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Impact of Rare Earth Mining and Processing on Soil and Water Environment at Chavara, Kollam, Kerala: A case study

Tekedil Zeenat Humsa*, R. K. Srivastava

Department of Civil Engineering, MNNIT Allahabad, PO 211004, UP, India

Abstract

The mining and processing of rare earth minerals along the coastline of Chavara, Kollam, Kerala has been a significant step in self reliance for the country in terms of being a strategically important industry but at the same time the grave environmental consequences because of the improper management of the industrial waste from the titanium dioxide (TiO₂) pigment producing industry is a cause of concern. This has led to the geo-environmental degradation of surrounding area which is also a high background radiation area. This study attempts to compare the geochemical variation in the soil due to contamination and the extent of water pollution from different water sources in the study area. Analysis of the surface soil (0-30cm) from contaminated land and inhabited land (supposedly less contaminated) provide a measure of the total concentrations of the elements present in the soil. XRF results indicate the increase in the concentrations of toxic heavy metals (e.g. Fe, Cr, V, Ni, Cu, Zn, Pb, Sr etc.) while concentrations of essential elements (e.g. K, Ca, Si, Ti, Zr) decreased due to contamination. Elements Mg, Ag, Au, Hf, Te, Nd, Yb, Ga present in inhabited area soil were found to be absent in contaminated soil. Co, Sn, W, Se, Br, Sm, Tb, Dy were detected only in contaminated soil. SEM analysis of the soil from residential area showed distinct mineral assemblage and that of contaminated soil, the signs of chemical weathering. The observed health problems in the local area indicate urgent need for health risk assessment and subsequent remediation of contaminated soil.

Keywords: Contaminated soil; industrial waste; SEM; TiO₂ industry; XRF.

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1. Introduction

Indiscrete disposal of industrial waste leads to several geo-environmental disasters on land and it has huge socio-economic effects on the population residing in the impacted area especially in terms of

* Corresponding author. Tel.: +91 8948313617
E-mail address: dearsist@yahoo.co.in

livelihood and health. Once this happens, it becomes a news item and comes into focus for geo-environmental evaluation. Mining and processing of heavy and rare earth minerals inevitably involves distress of the land environment, the magnitude and intensity of which depends on the type of chemicals and processes used, the efforts taken in the management of waste as well as on environmental fragility of location. It also involves extreme disturbance to local residents by increased diseases, water pollution and destruction of farmland thereby violating the rights of local communities¹. Some of the contaminants are even classified as human carcinogens by international and federal health agencies².



Fig. 1. Vegetation and soil destruction due to acidic discharge³

Fig. 2. Skin problems to residents³

The occurrence of heavy mineral rich placer deposits along Chavara-Neendakara coastline of Kollam, Kerala are being mined since 1922. The introduction of titanium dioxide (TiO_2) pigment producing plant in 1984 made the industry strategically important. But the mining activities along with processing of heavy minerals and production of TiO_2 pigment resulted in the release of a number of contaminants specific to the industry. These contaminants combined with the accidental leakage of tickle, raw material for TiO_2 from Kerala Minerals and Metals Ltd. (KMML) has led to the geo-environmental degradation of surrounding area of industry within a radius of 16 km square. Severe resentments by the local population & environmentalists have drawn attention of media and public in general^{3, 4}. The people living in the area had been experiencing air, land and water pollution problems since last 10 years. The signs of land contamination are visible in the form of complete destruction of vegetation (Figure 1). The wells have become useless. The people are warned not to use the water for drinking, bathing or even for toilets⁵. In addition to the land and water pollution, there are frequent gas leaks that results in residents being hospitalized⁶. Incidence of cancer is prevalent in the area and it is among the highest in India and those residing near the industrial area are suffering from diseases such as bronchitis, asthma, cancer and skin ailments⁵ (Figure 2). The air and water quality assessments of this area had revealed the pollution^{7, 8}. In addition, the area falls into a high background radiation area⁹. This study aims to assess the soil quality and update the water quality parameters of various water sources in the area.

The wastes produced from the industry are iron oxide sludge and a slurry containing chlorides of metals in the liquid state and un-reacted ore and coke in the solid state which are then pumped and stored in large settling ponds¹⁰. The crack in this pond has led to leakage of iron oxide sludge. This combined with unintentional release of Tickle (titanium tetra chloride: TiCl_4) kept in the storage vessels led to the rapid spreading of the acidic effluent to the nearby wells and groundwater and also turning existing

moderately acidic sandy soil¹¹ (pH ranging from 4.5 to 6.0) into extremely acidic soil changing the physico-chemical and biological properties of the same.

Soils are essential for food production, storage and filtration of water and nurturing multitudes of species by providing a habitat. Therefore, environmental upkeep of soils is fundamental¹. It is very important to understand the physical, chemical and biological changes that occurred in the natural soil due to contamination as each contaminant interacts with soil in its own way¹². The occurrence and geographical distribution of certain diseases could be correlated with the presence of toxic elements in the geologic environment¹³. Heavy metals are classified among the most dangerous groups of environmental pollutants due to their toxicity and persistence in the environment¹⁴. High rainfall areas have low pH¹⁵. The processes involved in heavy metals partitioning between solid and liquid phases are dependent on the pH of the soil suspensions. At acidic pH values, heavy metals become mobile and adsorption onto soil particles becomes less effective¹⁶. The mobile heavy metals hence can easily reach the ground and surface water and contaminate them. In view of this, it becomes imperative to continually assess and monitor the fate and transfer of metals species in soils for the evaluation of extent of contamination and health risk assessment of nearby population.

2. Material and methods

2.1. Study area

The study area (Figure 3) is the inhabited area surrounding KMML, located at Sankaramangalam in Chavara taluk (Panmana Panchayat), Kollam (Quilon) district, Kerala State, South India, on NH-47, at a distance of about 32km from the Kollam Central Railway Station and about 5km from the Neendakara Port in the southwest direction. The geographical coordinates are extending between Latitude $8^{\circ} 58'$ to $9^{\circ} 1'$ North and Longitude $76^{\circ} 30'$ to $76^{\circ} 33'$ East. The affected wards of the Panmana panchayat are highlighted in figure 3.

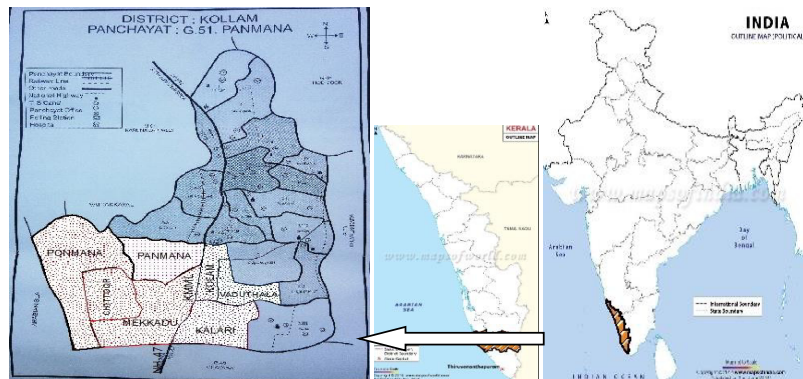


Fig. 3. Study area

2.2. Geology & climate

The area experiences an oppressive summer and plentiful seasonal rainfall. The hot season lasting from March to May is followed by the southwest monsoon from June to September. The northeast monsoon occurs from October to November. The rest of the year is generally dry. The climate is humid tropical with mean annual temperature 27.6°C and average annual rainfall of 1936 mm. Because of high rainfall and temperature conditions which are conducive to rapid removal of bases from the soil, the soils are predominantly acidic in nature and belong to Neendakara series which is a member of coated, isohyperthermic, aquic Quartzipsamments. Neendakara soils have very dark brown to dark grayish brown, neutral, sand to loamy sand A horizon and dark grey to reddish grey, neutral, sand C horizons. These soils are formed on coastal alluvium and occur on level to gently sloping lands of Kollam district lying at an elevation of less than 20m from mean sea level (lowland region). The 0-30 cm depth pedon description is very dark brown sand; weak fine granular; loose, non sticky and non plastic; many fine roots; many medium interstitial pores; rare earth minerals present; rapid permeability; pH 7.1¹¹.

2.3. Soil sample collection

After a thorough reconnaissance of the affected area, representative surface soil samples were collected from the inhabited area as a control point (depth 0-30cm) and designated as sample I. Similarly sample from contaminated area was collected (Figure 4, 5) and designated as sample II. The sampling was done in pre-monsoon season (May 2014). Both the samples were collected with plastic spatula in labelled self locking polythene bags and oven dried in laboratory at 105°C.



Fig. 4. Affected coconut tree



Fig. 5. Contaminated land

2.4. Water sample collection

Water samples were collected from five different sources from the study area, in the month of October (monsoon season). Sample no.1 is collected from the open well in the study area. Residents do not use the well water in this area for any domestic use. Paddy field water i.e. sample no. 2 is collected and analysed to check the level of contaminants (Figure 6). The sample no.3 is the water or discharge from KMML which is discharged into TS canal. Sample no.4 is collected from Thiruvananthapuram-Shoranur canal popularly known as TS canal which was once used as a waterway and even for drinking and bathing (Figure 7). The supply water i.e. sample no. 5 is the water supplied to the residents by KMML.



Fig. 6. Paddy field water



Fig. 7. T. S. Canal

2.5. Methodology used

- Laboratory tests for determination of specific gravity and grain size analysis for classifying soil were performed as per IS: 2720 part 3/section 1-1980 and IS: 2720 part 4-1985 respectively¹⁸.
- Soil pH was determined on the site using pH paper and in laboratory using pH meter.
- To study the surface morphology and contamination effects on elements, scanning electron microscopy (SEM) test was done using ZEISS EVO series Scanning Electron Microscope Model EVO15. Gold-Palladium sputter coating unit was used for sample coating.
- X-ray fluorescence (XRF) technique was used for the determination of elemental concentrations of both the soil samples using Thermo scientific, ARL OPTIM X, X-ray Analyzer.
- Physico-chemical parameters of water like pH, conductivity, total dissolved solids (TDS), turbidity, total hardness, alkalinity, acidity, sodium, potassium, chloride, iron, sulphate, nitrate etc. were determined as per standard procedures¹⁹.

2.6. Data analysis

2.6.1. Soil contamination assessment using single pollution indices

Various researchers have assessed the soil quality from the heavy metal concentration in different ways like pollution index, principle component analysis, gray correlation, fuzzy computing etc. Pollution index is an approximate method from which an idea of extent of pollution due to the presence of heavy metals in the soil could be made¹⁷. In the present paper, as a large number of contaminants are present both single pollution indices and integrated pollution indices are calculated and the contamination classes suggested by Gong (table 1) are used²⁰.

Considering the natural geochemical variability of soils particularly in this case, in view of the peculiar heavy mineral rich deposits, it is better to compare the metal concentrations in inhabited area and contaminated soils as they are texturally and mineralogically similar or identical²¹ and hence the

heavy metal concentration of the inhabited area is used as background or reference values for calculation. Single pollution indices like contamination factor, enrichment factor and geo-accumulation index are the measures of the contamination caused by individual elements. Integrated pollution indices on the other hand give the overall environmental quality due to the presence of a number of elements.

Table 1. Contamination classes based on single indices

Indices	1-unpolluted	2-low polluted	3-moderately polluted	4-strongly polluted	5- extremely polluted
Cf	< 2	2-4	4-16	16-32	> 32
EF	< 2	2-4	4-16	16-32	> 32
I _{geo}	< 0.42	0.42-1.42	1.42-3.42	3.42-4.42	> 4.42

a. Contamination factor

A contamination factor suggested by Hakanson²² and modified by Cabrera²³ is as follows, equation (1)

$$C_f = C_i / C_{bi} \quad (1)$$

Where C_i and C_{bi} are the metal content in the contaminated and background soil of metal i respectively.

b. Enrichment factor

An enrichment factor developed by Zoller et al.²⁴ and further used by Salomons and Forstner²⁵, Reimann and de Caritat²⁶ is as follows, equation (2)

$$EF = (C_i / C_{ref})_{\text{contaminated soil}} / (C_i / C_{ref})_{\text{background soil}} \quad (2)$$

Where $(C_i / C_{ref})_{\text{contaminated soil}}$ and $(C_i / C_{ref})_{\text{background soil}}$ are the concentration ratios of element i to the reference element in the contaminated and background soil respectively. Generally, relatively immobile elements like Fe, Si, Al, Li, Ti etc. which are not affected by the anthropogenic pollution in the background soil are taken as reference element. In the present study, Al is the only element which is not showing great variations in concentrations in contaminated soil from the background soil and hence it is taken as the reference element for enrichment factor calculation.

c. Geo-accumulation index

Geo-accumulation index proposed by Muller²⁷ is as follows, equation (3)

$$I_{geo} = \log_2 (C_i / (1.5 * C_{bi})) \quad (3)$$

Where C_i and C_{bi} are the metal content in contaminated soil and in the background soil of metal i respectively. The factor 1.5 is used to account for the variations in the background values due to lithological variations or anthropogenic influences.

2.6.2. Soil contamination assessment using integrated pollution indices

The integrated pollution indices are used to calculate the extent of contamination due to more than one contamination. In this study, three indices namely degree of contamination, average pollution index and pollution load index are calculated.

a. Degree of contamination

Degree of contamination defined by Hakanson²², Kwon and Lee²⁸ is the sum of the contamination factors of all the contaminants present in the soil and is given by equation (4)

$$Cd = \sum_{i=1}^m C_f \quad (4)$$

Where C_f is the contamination factor for metal i and m is the number of heavy metals present in the soil. To assess the extent of pollution, the following classes have been made. $C_d < m$, low degree of contamination; $m \leq C_d \leq 2m$, moderate degree of contamination; $2m \leq C_d < 4m$, considerable degree of contamination and $C_d > 4m$, very high degree of contamination¹⁶.

b. Average pollution index

Average pollution index developed by Bhattacharya²⁹, is given by equation (5)

$$PI_{avg} = \left(\frac{1}{m}\right) \sum_{i=1}^m P_i \tag{5}$$

Where P_i is the single pollution index of metal i and m is the number of heavy metals present in the soil. A $PI_{avg} > 1$ indicates low quality of soil because of contamination.

c. Pollution load index

Pollution load index used by Liu³⁰, is a simple and comparative method for assessment of heavy metal pollution and is given by equation (6)

$$PLI = (CF_1 * CF_2 * CF_3 * \dots * CF_m)^{(1/m)} \tag{6}$$

$PLI \leq 1$ indicates heavy metal concentrations close to background values and hence no pollution. $PLI > 1$ indicate pollution²².

2.6.3 water quality assessment using water quality index

The water quality index developed by Horton³¹ and later modified and used by various researchers³² to express the quality of water resources is applied and used to compare the water qualities from different sources of water in the study area. One such method suggested by Tiwari and Mishra³³, is used here and is given by equation (7)

$$WQI = antilog_{10} \left(\sum_{i=1}^n W_i * \log Q_i \right) \tag{7}$$

Where W_i i.e. unit weight or the weighting factor for the selected parameter i and given by equation (8)

$$W_i = \frac{K}{S_n} \tag{8}$$

Where K is the constant of proportionality given by equation (9)

$$K = 1 / \sum_{i=1}^n \left(\frac{1}{S_n} \right) \tag{9}$$

And S_n is the drinking water quality standards prescribed by World Health Organization (WHO)³⁴ or Indian Council of Medical Research (ICMR)³⁵ for n^{th} parameter. In the equation (7), Q_i is the quality rating given by equation (10)

$$Q_n = 100 * \frac{(V_{actual} - V_{ideal})}{(V_{standard} - V_{ideal})} \tag{10}$$

Where V_{actual} = Value of water quality parameter obtained from the laboratory analysis
 $V_{standard}$ = Value of water quality standards obtained from the standard tables i.e. S_n
 V_{ideal} = 0 for all parameters except for pH
 V_{ideal} = 7 for pH

After taking into account the various physico-chemical parameters in assessing the water quality, the status of water quality is decided based on the water quality index. The following categories are made³⁶. $WQI < 50$: fit for drinking; $50 \leq WQI < 80$: moderately contaminated; $WQI > 80$: excessively contaminated and $WQI > 100$: severely contaminated.

3. Results and discussion

3.1. Physical properties of soil

The colour is observed to have changed from grey black (Sample I) to brownish red (Sample II) (Refer figure 8). The contaminated soil gives a very distinct, pungent odour while mixing with water and very fine, heavy dust spreads in the area while sieving. The specific gravity of sample I was found to be 2.88 and that of sample II was 2.73. The grain size analysis revealed that contamination decreased the sand fraction i.e. 4.25mm to 75 μ of sample I from 93.76% to 76.96% in contaminated soil and increased the silt fraction i.e. from 75 μ to 2 μ from 5.86% to 21.05% in contaminated soil. As per Indian Standard Classification system, the sample I was poorly graded sand i.e. SP and contaminated soil was SM i.e. silty sand. Both soils had majority medium- fine sand fraction (Table 2). The average pH of the sample I & II on site was 6 and 2 respectively and in the laboratory was 5.87 and 2.55 respectively.

Table 2. Results of sieve analysis

Description	Sample I	Sample II
Gravel fraction	0.38%	0.04%
Sand fraction	93.76%	76.96%
Silt fraction	5.86%	21.05%
Clay fraction	0%	1.95%



Fig. 8. Contaminated soil & sample I in tray

3.2. Sem analysis

SEM image of sample I (Figure 9) and sample II (Figure 10) at 10 kv under 1000 magnification is given below. In the SEM image of sample I the shapes of different elements are distinct, their boundaries are clearly identifiable and surface morphology is visible. However for sample II, distinct mineralogical composition could not be observed indicating signs of weathering.

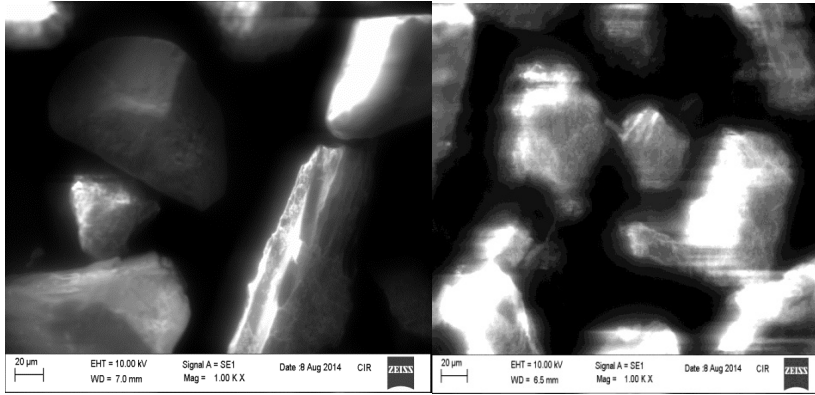


Fig. 9. SEM image of sample I

Fig. 10. SEM image of sample II

3.3. Xrf analysis

The result of XRF analysis for both sample I and sample II has been presented in table 3.

Table 3. Elemental concentrations (mg/kg) in soil samples

Element	I	II	Element	I	II	Element	I	II	Element	I	II
Mg	1610	-	Cr	185	386	Rb	21	35	Hf	304	-
Al	62100	64900	Mn	225	218	Sr	138	524	W	-	252
Si	360000	198000	Fe	12600	181000	Y	140	66	Au	60	-
P _x	7670	12200	Co	-	142	Zr	21100	6250	Pb	122	562
S _x	7220	36300	Ni	134	262	Nb	362	101	Nd	102	-
Cl	2050	53400	Cu	191	592	Mo	160	45	Sm	-	420
K	248	170	Zn	205	327	Ag	82	-	Tb	-	423
Ca	378	228	Ga	28	-	Sn	-	191	Dy	-	400
Ti	12500	4250	Se	-	46	Te	158	-	Yb	105	-
V	175	427	Br	-	44	Ba	400	340	Th	924	220

The result of XRF analysis has been separated and presented in tables 4 to 7 based on their presence and concentrations in sample I and II.

Table 4. Elemental concentrations which increased in sample II (mg/kg)

Elements	Fe	Al	Cl	Cu	Ni	Zn	Pb	Sx	Px	V	Cr	Rb	Sr
Sample I	12600	62100	2050	191	134	205	122	7220	7670	175	185	21	138
Sample II	181000	64900	53400	592	262	327	562	36300	12200	427	386	35	524

From table 4, it is observed that the amount of major elements like iron (Fe) and aluminium (Al) increased in sample II, but the increase of Fe was very high. (Fe) is the fourth most abundant element in the Earth's crust comprising nearly 4.3% by mass³⁷. Iron concentrations of a soil are region specific and can vary considerably locally due to soil types and presence of other sources. Sandy soils have the lowest overall iron content³⁸. In the present study, the iron content of the sample I is found to be 12,600 mg/kg which is very low when compared with the 181,000 mg/kg of the contaminated soil, clearly indicating the anthropogenic pollution by the industry. On acid soils, where Fe is most available, Fe²⁺ can become

toxic to plants. The aluminium content for sample I and sample II are 6.21% and 6.49% respectively which is even though greater than the average values for coastal and eustarine sediments in India³⁹ but are in line with the world average soil or rock concentration values. The accumulation of iron and aluminum gives the soil a red colour. The main concerns with iron flocculation from a human health perspective include unsightliness, staining and its effect on the taste of potable water. The iron stains the surface of the soil and can be carried to other areas via surface water routes. From an ecological point, the concern is not direct chemical toxicity, but the effect of iron as a mediator of the geochemistry of other (potentially toxic) metals and the potential physical hazard of depositing flocculent. Decrease in soil particle size causes decrease in Si content and increase in Al content⁴⁰ and the same was validated in this study also.

Rainwater, dust, air pollution and sea spray add chlorine naturally to soil. Anthropogenic sources include irrigation, fertilizers, manures etc. Chlorine occurs predominantly as chloride in the soils⁴¹. As coastal regions receive enormous quantities of chloride from rain, atmospheric chloride deposition is rather high. Chloride is neither adsorbed nor held back by soils leading to ready movement with soil water hence often used as a tracer for soil water movement. Chloride though a micronutrient, excessive levels of it in the soil can result in chloride sensitive crops accumulating excessive amounts of it, which can be toxic. In areas with high rainfall and high soil permeability, it may be leached from the soil profile. In the present case, the natural soil shows concentration of 2050mg/kg of Cl and that of contaminated soil is 53,400mg/kg which is enormous showing clear evidence of pollution. Considering the disposition and distribution of chloride in such a sensitive area, the fate and transfer of this element to the nearby soil and water sources is inevitable.

Cu concentrations in soil vary considerably with soil type, soil amendments, distance from polluting sources, distance from natural ore bodies and composition of bed rock and parent material among other factors⁴². Compared to other trace metals Cu is the least mobile as it is strongly adsorbed to soil particles⁴³ and hence accumulates in the soil surface due to contamination⁴⁴. Cu is more mobile under acidic conditions than alkaline conditions⁴⁵. Results in this study show that, Cu concentration in the background as well as contaminated soil exceeds the threshold value by WHO & CCME. High copper content in residential area soil may be either due to the presence of Cu in parent material or mobilization of Cu from contaminated site to inhabited area.

Ni concentration in contaminated soil is double that of inhabited area soil i.e. 262 and 134 mg/kg respectively both of which exceed the threshold value i.e. 80mg/kg. Acidic soil environment increases Ni solubility and mobility. The concentration of Cr in both virgin and contaminated soil (185 and 386mg/kg respectively) exceeds the maximum permissible limit set by WHO. Sandy soils are often low in sulphur as sulphur is leachable, plus sandy soils are typically low in organic matter which is a reservoir for sulphur⁴⁶. Lead in sample I is below the threshold limit and that in the contaminated soil is nearly 5 times higher than the sample I clearly indicating its origin to accidental dumping of lead containing wastes. Lead exists in the +2 oxidation state and becomes more soluble under low soil pH conditions. Zn in sample I is just at threshold value i.e. 200mg/kg while Zn in contaminated soil exceeds it. Under acidic conditions, Zn is the most mobile and soluble trace element. Problems related to Zn toxicity are adverse effects on crops, animals and human⁴⁷.

Phosphorous is a macro-nutrient and total phosphorous concentration in soils is around 1000mg/kg. But in the present study both residential area soil and contaminated soil showed high amounts of phosphorous i.e. 7670mg/kg and 12200mg/kg respectively. The concentration of vanadium in the soil ranges between 3-310mg/kg and high values up to 400mg/kg are found in areas polluted by fly ash⁴⁸. It is evident from table 4 that contamination increased the concentration of vanadium from 175mg/kg to 427mg/kg. Inhalation exposure to vanadium and vanadium compounds results primarily in adverse effects on the respiratory system. Typical concentration of strontium (Sr) in soil is 0.2mg/kg but higher concentrations may be found due to industrial, hazardous or radioactive waste disposal⁴⁹. In the present case Sr in background soil as 138mg/kg increased to 524mg/kg in contaminated soil.

Table 5 presents the concentration of elements found only in sample I. The following observations are made:

Table 5. Concentration of elements in natural soil but absent in contaminated soil (mg/kg)

Elements	Mg	Ag	Au	Hf	Te	Yb	Nd	Ga
Sample I	1610	82	60	304	158	105	102	28

Magnesium (Mg) is very abundant in nature, chemically very active, combines with almost every acid⁵⁰. This might be the reason that Mg was found absent in contaminated soil (Table 5). Magnesium is not considered to be carcinogenic, mutagenic or teratogenic⁵⁰. Hafnium (Hf) used in nuclear reactors and manufacturing of microprocessors is found with zirconium minerals in nature and used with other metals like titanium, iron, niobium etc. to make alloys. Hafnium has no known toxicity and poses no threat to plants⁵⁰. Till now no negative environmental effects of Hafnium have been reported⁵⁰. Ytterbium (Yb) and Neodymium (Nd) are rare earth minerals. Nd dust and salts are very irritating to the eyes. Nd can cause lung embolisms, especially during long term exposure and can be a threat to the liver when it accumulates in the body⁵⁰. Yb is easily attacked and dissolved by mineral acids. Yb is a skin and eye irritant and is also a suspected teratogen⁵⁰. Tellurium (Te) and Gold (Au) are found in nature as chemical compound. Te is not harmful or can be readily converted into harmless by natural processes⁵⁰. Gallium (Ga) does not exist in pure form in nature and is not harmful in small quantities⁵⁰. All the above elements were found to be absent in contaminated soil.

Table 6 presents the concentration of elements found only in contaminated soil.

Table 6. Concentration of elements found only in contaminated soil (mg/kg)

Elements	Tb	Sm	Dy	W	Sn	Co	Se	Br
Sample II	423	420	400	252	191	142	46	44

It is interesting to note that the Co was absent in sample I but in contaminated soil concentration was 142mg/kg which is very high compared to the threshold values i.e. 17mg/kg (Table 6). Generally, highly leached acidic sandy soils are prone to Co deficiency. But the higher soil acidity also leads to greater potential for cobalt toxicity^{51, 52}. In soil, selenium content is highly variable ranging from 0.1 to 2 mg/kg. It is predominantly determined by its content in the native substrate. Besides this, rainfall plays an important role in determining selenium content in soil⁵³. In high rainfall areas, if the parent rock is rich in selenium, the soil contains high amount of selenium but it is bound to iron in a poorly soluble complex. It is found that selenium binds to clay fractions more readily because of its high specific area and selenium content is found decreasing with increasing depth. Selenium adsorbs less to coarse and fine sand fractions. Selenium binds well with organic matter in acid soils⁵⁴. In the present study, selenium is absent in natural soil but a concentration of 46mg/kg is found in contaminated soil.

Rare earth minerals like Terbium (Tb), Samarium (Sm) and Dysprosium (Dy) are found chiefly in monazite ore. Tb has no biological role and may be mildly toxic by ingestion⁵⁰. Terbium powder and compound are very irritating if they come into contact with the skin and the eyes. Its toxicity has not been investigated in detail⁵⁰. Samarium is a significant radionuclide in spent nuclear fuel, high-level radioactive wastes resulting from the processing of spent nuclear fuel and radioactive wastes associated with the operation of nuclear reactors and fuel reprocessing plants⁵⁰.

Table 7 presents the concentration of elements which got reduced in the contaminated soil.

Table 7. Concentration of elements found decreased in contaminated soil (mg/kg)

Elements	Si	Ti	Zr	Ba	Ca	Mn	Th	K	Nb	Y	Mo
Sample I	360000	12500	21100	400	378	225	924	248	362	140	160
Sample II	198000	4250	6250	340	228	218	220	170	101	66	45

Silicon (Si) is the second most abundant element in the Earth's crust. Si is non toxic but people exposed to siliceous dust can develop a serious lung disease called silicosis⁵⁵. Si in the present study reduced from 360000mg/kg to 198000 mg/kg. The grain size analysis has also revealed that contamination has weathered the soil particle decreasing the sand fraction from 93.76% to 76.96% in contaminated soil and hence increasing the silt and clay fraction leading to more dust particles in air.

Titanium is the ninth most abundant element on Earth. Titanium is known for its excellent corrosion resistance, high strength, high melting point and low density and hence a strategic metal in the production of spacecrafts, aero engines etc. Bio-medical implants, sports goods, automobiles architecture and consumer durables are some of the other emerging areas of titanium application. Titanium is produced from mineral ilmenite and Chavara ilmenite is richest in TiO₂ content (75.8%)⁵⁶. The Ti content in sample I was 12500mg/kg which reduced to 4250mg/kg in contaminated soil. Zirconium (Zr) is mined from the mineral zircon which is highly resistant to weathering. Zr

(21100mg/kg) is reduced to 6250mg/kg in contaminated soil. Zirconium is unlikely to present a hazard to the environment⁵¹. However, if radio-nuclides of Zr like Zr 95 produced, will pose increased cancer risks. Thorium (Th) is a naturally occurring radioactive metal found at low levels in soil, rocks and water. Thorium enters the body mainly through inhalation of contaminated dust. If a person inhales thorium into the lungs, some may remain there for long periods of time. Th has the ability to change genetic materials and can be stored in bones and hence may cause bone cancer even many years after the exposure has taken place⁵⁰. Th (924mg/kg) has been found reduced to 220mg/kg in contaminated soil.

XRF results presented in the tables 4 to 7 give the total metal concentration for individual metal. Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in soil metal concentration over time. However, this does not give an indication of chemical form of the metal in the soil. Some of these metals exist in soil in more than one oxidation state. The oxidation state of these metals determines their relative mobility, bioavailability and toxicity⁵⁷. And hence more studies in this regard will throw light on the specific nature of the contaminants. Further the wastes and sludges from the extraction of rare earths also contain radio-nuclides as some level of radioactive minerals is found in rare earth deposits². These wastes hence could give rise to unacceptable radiation levels which needs to be checked from the point of view of human exposure.

3.4. Pollution indices

Table 8 summarizes contamination factor (Cf), enrichment factor (E. F.) and geo-accumulation index (Igeo) for the contaminants. Also each element is categorized into various pollution classes based on these pollution indices. Based on the classification, it follows that the soil is strongly polluted with Cl, moderately polluted with Fe, S_x and Pb. Pollution class for Cu, Cr, V and Sr is 2 indicating a low pollution because of these elements. Al, P_x, Ni, Zn, Rb falls in class 1 indicating that soil is unpolluted of these elements. However, if the toxic limits or threshold values for toxicity are used, Ni, Zn, P_x, Cr, Cu, Pb etc. are exceeding the limits and hence the soil is heavily polluted of these elements as well, e.g.as per United States Environmental Protection Agency (USEPA)⁵⁸, Pb > 60mg/kg, Cr > 75mg/kg, Cu > 50mg/kg and Zn > 200mg/kg indicate heavily polluted soil or sediment. In the present case, Pb (122-562mg/kg), Cr (185-386mg/kg), Cu (191-592mg/kg) and Zn (205-327mg/kg) exceed the threshold values for toxicity for both reference and contaminated soil.

In this industry, the chloride route process is used in the beneficiation of ilmenite which produces the wastes like iron oxide sludge and a slurry containing chlorides of metals in the liquid state and un-reacted ore and coke in the solid state¹⁰ which leaked from the settling ponds. The single pollution indices shows that the soil is strongly polluted with Cl, Fe and S_x, hence confirming or validating the accidental leakage of industrial waste as the source of contamination.

Table 8. Single pollution indices

Sr .No.	Element	Background soil in mg/kg	Contaminated soil in mg/kg	Cf	E.F.	Igeo	Class
1	Al	62100	64900	1.05	Ref.	-0.52	1
2	Fe	12600	181000	14.37	13.75	3.26	3
3	Cl	2050	53400	26.05	24.92	4.12	4
4	Px	7670	12200	1.59	1.52	0.08	1
5	Sx	7220	36300	5.03	4.81	1.74	3
6	Cu	191	592	3.10	2.97	1.05	2
7	Ni	134	262	1.96	1.87	0.38	1
8	Zn	205	327	1.60	1.53	0.09	1
9	Pb	122	562	4.61	4.41	1.62	3

10	Cr	185	386	2.09	2.00	0.48	2
11	V	175	427	2.44	2.33	0.70	2
12	Sr	138	524	3.80	3.63	1.34	2
13	Rb	21	35	1.67	1.59	0.15	1

The three integrated pollution indices viz. degree of contamination, average pollution index and pollution load index are calculated and presented in table 9. The degree of contamination value is greater than 48 and hence very high. Similarly, average pollution index and pollution load index values are greater than 1 and hence indicate low quality or polluted soil.

Table 9. Integrated pollution indices

Pollution Indices	Degree of contamination	Average pollution index	Pollution load index
Values	68.31	5.69	3.57
Remarks	Very high	Low quality soil	Polluted

3.5. Water analysis

The results obtained for various physico-chemical parameters are presented in table 10. The results are examined and the following observations are made:

Table 10. Results of physico-chemical parameters of water samples

Parameters	Open Well	Paddy Field	Factory Canal	T. S. Canal	Supply Tap
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
pH	6.8	1.9	6.5	6.5	6.6
Electrical Conductivity ($\mu\text{mhos/cm}$)	412	6700	346	2500	211
Total Dissolved Solids (mg/l)	247	4020	208	1500	84
Turbidity (NTU)	1	>5	1	2	1
Total Hardness (mg CaCO_3/l)	200	Difficult to get end point	105	310	85
Calcium (mg/l)	64		18	30	24
Magnesium (mg/l)	9.8		14.6	57	4.9
Sodium (mg/l)	13	46	25	436	9
Potassium (mg/l)	3.1	4.5	2.5	10.4	1.4
Total alkalinity (mg CaCO_3/l)	176	0	80	218	76
Carbonate (mg/l)	0	0	0	0	0
Bicarbonate (mg/l)	215	0	98	266	93

Sulphate (mg/l)	9.1	810	20	49	0.5
Chloride(mg/l)	17	2500	67	660	35
Iron (mg/l)	0.52	5	7	3.3	0.43

The paddy field water, in spite of heavy rains, showed pH 1.9 i.e. extremely acidic indicating the sources subjected to clear industrial pollution. Though this water is not for domestic use, the risk posed by this water via infiltration and contamination of the ground water aquifer, dermal contact etc. is equally important as there is no control of flow of this water especially in rainy season when the paddy fields are flooded and overflowing, sometimes even entering the houses of the residents. The conductivity of paddy field water recorded the highest which is 6700 μ mhos/cm. The extremely high values of conductivity in paddy field and T. S. canal water clearly indicate the presence of contaminants and that pollutants are spreading to the nearby T. S. canal also. Also paddy field water and T. S. canal water showed total dissolved solids as high as 4020mg/l and 1500mg/l respectively which are 8 and 3 times higher than the permissible limit. The chloride and sulphate concentration in paddy field water exceeded the permissible limit⁵⁹. The extremely elevated levels of the chlorides and sulphates can be attributed to the industrial discharge or accidental leakage of tickle (TiCl₄) that had taken place. Mg content in T. S. canal water was almost double the permissible limit. Sodium content was also found to be highest in TS canal water sample. The iron content in all the water samples was above 0.3mg/l, which is the desirable limit⁵⁹. The maximum iron content was found in the factory canal (7 mg/l) and then in the paddy field water (5mg/l) followed by T.S. canal water (3.3 mg/l). The elevated levels of iron in the water samples of factory canal, paddy field and T.S. canal points to the source of pollution as iron oxide sludge released from factory.

The water quality index (WQI) calculated is presented in table 11. The WQI for open well water is 81 indicating excessive contamination, whereas for supply water is 70 indicating moderate contamination. As per the WQI, the water samples from paddy field, factory drainage canal and T. S. canal are severely contaminated and not fit for use for any domestic purposes.

Table 11. Calculated values of water quality index (wqi)

Sample	1	2	3	4	5
WQI	81	692	741	427	70

4. Conclusion

Mining and related processes can disturb and alter large areas of land. The magnitude of such disturbance depends on variability in natural site conditions like geology, vegetation, topography, climate and proximity to and characteristics of surface waters. In the present study, the following observations are made:

- The discharge from the industry has resulted in the lowering of pH of water and soil, leading to loss of vegetation, water and soil quality deterioration.
- The soil and water are heavily polluted with iron and chlorine.
- The trace metals like Cu, Ni, Zn, Pb, V, Cr, Sr, Se, Co have found to be increased in soil which in turn may mobilise, increasing the heavy metal loading in surrounding subsoil and surface water sources.
- The fugitive dust poses risk to the nearby residents as radioactive elements can concentrate in these dusts.
- The calculated pollution indices and water quality index also confirmed the water and soil pollution in the area.

However no serious attention has been given to the potential threats of environmental deterioration. This is partly due to the difficulty associated with regulating resources of high strategic importance. In developing countries like India, preventive and curative measures against pollution and contamination of soil, water and land must receive high priority in coming years. As in a state like Kerala, because of the very high population density, all forms of biotic pressure on soil are high and hence it is an immediate and critical necessity to map and monitor soil quality and promptly take remedial measures. The pollution has affected the life and livelihood of the people in the surroundings of KMML. To solve the issues of contamination, a multidisciplinary approach involving in depth studies in geology, hydrology, soil chemistry, toxicology are required. On a priority basis, health risk assessments due to the contaminated

soil and water from various exposure pathways should be taken to evaluate the health impacts on the population.

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