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Uranium and polonium radio-isotopes activities in surface waters of the Upper Moulouya mining districts: Environmental Implications

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The Upper Moulouya River holds the largest abandoned mining deposits in Morocco that generate significant amounts of heavy metal wastes including stable and radioactive elements. They represent by far a significant source of pollution threatening the surrounding environment. The purpose of this study is to assess the contamination levels of ^{238}U, ^{234}U, and ^{210}Po in surface waters crossing the famous mining districts of Zaida, Mibladen, and Aouli, and eventually identify its sources. Ten sampling sites were carefully selected along the study area. The sampling technique consists to collect 20 liters of water. Samples underwent specific treatments to assess the sought activities of Uranium and Polonium radioisotopes. Results showed that the surface waters of the Upper Moulouya show variable activity values of Uranium and Polonium radioisotopes from one site to another. The spatial distribution of these values is defined by the intervention of several factors influencing the mobility of these radionuclides.

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1. Introduction

1.1. Geography

The Moulouya Basin, Este of Morocco, is a vast plain delimited by Middle Atlas and High Atlas Mountains from the Northwest and the South respectively. It represents the biggest water catchment in the country (Diani et al., 2017).The River of Moulouya, with a length of 600 km, crosses various geological features before reaching the Mediterranean Sea. In the upper part, called Upper Moulouya (Fig.1), the main of its tributaries including Ansegmir, Mibladne, Bouhafs, and Derhwal, go through old mining sites, marked by the presence of many lakes formed by the old quarries.

1.2. Geology

The geology of Upper Moulouya (Fig. 2) is constituted by a *Paleozoic* bedrock essentially in *Hercynian* structures, surmounted in discordance with the Permian, the Secondary (*Triassic* to Upper *Cretaceous*), the *Pontico-Pliocene*, and the *Quaternary structures*. The *Paleozoic* bedrock is composed of a granitic massif, amphibolites, and metamorphic shales. The Permo-Trias deposits consisted of conglomerates, arkoses, mudstones, argillite, and basaltic flows. Various sediments

such as conglomerates, dolomitic limestone, marl, limestone, and gypseous facies are representing the Triassic, Jurassic, and Upper Cretaceous. The Pontico-Pliocene and quaternary deposits are slightly thicker. They were materialized mainly by encased terraces in several places

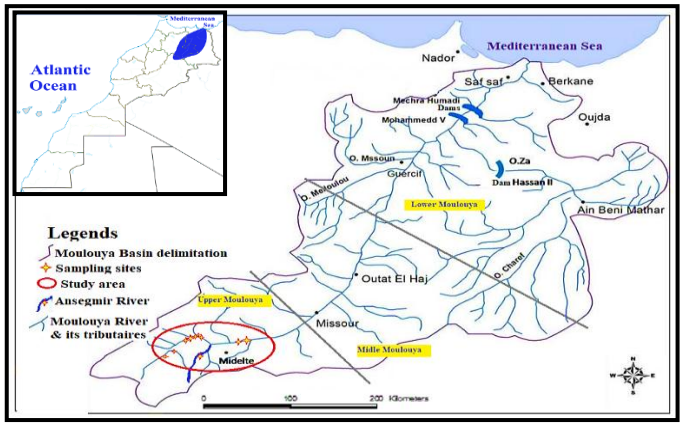

Fig.1: Location of the study sites in the Upper Moulouya *(Bellahbib et al., 2015 with amendments).*

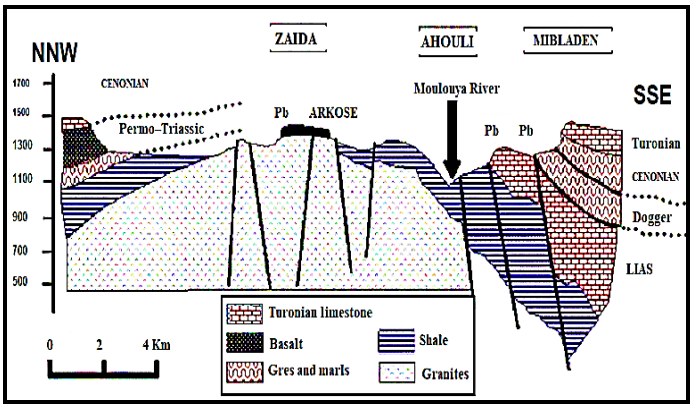

Fig. 2: Geological cut in the Upper Moulouya *(Emberger, 1965; amended).*

1.3. Climate

The climate of Upper Moulouya is characterized by an arid climate with cold winters and hot summers. The mean annual temperatures are between 12-14ºC, while the mean minimum is around 0ºC recorded in January and the mean maximum is between 32 to 33ºC recorded in July. The mean annual precipitations are about 200 mm frequently inform of stormy rainfall with short, sudden, and violent runoff causing a hazardous flood at the level of the main water course. Furthermore, soils fertility potential are very low leading to a little diversity of vegetation cover dominated mainly by steppes of Alfa, sagebrush, and a herbaceous vegetation. For these reasons, the population of the Upper Moulouya is concentrated in urban centers located either near the former mining sites or close to the permanent water sources.

1.4. Mining status.

The famous mining sites districts of Zaïda, Mibladen, and Aouli (or Ahouli) are located in Upper Moulouya. Extensively and massively exploited, these mineral deposits were rich in ore of lead and zinc which marked this region as the largest lead reserve in Morocco (Bouabdellah and Margoum, 2016). In 1975, the mining centers of Mibladen (stratiform cluster of Pb-Zn) and Aouli (base sill of Pb (Zn) (Cu)) were exhausted. The Zaida mine (mineralized arkoses) was also closed eleven years later (1986). These abandoned mining deposits, full of heavy metal wastes, remained without any rehabilitation. They represent by far a significant source of pollution threatening the surrounding environment. Several works have been carried out in the region in order to assess heavy metals contamination levels in waters, sediments, soils, and vegetation (El Founti et al., 2003; Bouabdli et al., 2004; Saidi, 2004; El Hachimi, 2006; Al Ibrahimi, 2009, Baghdad, 2015; Argane et al., 2016; El Azhari et al., 2017).

1.5. Objectives

This study aims to evaluate Uranium and Polonium radioisotopes activities in surface waters sampled in the mining districts of Upper Moulouya (Fig. 1). We will also establish the possible relationships between these mining districts, the geological structures on the distribution and the concentration of these radioactive elements.

2. Methodology

To measure the activity of Uranium and Polonium (^{238}U, ^{234}U and ^{210}Po) radioisotopes, samples were collected along the watercourses crossing the upper Moulouya as well as at the quarry lakes of the mining districts (Fig. 1 and 3).

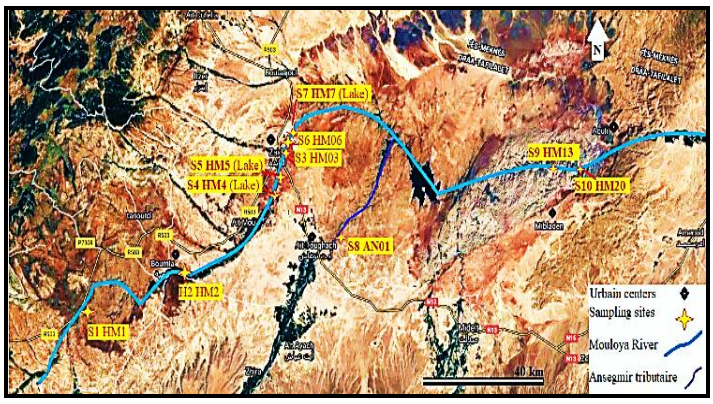

Fig 3. Sampling sites along the Upper Moulouya Basin

The sampling sites were precisely selected to cover and reflect the characteristics of the study region. Thus, ten sampling sites (S1-S10) were selected: three sites cover the lakes of the old careers of Zaida district and seven sites at the level of the main watercourse of Moulouya River and its tributaries crossing the

study area. The site S1 (HM 01), a reference site, is located at the upstream end of the Moulouya River to approximately 33 km south of Zaida far from any mining and urban contaminations. The site S2 (HM 02) is also located upstream of the Moulouya River but near the city of Boumia. The sites S3 (HM 03) and S6 (HM 06) are closer to the mining district of Zaida City. The sites S4, S5 and S7 (HM 04, HM 05 and HM 07) correspond to the old quarry lakes. The site S8 (AN 01) is chosen on the Ansegmir River in an agricultural region. The sites S9 (HM 13) and S10 (HM 20) are selected on the Moulouya River, near the mining area of Aouli-Mibladen.

The sampling technique (Skwarzec B., 1997 and Boryło A. 2013); consists to collect 20 liters of water in polyethylene cans. Later on, samples underwent specific treatments to assess the sought activities of Uranium and Polonium radioisotopes. Concentrated hydrochloric acid was added to the samples to make their pH = 2. A quantity of tracers (232U, 228Th, 209Po) of known activity is introduced to know the overall performance and to calculate the sought activities. Then, ammonia (NH_3) was added to the samples solution in the presence of a $FeCl_3$ to reach pH= 8-9, so Uranium and Thorium co-precipitated in alkaline solution. The complexation occurs according to the following reaction.

$$(FeOH + UO_2^{2+}) + H_2O \Leftrightarrow (FeO^{-}U\,O_2OH^{+}) + 2H^{+} \quad (1)$$

In an acid (pH=2) solution, after evaporation at 80-90°C, Polonium deposited on a silver disc by auto-deposition, it is a so-called spontaneous deposit since no current is applied.

The Uranium and Thorium, remained in the sample solution, were dissolved with iron hydroxides by adding HCl on a resin column (Dowex (1x8)). This process is followed by several extractions using different organic solvents until a radioactive source of Uranium was obtained in the form of ultra-thin layer on a copper support wrapped by a sheet of Aluminum, adaptable to the used window of the alpha detector.

The remained solution (Uranium and Thorium conditioned with 8N HCl) is injected onto an anionic ion exchange column. This solution flows in contact with the grains and undergoes anion exchange. The anions are fixed by the resin, while the cations are collected with the solution at the other end of the column.

In concentrated hydrochloric acid solutions, the Uranyl ion form anionic complexes (UO_2Cl^{3-}, $UO_2Cl_4^{2-}$) and fixed with the iron (Reyss et al., 1993; Choukri, 1994; Azougagh, 1996). The isotopes activities of Polonium (Jia et al., 2000) and Uranium are measured by the alpha spectrometry.

3. Results and discussions

The results of radioisotopes activities in surface waters carried out in Upper Moulouya are summarized in Table 1.

The lowest activity of Uranium ^{234}U is measured at S8 (7.57±0.59 MBq/kg) located in Ansegmir river and at S1 (21.40±0.80) located in upstream of the Moulouya river. The two sites are far from the town of Boumia (S2), as well of any influence of the mining districts of Zaida, Mibladen, and Aouli. Moving progressively toward the Boumia city (S2), downstream of the Upper Moulouya (S10) and the mining area of Aouli, the activity of ^{234}U increases without reaching significant values.

It is also clear from these results that the activity of the Uranium ^{234}U is significantly higher in S3 (**576.15±13.02**) and S6 (**701.88±11.8**), and extremely higher in the mining lakes of Zaida; S4 (**8564±671**), S5 (**1921±32**) and S7 (**1267±62**).

Tab 1: Activities of radioisotopes of uranium and polonium coupled with physico-chemical parameters in water samples in Upper Moulouya.

Sample	^{234}U (mBq/Kg)	^{238}U (mBq/Kg)	^{210}Po (mBq/Kg)	TºC	PH	CE (ms/cm)
S1-HM 01	**21.40±0.8**	9.38±0.51	0.96±0.16	14	8.14	3.5
S2-HM 02	34.32±1.6	17.87±1.08	2.00±0.28	13	7.56	3.6
S3-HM 03	**576.15±13.02**	**177.26±4.57**	**1.13±0.21**	14	8.07	3.6
S4-HM 04 (**Lake**)	**8564±671**	**1979±169**	**2.75±0.34**	17	9.15	3.5
S5-HM 05 (**Lake**)	**1921±32**	**443±8**	**2.33±0.32**	16	9.57	3.6
S6-HM 06	**701.88±11.8**	**203.34±3.74**	**2.54±0.31**	12	8.09	3.6
S7-HM 07 (**Lake**)	**1267±62**	**235±14**	**4.74±0.53**	13	9.23	3.4
S8-AN 01	**7.57±0.59**	235±0.4	2.69±0.30	12	8.28	3.7
S9-HM 13	117±3	57±2	2.29±0.27	13	7.86	3.3
S10-HM 20	28±1.0	14±1	0.73±0.14	15	8.58	3.3

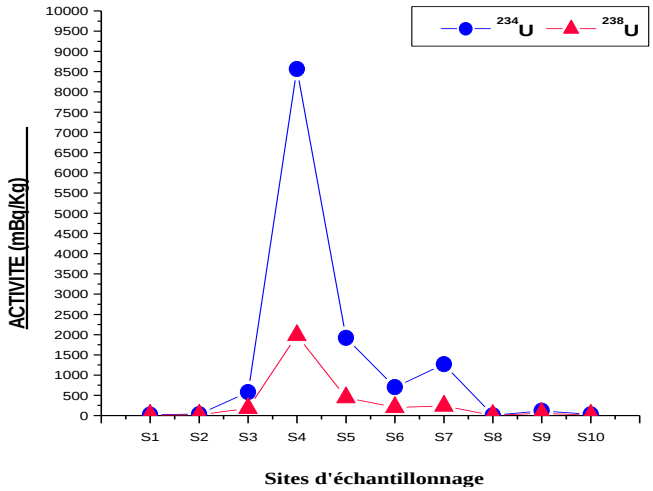

Fig. 4 : Activity *of radio-isotopes of uranium.*

The quarry lakes are mainly fed by runoff that drains mineralized zones and terrains of varied lithology. Once in the lake, these waters become stagnant and remain in permanent contact with the mineralized substratum, which induces a strong migration of radionuclides. These characteristics explain the very high values of ^{234}U measured particularly in lakes S4 and S5 located upstream of the massive granite of Zaida district. Some veins quartzo-ferruginous and few cracks in this massif show indices of Uranium (Annich et al., 1980).

The activity of 234U in Lake S7, located downstream of the granite, is significant but remains considerably lower than that measured in the aforementioned lakes (S4 & S5). Hence, there is obvious relationship between the geochemical composition of bedrocks and soils, and the phenomenon of drainage and leaching in one hand, and the values of uranium activities measured in different selected sites in other hand.

The high activities of Uranium within the mining area of Zaida: S3 (576.15±13.02) and S6 (701.88±11,80) are Justified by the important leaching phenomenon of trace metals from the abandoned mining sites. In fact, before its closure, this mining district witnessed an important extraction and exploitation of heavy metals such as Pb, Zn, Cu, and Cd (El Hachimi, 2006). These metal traces (stable and/or radioactive) reach easily the Moulouya River.

In specific physico-chemical conditions, the drainage promotes the dissociation of Uranium. According to Langmuir (1978), El obstructed (1996), and Hakam (2000), the distribution of hydroxides of uranyl [UO_2OH^+ and $(UO_2)_3(OH)^{3+}$] and carbonates of uranyl [$UO_2(CO_3)_2$ and $UO_2(CO_3)^{3+}$] is achieved at pH 8-9. This system disrupts the environment by the change of the Oxidation Number and subsequently a disorder ion or ion exchange that can occur in the mesh of the crystals. The latter may cause the decline of alpha particles and therefore a strong activity in uranium located in the matrix.

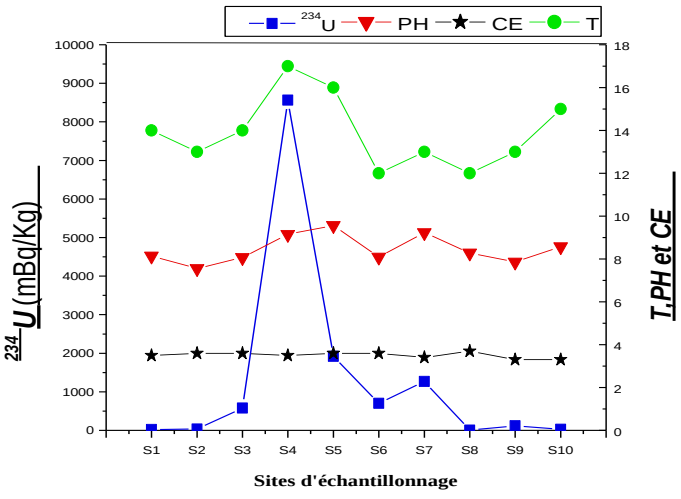

Fig. 5: Activity of ^{234}U and the parameters (T, PH, EC) spread on the sampling sites.

This is the case of the station S3 and S6 (**Fig. 5**) where the concentration of heavy metals, the pH (8.2 and 8.09), and the conductivity (3.6 ms/cm) are favorable to the ionic disorder in the crystals mesh and therefore the increase of uranium activity. Knowing that the uranium may precipitate with the carbonates in the form of (UO_2) at high pH (>7.5) (Langmuir, 1978; El Bouch, 1996). On the other hand, a high conductivity leads to the adsorption of metals with the colloids of iron, relatively abundant in the region (Bouabdli et al., 2004). Iron can attach the uranium in large proportions. The lowest activity is measured in the site of Ansegmir River (S8), even lower than the reference site (S1). This is can be explained by the fact that the sampling of S1 was taken from the upstream of Ansegmir River, far from any possible contamination from chemical fertilizers used in agriculture. These fertilizers contain phosphate ions carbonate, sulphate, and fluorinated, which can attach the uranium and subsequently drain it in the water streams toward the Ansegmir River.

The two sampling sites in S9 and S10, located respectively upstream and downstream the mining district of Aouli, show moderate values of uranium activity. They are not as high as those measured in the lakes Zaida, but are superior to that of the reference site S1 and S8. However, the activity of ^{234}U in S9 is superior to that of the S10, which show the direct impact of the mining area on the radionuclides mobility. It is wise to mention that the sampling period affect also the activity values. In this study, the sampling of water occurred during a flood period, which explain relatively moderate levels of ^{234}U activity.

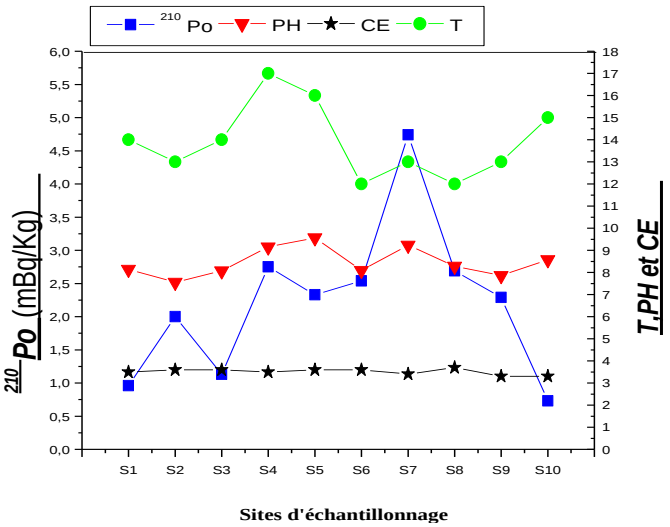

Fig. 6: Activity *of* ^{210}Po *and the parameters (T, PH, EC).*

The uranium activity is strongly higher than that of polonium. This is true for different sampling sites. The decrease of uranium concentrations is due to the regression stability of carbonates of uranyl complexes, while that of polonim results

from the decline of adsorption coefficient of polonate (PoO^{2-}) ions of polonium with barium and sulphate elements (Beaucaire et al., 1987; Al-Masri and Al-Bich, 2002). The polonium requires a strong acidity (3 <pH< 5) and a high temperature to be completely dissociated (Ulrich and Degueldre, 1993). The tests carried out on the surface waters of the High Moulouya show that the pH of the different sites is > 7 (**Fig. 5 & 6**). The most important values correspond to sites relatively mineralized. It is the case of the S7 site corresponding to the lake located downstream of the mining district of Zaida and S8 located in an area of agricultural activity (presence of sulphate fertilizers).

LaRock et al. (1996) show that the sulfate-reducing bacteria release the ^{210}Po during the reduction of sulphate in the phosphor-gypsum; however, when the concentration of sulphides exceeds 1M, a precipitate of PoS_2 is formed. In this case, the role of bacteria would be to stabilize the ^{210}Po in the mineral phase. In addition, the ^{210}Po, known to form complexes in the presence of organic matter (Vaaramaa et al., 2000), can be combined with organic metabolites, microbial, and then be remobilized in this form. The microbiological activity also acts on the behavior of the ^{210}Po in the hydro-systems (Momoshima et al., 2002; Swarzenski et al., 1999).

4. Conclusion

The surface waters of the Upper Moulouya show the activities of radioisotopes of uranium and polonium which values are quite variable from one site to another. The spatial distribution of these values is defined by the intervention of several factors influencing the mobility of these radionuclides. The geological factor intervenes by the nature of the geochemical composition of the bedrock drained by water runoff (case of sites S4 and S5).

The physico-chemical parameters (pH and conductivity) explain well the relatively low activities of Polonium compared with significant activities of Uranium (the case of the site S3). The important leaching of trace metals from abandoned mine residues intervenes by the release of stable or radioactive trace metals waste in the Moulouya River and its tributaries (case of sites S7, S9 and S10).

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