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Assessment of the ecological and geochemical conditions in surface sediments of the Varzob river, Tajikistan

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ABSTRACT

The aims of present study consist of collecting more information on the geochemistry of the Varzob river unconsolidated sediments as reflecting the diversity of the South-Hissar range together with a comprehensive evaluation of the anthropogenic contamination of the same sediments. Accordingly, the content of nine major, rock forming elements - Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe as well as of other 27 trace ones - Sc, V, Cr, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Hf, Ta, W, Th, and U was determined by Epithermal Neutron Activation Analysis. A special attention was given to potential heavy contaminants - V, Cr, Mn, Co, Ni, Zn, As, Sb and Ba whose content was used to calculate more environmental contamination proxies i.e. contamination factor, geoaccumulation, and pollution load indices. At the same time, the content of Cr, Ni, Sc, Zr, REE, Th and U were used to establish the nature and origin of recent sediments. The increased values of some pollution indices characteristic of industrial activity in the upper part of the Varzob River indicate an anthropogenic origin of As, Sb and Mn while the increased contents of Th and U in the lower reaches of the Varzob River could be attributed to the pegmatite field of the Odjuk tributary.

1. Introduction

The Varzob river, as many others rivers of Tajikistan, collects rain and melt water from large and small mountainous catchment areas (Fig. 1). According to [1] the water quality of the Varzob river relates to the first and second class of purity. The river, with a length of 71 km [2] crosses the Khoja-obi Garm geological fault which divides the river basin into two geochemically different subzones. Here, one of the most important features consists of a 27.5 km^2 pegmatite field located between the upper reaches of the Odjuk and Takob tributaries. The minerals of this area are characterized by increased contents of thorium and uranium found in some rare earth elements (REE) accessory minerals such as monazite, samarskite, gadolinite, etc. The weathering of this outcrop could be an explanation of the increasing of content of heavy and radioactive elements in water and surface sediments of the Varzob river [3–5]. On the contrary, the inferior Varzob river flows in a densely populated region including the Municipality of Dushanbe, the Tajikistan capital. With about 680 000 inhabitants [6] the City of Dushanbe contributes with a significant amount of biogenic and chemical pollutants discharged into the river [1]. At the same time, the Varzob river gorge, due to its proximity to the Municipality of Dushanbe, represents a well appreciated recreational area with a great tourist potential, especially for hiking and trekking.

Excepting general data concerning the geo-morphology [2], natural radioactivity [4] or mosses biomonitoring [7], until present there are no other systematic studies of Varzob catchments basin and related river sediments. Given the circumstances, a detailed investigation of the spatial distribution of one of the most important contaminant elements such as V, Cr, Mn, Co, Zn, As, Sb and Ba, could be helpful in assessing the ecological status of Varzob valley. Concurrently, the distribution of some lithophile elements such as incompatible and immobile Sc, Ti, V, Zr, REE, Th or more soluble U together with siderophile Ni could bring useful information about the origin of sedimentary material [8–10]. For this reason, during the 2017 spring-summer season, a field expedition

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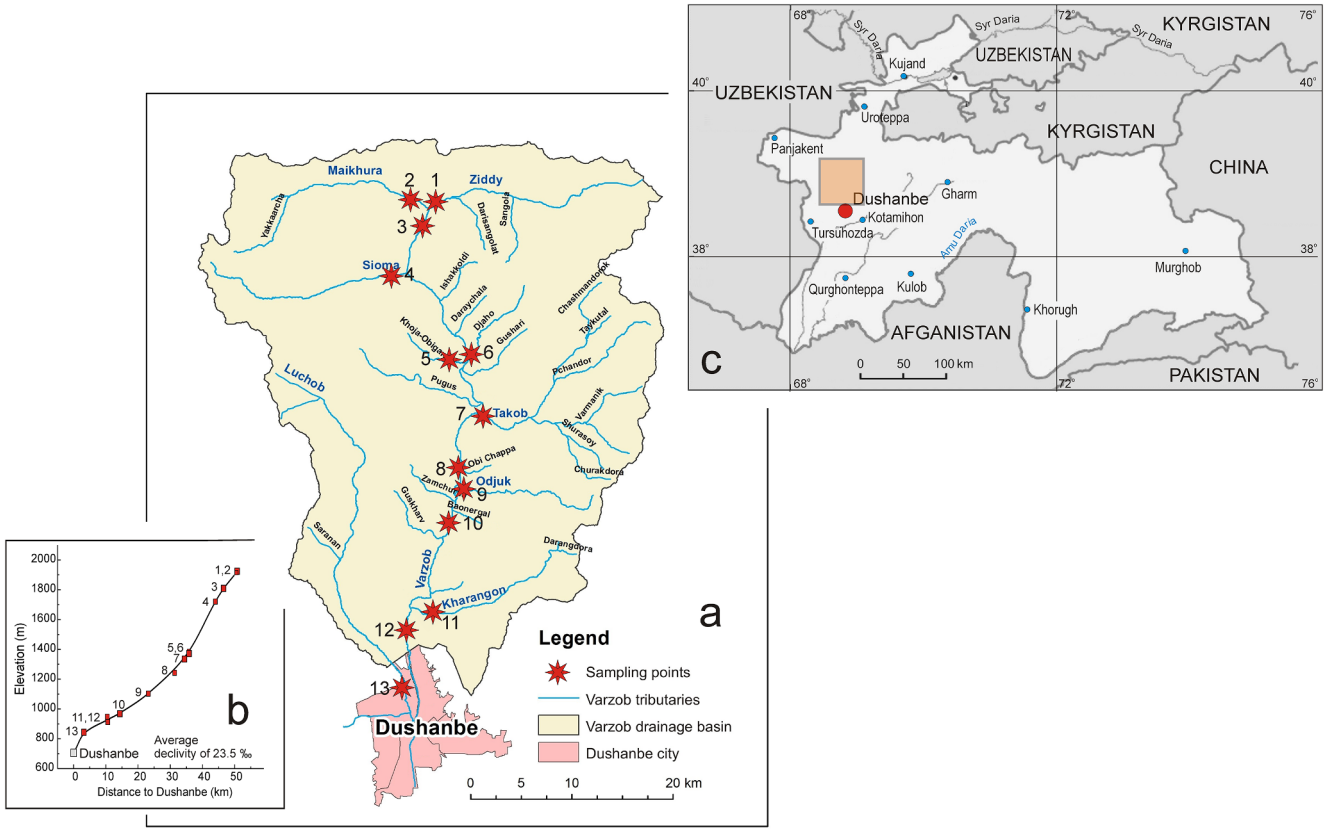

Fig. 1. The Varzob catchment basin with the location of sampling points (a) whose elevation are indicated on the valley vertical profile (b). The inset (c) illustrates the position of the Varzob basin on Tajikistan map. It should be remarked the step vertical profile of the Varzob valley characterized by an average declivity of 23.5%.

was organized by the Institute of Water Problems, Hydropower and Ecology of the Academy of Science of Tajikistan to collect representative sediments samples for this study. To be representative for the entire catchments basin, 13 specimens of sediments were carefully collected along the Varzob valley, especially at the confluences with its main tributaries (Fig. 1).

To determine with high accuracy the elemental content of the sediments, the Epithermal Neutron Activation Analysis (ENAA) showed to be one of the most suitable technique. Its main advantages consist of the possibility of a simultaneous determination of about 40 elements beginning with Na and ending with U whose contents vary from tens of percents to mg/kg, without any chemical pre-treatment susceptible to induce unwanted systematic errors. This option was facilitated by the permanent access to the Neutron Activation Analysis Section of the Frank Neutron Physics Laboratory (FNPL) of the Joint Institute for Nuclear Research (JINR), Dubna, Russian Federation. On the other hand, ENAA can not be used to determine with enough precision and accuracy the content of some common contaminants such as Cu, Cd or Pb [11,12].

Given the multitude of elements whose content could be determined by ENAA, our project has two main aims: – i. to evidence to what extent the geochemistry of Varzob river sediments reflects the geochemistry of different formations covered by the Varzob River catchment basin, adding new data concerning the geochemistry of Central Tajikistan [13–15]; i ii. to asset the influence of elements considered as contaminants on the sediment quality from the point of view of environmental toxicology.

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

2. Epithermal Neutron Activation Analysis

ENAA represents a variant of the classical Instrumental Neutron Activation Analysis (INAA) which was developed in '70. Its progress was stimulated by the improvement of neutron beams monochromatization by filtering and shielding with materials having high cross section for thermal neutrons such as B and Cd [11,12]. Epithermal neutrons conventionally have an energy range between 1 eV and 1 MeV including the resonance domain around 5 keV. For this reason, epithermal neutrons do not activate the elements with higher cross section for thermal neutrons, but those with high resonance cross sections. This particularity significantly increases the analysis sensitivity by reducing the background. Practically, this is achieved by using two reactor channels, one of them lined with Cd to absorb thermal neutrons, the other one without Cd padding. The second one which delivers neutrons with full spectra is used for short time activation, (0.5 to 5 min) specific for elements such as Mg, Si, Al, Ca, V, Ti, Mn, Cu, In, and I which are activated by the thermal component of neutron flux (Table 1). Distinct from this, the Cd –coated channel which retains thermal neutrons but

Table 1
The main parameter of the IBR 2 neutron fluxes at REGATA facility.

Irradiation channels	Irradiation time	Neutron flux density (in 10^{12} m^{-2} s^{-1})		
		0–0.55 eV	0.55–10^5 eV	10^5-25·10^6eV
C1 (Cd lined)	Long (1 h to 4 days)	0.023	3.3	4.2
C2 (without Cd)	Short (1–6 min)	1.23	2.9	4.1

contain a significant amount of epithermal neutrons (Table 1), is utilized for long term activation (one hour up to several days) which allows the determination of more than 40 elements, i.e. Na, K, Sc, Cr, Fe, Co, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Th, and U. Some elements which have more stable isotopes can be activated by both short and long term irradiation offering a higher precision. Under such conditions, the maximum sensitivity of ENAA is about 1 mg/kg, which makes this analytical method on of the most sensitive elemental analytical method still in use [11,12]. Due to these particularities, the ENAA sensitivity is 1.5–7 times better then those of the current INAA [16,17].

3. Varzob river catchment basin

The Varzob River catchment basin, with a total area of 174 km^2, covers the South-Hissar formation of Central Tajikistan (Southern Tien Shan range) [2]. This formation consists of a multi-phases Gissar batholith, with different granites of Middle Carboniferous-Early-Permian age. Locally, the formation is fractured and penetrated by early Triasic dikes of lamprophyres, pegmatites and explosion tubes filled with alkaline basalts [18]. The southern sector of the Varzob valley crosses the Tajik depression, rich on coastal-marine, terrigenous and chemogenics, sometimes coal-bearing, salt-bearings and gypsiferous sediments of late Mezozoic-early Cenozoic age, significantly deformed by the collision of Indo-Asian plates which taken part between 55 and 35 My [19]. Further, the Southern Tien-Shan and Pamir mountains formed during this collision supplied a significant amount of detritic material.

4. Materials and methods

4.1. Samples

A number of 13 surface sediments samples were collected using an AMS 12 Multi Stage Sediment Sampler (AMS Inc. American Falls, ID) [20] provided with tubular glass samplers. Unconsolidated sediments, 15 to 20 cm long, were directly collected from the riverbeds during the high-water period. For a better statistic, at each sampling point, three sub-samples were collected from an area of about 10 m^2 and blended to form a composite sample. To avoid any recent contamination, the top sediment layers were removed with an acid washed plastic spatula. Moreover, before being re-utilized, each collector sampler was intensively washed with clean water and soaked with single use cellulose napkins.

4.2. Epithermal Neutron Activation Analysis

After collection, all samples consisting of thin, grayish, sand-like matter devoid of vegetal detritus were placed into plastic containers and kept at 4 °C with cooled refrigerant. In the laboratory, each sample was clean from alien materials and dried at 70 °C at constant weight. After that, the resulting material was sieved by using a 0.425 mm (46 mesh) sieve, ground, homogenized and sent to the FLNP of the JINR for ENAA. Here, 10 g of each sample were again weighted and homogenized in a - PULVERISETTE 6 (Fritsch Laboratory Instruments GmbH, Germany) planetary ball mill at 400 rpm for 15 min.

Further, to increase the precision and accuracy of measurements, we have randomly selected from each sample six aliquots of about 0.3 g to be independently analyzed. For irradiation at the IBR-2 reactor of the JINR FLNP in Dubna, each aliquot was packed in polyethylene bags for the determination of short-living isotopes (three aliquots) and in aluminum foil (three aliquots) for long-living ones. The characteristics of the neutron fluxes in the irradiation channels 1 and 2, both of them connected with the pneumatic conveying unit “REGATA” [21], are presented in Table 1. The gamma spectra of each samples were measured with a HPGe detector with a resolution of 1.9 keV for the ^{60}Co 1332 keV line and analyzed using the Canberra software Genie 2000. In the case of short time irradiation, the gamma spectra were recorded and measured immediately after irradiation, while in the case of the long term irradiation, the gamma spectra were recorded and measured twice, after 4 and respectively 20 days after irradiation, time necessary for the short-living radioisotopes to disintegrate completely. The content of each element was calculated using proper software developed by the FLNP [22]. This software calculates the content of each element as well as the associated Combined Standard Uncertainty (CSU) [23] by taking into account the statistic error, influence of measurement geometry, detector efficiency, the content as well the error of each element for all Certified Standard Material (CSM) utilized for calibration. After gamma-ray spectroscopic measurements, all activated samples were sent to a permanent low activity repository.

Final results for each sample as well as the associated CSU, were calculated as the arithmetic media of three independent determinations corresponding to each aliquot [23,24].

4.3. Quality assurance

The quality control was provided by simultaneous analysis of the following CRM: National Institute for Standard and Technologies (NIST) Standard Reference Materials (SRM): SRM 1633c (Coal fly ash), SRM 2710a (Montana I Soil) for short-life isotopes and 2709a (San Joaquin Soil), International Atomic Energy Agency (IAEA): 433 (Marine sediment) as well as European Commission – Joint Research Center (EC-JRC): 690CC (Calcareous soil) for the long-life isotopes [24,25].

All mentioned CRM have been used to create the Group Standard Sample (GSS) which were irradiated together with the investigated samples. This procedure allowed to calculate the concentrations of about 40 elements of interest for this study. Final results concerning the concentrations were processed by means of the “Concentrations” proprietary software in order to check the accuracy and the precision of the experimental determinations. When applied to CRM, this procedure allowed to compare the corresponding values with the certified ones [22–24]. In this way, the accuracy expressed as the percentage of standard deviation of the mean for three determinations was lower than 10% while the deviation from the certified values, expressed by means of CSU varied between 3 and 26%, greater in the case of some REE (Table 2). This happened because in very few cases, the CRM provided only recommended values whose interval of uncertainty was significantly larger.

5. Results and discussion

The results concerning the main statistic parameter of all investigated elements are provided in Table 2 together with the corresponding values for Upper Continental Crust (UCC) [26] and Average World Suspended Sediment (AWSS) [27], both of them considered as reference systems. Moreover, for a better description of sediments geochemistry, in the column chart reproduced in Fig. 2 we have illustrated the content of the investigated elements as well as of WASS, all of them normalized to UCC [26]. At the same time, a complete set of experimental data concerning the content of all elements as the average value of all three determinations as well as the name and coordinates of sampling points can be found in [28].

To answer to the first task of our project, we have compared, by using more ANOVA tests (Tukey’ pairwise Q, Kruskal-Wallis, Mann-Whitney U as well as Dunn’ post hoc), the resemblance between Varzob on one hand and UCC and WASS on the other. Final results pointed towards a closer similarity between Varzob sediments and UCC than between Varzob sediments and WASS. For this reason, we have considered for future analysis only the UCC as reference system.

In view of this, we have calculated for each element the corresponding Coefficient of Variation (CV) [29] defined as ratio of the

Table 2
Average ± St.Dev., Coefficient of variation (CV), Total combined uncertainty (TCU) [21], regarding the distribution of 35 major and trace elements in surface sediments. For comparison, the corresponding values of Upper Continental Crust (UCC) [26] and World Average Suspended Sediments (WASS) [27] are provided too. CV, TCU as well as the content of nine major oxides are expressed in % while the contents other trace elements are expressed in mg/kg. In the case of the elements marked by asterisk (*), the increased values of TCU is due to the fact that Certified Reference Material (CRF) provided recommended values.

Element	Irradiationtime	Average ± St.Dev.	CV	TCU	UCC	WASS
SiO_2	short	62.55 ± 4.01	6	4.7	66.62	60.27 ± 27.75
TiO_2	short	0.35 ± 0.07	19	5.2	0.54	0.78 ± 0.56
Al_2O_3	short	13.9 ± 2.07	20	5.2	15.4	18.32 ± 12.65
FeO	long	4.82 ± 0.95	25	2.3	5.04	8.33 ± 6.88
MnO_2	short	0.11 ± 0.03	26	4.2	0.1	0.22 ± 0.22
MgO	short	0.92 ± 0.25	25	6.9	2.48	2.33 ± 2.11
CaO	short	8.05 ± 6.88	80	2.9	3.59	8.05 ± 8.80
K_2O	long	3.91 ± 1.51	37	3.4	2.8	2.2 ± 1.44
Na_2O	long	3.39 ± 1.29	38	5.8	3.27	3.39 ± 1.29
Sc	long	8.7 ± 3.3	38	3.1	14	18.2 ± 9.3
V	short	63 ± 23	38	1.3	140	129 ± 100
Cr	long	43 ± 32	74	1.3	69	130 ± 155
Co	long	7.5 ± 2.2	29	6.6	17	22.5 ± 19.6
Ni	long	19 ± 8	55	8.8	74.5	74.5 ± 100
Zn	long	87 ± 52	60	5.3	67	208 ± 237
As	long	13.2 ± 11.4	86	5.3	1.6	36 ± 27
Br	long	0.9 ± 0.4	51	5.3	2.1	21.5 ± 17.3
Rb	long	117 ± 66	56	8.7	110	78.5 ± 53.9
Sr	long	200 ± 52	26	4.3	350	187 ± 172
Zr	long	255 ± 160	63	15.3 *	162	160 ± 67
Sb	long	1.1 ± 0.9	89	12.8	0.2	2.2 ± 2.4
Cs	long	4.5 ± 2.8	62	4.2	3.7	6.3 ± 6.5
Ba	long	570 ± 200	36	6.8	570	522 ± 427
La	long	45 ± 35	78	10.3	30	37.4 ± 24.1
Ce	long	86 ± 66	77	12.1 *	58	73.6 ± 38.4
Nd	long	27 ± 18	68	15.5 *	27	32.2 ± 15.5
Sm	long	5.9 ± 3.3	55	20.5 *	4.6	1.3 ± 2.8
Eu	long	1 ± 0.3	30	20.5 *	1	1.3 ± 0.6
Gd	long	8.8 ± 9	102	25.9 *	4	5.3 ± 2.7
Tb	long	0.8 ± 0.6	71	29.5 *	0.6	0.8 ± 0.4
Yb	long	2.1 ± 1.9	92	24.5 *	2	2.1 ± 1.3
Hf	long	6.6 ± 4.5	68	5.1	4	4 ± 1.7
Ta	long	1.7 ± 3.2	182	20.1 *	1.5	12.1 ± 0.5
W	long	15.6 ± 27	170	9.8	1.9	2 ± 2.1
Th	long	26 ± 32	125	5.6	11	12.1 ± 5.7
U	long	5 ± 4.9	95	2.4	2.8	3.3 ± 3.1

standard deviation to the mean value. The final data reproduced in Table 2 showed for CV values between 6% for SiO_2 and 170% for W the smallest variability being noticed in the case of major, rock forming elements Mg, Si, Ti, Al, Fe, Mg, Ca, Na and K, while REE, Th and U evidenced themselves by a significantly higher variability. This fact could be attributed, in our opinion, to the presence of a coal deposit, a tungsten deposit, as well as of a massive pegmatite outcrop along the Takob and Odjuk valley. In this regard should be mentioned that the sediments collected from tributaries far away from granitoide Sioma valley or Takob and Odjuk pegmatite riches formation, i.e. Ziddi, Maykhura, Khoja Obi Garm, Djaho, Kharagon, and Luchob, were comparable with the UCC ones (Fig. 3). Moreover, the content of Zr together with all eight REE as well as Hf, W, Th and U were significantly higher only in sediments collected from the Sioma, Takob and Odjuk

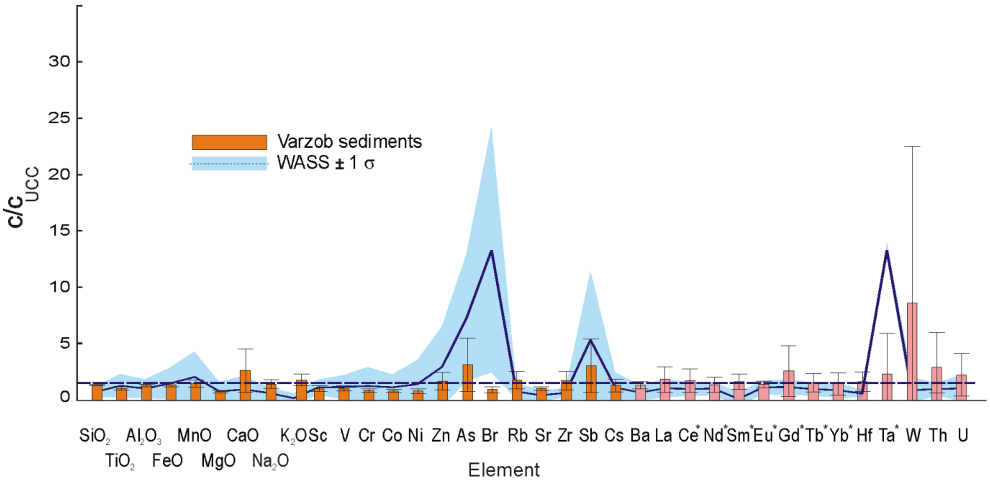

Fig. 2. Column chart illustrating the distribution of investigated elements as well as corresponding World Average Suspended Sediments (WASS) [27] data (mean ± St. Dev.) normalized to Upper Continental Crust (UCC) [26].

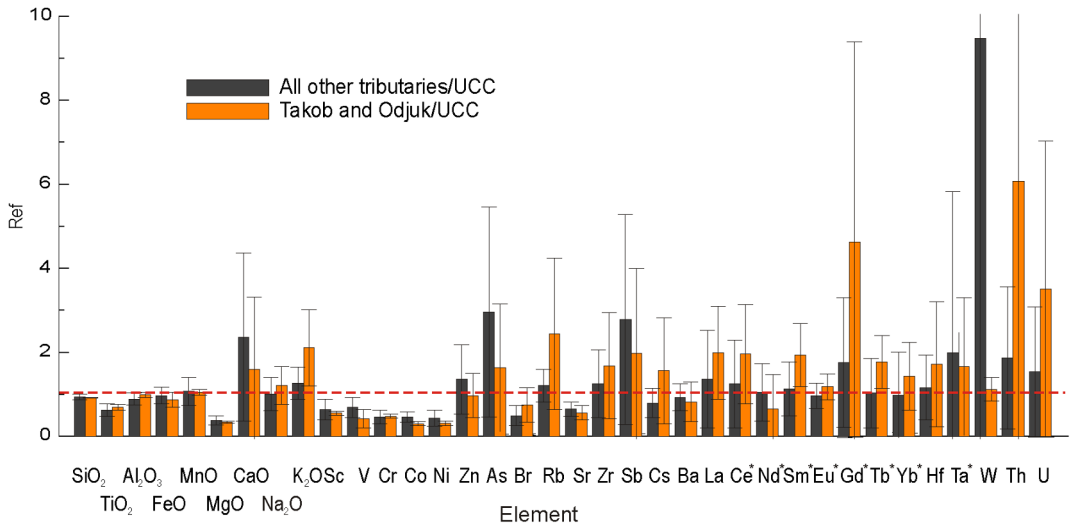

Fig. 3. Column chart illustrating the influence of pegmatite outcrop on the geochemistry of Varzob river sediments. The content ± St. Dev. of all elements are normalized to Upper Continental Crust (UCC) [26]. The increased content of As and Sb are due to the coal mine at the confluence of Ziddi, Maykhura and upper Varzob river, while the W peak reflects the presence of Maykhura tungsten deposit.

valleys, i.e. in immediately vicinity of pegmatite outcrop (see further discussion).

With the exception of K_2O and CaO, the other major elements showed contents slightly lower than the UCC one. One possible explanation could be related to the presence of limestone in the Hissar ridge as well as in the Ziddi and Maykhura river basins. Ca content decreases in southern tributaries through granitoids formations but again increases in the vicinity of Kharangon ridge where an important limestone quarry supplies raw material for the Dushanbe Cement Plant. It could also be remarked that, according to [30], the majority of Al and Ti enter into the Varzob river due to the washing of Ziddi kaolin outcrop, Takob granites and other aluminum and titan rich rocks of the upper Varzob gorge.

In the case of trace elements, it should be remarked a significant increased content of As whose presence can be identified in sediments collected in the vicinity of Ziddi, Maykhura (26.7 and 22.3 mg/kg, respectively) and especially of Varzob 1 confluence (36.6 mg/kg). Also its presence was observed on Varzob river downstream Varzob 3 and varzob 4 locations (20.6 and 23.6 mg/kg, respectively), where there are some industrial zones [26]. The most plausible explanation of this finding consists of the existence of a significant coal reservoir at the confluence of Ziddi, Maykhura and upper Varzob river (Fig. 1). A similar high content of Sb (between 1.0 and 3.0 mg/kg) was observed for the same triple junction.

Tungsten, whose content overpass the UCC one, was evidenced in sediments collected from Maykhura and Varzob 1, situated in the immediate vicinity of Maykhura tungsten deposit [30]. The same peculiarity was evidenced in sediments collected at Varzob 4 sampling point. Here, due to a significant reduced declivity and slow water flow, the suspended sediments containing W heavy minerals are deposited on the river bed (Fig. 3).

The influence of pegmatite deposits on the Varzob sediments can be evidenced also by the increased presence of REE La, Ce, Nd, Sm, Gd, and Yb as well as Hf together with natural radioactive Th and U whose content in sediments belonging to Takob, Objuk, Varzob 3 and Varzob 4 sampling points varied between 38 mg/kg for Gd and 119 mg/kg in the case of Th (Fig. 4) [26–28]. Moreover, we have noticed an increased Th/U ratio whose maximum value in the case of Takob, Odjuk and Varzob 3 samples reaches values of 11.3, 7.4 and 10.3 mg/kg respectively, higher then the 3.9 value for the UCC [28]. This peculiarity proves that in Odjuk and Takob pegmatite fields are significantly developed thorium mineralization (Fig. 3,4) [28].

Zirconium occurs in nature mainly as zirconium silicate by forming the mineral zircon, extremely resilient to abrasion due to its 7.5 hardness on Mohs scale. For this reason, Zr represents a good proxy for the sediments reprocessing. In this regard, the discriminating diagram Th/Sc vs. Zr/Sc (Fig. 5a) can be useful in estimating the degree of sediments recycling [9]. In our case, the majority of investigated sediment, excepting those collected in the vicinity of Odjuk pegmatite field, appeared less affected by sedimentary sorting and recycling, suggesting the predominance of a fresh sedimentary material [9].

The immobile or incompatible trace elements Sc, Zr, REE, Hf or Th can be used to trace the origin of sedimentary material [8]. In our case, the discriminating diagrams Th/Sc vs. Zr/Sc [8] , Sc-La-Th or La vs. Th [8] allowed evidencing the presence of two distinct fractions in the Varzob river sediments: one closer to the UCC which in the discriminating diagrams reproduced in Fig. 5a-d correspond to downstream collected sediments until the confluence with Sioma creek and the other one, collected upstream Sioma creek junction, significantly enriched in REE, Th and U, most probably due to the tributaries crossing the Odjuk pegmatite field (Table 2) [28].

Accordingly, as bi-plots reproduced in Fig. 5a and 5c prove, both Th/Sc to Zr/Sc as well as La to Th ratios presented values closed to UCC ones for the Varzob sediments collected up to Sioma confluence while, the same ratios were significantly higher downstream this point (Fig. 5a and 5c - insets). In our opinion, this finding favors the hypothesis of the contribution of the pegmatite material to final Varzob sedimentary material. Moreover, the La/Th vs. Hf [31] discriminating diagrams suggests once more the felsic origin of Varzob sedimentary material, including the Odjuk pegmatite whose increased content in zircon explains the enhanced content in U and Th (Table 2).

As previously mentioned, the second main aim of this study was the assessment of the presence of possible contaminants elements in Varzob river sediments. In this regard we have considered only those elements whose content, in the absence of a set of National Regulations, are considered as contaminant by the National Regulation of neighboring Russian Federation [32] as well as Romania, an EU member [33], i.e. V, Cr, Mn, Co, Ni, Zn, As, Sb and Ba.

To evidence the possible sources of anthropogenic or natural contamination, we have calculated the corresponding matrix of the Spearmans' correlation coefficients (Table 3). As the data reproduced in Table 3 confirm, we have noticed that As significantly correlates with Sb and Ni which suggests a common source [34]. The significantly positive correlations V-Co (ρ = 0.722), V-Ni (ρ = 0.743) and V-Zn

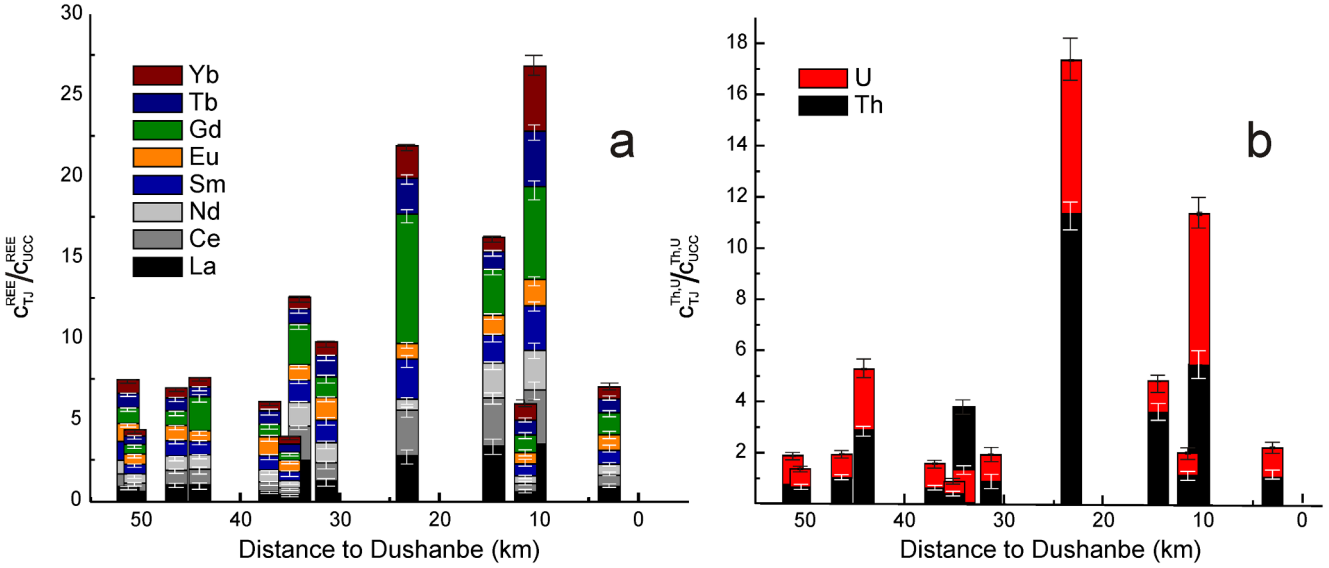

Fig. 4. Two bar-diagrams illustrating the content of REE (a) as well as Th and U (b) normalized to Upper Continental Crust (UCC) [26].

(ρ = 0.702) suggest also that these metals are redistributed in the surface sediments by the same processes or had a similar source.

To estimate the degree of contamination, we have use the indices most frequently reported in literature, i.e. Geoaccumulation index (I_{geo}) [35], Contamination factor (*CF*) [36] and Pollution Load Index (*PLI*) [37].

According to [33–35], for a given element *i* the I_{geo} is defined as:

$$I_{geo} = \log \frac{c_i}{1.5B_i} \quad (1)$$

where c_i is the content of the element *n* in investigated medium and B_i is the geochemical background content of the same element in a reference medium, in our case the UCC [26]. The factor 1.5 is used to compensate possible fluctuations which could be attributed to lithological variations of the sediment composition. A zero on negative value of I_{geo} could be interpreted as the absence of any contamination.

In the case of Varzob sediments, we have noticed for the I_{geo} positive values lower than 2 only for As, Zn and Sb, and restricted to few places such as Ziddi, Maykhura and Varzob 1 (Fig. 5). For As, a value of 2 signifies minor to moderate contamination [35], and by taking into account their location, the uncontrolled waste discharge from coal mining in Ziddi and Maykhura could be the main source of episodic pollution.

Almost similar to I_{geo}, index there is the contamination factor *CF* proposed by Hakanson [36]

$$CF_i = \frac{c_i}{B_i} \quad (2)$$

where c_i and B_i have the same signification as in the case of I_{geo}. According to [34–36], a *CF* less than one shows no contamination, a *CF* between 1 and 3 indicates a moderate contamination, between 3 and 6 a considerable contamination which for a *CF* greater than 6 is considered very high.

As in the case of I_{geo}, the *CF* presented increased values slightly exceeding six only in the case of As and Sb for the same Ziddi, Maykhura and Varzob 1 locations, which according to [36], indicates a very high contamination too (Fig. 6a). Here, the observed discrepancy between the level of contamination assessed by I_{geo} and *CF* could be explained by the absence of some unitary criteria to characterize the contamination level.

The *PLI* [37] was the last index we have used to characterize the Varzob valley environment. With respect to I_{geo} and *CF*, the *PLI* provides a global information concerning the local contamination. Hence the *PLI* for a number of *n* contaminants is defined as the geometric mean of the individual *CF*:

$$PLI = \sqrt[n]{\prod_{i-1}^{n} CI_i}$$

where CF_i refers to the *i*-th element. By following the recommendations provided in [32–34] the environment could be interpreted as polluted if $PLI \geq 1$ and as unpolluted if $PLI < 1$.

In our case, the final results concerning the distribution of the *PLI* along the Varzob valley show values ranging from 0.60 to 1.55 with an average value 0.98 (Fig. 6b). Higher than unity values were observed either in the vicinity of coal mining and W outcrop, i.e. Ziddi, Maykhura and Varzob 1 sampling points as well as at the confluences of Varzob river with tributaries crossing the Odjuk pegmatite field.

On this subject it should be remarked that the *PLI* at the Varzob 4 sampling point located in the immediate vicinity of Dushanbe city was of 0.76, which prove a negligible influence of the anthropogenic contamination.

6. Conclusions

The Epithermal Neutron Activation Analysis was used to determine the content of 35 major and trace elements in 13 samples of surface sediments collected from Varzob River. For a better assessment of the environmental situation, all experimental data were compared with corresponding ones of the Upper Continental Crust (UCC) and Average World Suspended Sediment (AWSS).

With some exceptions, the elemental content of sediments was closer to the UCC than to AWSS one which enabled us to consider the UCC as the most appropriate reference.

A more detailed analysis revealed a felsic origin of sedimentary material locally enriched in As, Sb and W. We explained this finding by the presence of a tungsten deposit and coal mining in the Varzob superior valley. In the case of Gd, Th and U, the most probable explanation considers the Odjuk pegmatite field as the main source the Takob tributary as carriers.

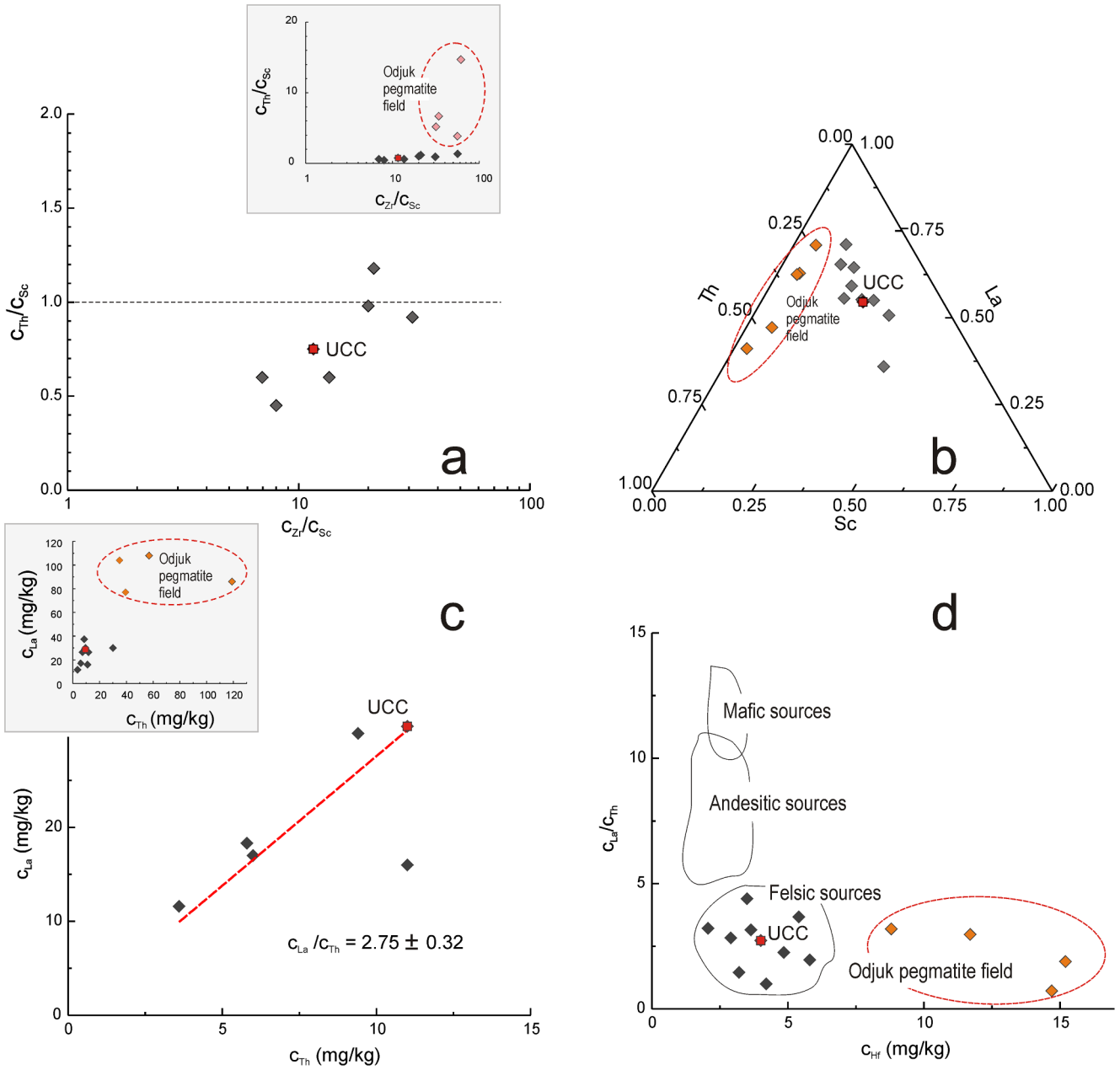

Fig. 5. Discriminating diagrams Th/Sc vs. Zr/Sc (a), Sc-La-Th (b), La vs. Th [8] (c) and La/Th vs. Hf [9] illustrating the influence of Odjuk pegmatite field on the Varzob river sediments. It can be remarked that the points corresponding to the samples not influenced by the Odjuk pegmatite are very close to Upper Continental Crust (UCC) [26].

Table 3
Matrix of the Spearman's correlation coefficient of presumed contaminant elements (in bold correlation coefficients at $p < 0.05$).

	V	Cr	Mn	Co	Ni	Zn	As	Sb
Cr	0.40							
Mn	0.31	0.36						
Co	**0.72**	**0.62**	0.15					
Ni	**0.74**	0.35	0.30	0.27				
Zn	**0.70**	0.11	**0.53**	0.22	**0.63**			
As	**0.46**	0.35	0.21	0.06	**0.74**	0.42		
Sb	0.31	0. 33	0.13	−0.01	**0.68**	0.20	**0.91**	
Ba	−0.08	**−0.59**	**−0.56**	−0.08	−0.31	−0.21	−0.24	−0.29

The contamination status of toxic elements V, Cr, Mn, Co, Ni, Zn, As, Sb and Ba was assessed based on Geoaccumulation index I_{geo} and Contamination Factor *CF*. Higher As and Sb I_{geo} values suggest a moderate contamination of surface sediment mainly upstream Varzob river. Most probably this particularity could be related to the coal mining and storage. In other sampling points along the Varzob river, a significant accumulation of these toxicants was not evidenced.

CRediT authorship contribution statement

Daler Abdusamadzoda: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Funding acquisition. **Djamshed A. Abdushukurov:** Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing, Visualization, Funding acquisition. **Inga Zinicovscaia:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing,

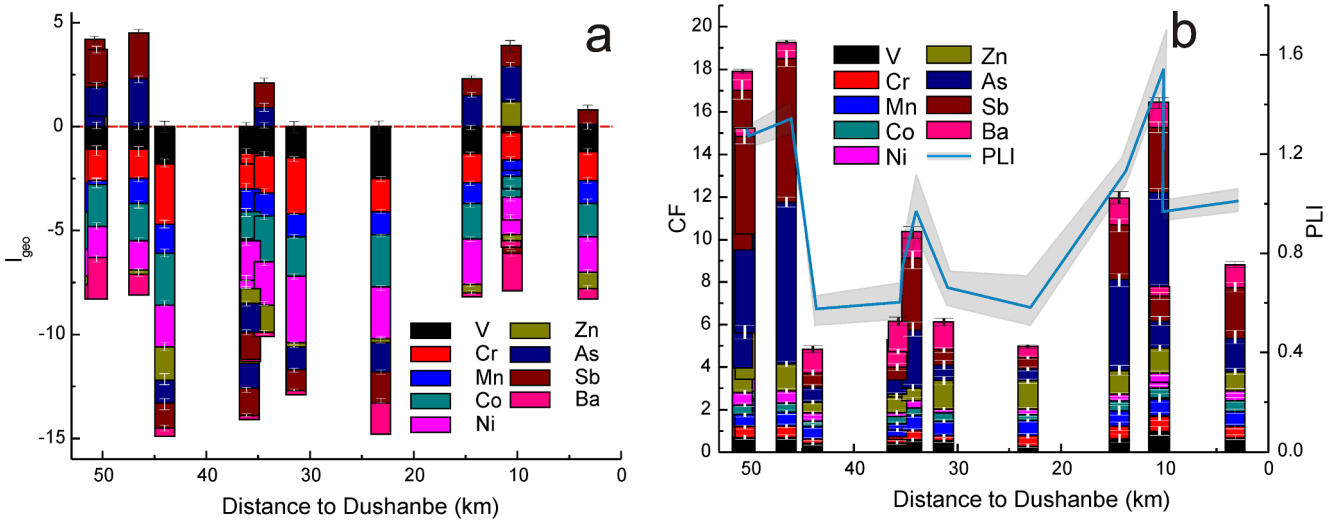

Fig. 6. The distribution of the Geoaccumulation index (a) as well as of the Contamination Factor *CF* and the corresponding Pollution Load Index *PLI* (b) of V, Cr, Mn, Ni, Zn, As, Sb and Ba considered as contaminating elements along the Varzob valley. The gray strip around PLI signifies ond St.Dev.

Visualization, Funding acquisition. **Octavian G. Duliu:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Konstantin N. Vergel:** Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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