



Mineral-leaching chemical transport with runoff and sediment from severely eroded rare-earth tailings in southern China

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Abstract. Rare-earth mining has led to severe soil erosion in southern China. Furthermore, the presence of the mineral-leaching chemical ammonium sulfate in runoff and sediment poses a serious environmental threat to downstream water bodies. In this paper, the characteristics of mineral-leaching chemicals in surface soil samples collected in the field were studied. In addition, NH_4^+ and SO_4^{2-} transport via soil erosion was monitored using runoff and sediment samples collected during natural rainfall processes. The results demonstrated that the NH_4^+ contents in the surface sediment deposits increased from the top of the heap (6.56 mg kg^{-1}) to the gully (8.23 mg kg^{-1}) and outside the tailing heap (13.03 mg kg^{-1}). The contents of SO_4^{2-} in the different locations of the tailing heaps ranged from 27.71 to 40.33 mg kg^{-1} . During typical rainfall events, the absorbed NH_4^+ concentrations (2.05 , 1.26 mg L^{-1}) in runoff were significantly higher than the dissolved concentrations (0.93 , 1.04 mg L^{-1}), while the absorbed SO_4^{2-} concentrations (2.87 , 1.92 mg L^{-1}) were significantly lower than the dissolved concentrations (6.55 , 7.51 mg L^{-1}). The dissolved NH_4^+ and SO_4^{2-} concentrations in runoff displayed an exponentially decreasing tendency with increasing transport distance ($Y = 1.02 \cdot \exp(-0.00312X)$; $Y = 3.34 \cdot \exp(-0.0185X)$). No clear trend with increasing distance was observed for the absorbed NH_4^+ and SO_4^{2-} contents in transported sediment. The NH_4^+ and SO_4^{2-} contents had positive correlations with the silt and clay ratio in transported sediment but negative correlations with the sand ratio. These results provide a better understanding of the transport processes and can be used to develop equations to predict the transport of mineral-leaching chemicals in rare-earth tailings,

which can provide a scientific foundation for erosion control and soil management in rare-earth tailing regions in southern China.

1 Introduction

Soil erosion is a global issue of great importance (Morgan, 2005) because it not only degrades soil quality but also leads to pollution associated with runoff and sediment, posing a risk to water and soil quality and human health. Human-driven production activities, especially mining, severely disturb the land and generate tailings, often leading to extremely serious soil erosion (Duque et al., 2015; Zhang et al., 2016; García-Gómez et al., 2014; Gharibreza et al., 2013; Meng et al., 2012; Riley, 1995). The soil erosion process in mining regions releases complex chemical substances into the surrounding environment, including nutrients, heavy metals, radioactive elements, and other contaminants, thereby threatening ecological security (Pascaud et al., 2015; Nascimento et al., 2012; Weng et al., 2012; Gao and Zhou, 2011; Mol and Ouboter, 2004; Razo et al., 2004).

The term “rare-earth element” (REE) refers to 17 elements containing lanthanide series along with scandium and yttrium (Khan et al., 2016). China is the dominant rare-earth element provider and accounts for over 95 % of the world production (Tse, 2011). Southern China contains large amounts of lateritic ion-adsorption clay deposits, which are relatively enriched in heavy rare-earth elements (HREEs; Gao and Zhou, 2011). HREEs, which are widely used in aviation, electronics, transportation, and health care, have great signifi-

importance for industry and the economy (Kanazawa and Kamitani, 2006). The ion-adsorption deposits were formed by chemical weathering decomposition and dissolution of granite and granite porphyry (containing a relatively high abundance of REE) (Yang et al., 2013). The main ore body contains 0.05–0.2 wt % REE grades, and strong cerium anomalies are found. These ion-adsorption clay deposits have been mined since the 1970s. Thirty years of weakly regulated HREE mining have left a legacy of environmentally damaging accidents and contamination due to mining and ore processing (Kynicky et al., 2012). The regional humid subtropical climate and intense rainfall lead to considerable surface runoff, which leads to the erosion of tailings, high suspended sediment loads in streams, and subsequent sediment deposition. The soil erosion is extremely intensive, with an average annual value of approximately $3.8 \times 10^4 \text{ t km}^{-2} \text{ a}^{-1}$ (Lu et al., 2015), which far exceeds the severe erosion standard of $1.5 \times 10^4 \text{ t km}^{-2} \text{ a}^{-1}$ (SL190-2007, Ministry of Water Resources, PRC, 2008). In addition, as the HREEs are adsorbed onto the clay surface, large amounts of the mineral-leaching chemicals are used to exchange the REE during ion-adsorption mining (Packey and Kingsnorth, 2016). The abandoned tailing heaps contain abundant acidic ammonium sulfate. These ions can lead to eutrophication in surface water, groundwater, and farmland, which are important for plant growth, animal livelihood, and human health in southern China (Zhang et al., 2016; Nie et al., 2009; Fu et al., 2004; Schlesinger et al., 2000; Schoumans et al., 2014; Tian et al., 2007; Gangbazo et al., 1995; Richardson and King, 1995; Lambert et al., 1985). Therefore, it is necessary to simulate and predict sediment yield and the leaching of chemical contents in rainfall runoff on and near the tailings.

Chemical transport during the erosion process is a complex process. This transport includes substance concentration variations, enrichment ratio variations, and both transport and transformation in runoff and sediment (Reddy and Patrick, 1984; Palis et al., 1990). It is influenced by many factors, such as rainfall intensity, runoff discharge, topography, soil characteristics, land use, vegetation cover, and anthropogenic or natural disturbances. Analysis of the chemical transport mechanism during the soil erosion process is very important for determining the potential chemical contents in both runoff and sediment. The methods used to study soil erosion and chemical transport include laboratory experiments, plot-based experiments, field observations, and watershed-level modeling (Lü et al., 2007). These methods have spatial scale differences, from the slope scale to the catchment scale (Palis et al., 1990; Razo et al., 2004; Ojeda et al., 2006; Zheng et al., 2016). Findings from small spatial-scale experiments should be treated with caution when up-scaling to describe chemical transport because they do not consider changes in the factors with increasing spatial scale. The simplified assumptions of models may fail to capture the chemical transport process, resulting in less accurate predictions of the chemical loads. Existing models, such as

AGNPS (Agricultural Non-Point-Source Pollution Model), CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems), and SWAT (Soil and Water Assessment Tool), calculate sediment yield based on the empirical USLE (Universal Soil Loss Equation) model, which does not include substance transport processes (Wu and Chen, 2012; Chaplot, 2005; West and Wali, 1999). In addition, the majority of the studies and models focus on non-point-source pollution in agricultural conditions, such as arable farming, tillage, and row cropping (Ongley et al., 2010). However, relatively few studies have focused specifically on extremely disturbed areas with intense rainfall. Therefore, our current knowledge of the chemical transportation process under serious erosional conditions is inadequate, especially in the lateritic ion-adsorption clay deposits of south China. The contamination situation is unclear, and the mechanism of mineral-leaching chemical transport during the soil erosion process has not been studied. As a large quantity of ammonium sulfate and ammonium bicarbonate were added in the production process, NH_4^+ and SO_4^{2-} still remain in the REE mining region. It is estimated that the process has generated about 20–25 000 t of wastewater and $300\text{--}500 \text{ mg L}^{-1}$ total ammonia nitrogen concentration up until 2005 (Khan et al., 2016). NH_4^+ tends to adsorb onto soil, and excess NH_4^+ would accelerate soil acidification, reduce soil mineral element content, change soil solution ion composition, and aggravate the soil contamination (Zhou et al., 2014). SO_4^{2-} is water soluble, and a high concentration could lead directly to death for plants (Yang, 2009). Different chemicals have unique transportation pathways and primary carriers in runoff. Thus, it is necessary to compare the differences between NH_4^+ and SO_4^{2-} .

The aim of a 2-year field study of runoff and sediment during natural rainfall events in a rare-earth tailing area was to (1) gain an insight into the two leaching chemicals' spatial distributions at different locations around the tailing heaps and (2) determine the transport characteristics and influencing factors of the two leaching chemicals in runoff, including both dissolved and adsorbed components.

2 Materials and methods

2.1 Study area

The experiment area is located in the Longshe soil erosion warning zone of rare-earth tailings (Fig. 1) in Xinfeng County, Ganzhou, Jiangxi Province, south China ($25^\circ 23' 10'' \text{ N}$, $115^\circ 0' 26'' \text{ E}$). The region features a subtropical moist monsoon climate with an average annual precipitation of 1500.4 mm, nearly half of which occurs from April to June. The intense rainfall leads to severe soil erosion and substance loss. The annual runoff modulus is 874 mm, and the total amount of annual runoff is approximately 5.2 billion m^3 . The mean annual temperature is 19.5° C , with monthly

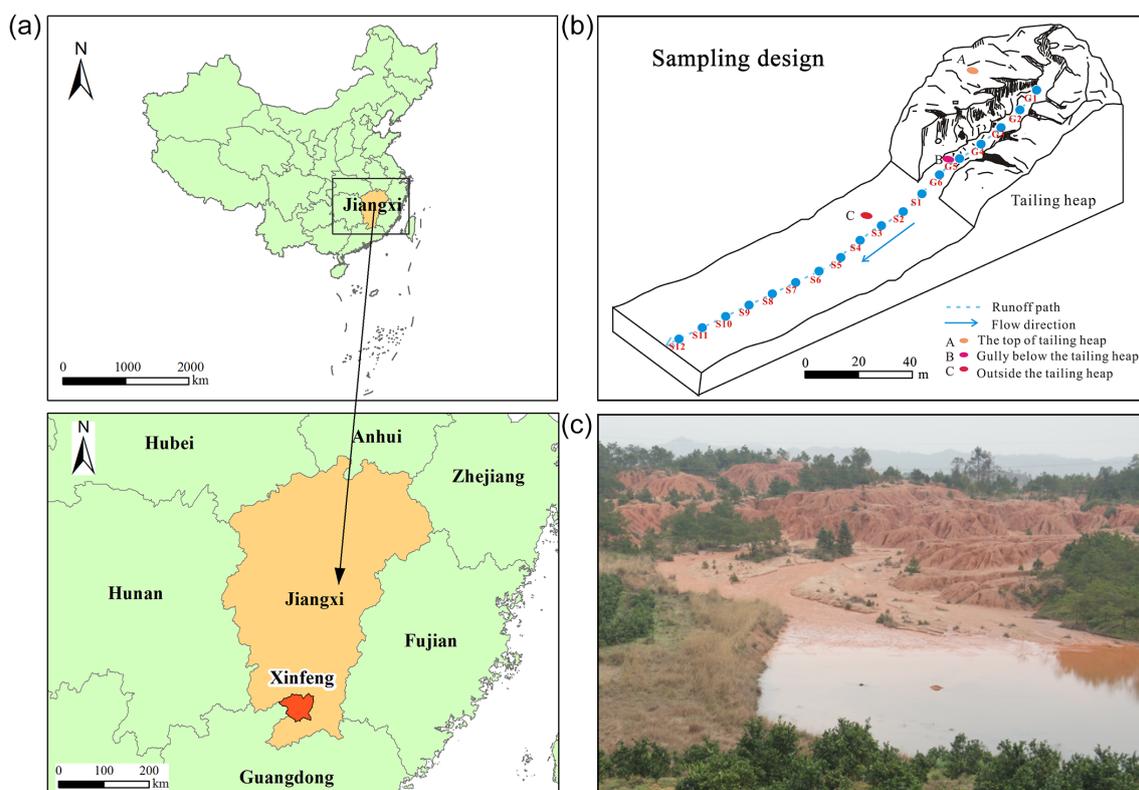


Figure 1. Study area (a), sampling design (b), and detailed view of the experimental area (c).

averages ranging from -4 to 39.4°C . The pristine soils are red soils developed from weathered residual granite.

The tailing area is approximately 0.26 km^2 . The tailings were formed in 1986, and the height of the tailings range from 0.83 to 3.45 m. A chain of undulating hills characterizes the topography due to mining and erosion. The mining technique for rare-earth ore is pond leaching, and ponding is one of the most prevalent mining methods. First, the subsurface ore body is mined, and the material is placed in an ammonium sulfate leaching pond to create a rare-earth solution. The REEs in the collected leaching solution are then precipitated with oxalic acid. Finally, the precipitates are turned into R_2O_3 via burning (Chi and Tian, 2007). After this mining process, residual tailing heaps containing acid leaching solution pollutants are formed. The production of 1 t of rare-earth oxide can create 1600–2000 t of tailings (Peng, 2005). There will be 302 abandoned mines and 191 million tons of tailings by 2020 in the Ganzhou region alone (Packey and Kingsnorth, 2016). No effective measures were taken, and the tailing heaps have experienced considerable soil loss. The tailing sediments in the region are poor in nutrients, strongly acidic, and subjected to substantial active erosion in areas where the original forest vegetation has been totally removed. Plants are rare, and only a few acid-resistant species, such as *Dicranopteris* and *Pinus massoniana*, are able to grow beside the tailing heaps. The tailing plots feature two

major water erosion forms: gully erosion and slope erosion. The slope erosion can be divided into three types: slopes on the tailing heap surface, slopes in the gully below the tailing heap, and slopes outside the tailing heap. The average gully density is 0.13 km km^{-2} , and the average gully sediment bulk density is 1.29 g cm^{-3} .

2.2 Sampling procedure

We designed the sample paths and points based on the erosion types and flow direction. Figure 1 showed that one path along a gully (G) and tailing heap (S) was designed. The G–S path was chosen because it had a relatively complete flow track, a long distance, and was not affected by other flow routes. The path length was 170 m, and we set several sample points at intervals of 10 m. The G–S path samples included natural rainfall runoff samples. Three rainfall events were recorded on 16 June 2012 and 15 and 16 May 2013. The precipitation intensities were measured with rainfall gauges and were 0.9 , 1.0 , and 1.2 mm min^{-1} , respectively. These values are typical of the high intensities common during the rainy season in the red soil region in southern China (Ma et al., 2014). The runoff samples were collected close to the surface using pre-cleaned polyethylene bottles. The bottles were immediately placed in dark boxes and processed within 6 h of collection. At least two samples were taken at every sampling point. There were a total of 67 rainfall runoff samples. More-

Table 1. NH_4^+ and SO_4^{2-} contents and soil textures in the surface soil samples collected in different locations. Locations A, B and C are the top of the tailing heap, the gully below the tailing heap, and the area outside the tailing heap, respectively. The texture classification standard is according to the USDA (United States Department of Agriculture).

Locations	NH_4^+	SO_4^{2-}	Sand 2–0.05 mm	Silt 0.05–0.002 mm	Clay < 0.002 mm	Soil texture
	mg kg ⁻¹					
A	6.56 ± 1.87	40.33 ± 4.58	60.35 ± 4.35	36.07 ± 4.26	3.59 ± 1.83	sandy loam
B	8.23 ± 1.46	27.71 ± 3.95	92.63 ± 1.31	7.17 ± 1.18	0.20 ± 0.19	sandy soil
C	13.03 ± 3.42	32.11 ± 4.42	83.84 ± 5.44	15.56 ± 5.19	0.61 ± 0.36	loamy sand

over, 20 surface sediment samples were collected on the top of the tailing heap (Fig. 1b), 6 deposited surface sediment samples were collected from the G path (G1–G6) (Fig. 1b) before the natural rainfall events, and 12 deposited surface sediment samples were collected from the S path (S1–S12) outside the tailing heap (Fig. 1b) after the rainfall events. All surface sediment samples were taken from 0 to 5 cm depths using small shovels and were stored in polyethylene bags. One sample was a mix of three parallel samples. The mixed surface sediment sample weight was approximately 500 g.

2.3 Analytical methods

Runoff samples were measured as two phases, i.e., runoff water and sediment. The samples were filtered in the field with a 0.45 µm pore-size membrane to separate the sediment from the water and measure dissolved and absorbed substances. Dissolved NH_4^+ and SO_4^{2-} concentrations and pH values were measured in the runoff water, and absorbed NH_4^+ and SO_4^{2-} contents, sediment concentrations, and particle distributions were measured in the runoff sediment samples. The precipitation intensities differed among the rainfall events, and the dissolved chemical concentrations increased with increasing precipitation intensity (Zhang et al., 2016). Thus, the data were standardized according to the precipitation intensities, i.e., the standardized concentrations were equal to the real concentrations divided by the corresponding precipitation intensity. The NH_4^+ and SO_4^{2-} contents and particle size distributions were also measured in the surface.

The pH values were determined using the glass calomel electrode method. The dissolved and absorbed NH_4^+ concentrations were analyzed colorimetrically using a flow injection analyzer. The dissolved and absorbed SO_4^{2-} concentrations were determined using turbidimetry through the formation of BaSO_4 via the addition of BaCl_2 . The sediment particle distribution was determined by sieving in combination with the sieve–pipette method (Lu, 2000). Each sediment sample was divided into three sediment size groups: sand (2–0.05 mm), silt (0.05–0.002 mm), and clay (< 0.002 mm).

2.4 Data analysis

One-way analysis of variance (ANOVA) was used to compare the difference between the leaching chemicals at different locations. Linear and nonlinear regressions were conducted to establish the relationship between the NH_4^+ and SO_4^{2-} concentrations and the influencing factors. The coefficient of determination (R^2) was used to evaluate the performance of the applied regression equations. All of the analyses were performed using IBM SPSS statistics for Windows Version 19.0 (IBM Corp., Armonk, NY, USA), and all graphical displays were prepared using ORIGIN8.0 (OriginLab, Northampton, MA, USA) and ArcGIS 9.3 (ESRI, Redlands, CA, USA).

3 Results

3.1 NH_4^+ and SO_4^{2-} spatial distributions in surface soils

The NH_4^+ and SO_4^{2-} contents in surface runoff depends on the corresponding content in the tailing heaps. Therefore, the NH_4^+ and SO_4^{2-} content of surface sediments must be determined in different locations. Due to the long duration of runoff and sediment transportation, the surface sediment on the top of the tailing heap moved first to the gully below the tailing heap and then beyond the tailing heap along the flow direction (Fig. 1). Table 1 shows the average NH_4^+ and SO_4^{2-} contents in the surface sediment samples collected at different locations. From A to B and C, the NH_4^+ contents increased. The value on top of the heap was 6.56 mg kg⁻¹, and the values outside the heap reached as high as 13.03 mg kg⁻¹. The trend observed for the SO_4^{2-} values did not agree with that of the NH_4^+ values. The SO_4^{2-} content was highest on top of the tailing heap, lowest in the gully below the tailing heap, and intermediate outside of the tailing heap. The SO_4^{2-} content in the gully below the tailing heap was similar to that outside the tailing heap. The different sediment particle distributions led to different textures in the three locations (Table 1). The sediment on top of the tailing heap had the highest silt and clay contents, and its texture was sandy loam. The texture in the gully below the tailing heap was sandy soil be-

cause the sand content exceeded 90 %. Similarly, the texture outside the tailing heap was loamy sand. The texture difference between positions A, B, and C might be due to the long period of time associated with the runoff process.

3.2 Dissolved and absorbed NH_4^+ and SO_4^{2-} concentrations in runoff

Dissolved and absorbed NH_4^+ and SO_4^{2-} concentrations in the runoff samples at different locations can be found in Table 2. Runoff is the main driving force for soil erosion and chemical transport. In the case of runoff movement, the chemicals adsorbed onto the sediment particles enter overland flow. Additionally, the dissolved chemicals also enter the sediment surface. After more than 20 years of leaching and weathering, the runoff was still acidic. The runoff pH values were nearly the same at locations B (4.51) and C (4.56). The results of the ANOVA (Table 2) indicated that highly significant differences were observed between the dissolved and adsorbed leaching chemicals. The adsorbed NH_4^+ concentrations at sites B (2.05 mg L^{-1}) and C (1.26 mg L^{-1}) were significantly higher than the dissolved NH_4^+ contents at sites B (0.93 mg L^{-1}) and C (1.04 mg L^{-1}), respectively (ANOVA, $p = 0.001$ and $p = 0.000$). This phenomenon shows that NH_4^+ was mainly transported by sediment in the runoff. In addition, the dissolved SO_4^{2-} concentrations at sites B (6.55 mg L^{-1}) and C (7.51 mg L^{-1}) were significantly greater than the adsorbed SO_4^{2-} at sites B (2.87 mg L^{-1}) and C (1.92 mg L^{-1}), respectively (ANOVA, $p = 0.001$ and $p = 0.000$). It is evident that SO_4^{2-} was mainly transported in runoff. The primary transportation mechanisms for NH_4^+ and SO_4^{2-} in runoff were different. Moreover, the dissolved NH_4^+ and SO_4^{2-} concentrations (0.93 and 6.55 mg L^{-1}) at location B were smaller than those at location C (1.04 and 7.51 mg L^{-1}), whereas the adsorbed NH_4^+ and SO_4^{2-} concentrations at location B (2.05 and 2.87 mg L^{-1}) were greater than those at location C (1.26 and 1.92 mg L^{-1}). This pattern is likely due to enrichment of the mineral-leaching chemicals in the gully and lower enrichment ratios outside of the gully. However, only adsorbed NH_4^+ concentrations displayed significant differences at location B and C (ANOVA, $p = 0.04$). The gully sediment concentration (288.29 g L^{-1}) was also significantly greater than that outside the gully (157.28 g L^{-1}) (ANOVA, $p = 0.01$).

3.3 Dissolved and adsorbed NH_4^+ and SO_4^{2-} transport characteristics along flow route

Data for the two rainfall days in 2013 were used for a trend analysis. The dissolved NH_4^+ transportation characteristics are shown in Fig. 2a. We took the representative G–S path as an example to analyze the transport characteristics. The NH_4^+ concentrations gradually decreased with transport distance along the sample path. Exponential functions

were used to fit the tendency because the concentrations approached 0 at long distances. The dissolved NH_4^+ concentrations decreased exponentially ($Y = 1.023 \cdot \exp(-0.00312X)$; $R^2 = 0.57$) as a function of the transport distance along the G–S path. The dissolved SO_4^{2-} transport trend was consistent with that of NH_4^+ in the sampled runoff. Figure 2b shows the SO_4^{2-} migration. The SO_4^{2-} concentrations also decreased exponentially ($Y = 3.34 \cdot \exp(-0.0185X)$; $R^2 = 0.57$) with increasing transport distance along the G–S path. However, the relationships for NH_4^+ and SO_4^{2-} transport differed. The dissolved NH_4^+ concentrations ranged from 0.45 to 1.17 mg L^{-1} , while the dissolved SO_4^{2-} concentrations ranged from 2.19 to 3.45 mg L^{-1} . Moreover, the attenuation coefficients of the SO_4^{2-} transport fit (3.34 and 0.0185) were greater than those of NH_4^+ (1.023 and 0.00312), indicating that the SO_4^{2-} concentrations decreased faster than the NH_4^+ concentrations.

The adsorbed NH_4^+ and SO_4^{2-} transport was influenced not only by precipitation intensity and flow energy but also by the erosion amount and sediment transport capacity. The sediment runoff process was so complex that a standardization of NH_4^+ and SO_4^{2-} concentrations using precipitation intensities was impossible. Thus, rainfall data for 15 May 2013, were used as an example to analyze the adsorbed chemicals in the runoff sediment samples. The adsorbed NH_4^+ transport characteristics are shown in Fig. 3a. Initially (transport distance 0–120 m), the adsorbed NH_4^+ concentrations showed a weak descending trend. However, when the sediment moved beyond 120 m, the concentrations increased to a distance of 180 m. Figure 3b shows that the adsorbed SO_4^{2-} transport was quite different from that of NH_4^+ in the sampled runoff sediment. The adsorbed SO_4^{2-} concentrations exhibited substantial variability as a function of the transport distance. The transport characteristics of the adsorbed NH_4^+ and SO_4^{2-} in the runoff sediment cannot be described as a linear function because it is difficult to identify a distinct trend.

3.4 Variations in adsorbed NH_4^+ and SO_4^{2-} contents with sand, silt, and clay particles

The grain size analysis was carried out in order to find correlation between leaching chemicals and the sediment particle size distributions. Figures 4 and 5 showed that the adsorbed NH_4^+ and SO_4^{2-} concentrations in the sampled runoff exhibited similar relationships with the sediment particle size distribution. The NH_4^+ and SO_4^{2-} content displayed linearly decreasing trends with increasing sand content and linearly increasing trends with increasing silt and clay contents.

4 Discussion

In this paper, to study the transport characteristics of mineral-leaching chemicals, soil on rare-earth tailings was sam-

Table 2. Average dissolved and absorbed NH_4^+ and SO_4^{2-} concentrations in the runoff samples at different locations. Locations B and C represent the gully below the tailing heap and outside the tailing heap, respectively. The asterisk refers to the very significant difference between the two statuses (dissolved and absorbed) of the same chemical at the same location at the 0.01 level.

Positions	Dissolved	Absorbed	Dissolved	Absorbed	Runoff volume	Sediment concentration	Runoff pH
	NH_4^+	NH_4^+	SO_4^{2-}	SO_4^{2-}			
	mg L^{-1}				L	g L^{-1}	
B	0.93	2.05*	6.55	2.87*	0.37	288.29	4.51
C	1.04	1.26*	7.51	1.92*	0.39	157.28	4.56

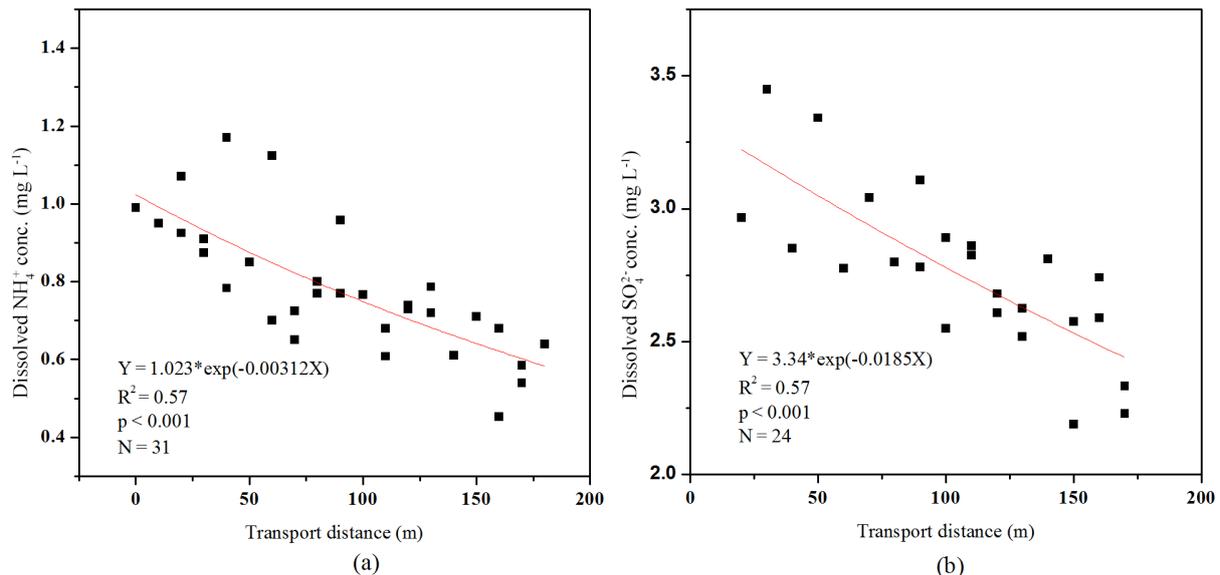


Figure 2. Dissolved NH_4^+ and SO_4^{2-} concentrations variations with increasing transport distance in runoff.

pled in different positions, and runoff and sediment samples were collected along flow routes during three typical rainfall events in the field. The results revealed the mineral-leaching chemicals' spatial distributions driving mechanism and transportation dynamic in flow and sediment processes.

4.1 The driving mechanism of the NH_4^+ and SO_4^{2-} spatial distributions

This study examined the transportation characteristics of NH_4^+ and SO_4^{2-} in runoff in order to explain their distribution in the surface soil at different locations. The main carrier mechanism is an important factor influencing chemical contents along the transport path. NH_4^+ was mainly transported with the sediment in the runoff (Table 2), which was especially enriched in fine particles (Fig. 4). It is possible that NH_4^+ has a strong affinity to the negatively charged particles (Tian et al., 2007). The NH_4^+ contents exhibited an increasing trend from the top of the tailing heap to beyond the heap (Table 1). Similar results have been reported by other studies. Particulate N was the main form in runoff in some ecosystems (Douglas et al., 1998; Zheng et al., 2005). Zhang and

Shao (2000) revealed that NH_4^+ was mainly adsorbed onto soil particles, whereas nitrate N may more easily exist in soil solution. Zheng et al. (2005) also found that NH_4^+ was concentrated in clay, which was transported with the eroded sediment in newly deforested areas on the Loess Plateau. However, our results differ from those of Fu et al. (2004), who reported that NH_4^+ is mainly transported in its dissolved form in runoff. Differences in land use, especially tillage and fertility management, may be responsible for these differences.

The main transport medium of SO_4^{2-} was runoff, and Table 2 demonstrated that SO_4^{2-} moved primarily in a dissolved state, which resulted in a non-significant transport trend from locations A to C in deposited sediment (Table 1). Our results demonstrate that SO_4^{2-} absorption occurred rarely in the upper soil; Alewell and Giesemann (1996) also reported that SO_4^{2-} sorption was not observed in the upper soil (≤ 1 m depth), and SO_4^{2-} solutions may have infiltrated from upper soil layers into deeper soil layers (1–12 m depth), where more SO_4^{2-} sorption was present. The dissolved SO_4^{2-} concentration may be related to pH values. Sharpley et al. (1991) conducted a 4-year field experiment to study the SO_4^{2-} transport

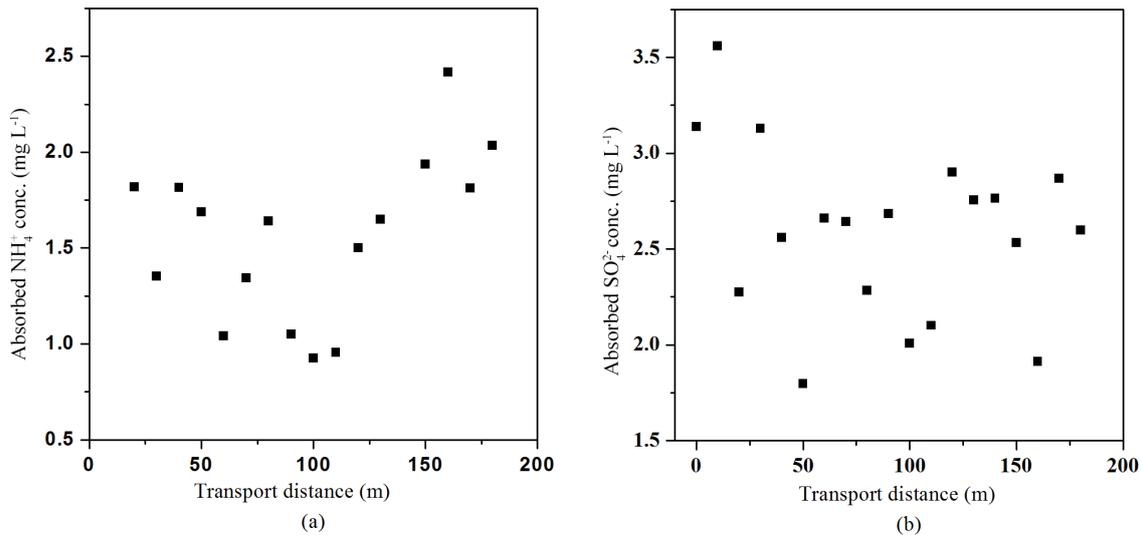


Figure 3. Absorbed NH_4^+ and SO_4^{2-} concentrations variations with increasing transport distance in runoff.

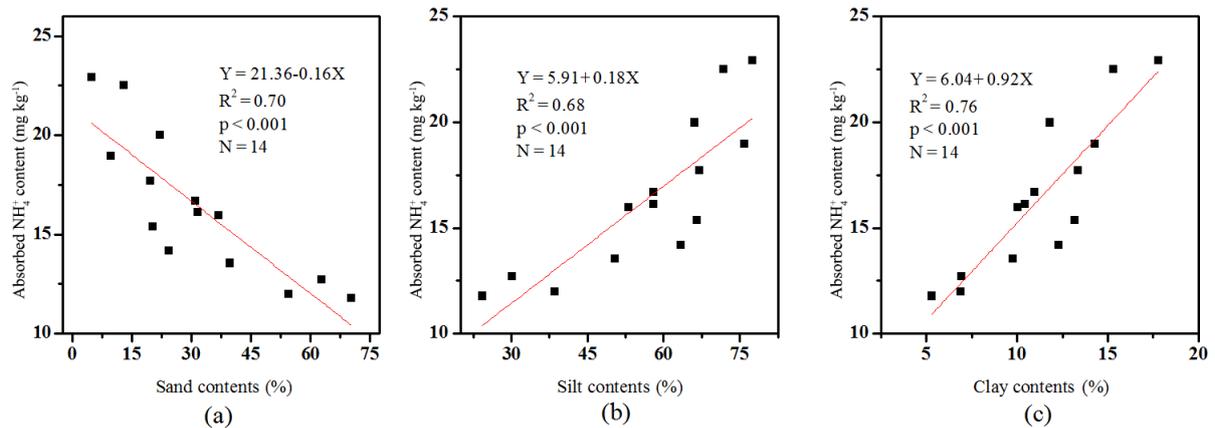


Figure 4. Absorbed NH_4^+ concentrations as a function of sand, silt, and clay contents.

in runoff and reported that the SO_4^{2-} concentration increases with decreasing pH in runoff.

4.2 NH_4^+ and SO_4^{2-} transport dynamic in flow and sediment process

Although the main pattern of transport differed between NH_4^+ and SO_4^{2-} in the runoff, the total concentrations involved both dissolved and absorbed states. The release of chemicals to the runoff involves the adsorption and desorption between the sediment surface and their transport by advection or by ordinary or enhanced diffusion (Wallach et al., 1989). The dissolved NH_4^+ and SO_4^{2-} decreased exponentially during the runoff transport process (Fig. 2) because the dilution associated with increasing runoff discharge and flow diffusion dominated the dissolved chemical transport under these conditions. Schlesinger et al. (2000) reported that the concentrations of dissolved constituents declined with in-

creasing total runoff volume, reflecting a rapid dilution of dissolved constituents with increasing discharge. Razo et al. (2004) also observed an inverse relationship between the distance and the concentration of metals in water from the pollution sources. However, the dissolved SO_4^{2-} concentration decreased faster than that of NH_4^+ , which was probably because dissolved SO_4^{2-} was mainly transported in runoff water. Thus, runoff discharge had a larger influence on the dissolved SO_4^{2-} transportation. Abu Bakar et al. (2015) found SO_4^{2-} was diluted by the large amounts of water observed during high-flow events. In addition, the chemical desorption kinetics, which may be limited by the contact time and sediment surface, should be an important control for dissolved chemicals in runoff (Gilley et al., 2012).

The absorbed NH_4^+ and SO_4^{2-} transport was more complicated in the runoff sediment. Tailing heaps provided a large quantity of sediments to the gully at the beginning of erosion.

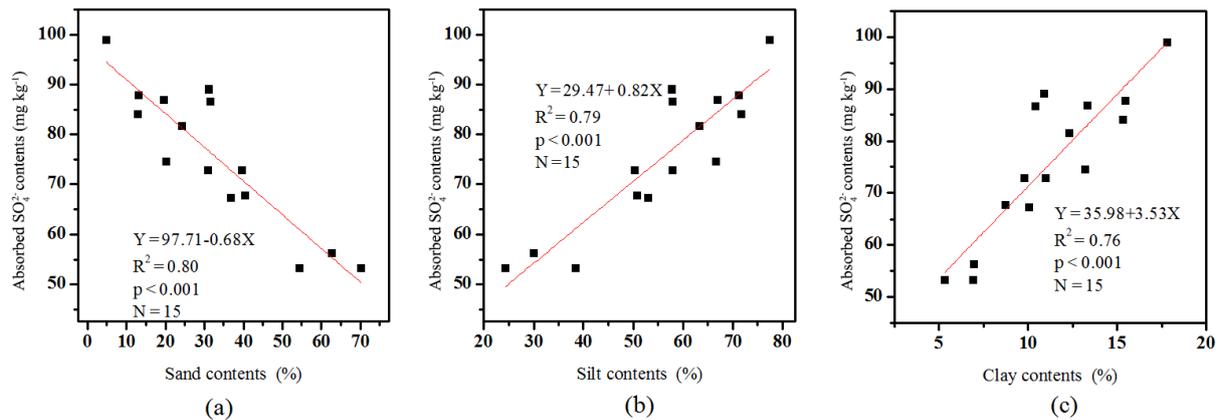


Figure 5. Absorbed SO_4^{2-} concentrations as a function of sand, silt, and clay contents.

Thus, the sediment concentration and the absorbed leaching chemicals continued to accumulate. When the runoff and runoff-associated sediment flowed beyond the heaps, the sediment concentration exceeded the runoff transport capacity as the flow decreased, resulting in gradual deposition of the sediment. Accordingly, the sediment concentration and absorbed NH_4^+ and SO_4^{2-} concentrations decreased (Table 2). As mentioned above, NH_4^+ was transported in an adsorbed state on fine particles (Fig. 4). Finer particles, especially clay, are typically considered to be the sediment size fraction that is most important in transporting adsorbed chemicals in soil and overland flow (Slattery and Burt, 1997; Young and Onstad, 1978; Hardy et al., 2016). Smaller particles, particularly silt and clay, have relatively greater specific surface areas and can therefore adsorb and transport large quantities of chemicals (Lü et al., 2007). Finer particles are more easily transported in runoff, resulting in increased fine-particle levels with transport distance along the path (Flanagan and Nearing, 2000; Parsons et al., 2006). More finer sediment reached the end of the deposition region than did coarser particles, and more chemicals were adsorbed on fine sediment particles. This is known as the selectivity of the erosion process (Sharpley, 1985; Zhang et al., 2016). Although the absolute quantity of sediment decreased, the percentage of relatively fine particles increased. This process explains why the adsorbed NH_4^+ transport characteristics in runoff showed an increasing trend over the last several meters (120–180 m; Fig. 3a). The trend slightly decreased at first; thus, the dynamic accumulation, remobilization, and adsorption-desorption in the transport process may influence the adsorbed NH_4^+ trend over the first few tens of meters (Ashraf and Borah, 1992; Huang et al., 2007). Although the adsorbed SO_4^{2-} concentration in the runoff also increased with finer particles and decreased with more sand particles (Fig. 5), the dissolved state is the major SO_4^{2-} transport form. The reason for this may differ from that for NH_4^+ , which was mainly transported in its adsorbed state. Flow energy attenuation

may also have enriched finer particles in adsorbed SO_4^{2-} in the sampled runoff. The SO_4^{2-} continuously dissolved in the runoff and infiltrated into deeper soil layers; hence, the adsorbed SO_4^{2-} concentrations were highly variable with distance (Fig. 3b). No clear transport features exist for adsorbed chemical in the sampled runoff. Pascaud et al. (2015) found that the effect of mining contamination decreased in sediment over a distance of 8000 m. Our study scale may not be large enough; moreover, earlier deposited sediment may have affected the runoff samples.

4.3 Implications and prospects of this study

The mineral-leaching chemicals' characteristics in rare-earth tailing heaps were discussed in this study. The results of this study indicate that leaching chemicals (NH_4^+ and SO_4^{2-}) transport characteristics as dissolved and adsorbed state in runoff and sediment along the flow route during natural rainfall. Besides the leaching chemicals we found, Pb, Cd, Zn, Cu and radioactive elements also existed (Gao and Zhou, 2011). The pollutants were transported from the mining area to the surrounding soil and surface water bodies through surface runoff water. Even after mining activities stopped, the ecological environment may still suffer a series of serious problems, such as the loss of farmland by sediment deposition due to soil erosion and damaged soil because of low pH and high chemical concentration. Measures for soil erosion and soil remediation must be urgently taken within the mining area. Vegetation and mulches have been proved to effectively reduce runoff energy and trap sediment (Cao et al., 2015). Meanwhile, ditches and terracing should also be conducted to intercept runoff. Soil amendment and fertility can be applied to improve the soil quality. These practices may control the influence of leaching chemicals, rare-earth elements, and sediments on the surrounding environment. Furthermore, there are also many other factors that influence pollutant transport behavior besides transport distance, e.g., the flow energy and topography factors. In future research, field-

simulated experiments should be conducted to establish the relationship between flow hydraulic parameters and chemical transport characteristics. All of these studies may provide a scientific foundation for erosion control and soil management in rare-earth tailing regions in southern China.

5 Conclusions

Large amounts of mineral-leaching chemicals (NH_4^+ and SO_4^{2-}) were still remaining in rare-earth tailings in southern China. By collecting field runoff samples during typical rainfall events in a rare-earth tailing area, this study assessed the contents of two mineral-leaching chemicals in surface sediments at different positions and provided insights regarding runoff- and sediment-related transport characteristics along the flow route. During typical rainfall events, the absorbed NH_4^+ concentrations in runoff were significantly higher than the dissolved concentrations, while the absorbed SO_4^{2-} concentrations were significantly lower than the dissolved concentrations. The driving mechanism of the NH_4^+ and SO_4^{2-} resulted in their spatial distributions in different locations. NH_4^+ is mainly transported with sediment in an absorbed state, and NH_4^+ content in the surface sediment samples showed an increasing trend from the top of the tailing heap to the area beyond the tailing gullies. Whereas SO_4^{2-} is mainly dissolved and transported with runoff, the SO_4^{2-} content did not show an observable trend. The dissolved NH_4^+ and SO_4^{2-} concentrations in runoff showed exponentially decreasing trends with transport distance from gully outlets to the nearby water body as a result of dilution. The absorbed chemicals' transport process may be more complex. The absorbed NH_4^+ and SO_4^{2-} concentrations in runoff showed no clear trends with transport distance. Linear regressions were conducted to establish the relationship between the NH_4^+ and SO_4^{2-} concentrations and the sand, silt, and clay contents. The NH_4^+ and SO_4^{2-} concentrations tended to be enriched in the silt and clay particles of transported sediment. The above results will aid a better understanding of the transport characteristics of mineral-leaching chemicals during the erosion process and the development of predictive equations in rare-earth tailing areas. Our results suggest that management practices for soil remediation should be mandatory in rare-earth tailings in southern China.

Data availability. All data obtained can be accessed by e-mailing the first author (hzlu@issas.ac.cn).

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Author contributions. LC, HL, and YL designed the research sample methods. LC, HL, JY, YZ, YW, and YG carried them out in the field. HL, LC, and YL developed the model code and performed the simulations. HL and LC prepared the paper. QZ and YL provided constructive suggestions for the paper.

Competing interests. The authors declare that they have no conflict of interest.

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