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

Huizhong Lu1,2, Longxi Cao1, Yin Liang1, Jiuqin Yuan1,2, Yayun Zhu1,2, Yi Wang1,2, Yalan Gu1,2, Qiguo Zhao1

1State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
2University of Chinese Academy of Sciences, Beijing 100049, China

Corresponding to: Yin Liang (yliang@issas.ac.cn)

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. To study the transport characteristics of mineral leaching chemicals, soil on rare earth tailings was sampled in different positions, and runoff and sediment samples were collected along flow routes during three typical rainfall events. The results demonstrated that the NH\(_4^+\) contents in the surface sediment deposits increased from the top of the heap (6.56 mg/kg) to the gully (8.23 mg/kg) and outside the tailing heap (13.03 mg/kg). The contents of SO\(_4^{2-}\) in the different locations of the tailing heaps ranged from 27.71 to 40.33 mg/kg. During typical rainfall events, the absorbed NH\(_4^+\) concentrations (2.05, 1.26 mg/L) in runoff were higher than the dissolved concentrations (0.93, 1.04 mg/L), while the absorbed SO\(_4^{2-}\) concentrations (2.87, 1.92 mg/L) were lower than the dissolved concentrations (6.55, 7.51 mg/L). The dissolved NH\(_4^+\) and SO\(_4^{2-}\) concentrations in runoff displayed an exponentially decreasing tendency with increasing transport distance (Y=1.02*exp(-0.00312X), Y=3.34*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.

Keywords: Mineral leaching chemicals; Soil and water loss; Ionic rare earth element mine; Tailing heap; chemical transport

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; 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).

China is the dominant rare earth element (REE) 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 significance for industry and the economy (Kanazawa and Kamitani, 2006). 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 3.8×10^4 t/(km² a) (Lu et al., 2015), which far exceeds the severe erosion standard of 1.5×10^4 t/(km² a) (SL190-2007, Ministry of Water Resources, PRC, 2007). In addition, as the HREEs are adsorbed onto the clay surface, large amounts of the mineral leaching chemicals ammonium sulfate and ammonium bicarbonate are used during ion-adsorption REE 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 et al., 1995; Lambert et al., 1985). Therefore, it is necessary to simulate and predict sediment yield and the leaching 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 modelling (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 upscaling 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, CREAMS and SWAT, calculate sediment yield based on the empirical USLE 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. Furthermore, different chemicals have unique transportation pathways and primary carriers in runoff. Thus, it is necessary to compare the differences between NH$_4^+$ and SO$_4^{2-}$.

We conducted a 2-year field study of runoff and sediment during natural rainfall events in a rare earth tailing area to (1) quantify the content of two leaching chemicals in the surface soil at different locations around the tailing heaps and (2) determine the transport characteristics 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 Xineng County, Ganzhou, Jiangxi Province, South China (25°23′10″ N, 115°0′26″ E). The region features a subtropical moist monsoon climate with an 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 averages ranging from -4°C 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$_2$O$_3$ via burning (Chi and Tian, 2007). After this mining process, residual tailing heaps containing acid leaching solution pollutants are formed. The production of one ton of rare earth oxide can create 1600-2000 tons 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 Sample collection

We designed the sample paths and points based on the erosion types and flow direction. One path along a gully (G) and tailing heap (S) was designed (Fig. 1). 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 and deposited sediment samples. Three rainfall events were recorded on June 16, 2012, May 15, 2013, and May 16, 2013. The precipitation intensities were measured with rainfall gauges and were 0.9, 1.0 and 1.2 mm/min, 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. Moreover, 20 surface sediment samples were collected on the top of the tailing heap (Fig. 1A), 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. 1C) after the rainfall events. All surface sediment samples were taken from 0-5 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 five hundred grams, and each deposited surface sediment weight was approximately one hundred grams.
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 $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ concentrations and pH values were measured in the runoff water, and absorbed $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ contents, sediment concentrations and particle distributions were measured in the runoff sediment samples. The $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ contents and particle size distributions were also measured in the surface and deposited sediment samples.

The pH values were determined using the glass calomel electrode method. The dissolved $\text{NH}_4^+$ concentrations were analyzed colorimetrically using a flow injection analyzer. The dissolved $\text{SO}_4^{2-}$ concentrations were determined using turbidimetry through the formation of $\text{BaSO}_4$ via the addition of $\text{BaCl}_2$.

The $\text{NH}_4^+$ concentrations of the sediment samples were also measured via colorimetry in a flow injection analyzer after extraction with a 1 mol/L $\text{KCl}$ solution. The $\text{SO}_4^{2-}$ concentrations were determined using turbidimetry through the formation of $\text{BaSO}_4$ via the addition of $\text{BaCl}_2$. The sediment particle distribution was determined by sieving in combination with the sieve-pipette method (Lu, 2000).

2.4 Data analysis

Linear regressions were conducted to establish the relationship between the $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ concentrations and the influencing factors. The coefficient of determination ($R^2$) was used to evaluate the performance of the applied regression equations. The analyses and graphical displays were prepared using ORIGIN8.0 (OriginLab, Northampton, MA, USA) and ArcGIS 9.3 (ESRI, Redlands, CA, U.S.A.).

3 Results

3.1 $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ distributions in surface soils in different positions

The $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ contents in surface runoff depends on the corresponding content in the tailing heaps. Therefore, the $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ 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 $\text{NH}_4^+$ and $\text{SO}_4^{2-}$ contents in the surface sediment samples collected at different locations. From A to B and C, the $\text{NH}_4^+$ contents increased. The value on top of the heap was 6.56 mg/kg, and the values outside the heap reached as high as 13.03 mg/kg. The trend observed for the $\text{SO}_4^{2-}$ values did not agree with that of the $\text{NH}_4^+$ values. The $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$ 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 because 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.
Table 1. NH$_4^+$ and SO$_4^{2-}$ contents and soil textures in the surface soil samples collected in different locations.

<table>
<thead>
<tr>
<th>Locations</th>
<th>NH$_4^+$</th>
<th>SO$_4^{2-}$</th>
<th>Sand 2-0.05 mm</th>
<th>Silt 0.05-0.002 mm</th>
<th>Clay &lt;0.002 mm</th>
<th>Soil texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.56±1.87</td>
<td>40.33±4.58</td>
<td>60.35±4.3</td>
<td>36.07±4.26</td>
<td>3.59±1.83</td>
<td>sandy loam</td>
</tr>
<tr>
<td>B</td>
<td>8.23±1.46</td>
<td>27.71±3.95</td>
<td>92.63±1.3</td>
<td>7.17±1.18</td>
<td>0.20±0.19</td>
<td>sandy soil</td>
</tr>
<tr>
<td>C</td>
<td>13.03±3.42</td>
<td>32.11±4.42</td>
<td>83.84±5.4</td>
<td>15.56±5.19</td>
<td>0.61±0.36</td>
<td>loamy sand</td>
</tr>
</tbody>
</table>

* 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).

3.2 NH$_4^+$ and SO$_4^{2-}$ concentrations in runoff and sediment

Runoff is the main driving force for soil erosion and chemical transport (Table 2). In the case of runoff movement, the chemicals adsorbed on the sediment particles enter overland flow. Additionally, the dissolved chemicals also enter the sediment surface. After more than twenty 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 absorbed NH$_4^+$ concentrations at sites B (2.05 mg/L) and C (1.26 mg/L) were higher than the dissolved NH$_4^+$ contents at sites B (0.93 mg/L) and C (1.04 mg/L). 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) and C (7.51 mg/L) were nearly three times higher than the absorbed SO$_4^{2-}$ at sites B (2.87 mg/L) and C (1.92 mg/L). 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 mg/L and 6.55 mg/L) at location B were smaller than those at location C (1.04 mg/L and 7.51 mg/L), whereas the absorbed NH$_4^+$ and SO$_4^{2-}$ concentrations at location B (2.05 mg/L and 2.87 mg/L) were greater than those at location C (1.26 mg/L and 1.92 mg/L). This pattern is likely due to enrichment of the mineral leaching chemicals in the gully and lower enrichment ratios outside of the gully. The gully sediment concentration (288.29 g/L) was also significantly greater than that outside the gully (157.28 g/L).

Table 2. Average dissolved and absorbed NH$_4^+$ and SO$_4^{2-}$ concentrations in the runoff samples at different locations.

<table>
<thead>
<tr>
<th>Positions</th>
<th>Dissolved NH$_4^+$ mg/L</th>
<th>Dissolved SO$_4^{2-}$ mg/L</th>
<th>Absorbed NH$_4^+$ mg/L</th>
<th>Absorbed SO$_4^{2-}$ mg/L</th>
<th>Runoff volume L</th>
<th>Sediment concentration g/L</th>
<th>Runoff pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.93</td>
<td>6.55</td>
<td>2.05</td>
<td>2.87</td>
<td>0.37</td>
<td>288.29</td>
<td>4.51</td>
</tr>
<tr>
<td>C</td>
<td>1.04</td>
<td>7.51</td>
<td>1.26</td>
<td>1.92</td>
<td>0.39</td>
<td>157.28</td>
<td>4.56</td>
</tr>
</tbody>
</table>
b. Locations B and C represent the gully below the tailing heap and outside the tailing heap, respectively.

3.3 Dissolved NH$_4^+$ and SO$_4^{2-}$ transportation characteristics in runoff

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. Data for the two rainfall days in 2013 were used for a trend analysis. The dissolved NH$_4^+$ transportation characteristics are shown in Figure 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 zero at long distances. The dissolved NH$_4^+$ concentrations decreased exponentially ($Y=1.023\times\exp(-0.00312X)$, $R^2=0.57$) 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 ($Y=3.34\times\exp(-0.0185X)$, $R^2=0.57$) 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, while the dissolved SO$_4^{2-}$ concentrations ranged from 2.19 to 3.45 mg/L. 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.

![Figure 2](image1.png)  
![Figure 2](image2.png)  

Figure 2. Dissolved NH$_4^+$ and SO$_4^{2-}$ concentrations in runoff as a function of distance along the sample paths.
3.4 Absorbed NH$_4^+$ and SO$_4^{2-}$ transport characteristics in runoff

The absorbed 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 May 15, 2013, were used as an example to analyze the absorbed chemicals in the runoff sediment samples. The absorbed NH$_4^+$ transport characteristics are shown in Figure 3a. The absorbed NH$_4^+$ concentrations ranged from 14.34 to 36.28 mg/kg in the runoff sediment. Initially (transport distance 0-120 m), the absorbed 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. The absorbed SO$_4^{2-}$ transport was quite different from that of NH$_4^+$ in the sampled runoff sediment (Fig. 3b). The absorbed SO$_4^{2-}$ concentrations exhibited substantial variability as a function of the transport distance, ranging from 58.28 to 163.14 mg/kg. 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.

Figure 3. Absorbed pollutant concentrations in runoff as a function of distance along the specific sample paths.

3.5 Relationship between absorbed NH$_4^+$ and SO$_4^{2-}$ and sediment particle size distributions in runoff

The absorbed NH$_4^+$ and SO$_4^{2-}$ concentrations in the sampled runoff exhibited similar relationships with the sediment particle size distribution (Figs. 4 and 5). 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). 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. 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).
Discussion

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.

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 deposited fine particle contents (silt and clay) increased with distance. Meanwhile, the NH$_4^+$ content increased with increasing transport distance in deposited sediment. Thus, 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 on 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 SO$_4^{2-}$ moved primarily in a dissolved state (Table 2), which resulted in a non-significant transport trend from locations A to C (Table 1). Our results demonstrate that SO$_4^{2-}$ absorption occurred rarely in the upper soil, although it was found in deeper soil layers, which was also reported by Alewell and Giesemann (1996). SO$_4^{2-}$ solutions may have infiltrated from upper soil layers into deeper soil layers, where more absorbed SO$_4^{2-}$ was present. The dissolved SO$_4^{2-}$ concentration may be related to pH values. Sharpley et al. (1991) conducted a four-year field experiment to study the SO$_4^{2-}$ transport in runoff and reported that the SO$_4^{2-}$ concentration increases with decreasing pH in runoff.

4.2 NH$_4^{+}$ and SO$_4^{2-}$ transportation 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 increasing 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. 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. 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 absorbed 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). 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 absorbed 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 absorbed 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 absorption-desorption in the transport process may influence the absorbed NH$_4^+$ trend over the first few tens of meters (Ashraf and Borah, 1992; Huang et al., 2007). Although the absorbed SO$_4^{2-}$ concentration in the runoff also increased with of 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 of NH$_4^+$, which was mainly transported in its absorbed state. Flow energy attenuation may also have enriched finer particles in absorbed SO$_4^{2-}$ in the sampled runoff. The SO$_4^{2-}$ continuously dissolved in the runoff and infiltrated into deeper soil layers; hence, the absorbed SO$_4^{2-}$ concentrations were highly variable with distance (Fig. 3b). No clear transport features exist for either absorbed 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 for the first time. However, many factors that influence pollutant transport behavior besides transport distance remain. Therefore, the next step is to study the effects of rainfall, slope and depth on chemical transport using a series of simulated experiments in the field.

5 Conclusions

By collecting field runoff samples during typical rainfall events in a rare earth tailing area in South China, this study assessed the contents of two mineral leaching chemicals, i.e., NH$_4^+$ and SO$_4^{2-}$, in surface sediments at different positions and provided insights regarding runoff- and sediment-related transport characteristics along the flow route. The results reveal that NH$_4^+$ is mainly transported with sediment in an absorbed state, whereas SO$_4^{2-}$ is mainly dissolved and transported with runoff. The 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 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. The absorbed NH$_4^+$ and SO$_4^{2-}$ concentrations in runoff showed no clear trends with transport distance. The NH$_4^+$ and SO$_4^{2-}$ concentrations tended to be higher in the finer particles of transported sediment, and runoff had a sorting effect on the sediment size distribution.

The above results will aid in better understanding the transport characteristics of mineral leaching chemicals during the erosion process and in developing predictive equations in rare earth tailing areas.

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Data availability

All gained data can be assessed by asking for them the author via an e-mail (hzlu@issas.ac.cn)

Author contribution
Longxi Cao, Huizhong Lu, and Yin Liang designed the research sample methods. And Longxi Cao, Huizhong Lu, Jiujin Yuan, Yunyun Zhu, Yi Wang, Yalan Gu carried them out in the field. Developed the model code and performed the simulations. Huizhong Lu and Longxi Cao prepared the manuscript. Qiguo Zhao and Yin Liang provided constructive suggestions for the manuscript.

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

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