

Distribution coefficients water sediment for uranium and polonium in the Moulouya River (eastern Morocco), a river affected by abandoned mines of lead and zinc

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Abstract.

The Upper Moulouya Lead district is a region of Morocco affected by the presence of mining deposits, pit lakes and other mining wastes, due to the former mining activities developed in the 20th century. The Middle Moulouya is a region not affected by human activities and is studied for a better comprehension of results obtained in the Upper Moulouya region.

Activity concentration of U-isotopes and ²¹⁰Po in water and sediments was determined in samples collected from the Moulouya River (Eastern Morocco) and two tributaries. These results were used for the evaluation of distribution coefficient in the river.

Some pit lakes resulting of former mining activities were also sampled and distribution coefficients were calculated for the mentioned radioisotopes. Sampling was made twice in different years. In the second sampling campaign a longer river area was studied.

Introduction

Determination of distribution coefficients for Uranium and Polonium (between water and sediment phases) is the main objective of this work. Natural radionuclides (²³⁸U, ²³⁴U and ²¹⁰Po) were measured in water and sediment samples collected along the Moulouya River (Oued Moulouya) and in three pit lakes at abandoned mines of Zn and Pb located in the Upper Moulouya Mining District (Eastern Morocco). Mining activities generated waste material that can affect to natural conditions of this environment.

The Upper Moulouya Lead district is crossed by the Moulouya River (Oued Moulouya), which is the most important river in Morocco. The region is characterized by a low population density. The geological and geographical description of the area is presented in Ivazzo et al., 2012. In the Upper Moulouya Lead district there are three main Lead deposits: Zeida, Mibladen and Aouli (Figure 1) that were exploited from 1972 to 1985, 1936 to 1985 and 1926 to 1985 (Ivazzo et al, 2012). Mining activities have created abandoned mine sites comprising: waste deposits, pit lakes, processing plants and waste tailings. Erosion and transport of mining materials are experienced in this region and they could reach the Moulouya River and its tributaries where heavy metals and natural radionuclides could be increased.

Materials and Methods

Sampling

Two sampling campaigns (July 2007 and June 2010) were carried out. Water was directly collected from the Moulouya River, some tributaries and three pit lakes. These waters were transferred into 25 l plastic bottles and a few ml of HNO₃ were added to avoid adsorption by plastic walls. Sediment

samples were directly collected in the same points than waters were sampled and stored in plastic bags.

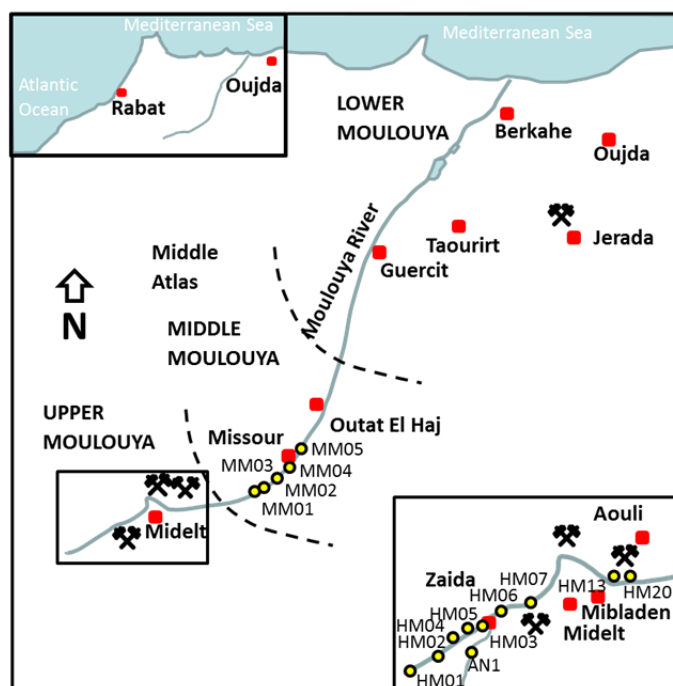


Figure 1. Map of Morocco where Moulouya River and sampling area are remarked

The sampling stations are shown in Figure 1. The sampling stations from the Upper Moulouya Lead District were the same in the two sampling campaigns, while the Middle Moulouya samples were collected only in the 2010 campaign.

The pH, of the water samples, shows slight alkalinity due to the presence of carbonates (Makhoukh, 2011). Higher pH values (around pH=9) were measured in pit lakes where the mineral is carbonated (Makhoukh, 2011; Ivazzo et al., 2012). The dominant mineral is Cerussite (Lead carbonate).

Analytical methods

The objective of the analytical method is to obtain both radioactive sources of U-isotopes and radioactive sources of ^{210}Po , which can be measured by alpha-spectrometry using an Alpha Analyst equipment based on PIPS semiconductor detectors. Although it is possible to obtain also radioactive sources of Th-isotopes, which is commented below, these results are not considered in this paper.

Concentration of actinides and polonium in water samples

An aliquot of 1 l of water, previously acidified, is taken for analysis. A well-known activity of ^{232}U , ^{229}Th and ^{209}Po is added for determination of radiochemical yield, and the actinides and polonium are co-precipitated with $\text{Fe}(\text{OH})_3$ (Holm and Fukai, 1977). Precipitate is separated from aqueous solution by centrifugation, then dried and dissolved with 10 ml of 8M HNO_3 .

Concentration of actinides and polonium in sediment samples

After collection, sediments are dried, powdered and sieved. If the polonium is not going to be measured the organic matter is eliminated by calcination of about one gram of sediment at 600 °C for 24 hours. The sieved soils or the resulting ashes are then traced with a well-known activity of ^{232}U , ^{229}Th and ^{209}Po and dissolved with acid (Lee and Lee, 2001). The dissolution is performed using first aqua regia with H_2O_2 and afterwards nitric acid 60 %, being the obtained solution conditioned in 8M HNO_3 . From this solution, actinides are co-precipitated with Fe^{3+} , and the precipitate is separated from solution by centrifugation, dried and finally dissolved in 10 ml of 8M HNO_3 .

Isolation of uranium, thorium and polonium

Two alternative methods have been used in this work for the sequential isolation of the Uranium-isotopes, the Thorium-isotopes, and ^{210}Po which are based either in the performance of solvent extractions with Tributyl-n-phosphate (TBP) or in the use of UTEVA (Uranium und TEtraValents Actinides, Eichrom trade mark) chromatographic resins.

The radiochemical procedure based in the use of TBP as solvent extract are described in Lehitani et al., 2012, and follows the original work performed by Holm and Fukai, 1977. The application of this procedure results in three aqueous solutions containing, respectively, the isolated Uranium, Thorium and Polonium. The purification of the isolated Thorium aliquot uses anion exchange resin (AG1×8, 100 – 200 mesh, Cl⁻ form) as described in Lehitani et al., 2012.

The radiochemical procedure based in the use of UTEVA chromatographic resins from Eichrom is described in Casacuberta et al., 2012, giving three aqueous solutions containing in isolated form the Uranium-isotopes, the Thorium-isotopes and the Po-210. In this procedure, no additional purification of any of the fractions is required.

Uranium source preparation for alpha-particle spectrometry

The Uranium sources for alpha-particle spectrometric measurements were prepared by electrodeposition of the elements onto stainless steel planchets following the method of Hallstadius (1984). The aqueous solutions containing the Uranium after application of the selected radiochemical procedure are evaporated until near dryness and conditioned as described in Mantero, 2010 then followed by electrodeposition.

The electrodeposition arrangement depends on the radionuclide of interest (Lehitani et al., 2012), using the electrical intensity 1.2 A in the case of Uranium.

Self-deposition of ^{210}Po

A well-established method (Flynn, 1968) based on the self-deposition of Polonium on several metal discs (Silver or Copper) is used for obtaining radioactive sources of ^{210}Po from the aqueous solutions containing this radionuclide. The adaptation of the Flynn method to our laboratory conditions is described in detail in Díaz-Francés et al., 2013.

Alpha-particle spectrometric measurements

Uranium-isotopes (^{238}U , ^{235}U , ^{234}U) and ^{210}Po activity determinations have been performed by applying the alpha-particle spectrometric technique using an Alpha-Analyst, spectrometer manufactured by Canberra Co. The system comprises eight independent chambers, each chamber being equipped with a 450 mm² PIPS detector, model A450-18AM. Only two chambers were used for ^{210}Po measurements, other two chambers for Thorium-isotopes measurements and the remaining four chambers have been used for Uranium-isotopes determinations. Activity determinations have been performed by applying the well-known isotope-dilution technique.

Results and Discussion

Activity concentration of U-isotopes

Activity concentrations of ^{238}U in water samples collected in 2007 and 2010 are presented in Figure 2. Higher activity concentrations correspond to pit lakes (HM04) or Moulouya water samples probably affected by mining wastes (HM06 and HM13). In the case of results of 2010, a different range of activity concentration is observed in the mining area (High Moulouya) and the rest of the river (Middle Moulouya). This fact can be also related to an enhancement due to mining wastes.

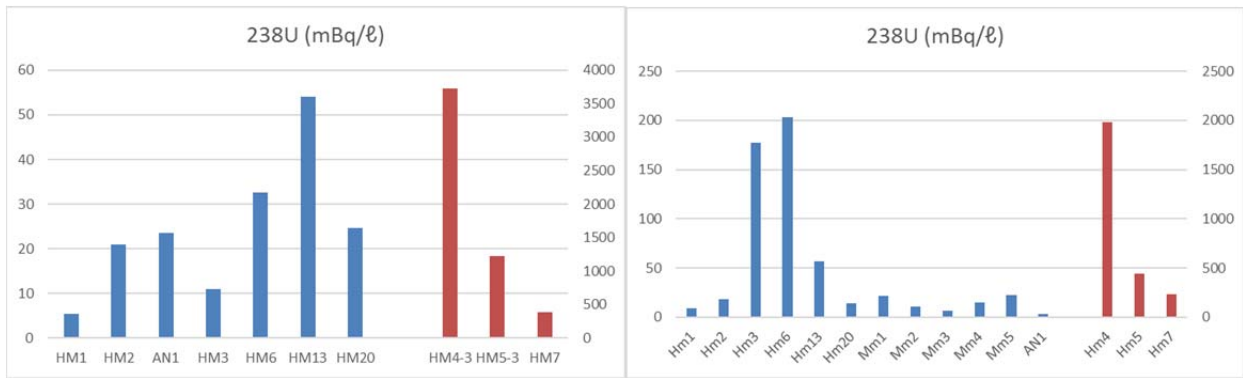


Figure 2. Activity concentration in river water (blue) and small lake water (red) samples collected in 2007 (left) and 2010 (right).

Figure 3 shows the $^{234}\text{U}/^{238}\text{U}$ activity ratio in water samples collected in 2010. A typical activity ratio around 2 can be inferred in water samples collected along the river. However, the activity ratio reaches more than 4 in water samples collected in the pit lakes.

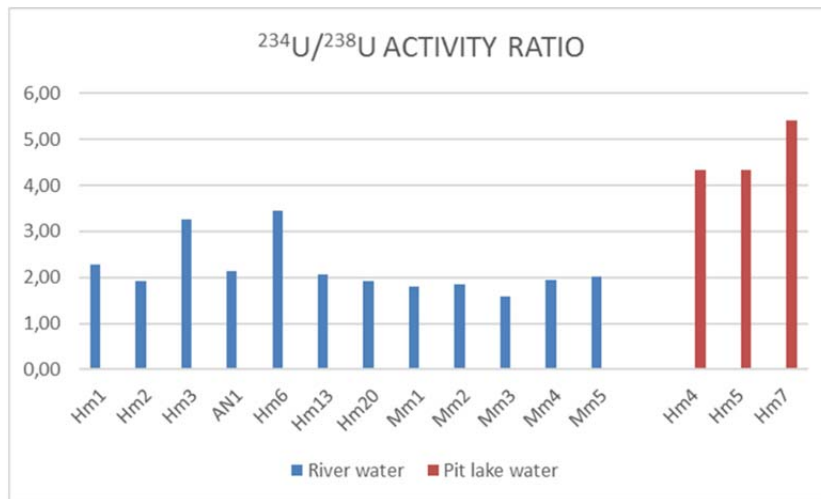


Figure 3. Activity ratio ($^{234}\text{U}/^{238}\text{U}$) in samples of water collected in 2010 in different sites along the Moulouya River (blue) and artificial lakes (red) caused by former air opened mines.

Sediment water distribution coefficient

The determinations performed at the same sampling point in both waters and sediments enable a discussion on the mobility of Uranium in the water – sediment system (Winde, 2002) using the distribution coefficients (K_d), defined as the quotient of ^{238}U activity concentration in sediment (mBq/kg) and water (mBq/l). Distribution coefficients of Uranium are compared with distribution coefficient of Polonium.

The values of distribution coefficients for Uranium and Polonium, in the samples collected in 2010 are shown in Figures 4 and 5. The following comments are made:

- as expected the K_d obtained for Po-210 are clearly higher than the K_d of Uranium due to the known tendency of the Po to bind to particulate matter in opposition to the more conservative behavior of Uranium,
- A good correlation is found between the $K_d(\text{U})$ and the Uranium concentrations determined in the waters, as it is shown in Figure 4. K_d decreases when the Uranium concentrations in waters increase. The higher $K_d(\text{U})$ values, in the order of 10^3 , were determined in the sampling points less affected by the impact of the mining areas while values as low as 10^1

were determined in the pit lakes, indicating the tendency of the Uranium to be in dissolved form in environments rich in carbonates.

- c) The K_d 's of Po are less sensitive to the concentrations found for this radionuclide in the waters as can be observed in Figure 5.

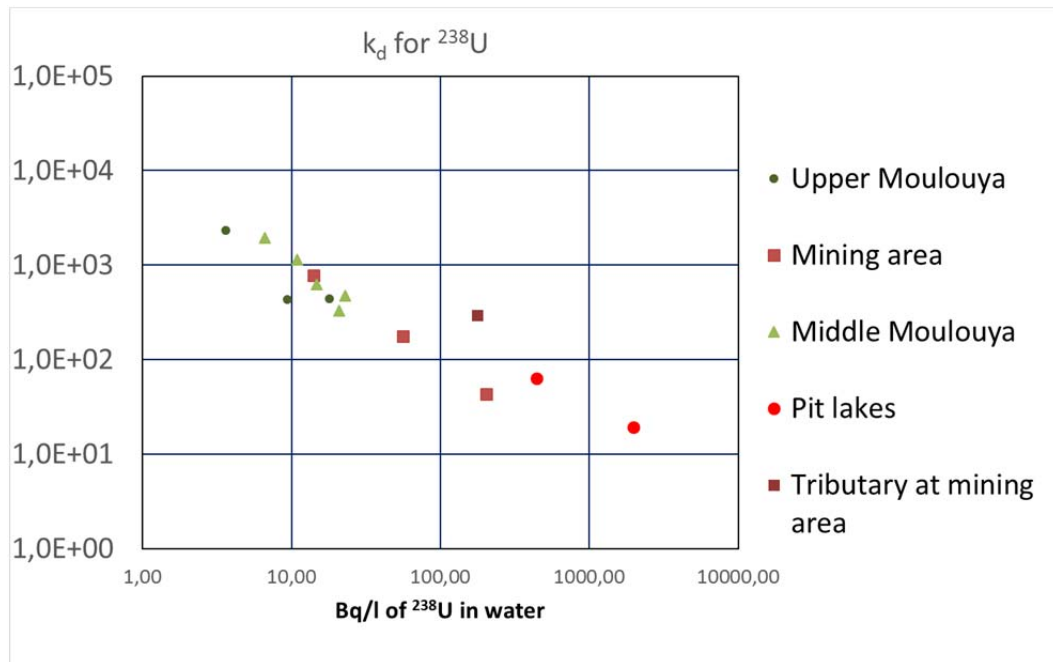


Figure 4. Distribution coefficient k_d for ²³⁸U in samples collected along the Moulouya River and two pit lakes.

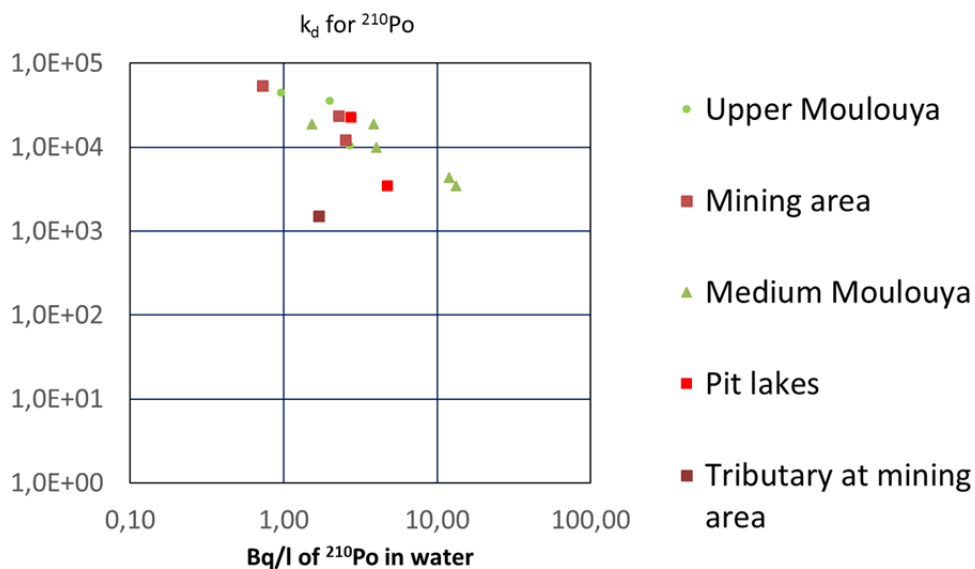


Figure 5. Distribution coefficient k_d for ²¹⁰Po in samples collected along the Moulouya River and two pit lakes.

Conclusions

Environmental impact on Moulouya River, with origin in mining activities, has been observed through the determination of U-isotope levels in water and sediment samples.

Distribution coefficient, k_d , in Moulouya River and pit lakes has been calculated. In the case of ^{238}U , the distribution coefficient ranged from 10^1 to 10^3 . This coefficient was between 10^3 and 10^5 for ^{210}Po .

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