

Article

Distribution of Uranium and Molybdenum in River Sediment near Molybdenite Mining Region: A Case Study in SW China

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Abstract: This work aims to understand the distribution and migration mechanisms of U and Mo between surface sediment and water in acid mine drainage (AMD) regions near a molybdenum mining region. A series of river sediment and water samples near the Jinduicheng mining area, one of the largest deposits of molybdenite ore in Asia, were collected and analyzed. Our results indicate that: (1) The pH value of river water samples increases with distance from upstream to downstream, while the pH has poor correlation with Mo and U; (2) The content of Mo and U in the sediment are significantly higher than the background value, which suggests potential pollution; (3) The content of Mo and U in the water and sediments in the lower reaches of the Wenyu river is significantly linearly related with the distance from the mining area, suggesting that AMD is a potential source; (4) BCR analysis shows that Mo in river sediments mainly existed as the residual, while U mainly existed as the non-residual; (5) The distribution coefficient $K_d(\text{Mo})$ exceeds $K_d(\text{U})$, indicating that Mo is enriched in sediments while U is more prone to porewater.

Keywords: surface waters; distribution; enrichment of molybdenum; porewater; sediment



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1. Introduction

The distribution between sediment and its surface water largely controls the enrichment characteristics and migration direction in the aquatic environment [1–4]. The geochemical distribution involves processes including adsorption–desorption, dissolution–precipitation, and ion exchange. The sediment acts not only as a sink for potentially toxic elements in the water but also as a source for the release of metals [5]. The potentially toxic elements migrated into the sediments will be released if there is a significant change in the physical–chemical properties of the overlying water, e.g., pH [3,6] and redox potential [7].

The Jinduicheng molybdenite ore is the second largest Mo deposit in Asia [8]. Long-term open-pit mining, accumulation and transportation of ore, and rain erosion can lead to a migration of main and trace elements from ore to aquatic sediment and soil [9–13]. The magmatic rocks in the Jinduicheng mining area are well developed, mainly acidic rocks like those of the granite porphyry series. There are extensive studies reporting the heavy metal pollution of different types of metal mines [14,15], while the distribution of these metals in molybdenite mining regions is poorly known. Molybdenite is a typical sulfide ore resource with a high content of redox-sensitive elements like Se, U, and Mo. Mo is one of the essential trace elements for humans, animals, and plants. According to WHO (2011), the maximum value of Mo in drinking waters is 70 µg/L. U is typically a toxic and radioactive element with strong carcinogenic effects [16]. U in sediments mainly comes from ore-bearing rocks, like ore-bearing potassium feldspar minerals [14,15]. Natural waters are the main medium for the migration of U [17,18]. The acid mine discharge not only affects the content of these elements but also the physicochemical conditions of river water [19].

Many researchers have found that a high content of Mo is often observed in U ore [19,20] because U and Mo have similar geochemical properties as redox-sensitive elements. Therefore, Mo isotopes can be used to trace U ore. In addition, it is found that molybdenite or

associated molybdenum polymetallic deposits in China are rich in U, Zn, Pb, and other elements [18]. For example, the U content of molybdenite is abnormally high in the Dawangshan Tungsten-Mo polymetallic ore, Jiangxi province, China, being up to 13.3×10^{-6} (Wb). Yang et al. (2018) [21] and Sun et al. (2017) [22] have discovered that, in Jinduicheng molybdenite, U is enriched with an average content of 19.77×10^{-6} (Wb). Moreover, relative to the study of the content of Mo and U in the ore, Kayzar et al. (2014) [23] found that there is a strong correlation between U and Mo in water, $R^2 = 0.96$. Research on the trace element (Re) in molybdenite has also made great progress, but there are few studies on the high content of U in molybdenite.

Therefore, we collected the water and sediments following the molybdenite migration direction at the Jinduicheng molybdenite mining area in Shaanxi Province, China (Figure 1). The objectives of this study include: (1) to clarify the distribution characteristics of Mo and U in the water and sediments near the molybdenite mining; and (2) to discuss the source and migration of these toxic elements in the water and sediments downstream of the mining area.

2. Materials and Method

2.1. Study Area Background

The study area is located in Jindui Town, Hua County, Weinan City, Shaanxi Province ($109^{\circ}57'22''$ E, $34^{\circ}19'41''$ N). It has a high occurrence of Mo ore. At present, the output of Mo ore in Jinduicheng Molybdenite has reached 1 million tons. It is the largest Mo mining area in China and Asia, with an average grade of 0.099% [24]. The mining area is contained in andesite and granite porphyry. The rock contains polymetallic sulfide minerals. In addition to molybdenite, the rock also contains pyrite, chalcopyrite, limonite, hematite, etc. The U content is relatively high in granite porphyry, especially in mineralized potassium feldspar porphyry [14,25]. The results of a sample analysis of the ore show that the maximum U content is about 50.94 mg/kg, and the average content is about 19.77 mg/kg [22].

The mining area is located in the Qinling Mountains in China. It is a mountainous terrain with an average altitude of about 1200 m [26]. The climate of this area is a temperate, semi-humid monsoon climate, with concentrated precipitation in summer and strong weathering of surface rocks. The Wenyu River flows through the mining area from north to south. Due to the influence of climate, the runoff of the river in flood season and dry season is quite different, and the runoff of surrounding hillsides is strong in summer. There are two tailing ponds in the south of the mining area, which are used for wastewater treatment.

The strata exposed in a large area in the study area are mainly the volcanic rocks of the Middle Proterozoic Xionger, and the lithology is basaltic andesite. Mesoproterozoic slate can be seen in the northeast and south. The southern stratum is the sedimentary rock of the Gaoshanhe formation of the Guandaokou group, which is mainly composed of quartz sandstone and mudstone, covering the volcanic rock of Xionger in the north [15]. The geological map of the mining area is shown in Figure 1.

The ore types of the Jinduicheng molybdenum ore body mainly include three types: granite porphyry, basaltic andesite, and a small amount of quartzite, of which the former two types are dominant [8,9]. Ore minerals include molybdenite, chalcopyrite, pyrite, pyrrhotite, magnetite, sphalerite, and a small amount of galena. Gangue minerals include quartz, biotite, muscovite, potassium feldspar, albite, fluorite, calcite, zircon, chlorite, epidote, actinolite, sphene, and apatite. The Jinduicheng granite porphyry body and its outer contact zone have developed a wall rock alteration, showing the zonation characteristics of typical porphyry-type deposits. According to the symbiotic association of minerals, porphyry body contact zone wall rock can be divided outwardly in turn into alteration zones such as potassium feldsparization, sericitization, silicification, and propylitization.

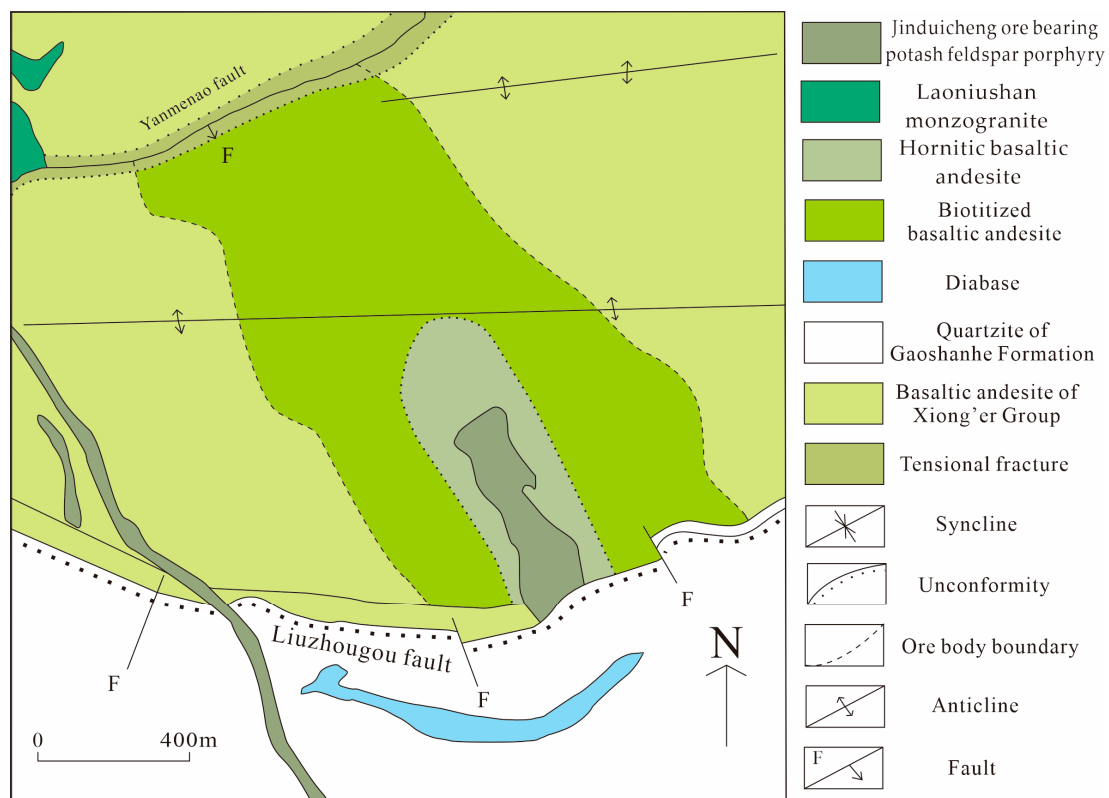


Figure 1. Geological map of Jinduicheng mining area (description and modification from Huang et al. (1987) [27]).

2.2. Sampling and Chemical Analysis

Surface water and sediment samples were collected along the Wenyu River and tailing pond in the mining area. According to the topographic and hydrological characteristics of the Wenyu River and the tailing pond, a total of 9 sampling sites along the river were collected. Table 1 (S1–S5) were distributed from north to south along the Wenyu River. Surface water and sediment samples were collected. Site S6 was located in the tailing pond in the southwest of the mining area and collected water samples from the tailing pond. Sites S7–S9 were located in the tailing pond in the southeast of the mining area. The specific distribution of sampling sites is shown in Figure 2.

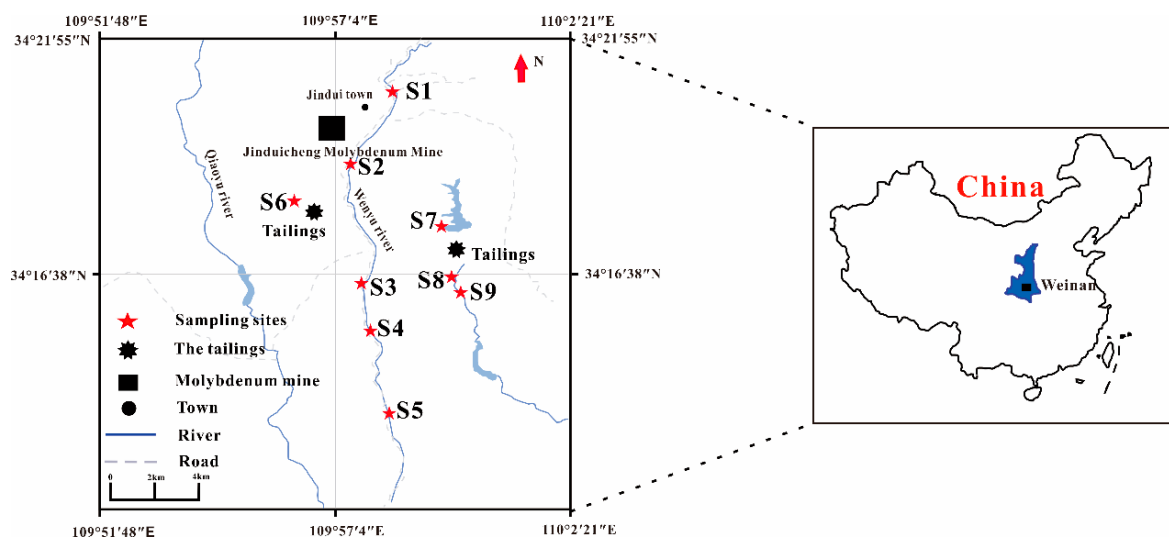


Figure 2. Study area and sampling sites in Jinduicheng molybdenite.

Table 1. Sample descriptions and details.

Site	Parameters		Electric Conductivity ($\mu\text{S}/\text{cm}$)	Sampling Description
	pH	Eh (mV)		
S1	7.04	8	150	S1 was located by the Wenyu River. The surface water (W1) and river sediment sample (SE1) of Wenyu River were collected at S1.
S2	6.18	52	270	S2 was located on the river course. The surface water (W2), river sediments (SE2) and soil on the banks of the river (S02) were collected at S2.
S3	6.34	35	300	S3 was located by the river with visible domestic waste. Surface water (W3), river sediment (SE3), and farmland soil (S03) were collected at S3. The soil sample(S03) was 10 m away from the river bank.
S4	6.21	35	320	Domestic garbage and smelly silt could be seen at S4 sampling site. River water (W4) and river sediment (SE4) were collected at S4.
S5	8.6	−77	350	S5 was located by the river, and the sediments in the river contained high levels of humus. River water (W5) and river sediment (SE5) were collected at S5.
S6	6.38	28	170	S6 was located in the tailing pond in the southwest of the molybdenite, with a few herbs. Tailing water sample (TW01) was collected at S6.
S7	6.12	51	1240	S7 was located on the north side of the tailing pond in the southeast of the molybdenite mine. The tailing pond water (TW02) was collected. Fish could be seen in the water.
S8	6.2	48	1090	S8 was located in the tailings pond in the southeast. Mainly collected drainage samples of tailing pond (TW03).
S9	6.19	52	940	S9 was located in the creek downstream of the tailing pond in the southeast. Collected water samples (T01) of the drainage channel of the mine and soil samples (TS01) by the creek.

The Eh and pH (YSI pH100A pH meter) values were immediately measured and recorded after sampling. Clean 500 mL polyethylene bottles were used for water sample collection (GB/T 5750.2-2006). There were three samples collected at each sampling site: one with a 2% analytical pure NaOH solution, one with a 2% analytical pure HNO₃ solution, and one field-blank sample with ultrapure water (resistivity 18.2 M Ω ·cm, 25 °C). All samples were brought to a portable refrigerator to be kept at low temperature. After collection, the water samples were directly sent to ALS Chemex (Guangzhou, China) for ICP-MS and ICP-AES detection. The sediment samples were collected and stored in a polyethylene zip-lock bag and dried in the shade in a nitrogen environment with an agate mortar to grind over 200-mesh nylon sieves. All samples were packaged and sent to ALS Chemex (Guangzhou, China) for detection and analysis using tetraacid digestion and the mass spectrometry/spectrometer integrated quantitative method. Extraction of potentially toxic elements was performed using the improved European Community Bureau of Reference (BCR) continuous extraction method. Other experiments were completed by the Geochemistry Laboratory of Chengdu University of Technology. The specific experimental steps are as shown in Table 2, and all concentrations of samples were determined by ICP-MS.

Table 2. BCR Sequential extraction steps.

Extraction Step	Extractant	T (°C)	pH	Incubation Time (Hours)
weak-acid soluble	40 mL 0.11 mol·L ^{−1} HAc	25 °C		16
reducible	40 mL 0.1 mol·L ^{−1} HONH ₃ Cl	25 °C	2	16
oxidizable	(a) 10 mL 30% H ₂ O ₂	85 °C		heat to dryness
	(b) 50 mL 1 mol·L ^{−1} NH ₄ OAc	25 °C		16
residual	10 mL HNO ₃ , 10 mL HF, 3 mL HClO ₄	25 °C		1
	1 mL V(HNO ₃):V(H ₂ O) = 1:1			cool down

2.3. Sample Details

Four tailing water samples, five river surface water samples, and five sediment samples were collected in the study area. The details about the sampling sites are in Table 2.

In fact, the S1 sampling site was located upstream of the mining area river, and the drainage of the mining area has a weak impact on the S1. Therefore, the pH and Eh values of the S1 water sample could be used as background values for the river water, which were 7.04 and 8, respectively. The electrical conductivity at site S6 was lower than at others (except S1) because the sampling site was in a relatively closed backfill pool.

2.4. Processing and Calculative Methods

Google Earth and CorelDRAW 2018 were used to locate the sample sites. Origin 2019b software was used to plot the data graphs. IBM SPSS Statistics 22 was used to analyze the data. The distribution coefficient of pollutants between sediment and water phases can reflect the actual migration capability of pollutants in a natural water body. The formula is:

$$K_d = C_s / C_w$$

where K_d is the distribution coefficient; C_s is the content of potentially toxic elements in the sediment; and C_w is the concentration of potentially toxic elements in the water.

3. Results and Discussions

3.1. Mo and U Enrichment in Surface Water

The upper reaches of the Wenyu River have a neutral pH and are weakly oxidized, but after flowing through the mining area, its characteristics have been changed. From sites (W2~W5), the pH value was between 6.18 and ~8.6 and the Eh value was between 55 and −77, indicating that the river water changed from weakly acidic to alkaline from upstream to downstream and from an oxidizing environment to a reducing environment. In addition, the farther away from the mining area, the higher the pH value and the lower the Eh value, showing a negative correlation between the pH value and the Eh value and showing that the pH value was negatively correlated with the Eh value. The Eh values ranged from 28 mV to 58 mV, with an average value of 44.75 mV, and Eh at each sampling site changed little, indicating an oxidative environment. Therefore, the water environment of the Wenyu River in the study area presented the characteristics of a neutral–weak, acid–alkaline, and weak oxidation–reduction environment from upstream to downstream. The pH of the tailing water ranged from 6.12 to 6.38, with a small change because the tailings may contain molybdenite [9,28], which is composed of many metal sulfide minerals (such as pyrite, etc.), and these minerals would increase the pH of the water after dissolving in the water. Molybdate in an acidic environment easily adsorb and precipitate metal ions in water, while in an alkaline environment, adsorption is not easy [29,30].

The average concentration of Mo in Chinese rivers ranges up to 20 µg/L, and the concentration of U is about 1 µg/L [31] (Zao et al., 1990). The contents of Mo and U from the tailing ponds in the four water sampling sites (TW01, TW02, TW03, and T01) were 2.62 mg/L and 0.03 mg/L, respectively, which were 131 times and 30 times the background value, respectively. The Mo content of TW01, TW02, TW03, and T01 exceeded the background value by 4, 32, 62, and 33 times, respectively (Table 3). The U content of the other three sampling sites (TW01, TW02, T01) was 2 times, 26 times, and 5 times the background value, respectively, except that TW03 had no value. The average content of U and Mo in TW01, TW02, TW03, and T01 was also 33 times and 30 times the background value, respectively (Table 3). The content of Mo and U in the surface water at the tailings ponds was significantly higher than the background values, indicating the potential pollution of the water body.

Table 3. The content of Mo and U in sediments and surface water.

	Sediments		River Water		Tailing Water	
	Mo	U	Mo	U	Mo	U
S1	13.2	4.60	<0.001	<0.001	-	-
S2	492	13.40	0.027	<0.001	-	-
S3	470	9.30	0.047	0.001	-	-
S4	429	6.90	0.049	0.001	-	-
S5	175.5	4.70	0.070	0.001	-	-
S6	-	-	-	-	0.083	0.002
S7	-	-	-	-	0.635	0.026
S8	-	-	-	-	1.245	<0.001
S9	-	-	-	-	0.660	0.005
Total	1579.7	38.9	0.193	0.003	2.62	0.03
Min	13.2	4.6	0	0	0.08	0
Max	492	13.4	0.07	0.001	1.25	0.03
Mean	315.94	7.78	0.039	0.001	0.66	0.01
S.D.	211.476	3.683	0.026	0.001	0.47	0.01
Median	429	6.9	0.047	0.001	0.65	0
RSD (%)	0.669	0.473	68.4	91.3	72	-
Background value	0.8 ^a	2.2 ^a	0.02 ^b	0.001 ^c	-	-
background value	13.2	4.6	0	0	-	-

^a indicates the soil background value of Xi'an [32]; ^b indicates background value data of Chinese rivers [33]; ^c indicates global river water background value. The units are mg/kg (soil and sediment samples) and mg/L (water samples), “-” means no data.

There may be many reasons for the high concentration of Mo. The average pH value of tailing water was 6.2, with no significant change, indicating a low correlation between Mo content and pH value (Figure 3a). With the increase in pH value in river water, the content of Mo appeared at the highest value of W5 (Figure 3a). According to previous studies, Mo is hardly adsorbed at pH > 8 [34], while the pH value of W5 was 8.6, so Mo in water cannot be adsorbed in this environment, resulting in an increase in molybdenum content detected in rivers. In addition to the influence of pH, the upper reaches of the Wenyu River had a narrow channel, a large river-specific fall, and a fast flow rate, while the lower reaches had a wide channel, a slow flow rate, and a superior condition for trace metal enrichment compared with the upper reaches, resulting in an increasing Mo concentration with the flow direction.

In general, the optimal pH for the adsorption and precipitation of U in water by clay minerals or metal minerals is 5 [35], and when the environment is oxidizing, U (VI) is relatively unstable and prone to migration. When the environment is a reducing environment, U (VI) will be reduced from a stable state to U (IV) and hydrolyze to precipitate. Although the pH value of the W5 sample increased to 8.6, the adsorption of U was also affected by the Eh value, and the Eh value at W5 reflected a reducing environment. Therefore, U (VI) was still reduced to U (IV) and precipitated [20,36–39]. Therefore, the U content in the river water was very low and did not change much (Figure 3b).

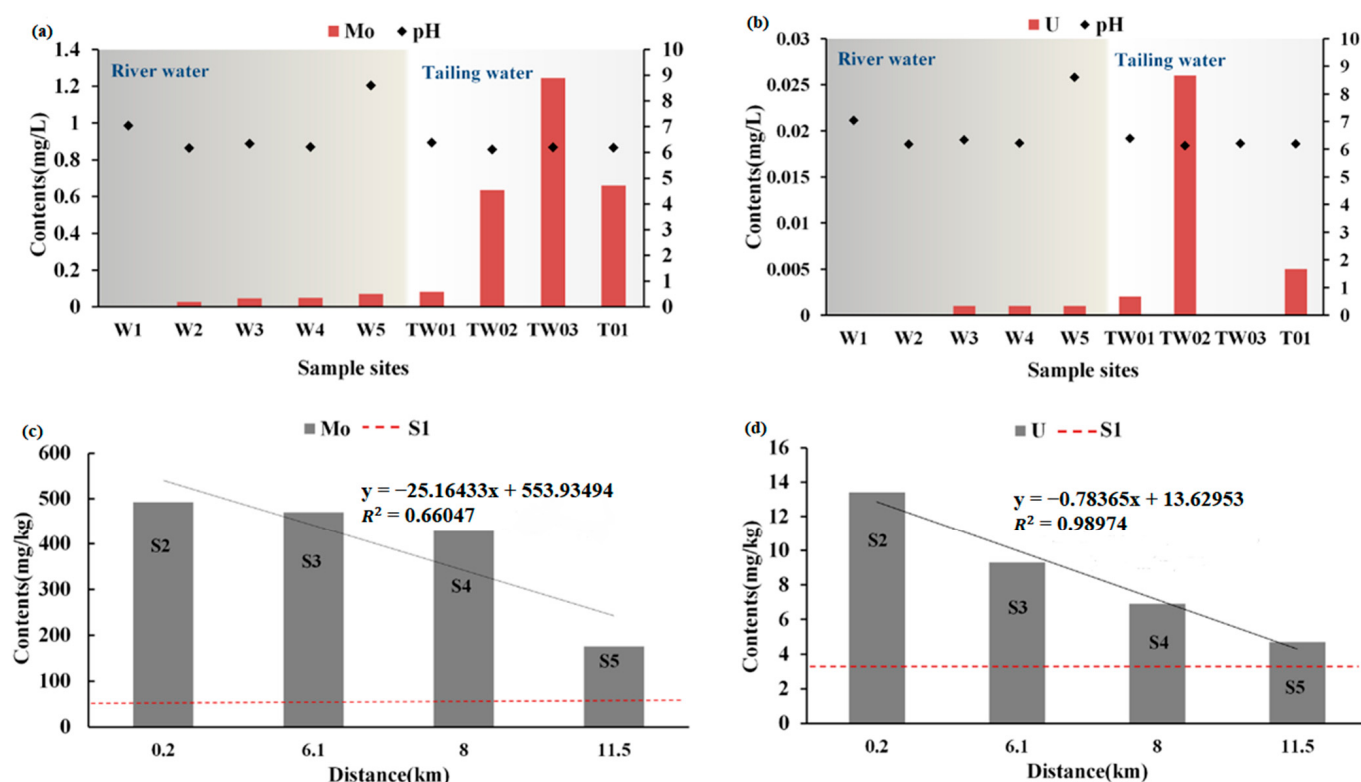


Figure 3. The relationship between the distribution of Mo and U in the river water and tailing water and the pH value (a,b). The relationship between the content of Mo and U in the sediments of Wenyu River and the distance (c,d).

3.2. Distribution of U and Mo in Downstream Sediment

The geochemical background values of Mo and U in soil in Xi'an are 0.8 mg/kg and 2.2 mg/kg, respectively [32]. Due to the proximity of the sampling point to the southeastern part of Xi'an, it was used as one of the reference factors for background values. S1 is located upstream of the mine and is not affected by mining wastewater, so the Mo and U contents in SE1 were used as the background values for the study area.

Through the analysis of sediment samples (SE2–SE5) from the Wenyu River, it was found that the total amounts of Mo and U in the sediment were 1566.5 mg/kg and 34.3 mg/kg, respectively, which were 119 times and 7.5 times higher than the background values (Table 3). The average contents of Mo and U were 391.6 mg/kg and 8.6 mg/kg, respectively, which were 30 times and 1.9 times the background values, respectively (Table 3). Compared to the contents of Mo and U in river water, the contents of Mo and U in sediments are significantly higher because colloids and clay minerals that enter the river may adsorb trace metals and precipitate them into sediments [40–43]. In general, the contents of Mo and U in the sediments of the Wenyu River exceeded the background values (SE1), and the content of Mo was significantly higher than the background value, indicating that Mo pollution in the Wenyu River sediments is severe (Figure 3a,b).

Figure 3a,b also show the distribution characteristics of Mo and U in the tailing ponds. The content of Mo in TW03 was higher than that in TW02, which was related to the collection site location of TW03. TW03 is in the drainage and sedimentation tank of the tailings pond. The fluidity and turbulence of the water flow made the Mo in the tailing sand enter the water and flow downstream, so that the content of Mo in T01, located downstream of the tailing pond, was high. The content of U in the tailing pond water was relatively low, and the content in TW02 was the highest. The content of U element at T01 was less than at TW02 and TW03, indicating that U element was concentrated in the tailing pond and that the migration amount decreased with the increase in drainage.

In general, Mo and U mainly exist in sediments in the study area, and the content of Mo and U in surface water was very low. As the mining area affected the lower reaches of the river, the Mo content in the river water increased with the distance, while the U content changed little. The content of Mo and U in river sediments gradually decreased with the increase in distance, and the distance and trace metal content showed a strong positive correlation.

The spatial analysis of sediments revealed that with an increase in distance, the content of U and Mo gradually decreased (Figure 3c,d); R^2 was 0.6605 and 0.9897, respectively. To predict the downward trend of Mo and U content in river sediments and the spatial impact range of molybdenite downstream, a linear regression equation was used to fit the data. It was calculated that the Mo content at about 21.5 km downstream of the Wenyu River was lower than the background value S1, while the U content was lower than the background value at 12 km; thus, the theoretical range of the polluted environment in the mining area was 21.5 km (Mo) and 12 km (U), respectively.

3.3. Migration of U and Mo Downstream

The enrichment and migration of trace metals mainly occurred by two mechanisms: (1) releasing from the minerals through weathering and rainfall erosion; and (2) diffusing, migrating, and transforming in the soil and water bodies through a series of physical and chemical processes, then flowing into the groundwater and sediments. In order to analyze the horizontal migration and distribution of Mo and U in river water bodies and sediments, this paper mainly analyzed the second mechanism.

The previous paper on the content of trace metal elements alone is not sufficient to explain the migration mechanism, and it is also necessary to analyze the morphology of Mo and U (Table 4).

Table 4. Speciation of Mo and U in sediments and surface water.

Sample Type	Speciation	Distribution of Various Potentially Toxic Elements		
		Mo	U	Mn
SE1	F1	0.01	0.11	0.53
	F2	0.24	0.61	2.70
	F3	7.16	0.44	7.84
	F4	7.24	3.25	30.74
SE2	F1	0.01	1.59	1.30
	F2	3.30	1.49	4.02
	F3	175.82	4.60	12.16
	F4	253.56	3.34	42.04
SE3	F1	1.63	2.10	8.31
	F2	4.34	1.85	2.79
	F3	113.51	2.87	8.98
	F4	342.77	2.16	36.86
SE4	F1	0.05	1.10	0.75
	F2	3.90	1.48	2.49
	F3	98.35	2.06	8.38
	F4	358.41	1.92	35.35
SE5	F1	0.03	0.24	1.17
	F2	4.53	0.79	3.80
	F3	34.77	0.56	13.00
	F4	157.25	2.30	56.91

The unit of water sample is mg/L; soil and sediment samples are mg/kg.

Many studies have suggested that the content of trace metal forms is closely related to the total amount of trace metals, and the organic matter content and pH value will also affect the content of trace metal speciation [44,45]. To examine if the speciation distribution

of Mo and U was related to the total content, we carried out a correlation analysis (Table 5) between the total amount and form of Mo and U. The result showed that the content of trace metals had varying degrees of influence on their speciation distribution. Except for the weak acid-soluble state, the morphological distribution of molybdenum was positively correlated with the total content. There was a significant positive correlation between molybdenum content and residual forms ($p = 0.974$).

Table 5. Correlation analysis between total content and speciation of Mo and U.

Speictation		Contents	F1	F2	F3	F4
Mo	F1	0.424	1			
	F2	0.72	0.357	1		
	F3	0.862	0.231	0.457	1	
	F4	0.974	0.47	0.77	0.724	1
U	F1	0.884	1			
	F2	0.811	0.975	1		
	F3	0.987	0.836	0.78	1	
	F4	0.205	−0.212	−0.385	0.2	1

According to Figure 4a, Mo in river sediments is mainly the residual fraction (F4), accounting for 68% of the total content. The residual fraction is the result of natural Mo ore rock weathering and soil erosion. It is hardly to migrate and has low pollution potential. S1 is in the upstream of the mining area, but the Mo of S1 had the same speciation characteristics as the Mo in the downstream of the mining area. Both were mainly the residual fraction, indicating that the Mo in the Wenyu River sediments was mainly the residual fraction. Mo has been stable in the sediment for a long time and is not easily absorbed by plants. Therefore, Mo in sediments of the Wenyu River migrated via runoff migration and deposition. In conclusion, Mo in the sediments of the Wenyu River mainly exists as a residual fraction.

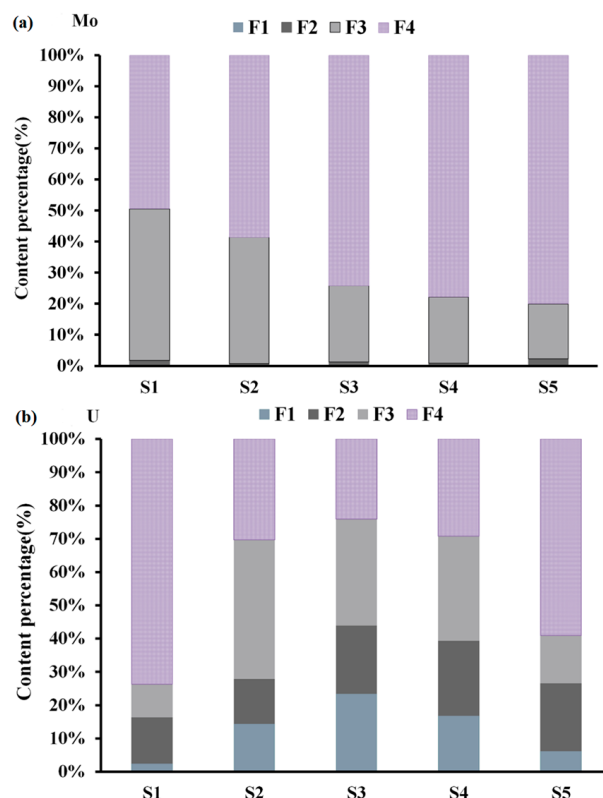


Figure 4. Speciation distribution of (a) Mo and (b) U in Wenyu River sediments.

Previous studies have shown that the speciation of U in natural water is mainly affected by pH and redox potential [18]. The U in SE1 and SE5 samples is mainly a residual fraction, accounting for 73.71% and 59.07%, respectively. However, the main morphology of U had changed downstream of the mining area. The U in three samples (SE2, SE3, SE4) were mainly non-residual fractions (F1 + F2 + F3), on average accounting for 65% (Figure 4b). In addition, U was a residual fraction at SE5, and the speciation distribution of SE5 and SE1 was highly similar (Figure 4b). This explains that the Wenyu River downstream was affected by the discharge of sewage from the mining area and the slag accumulation, resulting in the enrichment of U. It also showed that the migration and morphological transformation of U in water were affected by external factors, such as human activities.

The U speciation distribution also had a strong positive correlation with the total content in addition to the residual fraction of U. And the content of U had a high correlation coefficient with the oxidizable speciation ($p = 0.987$). Therefore, for the high proportion of the residual fraction of U in SE5 to have had little correlation with the total content, the explanation is that because U is a geochemically sensitive element and U (IV) is stable in a reducing environment and difficult to migrate, more of the residual fractions were embedded in the mineral lattice.

The distribution coefficient of trace metals in the water sediment phase reflects the migration ability of trace metals between the water phase and the sediment phase and also reflects the pollution potential of trace metals [46,47]. The distribution coefficients of Mo and U at five sampling sites in the Wenyu River were calculated. The results showed $K_d(\text{Mo}) > K_d(\text{U})$, indicating that Mo mainly exists in sediments and the migration of U in water is stronger than Mo (Table 6). Therefore, the pollution potential of U in the study area was stronger than that of Mo. The Mo and U in the sediment were about 5 orders of magnitude higher than those in the water, indicating that the sediment had a greater influence on the distribution and migration of Mo and U.

Table 6. Distribution coefficient of potentially toxic elements in downstream of Jinduicheng Mo mining area (L/kg).

Sites	$K_p(\text{Mo}) \times 10^3$	$K_p(\text{U}) \times 10^3$
S1	-	-
S2	18.2	-
S3	10.0	9.3
S4	8.8	6.9
S5	2.5	4.7

To gain a deeper understanding of the downstream migration of U and Mo, a linear correlation analysis was conducted on the Mo and U concentrations in the river water and sediments downstream of the mining area. The results show that the correlation coefficient is $R^2 = 0.6538$ (sediments) and $R^2 = 0.7529$ (river water), indicating that U and Mo in sediments and water had similar sources, especially natural mineral weathering (Figure 5). The results were consistent with the findings of Kayzar et al. (2014) [23,48]. On this basis, it is suggested that the high content of U downstream of the mining area may be the result of U enrichment in molybdenite.

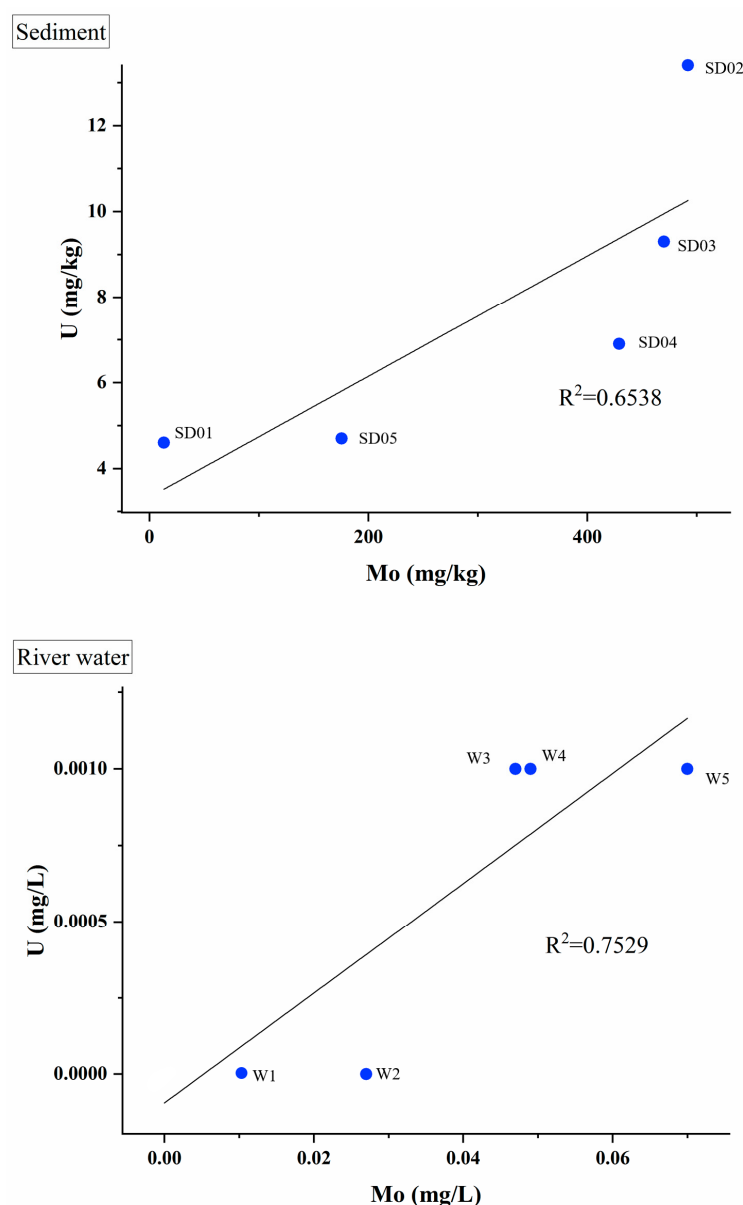


Figure 5. Linear fitting of Mo and U in Wenyu River water and sediments.

4. Conclusions

The results of bulk composition in the sediment and the river water samples suggests that the changes in physicochemical properties (e.g., pH) of the surface water can significantly affect the distribution of U and Mo between the sediment and its surface water. The Mo content of river sediment at Wenyuhe and the AMD pond can reach up to 0.193 mg/L and 2.623 mg/L, respectively. Compared to the background values, the Mo and U contents in the surface water of the tailing pond were significantly higher than in the river water. In particular, Mo and U are mainly enriched in the downstream sediment of the mining area. The spatial distribution characteristics indicate that the Mo content in the river sediment increases with distance, while the U remains stable. The contents of Mo and U in the sediments gradually decreased and were positively related to the distance of the mining area. The Mo in river sediments mainly existed as a residual fraction (F4), accounting for 68% in total. The U mainly existed as a non-residual fraction, accounting for an average of 65%. This indicates that the migration potential of U in Wenyu River sediment is stronger than that of Mo. The distribution coefficient of molybdate in the water exceeding that of

U suggests that Mo is more likely to be enriched in sediment, while U is more likely to migrate via water in the surface sediment near the AMD region.

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