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Trophic Transfer and Toxic Potency of Rare Earth Elements along a Terrestrial Plant–Herbivore Food Chain

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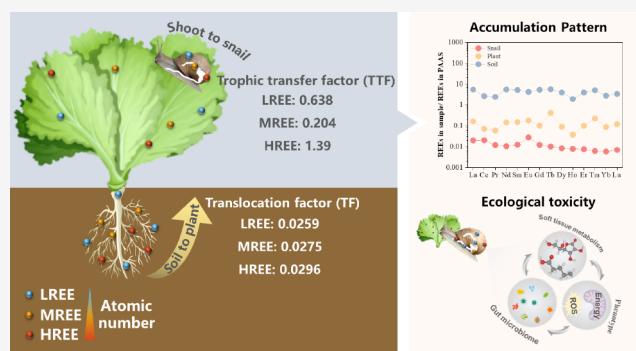
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Supporting Information

ABSTRACT: Extensive rare earth element (REE) mining activities have caused REE contamination of ambient agricultural soils, posing threats to associated food webs. Here, a simulated lettuce–snail food chain was conducted to evaluate the trophic transfer characteristics and the consequent effects of REEs on consumers. After 50-day exposure to soil, lettuce roots dose-dependently accumulated $9.4\text{--}76\text{ mg kg}^{-1}$ REEs and translocated $3.7\text{--}20\text{ mg kg}^{-1}$ REEs to shoots. Snails feeding on REE-contaminated shoots accumulated $3.0\text{--}6.7\text{ mg kg}^{-1}$ REEs with trophic transfer factors of $0.20\text{--}0.98$, indicating trophic dilution in the lettuce–snail system. REE profiles in lettuce and snails indicated light REE (LREE) enrichment only in snails and the varied REE profiles along the food chain. This was corroborated by toxicokinetics. Estimated uptake (K_u) and elimination (K_e) parameters were $0.010\text{--}2.9\text{ kg}_{\text{shoot}}\text{ kg}_{\text{snail}}^{-1}\text{ day}^{-1}$ and $0.010\text{--}1.8\text{ day}^{-1}$, respectively, with higher K_u values for LREE and HREE. The relatively high K_e , compared to K_w , indicating a fast REE elimination, supports the trophic dilution. Dietary exposure to REEs dose-dependently affected gut microbiota and metabolites in snails. These effects are mainly related to oxidative damage and energy expenditure, which are further substantiated by targeted analysis. Our study provides essential information about REE bioaccumulation characteristics and its associated risks to terrestrial food chains near REE mining areas.

KEYWORDS: rare earth element, trophic transfer, toxicokinetics, intestinal microbiome



1. INTRODUCTION

Rare earth elements (REEs), including lanthanides from La to Lu and Sc and Y, are indispensable in many fields, including metallurgy, petroleum industry, medical imagery, and agriculture. The global demand for REEs is increasing annually, leading to the excessive exploitation of REE resources. Numerous studies have proven that anthropogenic activities such as fertilizer application, mining operation, and industrial activities have resulted in elevated accumulation of REEs in the environment, particularly in agricultural soils surrounding mining areas.^{1,2} Beyond a certain threshold level, REEs in soils can be bioaccumulated by plants,^{2,3} posing potential risks to human health through trophic transfer. The trophic transfer and toxicological consequences of REEs are therefore attracting booming attention, especially for some hotspots with high levels of REEs.

Previous studies have shown the trophic transfer of REEs via aquatic food webs, with less information available for terrestrial food chains.^{3–5} However, some inconsistent conclusions still exist regarding the extent of transfer and biomagnification of REEs to higher trophic levels across food chains based on field investigations. For example, the transfer of REEs in a plant–snail food chain occurred with a maximum biomagnification

factor of 5.5.⁶ Other authors, however, concluded that REE concentrations decreased with trophic levels across aquatic and terrestrial ecosystems, i.e., trophic dilution.^{3,5,7,8} To enable a better comprehension of such debatable trophic transfer profiles of REEs, further investigation is needed, especially in laboratory-based studies across terrestrial food chains.

Individual REEs exhibited different bioaccessibility and bioaccumulation potentials in organisms,^{4,9,10} caused by the small but systemic dissimilarities in their physicochemical properties.¹¹ The difference in their bioaccumulation not only influenced the extent of transfer but also affected the REE profiles in organisms. For example, varying bioaccumulating potentials among light, medium, and heavy REEs, redox-independent REE anomalies (e.g., Gd) and redox-dependent REE anomalies (Ce and Eu) have been reported in plants^{12–14} and in aquatic organisms.⁸ Information about the change in

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REE profiles during their trophic transfer from producers to consumers is still lacking.

Trophic transferred REEs are in direct contact with the intestines of organisms at higher trophic levels, because they could only feed on REE-contaminated food. Dietary REE intake might negatively impact the intestinal morphology and disturb the intestinal flora in animals. For example, previous studies have demonstrated that the trophic transfer of pollutants, e.g., microplastics, pesticides, and metals, decreased the diversity and abundance of the gut *Bacteroidetes*^{15,16} and inhibited gut microbiota viability¹⁷ of organisms occupying higher trophic levels. There is also evidence indicating that dietary exposure to pollutants, e.g., Ag nanoparticles and Cd, adversely impacts consumers, including disturbances of metabolic profiles,¹⁸ inhibition of the growth of snails,^{19,20} impaired locomotion of springtails,²¹ and reduced reproduction of predatory mites.²² While much is separately known about the compositional changes in gut microbiota and toxic responses of consumers, significantly less is known about the interactions of REEs with the intestinal microbiome and the metabolism and health of consumers. A cohesive understanding of the relevance of gut microbial alternations and the health of the host, induced by dietary exposure to REEs, merits further investigation, contributing to the evaluation of how terrestrial ecosystems respond to REE exposure.

High levels of REEs in farmland soils around mining areas were frequently reported in recent years.²³ The REEs can finally enter the body of humans living near rare earth mines via the food chain.²⁴ However, data on the trophic transfer and toxicological consequences of REEs are scarce, especially along the terrestrial food chain. Hence, this study aimed to gain insight into the terrestrial trophic transfer and subsequent effects of REEs along a simulated lettuce–snail food chain in farmland soils collected near REE mining areas. Our specific objectives were to 1) quantify the bioaccumulation and trophic transfer factor of REEs in the lettuce–snail food chain, 2) explore the change of REE profiles during trophic transfer, and 3) evaluate the subsequent responses of higher-level organisms to the trophic transferred REEs. This study provides a more complete picture of the trophodynamic behaviors and environmental risks of REEs to organisms at the source.

2. MATERIALS AND METHODS

2.1. Test Soil. REE-contaminated soils (0–20 cm) were collected from farmlands in Lingbei (LB), Nanfeng (NF), Jianxia (JX), and Gaobei (GB) villages in Dingnan County, Jiangxi Province, China (Figure S1). The studied county experiences a subtropical monsoon humid climate, with an average annual temperature of 18.8 °C and a mean annual precipitation of 1609 mm. The four sampling locations in this study were selected in ascending order along the Yuezi River from upstream to downstream. Except for LB, these locations are situated within a distance of less than 2.5 km from the mining areas (Figure S1). After removing stones and plant debris, the soils were air-dried and 2 mm sieved. The soils had a sandy loam texture with 0.080–1.6% clay, 8.0–13% silt, and 85–92% sand. Soil pH-H₂O, organic matter (SOM), and NH₄⁺-N were 5.8–6.0, 15–16%, and 37–48 mg kg⁻¹, respectively (Table S1). Soil light (LREE, La, Ce, Pr, Nd, and Pm), medium (MREE, Sm, Eu, Gd, Tb, Dy, and Ho), heavy (HREE, Er, Tm, Yb, Lu, Y, and Sc), and total (TREE) REE concentrations were 3.2×10^2 – 1.1×10^3 , 30 – 1.9×10^2 , 32 – 3.1×10^2 , and 3.8×10^2 – 1.6×10^3 mg kg⁻¹, respectively

(Figure 1A). The raw data are listed in Table S2. The moisture content of the soils was adjusted to 60% of their maximum

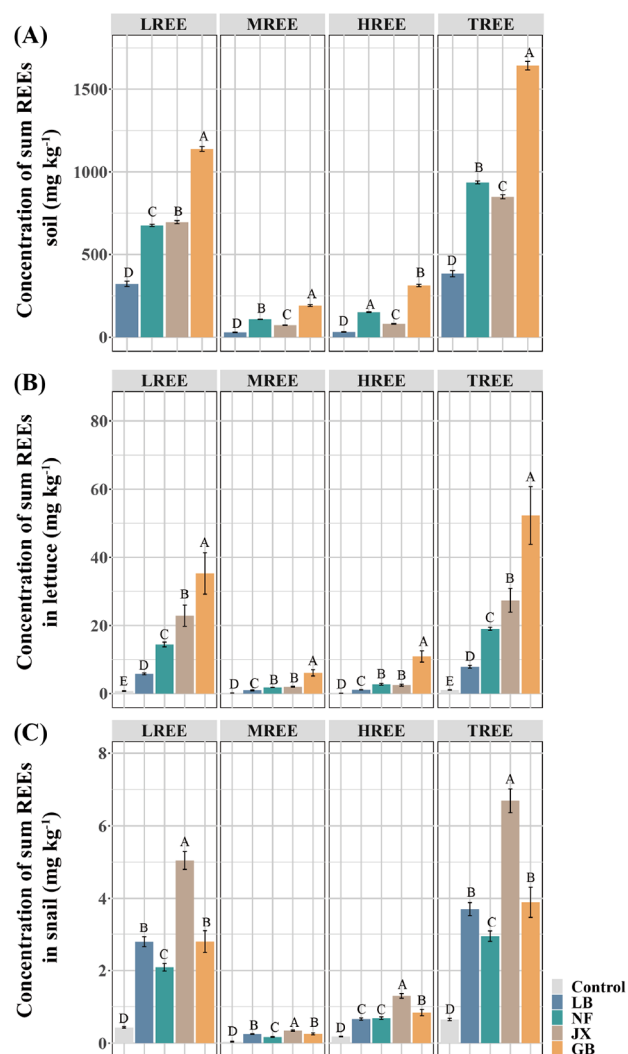


Figure 1. Concentrations of sum of rare earth elements (REEs) in soils (A), lettuce plants (*Lactuca sativa*) (B) exposed for 50 days to the soils, and in snails (*Bradybaena ravida*) (C) exposed for 28 days to lettuce shoots grown on the different agricultural soils collected from Lingbei (LB), Nanfeng (NF), Jianxia (JX), and Gaobei (GB) villages near REE mining areas in Dingnan County, Jiangxi Province, southern China. Potting soil was used as the control. Values are mean $\pm$ standard deviation ($n = 5$), and different letters indicate statistically significant differences between soils at the $p < 0.05$ level.

water holding capacity (WHC) and equilibrated for 2 days in the lab (25 °C, 60% humidity, and 24 h dark) before growing the plants.

2.2. Plant Cultivation. Lettuce seeds (*Lactuca sativa*) were purchased from the Chinese Academy of Agricultural Sciences. The seeds were sterilized with 0.5% NaClO for 10 min and then immersed in H₂O at 4 °C for 2 days to break the dormancy. Subsequently, the seeds were germinated and grown in dishes with moist filter paper at 25 °C for 2 days. Five seedlings of similar size were transferred into a PVC pot (height 13.5 cm; internal diameter 13.5 cm) containing 750 g of potting or test soil. The potting soil was used as a control to check for the performance of the plants and the snails. Five soils: (1) Control; (2) LB; (3) NF; (4) JX; and (5) GB were

tested in this study, with five replicates each. The plants were grown in a growth chamber at 25 °C, 60% humidity, and a 16 h/8 h light–dark cycle (600 Lux light intensity). During the experiment, the moisture content of the soils was kept at 60% of the maximum WHC.

The lettuce plants were harvested after growing for 50 days. The lettuce shoots were harvested, weighed, and stored at 4 °C for feeding the snails (storage for no longer than 1 week). The lettuce roots were washed with deionized water, submerged in 0.02 M Na₂EDTA for 15 min,²⁵ and washed with deionized water several times. A portion of the roots and shoots were killed by heating to 120 °C for 0.5 h and oven-dried at 60 °C to a constant weight. The oven-dried roots and shoots were ground (0.149 mm sieve) for further analysis.

2.3. Snail Exposure. The test snails (*Bradybaena ravidia*) were purchased from a snail company in Zhejiang Province, China. First, the snails were acclimated for 2 weeks to consume clean lettuce shoots in a growth chamber at 20 °C, 85% humidity, and 24 h dark. Then, healthy snails (fresh weight 1.7 ± 0.20 g) were selected and depurated for 48 h before starting the exposures. Twelve snails per replicate were transferred into four plastic containers (9 cm × 6 cm × 13 cm), with five replicates for each treatment. The snails were randomly assigned and fed with unexposed lettuce shoots (Control) or shoots grown on REE contaminated soils (LB, NF, JX, and GB) for 28 days. The presized shoots (1 cm × 1 cm) were fed to snails at 4% of the weight of the snails every 2 days. During the 28-day exposure, the unconsumed shoots were removed from each container at each feeding time point.

2.4. Soil, Plant, and Snail Analysis. Air-dried soil samples were sieved, weighed, and mixed with *aqua regia* in glass tubes at room temperature for 10 h. After that, the suspensions were digested using a graphite block digester at progressively higher temperatures (90 °C for 7 h, 160 °C for 2 h, and 180 °C for 2 h) to measure the total concentrations of REEs using ICP-OES and ICP-MS (Thermo Fisher Scientific, USA).²⁶ The dried root and shoot samples were separately sieved, weighed, and individually digested with HNO₃ at 90 °C for 2 h to determine the concentrations of REEs using ICP-OES and ICP-MS. The shell and soft tissue were freeze-dried, weighed, and individually digested with HNO₃ at 90 °C for 2 h to determine the concentrations of REEs using ICP-MS. To remove isobaric and polyatomic interferences, a quadrupole collision reaction cell is included in this type of ICP-MS. The reference material samples including soil (GBW07407 soil) and biological materials (BCR 668) were separately digested as described above. Additionally, 10 µg/L Rh was added to every sample as an internal standard. The standard was measured after every ten samples to control the instrumental drift. Every sample was measured with three replicates, and a relative standard deviation of <3% was obtained. Details of detection limits can be found in Table S3. The recovery rates of the REEs were between 90% and 110% (Table S4). Soft tissue of one snail per replicate was rinsed with an ice-cold physiological saline solution. Subsequently, the soft tissue was ground after addition physiological saline solution (soft tissue/total ratio of 10%), and the tissue homogenate was centrifuged at 2500 rpm for 10 min at 4 °C. The supernatant was collected for the determination of superoxide dismutase (SOD), Na⁺ K⁺-ATPase, and Ca²⁺-ATPase activities, and malondialdehyde (MDA), reduced glutathione (GSH), soluble sugar, lipid, and protein contents. Activities of SOD, Na⁺ K⁺-ATPase, and Ca²⁺-ATPase and contents of MDA, GSH, soluble sugar, lipid, and

protein in snail soft tissues were analyzed using assay reagent kits (Nanjing Jiancheng Bioengineering Institute, China).

2.5. Snail Metabolite Analysis. After the 28-day exposure and subsequent 48-h depuration periods, one snail soft tissue per replicate was frozen in liquid nitrogen and stored at −80 °C for further extraction. Detailed information on snail soft tissue metabolite analysis is given in He et al.²⁷

2.6. Snail Gut Microbial Community Analysis. After the 28-day exposure and subsequent 48-h depuration periods, one snail per replicate was dissected, and the gut was extracted on a super clean bench following Lőw et al.²⁸ and Zhang et al.²⁹ The snail guts were stored at −80 °C for DNA extraction. Detailed information on snail gut microbial analysis is given by Zhang et al.²⁹

2.7. Data Analysis. The translocation factor of REEs from soil to whole lettuce plants (TF_{soil–plant}) was calculated from the ratio of the REE concentrations in lettuce ([REE]_{plant}) and soil ([REE]_{soil}):

$$TF_{\text{soil–plant}} = \frac{[REE]_{\text{plant}}}{[REE]_{\text{soil}}} \quad (1)$$

The translocation factor of REEs from soil to lettuce root (TF_{soil–root}) was calculated from the ratio of the REE concentrations in the lettuce root ([REE]_{root}) and the soil:

$$TF_{\text{soil–root}} = \frac{[REE]_{\text{root}}}{[REE]_{\text{soil}}} \quad (2)$$

The translocation factor of REEs from lettuce root to shoot (TF_{root–shoot}) was calculated from the ratio of the REE concentrations in the lettuce shoots ([REE]_{shoot}) and roots:

$$TF_{\text{root–shoot}} = \frac{[REE]_{\text{shoot}}}{[REE]_{\text{root}}} \quad (3)$$

The trophic transfer factor (TTF) was calculated from the ratio of the REE concentrations in the shoots of lettuce and the snails ([REE]_{snail tissue}), i.e., shell, soft tissue, or the whole snail:

$$TTF_{\text{shoot–snail tissue}} = \frac{[REE]_{\text{snail tissue}}}{[REE]_{\text{shoot}}} \quad (4)$$

All concentrations are given in milligrams per kilogram of dry weight.

One-way analysis of variance (ANOVA) with Duncan's test in SPSS 22.0 was conducted to assess the significance of differences among the test soils. The construction and parametrization of REE uptake models by lettuce can be found in Text S1. The concentrations of REEs in the soil, plant, and snail samples were compared with the concentrations in the post-Archean Australian shale (PAAS). REE enrichment factors were calculated according to Liu et al.²³ and classified into four types: HREE enrichment (MREE/LREE > 1 and HREE/MREE > 1), MREE enrichment (MREE/LREE > 1 and HREE/MREE < 1), LREE enrichment (MREE/LREE < 1 and HREE/MREE < 1), and MREE depletion (MREE/LREE < 1 and HREE/MREE > 1).

Detailed information on toxicokinetic model construction and parametrization can be found in Text S2. Pearson's correlation analysis between TF, TTF, uptake, and elimination rate constants (*K_u* and *K_e*) and the atomic numbers of REEs was performed using SPSS. Details on the bioinformatics analysis are provided in Text S3.

3. RESULTS AND DISCUSSION

3.1. Accumulation and REE Profiles in Lettuce.

Concentrations in plants/roots/shoots of lettuce grown in the REE-contaminated soils were 5.8–35/6.9–51/2.8–13 mg kg⁻¹ for LREE, 0.97–6.1/1.2–8.6/0.52–2.7 mg kg⁻¹ for MREE, 1.1–11/1.2–16/0.39–3.7 mg kg⁻¹ for HREE, and 7.9–52/9.4–76/3.7–20 mg kg⁻¹ for TREE. These concentrations were significantly higher than those in lettuce plants grown in the Control soil (Figures 1B and S2). The REE concentrations in lettuce increased with increasing soil REE concentrations (Figures 1B and S2). The REEs followed the concentration order LREE > HREE > MREE in lettuce after exposure for 50 days (Figure 2A). This might be explained by

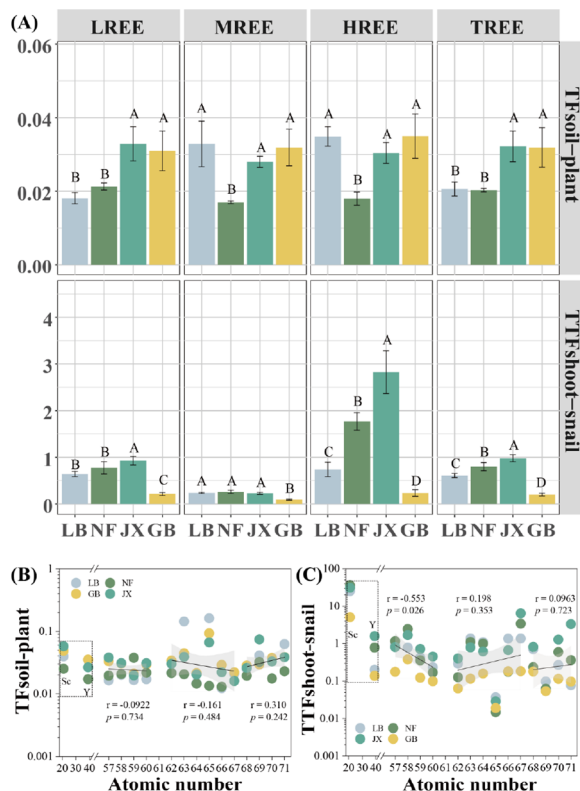


Figure 2. A: translocation factors (TF) of rare earth elements (REE) from soil to lettuce for plants (*Lactuca sativa*) grown for 50 days on soil, and trophic transfer factors (TTF) of REEs from lettuce shoots to snails (*Bradybaena ravida*) exposed for 28 days to lettuce shoots grown on different agricultural soils collected from Lingbei (LB), Nanfeng (NF), Jianxia (JX), and Gaobei (GB) villages near REE mining areas in Dingnan County, Jiangxi Province, southern China. B and C: the relationships between TF (B) and TTF (C) and the atomic number of the LREE, MREE, and HREE. In the figure A, values are mean $\pm$ standard deviation ($n = 5$), and different letters indicate statistically significant differences at the $p < 0.05$ level.

the REE uptake kinetic parameters calculated using the Michaelis–Menten equation for all of the data sets together (Table S5). The overall $V_{\max}$ values for both LREE and HREE (3.5 mg kg⁻¹ day⁻¹ for LREE and 0.077 mg kg⁻¹ day⁻¹ for HREE) were higher than that for MREE (0.069 mg kg⁻¹ day⁻¹) in the lettuce under different exposure concentrations of the test soil (Table S5). Similar to previous studies on the accumulation of REEs in plants,^{30,31} in our study, the accumulation of REEs was lower in the lettuce shoots than that in the roots (Figure S2). This indicates that REEs can

accumulate in plant roots, followed by the translocation of a small fraction of the accumulated REEs to other plant tissues. The calculated $TF_{\text{soil-plant}}/TF_{\text{soil-root}}/TF_{\text{root-shoot}}$ was 0.018–0.33/0.022–0.050/0.13–0.64 for LREE, 0.017–0.033/0.025–0.045/0.19–0.53 for MREE, 0.018–0.035/0.028–0.052/0.093–0.75 for HREE, and 0.020–0.032/0.025–0.049/0.13–0.64 for TREE (Figures 2A and S3). These values are comparable to the TF values for REE uptake in a variety of plants such as forest plants³¹ and vegetables.³² This suggests that REEs have a low potential for translocation in the soil–plant system. Additionally, the $TF_{\text{soil-plant}}$ of LREE and HREE was significantly higher in soils with higher REE concentrations i.e., JX and GB, than with lower REE concentrations i.e., LB and NF (Figure 2A). The same observation was reported by Kotelnikova et al.³³ for soil and by Saat et al.³⁴ for hydroponic exposures. Although the concentrations of the different REEs in lettuce differed from each other (Table S2), no significant relationship between $TF_{\text{soil-plant}}$ and REE atomic numbers was found (Figure 2B). Similar trends were observed for $TF_{\text{soil-root}}$ and $TF_{\text{root-shoot}}$ (Figure S4A,B). These results indicate that after exposure to REE-contaminated soil, the REEs were taken up by the plant roots and then partly translocated into the plant shoots, and this occurred in a dose-dependent manner.

The whole lettuce plants grown in REE-contaminated soil, except for the NF soil, were enriched in MREE and HREE (Figure 3A,B). Specifically, the PAAS-normalized REE profiles in the lettuce plants primarily mirrored those in the soil (Figure 3D,E). This study found that lettuce roots grown in REE-contaminated soil (pH 5.8–6.0), except for JX and NF soils, were enriched in MREE, compared to the contaminated soils (Figures S5A and S6A). Ding et al.³⁵ observed MREE enrichment in wheat roots due to phosphate precipitation of REEs in/on the roots as well as adsorption of REEs onto root cell walls at pH > 4.0. Additionally, HREE enrichment in wheat leaves generally decreased with the increase of EDTA levels.³⁵ These findings suggest that the change in REE patterns observed in plant roots might be attributed to the varying degree of phosphate precipitation of REEs in/on the roots or adsorption of REEs onto root cell walls, which are controlled by inorganic/organic ligand levels present in the soil environment. However, the REE profiles in the lettuce shoots mostly were similar to those in the roots, except for positive Tb anomalies (Figures S5B and S6B), since the REEs in the roots are the only source of REEs in the shoots. Obviously, other processes such as inorganic/organic ligand-mediated REE translocation in the plants may cause these changes. This needs further investigation.

Additionally, compared to the Control, significant reductions were observed in fresh shoot biomass along with decreased soluble sugar and protein contents in the shoots of lettuce grown in agricultural soils sampled near the REE mining areas (Figure S7). Similarly, previous studies have reported that when the accumulated REE concentrations in organisms exceed a certain threshold, adverse effects could be induced that disturb their physiological function.³⁶ This indicates that high levels of REEs may negatively impact the yield and quality of lettuce shoots, which could further influence the physiological function of snails through the food chain.

3.2. Trophic Transfer and REE Profiles in Snails. After exposure for 28 days, snails fed with REE-contaminated lettuce shoots also revealed a significant accumulation of REEs with 2.1–5.1 mg kg⁻¹ for LREE, 0.17–0.34 mg kg⁻¹ for MREE,

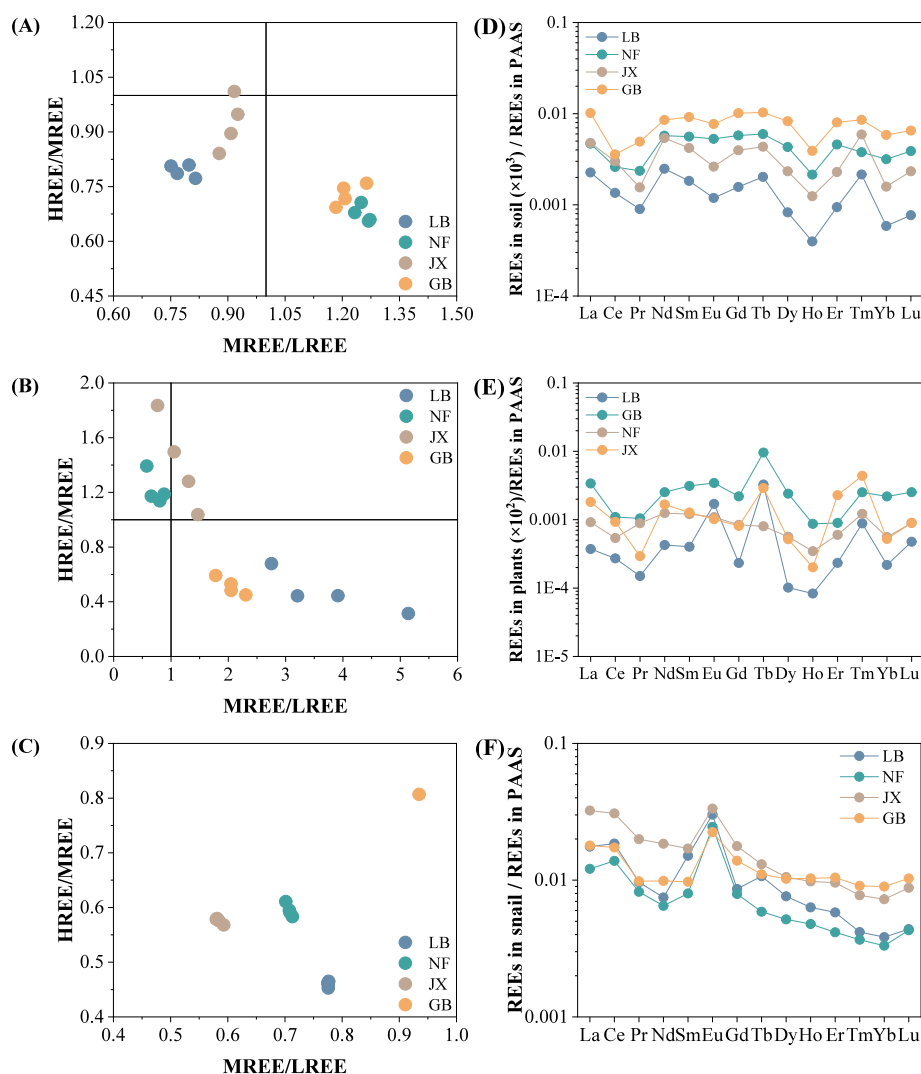


Figure 3. Rare earth element (REE) profiles in soils (A and D), lettuce plants (*Lactuca sativa*) (B and E), and snails (*Bradybaena ravida*) (C and F) normalized by post-Archean Australian average shale (PAAS) composite, and quantification of the REE enrichment profiles for exposures to different agricultural soils collected from Lingbei (LB), Nanfeng (NF), Jianxia (JX), and Gaobei (GB) villages near REE mining areas in Dingnan County, Jiangxi Province, southern China. The plants were exposed for 50 days to the different test soils, the snails were fed for 28 days with lettuce shoots grown on these soils.

0.66–1.3 mg kg^{−1} for HREE, and 3.0–6.7 mg kg^{−1} for TREE (Figures 1C and S2; Table S2). Specifically, LREE, MREE, HREE, and TREE concentrations in different snail tissues or the whole snails reached the highest values when exposed to 23 mg kg^{−1} LREE, 2.0 mg kg^{−1} MREE, 2.5 mg kg^{−1} HREE, and 27.4 mg kg^{−1} TREE in the lettuce plants and then decreased with ascending exposure level in the food (Figures 1C and S2; Table S2). The increased REE concentrations in the snails are in accordance with previous findings. Li et al.³⁷ reported a positive correlation between Cd concentrations in snail tissues and in lettuce, the significance of this correlation was further improved by considering Cd chemical forms ($F(i + ii + iii)$) in lettuce as variables. Apart from the exposure level, the bioavailability of metals is closely associated with the potential uptake capacity of consumers. Hence, the accumulation of metals in organisms could serve as a reliable indicator of the metal bioavailability. In our study, the observed trend of total REE concentrations in soils was inconsistent with those in plants and snails, indicating the variability of REE bioavailability and its effect on trophic transfer. These findings indicate

that REEs can be transferred to higher-trophic-level consumers through the food chain. The calculated $TTF_{\text{shoot–snail}}/TTF_{\text{shoot–shell}}/TTF_{\text{shoot–soft tissue}}$ was 0.21–0.93/0.23–0.81/0.20–1.0 for LREE, 0.092–0.26/0.092–0.29/0.091–0.28 for MREE, 0.23–2.8/0.31–3.2/0.18–2.5 for HREE, and 0.20–0.98/0.22–0.90/0.18–1.0 for TREE (Figures 2A and S3). Our results are in accordance with the range of 0.024–5.0 reported in previous studies on the REE transfer in terrestrial food webs based on field investigations.^{6,7,24} With the increasing REE concentrations in snail food, the percentage of REE transfer reached a maximum and then decreased with increasing exposure levels (Figure 2A). A similar trend has been found by Soliman et al.,³⁸ who observed that the trophic transfer factor of Cr increased initially and then decreased after peaking with the exposure concentration. Apart from the bioavailability of metals, the dynamics of metal accumulation, including uptake, internal sequestering, storage, and active excretion, could also be affected by elevated metal levels in organisms and subsequently affect their trophic transfer.³⁹ Our study also found a negative ($r = -0.55$) relationship between

$TTF_{\text{shoot} \rightarrow \text{snail}}$ and the atomic number for LREE ($p < 0.05$) (Figure 2C), which was consistent with the trends of $TTF_{\text{shoot} \rightarrow \text{soft tissue}}$ and $TTF_{\text{shoot} \rightarrow \text{shell}}$ (Figure S4C,D). The correlation trends of TTF between LREE might be due to their different metabolic fates in snails controlled by their specific physiochemical properties. Therefore, both the bioavailability of REEs in soil and lettuce and the metabolic processes of REEs in snails could affect their trophic availability.

During the trophic transfer of REEs from lettuce shoots to snail, the whole snail and tissue, i.e., shell and soft tissue, were enriched in LREE (Figures 3C and S5C,D). PAAS-normalized REE profiles in snails were characterized by positive Eu anomalies (Figures 3F and S6C,D). These features of LREE enrichment and positive Eu anomalies were not found in the shoots of the lettuce plants. Consistently, the detection of a positive Eu anomaly in organisms at higher trophic levels such as in bivalves and some crustaceans and plants is supported by previous studies.^{8,40} Eu^{3+} can form stable organic complexes thereby replacing Ca^{2+} in some biological matrices, such as in xylem fluid during normal nutrient fluxes, contributing to the positive Eu anomaly in plants.⁴⁰ This anomaly might be due to the mechanisms of uptake, distribution, and bioaccumulation in organisms.⁸ Previous studies explained the change of REE profiles from biological processes, influencing REE uptake by organisms.⁴¹ To test this hypothesis, the construction and parametrization of a toxicokinetic model were performed (Figures S8 and S9). The time course of REE bioaccumulation in snails was well fitted with one-compartment models with $R^2 = 0.46\text{--}1.0$ (Table S6). The estimated uptake (K_u)/elimination (K_e) rate constants in snails based on shoot concentrations were $0.030\text{--}1.6 \text{ kg}_{\text{shoot}} \text{ kg}_{\text{snail}}^{-1} \text{ day}^{-1}/0.12\text{--}1.8 \text{ day}^{-1}$ for LREE, $0.010\text{--}0.37 \text{ kg}_{\text{shoot}} \text{ kg}_{\text{snail}}^{-1} \text{ day}^{-1}/0.010\text{--}1.2 \text{ day}^{-1}$ for MREE, and $0.010\text{--}2.88 \text{ kg}_{\text{shoot}} \text{ kg}_{\text{snail}}^{-1} \text{ day}^{-1}/0.060\text{--}1.5 \text{ day}^{-1}$ for HREE (Figure 4A). These values are comparable to the K_u of $0.24\text{--}3.7 \text{ L kg}^{-1} \text{ day}^{-1}$ and K_e of $0.082\text{--}1.5 \text{ day}^{-1}$ reported for the toxicokinetics of REEs in enchytraeids exposed in a soil solution–quartz sand system^{10,42} but much higher than the rate constants for enchytraeids ($0.000821\text{--}0.122 \text{ kg}_{\text{soil}} \text{ kg}_{\text{worm}}^{-1} \text{ day}^{-1}$ for K_u and $0.0224\text{--}0.136 \text{ day}^{-1}$ for K_e) exposed to natural field soil.⁴³ This suggests that REEs are more bioaccessible to snails via trophic exposure.⁴⁴ Additionally, the K_u values were higher for LREE and HREE than for MREE. This suggests a higher accumulation of LREE and HREE than MREE in snails (Figure 4A). The K_u values were higher for Eu than for some elements in snails, which may contribute to explaining the positive Eu anomaly (Figure 4B). The correlation trend of K_u but not K_e with the atomic number of the HREE is also consistent with the trends of $TTF_{\text{shoot} \rightarrow \text{snail}}$ (Figure 4B,C). Overall, these findings illustrate that the differences in REE toxicokinetics, including uptake, distribution, metabolic processes, and elimination, result in different REE profiles in the snails.

3.3. Impacts of Dietary Exposure to REEs on Snail Health. Trophic transferred REEs had significant effects on the gut microbial community and global metabolic profiles of snails (Figure 5). After 28 days of exposure, the community structure of intestinal microbiota at the phylum level of snails was disordered as indicated by a decrease of *Proteobacteria* and an increase of *Firmicutes* (Figure 5A). Based on principal coordinates analysis (PCoA) analysis, gut microbiota from snails exposed to the lettuce grown at the highest REE concentrations, i.e., on soil JX, clearly separated from the

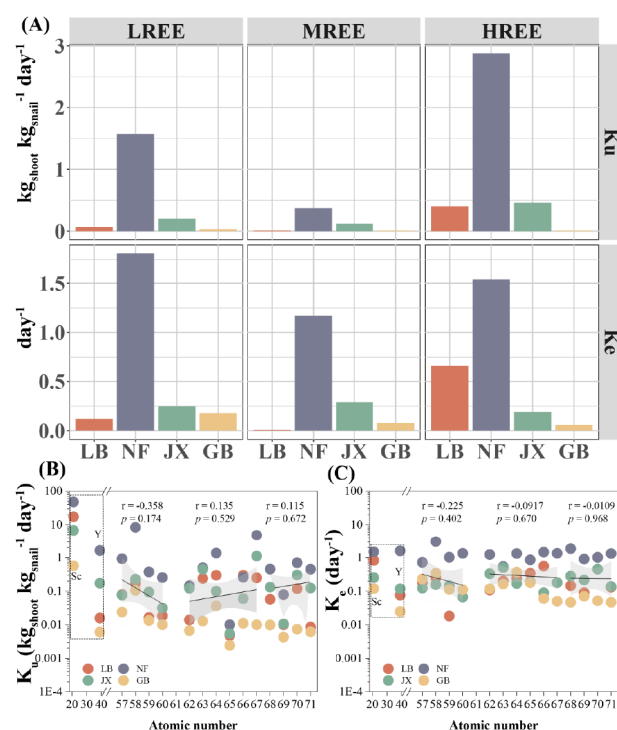


Figure 4. Uptake (K_u) and elimination (K_e) rate constants of rare earth elements (REEs) in snails (*Bradybaena ravida*) exposed for 28 days to lettuce shoots grown on different agricultural soils collected from Lingbei (LB), Nanfeng (NF), Jianxia (JX), and Gaobei (GB) villages near REE mining areas in Dingnan County, Jiangxi Province, southern China (A), and the relationships between K_u (B) and K_e (C) and the atomic number of the LREE, MREE, and HREE. In figure A, values are mean ($n = 5$); kinetics parameters were estimated by fitting a one-compartment model (eq S2) to the data based on shoot REE concentrations. In figures B and C, regressions are shown for light (LREE), medium (MREE), and heavy (HREE) weight REE.

Control, while those from snails exposed to lettuce grown at lower REE concentrations, i.e., NF soil, clustered with the Control (Figure 5B). Similarly, snail exposure to lettuce containing high concentrations of REEs, i.e., from JX soil, significantly changed the relative abundances of gut bacteria at the operational taxonomic unit (OTU) level compared to that of the Control (Figure 5C). Specifically, the relative abundances of microbes belonging to *Actinobacteriota*, *Chloroflexi*, *Desulfobacterota*, and *Firmicutes* phyla were profoundly increased compared to that of the Control (Figure 5C). Additionally, three prevalent ecological clusters (modules 1–3) were noted in the co-occurrence network based on the OTUs (Figure S10A), which were dominated by *Proteobacteria*, *Firmicutes*, *Actinobacteriota*, *Chloroflexi*, and *Bacteroidota* phyla (Figure S11A). These findings demonstrate a dose-dependent effect of trophically transferred REEs on the disruption of intestinal microbiota in the snails. Similarly, other researchers have reported that intestinal microbial flora has a high sensitivity to extraneous chemicals such as metals,⁴⁵ pesticides and antibiotics,^{46,47} and particles.^{15,48} This effect on the snail gut microbiome was not directly due to the fact that the snails were exposed indirectly to the REEs. Previous studies have shown that REEs directly affected the bacteria in the phyllosphere and leaf of a soil–rice system⁴⁹ and changed the metabolites in the leaves of plants.⁵⁰ However, our study, for the first time, revealed the indirect effects of REEs on

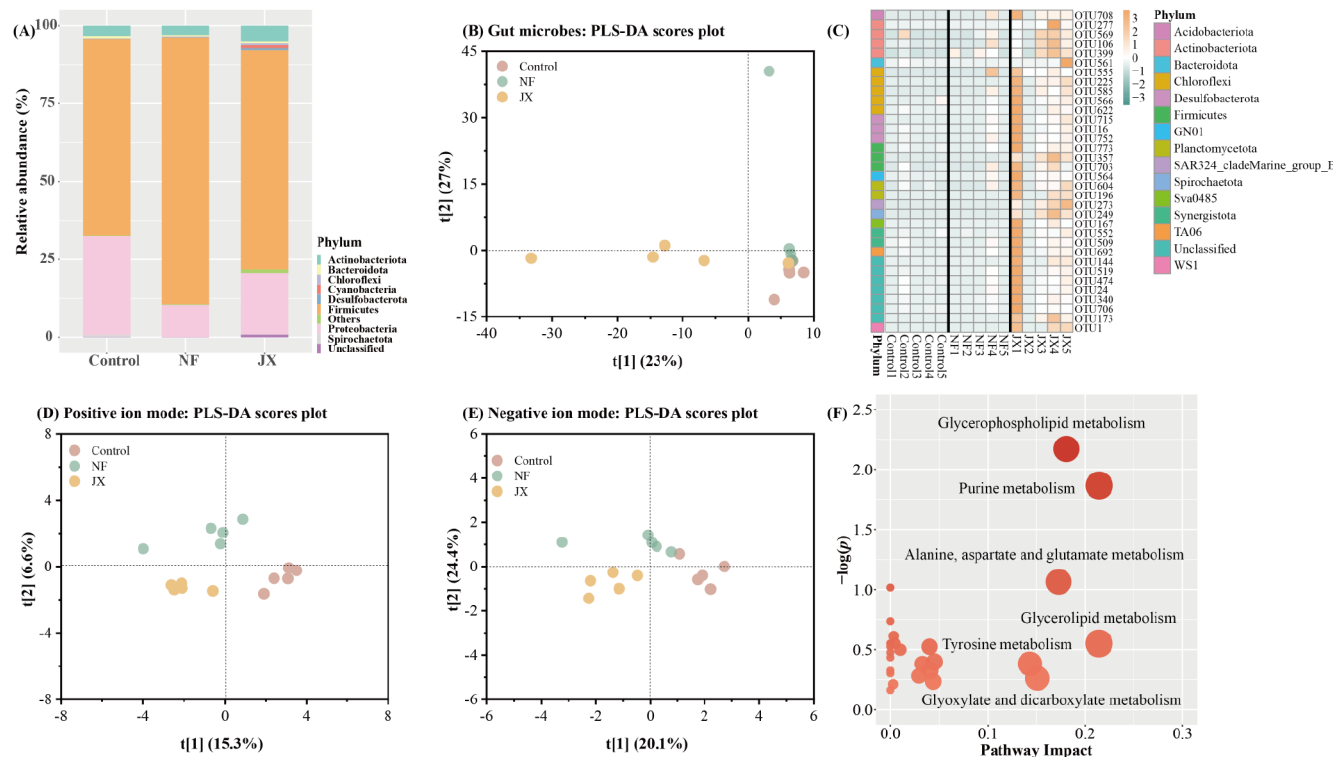


Figure 5. Gut microbial community composition (A for the relative abundance of phyla, B for partial least-squares-discriminant analysis (PLS-DA), and C for heatmap of significantly changed microbes) and soft tissue metabolites (D and E for PLS-DA in positive and negative ion modes and F for the pathway analysis of significantly changed metabolites) of snails (*Bradybaena ravida*) exposed for 28 days to lettuce shoots grown on agricultural soils collected from Nanfeng (NF) and Jianxia (JX) villages near rare earth element (REE) mining areas in southern China. See Figure S1 for sampling locations.

Table 1. Changes in Redox Homeostasis, Ion Transport, and Energy Storage of Snails (*Bradybaena ravida*) Exposed for 28 Days to Lettuce Shoots Grown on Agricultural Soils Collected From Nanfeng (NF) and Jianxia (JX) Villages Near Rare Earth Element (REE) Mining Areas in Dingnan County, Jiangxi Province, Southern China^a

		control	NF	JX
redox homeostasis	MDA (nmol mg _{protein} ⁻¹)	0.312 ± 0.120 A	0.385 ± 0.117 A	0.354 ± 0.0728 A
	SOD (U mg _{protein} ⁻¹)	89.6 ± 7.44 A	73.7 ± 5.43 B	70.1 ± 6.03 B
	GSH (μmol g _{protein} ⁻¹)	16.1 ± 1.39 B	16.6 ± 1.39 B	20.6 ± 1.60 A
ion transport	Na ⁺ K ⁺ -ATPase (U mg _{protein} ⁻¹)	3.55 ± 0.415 A	1.72 ± 0.333 B	3.37 ± 0.708 A
	Ca ²⁺ -ATPase (U mg _{protein} ⁻¹)	0.195 ± 0.0730 AB	0.105 ± 0.0272 B	0.241 ± 0.0981 A
energy storage	soluble sugar (mg mg _{protein} ⁻¹)	0.569 ± 0.135 B	0.817 ± 0.278 B	1.57 ± 0.268 A
	lipid (0.01 g g ⁻¹)	3.34 ± 0.472 B	4.68 ± 1.01 AB	5.49 ± 1.12 A
	protein (mg g ⁻¹)	49.7 ± 0.941 B	56.0 ± 2.88 A	36.9 ± 4.40 C

^aValues represent the mean ± standard deviation (*n* = 5). Values in each row with different letters indicate statistically significant differences of changes at *p* < 0.05 level.

microbiota through the food chain. This suggests the presence of bottom-up effects on the food chain via directly affecting the microbes and metabolites in the leaves of producers. This topic requires further investigation.

Numerous studies have reported that the intestinal microflora plays vital roles in the metabolism, immunity, and nutrient absorption of the host. To further focus on gut microbiota functions, we explored the metabolic profiles of the snails. Initially, the low-contaminated (NF), high-contaminated (JX) REE, and Control groups were separated along the first principal component, i.e., *t*[1], in a dose-dependent manner as shown in the partial least-squares-discriminant analysis (PLS-DA) (Figure 5D,E). There were 205 and 113 significantly changed metabolites (SCMs) with VIP > 1 under the positive and negative modes, respectively, contributing to

group separation (Table S7). The SCMs mainly included lipids and lipid-like molecules (fatty acyls and glycerophospholipids), organic acids and derivatives (amino acids, peptides, and analogues), organic oxygen compounds (carbohydrates and carbohydrate conjugates), phenylpropanoids and polyketides (flavonoids), organoheterocyclic compounds, and other metabolites (Table S7). These metabolites also were the keystone metabolites in the co-occurrence network based on metabolites (Figures S10BC and S11B). In addition, some of these SCMs mainly participate in a series of vital biological metabolic pathways, including glycerophospholipid metabolism, purine metabolism, alanine, aspartate, and glutamate metabolism, glycerolipid metabolism, tyrosine metabolism, and glyoxylate and dicarboxylate metabolism in snails (Figure 5F). Glycerolipid and glycerophospholipid are essential lipids for

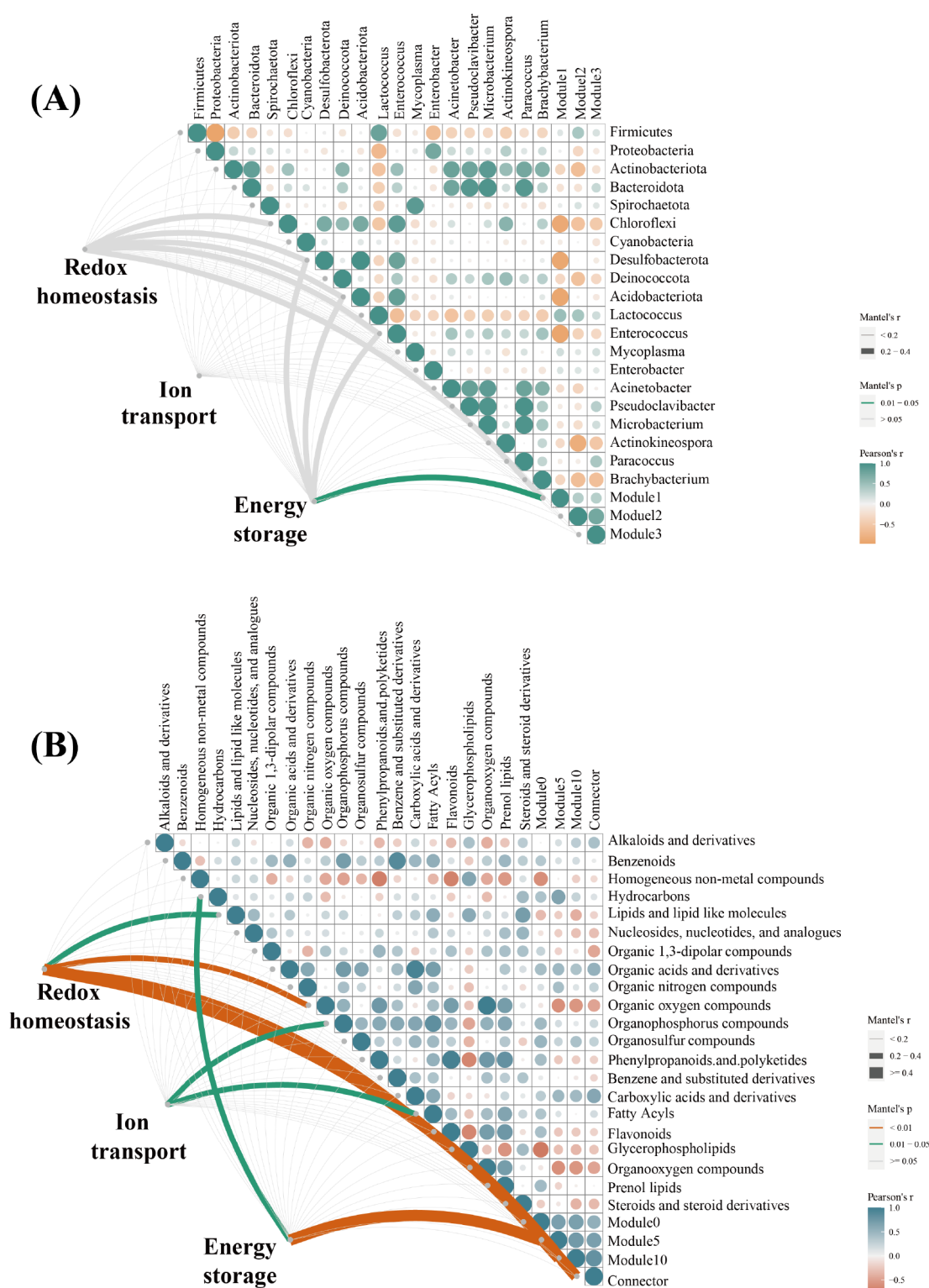


Figure 6. Correlation analysis between toxicity to snails and gut microbial community (A) and soft tissue metabolites (B) of snails (*Bradybaena ravidia*) exposed for 28 days to lettuce shoots grown on agricultural soils collected from Nanfeng (NF) and Jianxia (JX) villages near rare earth element (REE) mining areas in Dingnan County, Jiangxi Province, southern China.

membrane formation, energy storage, and some intracellular biological processes.⁵¹ Amino acids like aspartate and glutamate play important roles in promoting antioxidant levels in animals.⁵² To further validate the metabolic observations, such as redox homeostasis, ion transport, and energy storage, we performed a targeted analysis of the physiological and

biochemical responses of the snails (Table 1). The dietary exposure to REEs resulted in a significant increase in MDA and GSH contents ($p < 0.05$) and a reduction of SOD activities ($p < 0.05$), whereas the activities of $\text{Na}^+ \text{K}^+$ -ATPase and Ca^{2+} -ATPase remained unaffected, indicating an induced oxidative damage. Research has demonstrated oxidative stress-related

effects for some REEs in terrestrial organisms including plants and animals.⁵³ In terms of energy storage, the levels of soluble sugars and lipids in the snails decreased with increasing exposure concentration. However, a reduction in protein content was observed only in the high-dose REE group, specifically those exposed to lettuce shoots grown on soil JX. This finding clearly illustrates a decrease in energy storage. Overall, this study demonstrates the occurrence of oxidative stress and effects on energy expenditure induced by trophic transferred REEs through both nontargeted and targeted analyses.

The physiological functions of the host are regulated by gut microbiota and metabolites. Mantel tests showed that gut microorganisms, such as *Chloroflexi*, *Desulfobacterota*, *Acidobacteriota*, *Enterococcus*, and *module1*, and metabolites, such as hydrocarbons, lipids and lipid-like molecules, organic oxygen compounds, organophosphorus compounds, fatty acyls, *module 5*, and connectors, have close relationships with the phenotype of the snails (Figure 6). Besides, our study also found that benzenoids, benzene, lipids, and lipid-like molecules, fatty acyls, glycerophospholipids, prenol lipids, organic nitrogen compounds, organic oxygen compounds, and organophosphorus compounds have close relationships with the intestinal microbiome (Figure S12). This could be attributed to the fact that gut microbial metabolic processes regulate the close linkages between intestinal microbiome and host metabolism. Moreover, certain metabolites produced by the host act as the dominant organic substrates that could be utilized by gut microbes for growth. Consequently, the gut microbial alternations induced by dietary exposure to REEs might cause disturbances in host metabolism via their interactions. Additionally, the links of metabolites and the physiological functions in the snails were stronger than those of the gut microbial community, as shown by the higher Mantel's *r* (Figure 6). Overall, these perturbed metabolic profiles and gut microbial dysbiosis in snails exposed to REE-contaminated shoots are closely related to the physiological functions of the hosts.

4. ENVIRONMENTAL IMPLICATIONS

This study revealed that REEs can be transmitted from plants to terrestrial invertebrates by trophic transfer with changed REE profiles along the food chain. Furthermore, the mechanisms of variation in accumulation potential of different REEs at different trophic levels were illustrated by describing their uptake and elimination with toxicokinetic models. Subsequently, gut microbiome, nontargeted metabolomics, and targeted physiology analysis revealed that trophic transferred REEs may affect the redox homeostasis, energy storage, and ion transport processes in the snails in a dose-dependent manner, indicating the toxicity induced by dietary uptake of REEs. The findings of this study demonstrate that the cultivation of crops on agricultural soils surrounding REE mines may lead to dietary uptake and selective transfer of REEs within food chains, subsequently resulting in potential toxic effects associated with oxidative damage and energy expenditure in consumers. Our results also highlight that a toxicokinetic approach could be further applied to gain better insight into the mechanisms of contaminant transfer through the food chain and to better inform the regulatory framework for contaminant risk assessment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.3c09179>.

Additional details on the toxicokinetic models and bioinformatics analysis of sequencing and metabolomics data; the locations of the the sampling sites near REE mining areas (Figure S1); REE concentrations in roots and shoots of lettuce plants and in the soft tissues and shells of snails (Figure S2); TF of REEs from soil to lettuce and TTF of REEs from lettuce shoots to snail (Figure S3); relationship between REE TF and TTF and the atomic numbers of LREE, MREE, and HREE (Figure S4); REE profiles of lettuce and snails normalized by post-Archean Australian average shale (PAAS) composite (Figure S5); the quantification of the single REE enrichment profiles of lettuce and snails normalized by PAAS composite (Figure S6); changes in fresh biomass of shoot and soluble sugar and protein in shoot of lettuces (Figure S7); uptake of LREEs, MREEs, and HREEs in snails (Figure S8); uptake of REEs in snails exposed for 28 days to lettuce shoots (Figure S9); co-occurrence network of the gut microbes and soft tissue metabolites of snails (Figure S10); proportion of gut microbes and soft tissue metabolites in different categories of snails (Figure S11); relationship between soft tissue metabolites and gut microbes of snails (Figure S12); the basic physical and chemical properties of the test soils (Table S1); average concentrations (mg/kg) of single REEs in soil, lettuce plants, and snails (Table S2); mean detection limits for REEs (Table S3); certified and measured concentrations of REEs for the GBW07407 and BCR 668 certified material (Table S4); overall kinetic parameters for rare earth element uptake by lettuce plants (Table S5); the coefficient of determination for the fit of the one compartment model to data on the uptake of rare earth elements in snails (Table S6); SCMS in snails (Table S7) (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Gwenzi, W.; Mangori, L.; Danha, C.; Chaukura, N.; Dunjana, N.; Sanganyado, E. Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants. *Sci. Total Environ.* **2018**, *636*, 299–313.
- (2) Liang, T.; Li, K. X.; Wang, L. State of rare earth elements in different environmental components in mining areas of China. *Environ. Monit. Assess.* **2014**, *186*, 1499–1513.
- (3) MacMillan, G. A.; Chételat, J.; Heath, J.; Mickpegak, R.; Amyot, M. Rare earth elements (REE) in freshwater, marine, and terrestrial ecosystems in the eastern Canadian Arctic. *Environ. Sci.: Processes Impacts* **2017**, *19*, 1336–1345.
- (4) Wang, X. N.; Gu, Y. G.; Wang, Z. H. Rare earth elements in different trophic level marine wild fish species. *Environ. Pollut.* **2022**, *292*, 118346.
- (5) Amyot, M.; Clayden, M. G.; MacMillan, G. A.; Perron, T.; Arscott-Gauvin, A. Fate and trophic transfer of rare earth elements in temperate lake food webs. *Environ. Sci. Technol.* **2017**, *51*, 6009–6017.
- (6) Weltje, L.; Heidenreich, H.; Zhu, W.; Wolterbeek, H. T.; Korhammer, S.; de Goeij, J. J.; Markert, B. Lanthanide concentrations in freshwater plants and molluscs, related to those in surface water, pore water and sediment. A case study in The Netherlands. *Sci. Total Environ.* **2002**, *286*, 191–214.
- (7) Squadrone, S.; Brizio, P.; Stella, C.; Mantia, M.; Battuello, M.; Nurra, N.; Sartor, R. M.; Orusa, R.; Robetto, S.; Brusa, F.; et al. Rare earth elements in marine and terrestrial matrices of Northwestern Italy: Implications for food safety and human health. *Sci. Total Environ.* **2019**, *660*, 1383–1391.
- (8) Santos, A. C. S. S.; Souza, L. A.; Araujo, T. G.; de Rezende, C. E.; Hatje, V. Fate and trophic transfer of rare earth elements in a tropical estuarine food web. *Environ. Sci. Technol.* **2023**, *57*, 2404–2414.
- (9) González, V.; Vignati, D. A. L.; Leyval, C.; Giamberini, L. Environmental fate and ecotoxicity of lanthanides: are they a uniform group beyond chemistry? *Environ. Int.* **2014**, *71*, 148–157.
- (10) Huang, X. Y.; He, E. K.; Qiu, H.; Zhang, L. L.; Tang, Y. T.; Zhao, C. M.; Li, M.; Xiao, X.; Qiu, R. L. Do toxicokinetic and toxicodynamic processes hold the same for light and heavy rare earth elements in terrestrial organism *Enchytraeus crypticus*? *Environ. Pollut.* **2020**, *262*, 114234.
- (11) Neira, P.; Romero-Freire, A.; Basallote, M. D.; Qiu, H.; Cobelo-García, A.; Cánovas, C. R. Review of the concentration, bioaccumulation, and effects of lanthanides in marine systems. *Front. Mar. Sci.* **2022**, *9*, 920405.
- (12) Yuan, M.; Liu, C.; Liu, W. S.; Guo, M. N.; Morel, J. L.; Huot, H.; Yu, H. J.; Tang, Y. T.; Qiu, R. L. Accumulation and fractionation of rare earth elements (REEs) in the naturally grown *Phycolacca americana* L. in southern China. *Int. J. Phytorem.* **2018**, *20*, 415–423.
- (13) Ding, S. M.; Liang, T.; Zhang, C. S.; Huang, Z. C.; Xie, Y. N.; Chen, T. B. Fractionation mechanisms of rare earth elements (REEs) in hydroponic wheat: An application for metal accumulation by plants. *Environ. Sci. Technol.* **2006**, *40*, 2686–2691.
- (14) Semhi, K.; Chaudhuri, S.; Clauer, N. Fractionation of rare-earth elements in plants during experimental growth in varied clay substrates. *Appl. Geochem.* **2009**, *24* (3), 447–453.
- (15) Varg, J. E.; Outomuro, D.; Kuncze, W.; Kuehrer, L.; Svanbäck, R.; Johansson, F. Microplastic exposure across trophic levels: Effects on the host-microbiota of freshwater organisms. *Environ. Microbiome* **2022**, *17*, 36.
- (16) Li, J. M.; Yan, L. W.; Cao, X. H.; Luo, X. M.; Peng, X. T.; Wang, Z. R.; Zou, T. D.; Chen, J.; You, J. M. Effects of rare earth as feed additive on production performance, egg quality, serum biochemical parameters, antioxidant capacity, intestinal morphology, gut microbiota in late-phase laying hens. *Front. Sustain. Food Syst.* **2023**, *7*, 1155543.
- (17) Chae, Y.; An, Y. J. Nanoplastic ingestion induces behavioral disorders in terrestrial snails: Trophic transfer effects via vascular plants. *Environ. Sci. Nano* **2020**, *7*, 975.
- (18) Dang, F.; Li, C. C.; Nunes, L. M.; Tang, R. G.; Wang, J. S.; Dong, S. F.; Peijnenburg, W. J. G. M.; Wang, W. X.; Xing, B. S.; Lam, S. S.; et al. Trophic transfer of silver nanoparticles shifts metabolism in snails and reduces food safety. *Environ. Int.* **2023**, *176*, 107990.
- (19) Wu, J.; Bosker, T.; Vijver, M. G.; Peijnenburg, W. J. G. M. Trophic Transfer and Toxicity of (Mixtures of) Ag and TiO₂ Nanoparticles in the Lettuce–Terrestrial Snail Food Chain. *Environ. Sci. Technol.* **2021**, *55*, 16563–16572.
- (20) Scheifler, R.; Vaufléury, A. G.; Badot, P. M. Transfer of cadmium from plant leaves and vegetable flour to the snail *Helix aspersa*: Bioaccumulation and effects. *Ecotoxicol. Environ. Saf.* **2002**, *53*, 148–153.
- (21) Kwak, J. I.; An, Y. J. Trophic transfer of silver nanoparticles from earthworms disrupts the locomotion of springtails (*Collembola*). *J. Hazard. Mater.* **2016**, *315*, 110–116.
- (22) Zhu, D.; Ke, X.; Wu, L. H.; Li, Z.; Christie, P.; Luo, Y. M. Ecotoxicity of cadmium in a soil collembolan-predatory mite food chain: Can we use the ¹⁵N labeled litter addition method to assess soil functional change? *Environ. Pollut.* **2016**, *219*, 37–46.
- (23) Liu, W. S.; Guo, M. N.; Liu, C.; Yuan, M.; Chen, X. T.; Huot, H.; Zhao, C. M.; Tang, Y. T.; Morel, J. L.; Qiu, R. L. Water, sediment and agricultural soil contamination from an ion-adsorption rare earth mining area. *Chemosphere* **2019**, *216*, 75–83.
- (24) Dai, Y. B.; Sun, S.; Li, Y.; Yang, J. J.; Zhang, C. B.; Cao, R.; Zhang, H. J.; Chen, J. P.; Geng, N. B. Residual levels and health risk assessment of rare earth elements in Chinese resident diet: A market-based investigation. *Sci. Total Environ.* **2022**, *828*, 154119.
- (25) De Schampelaere, K. A. C.; Stauber, J. L.; Wilde, K. L.; Markich, S. J.; Brown, P. L.; Franklin, N. M.; Creighton, N. M.; Janssen, C. R. Toward a biotic ligand model for freshwater green algae: surface-bound and internal copper are better predictors of toxicity than free Cu²⁺-ion activity when pH is varied. *Environ. Sci. Technol.* **2005**, *39*, 2067–2072.
- (26) ISO 11466, *Soil quality: extraction of trace elements soluble in aqua regia*; ISO, 1995.
- (27) He, E. K.; Qiu, R. L.; Cao, X. D.; Song, L.; Peijnenburg, W. J. G. M.; Qiu, H. Elucidating toxicodynamic at the molecular scale between ZnO nanoparticles and ZnCl₂ in *Enchytraeus crypticus* via nontargeted metabolomics. *Environ. Sci. Technol.* **2020**, *54*, 3487–3498.
- (28) Lőw, P.; Molnár, K.; Kriska, G. Dissection of a Snail (*Helix pomatia*). In *Atlas of Animal Anatomy and Histology*; Lőw, P.; Molnár, K.; Kriska, G., Eds.; Springer: Cham, 2016; pp 4977.
- (29) Zhang, P. H.; Li, W. X.; Qiu, H.; Liu, M.; Li, Y.; He, E. K. Metal resistant gut microbiota facilitates snails feeding on metal hyper-accumulator plant *Sedum alfredii* in the phytoremediation field. *Ecotoxicol. Environ. Saf.* **2022**, *236*, 113514.
- (30) Tyler, G. Rare earth elements in soil and plant systems - A review. *Plant Soil* **2004**, *267*, 191–206.
- (31) Brioschi, L.; Steinmann, M.; Lucot, E.; Pierret, M. C.; Stille, P.; Prunier, J.; Badot, P. M. Transfer of rare earth elements (REE) from natural soil to plant systems: Implications for the environmental availability of anthropogenic REE. *Plant Soil* **2013**, *366*, 143–163.
- (32) Cao, X. D.; Chen, Y.; Gu, Z. M.; Wang, X. R. Determination of trace rare earth elements in plant and soil samples by inductively

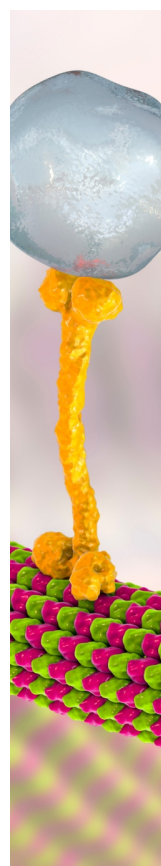
- coupled plasma-mass spectrometry. *Int. J. Environ. Anal. Chem.* **2000**, *76*, 295–309.
- (33) Kotelnikova, A.; Fastovets, I.; Rogova, O.; Volkov, D. S. La, Ce and Nd in the soil-plant system in a vegetation experiment with barley (*Hordeum vulgare* L.). *Ecotoxicol. Environ. Saf.* **2020**, *206*, 111193.
- (34) Saatz, J.; Vetterlein, D.; Mattusch, J.; Otto, M.; Daus, B. The influence of gadolinium and yttrium on biomass production and nutrient balance of maize plants. *Environ. Pollut.* **2015**, *204*, 32–38.
- (35) Ding, S. M.; Liang, T.; Zhang, C. S.; Yan, Y. C.; Zhang, Z. L. Accumulation and fractionation of rare earth elements (REEs) in wheat: Controlled by phosphate precipitation, cell wall absorption and solution complexation. *J. Exp. Bot.* **2005**, *56*, 2765–2775.
- (36) d'Aquino, L.; de Pinto, M. C.; Nardi, L.; Morgana, M.; Tommasi, F. Effect of some light rare earth elements on seed germination, seedling growth and antioxidant metabolism in *Triticum durum*. *Chemosphere* **2009**, *75*, 900–905.
- (37) Li, C. C.; Dang, F.; Cang, L.; Zhou, D. M.; Peijnenburg, W. J. G. M. Internal distribution of Cd in lettuce and resulting effects on Cd trophic transfer to the snail: *Achatina fulica*. *Chemosphere* **2015**, *135*, 123–128.
- (38) Soliman, M. M.; Hesselberg, T.; Mohamed, A. A.; Renault, D. Trophic transfer of heavy metals along a pollution gradient in a terrestrial agro-industrial food web. *Geoderma* **2022**, *413*, 115748.
- (39) McGeer, J. C.; Brix, K. V.; Skeaff, J. M.; DeForest, D. K.; Brigham, S. I.; Adams, W. J.; Green, A. Inverse relationship between bioconcentration factor and exposure concentration for metals: Implications for hazard assessment of metals in the aquatic environment. *Environ. Toxicol. Chem.* **2003**, *22*, 1017–1037.
- (40) Pourret, O.; van der Ent, A.; Hursthouse, A.; Irawan, D. E.; Liu, H. Y.; Wiche, O. The 'europium anomaly' in plants: facts and fiction. *Plant Soil* **2022**, *476*, 721–728.
- (41) Hirano, S.; Suzuki, K. T. Exposure, metabolism, and toxicity of rare earths and related compounds. *Environ. Health Perspect.* **1996**, *104* (Suppl 1), 85–95.
- (42) Gong, B.; He, E. K.; van Gestel, C. A. M.; Tang, Y. T.; Yang, W. J.; Yang, J.; Li, Y.; Qiu, H. Dynamic interaction processes of rare earth metal mixtures in terrestrial organisms interpreted by toxicokinetic and toxicodynamic model. *J. Hazard. Mater.* **2021**, *418*, 126281.
- (43) Li, W. X.; He, E. K.; van Gestel, C. A. M.; Peijnenburg, W. J. G. M.; Li, Y. S.; Liu, M.; Li, Y.; Li, X.; Qiu, H. A toxicokinetics approach using *Enchytraeus crypticus* to evaluate the efficiency of hydroxyapatite to remediate soils contaminated with rare earth elements. *J. Hazard. Mater.* **2023**, *460*, 132487.
- (44) Unrine, J. M.; Shoults-Wilson, W. A.; Zhurbich, O.; Bertsch, P. M.; Tsyusko, O. V. Trophic transfer of Au nanoparticles from soil along a simulated terrestrial food chain. *Environ. Sci. Technol.* **2012**, *46*, 9753–9760.
- (45) Zhu, D.; Zheng, F.; Chen, Q. L.; Yang, X. R.; Christie, P.; Ke, X.; Zhu, Y. G. Exposure of a soil collembolan to Ag nanoparticles and AgNO₃ disturbs its associated microbiota and lowers the incidence of antibiotic resistance genes in the gut. *Environ. Sci. Technol.* **2018**, *52*, 12748–12756.
- (46) Wang, H. T.; Gan, Q. Y.; Li, G.; Zhu, D. Effects of Zinc Thiazole and Oxytetracycline on the Microbial Metabolism, Antibiotic Resistance, and Virulence Factor Genes of Soil, Earthworm Gut, and Phyllosphere. *Environ. Sci. Technol.* **2024**, *58*, 160–170.
- (47) Zhu, D.; Xiang, Q.; Yang, X. R.; Ke, X.; O'Connor, P.; Zhu, Y. G. Trophic transfer of antibiotic resistance genes in a soil detritus food chain. *Environ. Sci. Technol.* **2019**, *53*, 7770–7781.
- (48) Li, W. X.; He, E. K.; Zhang, P. H.; Li, Y. S.; Qiu, H. Multiomics analyses uncover nanoceria triggered oxidative injury and nutrient imbalance in earthworm *Eisenia fetida*. *J. Hazard. Mater.* **2022**, *437*, 129354.
- (49) Zhang, X. Z.; Hu, Z. J.; Pan, H. H.; Bai, Y. J.; Hu, Y.; Jin, S. L. Effects of rare earth elements on bacteria in rhizosphere, root, phyllosphere and leaf of soil-rice ecosystem. *Sci. Rep.* **2022**, *12*, 2089.
- (50) Cheng, M. Z.; Wang, L. H.; Zhou, Q.; Chao, D. Y.; Nagawa, S.; He, D.; Zhang, J. Z.; Li, H.; Tan, L.; Gu, Z. H.; et al. Lanthanum(III)

triggers AtrbohD- and jasmonic acid-dependent systemic endocytosis in plants. *Nat. Commun.* **2021**, *12*, 4327.

(51) van Meer, G.; Voelker, D.; Feigenson, G. W. Membrane lipids: where they are and how they behave. *Nat. Rev. Mol. Cell Biol.* **2008**, *9*, 112–124.

(52) Ni, H.; Lu, L.; Deng, J. P.; Fan, W. J.; Li, T. J.; Yao, J. M. Effects of glutamate and aspartate on serum antioxidative enzyme, sex hormones, and genital inflammation in boars challenged with hydrogen peroxide. *Mediators Inflammation* **2016**, *2016*, 4394695.

(53) Pagano, G.; Guida, M.; Tommasi, F.; Oral, R. Health effects and toxicity mechanisms of rare earth elements-knowledge gaps and research prospects. *Ecotoxicol. Environ. Saf.* **2015**, *115*, 40–48.



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