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Additional Information

BEHAVIOR OF URANIUM ALONG
JUCAR RIVER (EASTERN SPAIN): DETERMINATION
OF ^{234}U/^{238}U AND ^{235}U/^{238}U RATIOS

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The uranium concentration and the ^{234}U/^{238}U, ^{235}U/^{238}U activity ratios were studied in water samples from Jucar River, using low-level α-spectrometry. The effects of pH, temperature and salinity were considered and more detailed sampling was done in the neighbourhood of Cofrentes Nuclear Plant (Valencia, Spain). Changes were observed in the uranium concentration with the salinity and the ^{234}U/^{238}U activity ratio was found to vary with pH. Leaching and dilution, which depend on pH and salinity, are the probable mechanisms for these changes in the concentration of uranium and the activity ratios.

In determining the activity ratios ^{234}U/^{238}U and ^{235}U/^{238}U in water samples collected along Jucar River, we found interesting results in the variation of ^{234}U/^{238}U with pH values. Temperature, pH and conductivity of water samples were measured "in situ".[1] Knowledge of these parameters is important for understanding the behavior of uranium concentration and activity ratios in water.[2] The secular equilibrium for the ^{234}U/^{238}U activity ratios is 1.00 and the value found in nature for the ^{235}U/^{238}U activity ratios is 0.046.[3,4] In this study, deviations in the ^{234}U/^{238}U ratio have been observed and the possible causes are discussed.

Experimental

Sampling: Samples were collected along Jucar River (Spain) in the 5th and 16th February 1993. The sites are shown in Fig. 1 (one sample was collected at each point). Samples were taken at the source of the River, upstream and downstream from the outlet of Cofrentes Nuclear Plant, at Cabriel River, the main affluent of Jucar River (Cabriel River flows into Jucar River after the outlet of Cofrentes Nuclear Plant) and finally at its mouth. Three samples have been taken close to the Cofrentes Plant (Fig. 2) in order to study a possible influence of the Nuclear Plant on the uranium levels. The samples were collected in 5 liter containers. Conductivity, temperature and pH were measured "in situ".

Procedure: The organic matter and sediment particles suspended in water samples were separated by filtration (≥ 2.5 μm) and the water was then immediately acidified
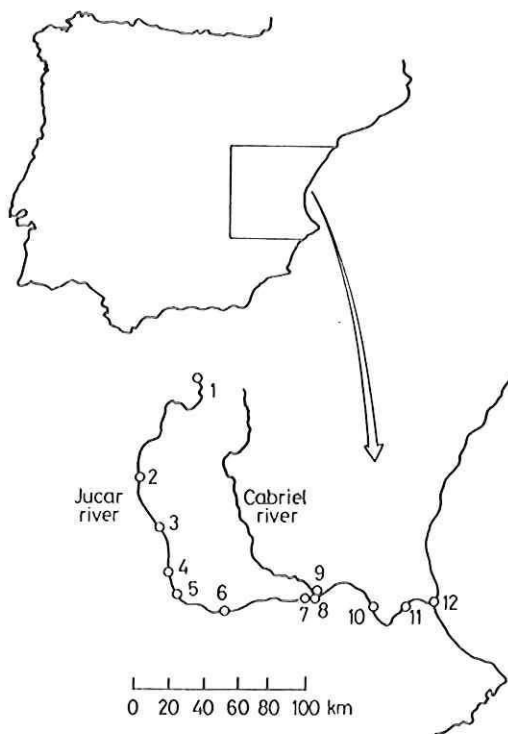
Fig. 1. Sampling points along Jucar and Cabriel Rivers

with HNO_3. ^{232}U was added as spike at start. Uranium was preconcentrated by coprecipitation[5] with added Fe(III) (15 mg of Fe/liter of sample), iron hydroxide was formed at pH 10 by adding NH_4OH. The precipitate was separated by centrifugation. Fe was then separated from uranium and other actinides by extracting with isopropyl ether,[6] the organic phase was rejected. This precipitate was dissolved with HCl 8M. The aqueous phase was evaporated to dryness and dissolved in 10 ml 9M HCl. Finally, uranium was separated from other actinides with Dowex AG 1×8 resin in chloride form.[7] Uranium and actinides are absorbed into the resin. Then thorium and other actinides are eliminated by passing HCl 9M through the resin, and uranium is finally eluted with 7.2M HNO_3. Uranium was then electrodeposited from the solution onto a disc of stainless steel with 2.5 cm diameter.[8,9] The plated samples are measured by low level α-spectrometry with a silicon surface barrier detector (active area 450 mm^2) coupled to a low noise preamplifier, linear amplifier and a multichannel analyzer. The resolution of the system is 21 keV (FWHM) for the 4824.2 keV α-emission of ^{233}U. The
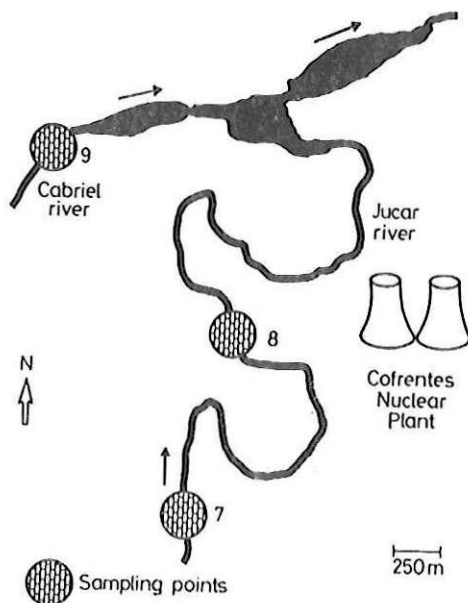
Fig. 2. Sampling points in Cofrentes Zone, Point No 8 corresponds to the location of the water outlet from Cofrentes Nuclear Plant. Arrows indicate the direction of flow of Rivers

efficiency of the detection system used in this work is $(6.6 \pm 0.1)\%$ as was determined with a calibrated planchet. Chemical yields between 50% and 90% were obtained.

The method has been checked with a calibrated sample of natural uranium. The activity ratios using this sample were 1.00 ± 0.04 and 0.049 ± 0.009 for $^{234}U/^{238}U$ and $^{235}U/^{238}U$, respectively.

Results and discussion

For each sample the ^{238}U, ^{235}U and ^{234}U activities were measured. The spectra were analyzed using ACURA program,[10] which was specifically developed for uranium α-spectra analysis. The total activity due to natural uranium and the $^{234}U/^{238}U$, $^{235}U/^{238}U$ activity ratios were calculated. The results are given in Table 1. Fig. 3 shows the activity of each isotope of natural uranium and the total uranium activity versus distance from the source of Jucar River.

The sample marked with * in Fig. 3 (No. 9) is not from Jucar River, but from Cabriel River, just before it flows into Jucar River, and the sample marked with ** (No. 8) was taken just before the outlet of Cofrentes Nuclear Plant.

Table 1
Uranium activities along Jucan River

No.	pH	Temperature, °C	Conductivity, μS	^{238}U, mBq/l	^{235}U, mBq/l	^{234}U, mBq/l	Total activity, mBq/l	$^{234}U/^{238}U$	$^{235}U/^{238}U$
1	7.51	6	671	7.05 ± 0.17	0.36 ± 0.05	13.4 ± 0.3	21.0 ± 0.3	1.90 ± 0.09	0.051 ± 0.008
2	7.60	7.5	710	11.78 ± 0.24	0.50 ± 0.07	22.2 ± 0.3	34.6 ± 0.4	1.88 ± 0.06	0.042 ± 0.007
3	7.86	7.5	720	13.22 ± 0.21	0.64 ± 0.09	21.8 ± 0.3	35.9 ± 0.4	1.65 ± 0.05	0.048 ± 0.008
4	7.87	8	695	13.08 ± 0.23	0.62 ± 0.09	21.4 ± 0.3	35.3 ± 0.4	1.64 ± 0.05	0.047 ± 0.008
5	7.64	7.5	715	13.0 ± 0.3	0.58 ± 0.09	22.0 ± 0.4	35.8 ± 0.5	1.69 ± 0.07	0.045 ± 0.008
6	6.97	7	697	16.4 ± 0.3	0.71 ± 0.11	34.3 ± 0.5	51.6 ± 0.6	2.09 ± 0.07	0.043 ± 0.007
7	7.33	8	745	14.0 ± 0.3	0.59 ± 0.09	26.0 ± 0.4	40.7 ± 0.5	1.86 ± 0.07	0.042 ± 0.007
8	7.40	8.5	734	13.01 ± 0.22	0.59 ± 0.09	23.0 ± 0.3	36.8 ± 0.4	1.77 ± 0.05	0.045 ± 0.008
9	7.71	8	712	12.0 ± 0.3	0.52 ± 0.08	16.0 ± 0.3	28.6 ± 0.4	1.33 ± 0.06	0.043 ± 0.008
10	7.35	8	720	9.5 ± 0.3	0.43 ± 0.06	16.1 ± 0.4	26.1 ± 0.5	1.69 ± 0.09	0.045 ± 0.008
11	7.20	8	688	15.5 ± 0.4	0.78 ± 0.12	25.5 ± 0.4	42.3 ± 0.5	1.64 ± 0.06	0.050 ± 0.009
12	7.52	8.5	$20 \cdot 10^3$	29.6 ± 0.4	1.30 ± 0.19	39.0 ± 0.5	70.0 ± 0.6	1.32 ± 0.03	0.044 ± 0.007
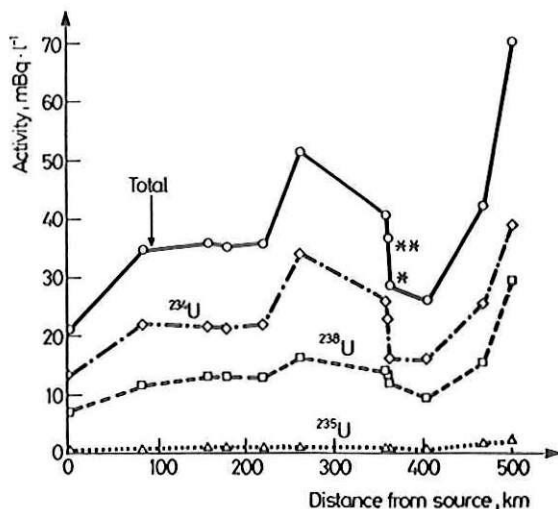
Fig. 3. Uranium activity along Jucar River
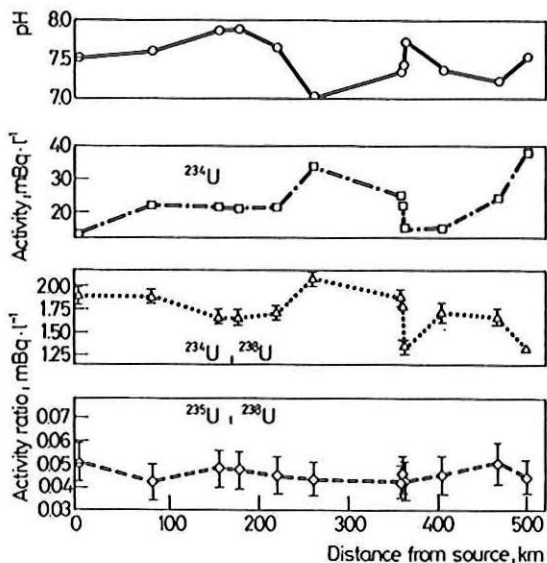
Fig. 4. ^{234}U activity, ^{234}U/^{238}U and ^{235}U/^{238}U activity ratios and pH along Jucar River

The pH values varied from 6.97 to 7.87. The drop of pH around sampling point No. 6 could be explained by changes in the composition of the River bed, although no significant changes in its composition have been observed. Nevertheless, the variation

of pH values is relatively small. The [234]U activity varies from 13.4 ± 0.3 mBq/l to 39.0 ± 0.5 mBq/l showing two maxima (Fig. 3). The maximum in [234]U obtained in sample No. 6 can be explained by pH considerations (see Fig. 4). This figure shows that an increase in [234]U activity is found when the pH value diminishes, and viceversa. This behavior has been observed by other authors[11,12] in acid waters (pH 3) but not in alkaline waters. In the sample collected in the mouth of Jucar River the [234]U activity increases in spite of pH (see Fig. 4), this is due to increased salinity. This effect will be explained later. The relationship between activity and pH found for [234]U is not found for [238]U. For this isotope the activity varies from 7.05 ± 0.17 mBq/l to 16.4 ± 0.3 mBq/l without considering the sample collected in the mouth of the River, which shows a significant increase of [238]U activity (29.6 ± 0.4 mBq/l). In this sample the increased salinity due to mixing with sea water produces high uranium activities, this effect being observed for each isotope measured. A similar behavior has been observed in the mouth of other Rivers (Guadalquivir, (Spain),[13] Forth (United Kingdom)).[14] Various studies have shown that the chemical interactions between Rivers and the ocean are complex. The adsorption/desorption chemistry of U has been studied by different authors[15–18] since 1969. The U activity increase could be attributed to uranium desorption from sediments brought about by an increase in salinity that occurs on mixing with ocean water. For [235]U we do not see any relation between the activity and pH, temperature or conductivity. The activity values measured by us are in general agreement with other authors for River waters in Spain.[11]

[235]U activity must be determined very carefully. One of the most important problems is to consider in a correct way the contribution of the low energy tails from [232]U added as tracer, in the [235]U determination. The normally poor accuracy when determining [235]U in environmental samples due to counting statistics and the wide band energy are to be considered (from 4218 keV to 4597 keV)[19] in the correct determination of [235]U isotope which makes the associated error higher than that of the other uranium isotopes.

We want to emphasize that we have not observed any release of uranium by Confrentes Nuclear Plant. In fact we observed a decrease in [234]U activity due to pH changes, as was already pointed out. We have found a direct relation between the [234]U/[238]U ratio and pH (see Fig. 4).

This behavior, i.e., that an increase in pH produces a decrease in [234]U/[238]U activity ratio, was reported by other in River waters.[20] The [234]U/[238]U activity ratios found by us were between 1.32 ± 0.03 and 2.09 ± 0.07, showing a clear divergence from the secular equilibrium ([234]U/[238]U = 1). These values are in general agreement with those for River waters in other geographic regions.[21] Complex processes are involved in this behavior. The deviations of the [234]U/[238]U activity ratio from secular equilibrium can be attributed primarily to an increased [234]U leaching rate (relative to the rate for [238]U), due to the [234]U being largely in unstable crystal locations.[22,23] Radioactive decays, especially by

α-emission, greatly disrupt the crystal lattice along the path of recoil and in the neighborhood of the displaced daughter.[22] Thus, atoms of ^{234}U become more vulnerable to leaching than ^{238}U atoms.

Direct α-recoil release of ^{234}Th can also produce disequilibrium.[22,24,25] In the case of ^{238}U, the daughter nuclide has a recoil energy of ≈ 72 keV, which is enough to displace the daughter nuclide ≈ 200 Å in crystalline materials. Direct recoil displacement may be a significant process in causing measurable disequilibrium where phase domains (particles) are small, as in the case of suspended material in River waters. The ^{234}Th can reach water by recoil process and if the pH conditions are adequate, will remain in water and finally decay there to ^{234}U. The relation found by us between pH and ^{234}U activity can then be explained by assuming that lowering of pH promotes leaching of ^{234}U from disordered crystal positions and reduces sorption of ^{234}Th and ^{234}U by sediment particles.

We have not found any relation between the ^{235}U/^{238}U activity ratio and pH, conductivity or temperature, (Table 1, Fig. 4).

Conclusions

We have measured by α-spectrometry the uranium activity in water samples from the Jucar River (East of Spain). We have found a direct relation between ^{234}U activity and pH, while this is not the case for the ^{235}U and ^{238}U activities. This produces also a direct relation between ^{234}U/^{238}U activity ratio and pH. Nearly all the uranium present in the water samples is coming from sediments by leaching. The ^{238}U present in the sediments decays by α-emission to ^{234}Th, which can reach water by α-recoil. The ^{234}Th will remain in water if pH conditions are adequate, and will finally decay to ^{234}U. Another process for the enrichment of ^{234}U as pH decreases is the recoil of ^{234}Th into instable crystal positions from which ^{234}Th or ^{234}U would be leached more easily, remaining again in water if pH conditions are adequate. These processes can explain the relation found by us between ^{234}U activity and pH.

Increasing salinity increases the activity for all uranium isotopes measured in the samples near the River mouth, thus no additional effect in ^{234}U/^{238}U and ^{235}U/^{238}U activity ratios arises. In the mouth of Jucar River the ^{234}U activity increases while pH increases too, showing that the effect of salinity in this case overrides the pH effect (Fig. 4).

Finally we want to emphasize that we have not found any evidence of uranium releases from Cofrentes Nuclear Plant.

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