

Biogeochemical cycles of nutrients, rare earth elements (REEs) and Al in soil-plant system in ion-adsorption REE mine tailings remediated with amendment and ramie (Boehmeria nivea L.)

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Graphical abstract



Highlights

- REE mine tailings are characterized by REE and Al excess and nutrient deficiency
- Phytostabilization practices decrease soil extractable REE and Al concentrations
- Phytostabilization practices improve physico-chemical properties of mine tailings
- Ramie root activity increases soil extractable nutrient but not REE and Al contents
- Ramie stores most of the plant REEs and Al in the thick roots

2	Biogeochemical cycles of nutrients, rare earth elements (REEs) and Al in
3	soil-plant system in ion-adsorption REE mine tailings remediated with
4	amendment and ramie (Boehmeria nivea L.)
5	
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The exploitation of ion-adsorption rare earth element (REE) deposits in South China 30 31 has left large areas of mine tailings. However, limited remediation practices on these 32 tailings have been reported, and how the remediation strategies and economic plants 33 cultivation affect the biogeochemical cycles of nutrients, REEs and Al remains unclear. 34 The aim of the present study was to investigate the effects of the combination of the 35 addition of soil amendment and the root development and activity of a fiber plant ramie 36 (Boehmeria nivea L.) on the availability and distribution of nutrients, as well as of REEs 37 and other potentially toxic elements (e.g. Al) in the soil-plant system. The results showed that the application of organic amendment and ramie planting induced a 38 significant increase in soil pH, total carbon (C), nitrogen (N), and other nutrient (e.g. P 39 40 and Ca) concentrations, while led to a decrease of 80-90% and 60-90% in soil extractable REE and Al concentrations respectively. Matrices of correlation showed 41 42 that soil pH, total C, N, and P concentrations were among the most important factors 43 controlling the availability of soil REEs and Al, and root characteristics (e.g. fine root length). The total C, N, P and extractable nutrient concentrations, and electrical 44 45 conductivity were higher in the rhizosphere soils of ramie than those in the bulk soils. Moreover, more than 60% of the quantity of REE and Al in the whole ramie plant were 46 stored within the thick roots. These results showed that, in addition to amendment, the 47 effects induced by the roots of ramie could further improve soil properties through C 48 49 input, nutrient mobilization and toxic element stabilization. Our study concludes that

- 50 ramie planting with organic amendment is a promising phytostabilization strategy for
- 51 the remediation of REE mine tailings in South China.
- 52
- 53 Keywords: fiber plant; mobilization; rhizosphere; root characteristic
- 54

Rare earth elements (REEs) are a group of metallic elements comprised of fifteen 56 lanthanide elements plus yttrium. The lanthanides are typically split into two sub-57 groups, light REEs (LREEs, La to Eu) and heavy REEs (HREEs, Gd to Lu) (Tyler 2004). 58 59 As the demand of REEs increases globally, the mining of REE deposits has rapidly 60 grown (Yang et al. 2013). Ion-adsorption REE deposits, resulting from the weathering 61 of granite under (sub)tropical climate, are mainly located in South China, and later 62 found in Vietnam, Myanmar and Madagascar (Borst et al. 2020). In these deposits, most 63 REEs exist as trivalent ions and are adsorbed onto the clay minerals (e.g. kaolinite) and Fe/Mn oxides originated from the granite. Thus, the REEs can be easily leached out 64 through a simple ion-exchange process using a salt solution: $2(Kaolin)^{3-}RE^{3+} +$ 65 $3(NH_4)_2SO_4 \rightarrow 2(Kaolin)^{3-}(NH_4)_3^+ + RE_2^{3+}(SO_4)_3^{2-}$. The heap leaching technology used 66 for decades in South China has consisted of: i) removing the vegetation and the topsoil; 67 ii) excavating the REE-rich clays (ores) from the (semi)weathered layers at a depth of 68 5–20 m; iii) pilling up the ores into a heap on a plastic sheet and leaching them with 69 70 ammonium sulfate solution; iv) recovering REEs from the leachates (Xiao et al. 2015). 71 This mining technology has induced many environmental damages, such as water and 72 soil erosion, vegetation destruction and mine tailings generation (Yang et al. 2013). For instance, it was reported that the area of REE mine tailings in Ganzhou city in the 73 Jiangxi province exceeded 100 km² (Liu et al. 2015). 74

76 Though some pioneer plants have begun to settle after several years of abandonment, the revegetation of these mine tailings under natural succession is quite slow (Liu et al. 77 78 2015). The poor physical conditions with soil compaction, low pH (4–5), low contents of nutrients (especially P) and organic matter (~0.1%), and low microbial activities are 79 80 considered as the main obstacles for plant colonization on these mine tailings (Liu et al. 81 2015). Moreover, these tailings still contain high residual REE concentrations (Chao et 82 al. 2016), which are highly exchangeable even after 10 years of abandonment (>20% 83 of the total REEs extracted with 1.0 mol/L MgCl₂) (Wen et al. 2013). This part of REEs 84 may leach out and enter into the surrounding rivers and farmland soils, posing potential risks to local living organisms (Li et al. 2013). Besides, the exchangeable Al^{3+} 85 concentration in the tailings soil is high and accounts for 80% of total cation exchange 86 87 capacity (CEC) (Liu et al. 2020a), which may also inhibit plant colonization. Up to now, the phytoremediation field trials at these mine tailings have mainly focused on the 88 restoration of soil fertility and microbial communities (Zhou et al. 2015; Liu et al. 2016; 89 90 Wei et al. 2019; Liu et al. 2020b), whilst the control of REE and Al availabilities and 91 the cycling of REE and Al are largely ignored.

92

Phytostabilization, one strategy of phytoremediation, aims to establish a plant cover on
the surface of contaminated soils, hence retaining contaminants within the vadose zone
through root accumulation or precipitation of contaminants within the rhizosphere. This
strategy can also reduce contamination dispersion by wind, water, and direct contact

97 with humans or animals (Bolan et al. 2011). Addition of organic amendments is a common practice in phytostabilization, which can improve soil structure, alleviate soil 98 99 nutrient deficiency, and effectively stabilize contaminants in mine tailings (Meeinkuirt 100 et al. 2016). A recent pot experiment showed that organic amendments are effective in 101 increasing the soil pH and organic matter concentration, thus reducing the REE 102 concentrations in tailing soil solution (Liu et al. 2020a). However, organic amendment 103 would induce an enrichment of dissolved organic carbon (DOC) in soil solution. As a result, heavy metals that are adsorbed on soil particles can be complexed by DOC and 104 105 solubilized into the soil solution. For example, it was found that manure amendment 106 was less efficient to stabilize heavy metals (e.g. Cd and Zn) (Houben et al. 2012). Nevertheless, the effectiveness of phytostabilization practice with organic amendment 107 108 in stabilizing REE and Al on the mine tailings needs further examination in the field.

109

110 Root development and activities are critical for the growth of plant and the cycling of 111 nutrients and pollutants in the soil-plant system since roots are the interface between 112 the plant and the soil environment (Abe 2001). Plants can adapt to harsh soil condition 113 through the manipulation of root morphology and metabolites (Sasse et al. 2019). Root morphological architectures and physiological adaptations are easily altered by 114 nutritional stress (Lambers and Colmer 2005). A number of studies found that the 115 changes of root morphology (e.g. fine root length) are critical for plant nutrient 116 117 acquisition (Hill et al. 2006; Christopher and Jonathan 2020). Plant root exudates,

118 consisting of a complex mixture of metabolites, play a fundamental role in regulation of soil nutrient availability and detoxification of undesirable metal pollutants for plants 119 120 (Dakora and Phillips 2002; Chen et al. 2017). Under conditions of nutrient deficiency 121 (e.g. P), plant roots would release carboxylates and lower soil pH, thus solubilizing P. 122 and Mn (or heavy metals) accidently (Lambers et al. 2015). Although the availability 123 of heavy metals can be largely reduced in the early stage of phytostabilization practices, a subsequent re-mobilization of heavy metals may happen as a result of root secretion 124 (Pierzynski et al. 2002; Cui 2011). However, there are no detailed studies reporting the 125 126 in situ effects of root activities on soil properties and on the change of REE and Al availabilities in mine tailings. 127

128

129 The cultivation of economic crops in the mine tailings can produce biomass of industrial interest (e.g. fibers and bioenergy) and contribute to the socio-economic redevelopment 130 of these mining areas (Ding et al. 2018). However, most studies focused on native or 131 132 pioneer plants (Wang et al. 2017), and the potential use of the economic crops for the remediation of mine sites is largely ignored. The fiber plant ramie (Boehmeria nivea L.) 133 134 is a perennial herb, with a complex underground system composed of fine fibrous roots, radish roots and rhizome. In previous studies, ramie is regarded as a multi-metal tolerant 135 plant, with strong tolerance to Pb, Zn, Cd, As, and has strong adaptability to harsh 136 environment such as drought (Yang et al. 2010). Ramie has also been found to have 137 138 great REE tolerance and retain most of the REEs in roots under hydroponic culture (Liu

et al. 2021a). Therefore, it could be a potential candidate for the phytoremediation of
ion-adsorption REE mine tailings and for the production of fibers of economic value.

In this work, a field trial of phytostabilization combining addition of soil amendment and cultivation of the fiber plant ramie were conducted on ion-adsorption REE mine tailings in South China with the aim of investigating: (i) the effects of phytostabilization practice on the changes of soil physico-chemical properties, including nutrients, REE and Al availabilities; (ii) the root development and the role of root activities in the changes of nutrients, REE and Al availabilities; (iii) the distribution, transfer and fractionation of REEs in the soil-plant system.

149

150 2. Materials and Methods

151 2.1 Site description

The study area is located in the Dingnan county of Ganzhou city, Jiangxi province, 152 China (latitude: 24.99°, longitude: 115.05°). The terrain is hilly with an altitude ranging 153 between 200 and 1200 m. It is situated in the subtropical monsoon humid climate zone 154 with an average annual temperature of 18.9 °C and annual rainfall of 1620 mm (Shi et 155 al. 2020). Dingnan is famous for its abundant reserve of ion-adsorption REE deposits, 156 which have been mined since the 1980s. The studied REE mine tailings were resulted 157 from the exploitation of REE deposits by heap leaching technology until 2008. The 158 tailings were further terraced to protect them from landslides in 2012 (Fig. 1a). 159

161 The studied mine tailings covered a surface area of about 0.53 km², some parts of which 162 were featured with steep slopes (> 45°) and subjected to strong erosion (Fig. 1). In 2015, 163 the vegetation coverage was limited (< 5%) and composed mainly of pioneer species 164 (*e.g. Miscanthus sinensis, Pinus massoniana*). Since 2015, this site has been used as a 165 demonstration base to implement remediation projects using amendments and different 166 plants.

167

168 2.2 Field plot description and samplings

169

170 *Remediation practices*

171 Two field plots (zones A and B) were set at the demonstration base in July 2015 to test the feasibility of cultivating fiber plants on ion-adsorption mine tailings (Fig. 1). 172 173 Different remediation practices in terms of fertilization, tillage and planting have been applied in both plots (about 2000 m^2 for each). Before planting, organic amendment 174 (pig manure and sawdust with a ratio of 2:1, v/v) was added at a rate of 5–6 kg/m² and 175 mixed with the first 10-12 cm of the tailings by tillage. Based on laboratory 176 177 experiments, this organic amendment was shown to be efficient in supporting the growth of fiber plants in these mine tailings. Compared to manure, the mixture of 178 179 manure and sawdust showed a slower release of DOC and nutrients (Chen et al. 2018). Plant resources (seeds and seedlings) for cultivation were brought from the Institute of 180

181 Bast Fiber Crops (Changsha, Chinese Academy of Agricultural Sciences).

182

183	In the zone A, an annual fiber plant was sown with a density of 3 g/m^2 in July 2015. In
184	June 2016, plants were removed, and organic amendment was further added at a rate of
185	5-6 kg/m ² and mixed in the first 10-12 cm. And then, one-year ramie seedlings of about
186	35 cm in height (cultivar Zhongzhu No.1), were planted in rows (3–5 plants per m ²). In
187	the zone B, ramie seedlings (one-year plants, about 35 cm in height) were planted in
188	rows (3-5 plants per m ²) in July 2015. In June 2016, the aboveground parts of ramie
189	plants were cut and granules of inorganic fertilizers (N/P/K) were introduced at a rate
190	of 30–45 g/m ² .

191

192 *Soil and plant sampling*

The sampling of both field plots was performed in November 2017. For each zone (A 193 and B), five whole ramie plants with soils associated to roots were sampled. 194 Rhizosphere soils were separated into two fractions: (i) the soil loosely adhering to the 195 196 roots (LAR) which was collected by shaking the roots for 3 min until almost no soil particles dropped and (ii) the remaining soil tightly adhering to the roots (TAR) which 197 was then recovered by brushing the roots (Otero et al. 2012). For comparison, bulk soils 198 199 were collected between two plants in each zone. In addition, bare tailing samples were 200 collected at three locations situated near the field plots and were considered as controls 201 without amendment and planting (Fig. 1b).

203 2.3 Analyses

204

205 Preparation and analysis of soil samples

Soil samples were air-dried for two weeks and sieved through a mesh of 2 mm. Roots 206 207 and stones were discarded from soils. An aliquot of 2-mm sieved soil sample was 208 further ground (<0.15 mm) for the elemental analysis. The total carbon (TC) and nitrogen (TN) were analyzed by dry combustion using an elemental analyzer 209 210 (Elemental, Vario EL, Germany). The concentrations of soil total REEs and other major 211 and trace elements (e.g. Al, Fe, Ca, P, Mn) were measured at ALS Chemex (Guangzhou) Co., Ltd. Namely, about 1 g of the air-dried soil was digested by lithium borate fusion 212 213 method and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent VISTA, USA) for REEs and X-ray fluorescence spectrometry (XRF) 214 215 (PANalytical PW2424, Netherlands) for major elements (Liu et al. 2020a).

216

The soil pH was measured at a ratio of 1: 2.5 (soil: deionized water, w/v) (Mettler Toledo, LE438 pH, Germany). An extraction using 0.001 mol/L CaCl₂ solution with a ratio of 1: 2 (soil: CaCl₂ solution, w/v) was performed to mimic the soil solution (Groenenberg et al. 2010). Namely, 20 g of air-dried and < 2 mm soil was mixed with 40 mL 0.001 mol/L CaCl₂ solution. The suspensions were shaken horizontally at 80 rpm for 48 h. After centrifugation and filtration through a 0.45- μ m membrane, the extracts were analyzed for the electrical conductivity (EC) using an electrochemical analyzer
(INESA DDS-307A, China), for the CaCl₂-extractable concentrations of organic
carbon (CaCl₂-EOC) using a TOC analyzer (Elemental, Vario TOC, Germany) and for
the CaCl₂-extractable concentrations of major and trace elements at ALS Chemex
(Guangzhou) Co., Ltd using ICP-MS and inductively coupled plasma optical emission
spectrometry (ICP-OES) (Agilent VISTA, USA).

229

230 *Preparation and analysis of plant samples*

For plant sample analyses, each plant was separated into leaves, stems, fine roots (0-5 231 mm in diameter) and thick roots (>5 mm, including radish roots and rhizomes) (Fig. 1d) 232 (Boehm 1979; Bai et al. 2016). In order to eliminate the dust from the surface of the 233 234 plants, and the soil particles adhering to the roots, each plant part was carefully washed 235 with tap water and deionized water. After cleaning, the fine roots were scanned (Epson perfection, V700 photo, Indonesia) and analyzed using a WinRHIZO software to 236 measure the fine root total length (TL), surface area (SA), average diameter (AD), root 237 volume (RV), root length depending on the diameter classes (0–0.2 mm, 0.2–1 mm, 1– 238 2 mm, 2–3 mm, 3–4 mm, 4–5 mm). The small fine root (<1 mm) and fine root (<5 mm) 239 240 morphological parameters are defined as follows:

241
$$specific root length (SRL, cm/g) = {fine root length (cm) \over fine root biomass (g)}$$

242 specific root suface area (SRA,
$$cm/g$$
) = $\frac{\text{fine root surface area (cm}^2)}{\text{fine root biomass (g)}}$

243 $small fine root percentage (SFRP, \%) = \frac{small fine root length (cm)}{fine root length (cm)} \times 100$

244 root tissue density
$$(RTD, g/cm^3) = \frac{\text{fine root biomass (g)}}{\text{fine root volume (cm^3)}}$$

Plant materials were dried at 105 °C for 30 min and 60 °C for 48 h and then ground to
<1 mm and preserved in polyethylene bags. The plant samples were digested by HNO₃
(65%, 6 ml) and HCl (37%, 2 ml). Afterwards, the trace and major elements in the
digested solutions were analyzed by ICP-MS and ICP-OES at ALS Chemex
(Guangzhou) Co., Ltd as described above.

251

252 *REE fractionation analysis*

253 The REE fractionation in the soil-plant system results from the small variations in the behaviors of individual REEs during soil and plant physiological processes (Tyler 254 255 2004). The Ce anomaly and REE fractionation pattern (*i.e.* LREE or HREE enrichment) 256 are widely used indicators in the soil-plant system. The transfer factors (K_n), which are defined as the REE concentrations in one compartment divided by the concentrations 257 258 in another compartment, were also calculated along the REE transfer route. The REE transfers in the soil-ramie system can be divided into 5 steps: I, from rhizosphere soil 259 260 (TAR) to soil solution; II, from rhizosphere soil solution to fine roots; III, from fine roots to thick roots; IV, from thick roots to stems; V, from stems to leaves. The transfer 261 factors of these steps are calculated as follows: 262

263
$$K_{I} = \frac{[\text{REE}]_{\text{CaCl}_{2}-\text{extractable in TAR soil}}}{[\text{REE}]_{\text{total in TAR soil}}}$$

264
$$K_{II} = \frac{[\text{REE}]_{\text{fine roots}}}{[\text{REE}]_{\text{CaCl}_2-\text{extractable in TAR soil}}}$$

265
$$K_{III} = \frac{[\text{REE}]_{\text{thick roots}}}{[\text{REE}]_{\text{fine roots}}}$$

266
$$K_{IV} = \frac{[\text{REE}]_{\text{stems}}}{[\text{REE}]_{\text{thick roots}}}$$

267
$$K_V = \frac{[\text{REE}]_{\text{leaves}}}{[\text{REE}]_{\text{stems}}}$$

269 The REE fractionation during each transfer process can be roughly estimated by270 (La/Yb), and Ce anomaly.

271
$$K_n(*Ce) = \frac{2 \times K_n(Ce)}{K_n(La) + K_n(Pr)}$$

272
$$K_n (La/Yb) = \frac{K_n(La)}{K_n(Yb)}$$

273

The Ce anomaly value (*Ce) >1 and <1 means positive and negative anomaly, respectively, and the ratio of La to Yb >1 and <1 means a LREE and HREE enrichment pattern, respectively (Wei et al. 2001; Liu et al. 2021b).

277

278 *2.4 Data analysis*

The SPSS 20.0 statistical analysis software was used for data analysis. All results were presented as arithmetic means with standard deviation calculated on three or five samples. Soil physico-chemical properties, plant growth characteristics, element concentrations in plant organs were compared using one-way analysis of variance (ANOVA) followed by a Duncan test at a significance level of 0.05. For one parameter, values with different letters refer to significant differences between the different samples from zones A and B and the controls. For some parameters, if the data were not normally distributed, they were transformed by normal score to follow a normal
distribution before being tested. Matrices of correlation were performed on the soil
physico-chemical properties and plant elemental composition or root morphological
characteristics using a Pearson correlation two-sided test.

290

291 **3. Results**

292



294 The general physico-chemical characteristics of the bare tailings, bulk and rhizosphere (LAR and TAR) soils are shown in Fig. 2. The pH values of the mine tailings after 295 planting and amendments (4.80-6.00) were significantly higher than those of the bare 296 297 tailings (4.38–4.47). There was no significant difference in pH between the bulk, LAR 298 and TAR soils in both zones A and B. The TC and TN concentrations showed significant differences between different soil fractions, and were in the order of bare tailings < bulk 299 300 soil < LAR < TAR in both the zones A and B. Whatever the soil fraction, the concentrations of TC and TN were higher in the zone A compared with the zone B. The 301 total P concentrations were higher in the LAR (30–100 mg/kg) and TAR (20–120 mg/kg) 302 soils than in the corresponding bulk soil (20–80 mg/kg), and much higher than that in 303 bare tailings (4.36 mg/kg). The total concentrations of other nutrients (Ca, K) showed 304 similar trends as the total P concentrations (Table S1). Concerning the bulk soils, some 305 chemical properties (pH, EC and total N, P, Ca, K, REE concentrations) were 306

307 significantly higher in the zone A than in the zone B.

308

309 The reclaimed tailings generally presented higher EC values in soil CaCl₂ extracts (154–693 µS/cm) than the bare tailings (185–200 µS/cm). For each zone, the EC values 310 311 of rhizosphere soils were higher than the corresponding bulk soils. The concentrations 312 of soil CaCl₂-EOC showed significant differences between the soil fractions and were 313 in the order of bare tailings < bulk soil < LAR < TAR in both the zones A and B. The concentrations of soil CaCl₂-EOC were higher in the zone A compared with the those 314 315 in the zone B for the corresponding soil fractions. The extractable nutrient 316 concentrations (K, Mg, Mn, Na, S, Zn) were significantly higher in the rhizosphere soils 317 (LAR and TAR fractions) compared with the corresponding bulk soils and the bare 318 tailings (Table S2).

The total REE concentrations varied in the bare tailings (281-729 mg/kg) and the 320 reclaimed tailings (zone A: 926-3460 mg/kg; zone B: 551-1030 mg/kg), revealing the 321 heterogeneity of the distribution of residual REEs in the tailings. The total Al 322 323 concentrations were around 8.5% in all the soil samples. The CaCl₂-extractable REE concentrations in the bare tailings (controls) were ten times higher than those in the 324 reclaimed tailings. The proportions of extractable REE concentrations out of the total 325 REE concentrations in the soils followed the order of control (0.11-0.79%) > zone B 326 327 bulk soil (0.04-0.13%) > zone A bulk soil (0.01-0.06%). Similar to those of REEs, the

328 extractable Al concentrations and the proportions of extractable Al out of the total Al

329 concentrations were both ten times higher in the controls than in the reclaimed tailings.

330 No significative difference in the extractable REE and Al concentrations or proportions

- 331 was found between bulk and rhizosphere soils in both zones A and B (Fig. 3).
- 332

333 *3.2 Plant growth and elemental distribution*

The biomass and root characteristics of ramie plants are shown in Fig. 4 and Table S3. Among the different ramie organs, the thick roots showed the highest dry biomass both in the zone A (159–406 g per plant) and the zone B (251–1090 g per plant). The thick roots accounted for 85–89% of the total dry biomass of ramie, followed by the stems (9.6–14.4%), fine roots (1.3–3.0%) and leaves (0.02–0.12%). Each ramie plant had an average ramet number of 6 in both zones. The average height of these ramet stems was 170 and 163 cm in the zones A and B, respectively.

341

The characteristics of the fine roots (< 5 mm in diameter) of ramie plants are presented in Table A3. The root morphological parameter AD was higher in the zone B than the zone A, while the TL, SA, and RV of the fine roots showed no significant difference between the zones A and B. The length of the small fine roots (<1 mm in diameter) represented more than 99% of the total fine root length, including 27 % for the very fine roots with a diameter <0.2 mm. The SRL was significantly higher in the zone A than that in the zone B, while the SRA and RTD were similar in both zones.

The distribution of nutrients varied greatly between the ramie organs and between the 350 351 zones A and B (Tables S4 and S5). The major elements accumulated by ramie plants 352 were Ca, K and P, and to a lesser extent Mg and Fe. Phosphorus (P) concentrations in 353 the organs showed the order of leaves \approx stems > thick roots > fine roots in the zone A, 354 and leaves > thick roots > stems > fine roots in the zone B. The amount of P (elemental concentration \times dry biomass) accumulated in the different organs of ramie generally 355 showed the order of thick roots (76.6-91.7%) > stems (7.33-21.3%) > fine roots (0.54-356 357 2.60%) > leaves (0.02–0.14%) in both the zones A and B.

358

The concentrations and amount of REEs and Al in plants are presented in Fig. 5. The 359 360 concentrations of REEs in the different organs of ramie were distributed in the order of fine roots (248-590 mg/kg) > leaves (160-312 mg/kg) > stems (36-172 mg/kg) > thick361 roots (31–59 mg/kg) in both the zones A and B. Despite the high REE concentrations 362 363 in leaves, the amount of REEs accumulated in leaves was low, being 0.01–0.30 mg per plant for both the zones A and B, and only accounted for about 0.5% of the total amount 364 365 of REEs accumulated in the whole plant. The amount stored in the thick roots reached 366 12.9–21.3 mg per plant, and represented approximately 67.0% and 80.2% of the total amount of REEs accumulated in the whole plant in the zones A and B, respectively. The 367 concentrations of Al in different organs of ramie showed the order of leaves (2920-368 10800 mg/kg > fine roots (1690–6300 mg/kg) > thick roots (495–3140 mg/kg) > stems 369

370 (641–2050 mg/kg) in the zones A and B. The amount of Al accumulated in the different
371 organs showed similar trends to those of REEs. Namely, most of the Al (67–94%)
372 accumulated by ramie plant was stored in the thick roots in the zones A and B (Fig. 5).
373

374 *3.3 Transfer and fractionation of REEs in the soil-ramie system*

375 The transfer factors in the soil-ramie system are shown in Fig. 6 and Table S6. The 376 results showed that $K_{II} > K_V > K_{IV} > K_{III} > K_I$, indicating a REE accumulation in fine roots compared with the soil extractable REE fraction (step II) and a slight enrichment 377 378 in the leaves compared with the stems (step V). The slopes of K_I (La/Yb) and K_V (La/Yb) were 0.4–0.5 in the zones A and B, indicating a selective transport of HREEs during 379 soil-solution and stem-leaf transfers. While the slopes of K_{II} (La/Yb) (~4) suggested a 380 381 selective absorption of LREEs by ramie roots. The Ce anomaly values was <1 for the steps I and IV, and >1 for steps II, III and V. In addition, there were no significant 382 differences of transfer factors and line slopes between the zones A and B. 383

384

385 *3.4 Relationships between soil properties and plant characteristics*

A correlation matrix analysis was performed on selected physico-chemical properties and extractable REEs of the bare tailings, the bulk and rhizosphere soils (Table 1). Results showed that extractable REE concentrations were positively correlated with extractable Al concentrations, and negatively correlated with soil pH and soil total C, N, P and Ca concentrations (p<0.05).

A correlation matrix analysis was also performed on selected physico-chemical 392 properties of TAR soils and plant parameters (Table 2 and Table S7). In plants, four root 393 characteristics (length for the different diameter classes, TL, SA, RV) were positively 394 395 correlated with REE, Al and nutrient (Ca, P) concentrations of fine roots (p<0.05). The 396 amount of REEs accumulated in the whole plant was also positively correlated with these four root characteristics. Moreover, these four root characteristics were positively 397 correlated with soil pH, TC, TP, and soil extractable Mg concentration. The SRL was 398 positively correlated with pH, TC, and TP in soils, and the SRA was positively 399 correlated with TC in soils. However, the AD and SFRP were positively and negatively 400 correlated with the extractable REE concentrations in the soil, respectively. 401

402

403 **4. Discussion**

4.1 Effects of phytostabilization practices on dynamics of REEs, Al and nutrients in soil 404 In line with previous studies, our results confirmed that the soils of bare tailings exhibit 405 low pH, low concentrations of CaCl₂-EOC, TC, TN, and nutrients (Ca, Mg, P, S, etc.), 406 407 but high concentrations of extractable REE and Al (Fig. 3). The REE concentrations in the tailings were higher than the background values in the soils of mainland China (188 408 mg/kg) or Jiangxi province (221 mg/kg) (Wei et al. 1991), and showed high proportions 409 of available REEs. A pot experiment has shown that plants can hardly grow on these 410 tailings without soil improvement (Liu et al. 2020a). Our results showed that the 411

412 application of organic amendment and planting with ramie resulted in an increase in 413 soil pH, soil CaCl₂-EOC, TC, TN and nutrient concentrations. The organic amendment 414 is a source of organic matter as well as macronutrients and micronutrients, which are 415 critical for supporting plants growth and adaptation in contaminated soils (Meeinkuirt 416 et al. 2016). The introduction of plant and organic amendment may also promote the 417 formation of stable aggregates, providing space for root growth and for the survival and 418 breeding of soil invertebrates and microorganisms (Chiang et al. 2006).

419

420 The soil pH was among the most obvious factors controlling the concentrations of extractable REE and Al in the mine tailing soils (Table 1). Under strong acid soil 421 422 conditions in the bare tailings (pH 4.4), REEs and Al that adsorbed on clays, organic 423 matter and Fe-/Mn- oxides may be released into the soil solution. With the increase of soil pH in the reclaimed soils, the REEs and Al in the soil solution would be precipitated 424 by REE/Al hydroxides and Fe-/Mn- oxides (Dinali et al. 2004). Significant correlations 425 426 between soil REE/Al and TC concentrations were also observed, indicating that REEs and Al could be bound by the functional groups (e.g. hydroxyl and carboxyl) of organic 427 428 matter (Migaszewski and Gałuszka 2015). Moreover, with the increase of P 429 concentrations, the REE and Al ions may also be precipitated by phosphates. The reasons why REE and Al showed a similar behavior could be that both REEs (except 430 Ce and Eu in some conditions) and Al are trivalent elements, which show many 431 similarities of chemical properties during the geochemical processes (Pletnev and 432

Zernov 2002). Therefore, the phytostabilization practices with ramie planting and organic amendment can protect the plants from REEs and Al toxicity, and may reduce the risk of groundwater contamination and other biological exposure. The significant differences of soil pH, EC, TN, and soil total P, Ca, K, REE concentrations between the zones A and B may be ascribed to the different planting strategies and amendment additions. The higher percentages of extractable REE and Al in the soils of zone B than zone A may be due to the lower soil pH, and soil TC and P concentrations of zone B.

- 440
- 441 4.2 Root development and effects of root activities on dynamics of REEs, Al and
 442 nutrients in soil

443 Soil properties may constrain the plant and root development and the morphological 444 characteristics of the root system. Matrices of correlation (Table 2) indicate that the beneficial soil physico-chemical properties (pH, TC and nutrients) promote the fine root 445 growth of ramie, however, the potential toxic REE and Al have adverse effects on the 446 fine root length. Previous studies have reported that the most obvious toxicity 447 phenomenon of Al and REE to plant is the inhibition of root elongation and activities 448 449 (Tyler 2004; Abdulaha-Al et al. 2018). A recent study found that the rice root morphological features (e.g. the number of lateral root of adventitious roots) were 450 sensitive to high concentration of REE (Shi et al. 2021). The difference of age of ramie 451 could also contribute to the differences in root morphology observed between the zones 452 453 A and B. Physical properties could also be a limiting factor for root development in the 454 mine tailings and should be taken into consideration in future studies.

455

456 In turn, the root activity and changes of the root morphological parameters may affect the soil properties in the rhizosphere. Significant enrichment of C and nutrients can be 457 458 seen in the rhizosphere samples compared to bulk soil samples (Fig. 2), indicating that 459 in addition to soil amendment, ramie planting could further improve the soil properties. 460 This enrichment of C and nutrients in rhizosphere soils has been previously reported for other mine soils phytoremediation practices by the planting of *Digitaria sanguinalis*, 461 462 Picris hieracioides, Conyza albida, Setaria viridis (Campillo-Cora et al. 2019). On the one hand, plant roots can directly release exudates or protons into the rhizosphere zone, 463 thus influencing nutrient mobility and bioavailability, and other physico-chemical 464 465 properties (Hinsinger et al. 2005; Qasim et al. 2016). In fact, ramie has been found to enhance soil fertility by fine root turnover and root exudation (Bene et al. 2011). On the 466 other hand, the plant would recruit certain beneficial microbes (e.g. P solubilization 467 468 microbes) in the rhizosphere under nutrient deficiency, thus indirectly increasing nutrient availabilities (Alori et al. 2017). Our former study found that the combination 469 470 of amendment and ramie planting treatment recruited much more beneficial microbes compared to the only amendment treatment (Liu et al. 2020b). 471

472

473 A number of studies reported that the planting induces strong rhizosphere effects, which474 finally induces an increase of available REEs in the soils (Wang et al. 2001; Wiche et

475 al. 2016). Compared to no planting treatment, it was found that planting of a REE hyperaccumulator Phytolacca americana significantly decreased soil pH and increased 476 477 extracted REE concentrations of the REE mine tailings (Liu et al. 2020a). However, in the present study, no significant differences of extractable REE and Al concentrations 478 479 were found between the rhizosphere and bulk soil samples (Fig. 5). One possible reason 480 is that the rhizosphere effect did not induce a significant decrease of soil pH (Fig. 2a). Another possible reason is that ramie absorbed high amount of REEs and Al from the 481 soil solution and retained them within the roots. Moreover, the REEs show high 482 483 affinities to oxalate (a root exudate for many plants), forming stable REE-complexes or even precipitates that are insoluble (He et al. 2021). 484

485

486 *4.3 REE accumulation and fractionation of soil-ramie system*

In this study, ramie presented large biomass in underground parts, especially the thick 487 488 roots (Fig. 4). Consequently, the quantity of REEs and Al accumulated by the plant was mostly retained within the thick roots for both zones. The thick roots are a "storehouse", 489 which can store a series of nutrients (e.g. N, P, K, etc.) (Table S5) (Bai et al. 2016). 490 491 Ramie might use these nutrients for next growth season, especially under nutrient deficiency (Wu et al. 2021). Most of the REEs and Al in the plant roots are usually 492 tightly complexed by the cell walls (e.g. REE hyperaccumulator Dicranopteris linearis 493 and normal plant cucumber) (Zhang et al. 2012; Liu et al. 2021c). Thus, the stored REEs 494 495 and Al in the thick roots of ramie are unlike to be redistributed in the plant any more. 496 Contrary to the "storehouse" role of the thick roots, the fine roots function as a "capturer"
497 of nutrients and contaminants from the soil (Bai et al. 2016). This can be explained by
498 the positive correlations between the fine root characteristics and the root
499 REE/Al/nutrient concentrations (Table 2).

500

501 With the increase of atomic number of REE ions, their ability to adsorb on clay minerals decreases gradually, while their ability to be complexed and leached out increases 502 (Tyler 2004). Therefore, soil-to-soil solution step showed a HREE enriched pattern (Fig. 503 504 6), which was similar to that of soil-D. linearis system (Wei et al. 2001). The negative Ce anomaly during soil-to-soil solution process may be due to the fact that Ce mostly 505 exists as Ce oxides in the soil (Tyler 2004). The reason why soil solution-to-fine root 506 507 process showed an LREE enriched pattern may be ascribed to the preferential uptake of LREE by plant root through Ca^{2+} channel, while the uptake of HREE may be 508 inhibited by the high concentration of Al (Yuan et al. 2017). The HREE enrichment in 509 510 the leaves compared to the stems measured in ramie was also observed in the REE hyperaccumulator P. americana. A previous study carried out on this plant has revealed 511 512 that organic ligands such as citric acid play an important role in long-distance transport 513 of REEs in the xylem, leading to a preferential enrichment of HREE in the leaves (Yuan et al. 2017). The positive Ce anomalies during the uptake processes (solution-to-fine 514 roots, fine root-to-thick roots, and stems-to-leaves) were also found in our former 515 hydroponic experiment (Liu et al. 2021a). It may be ascribed to the preferential 516

enrichment of CeO₂ precipitation on the root surface. These particles may further
activate REE endocytosis at the root cells membrane (Wang et al. 2014). Brioschi et al.
(2013) speculated that the REE-oxyhydroxide particles in plant xylem sap could lead
to the positive Ce anomaly during the transport process.

521

522 Though the HREE concentrations in the mine tailings are much lower than the LREEs, 523 the HREEs are easier to migrate from soil into the soil solution, and transport from underground part to the shoots. Further studies should not ignore the potential 524 525 environmental risks of HREEs. Based on the current field trial, high mechanical strength fibers with low REE concentrations have been extracted from the ramie plants 526 grown on the tailings (Segovia et al. 2021). However, further work is needed to ensure 527 528 sustainable management of this crop and long-term REE/Al phytostabilization of the 529 mine tailings.

530

531 5. Conclusion

The wide exploitation of ion-adsorption REE deposits in South China have led to a large area of mine tailings with limited remediation. In the present study, a 2-year field trial of phytostabilization combining addition of organic amendment and cultivation of ramie was conducted on a typical ion-adsorption REE mine tailing. Our results showed that this phytostabilization strategy not only improves soil properties, but also decreases the extractable concentrations of potentially toxic elements (REEs and Al). By 538 comparing the soil physico-chemical properties between the rhizosphere soils and the corresponding bulk soils, our study also showed that ramie planting and the root 539 activities further improve soil properties through C input and nutrient mobilization. 540 Moreover, this fiber plant succeeded to grow on the amended mine tailings and the 541 542 major quantity of REEs taken up by the plant were restricted within the thick roots. In 543 sum, we conclude that phytostabilization practice with organic amendment and ramie cultivation is a promising strategy for the remediation of ion-adsorption REE mine 544 tailings in South China. 545

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Fig. 1. Location of the experiment plots in an ion-adsorption rare earth element mine
tailing in South China (a); bare tailings without remediation (b); tailings after
remediation by the addition of organic amendment and the planting of ramie (c); root
structure of ramie plant grown in the tailings (d).

757 Zone A: the tailings were amended and planted with an annual fiber plant in 2015; plants were then

- removed, and the tailings were amended again and planted with ramie in 2016; Zone B: the tailings were
- amended and planted with ramie in 2015; the aboveground parts of ramie plants were harvested and
- 760 fertilizers (N/P/K) was added in 2016.



Fig. 2. Selected chemical properties in bulk and rhizosphere (LAR and TAR) soil
fractions in amended and planted tailings (zones A and B) and in bare tailings (control):
pH (a); electrical conductivity in soil CaCl₂ extracts (b); total concentrations of C (c);
total concentrations of N (d); CaCl₂-extractable concentrations of organic C (e); total P
concentrations (f).

The bars represent the mean values and the error bars the standard deviation calculated on five samples
per zone. LAR, loosely adhering soil to roots; TAR, tightly adhering soil to roots. The significance tests
were conducted between all the soil groups (TAR, LAR and bulk soils from zones A and B and the
controls).



Fig. 3. CaCl₂-extractable concentrations of rare earth elements (a) and of Al (b) in bulk

and rhizosphere (LAR and TAR) soil fractions in amended and planted tailings (zones

A and B) and in bare tailings (control).

The bars represent the mean values and the error bars the standard deviation calculated on five samples
per zone. LAR, loosely adhering soil to roots; TAR, tightly adhering soil to roots. The significance tests
were conducted between all the soil groups (TAR, LAR and bulk soils from zones A and B and the
controls).



Fig. 4. Dry biomass of different organs of the ramie plant (mean \pm s.d. n=5)



Fig. 5. Rare earth elements concentrations (mg/kg) (a) and accumulated quantities mg/plant) (b), Al concentrations (mg/kg) (c) and accumulated quantities (mg/plant) (d) in the different plant organs of ramie grown on two zones (A and B) of reclaimed ionadsorption REE mine tailings. The elemental accumulation was calculated as the product of elemental concentration and the organ biomass of ramie.



Fig. 6. Patterns of rare earth elements (REE) transfer factors in the soil-ramie system in the zone A (a) and the zone B (b). Steps I, TAR soil total REE concentrations to TAR soil CaCl₂-extractable REE concentrations; II, TAR soil CaCl₂-extractable REE concentrations to fine root REE concentrations; III, fine root REE concentrations to thick root REE concentrations; IV, thick root REE concentrations to stem REE concentrations; V, stem REE concentrations to leaf REE concentrations.

THE LAR, loosely adhering soil to roots; TAR, tightly adhering soil to roots.

	рН	EC	TC	TN	Fe	Al	Mn	Κ	Ca	Р	Si	REEs	E-Al	E-REEs
pН	1													
EC	0.75^{*}	1												
TC	0.77^{*}	0.85^{*}	1											
TN	0.75^{*}	0.87^{*}	0.99^{*}	1										
Fe	0.17	0.11	0.10	0.10	1									
Al	0.28	0.23	0.22	0.26	0.14	1								
Mn	0.59^{*}	0.67^*	0.58^{*}	0.59^{*}	0.27	0.46*	1							
Κ	0.07	-0.14	0.14	0.09	-0.05	-0.00	-0.30	1						
Ca	0.90^{*}	0.91*	0.89^{*}	0.90^{*}	0.14	0.29	0.66*	-0.06	1					
Р	0.83*	0.90^{*}	0.90^{*}	0.90^{*}	0.14	0.27	0.70^{*}	-0.03	0.95^{*}	1				
Si	-0.70^{*}	-0.72^{*}	-0.79^{*}	-0.80^{*}	-0.24	-0.76^{*}	-0.70^{*}	-0.06	-0.78^{*}	-0.77^{*}	1			
REEs	0.76^{*}	0.78^{*}	0.64^{*}	0.67^{*}	0.09	0.50^{*}	0.74^{*}	-0.28	0.83*	0.82^*	-0.74^{*}	1		
E-Al	-0.71*	-0.45*	-0.58^{*}	-0.55^{*}	-0.31	-0.31	-0.26	-0.28	-0.59^{*}	-0.59^{*}	0.62^{*}	-0.38^{*}	1	
E-REEs	-0.69*	-0.39*	-0.55^{*}	-0.52^{*}	-0.20	-0.35*	-0.13	-0.50^{*}	-0.54^{*}	-0.52^{*}	0.59^{*}	-0.34*	0.93^{*}	1

797 Table 1 Correlation matrix of selected physico-chemical properties of bare and reclaimed tailings (bulk and rhizosphere soils)

798 The values in the matrix are the Pearson correlation coefficient (R) between element concentrations. The higher the R value is, the higher degree of correlation (positive or

negative) between the two physico-chemical properties. The * refers to the significance level of the correlation (p-value), * p<0.05.

800 E: CaCl₂-extractable concentration

801	Table 2 Correlation	matrices o	of TAR a	soil j	physico-chemical	properties,	fine	root	morphology	indicators	and	composition,	and	plant	REE

802 accumulation

	Fine ro	ots			Whole plant	TAR						
	REE	Р	Ca	Al	REE	pН	TC	Р	E-Al	E-Mg	E-Si	E-REE
TL	0.71^{*}	0.96^{*}	0.92^{*}	0.83*	0.65*	0.84^*	0.68^{*}	0.71^{*}	-0.37	0.82^{*}	0.65^{*}	-0.30
SA	0.71^{*}	0.97^{*}	0.95^{*}	0.86^{*}	0.71^{*}	0.80^{*}	0.64^{*}	0.67^{*}	-0.32	0.80^{*}	0.60	-0.25
RV	0.70^{*}	0.98^*	0.97^{*}	0.88^{*}	0.77^{*}	0.74^*	0.58	0.62	-0.25	0.76^{*}	0.53	-0.17
AD	-0.31	-0.58	-0.46	-0.40	0.01	-0.79^{*}	-0.65^{*}	-0.66^{*}	0.71^{*}	-0.67^{*}	-0.80^{*}	0.72^*
L (0–0.2)	0.69^{*}	0.89^{*}	0.82^*	0.80^{*}	0.55	0.81^*	0.62	0.67^{*}	-0.44	0.70^{*}	0.56	-0.49
L (0–2)	0.70^{*}	0.96^{*}	0.93*	0.81^*	0.67^{*}	0.82^*	0.68^{*}	0.71^{*}	-0.34	0.85^*	0.67^{*}	-0.22
SRL	0.47	0.49	0.29	0.23	-0.10	0.73^{*}	0.77^{*}	0.73^{*}	-0.60	0.62	0.83*	-0.58
SRA	0.43	0.34	0.14	0.08	-0.16	0.54	0.67^{*}	0.62	-0.44	0.46	0.70^{*}	-0.43
SFRP	-0.26	0.15	0.08	0.05	-0.29	0.26	0.11	0.20	-0.76^{*}	0.11	0.37	-0.84^{*}
RTD	-0.01	-0.34	-0.08	0.19	0.18	-0.05	-0.31	-0.23	-0.05	-0.05	-0.24	-0.03

803 The values in the matrix are the Pearson correlation coefficient (R) between element concentrations and plant characteristics. The higher the R value is, the higher degree of

804 correlation (positive or negative) between the two physico-chemical properties. The * refers to the significance level of the correlation (p-value), * p<0.05.

805 E: CaCl₂-extractable concentrations; L (0–0.2): root length for roots with a diameter 0.00 < d <= 0.20 mm; L (0–2): root length for roots with a diameter 0.00 < d <= 2.00 mm. TL,

806 fine root length; SA, surface area; AD, average diameter; RV, volume (RV); SRL, specific root length; SRA, specific root surface area; SFRP, small fine root percentage.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

None.

Credit authorship contribution statement

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Visualization. When-Shen Liu, Hermine Huot: Methodology, Investigation, Writing
Review & Editing. Mei-Na Guo, Shi-Chen Zhu, Hong-Xiang Zheng:
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