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GEOCHEMICAL AND ISOTOPE ANOMALIES IN SIOMA RIVER GORGE, CENTRAL TAJIKISTAN

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Abstract: For a better understanding of the previously observed increased natural radioactivity at the confluence of Varzob and Sioma rivers, the activity concentration of natural radioactive ^{40}K, Th and U daughters as well as of the anthropogenic ^{137}Cs were determined in nine sampling points covering the entire Sioma river. The radiometric determinations evidenced, beside increased activity concentrations of Th and U daughter radionuclides, an anomalous accumulation of anthropic ^{137}Cs and natural ^{210}Pb in the middle of the Sioma gorge. Complementarily, the mass fractions of natural Th and U determined by Instrumental Neutron Activation Analysis (INAA) evidencing an increased presence of Th and U which, in some places overpasses six times the average mass fraction found in the Upper Continental Crust. The ^{137}Cs and ^{210}Pb activity concentrations did not correlate with the other radionuclides or Th and U presence, but were reciprocally correlated suggesting an active air transport from the southern Tadjik plane most probably during the Afgan storms. At their turn, the increased presence of Th and U as gamma-ray spectroscopy and INAA determinations proved could be attributed to the existence of actinides rich minerals, similar to those fond on neighbouring Odjuk pegmatite field.

Keywords: Sioma river; Tajikistan; natural radioactive elements; radiocesium; pegmatite; gamma ray spectrometry; instrumental neutron activation analysis.)

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1. Introduction

The Sioma River, a right-bank tributary of the Varzob River flows into Varzob about 50 kilometers north of city of Dushanbe, the capital of Tajikistan. The Sioma River Gorge stretches parallel to the Hissar Range having an east-west orientation. The gorge is about 17 km long and rather narrow, its width not exceeding 500 meters. It is framed by mountains with snow and glacial peaks 3500 - 4600 meters high while the gorge altitude varies between 2500-2700 m (Fig. 1).

The basin of the Sioma River, in geological terms, belongs to the South Hissar structural-formational zone of Central Tajikistan (Southern Tien Shan Mountains). Its catchment basin is located in the multi-phase Hissar batholith, composed of various granitoids of the Middle Carboniferous-Early Permian age and broken in places by Early Mesozoic lamprophyre dikes and explosive tubes with alkaline basalts [1]. The climate is cold and temperate, classified as Dfb according to the Köppen-Geiger climate classification [2].

Sioma basin is located in an area of aerosol deposition by the Afghani dust storms, but due to the steep banks of the gorge and abundant precipitation, dust particles are washed into the river, although in some places they form shallow loess soils [3,4]. During this aerosols transport, first of all, large particles and heavy minerals fall out, the remaining dust is enriched with light minerals, including potassium. At the entrance to the Sioma Gorge, there is a sharp change in the direction of the wind, and it, literally licks the surface of the rock leading to increased fallout of aerosols. At the end of the gorge, winds and dust hit higher rocks, which could also determine an increased aerosol deposition.

Previous studies performed within the Cooperative Transboundary Monitoring Data Sharing and Modeling of Water Resources in Central Asia (NAVRUZ) project [5], have evidenced along Varzob river an increased gamma ray activity at the confluence of the Sioma and Varzob rivers [6,7]. This finding was analyzed by taking into account the existence of post Soviet Era of a significant number of former uranium mines mainly located in the northern Tajikistan ridges as well in the other neighbouring mountainous regions of Central Asian states [8–10].

In view of these findings, during the summer season of 2019 it was organized by the Institute of Water Problems, Hydropower and Ecology of the Academy of Science of Tajikistan to collect more 9 samples representative for the environmental radioactivity of Sioma river sediments. High resolution gamma ray spectroscopy as well as Instrumental Neutron Activation Analysis (INAA) were used to determine the activity concentration of ^{232}Th and ^{238}U radioactive daughter as well as the mass fractions of natural Th and U in collected sediments.

The final aim of this study consists in realizing a detailed description of the natural radioactivity distribution along the Sioma river evidencing the contribution of local petrology as well as the long distance airborne transport, mainly by the Afgani storms [11].

The results of this project will be further presented and discussed.

2. Materials and Methods

2.1. Sampling

The position of sampling points are shown in Figure 1 and presented in Table A1. It should be noted that, due to water fast flow and granite bed of the river, sometime it was relatively difficult to collect samples of bottom sediment. At the same time, to increase the sampling accuracy, the distances between collecting points were chosen as possible as equal and spread on both river sides.

Therefore, nine surface sediments samples were collected by means of an AMS 12 Multi Stage Sediment Sampler (AMS Inc. American Falls, ID) [12]. At each sampling point, three independent samples were collected from an area of about 10 m^2 and mixed together which resulted in an average specimen. To avoid any cross contamination, after each operation, sampling tubes were intensively cleaned with water and soaked with paper napkins. Collected sediments of about 1 kg consisting of a silty greyish sand without visible vegetal debris, were kept in clean polyethylene bags and transported to Dushanbe laboratory. Here, the large fragments of rocks and pebbles were removed, the remaining sedimentary material being air dried, sieved through 18 mesh sieve and stored for future analysis [7,13].

2.2. Radiometric Measurements

Sediment samples, prepared as mentioned before, were poured into 500 cm^3 Marinelli backers, sealed and kept four weeks to reach the radioactive equilibrium. Measuring time was of 6 hours for sediment and 24 hours for the background.

High resolution gamma-ray spectrometry was used to determine the activity concentration of anthropogenic ^{137}Cs, natural ^{40}K as well as ^{212}Bi and ^{212}Pb (^{232}Th daughters) and ^{214}Bi, ^{214}Pb and ^{210}Pb (^{238}U daughters) Al measurements were done using an Ex-

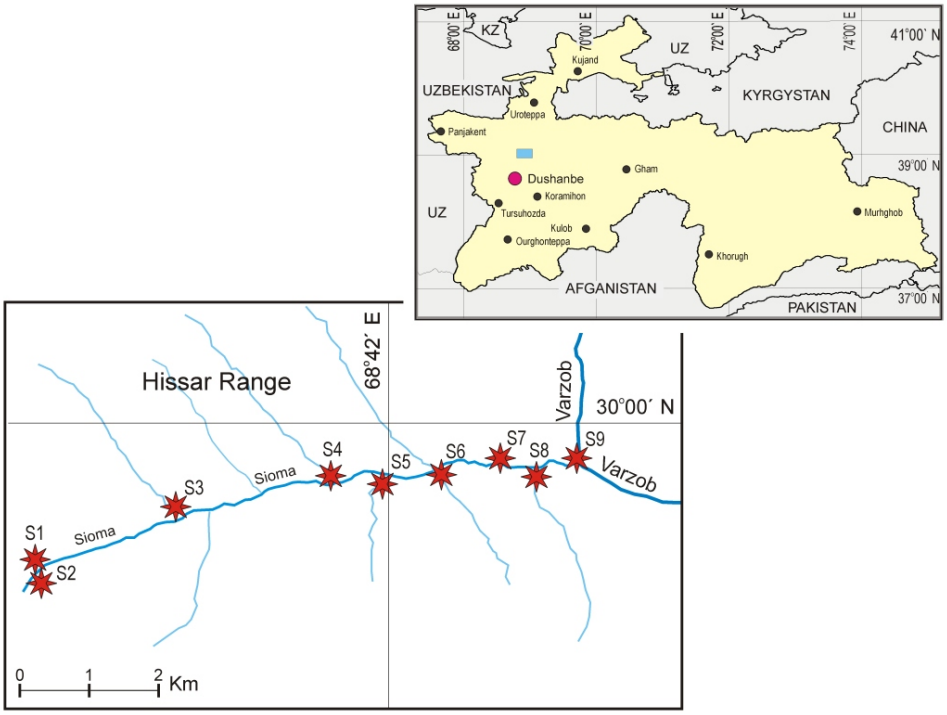

Figure 1. The locations of sampling points along the Sioma gorge whose position with respect to Tajikistan is illustrated in the inset. The tributaries of the Sioma river are in fact small creeks, majority without names.

tended Range Coaxial Ge Detector (XtRa) with an energy resolution of 1.78 keV for the ^{60}Co 1.33 MeV line. More details concerning efficiency calibration can be found in [7]. Under these circumstances, the total uncertainty concerning the activity concentrations was no greater than 7%

2.3. Instrumental Neutron Activation Analysis

The mass fractions of Th and U in considered sediments were determined by INAA carried out at the research nuclear reactor of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan [14]. Sediments samples and reference materials weighting about 0.5 g were wrapped in polyethylene bags and irradiated twice at a thermal neutrons fluency density of $5 \cdot 10^{13}$ neutrons cm^{-2}s^{-1}; for 15 s for short living radionuclides and after two weeks for 15 h in the same conditions, for the long living ones.

Spectra calibration was done by using internal reference material by micro-pipetting a determined volume of chloride or nitrate of considered elements on an ashless filter paper. Zn was used as secondary reference element. The quality control of all determinations was done by measuring in the same condition the certified reference material IAEA-336 (Trace and minor elements in lichen). In these conditions, the combined uncertainty concerning Th and U mass fractions was no greater than 6%. More details concerning INAA measurements can be found in [6].

3. Results

Final data concerning the experimentally determined activity concentrations as well as INAA determined mass fractions of Th and U are reproduced in Table A2, and, illustrated as stacked columns in Fig. 2a (activity concentration) and Fig. 2b (Th and U mass fractions). In the last case, we have reproduced for comparison the mass fractions of Th and U corresponding to the Upper Continental Crust (UCC) as provided in [15].

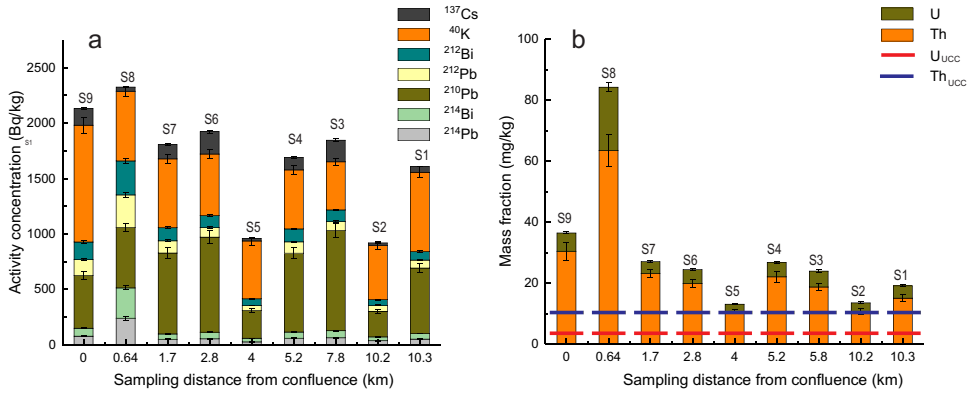

Figure 2. The activity concentration distribution of the main radioactive natural as well as anthropogenic isotopes (a) and the mass fractions of Th and U (b) along the Sioma valley from the confluence with the Varzob river. For comparisons, on fig 2b, the UCC [1] Th and U mass fractions are illustrated too.

In the last case, it can be remarked that both Th and U reached maximum mass fractions for the S8 sampling point slowly decreasing upstream, Th mass fraction significantly overpassing with two exceptions, S2 ad S5 sampling points, the UCC one [15]. At the same time, the Th/U mass fraction ratio varied more or less closer to the UCC one of 3.9 (Table A2).

4. Discussion

At a more carefully analysis of experimental results illustrated in Fig. 2 and Table A2, it can be remarked that, the ^{40}K activity concentration presents a relative maximum at the western end of Sioma Gorge reaching a maximum value of 1060 $\pm$ 70 Bq/kg, slightly higher then the UCC average value of 870 Bg/kg. This value correspond to the mass fraction of 2.80 % w specific to UCC [15].

It worth mentioning that the ^{40}K activity concentration presented two peaks, one at the entrance in the gorge (S1) and the other one at the confluence with the Varzob river (S9 on Fig. 1). This behaviour could be associated with the fallout of dusty aerosols. Indeed, the dust storms known as Afghans [3] originate in the Sahara Desert and fly a long way through the Arabian Peninsula, Iran and Afghanistan. The approximate equality of the ^{40}K isotope in the samples from the middle part of the gorge indicates approximately the same geological and geochemical origin of the soils throughout the gorge. These are, as mentioned before, loess soils of shallow depth [4].

Another evidenced peculiarities concern the mass fraction as well as the activity concentration of Th and U in conjunction with their daughter radionuclide ^{212}Bi, ^{212}Pb as well as ^{212}Bi and ^{212}Pb respectively. According to Figure 2a and Table A2, it should be noted their elevated presence for S8 sampling point. A corresponding sharp increase of Th and U mass fractions, as illustrated by both INAA and radiometric measurements (Fig. 2b), excludes, at this point, the possibility of an accidental statistical outlier. To this remark it should add the fact that ^{212}Pb activity concentration significantly overpasses, for entire Sioma valley sediments, those of the ^{212}Bi and ^{212}Pb daughters of natural Uranium (Table A2).

On the other hand, ^{212}Pb activity concentration dose not correlates neither with Th and U daughters radioactivity, nor with the ^{40}K, but only with the anthropogenic ^{137}Cs one (Table 3a,b). A similar behaviour of the ^{212}Pb activity concentration was previously reported for the entire length of the Varzob River gorge [7].

In spite of this, ^{212}Pb activity concentration presented a maximum at sampling point S8 where the U mass fraction showed a maximum. This somehow contradictory finding

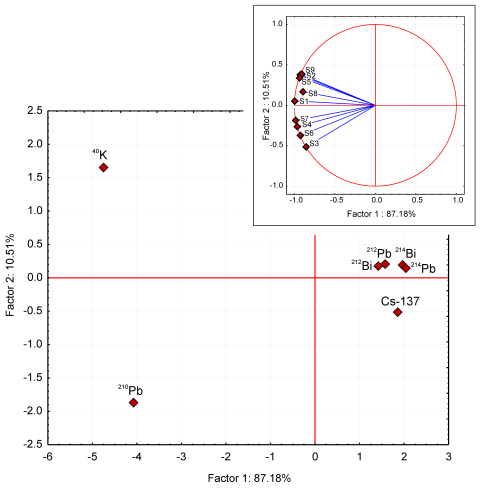

Figure 3. The result of PCA of the activity concentration of investigated radionuclides. While ^{232}Th and ^{238}U daughter, excepting ^{210}Pb form the same cluster proving a correlated distribution of naturel Th and U, ^{40}K, ^{137}Cs and ^{210}Pb form different individual clusters suggesting either different parent rocks as the case of ^{40}K or an external source as ^{137}Cs and partially ^{210}Pb.

could be explained by an active air transport of radon from the Odjuk pegmatite field as well as from the entire Hissar granite batholith superposed on the local U sources.

Concerning ^{137}Cs, its average activity concentration along Sioma valley of 100Bq/kg is significantly higher than the average value of 2Bq/kg reported for the entire Central Asia, most probably the reminiscence of Lob Nor atmospheric nuclear tests [16].

Despite different origin and source, between the activity concentrations of both ^{137}Cs and^{210}Pb there is a good correlation characterized by a Pearson's correlation coefficient of 0.824 and a corresponding nonparametric Spearman's correlation coefficient of 0.812, bot at $p < 0.05$ (Table 1). At the same time, between both ^{137}Cs and^{210}Pb activity concentrations and the other investigated radionuclide there are no correlations (Table 1).

This fact is well illustrated by the Principal Component Analysis (PCA) whose result, expressed by a Principal Component (PC) 2 vs PC1 bi-plot documents the existence of at last four clusters, consisting of ^{40}K, ^{137}Cs,^{210}Pb and ^{212}Bi, ^{212}Pb, ^{212}Bi and ^{212}Pb respectively (Figure 3).

In this regard is of interest to remark that, by analysing the Factor 2 vs. Factor 1 bi-plot reproduced in Figure 3, inset, results that the major contribution to discrimination between radionuclides comes, in a more or less equal measure, from all sapling points, Factor 1 being responsible for more than of 81 % of total variance.

The increased presence of Th and U indicates the existence of some enriched natural actinides deposits or ore occurrences which are located on the Sioma gorge in the vicinity of sampling point S-8, deposits which are either close to the surface or of high thickness, in good correlation with the previous reported data [7,13] concerning natural radioactivity along Varzob river

The fact that everywhere along the Sioma river, the Th/U ration varied around 4.3 $\pm$ 0.8, *i.e.*, not far from the 3.9 characteristic of the UCC[15], suggests the presence of the same type of acid rocks such as granitoids of pegmatites, the last one found, as mentioned before, in neighbouring Odjuk pegmatite field [7,13]. This observation is sustained by the evidenced good correlation between Th and U mass fractions characterized by both Pearson's and Spearman's correlation coefficients of 0.969 and respectively of 0.778 at $p < 0.05$.

Table 1. The matrix of Pearson's (lower diagonal) and Spearman's (upper diagonal) correlation coefficients of activity concentration distribution of investigated radionuclides. The correlations valid at $p < 0.05$ are represented in red ink.

	^{214}Pb	^{214}Bi	^{210}Pb	^{212}Pb	^{212}Bi	^{40}K	^{137}Cs
^{214}Pb	—	0.983	0.307	0.783	0.767	0.383	0.450
^{214}Bi	0.998	—	0.305	0.767	0.750	0.400	0.517
^{210}Pb	0.065	0.048	—	0.250	0.267	-0.117	0.817
^{212}Pb	0.970	0.959	0.099	—	0.983	0.600	0.383
^{212}Bi	0.966	0.955	0.163	0.994	—	0.617	0.400
^{40}K	0.152	0.111	-0.159	0.304	0.293	—	0.133
^{137}Cs	-0.175	-0.203	0.824	-0.086	-0.009	0.090	—

5. Concluding Remarks

Gamma ray spectrometry was used to determine the distribution of specific activity of Th and U daughter radionuclides ^{212}Bi, ^{212}Pb, and ^{212}Bi, ^{212}Pb as well as^{210}Pb respectively together with ^{40}K and anthropogenic ^{137}Cs along the Sioma river, a high mountain tributary of the Varzob river. These results were analysed in correlation with the Th and U mass fraction distribution determined by INAA for the same sampling points.

The final results showed an increased presence of Th, U and their daughter radionuclides near the confluence of Sioma and Varzob rivers attesting the presence of some mineral fractions, most probable pegmatite similar to those existing not far away on the Odjuk river valley.

Quite different was the situation of ^{137}Cs and^{210}Pb whose content was significantly higher than those reported outside the mountainous areas of Tajikistan, which, most probable, are transported by the local Afgan storms and deposited when the air mass intercept the Hissar range whose, east-westward orientation facilitate the aerosol deposition.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Coordinates of sampling points, altitude above sea level (m) and distance from the entrance to Sioma gorge - confluence with Varzob river (km)).

Sampling point	Latitude	Longitude	Altitude	Distance	Position
S1	38.9668	68.7503	2631	10.3	Left bank
S2	38.9668	68.7422	2705	10.2	Right bank
S3	38.9651	68.7284	2478	7.8	Left bank
S4	38.9638	68.7154	2184	5.2	Right-bank
S5	38.9642	68.7014	2123	4.0	Left-bank
S6	38.9561	68.6716	2057	2.8	Left-bank
S7	38.9444	68.6482	1893	1.7	Left-bank
S8	38.9478	68.6467	1871	0.6	Right-bank
S9	38.9683	68.7596	1751	0	Varzob confluence

Table A2. The distribution of activity concentration of investigated radionuclides (in Bq/kg) as well as the corresponding mass fractions of Th and U (in mg/kg).

Sampling point	^{40}K	^{137}Cs	^{214}Pb	^{214}Bi	^{210}Pb	^{212}Pb	^{212}Bi	Th
S1	710±50	53±3	51±3	51±3	590±38	71±5	78±7	15.1±1.1
S2	490±35	21±2	37±3	35±3	230±9	54±3	52±4	10.7±0.9
S3	430±30	195±13	64±4	64±4	900±55	80±8	106±8	18.8±1.2
S4	530±35	113±7	59±4	56±4	710±42	102±7	117±10	22.1±1.8
S5	520±30	24±2	27±2	32±2	250±15	45±3	61±6	10.7±0.7
S6	550±40	200±12	55±4	59±4	860±55	88±4	109±8	19.9±1.3
S7	620±40	130±7	49±3	49±3	730±35	111±9	118±10	23.2±1.4
S8	630±40	37±3	240±15	274±19	550±30	293±21	306±25	63.5±5.3
S9	1060±70	150±9	77±4	72±5	480±30	143±11	159±11	30.5±3.0

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