

Ecological and health risk assessments of rare earth elements in soil from gold mining areas in Sudan

Minas Elfatih Ahmed^{1,*}, *Hamid Bounouira*², *Mohamed Adam Abbo*¹, *Hamid Amsil*², *Abdessamad Didi*², *Abdelwahab Badague*² and *Iliasse Aarab*^{2,3}

¹Sudan University of Sciences and Technology, Faculty of Science, Department of Chemistry, Khartoum, Sudan

²National Center of Energy, Sciences and Nuclear Techniques (CNESTEN, Rabat, Morocco

³Faculty of Sciences, Ibn Tofail University, Kenitra, Morocco

Abstract. The increasing demand for rare earth elements (REE) has led to increased mining activities, which may result in potential ecological and health risks. Our objective was to evaluate the potential ecological and analyze the health risks associated with REE in soil samples obtained from the gold mining region, employing neutron activation analysis (NAA). The pollution load index (PLI) was carried out to evaluate the REE contamination. The findings indicated that the soils in gold mining regions were generally uncontaminated, with the exception of two specific locations. The correlation among of the REE with Au were carried out taking into account the chemical weathering indices (CIA). The potential ecological risk was calculated to conduct an ecological risk assessment of REE in the soil. The outcomes revealed that the RI values for the soil samples gathered from the mining area were within safe limits, signifying a low ecological risk, With the exception of Lutetium in three specific sample sites, suggesting a low to moderate level of ecological risk. Also, non-carcinogenic and carcinogenic health risk assessment was conducted in order to investigate potential adverse health risks. The hazard quotient values for both adults and children remained below 1, indicating that there were no significant non-carcinogenic risks to the inhabitants associated with all REE in the soil through ingestion, dermal contact, and inhalation pathways.

Keywords: Gold mining in Sudan, Soil samples, NAA, REE, Ecological and health risks.

1 Introduction

The soil is considered essential component of the environment, and it can be exposed to contamination by trace elements. Generally, the topsoil distinguishes by the high content of trace elements; due to the surface layer having the greatest ability to bond trace elements [1]. The origins of REE and trace elements in soils can be attributed to either natural processes (such as lithogenic and pedogenic processes) or human activities (anthropogenic sources) [2]. Nevertheless, when it comes to the accumulation of trace elements in soils, anthropogenic sources are the primary contributors, surpassing the influence of natural lithogenic processes [3].

*e-mail: minaselfatih11@gmail.com

This study was focused on the trace elements and REE. Recently, there has been a growing interest in the biogeochemistry of REE [4]. However, there is a scarcity of published information regarding the presence of REE in urban environments. The REE has environmental pollution indicators [5]. Rare earth elements (REE) hold significant importance in the field of geochemistry research, serving as crucial indicators of geochemical processes taking place not only on Earth but also on other celestial bodies. Due to their distinctive chemical characteristics, REEs have found extensive application in comprehending geological and geochemical phenomena, which encompasses the examination of the chemical evolution of the Earth's crust [6], weathering processes in watersheds [7], as well as pollution indicator [8].

Heavy metals and REE are both potentially harmful pollutants [9]. REE are categorized as heavy metals depending on which these elements possess atomic numbers exceeding 20 [10]. REE exhibit comparable environmental behaviors to heavy metals and can potentially accumulate in plant leaves or be absorbed by plant roots from the soil, thus presenting potential ecological risks [9] and [10]. Generally, REE are regarded as emerging contaminants with low toxicity; however, prolonged accumulation may give rise to certain environmental issues [11].

The contamination of soils by trace elements has evolved into a significant concern in numerous regions across the world [12]. Assessing the human health risks associated with REE should rely on toxicology assessments and population exposure evaluations. Numerous studies have documented the concentrations of REE in the human body [13]. Indeed, reports on population exposure assessments are infrequent. Presently, there exists a dearth of data concerning the ecological risks associated with Rare Earth Elements (REE) and their impact on human health [14].

Pagano et al. reported that REE toxicity could lead to inflammation and significant damage to vital organ tissues [15]. The introduction of REE into the human body through food consumption and skin absorption pathways can result in substantial systemic harm [16]. Conversely, the same study noted that REE also have value in enhancing crop productivity and promoting animal health, as they are employed as feed additives [16].

In a recent study conducted by Ahmed et al. (2023), the distribution of REE in soil samples obtained from gold mining regions in Sudan was examined. Their findings revealed that the REEs in these areas exhibited an enrichment of light REE (LREE) in contrast to heavy REE (HREE). Furthermore, the study focused on assessing the pollution levels of these elements [17]. Brouziotis et al. (2022), was carried out a review study on the REE, they found that REE have the capacity to enter the human body through various pathways. They reported that REE are linked to several diseases, can induce DNA damage and cell death, and exhibit greater toxicity towards cancer cells compared to normal cells [18]. Thus, this paper concentrated on a comprehensive and ongoing investigation into the geochemistry of REE across various locations, aiming to evaluate contamination levels as well as investigate the ecological risks associated with REE in the soils of the gold mining region.

The primary objectives of this paper are determine the concentration of REE in gold mining areas, investigate and analysis of the relationship between gold mining activity and the interaction of these elements in nature, determine the contamination and potential ecological risk of REE, to offer insights into the potential origins of these elements and their correlation with weathering processes, and evaluate both non-carcinogenic and carcinogenic human health risks faced by residents exposed to REE in soils. This assessment will be based on hazard quotients (HQs) and the cancer risk method.

2 Material and Methods

2.1 Sample collection

A sampling plot measuring 1 meter by 1 meter was established for the study. From each plot, five selected soil cores were collected from a depth of 5 to 10 centimeters, which were combined to create a single sample. In the autumn of 2022, a total of 17 soil samples were gathered, as shown in Fig. 1. These samples included 3 from the Haiya area and 2 from Mesherbab, 2 from Halayeb, 2 from Noriaya, these locations located in Rea Sea State, 3 from Sinner, and finally 5 from Blue Nile State. From each sampling site, approximately 1 kilogram of soil was collected using a shovel. The soil samples were initially air-dried at room temperature and subsequently subjected to oven drying at 105°C for a period of 24 hours. After drying, the moisture contents have been determined and then crushed using an agate mortar, subsequently homogenized, passed through a sieve to remove pebbles, and keep it in polyethylene bags until analysis.

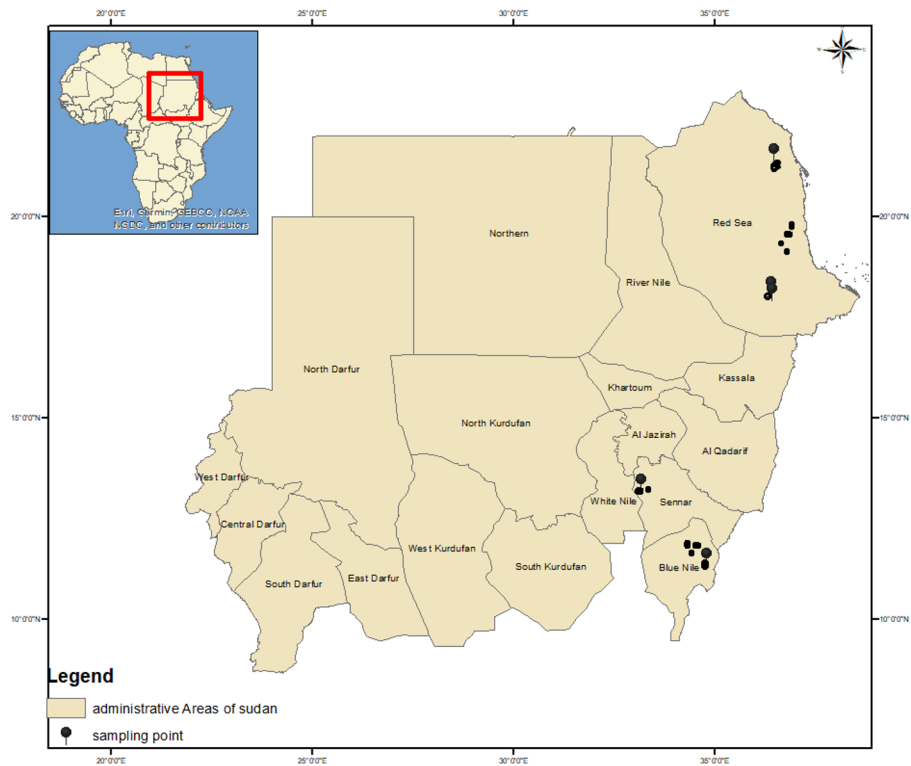


Figure 1. Sudan, sampling point in this study

2.2 Sample analysis

To determine the concentration of the elements, the soil samples were irradiated at the Neutron Activation Analysis Laboratory (NAAL) located within the National Center for Energy, Sciences, and Nuclear Techniques (CNESTEN). This laboratory is directly

linked to the Moroccan Triga Mark II research reactor, which is capable of supplying thermal neutrons, with a flux of $5.10^{12}n/cm^2.s$ at the pneumatic transfer system (PTS) and $2.10^{13}n/cm^2.s$ at the rotary specimen rack (RSR). 100 – 200 mg from each sample and standard reference materials were weighed into a polyethylene rabbit. Both short and long irradiation procedures were conducted (short irradiation to 30 s and long irradiation for 5 h). The flux monitor of 0.01% Au/Al was used to determine the flux variation in the system. For short irradiation; each sample was put alongside a flux monitor (approximately 10 mg), both of sample and flux monitor were put in a polyethylene container and sealed. These containers, known as rabbits, were conveyed to the reactor core using a pneumatic transfer system, enabling irradiation one sample at a time. For long irradiation, the polyethylene rabbits were filled with three soil samples and four flux monitors (sample sandwich between two flux monitors). These rabbit containers were moved to a rotary specimen rack system capable of accommodating up to 40 irradiation positions. Measurements of gamma rays emitted by these nuclides were conducted using a Hyper Pure germanium detector (HP-Ge), to recognize and identify the emitting isotopes and calculate the concentration of the elements of interest. Gamma vision software was used for data acquisition and the concentration of elements were calculated using the k0-IAEA software.

2.3 Chemical Index of Alternation (CIA)

The Chemical Index of Alteration is the commonly used index for assessing weathering profiles. This index is derived by combining the major element oxide chemistry of a sample into a single numerical value. It essentially quantifies the ratio of relatively immobile Al_2O_3 to the more mobile cations Na^+ , K^+ , and Ca^{2+} , expressed as oxides. The geochemical weather indices are calculated by the equation as:

$$CIA = \frac{Al_2O_3}{Al_2O_3 + K_2O + Na_2O + CaO}$$

CIA used to indicate the intensity of the silicate weathering in the soil [19].

2.4 Pollution load index (PLI)

The Pollution Load Index is a recognized method employed to assess the accumulation of REE in samples to determine the overall pollution. These calculations are essential for understanding geological processes, environmental changes. The PLI can be calculated by finding the geometric mean of the CF of each element analyzed as follows:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \dots \times CF_n}$$

CF is the contamination factor of each metal determined as:

$$CF = \frac{C_i}{Cb_i}$$

Where: C_i refers to the concentration of the elements; Cb_i denotes the concentration of the same elements in the background, and n signifies the quantity of analyzed REE. The Upper Continental Crust characterized by Taylor and McLennan [6] was used as background. If the PLI value is greater than 1, it signifies the existence of pollution, whereas a value < 1 indicates no pollution [20].

Table 1. Categorization of the potential ecological risk corresponding to Er and RI.

Er	RI	Ecological risk degree
$Er \leq 20$	$RI \leq 70$	Mild
$20 < Er < 40$	$70 < RI \leq 140$	Moderate
$40 < Er < 80$	$140 < RI \leq 280$	Strength
$80 < Er < 160$	$RI > 280$	Strong
$Er > 160$	—	Very strong

2.5 Ecological and health assessment methods

2.5.1 Risk Factor and Ecological Potential Index (RI)

The ecological risk index in soil samples was calculated using the toxic-response factor for a specific element and the concentrations of these elements within a study area are compared to those in a background or control area [21], One commonly employed method to assess and quantify the level of pollution [22]. Also, it can be used to assess the potential risks to the ecosystem, which is determined by the following equation:

$$Er = \frac{T_r^i \times C_m^i}{C_n^i}$$

Where: Er is the ecological risk factor, T_r^i is the toxic-response factor associated with a specific metal, which reflects the coefficient, C_m^i represents the concentration of the ith metal, while C_n^i denotes the concentration of ith metal in the background (UCC establish by Taylor and McLennan [6]).

In this study, the toxicity coefficients of REE determined by Chen (2020) were used to calculate the potential risk [23], which did not have equal value to the toxicity response coefficients, due to the toxic-response factor of REE did not establish yet. The toxicity coefficient were (La and Ce = 1, Nd = 2, Dy, Sm and Yb = 5, Eu and Tb = 10, Lu = 20). According to [23], Er ranges can be divided into five grades represented in Table 1. Lu has the highest toxicity coefficient in REE, it is represent the mild risk level. The potential ecological risk index (RI) is determined by adding up the ecological risk factors associated with all REE present in soils which is computed as:

$$RI = \sum_{i=1}^n Er$$

Where:

Er represents the ecological risk factor for each REE, and n stands for the number of REE in soil samples. Therefore, Chen reported that, the assessment standards for RI are the maximum allowable value was below 110, it pertains to the classification of a "mild ecological risk" level. In Chen's study from 2020, the combined toxicity response coefficients of the 15 REE pollutants were determined to be 96. In our study, we focused on assessing the ecological risk associated with 9 elements of REE and the summation of the toxicity coefficients was 59. The computation for adjusting to the "mild ecological risk" level was carried out in the following manner: RI (Risk Index) = $110 \times (59/96) \approx 67.6$ and the mild adjusted was taken as the integer 70. The RI's classifications are displayed in Table 1.

2.5.2 Health risk assessment

Human exposure to REE found in soil can potentially pose health risks through three distinct pathways, namely ingestion, inhalation, and dermal contact. The researchers utilized

several indices, including the Average Daily Dose (ADD), Hazard Quotient (HQ), Hazard Index (HI), and Carcinogenic Risk (CR), to estimate the potential non-carcinogenic and carcinogenic health risks associated with exposure to elements through ingestion, inhalation and dermal absorption pathways via soil. The amount of dose received can be determined by the following equations which were adopted by US Environmental Protection Agency [24].

$$ADD_{ing} = \frac{C \times R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} 10^{-6}$$
$$ADD_{inh} = \frac{C \times R_{inh} \times F_{exp} \times T_{exp}}{BEF \times ABW \times T_{avg}}$$
$$ADD_{derm} = \frac{C \times SAF \times A_{skin} \times DAF \times T_{exp}}{ABW \times T_{avg}} 10^{-6}$$

Where:

ADD is average daily dose (mg/kg/day) and C is the concentration of the element (mg/kg). A detailed explanation of the nomenclature and symbols utilized in the equations mentioned above can be found in Table 2. The reference values were taken from [25] and [26], this includes various biometric factors. The product of exposure concentration (C, mg/kg) and the exposure factors, as per the equation mentioned above, is considered as the reasonable maximum exposure [24].

The Hazard of the non-carcinogenic effect were calculated by the following equation:

$$HQ = ADD_i \div RfD_i$$

Where:

RfD is the reference dose (mg/kg/day) and ADD is the average daily for ith route of exposure.

The HQ was used to evaluate the potential for non-carcinogenic effects for each exposure pathway in the analysis. The overall non-carcinogenic risks for each recipient were determined by calculating the HI, this is represented by the summation of HQ for all the various exposure pathways considered in the analysis. It is computed using the following equation:

$$HI = HQ_{ingest} + HQ_{inhal} + HQ_{derm}$$

Where

HQ_{ingest} , HQ_{inhal} , and HQ_{derm} are the hazard quotient for exposure to REE by ingestion, inhalation, and dermal contact, respectively.

This approach operates on the premise that concurrent exposures to Rare Earth Elements (REE) below established thresholds could lead to negative health consequences. The extent of these adverse effects is thought to be directly linked to the cumulative total of the ratios between these sub-threshold exposures and the permissible exposure levels [24]. If the value of HQ and HI <1, it suggests that there is no substantial risk of non-carcinogenic effects. If HQ and HI >1, it implies the likelihood of non-carcinogenic effects occurring, and there is a higher probability of these effects becoming more pronounced as the HQ value increases [27].

The lifetime average daily dose (LADD) was implemented for the evaluation of cancer risk. The calculation involved determining a weighted average for each exposure pathway, utilizing the following equation:

$$LADD = \frac{C \times R_i \times F_{exp} \times T_{exp}}{ABW \times T_{avg}}$$

Where:

R is the intake of contaminated soil. The magnitude of carcinogenic was calculated using equations below [28]

Table 2. Explanation of symbols and the predefined values employed for calculating dose and assessing health risks.

Symbol	Meanings	children	adults	unit
R _{ing}	ingestion rate	200	100	mg/day
R _{inh}	inhalation rate	7.6	20	mg ³ /day
F _{exp}	Exposure frequency	365.25	365.25	day/year
T _{exp}	exposure duration	6	33	year
SA	Skin Area	2600	6030	cm ²
SAF	skin adherence factor	0.2	0.07	mg/cm ² .kg
DAF	dermal absrption factor	0.01	0.01	unit less
PEF	particle emission factor	1.36E+09	1.36E+09	m ³ /kg
ABW	average body weight	17.4	80	kg
T _{aver}	averaging time for non-carcinogenic	T _{exp} × F _{exp}	T _{exp} × F _{exp}	day
T _{aver}	averaging time for carcinogenic	78 × F _{exp}	78 × F _{exp}	day

$$\text{Carcinogenic Risk (CF)}=\sum LADD_i \times S F_i$$

Where

SF is the carcinogenic slope factor and i is the exposure pathway. For regulatory purposes, the acceptable or tolerable risk typically falls within the range of 1.10⁻⁶~1.10⁻⁴ [24]. By definition, the slope factor is the increased risk of cancer per unit of carcinogenic exposure over a lifetime.

3 Results and Discussion

3.1 Concentration of the elements in gold mining area

The concentrations of elements in soil samples collected from gold mining areas were assessed through the utilization of Neutron Activation Analysis. The concentrations of the elements are listed in Table 3.

The precision of the NAA was carried out by the analysis of reference material (SRM2586 NIST) with our sample and the z-score was determined for the elements. It was found to be less than 2 indicating this technique is reliable. The prediction of toxic effects across the entire REE series is often based on the chemical similarity of the Lanthanide group. The total concentrations of REEs have been employed to illustrate variations in REE abundance. The ∑REE concentration in this study were found to be ranged from 10.02 to 141.7 mg/kg. The occurrence of REE with even atomic numbers is more commonly found than those with odd atomic numbers. The LREE represent a range from 77.6% to 95.4%

The value is written as < means that the concentration was less than the limit of detection. of the ∑REE, while, HREE (Eu to Lu) represents less than 25%. Lutetium is a rare element that occurs in small concentrations, typically less than 0.65 mg/kg, making it one of the rarest elements. The variation and the wide range of values of the REE are observed in soil from gold mining, the highest contents can be found in M30, whereas M16 exhibits the lowest REE content. Despite the differences in absolute values, the relationships between the elements follow similar patterns in each location. Ce, La, and Nd comprise the main share of all REE and consist of between 69.2 and 90.7% of total REE. The highest contents were found at Ce followed by La, these findings align with prior reports indicating that Ce, followed by La, is the most abundant REE in the earth’s crust [29]. The elements Eu, Tb, and Lu do not exceed

Table 3. Explanation of symbols and the predefined values employed for calculating dose and assessing health risks.

Element	M02	M04	M06	M08	M10	M12
La	5.90 ± 0.12	6.55 ± 0.03	3.73 ± 0.10	6.56 ± 0.17	6.04 ± 0.13	5.28 ± 0.10
Ce	9.46 ± 0.63	9.67 ± 0.99	8.37 ± 1.00	12.88 ± 0.61	12.50 ± 0.85	3.80 ± 0.61
Nd	2.09 ± 0.08	2.31 ± 0.09	1.02 ± 0.09	12.1 ± 2.38	5.35 ± 0.85	10.65 ± 2.05
Sm	1.35 ± 0.06	1.20 ± 0.07	4.23 ± 0.08	3.28 ± 0.09	3.34 ± 0.13	1.32 ± 0.24
Eu	0.34 ± 0.02	0.42 ± 0.04	0.11 ± 0.01	1.05 ± 0.07	1.01 ± 0.05	0.34 ± 0.03
Tb	0.07 ± 0.02	0.16 ± 0.04	0.06 ± 0.01	0.39 ± 0.05	0.36 ± 0.99	0.06 ± 0.01
Dy	2.3 ± 0.17	2.22 ± 0.20	1.20 ± 0.04	3.40 ± 0.23	<6.80	1.57 ± 0.40
Yb	0.56 ± 0.06	0.58 ± 0.18	0.41 ± 0.09	1.58 ± 0.04	1.71 ± 0.17	0.42 ± 0.11
Lu	0.04 ± 0.01	0.17 ± 0.02	0.39 ± 0.01	0.07 ± 0.01	0.15 ± 0.03	0.23 ± 0.05
Au	12.02±0.22	8.27 ± 0.02	2.35 ± 0.04	3.06 ± 0.05	2.57 ± 0.05	168.3 ± 3.03
ΣREE	22.11	23.27	19.52	41.29	37.25	23.66
CIA	62.15	66.48	55.22	79.99	74.44	70.95

Element	M14	M16	M18	M20	M22	M24
La	12.13 ± 0.22	1.32 ± 0.06	12.63 ± 0.28	11.96 ± 0.25	4.42 ± 0.20	10.45 ± 0.32
Ce	29.53 ± 2.51	4.07 ± 0.36	27.65 ± 0.44	26.36 ± 0.42	13.26 ± 2.11	21.6 ± 0.93
Nd	6.43 ± 1.04	<2.53	13.15 ± 2.11	5.06 ± 0.99	8.99 ± 2.02	19.28 ± 1.50
Sm	23.78 ± 0.12	0.54 ± 0.05	4.04 ± 0.14	3.60 ± 0.16	3.40 ± 0.16	4.60 ± 0.27
Eu	1.72 ± 0.04	0.16 ± 0.02	0.92 ± 0.03	0.75 ± 0.05	0.92 ± 0.05	1.26 ± 0.04
Tb	0.85 ± 0.07	0.01 ± 0.001	0.31 ± 0.04	0.29 ± 0.07	0.44 ± 0.07	0.25 ± 0.04
Dy	3.31 ± 0.54	1.01 ± 0.27	3.40 ± 0.45	2.13 ± 0.44	<6.8	4.6 ± 0.91
Yb	2.99 ± 0.12	0.10 ± 0.002	1.47 ± 0.05	0.67 ± 0.11	0.42 ± 0.11	1.92 ± 0.23
Lu	0.52 ± 0.03	0.03 ± 0.01	0.46 ± 0.11	0.22 ± 0.04	0.29 ± 0.04	0.64 ± 0.14
Au	0.01 ± 0.002	0.35 ± 0.01	<0.37	<0.011	0.04 ± 0.01	0.07 ± 0.02
ΣREE	80.05	9.74	64.02	51.03	38.92	64.59
CIA	65.23	59.59	49.31	55.64	43.94	52.13

Element	M26	M28	M30	M32	M34
La	13.97 ± 0.16	5.95 ± 0.50	33.65 ± 0.37	22.98 ± 0.46	27.12 ± 1.12
Ce	24.4 ± 3.52	11.48 ± 0.62	58.46 ± 5.11	43.51 ± 0.78	48.83 ± 1.32
Nd	23.32 ± 2.11	7.21 ± 0.14	34.85 ± 2.07	42.04 ± 3.69	41.54 ± 5.23
Sm	5.15 ± 0.06	2.28 ± 0.13	7.59 ± 0.12	5.90 ± 0.15	6.64 ± 0.54
Eu	1.41 ± 0.07	0.39 ± 0.02	1.78 ± 0.09	1.39 ± 0.06	1.73 ± 0.06
Tb	0.91 ± 0.17	0.42 ± 0.06	1.38 ± 0.22	0.41 ± 0.07	0.74 ± 0.11
Dy	4.80 ± 1.11	2.82 ± 0.22	2.05 ± 0.18	2.08 ± 0.20	2.67 ± 0.33
Yb	2.01 ± 0.25	1.31 ± 0.14	2.05 ± 0.34	1.51 ± 0.22	1.81 ± 0.15
Lu	0.13 ± 0.03	0.43 ± 0.05	0.32 ± 0.04	0.15 ± 0.04	0.29 ± 0.08
Au	0.02 ± 0.003	0.01 ± 0.001	0.013 ± 0.004	0.012 ± 0.001	0.01 ± 0.003
ΣREE	76.09	32.27	142.12	119.98	131.36
CIA	49.22	47.30	57.15	46.01	46.80

4.82% in total. Concluding from data the REE contents in the gold mining area following order of M16> M06> M02> M04>M12> M10> M22> M08> M20> M24> M18> M26> M14> M32> M34> M30. The highest total contents observed in the clay soil ranged from 120 to 140, less than the content established by [30]. A distinction can be observed in the behavior of REE in soil. LREE are predominantly linked to clayey soils, while HREE are more commonly found in sandy soils. This phenomenon occurs due to the affinity of HREE for refractory minerals, which are highly resistant to weathering and consequently tend to stay within the coarser portion of the soil. The concentration of Au in soil from gold mining areas exhibits substantial levels across the majority of the examined locations. This variation is particularly noticed in the abundance, with observed maximum concentrations reaching significant levels (168 mg/kg).

3.2 Chemical alteration index

In this study, the samples range from an un-weathered CIA value of 43.9 to a maximum of 80 in their highly altered state. This suggests that even in the most weathered samples from gold mining areas, there is still a presence of labile major element cations, indicating an incomplete removal process. The CIA fails to effectively quantify or distinguish elemental changes that take place during the advanced stages of weathering. This limitation arises because the primary process involved in lateritization is desilication, where the removal of silicon (Si) plays a crucial role. Unfortunately, the CIA does not incorporate Si into its calculations, further undermining its accuracy in assessing lateralization processes [31].

3.3 Pollution load index

To assess soil contamination by these elements, the PLI was computed to gauge the extent of pollution; the results were shown in Fig. 2. Based on PLI evaluation, 14 sampling sites, no

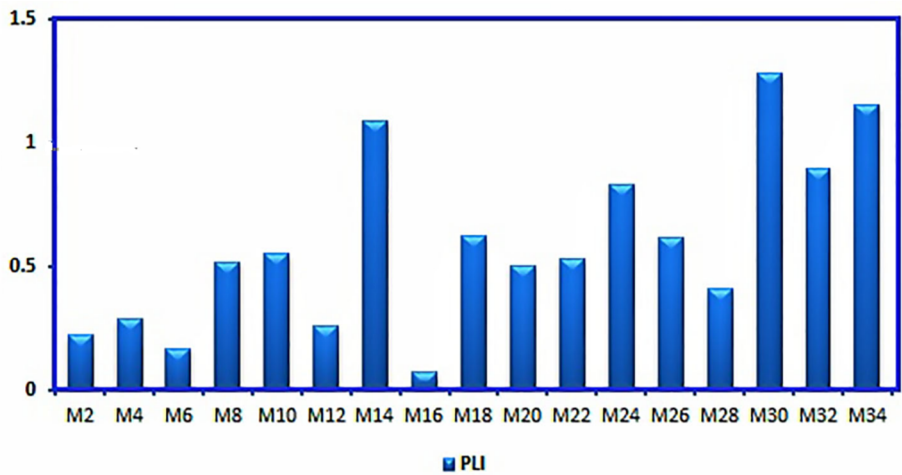


Figure 2. The pollution load indexes for the REE in soil from gold mining regions, Sudan.

contamination was detected (when $PLI > 1$) while 3 sites were in a very low contamination status (when $PLI > 1.5$). According to Muller $PLI \geq 1.5$ indicates that the metal concentration may be entirely from natural weathering processes [32]. PLI values recorded at the

Table 4. Correlation among REE, Au and CIA in soil from gold mining area.

Element	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Au	CIA
La	1										
Ce	0.98	1									
Nd	0.89	0.89	1								
Sm	0.87	0.92	0.88	1							
Eu	0.80	0.84	0.86	0.97	1						
Tb	0.77	0.78	0.69	0.84	0.83	1					
Dy	-0.06	0.04	0.02	0.28	0.34	0.19	1				
Yb	0.59	0.64	0.66	0.85	0.86	0.72	0.35	1			
Lu	0.13	0.20	0.18	0.31	0.31	0.22	0.11	0.41	1		
Au	-0.19	-0.30	-0.12	-0.30	0.21	-0.30	-0.37	-0.29	-0.09	1	
CIA	-0.34	-0.39	-0.37	-0.30	0.43	-0.22	0.87	0.98	-0.36	0.35	1

six stations studied fall less than 0.5 this may reflect the mobilization and loss of the measured elements relative to reference elements [33]. The PLI results helped narrow down the pollution range by reducing the impact of extreme values. These results illustrated that soil from gold mining areas showed free to low-level enrichment based on the category above, but enrichment of elements are natural origin.

3.4 Correlation Coefficient

The Person’s correlation was calculated to evaluate the correlation among the variables. It has a value between –1 and 1. The correlation among the REE with Au and CIA were determined by using the SPSS program and the outcomes were presented in Table 4.

The values that are highlighted in bold indicate a significant correlation between the elements of interest at the alpha = 0.05.

We noticed that the (La, Ce, Nd, Sm, Eu, and Tb) showed a strong positive correlation among them. Dy has a moderate positive correlation with the Tb. Yb recorded a significant correlation with the most of REE except Dy, while Lu was showed a weak correlation with most of REE. LREE were showed negative moderate correlation with CIA, however Yb and Dy were showed a strong positive correlation with CIA. This may indicate the HREE has a correlation with weathering results over LREE, this notice does not agree with the recorded by [34]. However [35], this observation demonstrates that the LREE that accumulates during alkaline phases of weathering can subsequently be leached or released during more acidic phases of weathering.

As for the correlation of REE with Au, it was revealed that a moderate negative correlation with Ce, Sm, and Dy.

3.5 Ecological and health risk assessment

3.5.1 Ecological risk

Ecological risk assessment holds great significance in identifying potential hazards and evaluating the level of risk posed by to both animals and the environment [36]. In this study, the ecological risk and potential ecological risk were determined, and their results are shown in Fig. 3 and Fig. 4 Based on the results in Fig. 3, the average Er values of individual REE in the gold mining area exhibited a decreasing order as follows: Lu> Eu> Sm> Tb> Dy> Yb>

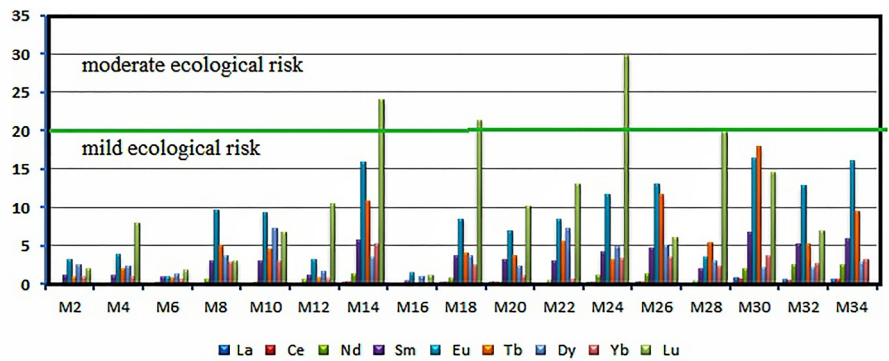


Figure 3. Individual potential ecological risk factor (E_r) of REE.

$Nd > La > Ce$. The E_{r_s} of the REE were below 30 with average values ranging from 0.04 to 29.76. As a result, the findings from this study indicate that there are no apparent ecological risks associated with the presence of elements such as La, Ce, Nd, Sm, Tb, Dy, and Yb in soil from gold mining areas in Sudan. However, the results of Lu showed mild ecological risk in most of the locations except in M14, M18, and M24 revealed moderate ecological risk, which can be attributed to a combination of factors related to natural geology, the extraction of gold; can contribute to the redistribution of lutetium, sandy soils; which often have low cation exchange capacities, may allow for the accumulation of lutetium, and the presence of igneous rocks are a known source of lutetium. As shown in Fig. 4, The RI of the REE was

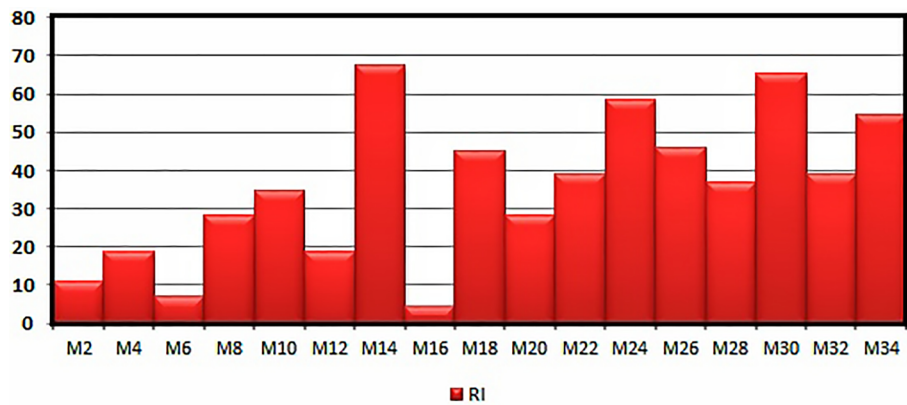


Figure 4. Potential ecological risk index (RI) of 17 soil located in gold mining area in Sudan.

within the range of 4.6 to 67.5. The RI of the REE was descending as following: $M16 < M6 < M2 < M12 < M4 < M28 < M8 < M20 < M10 < M22 < M32 < M18 < M26 < M34 < M24 < M30 < M14$. The RI of the REE were all below 70, which indicated no potential ecological risk in accordance with the classification of RI. The toxicity of HREE is relatively higher than LREE [37] because of the values of the toxicity coefficient of these elements (La, Ce, and Nd) are comparatively low compared to HREE, and the abundance of these elements in our soils ranging from 64.1 to 90.5% from the total REE, this might be the reason behind the lower toxicity of REE [28]. The toxicity coefficients of Lu, Eu, and Tb are greater than

Table 5. Average daily dose (µg/ kg/ day) of rare earth oxides via exposure to soil in gold mining area.

Element	Children		adult	
	range	average	range	average
La	1.78E-01_4.45E-01	1.51E-01	1.94E-03_4.93E-2	1.64E-02
Ce	5.11E-02_7.87E-01	2.89E-01	5.56E-03_8.56E-02	3.14E-02
Nd	2.80E-02_5.64E-01	2.04E-01	3.05E-03_6.13E-02	2.22E-02
Sm	6.77E-03_9.54E-02	4.56E-02	7.36E-04_1.04E-02	4.96E-03
Eu	1.45E-03_2.37E-02	1.23E-02	1.58E-04_2.57E-03	1.33E-03
Tb	4.00E-05_1.83E-02	5.51E-03	4.35E-06_1.99E-03	6.00E-04
Dy	1.32E-02_3.91E-02	4.01E-02	1.44E-03_9.76E-03	4.36E-03
Yb	4.79E-03_3.91E-02	1.68E-02	5.21E-04_1.82E-03	1.82E-03
Lu	3.19E-04_8.42E-03	2.94E-03	3.47E-05_9.16E-04	3.20E-04
ΣREE	1.15E-01_1.63E+00	6.56E-01	1.25E-02_1.77E-01	7.14E-02

those of heavy metal elements like Pb, Co, and Cu, but their content in our soil samples is relatively low. Also, their market demand is limited due to their low natural abundance in the environment [39] and their toxicity has not emerged. Lu caused ecological risk ranging from 10.9 to 55.66% of the total risks of all the REE analyzed.

3.5.2 Health risk assessment

Daily intake dose

This study focused on the health risk assessment of REE in soil from gold-mining areas. The daily intakes of REE-oxide were estimated for children and adults and the results are shown in Table 5.

The primary exposure route for metals entering the human body is typically through the ingestion of soil particles [40]. For children and adults, the maximum estimated daily intakes of REE-oxides were revealed in Ce ranging from (0.05 to 0.79 with an average of 0.29 µg/kg/day for children and from 0.01 to 0.09 with an average of 0.03 µg/kg/day for adults) followed by the La. Lu showed lower daily intakes ranging from (3.2E-4 to 8.4E-3 µg with an average 3E-3 µg/kg/day for children and from 3.5E-5 to 9.2E-4 with an average 3.2E-4 µg/kg/day for adults). The estimated daily intakes for the sum REE-oxides were found to be substantially the same and had little variation, ranging from 0.01 to 0.18 µg/kg/day for adults and 0.12 to 1.63 µg/kg/day for children. For both children and adults, were significantly lower than the estimated daily intake (70 µg/ kg/day) established by Zhuo [41]. According to these findings, the potential harm from Rare Earth Element (REE) exposure to adults and children through the consumption of these soils appears to be negligible. However, it may be prudent to focus attention on the effects of continuous exposure to low levels of REEs on human health, particularly in the case of children.

Carcinogenic and non-carcinogenic risk

Non-carcinogenic and carcinogenic effects of REE in gold mining areas on human beings were computed and shown in Fig. 5 and Table 6. The hazard index values of REE were calculated using respective a reference dose value (0.02 mg/kg/day) for LREE and REE, and (0.002mg/kg/day) for HREE [42]. In assessing the toxicity of REE through the inhalation route, reference doses are considered. The assumption here is that after inhalation, the absorption of toxicants bound to particles would lead to similar health effects as if the particles had been ingested [43]. However, it's worth noting that the slope factor for oral REE up-

take hasn't been published. In place of REE, the toxicological profile of Yttrium (Y) is used because its chemical and toxicological characteristics are similar to those of REE [44].

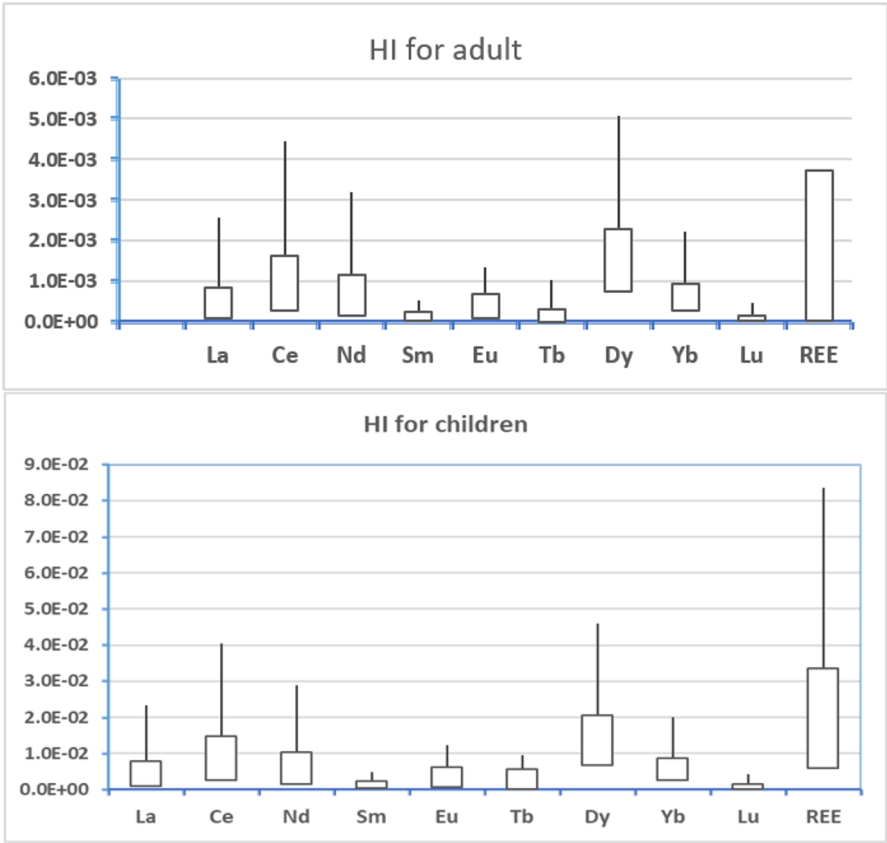


Figure 5. HI for children and adult cause by REE in gold mining areas.

The values of hazard quotient (HQ) for three pathways were computed and shown in Fig. 5, the occurrence of non-carcinogenic metals and REE in the children and adults among the different exposure routes are consequence $HQ_{ingest} > HQ_{derm} > HQ_{inhal}$. Non-carcinogenic effects for REE can observe a maximum dose of children and a minimum dose of adults.

HI values were found to be $\ll 1$ for the REE studied, indicating the absence of non-carcinogenic risks to adults and children and the soil is consider safe [26].

The total Hazard Index (HI) values for children were found to be nine times higher than those for adults. Consequently, we can conclude that children are more susceptible to the adverse health effects of trace elements present in soils. This study further highlighted that in gold mining areas, children face a higher risk from ingesting soil compared to adults. This can be attributed to the fact that children tend to ingest larger amounts of soil, often due to their hand-to-mouth activities while playing on the ground [45]. Additionally, children are considered the most sensitive subgroup [43] in terms of health risks. As a result, exposure to children could potentially pose greater health risks. It was also found that the ingestion

Table 6. Lifetime average daily dose (mg /kg/day) and cancer risk for $\sum$ REE and in gold mining areas.

exposure pathway		ingestion		inhalation		dermal		Total Cancer risk
		Cancer dose	cancer risk	Cancer dose	cancer risk	Cancer dose	cancer risk	
Child	Min	8.58E-06	3.52E-19	2.4E-10	1.32E-21	2.23E-07	0	3.54E-19
	Max	1.25E-04	5.14E-18	3.5E-09	1.93E-20	3.26E-06	0	5.16E-18
	average	5.05E-05	2.07E-18	1.41E-09	7.76E-21	1.31E-06	0	2.08E-18
adult	Min	5.13E-06	2.11E-19	7.55E-10	4.15E-21	9.96E-07	0	2.15E-19
	Max	7.49E-05	3.07E-18	1.1E-08	6.06E-20	1.45E-05	0	3.14E-18
	average	3.02E-05	1.24E-18	4.44E-09	2.44E-20	5.86E-06	0	1.26E-18

pathway contributed more significantly to the average dose compared to other exposure pathways.

Numerous studies have reported elevated Hazard Index (HI) values for children [12] and [46]. Jiang and et al. were determined the HI in soil from Province, China [47]; they were HI > 1 for adults and children. Our results were agreed with that obtained by Sun [45], who was studied hazard index cause from street dust a municipal industrial base in central China and they were found that the HI values < 1 for adults and children.

Carcinogenic risk levels for ingestion and inhalation pathways from $\sum$ REE were computed. From Table 6, in our observations, the level of cancer risk is found to be within a range that falls below the established threshold (10^{-4} – 10^{-6}), this level of risk is typically considered acceptable or tolerable according to environmental regulatory agencies, therefore, the health hazard of REE due to soil exposure in gold mining areas was low or indicating that the risk results from REE were acceptable. The findings indicate that cancer risks for children were consistently higher than those for adults, underscoring that children are considerably more vulnerable to the adverse effects of REE in soil. When assessing cancer risks through pathways such as ingestion, dermal contact, and inhalation, the order of risk levels followed this pattern: CR_{inhal} < CR_{ingest} for REE. Furthermore, REE was the primary contributor to cancer risks through the ingestion pathway, with the highest contribution percentages being 99.6% for children and 98% for adults.

4 Conclusion

In conclusion, this study utilized neutron activation analysis (NAA) to assess the potential ecological and health risks associated with rare earth elements (REE) in soil samples collected from gold mining areas. The results of the study indicated that the soils in the gold mining areas were free from contamination, as indicated by the Pollution Load Index (PLI). The correlation among the elements were carried out by using SPSS program, the results were showed that LREE has very strong correlation among each other, while Eu, Tb and Yb were recorded very strong positive correlation among them and also with LREE. The correlation REE with Au were weak to moderate negatively. The ecological risk assessment using the Potential Ecological Risk Index revealed that the soil samples from the gold mining areas generally have a low ecological risk, with the exception of moderate risk associated with Lu in three sample sites.

Furthermore, the health risk assessment conducted for both non-carcinogenic and carcinogenic risks indicated that the hazard quotient values for REE in the soil samples, through

ingestion, dermal contact, and inhalation pathways, fall in the impressible range. This suggests that there were no significant non-carcinogenic health risks to the inhabitants, for both adults and children; however the children affect more than adults. The study also identified gold mining and smelting activities, along with the excessive application of fertilizers as the main anthropogenic sources of trace metal releases. Overall, this research provides valuable insights into the sources, ecological risk levels, and health risk assessment of REE in surface sediments within a gold mining area. Additionally, it highlights the effectiveness of NAA as a tool for such assessments. These findings are crucial for informing and implementing measures to mitigate the potential ecological and health risks associated with gold mining activities.

Acknowledgement: The authors most grateful to the International Atomic Energy Agency (IAEA) for funding this work through Ph D Sandwich Program from the AFRA

References

- [1] R. Mazurek , Kowalska J, Gasiorek M, Zadrozny P, Jozefowska A, Zaleski T, Kepka W, Tymczuk M, Orlowska K, Chem. 168 (2017).
- [2] Y. Huang, Q. Chen, M. Deng, J. Japenga, T. Li, X. Yang, Z. He, J. Environ. Manag. 207 (2018).
- [3] R. Dong, Z. Jia, S. Li, Process Saf. Environ 113 (2018).
- [4] X. Ping, D. C. Cheng, A. Peng, Environ Sciand Poll Res. 9 (2002).
- [5] X. W Lu, L. J. Wang, K. Lei, J. Huang, Y. X. Zhai, J. Hazard Mat, 161 (2009).
- [6] S. R. Taylor, S. M. McLennan Oxford: Blackwell Scientific publications 312 (1985).
- [7] C. Laveuf, S. Cornu, F. Juillot, C. R. Geosci. 340, 8 (2008).
- [8] M. D. S. Elias, S. Ibrahim, K. Samuding, N. Kantasamy, S. Ab Rahman, A. Hashim, A. Rad. and Isot. 151 (2019).
- [9] W. Gwenzi, L. Mangori, C. Danha, et al., Sci Tot. Environ, 636 (2018)
- [10] E. Kothe, A. Varma, Springer, Berlin (2012).
- [11] Y. Chernysh, O. Yakhnenko, V. Chubur, H. Roubík, Appl. Sci. 11, 4 (2021).
- [12] Z. Jia, S. Li, W. Li, Sci. Rep. 8 (2018).
- [13] C. Chen, P. Zhang, Z. Chai, Anal. Chim. Acta. 439 (2001).
- [14] P. Arvela, Prog. Pharmacol. 2 (1979).
- [15] G. Pagano, F. Aliberti, M. Guida, R. Oral, A. Siciliano, M. Trifuoggi, F. Tommasi, Environ. Res 142 (2015).
- [16] B. H. Huang, Y. D. Zou, S. D. Bi, et al., Acta. Sci. Circum 29, 9 (2009).
- [17] M. E. Ahmed, H. Bounouira, M. A. Abbo et al., J Radioanal Nucl Chem 332 (2023).
- [18] A. A. Brouziotis, A. Giarra, G. Libralato, G. Pagano, M. Guida, M. Trifuoggi, Front. Environ. Sci. 10 (2022).
- [19] H. Nesbitt, G. Young, Nature. 299 (1982).
- [20] M. Zari, R. Smith, C. Wright, R. Ferrari, Norfolk, UK (2002).
- [21] Hakanson L, Water Res 14, 8 (1980).
- [22] Z. Q. Xu, S. J. Ni, X. G. Tuo, et al, Envir Sci Tech 31, 2 (2008).
- [23] H. Chen, Z. Chen, Z. Chen, X. Ou, X. Chen, Bull Environ Contam Toxicol 104 (2020).
- [24] US EPA, Human Health Evaluation Manual, EPA/540/1- 89/002. Office of Soild Waste and Emrgency Response 1 (1989).
- [25] [ATSDR] Agency for Toxic Substances and Disease Registry, Public Heal Ser. (2018).
- [26] Y. Faiz, N. Siddioue, M. Tufail, J. Envir. Sci and Heal, Part A 47 (2012).
- [27] US EPA, OSWER 9355.4-24. Office of Soild Waste and Emergency Response (2001).

- [28] US EPA, OSWER 9285.7-80 (2007).
- [29] Z. Hu et al., *Sci Plant Anal.* 37 (2006).
- [30] M. Scott, C. Verb, A. Falcon, J. Poston, M. McKoy, AGU Fall Meeting Abstracts, dec, PP13C-1786 (2017).
- [31] M. G. Babechuk, M. Widdowson, B. S. Kamber B, *Chem. Geo.* 363 (2014).
- [32] G. Muller, *Geol. J.* 2 (1969).
- [33] J. G. Zhang, C. L. Lui, *Coast. Shelf.* 54, 6 (2002).
- [34] B. Boulangé, F. Colin, *Appl. Geochem.* 9 (1994).
- [35] C. Huang, Z. Gong, *J. Rare Ear.* 19, 1 (2001).
- [36] F.O. Ohiagu, K.C. Lele, P.C. Chikezie, A.W. Verla, C.E. Enyoh, *Chem. Afr.* 4 (2020).
- [37] S. L. Jin, Y. Z. Huang, *As. J. Ecotoxicol.* 9, 2 (2014).
- [38] Z. Y. Chen, *Rur. Eco-Environ.* 20, 4 (2004).
- [39] K. M. Goodenough, F. Wall, D. Merriman, *Nat Res Res.* 27, 2 (2018).
- [40] L. Ferreira-Baptista, E. De Miguel, *Atm. Enviro.* 39 (2005).
- [41] W. F. Zhu, S. Q. Xu, P. P. Shao, H. Zhang, J. Feng, D. L. Wu, et al., *Environ. Sci. Tech.* 17 (1997). (In Chinese).
- [42] P. Damian, Union Blvd., Lakewood, Color. (2014).
- [43] N. Zheng, J. S. Liu, Q. C. Wang, Z. Z. Liang, *Sci Tot. Environ.* 408 (2010).
- [44] G. Sun, Z. Li, T. Liu, J. Chen, T. Wu, X. Feng, *Environ. Geochem. Heal.* 39, 6 (2017).
- [45] Z. Cao, Q. Chen, X. Wang, Y. Zhang, S. Wang, M. Wang, et al, *Envir. Geo. Heal.* 40 (2018).
- [46] J. Wu, J. Lu, L. Li, X. Min, Y. Luo, *Chemo.* 201 (2018).
- [47] Jiang, S. Chao, J. Liu, Y. Yang, Y. Chen, A. Zhang, H. Cao, *Chem.* 168 (2017).