Journal of Geochemical Exploration xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Potential human health impact of groundwater in non-exploited uranium ores: The case of Horta da Vilariça (NE Portugal)

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ARTICLE INFO

Article history:
Received 26 July 2016
Revised 15 March 2017
Accepted 19 March 2017
Available online xxxx

Keywords:
Groundwater
Hydrogeochemistry
Drinking water
Chemical elements
Radioisotopes
Water ingestion
Total effective dose
Portugal

ABSTRACT

The anomalous concentration of chemical elements in rocks can have consequences on the human health population even in the absence of anthropogenic activities. Uranium contamination of groundwater is being increasingly recognized as a health threat to rural residents relying on home wells for their drinking water, not only in communities with a legacy of mining, but also where there's naturally occurring uranium. In the Horta da Vilariça region (Torre de Moncorvo, Northern Portugal), a few uranium (U) ores were recognized in the metamorphic aureole of a hercynian granite; the host rocks are metasedimentary schists and greywacks of the pre-ordovician "Complexo Xisto-Grauváquico". To assess water-rock interaction 11 groundwater wells were selected and sampled, for major and trace elements as well as for radioisotopes ^{222}Rn, ^{226}Ra, ^{234}U, ^{238}U analyses. Analytical results point to Na-Ca-bicarbonate groundwater with a mean electric conductivity of 477 $\mu S \cdot cm^{-1}$ and pH between 5.4 and 6.5. The concentration of dissolved arsenic (As) reaches 15 $\mu g\ L^{-1}$, mostly in the oxidized form of As(V), and is above the parametric value for drinking water (10 $\mu g\ L^{-1}$) in 3 wells used for drinking and/or irrigation. The radioisotope activity (U, ^{226}Ra and ^{222}Rn) is also very high in the most of collected water samples. About 65% of the samples are above the WHO recommended limit for drinking water with respect to U, with a median of 129 $mg \cdot L^{-1}$ and a maximum of 3483 $mg \cdot L^{-1}$. About 30% of the samples are above the EU (2013) recommended limit for drinking water for ^{222}Rn (1000 $Bq \cdot L^{-1}$), with a median of 400 $Bq \cdot L^{-1}$ and a measured maximum of 9784 $Bq \cdot L^{-1}$. The human health impact was evaluated only for the water ingestion vector through calculation of the annual effective dose. As the health impact depends of the body mass the dose was calculate for different age groups of the population. The results indicate that, in 60% of the samples, the effective dose exceeds the limits suggested by existing guidelines. The use of groundwater for drinking and crop irrigation in the studied region should be subject to previous assessment for U, Ra, Rn and As. In the activity concentrations found in the present work they are clearly a potential health risk for the population.

1. Introduction

The geological and geochemical processes may lead to the accumulation of chemical elements that can reach several times their average crustal concentration (LeGrand, 1987). These elements may build up in such locations or be transferred to other environmental compartments (rock–soil–water–air–ecosystems), thereby enhancing human exposure to potentially toxic elements, such as heavy metals and radioisotopes (Brugge et al., 2005; Teixeira et al., 2015). Ingestion and inhalation are the primary route of entry into the body (Brugge et al., 2005). This exposure can occur naturally without human intervention, not involving the mining of mineral deposits, which are examples of geochemically anomalous sites (Arzuaga et al., 2010; Caldwell, 2008; Gomes et al., 2011; Pereira and Neves, 2012).

The involved processes in water-rock interaction can promote the transference of some elements into groundwater at high concentrations.

Different areas from north and central Portugal correspond to very high radiation levels with several times higher than regional background (Gomes et al., 2011; Pereira et al., 2015). These radiometric anomalies are due to the occurrence of high uranium and isotope concentrations integrating the isotopic decay sequence (Pereira et al., 2010; Pereira and Neves, 2012). In some of these anomalies (61 of which have been economically exploited in the past for extracting U), in addition to the U host-minerals (usually of secondary type), other metals such as sulfides also occur. In the north, near the Douro River, some U mineralization was identified near the village of Horta da Vilariça, but despite its high content it has not been subject to commercial exploitation. Previous studies show that ambient gamma radiation

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http://dx.doi.org/10.1016/j.gexplo.2017.03.010
0375-6742/

levels are very high in this area (up to 2.8 $\mu Gy \cdot h^{-1}$, with a background level of 0.25 $\mu Gy \cdot h^{-1}$) and soil gas radon concentration varies between 297 and 80,000 $kBq \cdot m^{-3}$ (Pereira and Neves, 2012). Horta da Vilariça village is located in the Vilariça valley, on the right bank of the homonymous river, where 310 inhabitants living in an area of 14.58 km^2 (INE, 2012). Soils are in use for agricultural purposes and groundwater is exploited for irrigation and human consumption.

The purpose of this research is to evaluate the chemical quality of groundwater in the naturally U-enriched area. This goal was achieved using data of physicochemical parameters, concentration of major ions and trace metals, arsenic speciation and radioisotopes of the U isotopic decay sequence.

2. Geological setting

The main geological feature is the occurrence of several uranium mineralization in the Horta da Vilariça, Horta da Eira I and Horta da Eira II locations hosted in the metamorphic aureole of porphyritic hercynian Vilariça granite (Fig. 1). The aureole is composed of metasedimentary schists and greywacks of the pre-ordovician "Complexo Xisto-Grauváquico" unit. Uranium is hosted in secondary minerals such as saleeite and autunite, but also in amorphous iron oxides and hydroxides (Bolle et al., 1988; Dias, 1984; Dias and Andrade, 1970; Moreira, 1985). Previous prospection works estimate a resource with >1000 tons of U_3O_8 with an average content of 0.08% (maximum 0.5%; Dias, 1984).

In the eastern margin of the studied area outcrop the Vilariça fault corresponding to a seismically active tectonic lineament with NE-SW striking. The associated "graben" is fulfilled of quaternary detritic sediments of variable thickness.

3. Materials and methods

The 11 groundwater wells with depths between 42 and 75 m were selected and sampled in April 2010, in order to evaluate the water-rock transfer of the elements (Fig. 1). The chemical analyses was performed in the National Laboratory of Energy and Geology (LNEG) in Oporto, whereas the radioisotopes activity in the Laboratory of Natural Radioactivity (LRN) of the University of Coimbra.

The parameters measured were pH, electric conductivity, alkalinity, SiO_2, anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, Fe^{2+}, Li^+). Trace analysis was made by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Total arsenic was measured using hydride generation atomic absorption spectrometry (AAS). The limit of quantification (LQ) is of 2 $\mu g \cdot L^{-1}$ with a reproducibility of about 20%. Arsenic speciation was made by Square Wave Cathodic Stripping Voltammetry and hydride generation HG-FAAS according to Ferreira and Barros (2002) methodology. The LQ is 0.2 $\mu g \cdot L^{-1}$ with a reproducibility of about 10%. The activitiy of uranium isotopes (^{238}U and ^{234}U), radium (^{226}Ra) and radon (^{222}Rn) were measured by liquid scintillation techniques using an ultra-low level spectrometer, Quantulus 1220, available in the Laboratory of Natural Radioactivity (LRN) of the University of Coimbra, following the procedures described in Pereira et al. (2015). In order to measure uranium isotopes, total uranium and ^{226}Ra, the samples were previously acidified with HNO_3 down to a pH of about 2 and filtered to remove suspended solid particles. For radon analysis, a 10 mL aliquot of each sample was carefully taken with a syringe, to avoid loss of gas, and immediately injected in a glass vial containing an immiscible scintillation cocktail. The ^{226}Ra was measured by an indirect method using ^{222}Rn as a tracer after isotopic equilibrium was reached as well as after pre-concentration by slow evaporation. The uranium isotopes were previously extracted with a mixture of a scintillation cocktail and Bis-(2-ethylhexyle) phosphate. The detection limits for the activity of uranium isotopes are 1.5 $mBq \cdot L^{-1}$ (0.15 $mg \cdot L^{-1}$, for $U_{natural}$), 0.01 $Bq \cdot L^{-1}$ for ^{226}Ra and 1 $Bq \cdot L^{-1}$ for radon. For all of these, analytical errors are, on average, under 15% of the measured value ($p = 0.95\%$). Following the approach of Desideri et al. (2007) described in Gonçalves and Pereira (2007), the radiological risk for the population derived from water ingestion was estimate taken in account mainly the body mass. Therefore, different age groups whereas

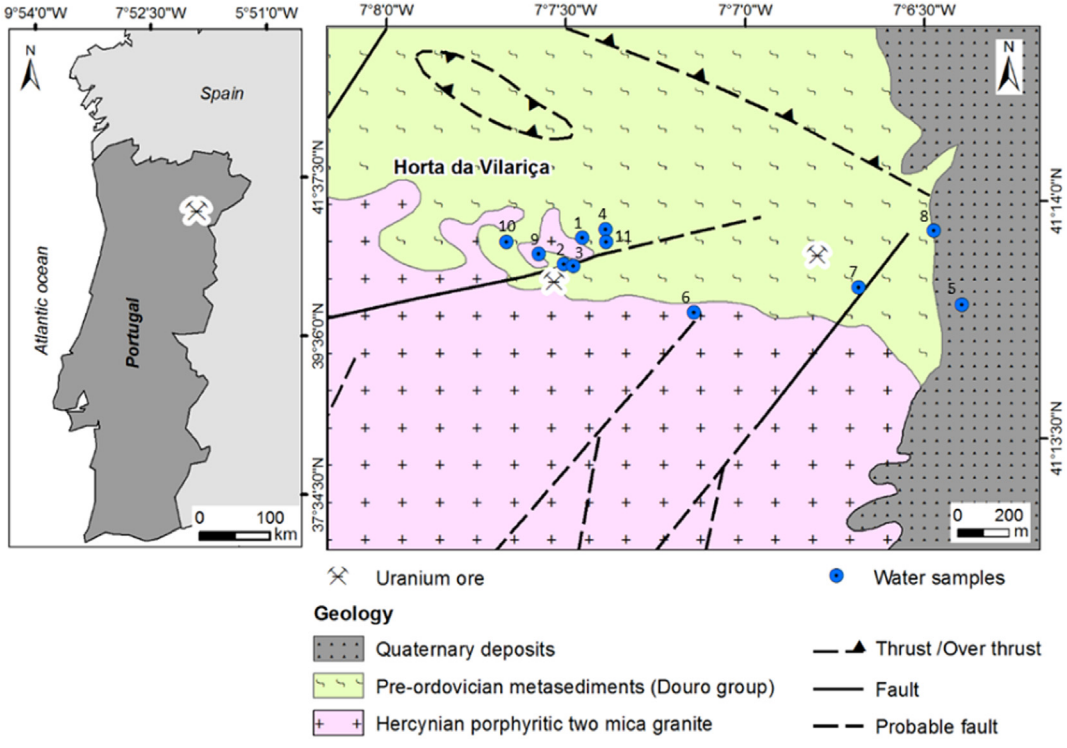

Fig. 1. Simplified geological map of Horta da Vilariça area (Northern Portugal). The numbered dots represent the location of groundwater sampling wells.

Please cite this article as: Costa, M.R., et al., Potential human health impact of groundwater in non-exploited uranium ores: The case of Horta da Vilariça (NE Portugal), J. Geochem. Explor. (2017), http://dx.doi.org/10.1016/j.gexplo.2017.03.010