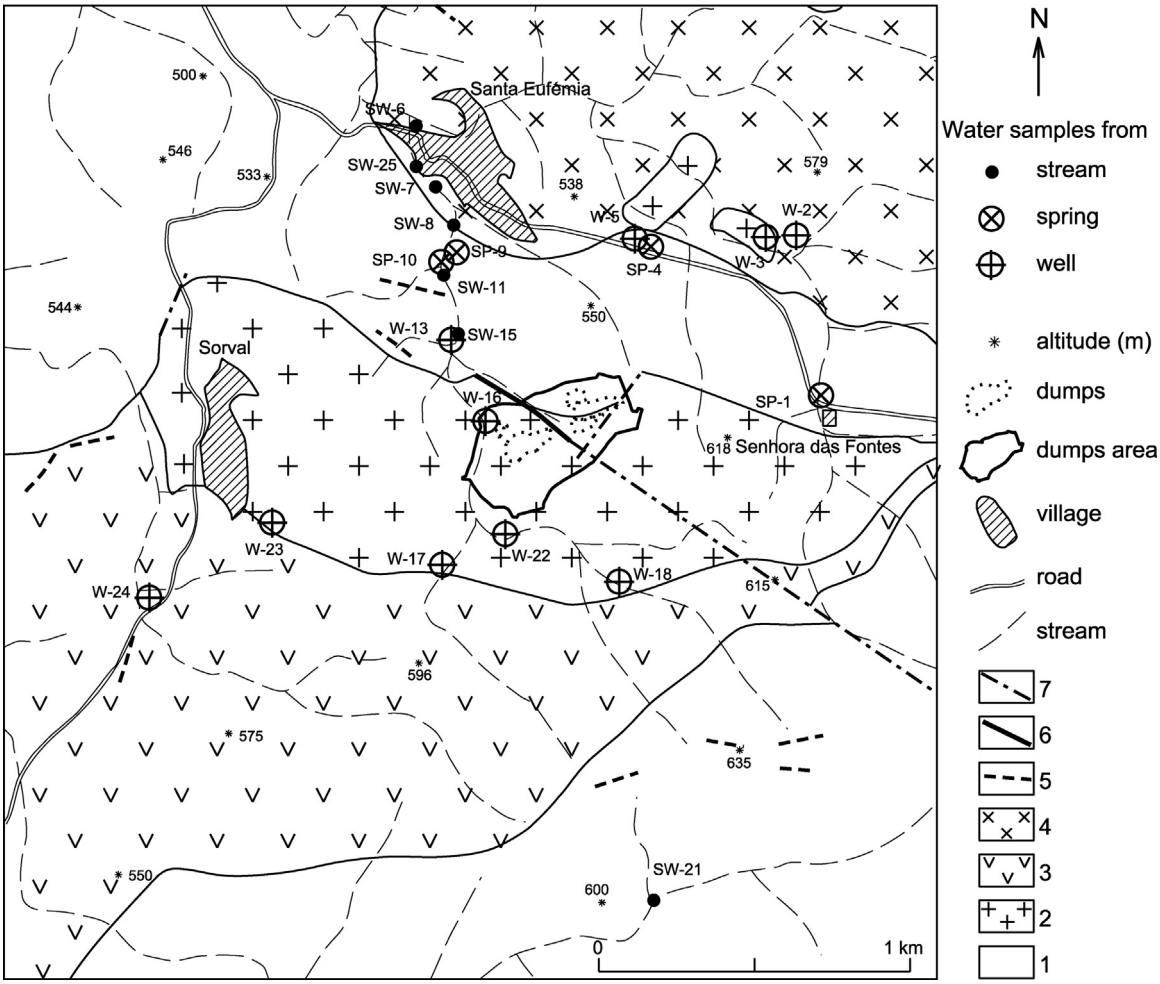

Fig. 2. Simplified map showing the locations of dumps and water samples. 1 – schist–greywacke complex; 2 – Senhora das Fontes–Sorval orthogneiss; 3 – Póvoa d'el Rei orthogneiss; 4 – Santa Eufémia granite; 5 – quartz vein; 6 – basic rock vein; 7 – fault.

Emission Spectrometer (ICP-OES), using a Horiba Yvon JY2000 2 spectrometer with a monochromator. Anions were determined in non-acidified samples by ion chromatography with a Dionex ICS 3000 Model. Duplicate blanks and a laboratory water standard were analyzed for quality control. The precision was better than 5%, but better than 15% for Na and Al. The detection limits in mg/L were 0.001 for K, Ca, Mg, Cd and F^-, 0.002 for Na, Sr and Zn, 0.003 for Co, Mn and Ni, 0.004 for Fe and Cr, 0.036 for Al and Li, 0.008 for Cu and Pb, 0.007 for U, 0.016 for Th and As, 0.051 for Cl^-, 0.015 for PO_4^{2-} and 0.066 for SO_4^{2-} and NO_3^-. Total dissolved solids (TDS) and total solids (TS), corresponding to the weight material obtained by evaporation of 100 mL of filtered and unfiltered water through 0.45 μm filters, respectively, were determined. The analytical results show ion balance errors within ±10% for most water samples. The modelling of metals and arsenic was carried out using the software Phreeq C and the minteq.V4.dat database, whereas for uranium modelling was used the sid.dat database. Moreover, for uranium modelling the alkaline earth elements reactions and log *K* values were added to the Phreeq C input file (according to Dong and Brooks, 2006; Geipel et al., 2008).

$$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3;\ \log K = 30.79$$

$$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-};\ \log K = 27.18$$

$$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} = MgUO_2CO_3^{2-};\ \log K = 26.11$$

$$Sr^{2+} + UO_2^{2+} + 3CO_3^{2-} = SrUO_2(CO)_3^{2-};\ \log k = 26.86$$

$$2Sr^{2+} + UO_2^{2+} + 3CO_3^{2-} = SrUO_2(CO)_3^{2-};\ \log k = 29.73$$

Spatial and temporal distribution (before, during and after the remediation) of uranium and thorium concentrations in surface water and groundwater from the Senhora das Fontes mine area are plotted in dot maps. Spatial distributions of U and Th contents in surface water and groundwater are not a continuous space field. The concentration of a particular point is only representative of that point, although it has also the contribution of the points located upstream in the stream line and in higher groundwater levels, respectively. Since the field is not continuous, the spatial distribution is mapped using dot contents and none contour lines. The distribution of U and Th contents in space are mapped using 7 samples of surface water and 14 samples of groundwater (wells and springs) and in time before ($n = 2$), during ($n = 2$) and after ($n = 2$) the remediation. The size of the dot increases with the increase in trace element content. As the element concentration varies significantly in space and time, the number of map classes and the metal content for the class limit were not fixed.

4. Results and discussion

4.1. Classification of surface water and groundwater from the Senhora das Fontes uranium mine area

Physico-chemical parameters and chemical analyses of waters from streams (SW-6, SW-7, SW-8, SW-11, SW-15, SW-21 and SW-25), wells (W-2, W-3, W-5, W-13, W-16, W-17, W-18, W-22, W-23 and W-24) and springs (SP-1, SP-4, SP-9 and SP-10) from the old Senhora das Fontes mine area are presented in Appendixes 1 and 2. The surface water sample SW-21 and the groundwater samples W-23 and W-24 represent the background or natural level (Fig. 2). According to the Piper classification, surface water samples SW-7, SW-8, SW-11 and SW-25 are of sulphate undefined type, whereas the other surface water samples SW-6, SW-7 and SW-21 and groundwater samples W-2, W-3, W-22, W-23, W-24, SP-1 and SP-4 are of bicarbonate sodium—potassium type. Groundwater samples W-13, W-18 and SP-10 are of bicarbonate undefined type. The groundwater samples W-5, W-16, W-17 and SP-9 are of undefined type.

Almost water samples are classified as metal poor and neutral to acidic (pH < 5.5), according to the Ficklin classification (Ficklin et al., 1992). Groundwater samples W-16 and W-13 are metal-enriched and acidic (Fig. 3). In general, there is a decrease in metal contents of groundwater and surface waters with the remediation processes (Fig. 3). However, almost groundwater samples and some stream samples (SW-7, SW-8, SW-11, SW-15 and SW-25) show pH variability with an initial decrease during the remediation phase and decreasing in the post-remediation (Fig. 3). This variability could be associated to the mobility of oxidizing trace elements on surface drainage from the mine area and consequent infiltration to groundwater levels, after the surface dumps mobilization and relocation. In general, the surface water samples SW-15, SW-11, SW-8, SW-7, SW-25 and SW-6 collected in the stream, which drains the area and receives the influence from several mine dumps, show that pH values and bicarbonate concentrations increase and sulphate and uranium concentrations tend to decrease downstream. The effect due to the dumps decreases with the increase in distance from them, due to the water dilution and also metals, metalloids and radionuclides precipitated in stream sediments.

4.2. The effect of remediation on the physico-chemical characteristics of surface water and groundwater from the Senhora das Fontes uranium mine area

Before the remediation processes, pH values of surface water are of 5.5–7.9, ranging from slightly acidic to alkaline (Appendix 3a), because secondary minerals were formed and retained the acidity. Metals and metalloids and the sulphide oxidation were not enough to produce an acid pH (e.g., Jerz and Rimstidt, 2003). The pH values of groundwater before remediation are generally lower, ranging from 4.2 to 7.3 and consequently from acidic to alkaline (Appendix 3a). After the remediation has started and also after it has finished, the pH values of surface water (4.1–7.3) and groundwater (3.5–6.4) are lower and Eh values are higher than before the remediation (Appendixes 1, 2). At Senhora das Fontes mine area, the pH values of water are lower and Eh values are higher after the remediation has finished in May and June of 2011 than in the respective month of 2010, when the remediation started, suggesting that the remediation caused those effects. pH, Eh and the type of complexing agents present mainly control the water chemistry (Langmuir, 1997).

The electrical conductivity (EC) of the surface water ranges from 43 to 276 μS/cm before the remediation and from 61 to 259 μS/cm, after the remediation has finished (Appendixes 1 and 3b). Only the highest value decreases. A similar effect occurs in the total dissolved solids (TDS) in the surface water, as they range from 34 to 175 mg/L before a significant remediation took place and are of 40–156 mg/L after the remediation has finished (Appendix 1). However, the remediation does not modify the EC of groundwater from wells (26–1103 μS/cm) and springs (52–158 μS/cm) and TDS of springs (37–99 μs/cm) (Appendixes 2 and 3b). The TDS values of groundwater from wells range between 19 and 496 mg/L before a significant remediation and are of 18–588 mg/L after the remediation (Appendix 2). The groundwater sample W-16, corresponding to the Senhora das Fontes mine well, shows the lowest pH values and highest EC, TS and TDS from the study area, independently of the remediation phase (Appendixes 2, 3a and 3b).

4.3. The effect of remediation on metals and metalloids of surface water and groundwater from the Senhora das Fontes uranium mine area

Before the remediation, uranium concentrations in surface water range from 17 to 83 μg/L and in groundwater from wells and springs mainly range from 17 to 116 μg/L, but are higher in two wells reaching 649 μg/L and in springs range from 34 to 53 μg/L (Appendixes 1 and 2; Fig. 4a). Most of these concentrations are typical of water from uraniferous areas (e.g., Iwatsukí and Yoshida, 1999; Landa, 1999), because only two groundwater samples have concentrations above 116 μg/L. When the remediation started, in May and June of 2010, the uranium concentrations generally increased up to 183 μg/L in surface water and also tended to increase in groundwater, up to 272 μg/L in wells and 116 μg/L in springs (Fig. 4a). Therefore, the high uranium concentrations found are attributed to the beginning of the remediation activities in the area, such as remobilization of mine dumps and sulphides exposure (pyrite and chalcopyrite) and consequently the pH values decrease slightly as already mentioned. In uranium areas, the highest concentration of uranium in surface water and groundwater commonly occurs in the wet season, when the flow is high and leaching from mineralized quartz veins and dumps takes place (e.g., Pinto et al., 2004; Neiva et al., 2014). After the remediation ended, in May and June of 2011, uranium concentrations decrease in almost surface water samples located at north of the uranium mine area. Otherwise, there is an increase in U content of eight times in a stream water (SW-21; Fig. 4a) and from 6 to 16 times in the groundwater samples (W-22, W-23 and W-24; Fig. 4a) after the remediation process.

Uranium mobility is mainly controlled by complexation and redox reactions (Langmuir, 1978). The dissolution of uranium minerals produces U(VI) by oxidation of U(IV) and forms strong complexes with the anions OH^-, F^-, Cl^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} (Langmuir, 1978), that increase the uranium mobility. Uraninite is the primary mineral exploited from the Senhora das Fontes mine. Autunite, uranium oxides and Fe-saleeite are the secondary uranium minerals found, containing uranyl ions (UO_2^{2+}), which are more soluble and mobilized in the environment than the unaltered uraninite. The UO_2^{2+} is the most stable under acidic or oxygenated conditions (Duff and Amrhein, 1996). The strong carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are formed under neutral or alkaline pH conditions (Grenthe et al., 2003). The alkaline earth uranyl carbonate species can also be formed in neutral waters with significant contents of alkaline earth elements (Vercouter et al., 2015). Some studies have shown that the dominant species of aqueous uranium changes from $UO_2^{2+} \rightarrow UO_2CO_3 \rightarrow UO_2(CO_3)_2^{2-} \rightarrow UO_2(CO_3)_3^{4-}$, as pH increases (Zhang et al., 2010). In the Senhora das Fontes mine area, uranyl ions (UO_2^{2+}) increase in most water samples in May of 2011 (Appendix 4), due to the low pH values. Moreover, uranyl ions are easily adsorbed into predominantly negatively charged surface sites of clays (Turned et al., 1996; Barnett et al., 2000) that decrease the uranium mobility. Dissolved

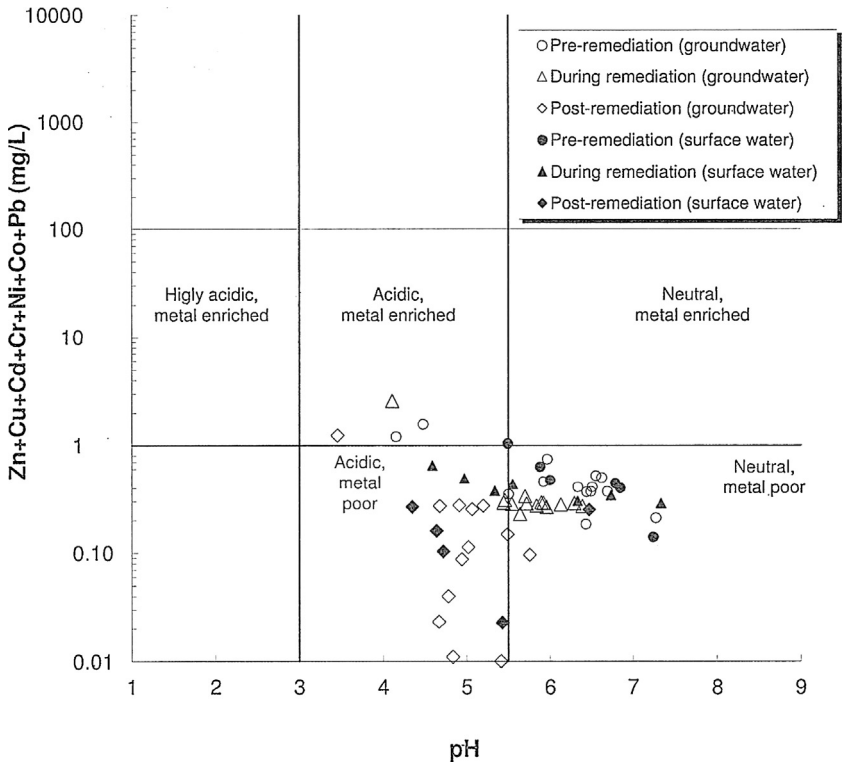

Fig. 3. Classification of waters from the Senhora das Fontes mine area in the Ficklin diagram (Ficklin et al., 1992).

thorium concentrations are lower than those of uranium, because thorium compounds are hardly soluble and easily precipitated in solid phases (Tutu et al., 2009). However, after the remediation, thorium reached the highest concentration of 261 μg/L in the surface water sample SW-21 (Appendix 1).

In general, most metals Co, Cr, Ni, Pb, Sr, Zn and Cu and the metalloid As show lower concentrations in the surface water after the remediation has finished than before the remediation process (Appendix 1; Fig. 4b–d), indicating that the remediation had a significant effect. In the groundwater samples W-2, W-3, W-5, W-13 and W-16, located at the north of the mine area (Fig. 2), generally As, Cd, Co, Cr, Mn, Ni, Pb, Sr, Zn and Cu also decrease their concentrations after the remediation has finished (Appendix 2; Fig. 4). In general, in springs, which are all located at north of mine area, the concentrations of U, Cd, Co, Mn, Ni, Pb, Sr, Zn, Cu and As also decrease after the remediation has finished. The speciation modelling also demonstrates that the dissolved metals Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+} tend to decrease in surface water and groundwater at north of the mine area, after the remediation (Appendix 4). Moreover, K, Ca and Mg also generally increase in surface water and groundwater in May and June of 2010, at the beginning of the remediation, but they decrease after the remediation ended (Appendixes 1 and 2). However, the formation of calcium and magnesium uranyl carbonates only occurs in the samples SW21 and SP9, due to the close to neutral pH values of these waters. At low pH values, $Ca_2UO_2(CO)_3O$ does not occur. Uranyl carbonates and uranyl sulphates are predominant.

Spatial and temporal U and Th distributions of surface water from the Senhora das Fontes mine area vary before, during and after remediation processes (Fig. 5a–f). Before and during the remediation, U content shows a spatial dispersion. After the remediation, the U contents move towards the south of the area, outside the mine influence (Fig. 5c). Before the remediation, the Th content in surface water shows a tendency to increase with the distance to the mine site (Fig. 5d). During the remediation, the highest Th concentration occurs in the mine site and after this process, the highest Th content occurs in the south of the area (Fig. 5e and f).

Uranium spatial distribution of groundwater (wells and springs) from Senhora das Fontes mine area varies before, during and after remediation processes (Fig. 6a–c). Before and during remediation, the highest U concentration is mainly around the mine site (water samples W-16 and W-13; Fig. 2). During the remediation, there is a global U enrichment in groundwater around the mine site, but the highest concentrations of 649 μg/L for W-16 and 645 μg/L for W-13 (in the mine area) decrease to 272 μg/L and 111 μg/L, respectively, about 2–6 times lower than the U concentration before remediation. After the remediation, there is a dispersion of U contents, with the highest values concentrated in the west of the area, where they increase up to 10 times (Fig. 6a–c). Before and during remediation, the highest Th content in groundwater is concentrated around the mine site (water sample W-16; Fig. 6d and e). After the remediation, there is a decrease in the Th content at the north of the area and around the mine site and an increase from not detected to 209 μg/L in the south, outside the mine influence (Fig. 6f). Therefore, although the remediation decreased U and Th contents of surface water and groundwater at the north and close to the mine site, it also increases their contents in both waters at the south.

In general, after the remediation, in June 2011, Cd, Al, Li, Pb, Sr and As concentrations also increased in groundwater samples W-17, W-18, W-22, W-23 and W-24 and the surface water SW-21 (Appendixes 1, 2; Fig. 4). After the remediation, the thorium concentration also increases in SW-21, W18, W-23, W-24 samples (Fig. 5d and f). These samples are located at S and SW of the mining area (Fig. 2). Some water samples were collected in orthogneisses, which belong to the Beira granitic batholith, which contains uranium minerals (Cotelo Neiva, 2003) and is an important source of uranium (Porcelli et al., 1997). But other water samples are located in the schist–greywacke complex, where uranium minerals mainly occur. Before the remediation,

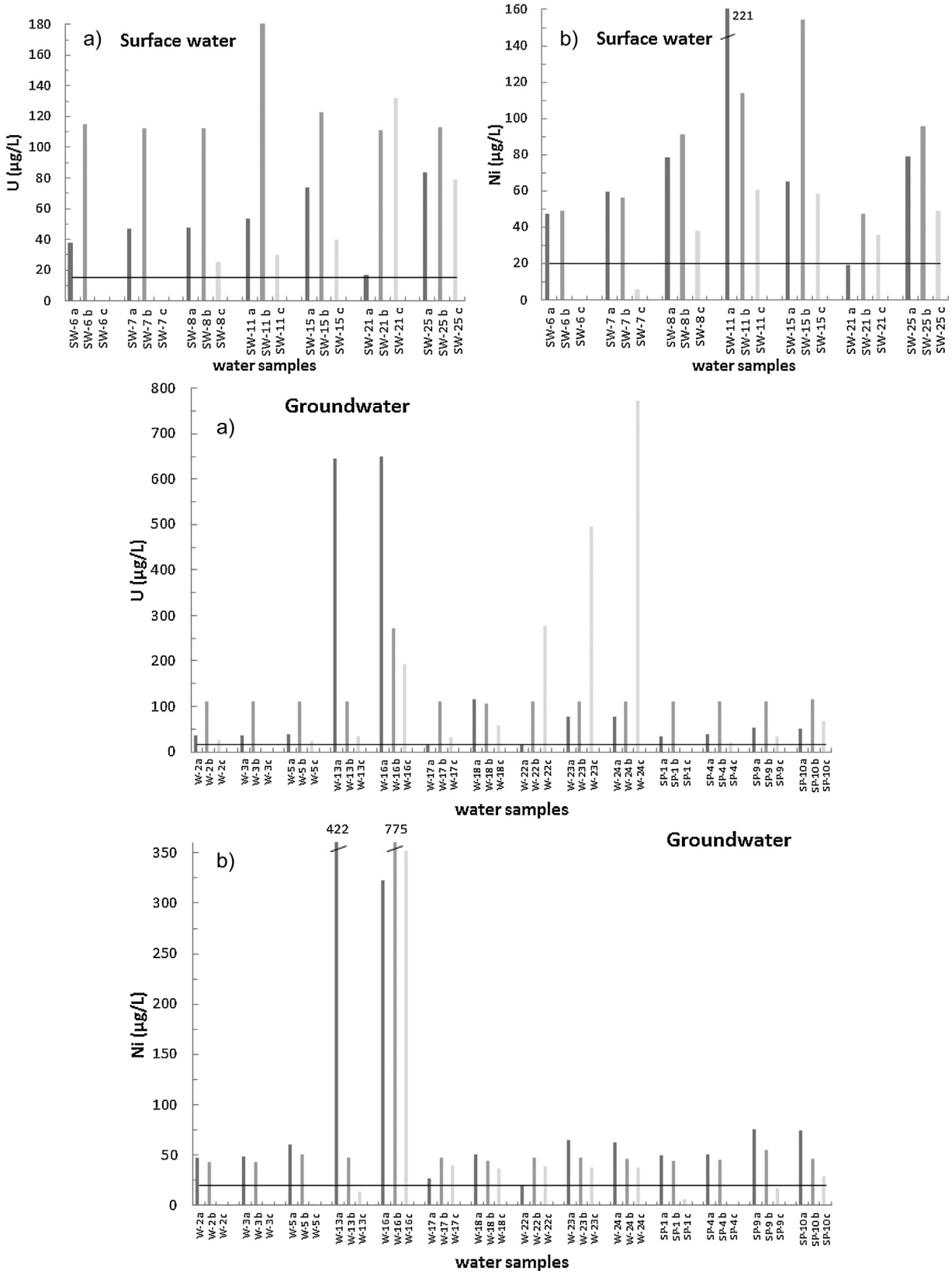

Fig. 4. Seasonal chemical variations in waters from the Senhora das Fontes uranium mine area. (a) U; (b) Ni; (c) Pb; (d) As; (e) Cd; (f) Mn; **- - - -** Recommended values for agriculture use; — permitted values for human consumption (Portuguese Law, 1998, 2007), except for As and U (WHO, 2010). Darker grey – before remediation, intermediate grey – at the beginning of remediation, lighter grey – after remediation.

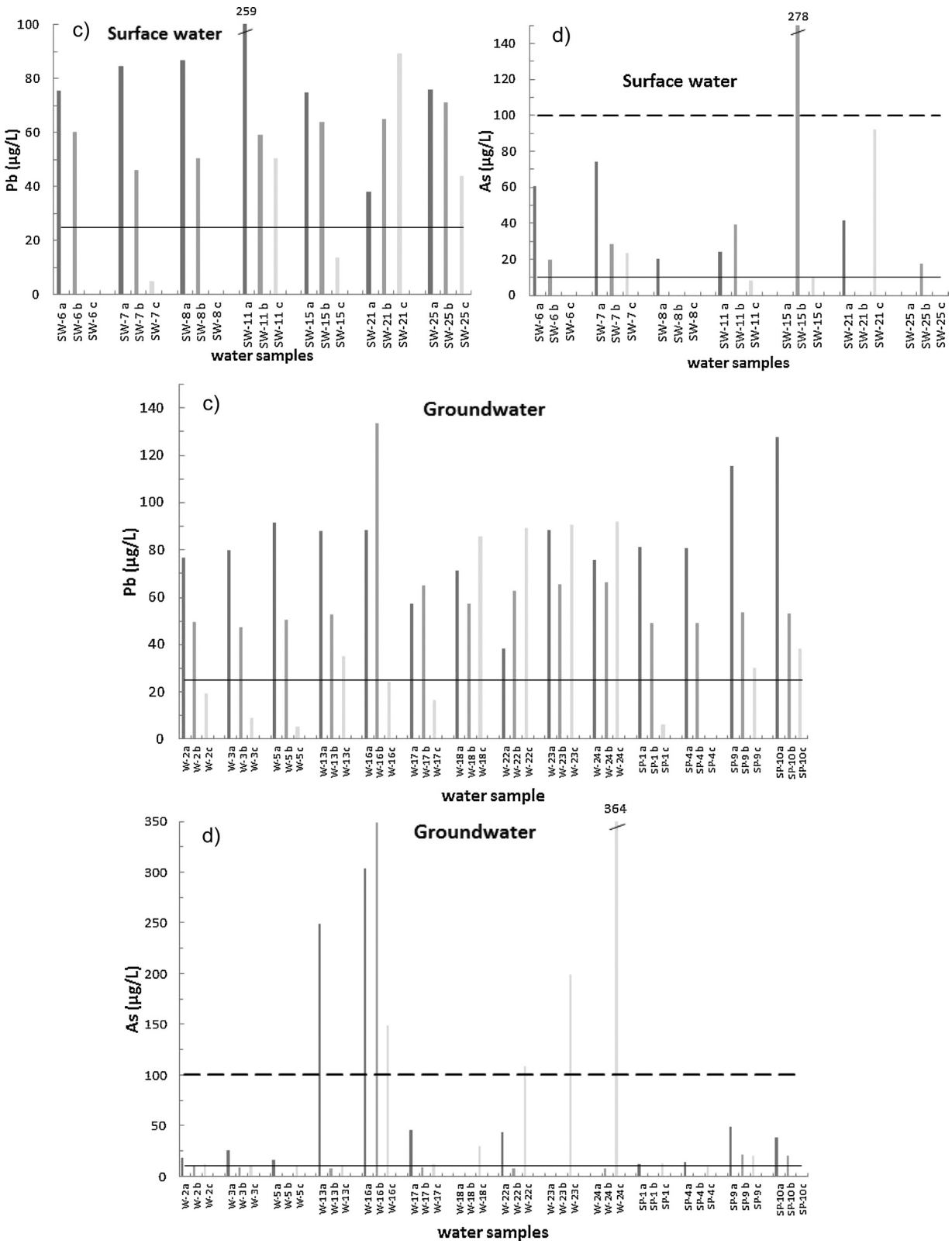

Fig. 4. (*Continued*).

heap-leached materials, mine dumps and tailings were spread over the area (Fig. 1c). But, during the remediation, they were relocated. Probably, the remobilization of dumps and tailings caused the infiltration of waste liquids in seepage and the release of contaminants, such as some metals, radionuclides and arsenic, probably favoured by the groundwater direction and the decrease in pH of the groundwater. The increase in the arsenic concentration indicates sulphides weathering, because its concentration tends to increase in groundwater samples after remediation (Appendix 2). The dissolved metals Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+} tend to increase in the groundwaters at S and SW of the mine area groundwater samples as shown by the speciation modelling

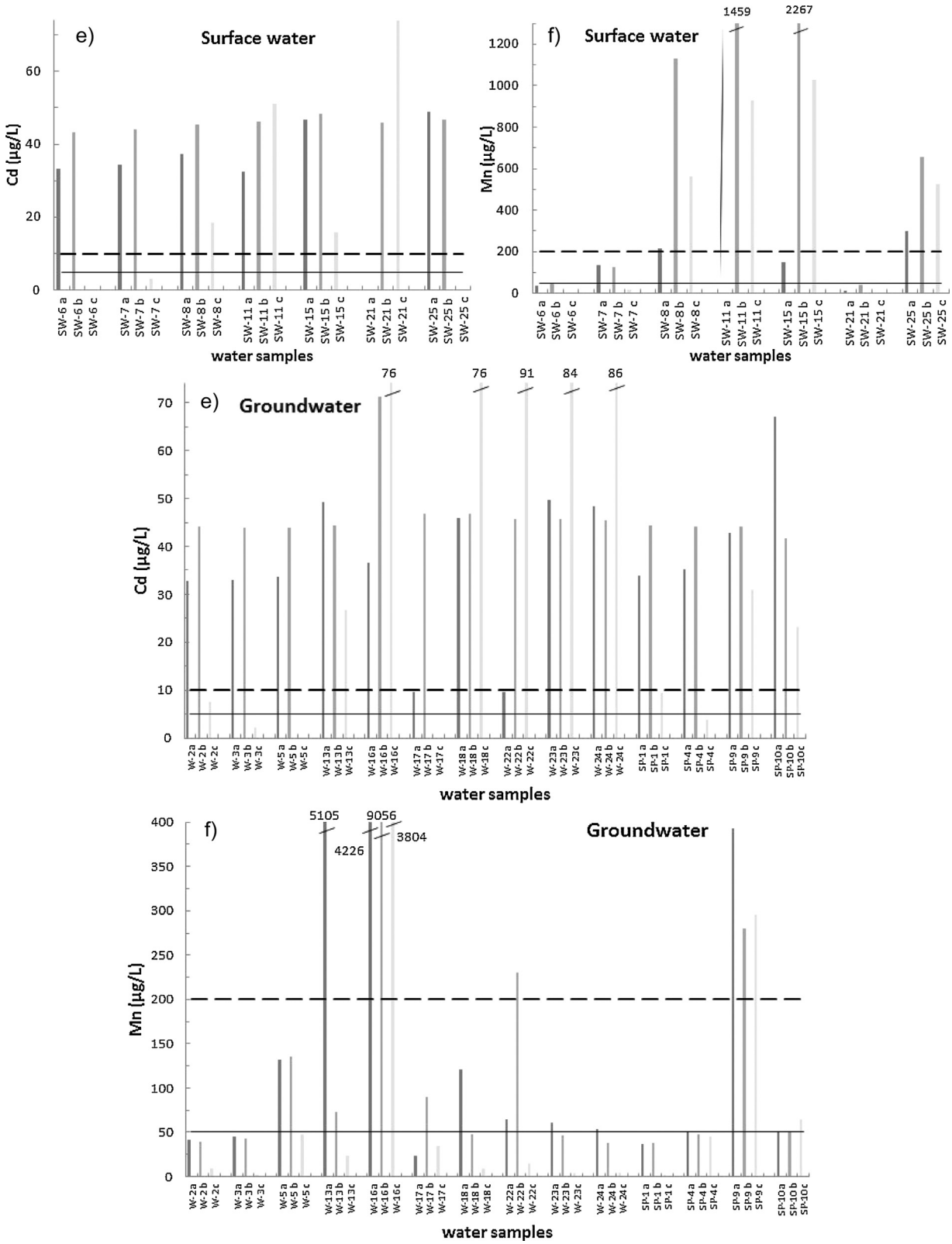

Fig. 4. (*Continued*).

(Appendix 4). Therefore, the remediation did not improve the water quality at S and SW of the mine area, but turned it worse than before.

The saturation indices obtained by geochemical modelling (Appendix 4) indicate the precipitation of Fe-oxides, as goethite (α-FeOOH), lepidocrocite (γ-FeO(OH)), hematite (Fe_2O_3) and magnetite ($Fe^{2+}Fe_2{}^{3+}O_4$), because they are saturated in surface water samples (SW-11, SW-15 and SW-21) and groundwater samples (W-5, W-13, W-16, SP-9 and SP-10). After the remediation, the saturation indices of those minerals decrease, mainly due to the decrease in the pH values. In those waters, uranium tends to be adsorbed in oxyhydroxides. Goethite is

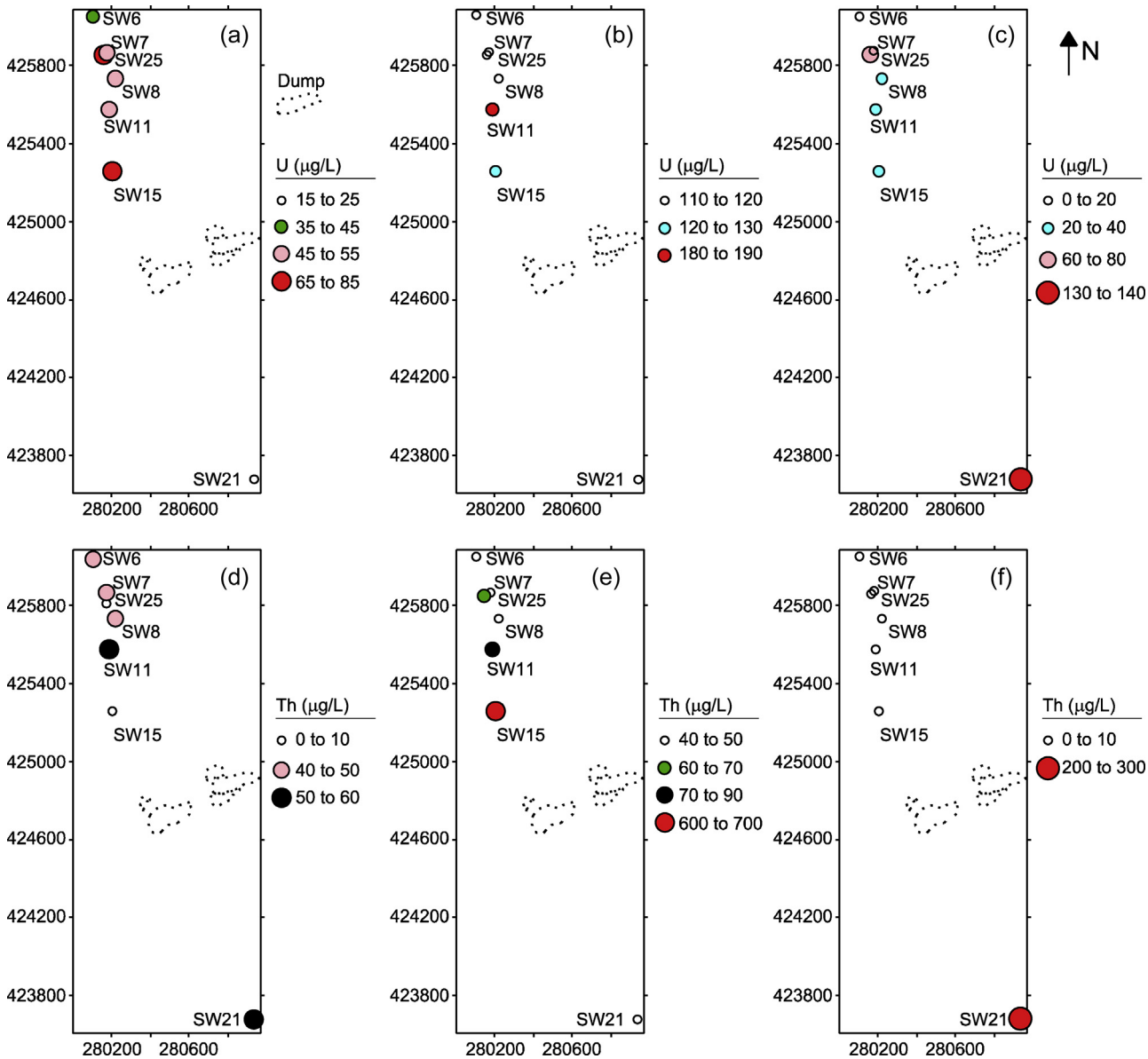

Fig. 5. Spatial distribution maps of U and Th concentrations (µg/L) in surface water from Senhora das Fontes uranium mine area. Uranium contents: (a) before the remediation, (b) during the remediation, (c) after the remediation; Thorium contents: (d) before the remediation, (e) during the remediation, (f) after the remediation.

among the most important inorganic adsorbent phases for U(VI) due to its ubiquity in waters, especially in mine areas, and their high surface areas (e.g., Bruno et al., 1995; Gabriel et al., 1998). The most effective sorption of the uranyl cation occurs at slightly acid to neutral pH conditions (Langmuir, 1978; Duff and Amrhein, 1996).

4.4. Contamination of surface water and groundwater from the Senhora das Fontes uranium mine area

Most surface water samples and groundwater samples have higher Cd, Cr, Al, Mn, Ni, Pb, Cu, As and U concentrations than the accepted levels for drinking water (Portuguese Law, 2007), before and after the remediation (Appendixes 1 and 2; Fig. 4). Most of them also have higher concentrations of these metals and the metalloid As than permitted for agriculture use (Portuguese Law, 1998). In some surface water samples (SW-6 and SW-7) and groundwater samples (W-3 and SP-1), uranium was not detected after remediation (June of 2011; Fig. 4a). However, in all the remaining waters the uranium concentration is higher than the level indicated by WHO (2010) (Fig. 4a). In the stream water sample SW-21 and groundwater samples W-22, W-23 and W-24, uranium concentration is higher after the remediation than before the remediation, and also higher than the level for human consumption (WHO, 2010) by an order up to 52 (Fig. 4a). The remediation eliminated the infiltration of rain and surface water into dumps. Therefore, the contamination of surface water decreases. But the groundwater located to the S and SW of the mine dumps (W-22, W-23 and W-24) became more contaminated after the remediation, probably due to the mobilization of metals and arsenic derived from the remobilization of sulphides, which caused a decreased in the pH of water that migrated towards the groundwater flow.

More research will be necessary to evaluate if at long-term the remediation was effective in the retention of the contamination. However, at S and SW of the mine area, the remediation must be properly applied taking into account the negative effect it already caused. Therefore, a good study of the whole area must be carried out before any remediation is applied in any mine area and the remediation process must be properly studied for each area.

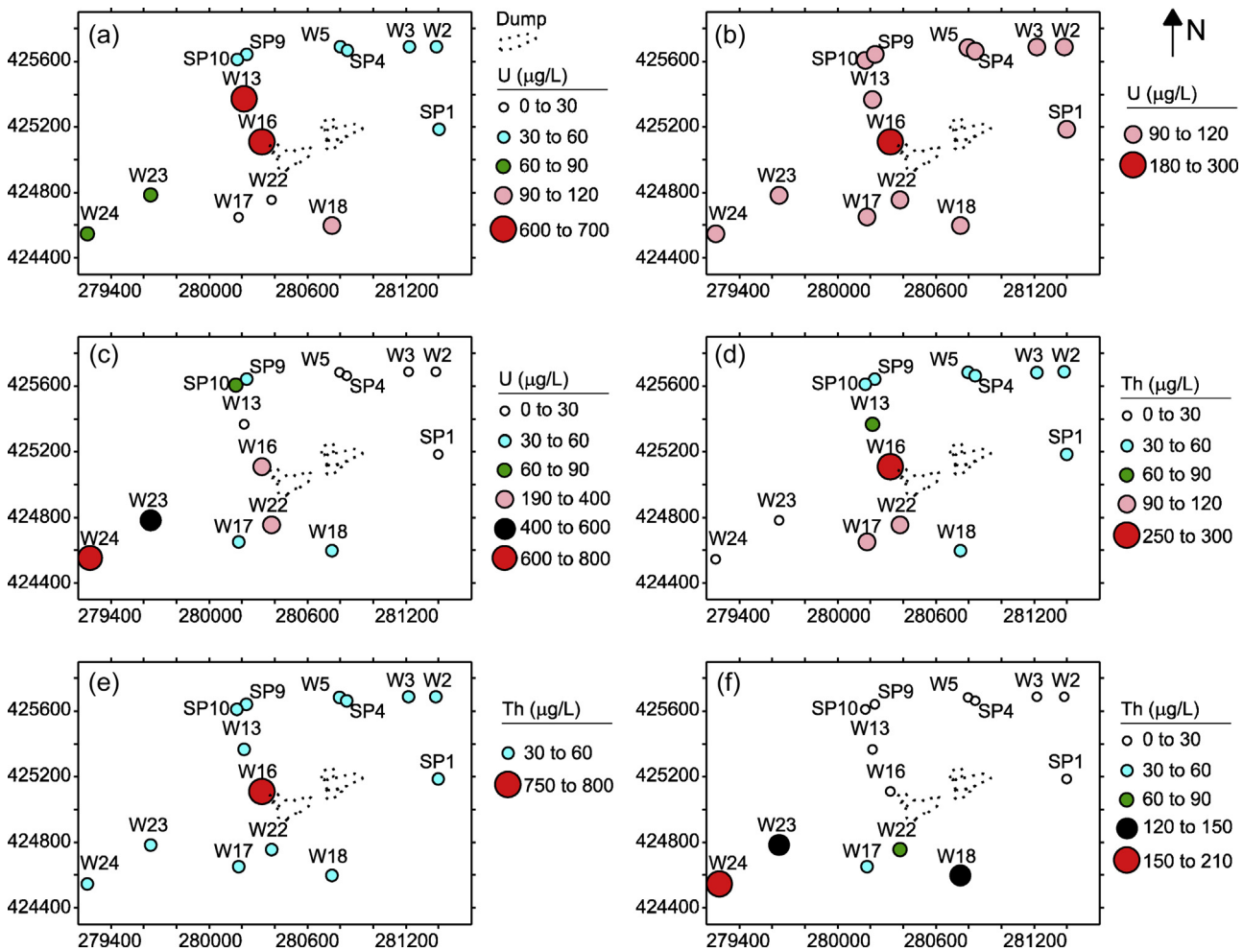

Fig. 6. Spatial distribution maps of U and Th concentrations (μg/L) in groundwater from Senhora das Fontes uranium mine area. Uranium contents: (a) before the remediation, (b) during the remediation, (c) after the remediation; Thorium contents: (d) before the remediation, (e) during the remediation, (f) after the remediation.

5. Conclusions

In general, the remediation caused a decrease in pH and an increase in Eh of surface water and groundwater. Before the remediation, in the wet season, the uranium concentration was up to 83 μg/L in the surface water and generally up to 116 μg/L in the groundwater, but was up to 649 μg/L in two wells. At the beginning of the remediation, in the dry season of 2010, the uranium concentration increased, probably due to the remobilization of mine dumps.

After the remediation has finished, in the dry season of 2011, U, Cd, Co, Cr, Ni, Pb, Zn, Cu, As, Sr and Mn concentrations decreased mainly in the surface water and groundwater from wells and springs, all located at north of the mine area. The speciation modelling shows that after the remediation, the dissolved metals Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} decreased in surface water and groundwater at north of the mine area.

After the remediation, in the dry season of 2011, U, Th, Cd, Al, Li, Pb, Sr and As concentrations generally increased in groundwater and surface water located at S and SW of the mine area.

Uranium is adsorbed in clay minerals. The geochemical modelling indicates that U is also adsorbed in oxyhydroxides, particularly goethite in some surface water and groundwater samples. But after the remediation, the saturation indices of these minerals decreased as pH decreases.

Before and after the remediation, most surface water and groundwater are contaminated in U, Cd, Cr, Al, Mn, Ni, Pb, Cu and As and must not be used for human consumption and agriculture. After the remediation, the groundwater at S and SW of the mine area is more contaminated than before the remediation. Therefore, the remediation caused only some improvement at north of the mine area.

The environmental rehabilitation of the uranium mining sites and milling facilities is still to be performed. The high trace element contents of waters used for human consumption or agriculture activities from Senhora das Fontes mine area should be controlled. The planning of remediation works and goals for environment rehabilitation must be site specific.

The radiological impact is the other main impact of uranium sites and, for the success of the rehabilitation measures, the radioactive contamination of sites and radionuclide content of waters must be evaluated beforehand (Carvalho et al., 2007). Environmental rehabilitation measures shall be adequate to the mine site in order to prevent the radioactive contamination of agriculture soils and water resources, and to ensure adequate radiological protection to the public and to the environment.

As many of the sites are located in remote areas and decades of abandon have modified the distribution of materials left around mines, a detailed geochemical water spatial distribution and a radiological characterization of the sites is needed.

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Appendixes 1, 2, 3 and 4. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemer.2015.06.001

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