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Trace elements and Pb isotopes in soils and sediments impacted by uranium mining

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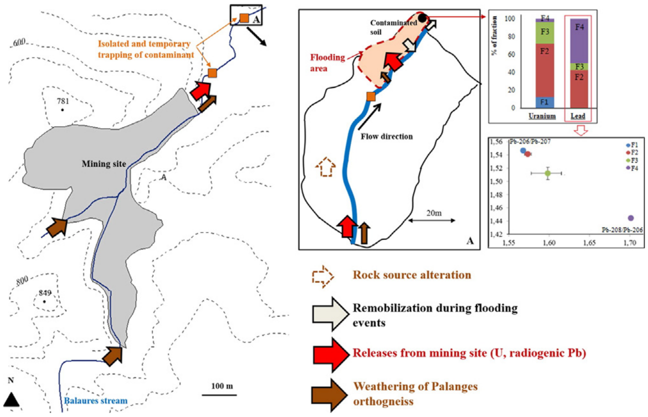
HIGHLIGHTS

- Contamination of soils is evidenced by a multiproxy approach.
- Enrichment factors highlight a low contamination except for U, S and Ba.
- Pb isotope ratios point out inputs of radiogenic Pb from the mine.
- Radiogenic Pb is mainly in the acid-soluble and the reducible fractions.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this study is to evaluate the contamination in As, Ba, Co, Cu, Mn, Ni, Sr, V, Zn and REE, in a high uranium activity (up to 21,000 $\mathrm{Bq\cdot kg^{-1}}$) area, downstream of a former uranium mine. Different geochemical proxies like enrichment factor and fractions from a sequential extraction procedure are used to evaluate the level of contamination, the mobility and the availability of the potential contaminants. Pb isotope ratios are determined in the total samples and in the sequential leachates to identify the sources of the contaminants and to determine the mobility of radiogenic Pb in the context of uranium mining.

In spite of the large uranium contamination measured in the soils and the sediments ($EF \gg 40$), trace element contamination is low to moderate ($2 < EF < 5$), except for Ba ($5 < EF < 15$), due to the precipitation of barium sulfate resulting from mining activities. Most of the trace elements are associated with the most mobile fractions of the sediments/soils, implying an enhanced potential availability.

Even if no Pb enrichment is highlighted, the Pb isotopic signature of the contaminated soils is strongly radiogenic. Measurements performed on the sequential leachates reveal inputs of radiogenic Pb in the most mobile fractions of the contaminated soil. Inputs of low-mobile radiogenic Pb from mining activities may also contribute to the Pb signature recorded in the residual phase of the contaminated samples. We demonstrate that Pb isotopes are efficient tools to trace the origin and the mobility of the contaminants in environments affected by uranium mining.

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1. Introduction

Mining activities contribute to approximately 46% of the total anthropogenic flux of uranium to the environment (Sen and Peucker-Ehrenbrink, 2012). Uranium mining is often associated with environmental releases of non-radioactive contaminants from ore, waste rocks and reagents used in the extraction process. In addition to uranium, Noller (1991) measured a significant increase of Mg, Mn and S (as sulfate ions) from milling process, in the aquatic ecosystem. U, V, Cr, Cd, Ni, Cu, Zn, As, Mo, W and Cd were found to be enriched in soils located on a former uranium ore heap in Germany (Carlsson and Büchel, 2005). Fe, K, U, Zn and lanthanides were enriched in Argentinian topsoils, due to a former open-cast operation uranium mine (Bermudez et al., 2010). As is commonly associated with uranium enrichment in sediments near former uranium mines (Kipp et al., 2009, Larson and Stone, 2011).

Different indices, like the enrichment factor (EF) (Chester and Stoner, 1973, Covelli and Fontolan, 1997), are used to evaluate the degree of contamination. These indices concern only the total concentration and do not provide any indication about the distribution in the different soil phases. If the degree of contamination is low, EF may not be significant, in particular if the material chosen as a reference is not appropriate (N'Guessan et al., 2009, Reimann and de Caritat, 2005). That is why these indices must be coupled with other procedures allowing the determination of the mobility and bioavailability of the contaminants.

Among indicators of contamination, sequential extractions offer a good compromise between information on the distribution of element among the solid fractions/components and the potential risks associated with their mobility or their bioavailability. In the framework of the Standards, Measurements and Testing Program (SMTP), an harmonization of extraction protocols led to a standardized 3-step procedure (Quevauviller et al., 1994, Rauret et al., 1999). This procedure allows the determination of three operationally extractable fractions that can predict the nature and the content of trace elements, potentially released in case of modifications of environmental parameters like pH or redox conditions. Its reproducibility and repeatability were confirmed by various studies (Davidson et al., 1998; Rauret, 1998; Whalley and Grant, 1994). The enhanced BCR sequential extraction protocol has been widely adopted and applied to different media including uranium contamination (Bartosiewicz et al., 2015, Dhoum and Evans, 1998, Howe et al., 2002, Martin et al., 1998, Meca et al., 2012, Smodiš et al., 2012, Štrok and Smodiš, 2013).

In the case of anthropogenic contamination, the origin and the mobility of Pb can be assessed by the measurement of Pb isotopes in sequential leachates (Bäckström et al., 2004, Bacon et al., 2006, Hirner, 1992, Probst et al., 2003, Steinmann and Stille, 1997). Water, soils, sediments or living organisms contaminated by U-ore or U-mining products show specific radiogenic Pb signatures. That is why Pb isotopes are frequently used as potential tracers of U-mining pollution (Bollhöfer and Martin, 2003, Bollhöfer et al., 2006, Frostick et al., 2008, 2011, Kyser et al., 2015, Santos and Tassinari, 2012). However, to our knowledge, no Pb isotope measurement has ever been made on sequential leachates of soil or sediment contaminated by U-ore or U-mining products. Clearly there is a lack of information about the mobility of radiogenic Pb in the context of uranium mining.

This study aims to combine enrichment factor, sequential extractions and Pb isotope ratios in soils and sediments highly contaminated by uranium as a result of past U-mining activities, in order to assess (1) other potential harmful trace element (PHTE) contamination, (2) the mobility of contaminants and (3) their potential source(s).

2. Methods

2.1. Studied site

The Bertholène mine is located in the Palanges forest, within the Palanges orthogneissic massif, an alkali monzogranite, mainly constituted by microclines, quartzs, plagioclase feldspars and micas (biotite and muscovite). Accessory minerals include sphenes, rutiles, apatites, allanites, thorites, zircons, monazites and yttrium phosphates. Uranium ore and associated weathering were described by Schmitt et al. (1984) and Lévêque (1988). The exploitation of the Bertholène uranium ore was performed as underground (1981–1992) and open pit (1983–1995) mines, leading to the production of 744 tons of uranium and 470,000 tons of tailings. The site was equipped with an in-situ uranium ore pre-processing unit, of which functioning is described in Humbert (1986). Since the beginning of the mine operation, effluent waters from mines, tailings dams and barren materials have been collected and neutralized with lime, sodium hydroxide and flocculating agents, before being released into the Balaures stream. A previous gamma spectrometry mapping of the radionuclide distribution has shown strong enrichments in U-decay products, downstream of the mine, in a flooding area frequently submerged by the Balaures stream (see the colorful inset in Fig. 1 and the supplementary material SI-1). Activity of U-238 as high as 21,000 $\text{Bq} \cdot \text{kg}^{-1}$ has been measured, with strong disequilibrium in the U-238 decay chain (Cuvier et al., 2015). The Balaures stream, flowing through the mining site, is contaminated by the mining activities and has been identified as the main vector of radionuclide transfer.

2.2. Sampling protocols

2.2.1. Soils and sediments

A total of seven soil surface horizons were sampled in the downstream area, using an 8 cm diameter stainless steel corer (Fig. 1). Two sampling points, namely P0 and P3, were located in the non-contaminated areas, on the left and on the right riverbanks of the Balaures stream respectively. Five sampling points, namely P1, P2, P8, P13 and P10 were sampled in the radionuclide accumulation area (see the supplementary material SI-1). All the profiles were 25 cm length except the uncontaminated profile P3 of 35 cm length. At each sampling site, three cores were collected and each core was sampled in sub-sections of 5 cm length all the way along the core. The three corresponding slices were then mixed together, in order to minimize heterogeneity.

1 kg of surface river bottom sediments of the Balaures stream was collected by hand upstream and downstream of the mine. Soil and sediment samples were collected in plastic bag and kept to 4 °C before preparation.

After air-drying the soils and sediments, coarse particles (gravels) and organic debris (roots) were removed. Soil and sediment samples were carefully homogenized, quartered and sieved at 2 mm using nylon sieves. The sieve analyses were performed on the representative aliquots by the Société du Canal de Provence (COFRAC accreditation), according to the standard AFNOR X31 107. Four grain sizes were identified: coarse sand (2 mm–0.2 mm), fine sand (0.2 mm–0.05 mm), silts (0.05 mm–0.002 mm) and clays (<0.002 mm). Trace element and Pb isotopes contents were determined on the <2 mm fraction using aliquots previously crushed with an agate mortar.

2.2.2. Vegetation

Aerial parts of ray-grasses and undifferentiated forage crops (1 m above the soil) were collected in uncontaminated and radionuclide contaminated areas (Fig. 1). Samples were cut using a ceramic knife on a surface covering around 1 m^2. Samples were rinsed with ultrapure H_2O before drying at 40 °C and crushing.

2.3. Sequential extraction procedure

Sequential extractions were performed on the 5–10 cm layer of the selected soils and sediments, according to the revised procedure of Rauret et al. (1999). All reactants were ultrapure grade and supplied by VWR. For each sample, three replicates were performed and the accuracy of the process was confirmed by analyses of CRM BCR-701 (see Supplementary Information SI-2). An internal check was also realized