Distribution and Potential Ecological Risk Assessment of Four Light Rare Earth Elements in the Anning River Located in Sichuan Province, China

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Abstract. In order to investigate the distribution of rare earth elements (REEs) in the Anning River, 48 surface water and 16 sediment samples were collected. The elements La, Ce, Pr and Nd were analyzed. Risk Quotient and Potential Ecological Risk index were used to assess the ecological risk in the Anning River. The results showed that total REEs concentrations (La, Ce, Pr, and Nd) varied from 1.43 μg/L to 24.30 μg/L in surface water, and from 74.86 mg/kg to 1542.16 mg/kg in sediments. Average RQ values displayed the order: Ce > La > Pr > Nd. The RQ values of all REEs exceeded 1 at 7 sites. In addition, the resulting RQ values for La were higher than 1 at 14 sites (87.50%). The average potential ecological risk of REEs in the Anning River indicated a high risk level (RI= 44.40), mainly in sections S4-S6. The rare earth element Pr was the element that contributed the most to the Potential Ecological Risk index. Ecological risk should not be ignored. Thus, further studies are urgently required.

1. Introduction

Rare earth elements (REEs) are new pollutants of emerging concern, which have been reported its occurrence in aquatic systems and other substance in recent studies [1]. REEs can be adsorbed onto different types of particles, accumulated by organisms, and interfere with cellular functions [2]. In view of their wide applications in modern electronics and industrial and medical products, it is expected that the emission of REEs into aquatic systems will increase in different forms [3]. However, few studies on the distribution and toxicology of REE in aquatic systems are available. Thus, more research is needed to determine the toxicity effects and potential risk of rare earth elements on aquatic environments.

Anning River, the largest tributary of the Yalong River in Sichuan Provence, China, is located in the most developed area of the Liangshan Prefecture, with intense industrial activity and agricultural production [4]. The Anning River Basin is rich in mineral resources, including light rare earth elements (LREE), iron ore, and copper, among others. However, disordered mining activities carried out in the past caused the accumulation of heavy metals in this area, especially rare earth elements [5]. Wastewater discharges from mineral processing, long-term hydraulic action of tailings and chemical weathering of ores under natural conditions [6] are the main source of LREE enrichment in the Anning river basin. Previous research has shown that total concentrations of REEs in the mining area of the Anning River basin reached 287-917 μg/L after HNO3 treatment. The main polluting elements are Lanthanum (La),
Cerium (Ce), Praseodymium (Pr) and Neodymium (Nd) [5]. These numbers are over a dozen times the world's average level for REEs in fresh water (0.52 ug/L). Thus, this type of pollution is threatening the environment of the Anning River Basin. The ecological environmental quality is directly related to the ecological security of the middle and lower sections of the Yangtze River and other vast areas in China. For this reason, in the present investigation, the Anning River was selected as study area. The purpose of the present study were (1) characterize the distribution of four light REEs including La, Ce, Pr and Nd, in sediments and surface water of the Anning River during the dry season; and (2) assess the potential ecological risk of four light REEs. The results presented herein will provide an important reference for environmental risk management of REEs in the Anning River.

2. Materials and methods
2.1. Study area and sample collection
Anning River is the largest tributary of the Yalong River, which to the east originates from Xiaoxiangling and to the south from the Maoniu Mountain. It flows from north to south through Mianning, Xichang, and Dechang counties (cities) in Liangshan Yi, the autonomous Prefecture of Sichuan Province. It also flows into the Yalong River in the Yanbian County of Panzhihua City. The main river is 320 km long and the drainage area is 11150 km$^2$. This is the most developed area in the Liangshan Prefecture dedicated to industrial activities and agricultural production [4].

Figure 1. Sampling stations along the Anning River.

During dry season in January 2020, surface water and sediment samples were collected from 16 stations. In each sampling station, three water sub-samples were collected from the river and a total of 48 water sub-samples were collected. Sediments were collected at 0-20 cm in each station using a plastic spade. Five sub-samples were mixed to form a sample. A total of 16 sediment samples were collected. The weight of each sample was 1kg. Samples were stored in a dark cool box for transport.
2.2. Sample analysis
Prior to analysis, sediments were air-dried and passed through a 100-mesh sieve in order to remove large pebbles. After sieving, 0.5 g of each sample were digested using an acid mixture comprised of 5 ml HNO₃, 8 ml HF, and 1 ml HClO₄ in a teflon crucible [7]. The 48 water sub-samples were filtered using a 0.45 μm membrane before quantitative elemental analysis. Concentrations of La, Ce, Pr, and Nd in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer) (GB/T 14506.30-2010). All data processing and Pearson correlation analysis were conducted on Excel 2016 and SPSS 25.0.

2.3. Ecological risk assessment

2.3.1. Risk quotient method. The risk quotient (RQ) was used to evaluate the ecological risk for surface water. For this purpose, the ratio of REEs concentrations in the environment (MEC) to the predicted no effect concentration (PNEC) was obtained (Eq.(1)):

$$ RQ = \frac{MEC}{PNEC} $$

An RQ value higher than 1 indicates a potential ecological risk that should not be neglected, while an RQ value equal to or less than 1 suggests a relatively small risk [8].

| Element | Species | Endpoint | La | Ce | Pr | Nd | References |
|---------|---------|----------|----|----|----|----|------------|
| Algae   | Raphidocelis subcapitata | LC50 | 51720.00 | - | - | 56990.00 | [11] |
|         | Chlorella vulgaris | LC50 | 47130.00 | - | - | 5504.00 | [11] |
| Crustaceans | Daphnia magna | LC50 | 24029.70 | 21960.68 | 9003.51 | 1384.32 | [12] |
|         | Daphnia similis | LC50 | 12920.00 | - | - | 9410.00 | [11] |
|         | Thamnocephalus platyurus | LC50 | 34600.00 | 33000.00 | 30800.00 | 31800.00 | [13] |
|         | Hyalella azteca | LC50 | 1655.00 | 651.00 | 441.00 | 511.00 | [14] |
|         | Hydra attenuata | LC50 | - | 560.00 | - | - | [15] |
| Fish    | Oncorhynchus mykiss | LC50 | 68311.02 | 54330.78 | - | 34752.20 | [16] |
|         | Danio rerio | LC50 | 83812.26 | - | - | - | [17] |
| Benthos | Tubifex | EC50 | 10556.40 | 11936.52 | 10637.95 | 10382.40 | [18] |
|         | Nannodrilus spp | EC50 | - | - | - | - | - |

PNEC*: not available; *: PNEC was calculated using acute toxicity data in table.

In the present study, the REEs PNEC values were calculated by the assessment factor according to Guidance on Information Requirements and Chemical Safety (European Chemicals Agency (RECHA) [9]). Reported REEs aquatic-acute-toxicity data for sensitive species were collected from Web of science (https://www.webofknowledge.com), ScienceDirect (https://www.sciencedirect.com), Springer (https://www.springer.com), and CNKI (https://www.cnki.net). The acute toxicity data from four different trophic-level aquatic species are displayed in Table 1. According to the guidance, when only short-term toxicity data are available, an assessment factor of 1000 will be applied on the lowest L(E)C₅₀ of the relevant available toxicity data [10].

2.3.2. Potential Ecological Risk index method. The potential ecological risk index is frequently used to evaluate the risk of heavy metal pollution [20], which was proposed by Hakanson [19]. This research selected this index to estimate the ecological risk in sediments. The comprehensive Potential Ecological Risk index (RI) is the sum of each elemental index (Eq.(2))

$$ RI = \sum E_i = \sum (T_i \times f_i) = \sum (T_i \times C_{wi}) / B_i \quad (i = 1, 2, \cdots n) $$
Where $E_i$ represents the potential ecological risk index of a single element; $T_i$ is the toxicity index, which reflects the coefficient, toxic level, as well as the water sensitivity of the element; $f_i$ is the pollution coefficient for a single element, and is calculated using $f_i = C_{io} / B_i$; $C_{io}$ is the measured concentration of the element; and $B_i$ is the background concentration.

According to the references, the toxicity index of La, Ce, Pr, and Nd are 1, 1, 5 and 2, respectively [21]. In addition, REEs background values in soils of the Sichuan Province were selected as the background value for risk assessment purposes. Table 2 presents the classification of potential ecological risk and pollution levels that were obtained considering the modifications proposed by Ma [22].

| Ecological risk degree | Mild | Moderate | Strength | Strong | Very strong |
|-----------------------|------|----------|----------|--------|-------------|
| $E_i$                 | <5   | 5-10     | 10-20    | 20-40  | >40         |
| $RI$                  | <9   | 9-18     | 18-36    | >36    |             |

3. Results and discussion

3.1. The distribution of La, Ce, Pr, and Nd in surface water and sediments of the Anning River

Figure 2 displays the distribution and REE concentrations in each sampling station. Total concentrations of REEs (La, Ce, Pr, and Nd) varied from $1.43 \mu g/L$ to $24.30 \mu g/L$ in surface water, and from $74.86 mg/kg$ to $1542.16 mg/kg$ in sediments. Among all the REE quantified in the present study, La was detected a mean concentration of $4.75 \mu g/L$ in water which was the most abundant. Ce was the most abundant REE in sediments, displaying a mean concentration of $167.38 mg/kg$. Because of the lack of relevant standards for REEs in China, in the present study the chosen reference ratios corresponded to the background values of: (a) Sichuan soils; (b) Yangtze River sediments; and (c) background value of different sediments. Our data indicated that concentrations of REEs in all sampling stations were higher than reference values.

In terms of spatial distribution, rare earth element pollution was mainly distributed in the middle and lower areas of the river. In addition, the highest REEs concentration occurred in S8, which is located downstream of the rare earth element industrial park. Data also indicated that sediments in the Nanhe section (s4-s7), a tributary of Anning River located in Maoniuping rare earth mining area, showed more rare earth elements enrichment than other sections. In fact, S5 displayed the highest enrichment factor. This phenomenon was mainly related to the accumulation of tailings caused by disordered development in the area. The long-term rain erosion and flood erosion lead to a large number of slag components flowing into the Anning River Basin, causing water and sediment pollution.

Individual REEs were analyzed in water and sediments using Pearson correlation with SPSS. According to the results, significant correlation was detected among the elements ($r_{water}=0.613-0.948$, $r_{sediment}=0.955-0.993$, $P<0.05$), indicating that the sources of individual REEs were homologous. However, the most abundant REE in water was La, and the highest concentration was observed in S8. In addition, the most abundant REE in sediments was Ce and the highest concentration was observed in S5. These differences indicated that the main pollution sources of REEs between water and sediment were different. The REE pollution in sediments was mainly related to tailings, while that in water was mainly related to industrial activities and agricultural production.
3.2. Ecological risk assessment

The RQ in water and \( E_i \) in sediments for four REEs of the Anning river are showed in Figure 3 and Table 3. The order of average RQ values was ranked as follows: Ce > La > Pr > Nd. The RQ values of all REEs exceeded 1 at S5, S8, S9, S10, S12, S15, S16, indicating the existing of adverse ecological effects. the resulting RQ values for La were higher than 1 at 14 sites (87.50%). It is important to note that the assessment was based on a single sampling event. Thus, only partial information for the real water environment was provided. However, these results suggested that the ecological risk should not be ignored in Anning River because the RQ value for La, Ce, Pr and Nd in most samples was higher than 1.

Average \( E_i \) values followed the order: Pr > Nd > Ce > La. Pr in sediments showed high ecological risk (12.13-114.62). The Potential Ecological Risk for sample stations S4-S6 reached a very high level, and the Potential Ecological Risk of S5 was the highest one. The ecological risks of La, Ce, Pr and Nd were small in the 13 station of the Anning River. In addition, a medium level risk was determined in the S4-S6 sections. Pr was the element that contributed the most to the risk index. According to previous reports, Pr also presents an ecological risk in the Pearl River basin [10], and Pr pollution should be further discussed.

According to our results, the average Potential Ecological Risk for REEs in the Anning River was RI= 44.40, which corresponds to a high risk level and was mainly observed in sections S4-S6 and S16. Agricultural activities in the middle and lower reaches of Anning River Valley, large-scale planting of crops, intensive soil erosion, among other factors, lead to non-point source pollution, also affecting the REE content in sediments. Accordingly, further studies are urgently required.

Hakanson’s potential ecological risk model, which was used to obtain the parameters is “water-sediment-plankton-fish-human”, was selected for the present research. However, due to the lack of data on REE ecotoxicology, during the assessment of the potential ecological risk the toxicity response coefficient was replaced by the toxicity coefficient calculated by Chen et al. [15]. This coefficient takes into account the “abundance effect” and the “sedimentation effect”. It is likely that this replacement resulted in some errors during the assessment, especially because of the impact of productivity in the study area. Moreover, because of the lack of acute-toxicity data of REEs for local species, this study selected relative sensitive species as reference, which might increase the uncertainty of the assessment results. Therefore, it is urgent to carry out local ecotoxicology research in order to more accurately assess the ecological risk of REEs in the Anning River Basin. With this information we will improve the comprehensive assessment technology of REEs ecological risk, and establish the environmental risk assessment and management system for the rare earth element industry.
Figure 3. RQ values for La, Ce, Pr, and Nd at the sampling stations in the Anning river water.

Table 3. Potential Ecological Risk coefficient (Ei) and risk indices (RI) of rare earth elements in sediments

| Sample station | La   | Ce   | Pr   | Nd   | RI     |
|----------------|------|------|------|------|--------|
| S1             | 0.67 | 0.15 | 0.23 | 0.22 |        |
| S2             | 1.19 | 0.15 | 0.23 | 0.20 |        |
| S3             | 2.07 | 1.49 | 0.36 | 1.00 |        |
| S4             | 3.57 | 2.86 | 0.48 | 1.33 |        |
| S5             | 5.83 | 7.63 | 2.09 | 6.13 |        |
| S6             | 2.61 | 0.18 | 0.23 | 0.20 |        |
| S7             | 1.60 | 0.15 | 0.23 | 0.20 |        |
| S8             | 8.32 | 7.19 | 4.08 | 7.75 |        |
| S9             | 3.65 | 9.80 | 1.88 | 5.44 |        |
| S10            | 3.80 | 7.04 | 1.45 | 3.58 |        |
| S11            | 1.32 | 2.89 | 0.61 | 1.68 |        |
| S12            | 3.24 | 5.67 | 1.11 | 2.94 |        |
| S13            | 2.05 | 4.98 | 0.82 | 2.52 |        |
| S14            | 0.70 | 3.79 | 0.63 | 1.76 |        |
| S15            | 1.83 | 6.14 | 1.04 | 3.11 |        |
| S16            | 3.20 | 7.19 | 1.13 | 3.58 |        |

4. Conclusion
According to the results obtained in the present investigation, mining activities are responsible for the presence of rare earth elements in surface water and sediment of the Anning River. Total REEs concentrations (La, Ce, Pr, and Nd) varied from 1.43μg/L to 24.30μg/L in surface water, and from 74.86 mg/kg to 1542.16 mg/kg in surface sediments. Among all the REEs, La and Ce displayed the highest concentration in water and sediments, respectively. In the case of La, mean value was 4.75 μg/L in water and Ce concentration in sediments was 167.38 mg/kg. We determined that REEs pollution in sediments...
was mainly caused by mine tailing. On the other hand, contamination present in downstream water was mainly related to industrial and agricultural activities. The average RQ values followed the order: Ce > La > Pr > Nd. RQ values of all REEs exceeded 1 at 7 sites. In addition, La RQ value was higher than 1 at 14 sites (87.50%). Results obtained for the average potential ecological risk of REEs in the Anning River indicated that this place is at high risk level (RI= 44.40), specifically in sections S4-S6. Pr was the element that contributed the most to the risk index. The ecological risk should not be ignored and further studies are urgently required.

References
[1] Gwenzi W, Mangori L, Danha C, Chaukura N, Dunjana N and Sanganyado, E 2018 Sources, behaviour, and environmental and human health risks of high-technology rare earth elements as emerging contaminants. Sci. Total Environ. 636 299-313
[2] Herrmann H, Nolde J, Berger S and Heise S 2016 Aquatic ecotoxicity of lanthanum – a review and an attempt to derive water and sediment quality criteria. Ecotox. & Environ Safety 124 213-38
[3] Jin S L, Huang Y Z, Wang F, Xu F, Hu Y, Wang X L and Gao Z 2016 Rare earth elements content in farmland soils, crops, and river near a typical Tungsten Ore in Jiangxi province. Acta Sci. Cricumstantiae 36 1328-35
[4] Wang X M, Lan Q, Wang H B and Hu J Z 2016 Pollution characteristics and potential ecological risk assessment of heavy metals in Anning river, Sichuan province. Earth & Environ. 44 472-7
[5] Fu X F, Hou L W, Yuan L P, Pu Y H, Hao X F and Pan M 2017 Proposals on development and application, the investigation and assessment of Nanhe-Machangcun REE tailings mining of Sichuan J. Chinese society of rare earths 35 272-82
[6] Chen R Y 2019 Environment pollution and protection in rare earth application. Metallic Functional Materials 26 60-8
[7] Wang L Q, Han X X, Ding S M, Liang T, Zhang Y Y, Xiao J, Dong L L and Zhang H D 2019 Combining multiple methods for provenance discrimination based on rare earth element geochemistry in lake sediment Sci. Total Environ. 672 264-74
[8] Meng Y, et al. 2019 A review on occurrence and risk of polycyclic aromatic hydrocarbons (PAHs) in lakes of China Sci. Total Environ. 651 2497-506
[9] European Chemicals Agency (RECHA) 2008 Chapter R.10: Characterisation of dose [concentration] - response for environment. Guidance on information requirements and chemical safety
[10] Gu Y G, Gao Y P, Huang H H and Wu F X 2020 First attempt to assess ecotoxicological risk of fifteen rare earth elements and their mixtures in sediments with diffusive gradients in thin films. Water Research 185 116245
[11] Bergsten-Torralba L R, Magalhes D P, Giese E C, Nascimento C R S and Buss D F 2020 Toxicity of three rare earth elements, and their combinations to algae, microcrustaceans, and fungi. Ecotox. & Environ Safety 201 110795
[12] Gonzalez V, Vignati D A L, Leyval C and Giamberini L 2014 Environmental fate and ecotoxicity of lanthanides: Are they a uniform group beyond chemistry? Environ. International 71 148-57
[13] Blinova I, Lukjanova A, Muna M, Vija H and Kahru A 2018 Evaluation of the potential hazard of lanthanides to freshwater microcrustaceans. Sci. Total Environ. 642 1100-7
[14] Borgmann U, Couillard Y, Doyle P and Dixon D G 2010 Toxicity of sixty-three metals and metalloids to Hyalella azteca at two levels of water hardness Environ. Toxic. Chemi. 24 113
[15] Christian B, Francois G, Manon H, Brian Q and Hanana H 2018 Ecotoxicity responses of the freshwater cnidarian Hydra attenuata to 11 rare earth elements. Ecotox. & Environ Safety 163 486-91

7
[16] Dubé M, Auclair J, Hanana H, Turcotte P, Gagnon C and Gagné F 2019 Gene expression changes and toxicity of selected rare earth elements in rainbow trout juveniles. *Toxic. Pharma.* **223** 88-95

[17] Cui J A. 2011 Qingdao: Qingdao University of Science & Technology

[18] Rucki M, et al 2021 Evaluation of toxicity profiles of rare earth elements salts (lanthanides) *J. Rare Earths* **39** 225-32

[19] Hakansson L 1980 An ecological risk index for aquatic pollution control: a sedimentological approach *Water Res*** **14** 975-1001

[20] Xu Z Q, Ni S J and Tuo X G 2008 Calculation of heavy metals’ toxicity coefficient in the evaluation of potential ecological risk index. *Environ. Sci. Technol.* **31** 112-5

[21] Chen H B, Chen X B, Chen Z Q, Ou X L and Chen J J 2020 Calculation of toxicity coefficient of potential ecological risk assessment of rare earth elements. *Bull. Environ. Contam. Toxicol.* **104** 582-7

[22] Ma J H, Han C X and Jang Y L 2020 Some problems in the application of potential ecological risk index. *Geographical Research* **39** 1233-41