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Uranium and thorium leachability in contaminated stream sediments from a uranium minesite

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ABSTRACT

The leachability and potential environmental risks of uranium (U) and thorium (Th) in aquifer sediments from a recent uranium minesite of northern Guangdong Province, China were investigated as part of ongoing environmental investigations. Data for the non-mineralogical portion of U, Th and of additional major elements (Mn, Fe, Ca, Mg, Na, Al and K) using a 0.5 mol/L HCl partial leach and inductively coupled plasma optical emission spectrometry (ICP-OES) were presented for the contaminated sediments and a background sediment. The contaminated sediments reported leachable contents of U between 22.85 and 2700 μg/g and those of Th between 4.800 and 102.1 μg/g, which exceed by a few to several hundred times the respective content found in the background. Generally, the leachable U and Th contents in the stream sediments decrease with distance from the potential contamination sources. A special case is the runoff gathering reservoir located around 1 km downstream of the U mine-site, representing the most severe metal contamination hotspot within the alpine watershed, where the highest leachable content of U and Th in the inlet sediment was observed. The highest leachability of U (68.6%) and Th (44.8%) was observed in this sediment as well, indicating a high potential of bioaccumulation and bioconcentration of U and Th under changing geochemical conditions. Correlations analysis indicates that the dilute HCl leachable fraction of U and Th bound in the sediments are strongly dependent on anthropogenic inputs from the U mining/milling activities, and Ca salts are the main vectors.

1. Introduction

Uranium (U) is a naturally occurring element, both chemically and radiologically toxic (Oughton et al., 2013), with an average abundance of 2–4 μg/g in the Earth's crust (Franz, 2009; Hu et al., 2010). It occurs with more concentrated amounts in rock formations which could be mined. In recent decades, the U mining and milling activities in China has been greatly enhanced due to escalated demands for nuclear energy. Extensive environmental degradation has resulted from these mining and milling operations (Shuai et al., 2001; Hu et al., 2010). The U ore and its associated tailings were exposed to the surface where weathering readily occurred, thereby liberating U and other potentially toxic metals to the environment at rates surpassing those typically observed in nature (Chen et al., 1999; Shuai et al., 2001; Hu et al., 2010). Meanwhile, large amounts of U waste-rock piles, dumps and wastewater have been generated and disposed randomly, facilitating massive release and widespread migration of U and other potentially toxic metals in the aquatic environment (Rios-Arana et al., 2004; Liu et al., 2015), leaving behind a persistent legacy of environmental degradation and contamination (Wu et al., 2005; Varol, 2011; Wang et al., 2012b).

In a rural district of Northern Guangdong Province, China, uranium was initially discovered in the 1950s, owing to a gamma radiation project for screening airborne radiation anomalies conducted by the Nanling Belt Geology Brigade (Franz, 2009; Davutluoglu et al., 2011). About fifteen medium-sized intragranitic deposits of U have been identified and intermittently mined in open pits, with little consideration for erosion controls in past decades. Operational U-bearing wastes, such as U-mill tailings, spent acids, mine wastewater and dumps were disposed and deposited at unlined ponds. Observable red spoil mud and lower grade ores were scattered over this area and left to more rapid weathering processes. Previous radiometric studies uncovered that significant elevation of gamma-activities emanated from the uranium

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decay series in these operational wastes, posing a serious threat to the surrounding eco-system (Wang et al., 2005; Zhang and Xian, 2007; Zhang et al., 2008). The emission and exposure of radionuclides and other potentially toxic metals to nearby habitats might also be possible due to the seepage of tailings and mine waters into local streams and alpine watersheds. However, only in relatively recent years, have concerns been voiced over the risks of environmental degradation and contamination in this area (Zhang et al., 2008; Wang et al., 2012a; Liu et al., 2015). In our preliminary survey, an obvious pollution of U and Mn in the water samples, and an evident enrichment of U in the sediments from a recipient stream near the metallurgy site were found (Wang et al., 2012a; Liu et al., 2015).

Sediment, composed of loose sand, clay, silt and other soil particles that precipitate at the bottom of the body of water, provides the best natural records of metal contaminations and relevant environmental changes (Abdel-Baki et al., 2013). It plays a critical role not only as a sink and carrier of pollutants, but also a possible secondary source of the pollutants. Specifically, the bioassimilation and bioaccumulation of metals may occur in the aquatic organisms due to the resuspension of sediment in the water column (Rios-Arana et al., 2004). However, it is increasingly recognized that total-element contents analysis is not sufficient to describe the geochemical behavior and potential environmental impact of a specific element (Kumar et al., 2011). From an exhaustive literature survey, a partial digestion procedure using dilute hydrochloric acid (HCl) is a fast, simple and useful technique for understanding the geochemical behavior and assessing the potential bioavailability and environmental risks of an element (Martins et al., 2013). The method of dilute HCl leach could be used because it approximates the bioavailable portion and determines labile forms of some metals typically in sediments or soils (Luoma and Bryan, 1982). To be specific, the dilute HCl can extract water soluble, exchangeable, carbonate, and a part of oxide fractions in the soil (Adriano, 1986), and minimally affect the silicate (residual) sediment matrix (Chester and Voutsinou, 1981; Sutherland and Tolosa, 2000).

As a part of on-going research on environmental assessment, the objectives of this work were to (1) quantify the level of U and Th in the leachable fraction of the sediments; and (2) identify possible migration and dispersion pathways of U and Th in the watershed surrounding the U mining and milling site.

2. Materials and methods

2.1. Site description

The sampling sites in the study were near a large uranium ore field, located in the eastern portion of Guidong Granite Massif (Guangdong Province, China), where fifteen intragranitic uranium deposits were identified. The polyphase granitic Guidong Massif is estimated to hold a length of 68 km, a width of 12–18 km, and cover 1000 km^2 at the intersection of the Cathaysian fold system with the Hunan–Guangxi fold system. It contains mostly granitic terrane with peripheral Paleozoic metasedimentary terranes as well as several intermontane Mesozoic basins (Franz, 2009). The occurrences of U were found to be mainly associated with diabase dikes and silicified fracture zones. Host rocks include various granites and intermediate to mafic dikes, with medium-grained, porphyritic two-mica granite in the Xiazhuang intrusion. The two-mica granite is composed of 25.3% felsic plagioclase, 32.9% microcline, 33.5% quartz, 4.8% biotite and 3.5% muscovite, with accessory minerals of apatite, zircon, pyrite, tourmaline, ilmenite and uraninite. The uraninite occurs as interfranular grains between and within the rock-forming minerals. The mean tenors of U range from 5 to 13 μg/g in different strata (Franz, 2009).

The district, where the ore field is situated, hosts about 50,000 people, partially scattered over the area or living in small villages (Zhang and Xian, 2007). The climate is subtropical–monsoonal with an average precipitation of 1600 mm/year and mean temperature ranging from 14 to 29 °C in a year (Chen et al., 1999; Zhang et al., 2008). The U mining and milling site is dusty and covered with rare vegetation, but croplands, paddies and some vegetables were observed along the bank of the downgradient streams. As shown in Fig. 1, our studied aquifer systems include a recipient stream, which flows through tailings footprints and directly collects various discharge effluent and tailings seepage (stream 2), an unaffected natural stream (stream 3), which shares a common granitic geological environment with stream 2, and a reservoir where the streams converge.

2.2. Sample collection and processing

Surface sediment samples were collected from the bottom of the waters in the studied aquifer systems. Among them, eight samples were collected along stream 2, as shown in Fig. 1, from the contamination sources to the reservoir (W1, W2, W12, W13, W14, W15, W16 and W17) and one from stream 3 above the stream confluences (W19). Sediment samples were gained by mixing several cores, which were collected by using a self-made sediment core sampler (inner diameter of 5 cm and length of 50 cm). For comparison and better understanding, a representative powdered uranium ore sample (UO), a uranium tailing sample (UT) and a tailing mud (TM) were gathered accordingly in the mining and milling site. All samples were assembled in plastic bags immediately after sampling and kept at −4 °C prior to laboratory analysis, then they were dried in an oven at 50 °C for 48 h, ground using an agate mortar and finally sieved to a size less than 100 μm. The detailed information of the samples was illustrated by Liu et al. (2015).

2.3. Partial leach of sediment by dilute HCl

In order to assess the leachable fraction and the environmental impact of the solid samples, single-step extraction schemes using dilute hydrochloric acid (HCl) were applied (Chester and Voutsinou, 1981; Sutherland et al., 2001). This involved shaking 1 g of each sample with 20 mL of 0.5 mol/L HCl for 1 h under room temperature. The systems were subsequently centrifuged at 4000 rpm for 20 min, and aliquots of the supernatant were taken for analysis on inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 7000 DV, PerkinElmer Inc., Waltham, USA).

3. Results and discussion

3.1. Spatial distribution of U and Th in the sediments

Table 1 presented extractable contents of U, Th and additional elements (Mn, Fe, Ca, Mg, Na, Al and K) in the source materials, near-source sediments in and around the wastewater storage pond, sediments from the discharged stream channel of mine wastes (stream 2), the background stream sideward (stream 3), and the runoff gathering reservoir where all streams converged. It is not surprising to find an extremely high content of leachable U (7760 μg/g) and Th (194.7 μg/g) in the original uranium ore (UO) from the mine pit. Tailing mud (TM) showed around four times higher content of leachable U (1943 μg/g) as well as Th (37.6 μg/g) than the dry tailing (UT). One possible reason is that tailing mud is composed of fine particles washed out from the dry tailing. In the near-source area, the sediment from the wastewater storage pond (W1) presented leachable U content as high as 246.6 μg/g, exceeding more than 35 times the background leachable content (W19, 6.900 μg/g). A comparatively high level of leachable Th (60.65 μg/g) was observed in this sediment (W1), which amounts to thirty times the background (W19, 2.050 μg/g). The sediment under the pipelined effluent (W2) retained relatively low content of leachable U (92.3 μg/g) and Th (29.8 μg/g).

Leachable content of U and Th in different sediment samples from stream 2, the background stream sideward (stream 3), and the reservoir varied as much as several orders of magnitude (shown in Table 1); all

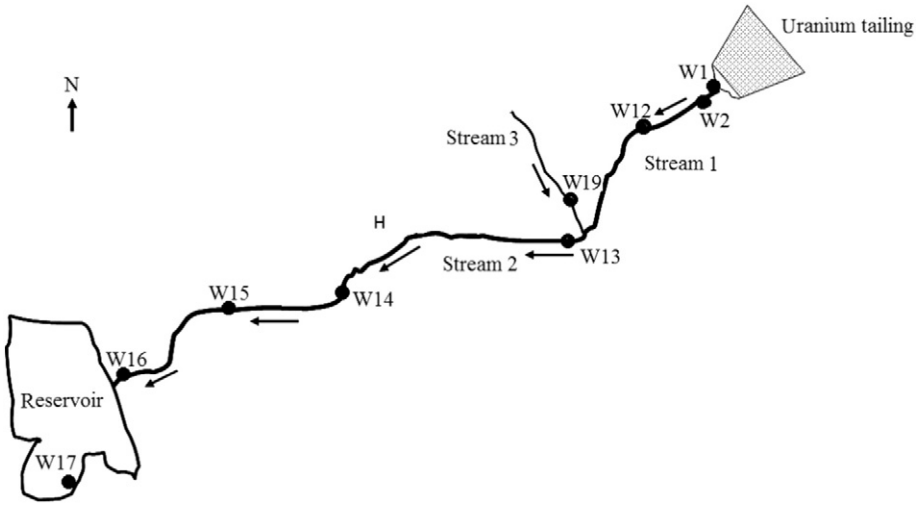

Fig. 1. Schematic display of sampling sites.

surface sediments from stream 2 and the reservoir exhibited significantly higher leachable content of U and Th than the background (W19). As expected, the background sediment from stream 3 presented low content of leachable U and Th. The total contents of U and Th in the corresponding sediment samples were given as well in Table 1 for comparison. As previously reported, an obviously inverse relationship was observed between the concentrations of U and Th in water samples from stream 2 and the distance from potential pollution sources (Wang et al., 2012a). A similar trend was generally found for leachable U and Th contents in the corresponding sediments (Table 1 and Fig. 2). However, a special case was found in the sediment collected from the inlet of the reservoir (W16), where the highest content of leachable U (2700 μg/g) and Th (102.1 μg/g) occurred, corresponding to the highest total U (3935 μg/g) and Th (227.8 μg/g) contents (Liu et al., 2015). The unexpected extremely high enrichment of U and Th discovered might be ascribed to occasional accumulation of U/Th-bearing waste material during events of tailing-dam failure or flooding. Alternatively, the reservoir inlet lies in the position lower than the streambed, thereby acting like an accumulation area of the contaminants. Leachable contents of U and Th dropped to 190.1 μg/g and 10.35 μg/g, respectively, in the surface sediment gathered from the down-gradient of the reservoir. The reduction of contaminants may be due to the dilution effects by sediments deposited before mining activities.

Due to the worldwide lack of environmental quality guidelines for sediment relative to water and soil, these results were compared with the recommended PNEC (predicted no-effect concentrations) value of 100 μg/g for sediment (Sheppard et al., 2005). It is evident, as exhibited in Table 1, that leachable U contents in most studied sediments slightly or highly exceeded the recommended value. The croplands around the aquifer system that received the sediments for landfill and plant nutrition might be at a risk of U pollution. High enrichment of U in the sediments might also release excessive U to the groundwater, exacerbating the local water quality and endangering the ecosystem.

3.2. Leachability of U and Th in the sediments

The leachability of U, Th and the analyzed elements were shown in Table 2 and summarized in Fig. 3. The source materials such as uranium ore, uranium tailing and tailing mud exhibited high extractability of U and Th, amounting to an average of 60% and 40%, respectively. The background sediment (W19), bearing low abundance of U and Th, showed relatively high leachability of U (39.7%), as well as Th (22.4%). The average leachability of U and Th in the contaminated sediments was found to be at a level similar to the background sediment. However, the sediment from the inlet of the reservoir (W16), displayed significantly higher leachability of U and Th, with 68.6% and 44.8%, respectively. The leachability of Mn, Fe, Ca and Mg in this sediment also reached around or even exceeded 50%. But the extractabilities of Na, Al and K were considerably lower, which were less than 10%. Therefore, U and Th in this sample may be predominantly adsorbed on or occluded in oxides of Fe or Mn and new precipitates of Ca and Mg. Apart from this, high partial leach percentages are environmentally relevant since U and Th associated in this fraction might experience bioaccumulation and bioconcentration under changing geochemical conditions. For the sediments from stream 2, the leachability of U, Th, Mn, Fe and Ca generally decreased from the source area to the downgradient zone.

Table 1
Extractable U, Th and other major elements by 0.5 mol/L HCl partial leach.

		U (total[a]), μg/g		Th (total), μg/g		Mn, μg/g	Ca (%)	Fe (%)	Mg (%)	Na (%)	Al (%)	K (%)
Source materials	UO	7760	(8472)	194.7	(466.0)	335.0	2.207	0.565	0.065	0.017	1.362	0.457
	UT	473	(546.7)	8.150	(17.70)	202.5	0.436	0.824	0.261	0.032	0.553	0.314
	TM	1943	(3440)	37.55	(98.32)	402.5	0.568	3.402	0.457	0.108	0.962	0.320
Near-source sediments	W1	246.6	(763.0)	60.65	(222.1)	245.0	0.054	2.807	0.038	0.046	0.615	0.258
	W2	92.30	(351.2)	29.80	(107.5)	422.5	0.055	1.338	0.045	0.057	0.488	0.274
Recipient stream sediments	W12	159.2	(422.6)	18.25	(71.41)	467.5	0.101	1.224	0.240	0.077	1.864	0.605
	W13	54.50	(183.8)	4.450	(41.15)	280.0	0.072	0.462	0.075	0.052	1.300	0.550
	W14	51.90	(209.5)	7.500	(37.73)	300.0	0.055	0.439	0.101	0.018	0.515	0.279
	W15	22.85	(154.8)	4.800	(50.96)	277.5	0.014	0.224	0.036	0.013	0.304	0.266
Reservoir sediments	W16	2700	(3935)	102.1	(227.8)	840.0	1.052	1.421	0.402	0.019	0.715	0.288
	W17	190.1	(477.8)	10.35	(97.74)	627.5	0.088	1.213	0.098	0.013	1.103	0.278
Background sediment	W19	6.90	(17.40)	2.050	(9.150)	177.5	0.017	0.190	0.023	0.009	0.403	0.267

[a] The comparable data on total contents of U and Th are cited from Liu et al. (2015).

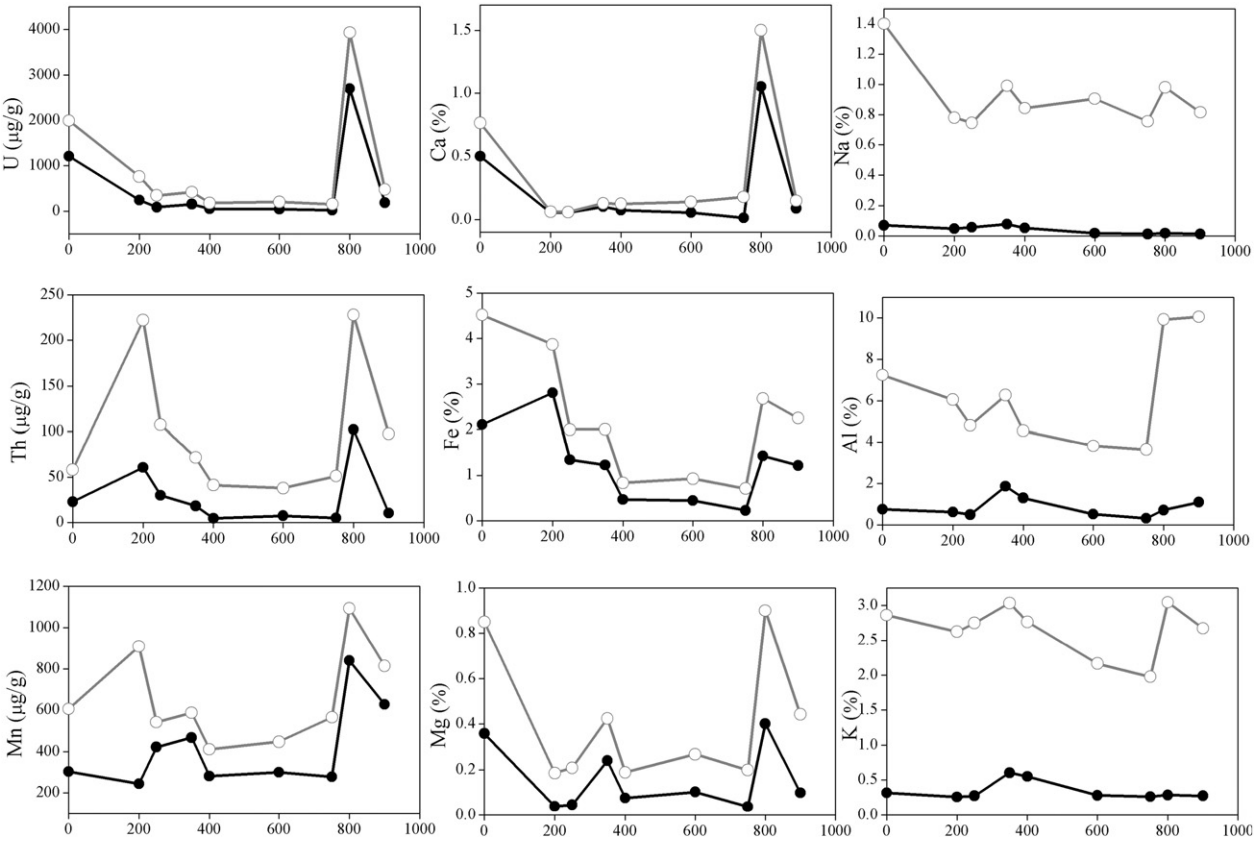

Fig. 2. Variation of total (open circles) and leachable contents (solid circles) of metals in the sediments versus distance from the uranium tailing site.

As shown in Fig. 3, the average leachability of metals in the sediments from stream 2 decreased in the order of Mn (65.3%), Ca (62.1%), Fe (55.3%), U (34.2%), Mg (32.7%), Th (22.0%), Al (14.8%), K (13.2%) and Na (4.4%). Generally, metals are transported in the aquifer system either as dissolved species from geochemical weathering of the source material, or by physical transport of materials bearing adsorbed metals. The differences in the spatial distribution of metals' leachability may be explained by their own physico-chemical characteristics and intricate geochemical and hydrogeological interactions that occurred between the sediments, surface water, ground water and biological systems. The two elements (U and Mn) suggested to be primarily related with anthropogenic inputs from U mining activities have overall high extractable percentages, which coincided with high extractabilities of Ca, Fe and Mg. An explanation for this may be that metals from anthropogenic origins are likely to form new precipitates with Ca, Fe and Mg and adsorbed on their associated minerals in surface coatings of sediments. Besides, the high ratio of extractability suggests that the sediments are vulnerable to releasing these elements when they are subjected to acidity, whether in contact with acid rain or acid mine water. Usually in a natural environment, Th occurred predominantly as a sparingly soluble oxide (ThO_2). The moderately high extractability of Th found in our studied sediments, however, indicates that they may also have the potential to remobilize Th to the aquatic phase and the surrounding eco-system.

Table 2
The ratio of extractability of U, Th and other major elements in the sediments.

	U (%)	Th (%)	Mn (%)	Ca (%)	Fe (%)	Mg (%)	Na (%)	Al (%)	K (%)
UO	96.3	41.8	54.9	85.7	40.8	23.3	2.5	24.7	20.1
UT	86.4	46.0	50.3	66.6	40.5	45.7	1.9	8.0	9.6
TM	56.5	38.2	49.6	65.0	48.6	40.4	9.6	12.8	13.1
W1	32.3	27.3	26.9	87.9	72.5	20.7	5.9	10.2	9.8
W2	26.3	27.7	77.9	93.7	67.0	21.5	7.7	10.2	10.0
W12	37.7	25.6	79.6	79.6	60.9	56.4	7.8	29.7	19.9
W13	29.7	10.8	68.0	58.8	55.8	39.9	6.1	28.6	19.9
W14	24.8	19.9	67.1	39.7	47.5	37.6	2.0	13.5	12.9
W15	14.8	9.4	49.0	7.7	31.7	18.4	1.8	8.4	13.5
W16	68.6	44.8	76.8	70.1	53.0	44.6	1.9	7.2	9.5
W17	39.8	10.6	77.0	59.1	53.8	22.1	1.6	11.0	10.4
W19	39.7	22.4	67.6	69.7	37.3	24.4	3.9	11.1	11.9
Aver	34.2	22.0	65.3	62.1	55.3	32.7	4.4	14.8	13.2
SD	14.9	11.2	17.3	26.3	11.7	13.1	2.6	8.4	4.1
Min	14.8	9.4	26.9	7.7	31.7	18.4	1.6	7.2	9.5
Max	68.6	44.8	79.6	93.7	72.5	56.4	7.8	29.7	19.9

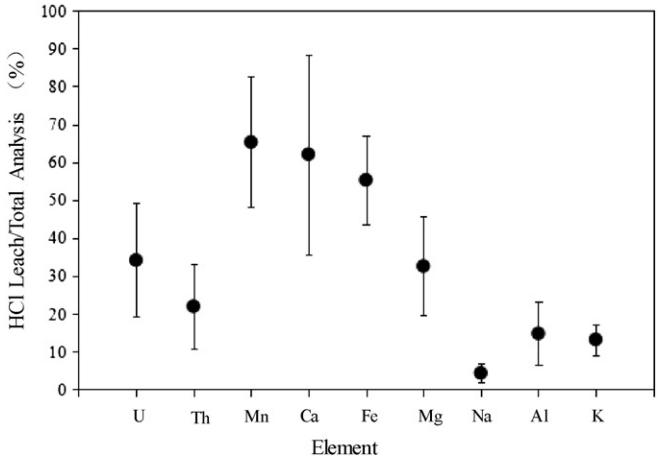

Fig. 3. Percentage of extractable metals from the recipient stream sediments. The solid circles represent the average value and the error bars show the standard deviation.

3.3. Fate and transport processes using multivariate analysis

It is well known that metals in sediments usually involve complicated interrelationships. Numerous factors may control their relative abundances, such as various anthropogenic and natural sources, and different processes of sediment formation. For the weak acid leachable contents, as displayed in Table 3, U was highly positively correlated with Th (0.867) and Ca (0.869) at $P < 0.01$; while Th was positively correlated with Ca (0.644) at $P < 0.05$ and Fe (0.755) at $P < 0.01$. Moderately positive correlations at $P < 0.01$ also occurred between the elemental pairs of Fe–Na (0.697) and Al–K (0.790). These significantly positive correlations between the leachable contents of U, Th and Ca by 0.5 mol/L HCl suggest that these metals may come from an identical source and encounter similar transport behavior. Besides, this result could be used to explain the high positive correlations between U and Th that occurred in the stream water, as reported previously (Wang et al., 2012a).

In order to better identify the transport pathways and mechanism of the metals, principal component analysis (PCA) was then applied to the whole dataset by applying Varimax rotation with Kaiser normalization (Cai et al., 2012). As shown in Table 4, three principle components, whose eigenvalues were higher than one, have been extracted, representing 82.4% of the cumulative variance. The first factor represents 33.9% of the total variance, which is strongly associated with U, Th and Ca. The second factor accounts for 25.6% of the total variance and is found to be dominated by Fe, Mg, Na and Mn. The third factor, predominantly loaded in K and Al, explains 23.0% of the total variance. Generally, the results of principal component analysis and correlation analysis coincided with each other.

Noting that the main source of U is from the uranium metallurgy wastes, we infer that the first factor loaded mainly in U, Th and Ca, could be basically explained as anthropogenic contribution. As shown in Fig. 3, these elements generally exhibited relatively high HCl extractability from the studied sediments, further confirming that they mainly originated from anthropogenic activities, since anthropogenic metals usually have high HCl leachability. Besides, high associations of Ca with the first factor, further indicates that these metals may be dominantly retained by calcium salts (e.g. carbonates, phosphates) in the sediments. It is well known that metals from anthropogenic sources are likely to form new precipitates with Ca and adsorbed on the surface coatings of sediments. In addition, as suggested by mineral composition analysis from XRD, precipitation of uranophane ($Ca[UO_2(SiO_3OH)]_2 \cdot 5H_2O$) was found in W16, the sediment with the highest content and leachability of U. Therewith, the leaching behavior of U and Th in the sediments might be dominantly controlled by anthropogenic contribution, following the process of deposition and dissolution along with calcium salts, which is quite different from the study that aluminum salt dominated clay minerals are the main transporters or vectors of such anthropogenic elements in the sediments (Chen et al., 2014). The second factor mainly loaded in Fe, Mg, Na and Mn, may be explained as geochemical processes related with dissolution and deposition of secondary Fe/Mn-(hydr)oxides. The third factor loaded primarily in K and Al, which usually come from parental rocks and primary minerals and exhibited comparatively low HCl extractability, can be suggested as a natural weathering process. It is worthy to note that the first factor explains the majority of the total variance, indicating a significant environmental impact of the uranium metallurgy wastes on the surrounding aquatic system.

Table 3
Spearmann correlation relationships between U, Th and other studied elements.

	U	Th	Mn	Ca	Fe	Mg	Na	Al	K
U	1								
Th	0.867**	1							
Mn	0.42	0.531	1						
Ca	0.869**	0.644*	0.536	1					
Fe	0.678*	0.755**	0.517	0.455	1				
Mg	0.587*	0.35	0.524	0.757**	0.524	1			
Na	0.312	0.34	0.284	0.319	0.697*	0.515	1		
Al	0.566	0.434	0.503	0.704*	0.364	0.476	0.399	1	
K	0.392	0.154	0.357	0.736**	0.112	0.636*	0.48	0.790**	1

Table footnotes show levels of significance.
* $P < 0.05$.
** $P < 0.01$.

Table 4
Principal component analysis (PCA) of the elements in the sediments.

	Component		
	1	2	3
Ca	**0.974**[a]	0.062	0.12
U	**0.965**	0.029	0.152
Th	**0.956**	0.083	0.073
Fe	−0.046	**0.888**	−0.051
Mg	0.158	**0.831**	0.073
Na	−0.255	**0.727**	0.475
Mn	0.328	0.498	−0.044
K	0.098	−0.079	**0.978**
Al	0.222	0.172	**0.912**
Percent of variance (%)	33.9	25.6	23.0
Cumulative loading (%)	33.9	59.5	82.4

[a] Number in bold represents mainly composed metals in each principal component.

4. Conclusions

This project was one part of an ongoing project for evaluation of environmental impacts stemming from uranium mining and metallurgy activities in a rural country of Guangdong Province, China. The leachability of radioactive elements (U and Th) in combination with some major elements (Mn, Fe, Ca, Mg, Na, Al and K) in the sediments is essential for predicting their mobility and bioavailability. The leachable contents of the studied elements by 0.5 mol/L HCl partial leach exhibited notable fluctuations across the recipient stream from the metal loading sources towards the reservoir confluence, with the maximum value found at the most distal points. The contaminated sediments exhibited leachable contents of U ranging from 22.85 to 2700 μg/g, which slightly or highly exceeded the recommended value of 100 μg/g. The relatively high leachability of U, with a mean value of 34.2%, suggests that the croplands, groundwater and even the ecosystem nearby might be at a risk of U pollution. Spearman correlation analysis suggests that the non-mineralogical U and Th bound in the sediments are predominantly associated with anthropogenic inputs from the U minesite and carried by Ca salts, which are vulnerable to bioaccumulation and bioconcentration under changing geo-environmental conditions. Therefore, it is high time to further investigate the status of U and Th contents in the food crops growing around the mining/milling area and their implications for human health. Besides, appropriate measures should be implemented to strictly supervise and prevent further contamination of U and Th in this area.

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