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

Huizhong Lu[1, 2], Longxi Cao[1], Yin Liang[*1], Jiuqin Yuan[1, 2], Yayun Zhu[1, 2], Yi Wang[1, 2], Yalan Gu[1, 2],

5   Qiguo Zhao[1]

[1]State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing

210008, China

[2]University of Chinese Academy of Sciences, Beijing 100049, China

10   **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

15   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

20   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

25   (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

30   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

35   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

40   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 $3.8{\times}10^4$ t/(km^2 a) (Lu et al., 2015), which far exceeds the severe erosion standard of $1.5{\times}10^4$ t/(km^2 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

5   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

10   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

15   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°23′10″ N, 115°0′26″ E). The region features is 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

20   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

25   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

30   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,

35   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

40   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.

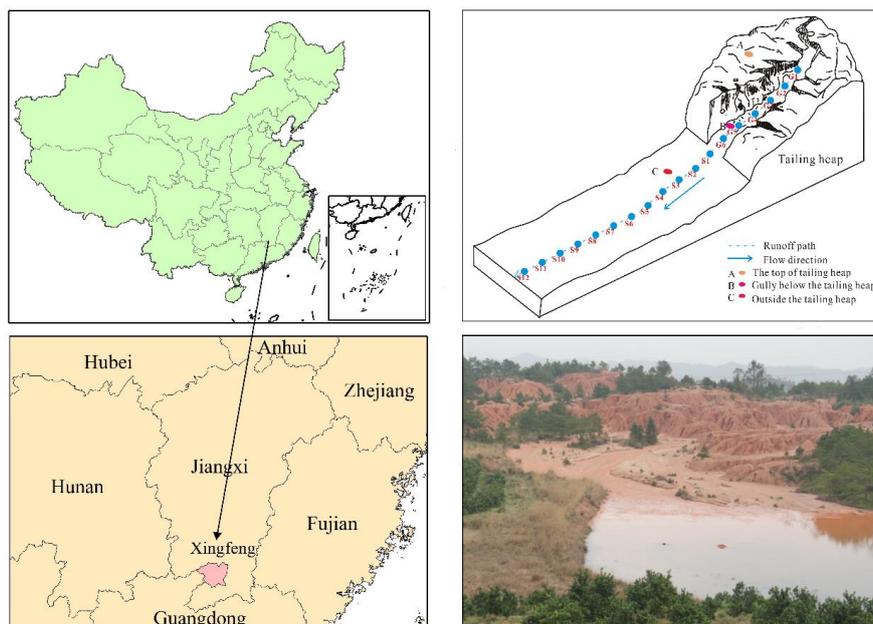



Figure 1. Sampling site.

2.2 Sample collection

5   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
10 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
15 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
20 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.

25 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 NH_4^+ and 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 NH_4^+ concentrations were analyzed colorimetrically using a flow injection analyzer. The dissolved SO_4^{2-} concentrations were determined using turbidimetry through the formation of $BaSO_4$ via the addition of $BaCl_2$.

The NH_4^+ concentrations of the sediment samples were also measured via colorimetry in a flow injection analyzer after extraction with a 1 mol/L KCl solution. The 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).

2.4 Data analysis

Linear 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. 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 NH_4^+ and SO_4^{2-} distributions in surface soils in different positions

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, and the values outside the heap reached as high as 13.03 mg/kg. 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 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.

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			%		
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

a. Locations A, B and C are the top of the tailing heap, the gully below the tailing heap, and the
5   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
10   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
15   (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
20   (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
25   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.

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

Location	Soluble NH$_4^+$	Soluble SO$_4^{2-}$	Absorbed NH$_4^+$	Absorbed SO$_4^{2-}$	Runoff pH
	mg/L				
B	0.93	6.53	2.06	2.85	4.51
C	1.03	7.53	1.26	1.91	4.56

b. Locations B and C represent the gully below the tailing heap and outside the tailing heap, respectively.

5   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

10   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

15   exponentially (Y=1.023*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*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$_4^+$

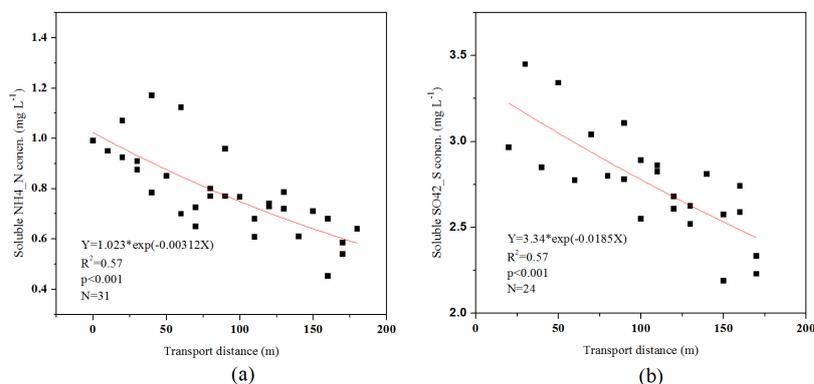
20   concentrations ranged from 0.45 to 1.17 mg/L, while the dissolved SO$_4^{2-}$ concentrations ranged from 2.19 to 3.45 mg/L. Moreover, the attenuation coefficients of the SO$_4^{2-}$ transport fit (3.34 and 0.0185) were greater than those of NH$_4^+$ (1.023 and 0.00312), indicating that the SO$_4^{2-}$ concentrations decreased faster than the NH$_4^+$ concentrations.

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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

5   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

10 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-}

15 in the runoff sediment cannot be described as a linear function because it is difficult to identify a distinct trend.
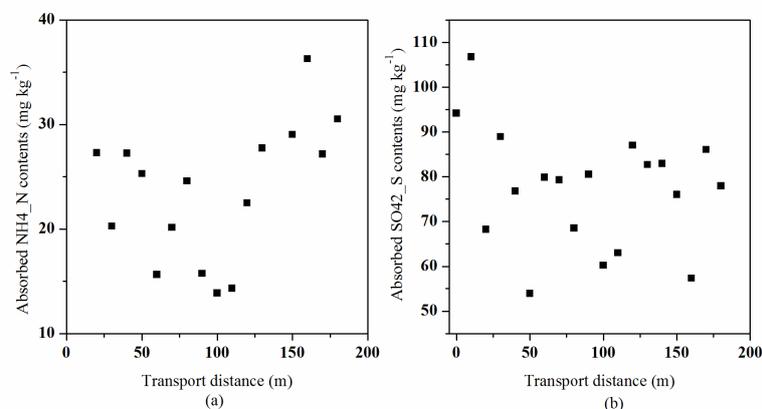
Figure 3. Absorbed pollutant concentrations in runoff as a function of distance along the specific sample paths.

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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

25 (<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).

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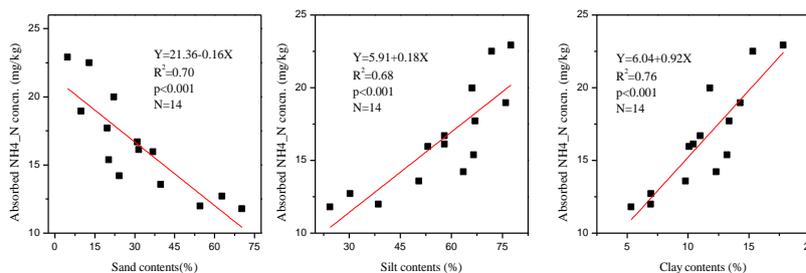
Figure 4. Relationships between the absorbed NH_4^+ and the sediment particle size distributions.
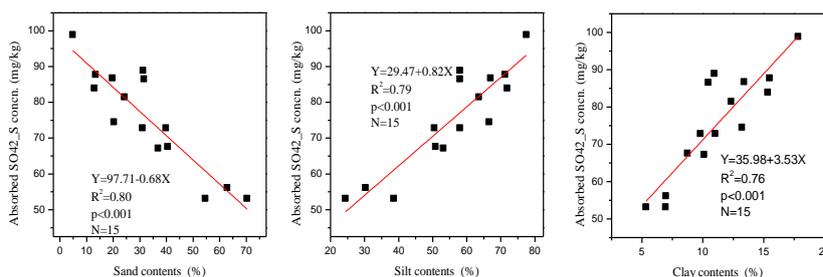
Figure 5. Relationships between the absorbed SO_4^{2-} and the sediment particle size distributions.

4   Discussion

10   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

15   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

20   (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

25   (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.

5   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

10   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

15   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

20   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

25   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

30   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

35   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

40   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

5   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

10   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.

15   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

20   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

25   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

30   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, Jiuqin Yuan, Yunyun Zhu, Yi Wang, Yalan Gu carried them out in the field. D developed the model code and periformed 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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