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# Toxicity, uptake, potential ecological and health risks of Thallium (Tl) in environmental media around selected artisanal mining sites in Nigeria

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## ABSTRACT

Thallium (Tl) in environmental media poses great threat to the environment and human health. Contamination, toxicity and potential ecological and health risks of thallium associated with mining activities were studied in this paper. Results showed that the average content of Tl in tailings, rocks, groundwater, surface water and mine water in Anka area are 7.89 µg/g, 8.82 µg/g, 0.04 µg/g, 0.006 µg/g, and 0.048 µg/g, respectively while in Ijero area, the mean concentration of Tl in tailings, rocks, groundwater, surface water and minewater are 9.78 µg/g; 18.99 µg/g; 0.004 µg/g; 0.003 µg/g and 0.03 µg/g respectively. The percentage concentration of K, Ca, Na and Mg in soils of the area are 0.66, 15.37, 0.42 and 3.21 while in sediments their concentrations are 0.74, 12.61, 0.59, and 2.61. In the tailings, the percentage concentration of K, Ca, Na and Mg are 0.81, 16.68, 0.68 and 2.97 respectively. Tl concentrations from the media are mainly from artisanal mining and mineral processing of gold (Au), lead (Pb), zinc (Zn) and minerals associated with pegmatites. Single factor pollution index is greater than 1 and revealed that soils and sediments are uncontaminated by Tl while tailings and water are contaminated by it. Tl was highly available in plants of the area and the content of Tl exceeded the recommended limits. Also, the daily intake of the metal is above the recommended limit. Tl poses low to very high ecological and health risk in the area.

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Ecological risk; health risk; mining; Nigeria; plant uptake; Thallium

## 1. Introduction

Thallium (Tl) which is of low abundance with an average concentration in continental crustal of 0.49 µg/g [1], has recently been a metal of environmental concern across the world [2] because of the enhanced awareness of its highly complex and serious toxicities to plants, animals and human health [3]. It is one of the 13 priority pollutants and more toxic than mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) even at a very minute concentration [1,4,5]. It is an exclusively monovalent and its toxicity is

attributed to its interaction with potassium (K) [6,7]. It is a non-degradable and stable metal [8,9] which rarely occur as an independent mineral, but are common in sulphuric mines in relation with copper (Cu), iron (Fe), lead (Pb), zinc (Zn) and other toxic metal [5,7,10]. Thallium can be released from both natural and anthropogenic sources [11]. Tl pollution have been recorded in many parts of the world such as China [12]; Belgium [13]; the United States [14]; Chile [15]. Tl is a poisonous and cancer causing metal [2]. For contaminated soils, a potential risk for humans can arise at levels above 1 µg/g [7]. Human health risk assessment is a technique used to evaluate the nature and likelihood of adverse health impacts in humans who may be exposed to metals in contaminated environmental media [16] while ecological risk assessment is a process that assess the possibility that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors. Studies have reported human health and ecological risks associated with toxic metals in environmental media [17]. Simultaneous calculation of ecological and health risks indices provides comprehensive view of the pollution in the environment [18]. Serious ecological and human health impacts are related with high grouping of heavy metals in the environment [19–21].

Mining activities release potentially toxic metals (PTM) into the ecosystem and degrade it [22]. Many studies in Nigeria focused on the impact of mining on their immediate environment [16,23–25]. Hitherto, scientific information pertaining to Tl contamination and toxicity in environmental media in Nigeria is still unknown. Therefore, the objectives of this study are to investigate the total concentration of Tl in media collected around active and abandoned artisanal mining areas in Nigeria. This study unravelled the extent of contamination, toxicity and risk associated with Tl in media collected from Anka, Arufu and Ijero mining areas. This study will give insight into thallium pollution in Nigeria and also propel interest in further study of this metal in the country.

## 2. Materials and methods

### 2.1. Description of the sampling areas

Sampling were carried out around three selected mining sites of Nigeria: Anka, Arufu and Ijero areas (Figure 1). Anka is located in Zamfara state, northwest Nigeria on latitude 12°06'30"N and longitude 5°56'00"E. It is a major gold mining site in the country. Arufu is located in Taraba state, northeast Nigeria on 7°50'59"N and longitude 9°5'00"E, approximately 295.10 km from Jalingo. This area is one of the main places where lead-zinc-fluorite mineralisation occur in the country. Ijero is located in Ekiti state, southwest Nigeria on 7°46'00"N and longitude 5°5'00"E. This area is renowned for pegmatite hosting mineral such as [26]. Nigeria typically has a tropical climate with rainy and dry seasons differing in several parts of the country. The topography of the country consists of plains (300 metres) in the north and south intersected by hills and plateaus (2,400 metres) at the centre. The Mandara Mountains are the major mountains in the country, while the main plateaus are Jos, Biu and Mambilla plateaus. Mining, mineral dressing and agricultural practices are major human activities observed in the area.

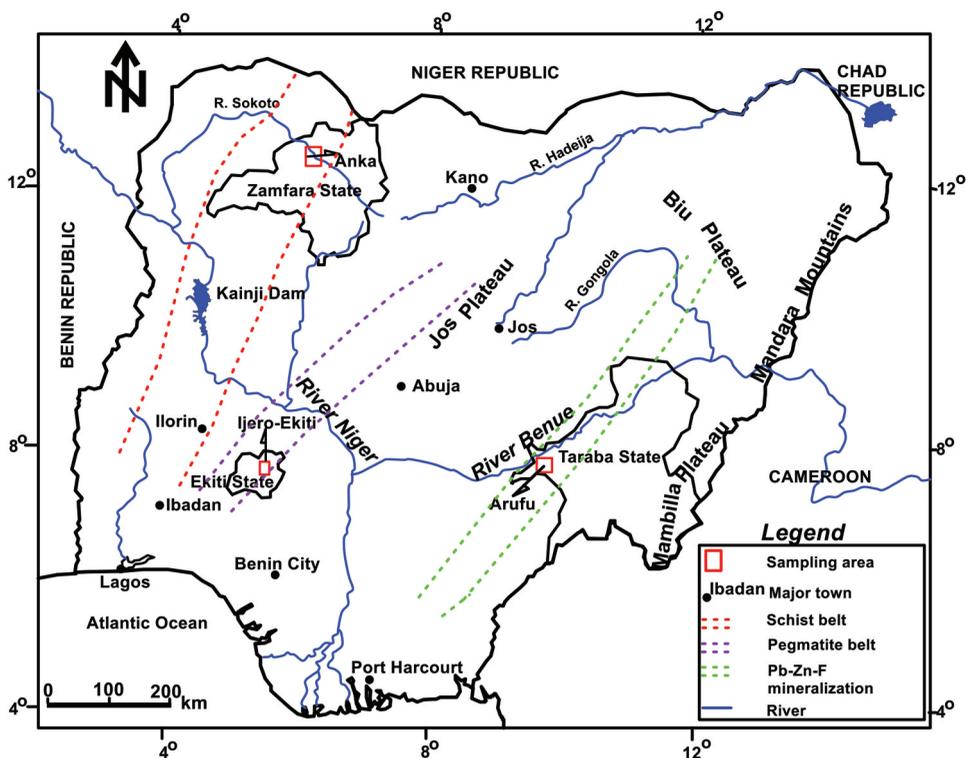


Figure 1. Location map of the study area.

## 2.2. Media sampling and reagents

A total of three hundred and thirty seven (337) samples consisting of soils, stream sediments, mine tailings, rocks, groundwater, surfacewater and mine water samples were collected around mining areas in Anka, Arufu and Ijero areas in January 2017. In total, 37 mine tailings, 66 soils, 71 sediments, 15 plants (which include: maize, *Zea mays*; sorghum, *Sorghum bicolor*; onion, *Allium cepa*; ewedu: *Corchorus olitorius*, soko: *Celosia argentea*), 40 rocks, 58 groundwater, 29 surface water and 21 minewater were collected. At each sampling area, soil and mine tailings samples were randomly collected at the upper horizon (0–20 cm) using a clean, uncontaminated hand auger while sediments were scooped using hand trowel. Unweathered rock samples were collected for this study. Water samples were collected into a clean 1 litre plastic bottles pre-washed in ultra-pure water and was acidified using diluted nitric acid. All liquid samples were kept in an ice filled container to maintain its original status. All solid samples were placed in a clean ziplock bags. All glassware and Teflon vessels used were soaked in a 0.2 mol/L nitric acid solution for 24 h and subsequently rinsed with deionised water. Hydrofluoric acid (HF), and nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl), perchloric acid (HClO<sub>4</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) were of super-pure grade. Analysis was carried out using ultra-pure water (18.2 mS/cm) obtained from a MilliQ-system (Millipore, Milford Corp., MA, USA).

### 2.3. Samples pre-treatment and chemical analysis

After transportation to the laboratory, the media were air-dried, pulverised and sieved through a 1 mm mesh to collect very fine particle size. These were used to measure the physico-chemical parameters following acceptable procedures. The entire plant samples were plants thoroughly washed with clean running tap and ultrapure water to remove associated dirt. The plants were separated into root, stem, leaf and grains parts with a stainless steel scissors, pulverised and sieved using a 0.15 mm sieve. Rocks were pulverised, sieved through a 1 mm sieve to collect fine particles. One hundred and fifty-one (151) water samples were kept in the refrigerator at temperature less than 4°C.

### 2.4. Laboratory analysis

Soil, sediment, tailings and water pH were determined with a 1:2.5 (w/v) ratio of soil to water using a digital pH metre (model) (PH100-V 0.01). Five grams of soils, stream sediments were digested using a solution of concentrated HCl-HNO<sub>3</sub>-HF-HClO<sub>4</sub> [27]. Dry powdered plant samples were digested with 60% HClO<sub>4</sub>, concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [28] while rock samples were digested using the procedures presented by 29. Digested samples were diluted using double-deionised water [30]. TI in samples were analysed using Agilent HPLC inductively coupled plasma-mass spectrometry (ICPMS) while mineralogical analysis for soils, stream sediments, rocks and mine-tailings were carried using ARL™ Equinox 6000 X-Ray diffractometer. All laboratory analysis were carried out at the State Key Laboratory of Environmental Geochemistry (SKLEG), Guiyang, China. Quality assurance was carried out following the standard set by the laboratory.

### 2.5. Data analysis

#### 2.5.1. Bioconcentration factor

The bioconcentration factor (BCF) reflects metal availability to plant from a given soil sample [31]. The concentrations of TI in soils, stream sediments and mine tailings were calculated on a dry weight basis. It was calculated as shown in Equation 1.

$$BCF = \frac{C_{Plant}}{C_{Soil}} \quad (1)$$

Where C<sub>plant</sub> and C<sub>soil</sub> represent the concentrations of TI in the plant and soil samples on a dry weight basis, respectively.

#### 2.5.2. Enrichment factor

Enrichment factor (EF) of an element in the studied samples was based on the standardisation of a measured element against a reference element. A reference element is often the one characterised by low occurrence variability [32]. *K* was used as normaliser in this study. The EF calculation is expressed in Equation 2.

$$EF = \frac{\left(\frac{Metal}{RE}\right)_{Soil}}{\left(\frac{Metal}{RE}\right)_{Background}} \quad (2)$$

Where RE is the Reference metal concentration. Background samples were collected from far from the mining zones where there is no human activities taking place. Five contamination categories are recognised on the basis of the enrichment factor:  $EF < 2$  states deficiency to minimal enrichment,  $EF = 2-5$  moderate enrichment,  $EF = 5-20$  significant enrichment,  $EF = 20-40$  very high enrichment and  $EF > 40$  extremely high enrichment [32].

### 2.5.3. Single factor pollution index

The extent of metal pollution in the media was calculated using the single factor pollution index (SFPI) method depending on the concentration of the metal in the samples. The SFPI was calculated using the following equation 3 as modified by [33].

$$SFPI = \frac{C_{Media(Samples)}}{C_{background(Samples)}} \quad (3)$$

Where  $C_{media}$  (samples) and  $C_{background}$  (samples) represent the concentrations of TI in media and their background samples respectively. Background samples were collected far from mining sites, where less human activities occur while the maximum contaminant level (MCL) for TI was used as background value for water samples [34].

### 2.5.4. Contamination factor

The assessment of soil contamination was also carried out using the contamination factor (CF) in equation 3. The CF is the single element index, and all four classes are recognised [35]. The classification of CF are:  $CF < 1$ : low contamination factor indicating low contamination;  $1 \leq CF < 3$ : moderate contamination factor;  $3 \leq CF < 6$ : considerable contamination factor and  $6 > CF$ : very high contamination factor.

$$Contamination\ Factor = \frac{Metal\ Concentration}{Concentration\ of\ Element\ in\ Background\ Soils} \quad (4)$$

### 2.5.5. Contamination load index

Degree of crop contamination for each metal was determined using contamination load index (CLI). Equation 5 was used to assess CLI level in crops.

$$CLI = \frac{C_{Crop}}{MPC} \quad (5)$$

Where  $C_{crop}$ : Heavy metal concentrations in the edible portion of plants and MPC: Maximum permitted concentration of heavy metal in crops. No MPC guideline for TI. In this study the MPC of Hg is used because of the TI is more toxic than it. The MPC for Hg is  $0.1 \mu\text{g/g}$  [36].

### 2.5.6. Chemical Index of Weathering (CIW)

Chemical index of weathering is an improved measure of the degree of weathering experience by a material relative to its parent rock. CIW for stream sediments were calculated using Equation 6 following [37], method.

$$CIW = \left( \frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O} \right) \times 100 \quad (5)$$

If CIW is between 50 and 60, it indicate incipient weathering but if it is between 60 and 80 indicate intermediate weathering, and values above 80 indicate extreme weathering.

### 2.5.7. Toxicity units

Toxic unit (TU) is defined as the ratio of the determined concentration to severe effect level (SEL) value [38]. The potential acute toxicity of contaminants in media can be estimated as the sum of the toxic units. If the sum of TU is greater than 4, metals in a media pose high potential acute toxicity, but if less than 4, they do not pose acute toxicity [39]. Although no TI has no low lowest effect level (LEL) and severe effect level (SEL) values as outlined by [40]. The LEL and SEL values of Hg was used for TI because of their similar toxicities. SEL values for Hg is 2 respectively [40]. It is mathematically expressed as shown in equation 6.

$$TU = \frac{\text{Concentration of metal in media}}{\text{Severe effect level}} \quad (6)$$

### 2.5.8. Potential ecological risk index

The potential ecological risk index proposed by Hakanson was employed to assess the degree of heavy metal pollution by heavy metals [35]. The method is used to understand ecological and toxicological effects that metals may cause. There are five classes (0–5 grade) of ecological risk [41] which range from background concentration to very heavy contamination [30]. The single-factor pollution index ( $C_f^i$ ) (Equation 3) and single-factor potential ecological risk index ( $E_r^i$ ) are calculated in Equation 7:

$$E_r^i = T_r^i \times C_f^i \quad (7)$$

$C_f^i$  is contamination factor while  $T_r^i$  is the toxic response parameter.  $C_f^i < 1$ ,  $1 \leq C_f^i < 3$ ,  $3 \leq C_f^i < 6$ , and  $C_f^i \geq 6$  represent slight, moderate, heavy and serious pollution respectively [42]. Five groups of are low ( $40 \leq E_r^i$ ), moderate ( $40 \leq E_r^i < 160$ ), considerable ( $80 \leq E_r^i < 160$ ), high ( $160 \leq E_r^i < 320$ ) and very high ( $E_r^i \geq 320$ ) [43].

## 2.6. Health risk index

The health risk index (HRI) for the inhabitants of this area via the ingestion of contaminated plants was assessed based on food chain and the reference oral dose (RfD: mg/kg/d) for the metal. If HRI is less than 1, it indicates that the exposed people are not in danger. HRI was calculated using Equation 8 [44]

$$HRI = \frac{DIM}{RfD} \quad (8)$$

The RfD of TI was taken to be 8.0E-5 mg/kg/d, as suggested by [45]. The daily intake of metals (DIM) was calculated using Equation 9 [44].

$$DIM = \frac{C_{\text{metal}} \times C_{\text{factor}} \times D \times EF \times ED}{BW \times AT} \quad (9)$$

Where  $C_{\text{metal}}$  is the amount of TI in the plant samples (mg/kg),  $C_{\text{factor}}$  is the conversion factor,  $D$  is the daily consumption rates for vegetables (kg),  $EF$  is the exposure frequency

(days/year), ED is exposure duration (years), BW is average body weight (kg) and AT is the averaging time (period over which exposure is averaged/days). A conversion factor of 0.085 was used to convert fresh green vegetable weight to dry weigh [46,47]. The average daily consumption of vegetables, root vegetables and grains were 0.08, 0.041 and 0.17 kg/person/day for adults and 0.025, 0.016 and 0.113 kg/person/day for children [47]. The weights for adults and children were 62.7 and 32.7 kg respectively, as used in previous studies by [47–49]. The value of EF, ED, and AT is 350 d/y, 30 years and 70 years, respectively in this work [44,47,50].

### 3. Results and discussion

#### 3.1. Physicochemical properties in soils, sediments and tailings

Physicochemical properties of soils, stream sediments and mine tailings from Anka, Arufu and Ijero area are presented in Table 1. In Anka area, the pH KCl for soils, sediments and tailings are 6.10, 6.40 and 4.20 while the pH water for media from this area is 6.80, 7.30 and 5.10. The cation exchange capacities (CEC) for soil, sediments and tailings are 15.64, 10.71 and 22.61. The soils and sediments are classified as sandy loam and sand. The percentage concentration of K, Ca, Na and Mg in soils of the area are 0.70, 13.58, 0.50 and 2.40 while in sediments their concentrations are 0.90, 14.28, 0.66, and 2.90. In the tailings, the percentage concentration of K, Ca, Na and Mg are 0.62, 16.18, 0.54 and 3.61 respectively. In Arufu area, pHKCl for soil, sediments and tailings are 5.50, 6.30 and 5.40 while the pH water for the media are 6.50, 6.80 and 6.32 respectively. The CEC for soil, sediments and tailings in the area are 20.92, 22.64 and 27.22 each. The soils and sediments in this area are classified as sandy loam and sand. The major oxides concentrations of soils, sediments and tailings are presented in Table 2. The percentage concentration of K, Ca, Na and Mg in soils of the area are 0.60, 16.18, 0.54 and 3.61 while in sediments their concentrations are 0.85, 13.66, 0.62, and 2.01. In the tailings, the percentage concentration of K, Ca, Na and Mg are 0.72, 14.16, 0.55 and 2.65 respectively. In Ijero area, pH KCl for soils, sediments and tailings are 6.60, 6.11 and 4.69 while the pH water is 6.80, 6.78 and 5.82 respectively. The CEC for soils,

**Table 1.** Selected chemical and physical properties of soils, stream sediments and mine tailings.

	Anka			Arufu			Ijero		
	Soil	Sediments	Mine Tailings	Soil	Sediments	Mine Tailings	Soil	Sediments	Mine Tailings
pH KCl	6.10	6.40	4.20	5.50	6.30	5.40	6.60	6.11	4.69
pH H <sub>2</sub> O (1:5)	6.80	7.30	5.10	6.50	6.80	6.32	6.80	6.78	5.82
CEC	15.64	10.71	22.61	20.92	22.64	27.22	16.28	20.21	24.15
NH <sub>4</sub> OAc Exc. Cations Cmol <sub>c</sub> Kg <sup>-1</sup>									
K	0.70	0.90	0.62	0.60	0.85	0.72	0.66	0.74	0.81
Ca	13.58	14.28	16.18	15.87	13.66	14.16	15.37	12.61	16.68
Na	0.50	0.66	0.54	0.51	0.62	0.55	0.42	0.59	0.68
Mg	2.40	2.90	3.61	1.62	2.01	2.65	3.21	2.61	2.97
Particle Size Distribution (%)									
Sand	70.00	80.00	-	75.00	85.00	-	70.00	75.00	-
Silt	20.00	10.00	-	20.00	10.00	-	20.00	15.00	-
Clay	10.00	10.00	-	5.00	5.00	-	10.00	10.00	-
Soil Texture	<b>SL</b>	<b>S</b>	-	<b>SL</b>	<b>S</b>	-	<b>SL</b>	<b>SL</b>	-

**SL** – Sandy Loam; **S** – Sand

**Table 2.** Major oxides of the selected soils, sediments and tailings (wt%).

Media	Location	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	MgO (%)	CaO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
Rock	<b>Anka</b>	48.49–90.22	1.06–12.93	5.41–21.18	0.03–5.64	0.13–7.64	0.07–2.64	0.01–1.11
	Mean	69.27	6.92	13.01	2.74	3.79	1.33	0.51
	<b>Arufu</b>	68.18–73.69	2.14–4.27	5.17–13.65	0.41–0.71	3.12–5.34	0.11–0.17	0.32–0.81
	Mean	70.85	3.19	9.34	0.42	4.2	0.13	0.54
	<b>Ijero</b>	68.34–75.69	3.28–8.48	6.69–8.74	0.01–3.00	0.01–3.89	0.04–0.14	0.54–0.89
	Mean	71.26	5.82	7.7	1.49	1.94	0.07	0.69
Soils	<b>Anka</b>	72.58–89.48	4.09–11.16	1.08–6.05	0.11–0.61	0.18–0.67	0.12–1.52	1.19–2.86
	Mean	80.17	6.27	3.51	0.29	0.39	0.79	1.98
	<b>Arufu</b>	78.23–94.63	2.13–4.33	0.71–1.79	0.04–0.12	0.05–0.83	0.03–0.12	0.76–2.20
	Mean	85.18	3.21	1.19	0.06	0.4	0.07	1.39
	<b>Ijero</b>	62.18–74.31	2.16–3.66	3.06–5.19	0.03–1.48	0.01–1.98	0.02–0.11	0.11–1.69
	Mean	67.24	2.89	4.1	0.72	0.91	0.04	0.87
Stream Sediments	<b>Anka</b>	62.74–85.99	4.13–15.74	3.66–7.04	0.18–1.34	0.49–1.64	0.20–0.97	1.12–3.58
	Mean	73.88	9.27	5.09	0.71	1.02	0.52	2.3
	<b>Arufu</b>	80.17–89.36	3.76–4.36	0.52–0.74	0.01–0.04	0.06–0.09	0.18–0.19	2.40–2.73
	Mean	83.77	3.99	0.6	0.02	0.07	0.18	2.49
	<b>Ijero</b>	64.22–79.08	5.12–7.28	4.27–5.56	0.05–4.12	0.28–2.17	0.02–0.16	0.17–0.65
	Mean	71.22	6.12	4.88	2.04	1.19	0.05	0.38
Mine Tailings	<b>Anka</b>	48.50–54.55	9.89–16.84	7.14–11.44	0.64–7.21	0.01–0.03	0.38–1.12	1.82–2.41
	Mean	50.19	12.19	9.17	3.17	0.02	0.69	2.09
	<b>Arufu</b>	73.88–92.69	5.24–10.05	1.81–2.65	0.29–0.57	1.42–4.28	0.05–0.11	1.09–2.45
	Mean	82.49	7.42	4.22	0.4	2.78	0.06	1.71
	<b>Ijero</b>	63.15–72.66	4.32–10.64	3.16–6.22	0.21–1.22	0.21–3.57	0.06–0.12	0.32–0.87
	Mean	67.28	7.38	4.16	0.67	1.81	0.08	0.51

sediments and tailings in the area are 16.28, 20.21 and 24.15 each. The soil and sediments in this area are classified as sandy loam. The percentage concentration of K, Ca, Na and Mg in soils of the area are 0.66, 15.37, 0.42 and 3.21 while in sediments their concentrations are 0.74, 12.61, 0.59 and 2.61. In the tailings, the percentage concentration of K, Ca, Na and Mg are 0.81, 16.68, 0.68 and 2.97 respectively. Results of physicochemical parameters in media are similar to those obtained by [51] and [7].

### **3.2. Mineralogical composition and extent of weathering of media**

The mineralogical composition of soils, stream sediments and mine tailings in the area is presented in Table 3. In Anka, quartz, microcline, kaolinite, albite and muscovite are the predominant minerals in the soils while in stream sediments, quartz, albite, microcline, muscovite, orthoclase, kaolinite, diopside and anorthite are the major minerals. In mine tailings, the main minerals are quartz, muscovite, haematite, pargasite, dolomite, chlorite and albite. In Arufu, quartz, microcline, muscovite and anatase are the principal minerals in soils while in sediments, the main minerals are quartz, rutile, magnetite, calcite, anatase and microcline and in mine tailings, the minerals are quartz, cerussite, fluorite and muscovite. In Ijero, quartz, kaolinite, microcline, muscovite, albite, clinocllore, marcasite and magnesite are the foremost minerals in soils, while quartz, microcline, pyrite, muscovite, diopside, orthoclase, clinocllore, phlogopite and albite are prominent in sediments and quartz, kaolinite and muscovite are the primary minerals in the mine tailings. It has been affirmed by several studies that Tl are present in ores especially copper, tin and zinc ores [52–54], sphalerite [55], pegmatites [56], silicate rocks [56,57] and minerals (such as micas and feldspars) [10,56,58].

### **3.3. Tl distribution and contamination in media**

The concentrations of Tl in mine tailings, stream sediments, soils, rocks, groundwater, surface water and minewater in Anka, Arufu and Ijero are shown in Table 4. The average concentration of Tl in mine tailings, stream sediments, soils, rocks, groundwater, surface water and minewater in Anka are 7.89  $\mu\text{g/g}$ , 0.38  $\mu\text{g/g}$ , 0.37  $\mu\text{g/g}$ , 8.82  $\mu\text{g/g}$ , 0.04  $\mu\text{g/g}$ , 0.006  $\mu\text{g/g}$  and 0.048  $\mu\text{g/g}$  respectively. In Arufu area, the mean concentration of Tl are 10.55  $\mu\text{g/g}$ , 0.40  $\mu\text{g/g}$ , 0.31  $\mu\text{g/g}$ , 7.95  $\mu\text{g/g}$ , 0.003  $\mu\text{g/g}$ , 0.004  $\mu\text{g/g}$  and 0.03  $\mu\text{g/g}$  in mine tailings, stream sediments, soils, rocks, groundwater, surface water and mine water from the vicinity. In Ijero, average concentration of Tl are: mine tailings (9.78  $\mu\text{g/g}$ ), stream sediments (0.66  $\mu\text{g/g}$ ), soils (0.82  $\mu\text{g/g}$ ), rocks (18.99  $\mu\text{g/g}$ ), groundwater (0.004  $\mu\text{g/g}$ ), surface water (0.003  $\mu\text{g/g}$ ) and minewater (0.03  $\mu\text{g/g}$ ). The concentration of Tl in samples obtained are above their values in the background samples but are lower compared to environmental quality standard set by the Canadian Council of Ministers of the Environment, [59]. However, the concentration of Tl in mine tailings and rocks are above their average crustal values [60]. Also, Tl in all water are above the maximum contaminant level goal (MCLG) and maximum contaminant level [MCL] set by [34] (Table 1). Average Tl concentration in the soil is higher than those reported in soils in Korea [0.30  $\mu\text{g/g}$ ] by [61], while it is lower than the averages reported in Turkey [170  $\mu\text{g/g}$ ] by [62], France [27.57  $\mu\text{g/g}$ ] by [57], Spain [2.60  $\mu\text{g/g}$ ] by [63]. Also, the average Tl in sediments from the Anka and Arufu are lesser than those reported in China [0.59  $\mu\text{g/g}$ ] by [64], but those in sediments from Ijero area are higher. However, the



**Table 3.** Mineralogical composition and chemical index of weathering (CIW) in soils, sediments and tailings.

	Soils		Stream Sediments		Mine Tailings	
Anka	<b>Minerals</b>	Quartz, microcline, kaolinite, albite, muscovite	Quartz, albite, microcline, muscovite, orthoclase, kaolinite, diopside, anorthite	Quartz, muscovite, haematite, pargasite, dolomite, chlorite, albite	84.65	
	<b>CIW</b>	87.15	83.02			
Arufu	<b>Minerals</b>	Quartz, microcline, muscovite, anatase	Quartz, rutile, magnetite, calcite, anatase, microcline	Quartz, cerrusite, fluorite, muscovite	81.81	
Ijero	<b>Minerals</b>	Quartz, kaolinite, microcline, albite, clinocllore, marcasite, magnetite	Quartz, microcline, pyrite, muscovite, diopside, orthoclase, clinochore, phlogopite, albite	Quartz, kaolinite, marcasite		
	<b>CIW</b>	95.82	86.07		98.35	

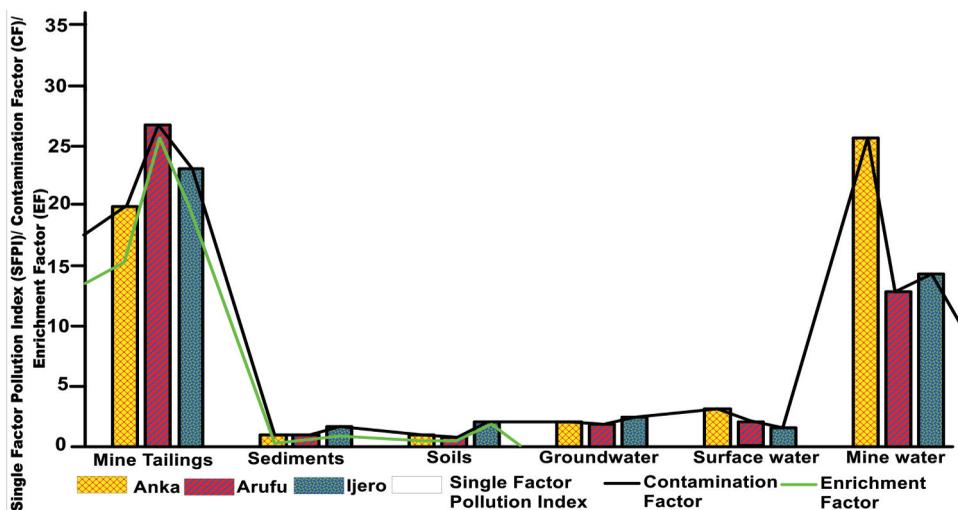
**Table 4.** Concentration of TI in Media from the sampling sites.

	Mine Tailings (µg/g)	Stream Sediments (µg/g)	Soils (µg/g)	Rocks (µg/g)	Ground Water (µg/l)	Surface Water (µg/l)	Mine Water (µg/l)
Anka	4.17	0.21	0.22	4.78	0.001	0.0013	0.0012
	<b>Maximum</b>	0.75	0.61	20.00	0.014	0.028	0.0017
	<b>Mean±SD</b>	0.38 ± 0.14	0.37 ± 0.08	8.82 ± 1.86	0.04 ± 0.003	0.006 ± 0.002	0.048 ± 0.03
Arufu	8.27	0.11	0.17	5.67	0.0015	0.0001	0.011
	<b>Maximum</b>	0.49	1.42	10.00	0.007	0.01	0.013
	<b>Mean±SD</b>	0.40 ± 0.15	0.31 ± 0.27	7.95 ± 1.44	0.003 ± 0.002	0.004 ± 0.005	0.03 ± 0.01
Ijero	4.17	0.2	0.54	4.98	0.002	0.002	0.016
	<b>Maximum</b>	0.91	1.5	70.00	0.009	0.007	0.018
	<b>Mean±SD</b>	0.66 ± 0.81	0.82 ± 0.24	18.99 ± 23.88	0.004 ± 0.002	0.003 ± 0.002	0.03 ± 0.013
Background	0.49 <sup>a</sup>	0.49 <sup>a</sup>	0.49 <sup>a</sup>	0.49 <sup>b</sup>	0.002 <sup>b</sup>	0.002 <sup>b</sup>	0.002 <sup>b</sup>
Korea	0.59 <sup>c</sup>	-	0.30 <sup>c</sup>	-	-	-	-
Turkey	-	-	170.00 <sup>d</sup>	-	-	-	-
France	-	-	27.57 <sup>e</sup>	-	-	-	-
Spain	-	-	2.60 <sup>f</sup>	-	-	-	-
Czech Republic	-	-	3.30 <sup>g</sup>	-	-	-	-

a – Average crustal value (ACV); b – Maximum contaminant level (MCL); c – [61], d – [62]; e – [57], f – [63], g – [86]

mean TI concentrations in mine tailings is higher than the average reported by [61]. TI concentrations from the media is mainly from artisanal mining and mineral processing of gold (Au), lead (Pb), zinc (Zn) and minerals associated with pegmatites. High TI concentrations are related with the epithermal, coal and silver deposits [65–67]. Study by [62], showed higher TI concentration in acidic rocks can also be related to the Ag, As, and Pb deposits. The chemical index of weathering (CIW) for soils, sediments and tailings in Anka are 87.15, 83.02 and 74.65 respectively while in Arufu it is 91.12, 92.88 and 81.81 and in Ijero it is 95.82, 86.07 and 98.35 (Table 3). The CIW revealed that extreme weathering of rocks and minerals play significant role in the concentrations of TI in the soils, sediments and mine tailings.

The enrichment and contamination factors of TI in the media are shown in Figure 2. The EF of tailings, soils and sediments in Anka area are 14.45, 0.98 and 0.85 respectively while in Arufu the EF are 25.01, 0.61 and 1.62 each while the EF for Ijero are 20.25, 1.13 and 2.08. According to [32], tailings in Anka are significantly enriched in TI while in Arufu and Ijero are very highly enriched in the metal. Soils in the area are minimally enriched in the metal while the sediments of Anka and Arufu area are minimally enriched in TI while in Ijero sediments they are moderately enriched in the metal. The single factor pollution index (SFPI) and contamination factor (CF) for TI in mine tailings, stream sediments soils, groundwater, surface water and mine water is shown in Figure 2. In Anka area, average SFPI in the media are in the following order: mine water (25.69) > mine tailings (19.94) > surface water (3.16) > groundwater (2.04) > stream sediment (0.98) > soil (0.93). In Arufu, SFPI in the media decreases in the following order: mine tailings (26.73) > mine water (12.92) > surface water (2.07) > groundwater (1.85) > stream sediment (1.02) > soil (0.81). In Ijero area, SFPI in samples are in the following order: mine tailings (23.15) > mine water (14.33) > groundwater (2.44) > soil (2.04) > stream sediment (1.66) > surface water (1.56). The study revealed that in Anka, mine water, mine tailings, surface water and groundwater are contaminated by TI (SFPI >1) while stream sediments and soils are not contaminated by TI (SFPI < 1). In Arufu, only soil is uncontaminated by TI while other media are contaminated by it. In this area, mine tailings are the most contaminated.



**Figure 2.** Single factor pollution index (SFPI), contamination factor (CF) and enrichment factor (EF) of TI in media.

However, in Ijero area all media are contaminated by TI, with mine tailings most contaminated and surface water least contaminated (Figure 2). Mine tailings which are waste products originating from host rocks housing the desired ores have higher degree of contamination than other media. This is possible due to the high concentration of TI in rocks which are above the background value (Table 4). Interactions of groundwater and surface water with TI laden rocks in the area provide avenues for TI to migrate into these media. Studies such as [2,11,63] have shown that TI pose very high degree of contamination in the environment.

### 3.4. Toxicity of TI in soils, sediments and tailings

The toxic units (TU) for TI in soils, sediments, tailings and rocks are shown in Figure 3. The results uncovered that TI in mine tailings and rocks were more toxic because the TU was above the severe effect level (SEL) of 4 while TU of TI in soils and sediments are below the SEL level. This showed that TI in soils and sediments of the area do not pose any toxicological effects on the ecosystem in the present condition [68]. TI occurs naturally in the environment at low concentrations [11]. It is easily attached to the soil and tailing matrix limiting its movement and may be introduced to the aquatic environment thus increasing the chronic exposure risks [11].

### 3.5. Distribution and contamination of TI in plants

The concentrations of TI in various plants grown around mining sites in the study area is shown in Table 5. The average values of TI in different parts of maize in Anka area: root: 1.78  $\mu\text{g/g}$ ; stem: 0.69  $\mu\text{g/g}$ ; leaf: 1.44  $\mu\text{g/g}$  and grain: 0.72  $\mu\text{g/g}$ . The total content of TI in plants are 4.63  $\mu\text{g/g}$ . For sorghum, the mean values of TI in different parts of the plant are: root: 1.06  $\mu\text{g/g}$ ; stem: 1.17  $\mu\text{g/g}$ ; leaf: 1.98  $\mu\text{g/g}$  and grain: 0.55  $\mu\text{g/g}$ . The total content of TI in plants are 4.76  $\mu\text{g/g}$ . In Arufu, the mean values of TI in different parts of maize are: root: 1.87  $\mu\text{g/g}$ ; stem: 0.95  $\mu\text{g/g}$ ; leaf: 1.67  $\mu\text{g/g}$  and grain: 0.71  $\mu\text{g/g}$ . with a total content 5.20  $\mu\text{g/g}$  while for sorghum the mean values of TI in different parts of maize are: root: 0.85  $\mu\text{g/g}$ ; stem: 0.46  $\mu\text{g/g}$ ;

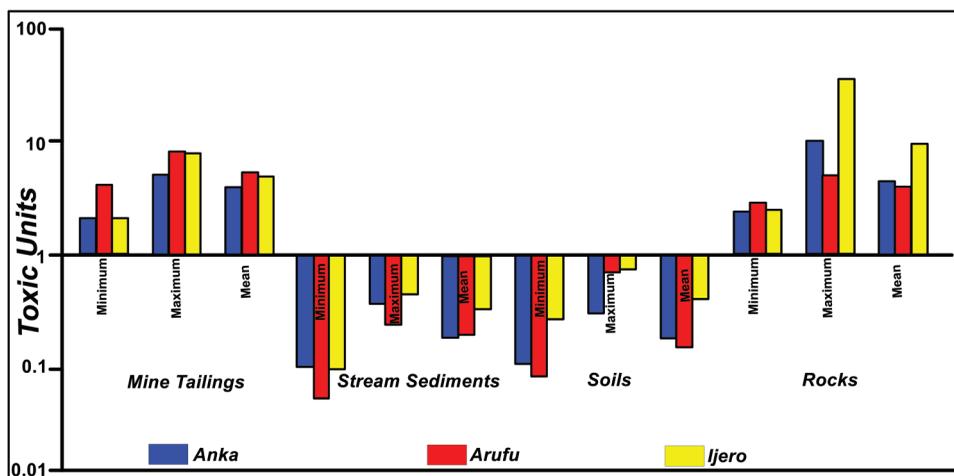


Figure 3. Toxicity values of TI in soils, sediments, mine tailings and rocks.

**Table 5.** Average Concentrations and Contamination Load Index (CLI) of Tl in Plants from the Mining Sites.

		Anka				Arufu				Ijero			
		Root	Stem	Leaf	Grain	Root	Stem	Leaf	Grain	Root	Stem	Leaf	Grain
Maize	<b>Conc.</b>	1.78	0.69	1.44	0.72	1.87	0.95	1.67	0.71	1.37	0.98	1.13	0.61
	<b>CLI</b>	17.80	6.90	14.40	7.20	18.7	9.50	16.7	7.10	13.7	9.80	11.3	6.10
Sorghum	<b>Conc.</b>	1.06	1.17	1.98	0.55	0.85	0.46	0.65	0.39	-	-	-	-
	<b>CLI</b>	10.60	11.7	19.80	5.50	8.50	4.60	6.50	3.90	-	-	-	-
Onion	<b>Conc.</b>	-	-	-	-	1.39	-	1.50	-	-	-	-	-
	<b>CLI</b>	-	-	-	-	13.9	-	15.00	-	-	-	-	-
Soko	<b>Conc.</b>	-	-	-	-	-	-	-	-	2.15	1.12	2.19	-
	<b>CLI</b>	-	-	-	-	-	-	-	-	21.5	11.20	21.9	-
Ewedu	<b>Conc.</b>	-	-	-	-	-	-	-	-	0.94	0.56	0.89	-
	<b>CLI</b>	-	-	-	-	-	-	-	-	9.40	5.60	8.90	-

leaf: 0.65  $\mu\text{g/g}$  and grain: 0.39  $\mu\text{g/g}$ , with a total content 2.35  $\mu\text{g/g}$ . Also in this area the average value of Tl in onions are: root: 1.39  $\mu\text{g/g}$  and leaf: 1.50  $\mu\text{g/g}$  with a total concentration of 2.89  $\mu\text{g/g}$ . In Ijero area, the average concentration of Tl in maize are: root (1.37  $\mu\text{g/g}$ ); stem (0.98  $\mu\text{g/g}$ ); leaf (1.13  $\mu\text{g/g}$ ) and grain (0.61  $\mu\text{g/g}$ ) with a total concentration of 4.09  $\mu\text{g/g}$  while the mean values in different parts of soko are: root: 2.15  $\mu\text{g/g}$ ; stem: 1.12  $\mu\text{g/g}$  and leaf: 2.19  $\mu\text{g/g}$  with a total of 5.46  $\mu\text{g/g}$ . Furthermore, the average concentration of Tl in ewedu are 0.94  $\mu\text{g/g}$ , 0.56  $\mu\text{g/g}$  and 0.89  $\mu\text{g/g}$  with a total value of 2.39  $\mu\text{g/g}$ . Total values are higher than average abundances compared to land plants worldwide which is between 0.008 and 1.00  $\mu\text{g/g}$  [69]. The results were also consistent with those obtained by [2,70]. Also, crops grown on soils and mine wastes in the area were contaminated by Tl, with edible parts above the acceptable limits for Tl as reported by Pavlickova et al. and [47]. High values of Tl in plants of the area indicate that crops in the area are highly contaminated with the metal from topsoils resulting from prolonged mining activities in the area. Also, the elevated concentration of Tl in plants also showed that Tl is preferentially assimilated by the plants because it has geochemical affinity with K [2,47]. Thallium enrichment in plants of the area are species dependent. In Anka Tl concentrations in plants were in the following order: sorghum > maize while in Arufu, it is in the following order: maize > onion > sorghum. In Ijero Tl concentration in plant is in the following order: soko > maize > ewedu (Table 5). The contamination load index (CLI) of Tl in plants of the area (Table 5) showed that the CLI is greater 1. This implied that plants in this area are contaminated by the metal.

The average BCF values for Tl in maize and sorghum in Anka are 11.28 and 15.46 respectively while in Arufu, BCF for Tl in maize, onion and sorghum are 10.58, 17.09 and 7.10 each (Table 6). In Ijero, The mean BCF values for Tl in maize, soko and ewedu are 4.35, 5.46 and 4.06 respectively. For Tl in crop sample, BCF were found to be high, all above 1, reflecting the availability from soils. In Anka, the highest BCF was found in sorghum, showing that Tl was more in it than in other crops while in Arufu, onion, a root plant had highest BCF more than other plants reflecting that Tl was more available in onion than other crops in the area. In Ijero, BCF in soko, a vegetable is higher than those of other plants. The average BCF values for Tl in different parts of maize and sorghum from Anka ranged from 1.72 to 4.34 and 3.41 to 6.39 while for different parts of maize, onion and sorghum in Arufu, it ranged from 1.04 to 4.30, 3.70 to 7.03 and 1.17 to 2.56. In maize, soko and ewedu from Ijero, the mean BCF ranged from 0.61 to 1.37, 1.12 to 2.19 and 0.95 to 1.59. The BCF values were greater than 1 in roots of all plants while it was higher than 1 in stems of plants except in maize and ewedu from Anka and

**Table 6.** Bioconcentration Factor (BCF) of Tl in plants cultivated around mining areas.

	Plant	Root	Stem	Leaf	Grains
Anka	<b>Maize</b>	3.63	1.60	4.65	1.99
	<b>Maize</b>	4.9	2.45	3.83	1.79
	<b>Maize</b>	4.06	0.94	2.89	2.17
	<b>Maize</b>	4.76	1.91	2.59	0.93
	<b>Mean</b>	<b>4.34</b>	<b>1.73</b>	<b>3.49</b>	<b>1.72</b>
Arufu	<b>Sorghum</b>	3.41	3.77	6.39	1.89
	<b>Maize</b>	1.62	1.26	1.38	1.03
	<b>Maize</b>	6.98	1.43	6.41	1.04
	<b>Mean</b>	<b>4.3</b>	<b>1.35</b>	<b>3.89</b>	<b>1.04</b>
	<b>Onion</b>	6.99	3.75	6.76	-
	<b>Onion</b>	5.73	3.65	7.29	-
	<b>Mean</b>	<b>6.36</b>	<b>3.7</b>	<b>7.03</b>	-
Ijero	<b>Sorghum</b>	2.56	1.39	1.98	1.17
	<b>Maize</b>	1.12	1.04	0.88	0.86
	<b>Maize</b>	1.62	0.93	1.38	0.36
	<b>Mean</b>	<b>1.37</b>	<b>0.99</b>	<b>1.13</b>	<b>0.61</b>
	<b>Soko</b>	2.15	1.17	1.99	-
	<b>Soko</b>	2.14	1.07	2.39	-
	<b>Mean</b>	<b>2.15</b>	<b>1.12</b>	<b>2.19</b>	-
	<b>Ewedu</b>	1.59	0.95	1.52	-

Ijero. BCF values in leaves of plants are greater than 1 in all samples except in maize from Ijero. Average BCF in grains of maize in Anka and Ijero are less than 1. In Anka, the trend of BCF in maize and sorghum are root > leaf > stem > grains while in Arufu the trend of BCF in maize and sorghum is roots > leaf > stem > grains while in onion the trend is leaf > root > stem. In Ijero, the trend of BCF in maize is roots > leaf > stem > grains while in soko the trend is leaf > root > stem and in ewedu the trend is root > leaf > stem. In study, Tl showed higher enrichment in roots and leaves than in the stems and grains in all crop samples from the study area. Higher concentration of Tl in leaves of plants in this area may be attributed to the presence of stomata which assimilate and interact with contaminated aerosols from the mines [16]. Presence of the metal in shallow soil also poses threats due to assimilation by plant roots and storage in plant biomass. As a result, thallium may enter the food chain and accumulate in living organisms, causing severe disorders and ultimately becoming fatal [11]. Tl is mostly enriched in the roots. This may be because roots are in direct contact with soils, tailings and/or surface waters, where Tl contents were found to be much higher compared to dusts [71]. Due to their high capacities to uptake Tl, these plants may be used for phytoremediation. Also, Tl is taken up by vegetation and the extent of uptake determined by soil acidity and plant species. Since soils, sediments and tailings in the area are mainly acidic, the mobility of the metal are highly affirmed.

### 3.6. Potential ecological risk assessment

Potential ecological risk index (PERI) is a known measurement that quantitatively reveals the overall potential ecological risk due to contamination [30]. PERI for Tl in media are shown in Table 7. In Anka, the mean values  $E_r$  in soil are 37.29. Of the total soil samples from this area, Tl pose low ecological risk in the 27 soil samples while it poses moderate ecological risk in 14 samples. For sediments, the mean  $E_r$  is 39.36. Tl pose low ecological risk in 13 of the samples while it poses moderate ecological risk in 9 of the samples. The

**Table 7.** Single potential ecological risk of samples.

		Minimum	Maximum	Mean	Er<40	40≤ Er<80	80≤ Er<160	160≤ Er<320	Er≥320
					Low	Moderate	Considerable	High	Very High
Anka	<b>Soil</b>	22.00	67.00	37.29	27	14	0	0	0
	<b>Sediments</b>	21.00	75.00	39.36	13	9	0	0	0
	<b>Mine tailings</b>	518.00	1000.00	797.78	0	0	0	0	14
	<b>Groundwater</b>	20.23	278.57	81.65	10	9	9	5	0
	<b>Surface water</b>	25.68	559.63	126.52	3	3	5	1	1
Arufu	<b>Mine water</b>	255.48	1790.47	1027.51	0	0	0	2	8
	<b>Soil</b>	17.00	142.00	32.47	29	1	2	0	0
	<b>Sediments</b>	11.00	49.00	40.71	1	6	0	0	0
	<b>Mine tailings</b>	827.00	1624.00	1069.25	0	0	0	0	8
	<b>Groundwater</b>	30.09	147.25	74.16	2	6	3	0	0
Ijero	<b>Surface water</b>	2.14	199.97	82.79	2	2	0	3	0
	<b>Mine water</b>	139.65	1062.21	516.73	0	0	1	2	3
	<b>Soil</b>	54.00	150.00	81.55	0	12	8	0	0
	<b>Sediments</b>	20.00	91.00	66.41	2	11	4	0	0
	<b>Mine tailings</b>	198.00	1568.00	925.93	0	0	0	1	14
	<b>Groundwater</b>	37.75	194.67	97.40	1	6	6	2	0
	<b>Surface water</b>	29.92	142.12	62.56	2	6	2	0	0
	<b>Mine water</b>	325.59	800.02	573.20	0	0	0	0	5

mean ecological risk for mine tailings from this area is 797.78. TI in all the tailing samples poses very high ecological risk. In groundwater, Er has an average of 81.65. TI poses low, moderate, considerable and high ecological risks in 10, 9, 9 and 5 groundwater samples respectively. For surface water, the mean Er is 25.68, 559.63 and 126.52 each. In the samples, TI poses low, moderate, considerable, high and very high ecological risk in 3, 3, 5, 1 and 1 samples respectively. Minewater have an average of 1027.51. TI poses high and very high ecological risks in 2 and 8 mine water samples respectively.

In Arufu, the mean Er in soils was 142 it pose low, moderate and considerable risks in 29, 1 and 2 samples each while in stream sediments, the mean Er were 49, posing low and moderate risks in 1 and 6 samples each. For mine tailings, the mean Er is 1624. TI in all the tailings poses very high ecological risks. For groundwater, the average Er of TI is 74.16, posing low, moderate and considerable risks in 2, 6 and 3 samples respectively. For surface water, the mean Er is 82.79, posing low, moderate, and high ecological risks in 2, 2 and 3 samples respectively. For minewater, average Er is 516.73 each. TI poses considerable, high and very high ecological risks in 1, 2, and 3 samples respectively.

In Ijero soils, the mean Er of TI is 81.55, posing moderate and considerable risks in 12 and 8 samples each while in stream sediments the mean Er is 66.41. TI poses low, moderate and considerable ecological risks in 2, 11 and 4 samples respectively. The mean Er for mine tailings are is 925.93 each, posing high and very high ecological risks in 1 and 14 samples respectively. For groundwater, the average Er is 97.40, posing low, moderate, considerable and high ecological risks in 1, 6, 6 and 2 samples each. For surface water, the average Er of TI was 62.56, posing low, moderate and considerable risks in 2, 6 and 2 each. For mine water, average of 573.02, posing very high ecological risks in all the samples. Results obtained from this study are similar to high ecological risks of TI in surface sediments, reported by [72], in Yangtze estuary and Poyang Lake, China, soils as presented by [30], in Henan province, China, wastewater reported by [47]. According to

[10], favourable geoenvironment may lead to dispersion of naturally occurring TI and may create environmental health hazards.

### 3.7. Human health risks of TI

To ascertain the health risk imposed by toxic elements on humans, it is necessary that exposure level of a metal must be determined [73]. There are many exposure pathways that aid the movement of toxic metals into humans, but the food chain is the most crucial pathway [74]. Crops grown in Anka, Arufu and Ijero areas are highly contaminated with TI, and the ingestion of food stuffs from such crops may contribute significantly to increase diseases in human beings. In this study, the daily intake of TI was calculated using the average vegetable and grain consumptions. The estimated daily intake of metals (DIM) through the food chain for adults and children are presented in Table 8. In Anka area, the estimated amounts of TI intake via consumption of maize and sorghum grains were 2.47E-02 and 2.02E-02 mg/kg/d for local adults and 3.15E-02 and 2.58E-02 for local children. In Arufu area, the estimated daily intake of onions, maize, and sorghum are 1.55E-02, 2.34E-02 and 1.33E-02 mg/kg/d for adults and 1.45E-02, 2.97E-02 and 1.67E-02 mg/kg/d for children respectively. In Ijero area, the average estimated daily intake of maize (grain), ewedu and soko (vegetables) are 2.44E-02, 3.25E-02, and 5.31E-02 mg/kg/d for adults and 2.28E-02, 4.15E-02 and 6.77E-02 mg/kg/d for children. In Anka and Arufu areas, for both adults and children, the highest intake of TI was through the ingestion of maize while in Ijero, the highest intake of TI for adult and children was from soko. In all the areas, it was observed that children consumed more TI from than adults.

In the study areas, crops are planted on contaminated mine wastes and soils, and are irrigated by contaminated mine water during dry seasons. For these reasons, the mean TI concentration in food crops were used to calculate HRI. The HRI of TI through the consumption of food crops for adults and children is given in Table 8. The HRI for TI ranged from 161 to 421 for adults and 205 to 537 for children in Anka while in Arufu, it

**Table 8.** Daily Intake of Metals (DIM) and Health Risk Index (HRI) of TI.

		Adults	Child	HRI Adult	HRI Child
Anka	Maize ( <i>Zea mays</i> )	2.89E-02	3.68E-02	3.61E+02	4.60E+02
	Maize ( <i>Zea mays</i> )	2.34E-02	3.00E-02	2.95E+02	3.76E+02
	Maize ( <i>Zea mays</i> )	3.37E-02	4.29E-02	4.21E+02	5.37E+02
	Maize ( <i>Zea mays</i> )	1.29E-02	1.64E-02	1.61E+02	2.05E+02
	<b>Average</b>	<b>2.47E-02</b>	<b>3.15E-02</b>	<b>3.10E+02</b>	<b>3.95E+02</b>
	Sorghum ( <i>Sorghum bicolor</i> )	2.02E-02	2.58E-02	2.53E+02	3.22E+02
Arufu	Onion ( <i>Allium cepa</i> )	1.99E-03	1.49E-03	2.49E+01	1.87E+01
	Onion ( <i>Allium cepa</i> )	2.91E-02	1.45E-02	3.64E+02	1.81E+02
	<b>Average</b>	<b>1.55E-02</b>	<b>8.00E-03</b>	<b>1.94E+02</b>	<b>9.99E+01</b>
	Maize ( <i>Zea mays</i> )	4.29E-02	5.46E-02	5.34E+02	6.83E+02
	Maize ( <i>Zea mays</i> )	3.84E-03	4.89E-03	4.80E+02	6.12E+01
	<b>Average</b>	<b>2.34E-02</b>	<b>2.97E-02</b>	<b>5.07E+02</b>	<b>3.72E+02</b>
Ijero	Sorghum ( <i>Sorghum bicolor</i> )	1.33E-02	1.69E-02	1.66E+02	2.12E+02
	Ewedu ( <i>Corchorus olitorius</i> )	<b>3.25E-02</b>	<b>4.15E-02</b>	<b>4.03E+02</b>	<b>5.18E+02</b>
	Maize ( <i>Zea mays</i> )	3.57E-02	4.54E-02	4.46E+02	5.68E+02
	Maize ( <i>Zea mays</i> )	1.31E-02	1.67E-02	1.64E+02	2.09E+02
	<b>Average</b>	<b>2.44E-02</b>	<b>2.28E-02</b>	<b>3.05E+02</b>	<b>3.89E+02</b>
	Soko ( <i>Celosia argentea</i> )	5.19E-02	6.61E-02	6.48E+02	8.26E+02
	Soko ( <i>Celosia argentea</i> )	5.43E-02	6.92E-02	6.79E+02	8.65E+02
<b>Average</b>	<b>5.31E-02</b>	<b>6.77E-02</b>	<b>6.64E+02</b>	<b>8.46E+02</b>	

ranged from 24.90 to 534.00 for adults and 18.70 to 683.00 for children. In Ijero, HRI for Tl ranged from 164 to 679 for adults and 209 to 865 for children. HRI values from all the crops in the three areas were above 1, which suggest that health risks associated with Tl are significant. This implied that health risks of Tl exposure through the food chain are generally assumed to be high in the mining areas. The estimated dietary intakes of Tl through maize, sorghum, onion, ewedu and soko exceeded recommended RfD for Tl which is pegged at  $8.00E-05$  mg/kg/d [45]. In general, RfD is an estimation of daily exposure of human beings at which no significant risk of dangerous metals can affect them during a life time [47]. The findings revealed that consumption of crops grown on toxic metals contaminated soils and tailings pose great human health problems, which may be aggravated through oral ingestion, dermal contact and inhalation of contaminated soils, sediments, water and weathered rocks by local inhabitants. Although Tl is not metabolised, studies in humans and animals revealed that thallium compounds are easily absorbed through various exposures routes. [75], reported that water soluble salts are rapidly and completely absorbed from the respiratory tract, gastrointestinal (GI) tract, or skin. [76,77], showed that Tl ions have been detected in the urine of exposed humans and animals [78,79] from environmental sources. [80], also revealed that Tl is rapidly distributed very early throughout the body regardless of the route of exposure, dose, and length of exposure [81]. Kidneys are known to absorb the highest amount of thallium whereas the brain have the lowest concentrations. Also, Tl it has been shown to pass through the placenta in humans [82]. Research have revealed that Tl have effects on testes and sperm and subsequently male fertility in rats [83] and mice [84]. Tl exposure during growth can cause abnormalities of the nervous system and bones and also cause reduced foetal body weight and is linked with oral ingestion of Tl contaminated water [85].

#### 4. Conclusions

The contamination of Tl with its possible toxicological, ecological and human health risks in soils, sediments, mine tailings, rocks, water and plants around selected mining areas in Nigeria were investigated in this research. It was observed mining activities led to Tl contamination of soils, sediments, mine tailings, water and plants. Average thallium concentrations in all media were higher compared with those in the background samples. The PI values indicated that soils are uncontaminated by Tl while mine tailings and mine water are extremely contaminated by Tl.

Ecological risk assessment revealed that Tl in samples poses low to considerable risk in soils and sediments in the study area while it poses high to very high ecological risk in mine tailings and mine water from these areas. Tl in groundwater and surface water in these areas poses low to very high ecological risks. This showed that Tl is a great threat to both living and non-living components of the ecosystem in these areas. Tl showed high accumulation in crops in the study area, and may possibly be adduced to the substitution of Tl for K. The enrichment of Tl is higher in vegetables than in grains. Due to excessive uptake of Tl by crops, Tl is may be considered as one of the main toxic metals that may instigate poisoning in the area. The DIM values of Tl for both adults and children through food crops were higher than the USEPA recommended RfD limits. HRI values were above 1 through edible plants, indicating that exposure of local inhabitants to Tl pose significant and generally dangerous health issues. It is important that investigations of Tl in

environmental media around mining and other high human activities areas in Nigeria and other parts of Africa should be stepped up to avert health issues related to Tl poisoning. Complete remediation of areas around contaminated mining sites should be carried and regular awareness of populace about the dangers of toxic metals is recommended.

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The authors declare that no conflict interest exist in this study.

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