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Original Article

Assessment of natural radionuclides and heavy metals contamination to the environment: Case study of Malaysian unregulated tin-tailing processing industry

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ABSTRACT

The tin tailing processing industry in Malaysia has operated with minimal regard and awareness for material management and working environment safety, impacting the environment and workers in aspects of radiation and heavy metal exposure. RIA was conducted where environmental samples were analyzed, revealing concentrations of ^{226}Ra, ^{232}Th and ^{40}K between the range of 0.1–10.0, 0.0–25.7, and 0.1–5.8 Bq/g respectively, resulting in the AED exceeding UNCEAR recommended value and regulation limit enforced by AELB (1 mSv/y). Ra_{eq} calculated indicates that samples collected pose a significant threat to human health from gamma-ray exposure. Assessment of heavy metal content via pollution indices of soil and sediment showed significant contamination and enrichment from processing activities conducted. As and Fe were two of the highest metals exposed both via soil ingestion with an average of 4.6×10^{-3} mg/kg-day and 1.4×10^{-4} mg/kg-day, and dermal contact with an average of 5.6×10^{-4} mg/kg-day and 6.0×10^{-4}. mg/kg-day respectively. Exposure via accidental ingestion of soil and sediment could potentially cause adverse non-carcinogenic and carcinogenic health effect towards workers in the industry. Correlation analysis indicates the presence of a relationship between the concentration of NORM and trace elements.

1. Introduction

Since the large drop in tin demands and process in the 80s, Malaysia, as one of the global tin producers has since focused on the extraction of valuable metals and minerals from the by-products of the industry that has accumulated over the years [1,2]. Said by-products (in the form of tailing) contains significant concentrations of Ilmenite, Rutile, Monazite, Zircon, and many other minerals containing rare earth elements and heavy metals that could be extracted using specific methods which could later be used in other applications [1,3–5]. However, the main challenge faced by the industry to this day is the safety conduct as the materials handled and produced contain significant concentrations of naturally occurring radioactive material (NORM) and harmful heavy metals that could result in adverse health effects [1,6–12].

The industrial practice applied in the tin tailing industry has been in use for several decades which, to this day, still employs several procedures that could introduce hazards to not only the workers but also to the environment; one of which is the lack of a processing storage facility and waste management systems [1,3] where the materials are kept in large stockpiles in the open air with neither bottom nor top cover, increasing the likelihood of inhalation or accidental ingestion of humans as well as leaching to the soil below for the environment [13,14]. Additionally, external exposure to radiation and heavy metal through the skin could also cause health complications if exposed continually [13,14]. As different heavy metals cause different reactions, cytotoxic heavy metals are the most concerning as they pose the risk of high damage to human

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cells and tissues due to their toxic and carcinogenic properties [15].

Several studies have also been conducted in other counties with regards to the impact that the industry poses; a study done in a Nigerian Tin mine shows an average annual dose (1.44 mSv) that exceeds the regulator limit, especially in mining pits and processing sites [11]. Supporting this is a study done by Abba where findings yield similar values in tin mining areas in Jos Plateau with an annual effect dose ranging between 0.31 and 1.2 mSv/year [16]. Several studies have also been done in Indonesian tin mining and processing sites revealing that concentrations of not only NORM but also heavy metals in the surrounding environment as well as the material indicate concerning values that could cause harm to human health [10,17–19]. The culmination of these studies indicates a common unresolved issue that presents a danger to the citizens involved in the industry.

At the present moment, the Malaysian regulatory body for radiation protection and safety, the Atomic Agency Licensing Board (AELB) does not have strong jurisdiction on the conduct of the tailing processing plant as the exemption order created in 1994 allowed said plants to continually operate without the need for a valid license. This allows them to bypass most prerequisites that the licensing act 1984 demands, which extends to the PPE provisions, exposure monitoring, and proper shielding of sites and facilities [20,21]. Though these processing plants operate in accordance with rules and regulations of the mineral development act 1994, which is heavily tied to the Environmental Quality Act 1974, the extent of supervision and monitoring by the governmental body is uncertain as the occurrence of environmental as well as radiological contamination would presumably be from the same source.

Studies in the last decade have provided significant evidence showing that the industry has caused a significant impact on the environment which subsequently leads to human exposure [22–26]. Recent studies on the other hand show results that are parallel but cover only a specific portion in terms of either human exposure or environmental pollution caused by the industry [1,3,11,18]. This study aims to provide a more comprehensive layout of the situation in tin tailing processing plants both in terms of radiological impact assessment and heavy metal contamination towards humans and the environment. To achieve this, the objective of the study is to measure the concentration of NORM and heavy metal in the environment as well as tailing samples to assess the presence of hazards and risks posed towards workers and the environment.

2. Materials and method

2.1. Sampling, sample processing, and analysis

The study was centred around four processing plants located in the state of Perak Malaysia, where three types of samples (soil, tailing, sediment) were collected compositely. Fig. 1 shows the study site with a visual representation of the stockpiles that could be found in most processing plants.

A total of 16 soil samples were collected at key routes within the processing plants at a depth of 5–15 cm below surface level using a hand auger while 23 tailing samples were collected similarly however was done directly on to the stockpiles found in the vicinity of the processing plant. 8 sediment samples in total were collected from pools containing water used during tailing processing using a handmade sampler. A total of 2 kg of each sample was collected and

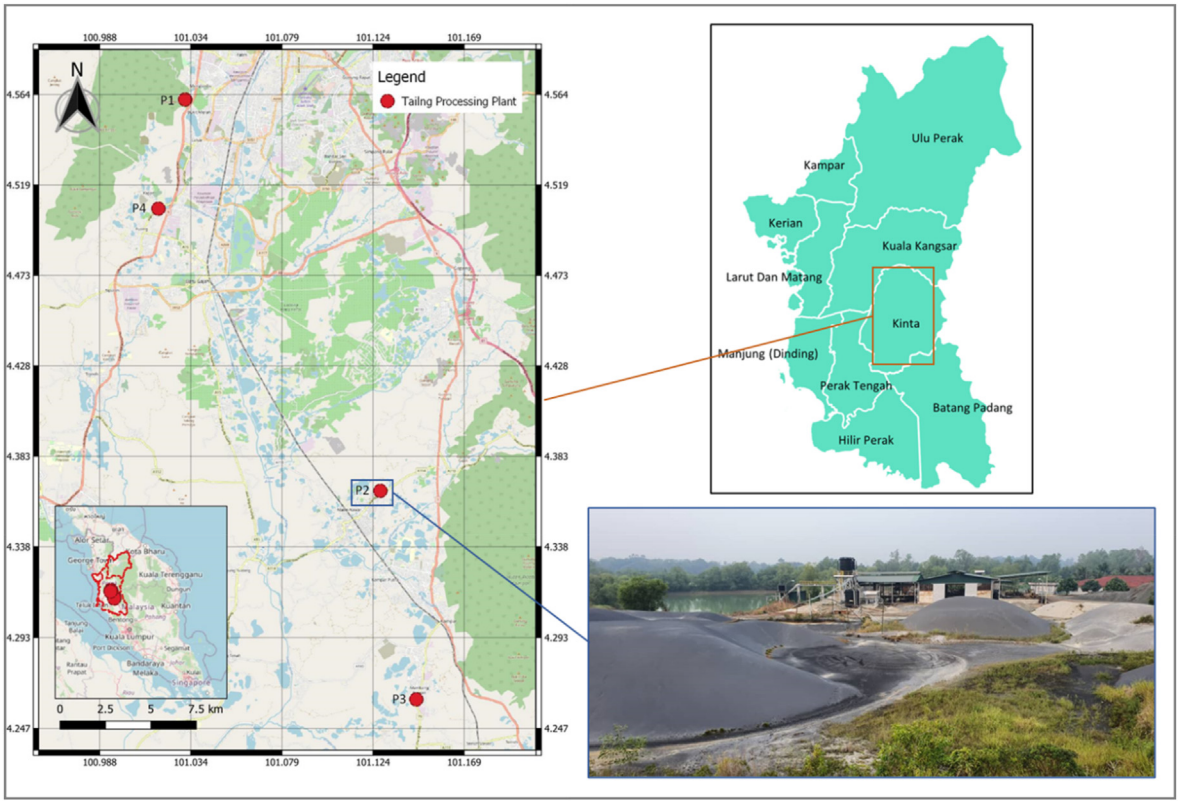


Fig. 1. Study site and visual representation of stockpiles commonly found in processing plants.

secured in polyethylene containers to ensure no cross-contamination occurs [27]. As a base of comparison, four control soil samples were also collected in publicly accessible clean, free from any processing activities. All samples were oven-dried for 24 h at a temperature of 105 °C until a constant mass was achieved. Samples were then ground and sieved using a 500 μm sieve to ensure complete homogeneity [28].

2.2. Natural radioactive analysis

Each sample was triplicated, bottled, sealed airtight, and stored for 3 weeks to ensure radionuclides and their respective progenies are in secular equilibrium. The concentrations of ^{226}Ra, ^{232}Th, and ^{40}K were determined by counting each sample for 12 h using a gamma spectrometry system which is equipped with a Hyper-Pure Germanium detector paired with the Genie 2000 data analysis software. Encased in a thick Pb housing to reduce interference from background radiation, the system was calibrated using a multi-nuclied standard. The photopeaks used in the study were the peaks of ^{214}Pb (351 keV) and ^{214}Bi (1764 keV) to determine concentrations of ^{226}Ra while the phototpeaks of ^{288}Ac (911 keV) and ^{208}Tl (2614 keV) for ^{232}Th while the photopeak used for ^{40}K is 1461 keV. The IAEA-375 soil was used as the known standard reference material in this study which was counted for 12 h as well.

$$DL = 2.71 + 4.66\sqrt{N_b} \quad (1)$$

$$MDA = \frac{DL}{T\varepsilon BM} \quad (2)$$

where N_b denotes the background count, DL denotes the detection limit, T being the counting time is seconds, B denoting the braching ratio factor and M being the mass of sample. The DL values calculated using equation (1) were 74.2 ± 9.54, 58.56 ± 7.43, 92.29 ± 10.36, 42.14 ± 6.68 and 58.78 ± 9.61while the calculated MDA values were 2.36 ± 0.3, 2.85 ± 0.36, 25.1 ± 2.82, 1.18 ± 0.19 and 0.56 ± 0.09 for photopeaks 2614, 1764, 1460, 911, and 351 keV respectively.

To ensure the data collected was reliable, the detection limit and Minimum Detectable values were also calculated using equation (2). were found to be in the acceptable range [29–31]. The concentration of radionuclide in samples could be determined using equation (3) [32,33].

$$C = \frac{M_{std} \times A_s}{M_s \times A_{std}} C_{std} \quad (3)$$

where C and C_{std} denote the concentration of radionuclide (Bq/g), M and M_{std}, refer to the mass (g), while A and A_{std} refer to the net count of both sample and standard respectively.

2.3. Heavy metal content analysis

A mass of 0.1g of each sieved sample was digested with both 6 ml of hydrochloric acid and 4 ml of nitric acid respectively and digested in the acid digestion oven at a pressure of 55.19, with stage 1 at 165 °C for 0–20 min and stage 2 at 195 °C for 20–35 min (set 10 min). The solution is then diluted to a final volume of 100 ml [34,35]. Each sample is then analyzed for heavy metal contradiction using the Induced coupled plasma-mass spectroscopy, (ICP-MS, model ELAN 9000; PerkinElmer SCIEX). The study is focused on 8 elements which are Cd, Cr, As, Pb Ni, Zn, Cu, and Fe.

To ensure the reliability of the data, the system was calibrated using the manufacturers multielement standard (PerkinElmer Pure Plus Multielement Calibration Standard 3) which achived a calibration curve with a correlation coefficient above 0.95 for the metals being analyzed. The quantification of the elements in the samples was based on the 7-point calibration curve. Quality control of system output was conducted by running analysis using a known standard as a sample and cross checking the output heavy metal concentration with the known concetration, which indicates to the study that the system used is operating within the acceptable ranges.

Since tailings are the main source of pollutants in this study, verification of mineral content was done on each tailing sample via X-ray diffraction analysis to determine the minerals present in the samples which affect the degree of pollution of the study site. All tailing samples were ground finely and sieved at a mesh of 250 μm before being placed into the sample holder and examined using Bruker D8-advance diffractometer with a Cu Kα source (λ = 0.1542 nm). The spectrum obtained from the analysis was analyzed by Diffrac.eva software by comparison with the International Centre Diffraction data.

3. Results and discussion

Table 1 shows the average concentration of NORM radionuclides measured in the samples collected from the study sites with the highest values are shown to be from tailing samples with an average of ^{238}U, ^{232}Th, and ^{40}K 3.0 ± 2.3 Bq/g, 4.7 ± 5.9 Bq/g and 0.7 ± 1.2 Bq/g respectively. The study also found that the average concentration of radionuclides in soil samples collected from the study site also contains comparable concentrations being 1.6 ± 0.2 Bq/g, 3.0 ± 0.4 Bq/g, and 0.3 ± 0.0 Bq/g respectively. When compared to the control soil samples, the soil samples from the processing plants show a large discrepancy as an observable elevation could be seen.

This could be attributed to the processing activities done on the study site itself where the materials and by-products containing minerals commonly associated with high NORM concentrations were stored in large stockpiles in direct contact with the earth as shown in Fig. 2, increasing the likelihood of contamination significantly, namely Monazite, Zircon Ilmenite and Rutile [1,24,36]. Studies towards these processing plants have been conducted nearly a decade ago with no new development to the present day, yet the results shown in this study shows that no significant improvements have been done to the industry as the findings show similar if not more severe contamination compared to older studies [22–24,37].

An analysis of variance was also conducted on the samples categorized by the specific plants they where collected from and showed that there was a large statistical difference in NORM concentration amongst all processing plants. The study would attribute this finding to the difference in operational states as well of each processing plant as the state of operations for each differs; at the time of study, P1, P2, and P3 were still in full operation while P4 was not actively processing and extracting heavy minerals. Though still in operation, samples collected from P1 was seen to be considerably lower compared to the other processing plants due to the presence of on-site safety officers that supervises the overall operations of the plant. The study discovered that the standard practice at P1 is that the safety officers would monitor the environmental conditions on-site and send monthly reports to the department of environment. The constant monitoring and close supervision would likely be the reason why NORM contamination levels were considerably lower compared to the rest.

Additionally, findings also revealed that a large portion of the total sample counted had already exceeded the radiation regulation limit set by the (AELB) [21]. The regulation set in place by the licensing board is based on the estimation made by the United

Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) that material an activity concentration of 1 Bq/g could result in an exposure of 1 mSv and beyond per year.

3.1. Radiological impact assessment of activities towards the industry

Radiological impact and risk assessment was conducted by first assessing the absorbed (D) and annual effective dose (AED) using equations (4) and (5) [40]:

$$D\ (nGyh^{-1}) = 0.462\ C_{Ra} + 0.604\ C_{Th} + 0.0417\ C_K \quad (4)$$

$$AED\ (mSv) = (D) \times T \times 0.7\ Sv/Gy \times 0.2 \times 10^{-6} \quad (5)$$

Where C_{Ra}, $C_{Th,}$ and C_K refer to the concentration of ^{226}Ra, ^{232}Th, and ^{40}K in a sample, respectively. 0.7 Sv/Gy denotes the conversion factor while 0.2 denotes the fraction of time workers spend outdoors out of the total time (T) of 8760 h/year [39].

Study findings show that both the calculated absorbed and annual effective dose were found to have exceeded the recommended values proposed by the UNSCEAR (20nGy/h − 200 nGy/h and 1 mSv/y respectively) [39] for most samples collected. Because the current regulations exempt the tin tailing processing industry from requiring a license to operate, the AED limit capped for the workers is limited similar to that of which as members of publics' (1 mSv/y) [20]. This indicates that workers in the industry are most likely to have received doses above the permissible level.

The assessment of radiological exposure hazard from environmental material was done by calculating the radium equivalent activity via equation (6) with the generally accepted assumption that gamma radiation exposure produced by 370 Bq/kg of ^{226}Ra, 259 Bq/kg of ^{232}Th, and 4810 Bq/kg of ^{40}K results in the equal dose rates [30,41]:

$$Ra_{eq=}C_{Ra} + 1.42C_{Th} + 0.077C_K \quad (6)$$

The average values obtained from each plant ranged between the $6.0 \times 10^2 \pm 4.9 \times 10^2$–$2.1 \times 10^4 \pm 8.0 \times 10^3$ Bq/kg for soil samples, $1.4 \times 10^3 \pm 4.6 \times 10^2$–$6.5 \times 10^3 \pm 5.5 \times 10^2$ Bq/kg for sediment samples, and $3.2 \times 10^3 \pm 4.2 \times 10^3$–$1.7 \times 10^4 \pm 1.4 \times 10^4$ Bq/kg for tailing samples. It is evident that the Ra_{eq} values were found to be over the recommended value of 370 Bq/kg. This finding indicates that exposure to samples collected from the study sites tends to cause an exposure rate of above 1 mSv/y, thus exceeding the recommended value for members of public [10]. The data collected was also found to be comparable to a study conducted by Gunawan on Indonesian tin slags.

Additionally, an assessment of risk towards the excess cancer occurrence was done to put the significance of exposure to the material studied. Calculation of the Excess Lifetime Cancer Risk (ELCR) was done according to equation (7) [40].

$$ELCR = AED \times LS \times RF \quad (7)$$

Where (LS) denotes the average life span of an individual while (RF) refers to the risk factor used as provided by the ICRP to be 0.05 [42]. Results found in the study showed the ELCR value ranges between 4.0×10^{-4} to 9.3×10^{-2}. A study done by Abdullahi showed that the results in this study have exceeded not only the average global external ELCR value (0.3×10^{-3}) but also the sum of both global average external and internal ELCR values (1.5×10^{-3}) [40]. This implies that workers in this industry exposed to such conditions pose a higher tendency of developing cancer compared to the average members of public who reaches the age of 70. However, it must be noted that despite the values, the significance of the elevation of risk is relatively small [11,40]. Table 2 shows the radiological impact assessment based on NORM concentrations in the samples.

Table 1
Concentration of NORM in samples collected from the study site.

Sample Types	Processing plants	No. of Samples	Concentration (Bq/g)			References
			^{226}Ra	^{232}Th	^{40}K	
Soil	P1	12	0.3 ± 0.3	0.2 ± 0.2	0.7 ± 0.4	This study
	P2	9	1.54 ± 0.3	1.7 ± 0.4	0.2 ± 0.0	
	P3	12	5.0 ± 1.5	11.1 ± 4.9	1.2 ± 0.6	
	P4	15	1.6 ± 0.2	2.0 ± 0.4	0.3 ± 0.0	
	F-Value[b]		81.8	54.1	25.3	
	F-Crit[a]		2.8	2.8	2.8	
Sediment	P1	15	0.7 ± 0.3	0.4 ± 0.1	1.4 ± 0.3	
	P2	3	1.1 ± 0.34	1.8 ± 0.4	0.3 ± 0.0	
	P3	3	1.9 ± 0.2	3.2 ± 0.3	0.4 ± 0.1	
	P4	3	0.5 ± 0.0	0.70 ± 0.0	0.2–0.3	
	F-Value[b]		11.3	9.5	5.4	
	F-Crit[a]		2.8	2.8	2.8	
Tailing	P1	9	2.47 ± 2.2	1.1 ± 0.3	0.1 ± 0.0	
	P2	18	3.04 ± 1.12	4.7 ± 4.4	0.5 ± 0.4	
	P3	24	4.47 ± 2.67	8.6 ± 7.7	1.3 ± 1.8	
	P4	18	1.11 ± 1.37	1.3 ± 1.7	0.2 ± 0.2	
	F-Value[b]		24.27	198.2	49.0	
	F-Crit[a]		3.10	3.0	3.1	
Min			0.1	0.0	0.1	
Max			10.0	25.7	5.8	
Control Soil			0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	
Malaysian tin tailing industry			0.0–1.8	0.0–4.5	0.0–0.7	[36]
Indonesian Tin Slag			3.0–7.7	9.9–22.8	0.7–2.2	[10]
Malaysian Soil Average			0.1	0.1	0.3	[39]
Regulatory Body limit			1.00		10	(AELB, 2010)

[a] F-crit denotes the statistical rejection region of the null hypothesis.
[b] F-values exceeding the F-crit values indicate significant statistical differences between NORM concentrations between processing plants.

Fig. 2. Tailing storage situation in tailing processing site.

3.2. Heavy metal concentrations in collected samples

Table 3 shows the concentration of heavy metals measured in collected samples from the processing plants and control locations. Results revealed an observable discrepancy in heavy metal concentration between the type of samples where sediment samples show the highest accumulation of heavy metals following the order of Fe > As > Zn > Pb > Cr > Cu > Ni > Cd. Second to this are the soil samples which follow the trend as sediment samples in terms of elemental concentrations. The average concentration of heavy metals in tailing samples was unexpectedly the lowest amongst the three following the order of Fe > As > Pb > Zn > Ni > Cu > Cr > Cd. XRD analysis shows a varied mineral composition with the most found being Ilmenite, Rutile, Cassiterite, Rare-earth bearing minerals, Pyrite, Zircon bearing minerals, and Quartz. Said minerals are commonly found in tin-bearing granitic veins, primarily in the Southeast Asian Tin belt [2,43]. Table A.1 shows the minerals found in tailing samples in the study. Similarly, the results are also parallel with findings from studies done by Andini and Farhana noting that As and Pb are one of the highest metal content [19,44].

Additionally, soil samples collected in the processing sites show observable contamination when concentrations were compared to control samples, specifically As, Pb, and Fe. This could be attributed to the processing activities conducted which caused the soil to be contaminated with the tailing itself, primarily due to poor storage management systems used [17,25]. A study done by Irzon in 2018 found similar results showing an increase in heavy metal concentration in tailing and mining-related soil.

The high concentration of metals in sediment samples could be attributed to the fact that minerals bearing these metals such as Arsenopyrite, (containing As), Wulfingite (containing Zn), Selenospinel (containing Cd), and Chromite (containing Chromceladonite and Cr) have lower specific gravity comparative to Cassiterite (containing Sn). Because shaker tables and jigs use the difference in specific gravity of material to separate them, the lighter unwanted material carried away by the water is separated and accumulates in the containment pools, and collects to the bottom [43,45,46].

In terms of processing sites, it is found that P4 shows the highest heavy metal concertation. It is worth noting that amongst all the four processing plants in which the study is based around, P4 is the only processing plant that is actively operational thus suggesting that the effects of tailing processing towards the environment persist even after processing activates have ceased. A study done by Irzon and Hamzah shows that soil and tailing samples collected from a former tin mining site showed concentrations that are in line with study findings [18,26]. Comparatively, concentration results found in this study are still parallel with older studies with the highest being from the accumulated tailing collected from North Bangka Island showed far a larger heavy metal content compared to study findings [19].

As a standardized base of comparison, the Dutch Standard is the most referred to in terms of determining permissible limits for heavy metal concentration in the environment. The findings found in this study show that the average concentrations of As, Pb, Ni, and Cu for soil have already exceeded the maximum permissible concentrations reported by the National Institute of Public Health and The Environment of the Netherlands [47]. For sediment As, Ni, and Cu have exceeded with the addition that As has also exceeded the intervention level proposed in the new dutch list [48].

In addition to this, a guide produced by the Malaysian Department of Environment reported screening levels as a gauge to see if there are potential subsurface impacts. It is found that the concentration of As has exceeded the screening level for industrial soil according to the guide, suggesting that As could potentially affect the soil in the lower parts and cause contaminate the groundwater that flows below [49].

Table 2
Radiological impact assessment of each sample type collected from each processing plant.

Sample types	Processing plants	D(nGy/h)	AED (mSv)	Ra_{eq} (10^{-3}) (Bq/kg)	ELCR (10^{-3})	Reference
Soil	P1	2.6×10^2	0.3	0.6	1.2	This Study
	P2	1.7×10^3	2.1	4.0	8.1	
	P3	8.9×10^3	11.0	20.9	42.0	
	P4	1.9×10^3	2.3	4.4	8.8	
Average		3.2×10^3	3.9	7.5	15.0	
Sediment	P1	5.8×10^2	0.7	1.4	2.8	
	P2	1.5×10^3	1.9	3.6	7.3	
	P3	2.8×10^3	3.4	6.5	1.3	
	P4	6.4×10^2	0.8	1.5	3.0	
Average		3.6×10^3	1.7	3.3	6.6	
Tailing	P1	1.7×10^3	2.1	4.0	8.1	
	P2	4.2×10^3	5.1	9.9	20.0	
	P3	7.2×10^3	8.8	17.0	34.0	
	P4	1.2×10^3	1.5	3.2	5.9	
Average		1.4×10^3	4.4	8.5	17.0	
Malaysian Tin Tailing		8.7×10^2–2.6×10^4	1.1–3.2 × 10	–	–	[1]
Nigerian Tin Mine Soil		–	0.4–3.8	–	1.3–3.8	[11]
Indonesian Tin Slag		8.6×10^5–2.1×10^6	1.5 × 10–3.8 × 10	1.9 × 10–4.0 × 10	–	[10]

Table 3
Concentrations of heavy metals in samples collected in this study and other studies.

Heavy Metal		Concentration (mg/kg)			
		Soil	Sediment	Tailing	Control
Cd	Mean	1.09	2.80	0.58	0.42
	SD	1.06	1.52	0.57	0.32
	Min	0.10	0.80	0.10	0.24
	Max	3.16	5.49	1.79	0.90
	*MPC	1–6	**30.00 (12)	–	–
Cr	Mean	77.62	135.75	24.39	78.88
	SD	64.35	135.65	19.81	63.93
	Min	10.79	35.64	6.17	26.96
	Max	263.68	269.08	80.21	170.16
	*MPC	100.00	**1720.00 (380)	–	–
As	Mean	634.46	2644.25	318.63	120.23
	SD	877.94	5859.72	455.00	104.05
	Min	57.81	96.99	30.93	61.37
	Max	3586.42	17121.36	1672.71	276.03
	*MPC	34.00	**190.00 (55)	–	–
Pb	Mean	147.77	265.82	130.91	40.12
	SD	108.39	236.16	52.80	26.07
	Min	16.76	11.35	44.10	6.80
	Max	461.96	642.84	208.77	67.53
	*MPC	140.00	**4800.00 (530)	–	–
Ni	Mean	38.71	55.22	33.32	26.02
	SD	38.47	47.57	42.50	8.34
	Min	2.47	10.15	4.11	18.84
	Max	102.43	146.26	161.08	35.87
	*MPC	38.00	**44.00 (210)	–	–
Zn	Mean	150.91	328.06	94.05	128.55
	SD	76.65	128.84	58.29	53.22
	Min	34.27	169.95	32.81	55.47
	Max	329.56	503.86	219.85	181.33
	*MPC	160.00	**620.00 (720)	–	–
Cu	Mean	56.67	96.77	33.10	14.34
	SD	47.37	41.27	34.80	12.89
	Min	10.97	41.29	8.81	6.47
	Max	132.84	162.93	155.98	33.62
	*MPC	40.00	**73.00 (190)	–	–
Fe	Mean	22599.54	35082.99	16083.33	4111.24
	SD	16863.82	19681.11	21631.05	3299.84
	Min	2384.25	11428.28	1225.40	785.64
	Max	46563.59	61140.70	52765.01	3409.28
	*MPC	–	–	–	–

MPC*- Maximum Permissible concentration obtained from the Dutch standard [47].
**(–) - Intervention concentration from the dutch list [48].

3.3. Radiological and toxicological pollution relationship

Statistical relationship analysis between the radionuclides and heavy metals was conducted by calculating the Pearson correlation coefficient for each pair. The analysis was conducted to ascertain the presence of a possible relationship amongst the elemental pairs. Generally, a positive value approaching 1 indicates a directly proportional relationship between the said pairs while a negative

Table 4
Shows the Pearson correlation coefficient calculated for (a) soil (b) sediment samples.

(a)

	^{226}Ra	^{232}Th	^{40}K	Cd	Cr	As	Pb	Ni	Zn	Cu	Fe
U	1.00										
Th	**0.92***	1.00									
K	**0.60***	**0.78***	1.00								
Cd	−0.38	−0.42	−0.37	1.00							
Cr	−0.18	−0.27	0.06	0.28	1.00						
As	−0.23	−0.27	−0.29	**0.75***	0.07	1.00					
Pb	−0.16	−0.20	−0.30	**0.64***	0.17	**0.63***	1.00				
Ni	−0.37	−0.41	−0.45	**0.89***	0.10	**0.68***	**0.70***	1.00			
Zn	−0.39	−0.07	0.15	0.37	−0.01	0.23	0.16	0.34	1.00		
Cu	−0.35	−0.38	−0.46	**0.92***	0.08	**0.67***	**0.66***	**0.93***	0.40	1.00	
Fe	−0.38	−0.47	**−0.64***	**0.76***	0.17	**0.53***	**0.69***	**0.87***	0.22	**0.79***	1.00

(b)

	^{226}Ra	^{232}Th	^{40}K	Cd	Cr	As	Pb	Ni	Zn	Cu	Fe
U	1.00										
Th	**0.90**[a]	1.00									
K	0.29	**−0.63**[a]	1.00								
Cd	0.18	−0.50	**0.61**[a]	1.00							
Cr	0.47	−0.44	0.38	0.10	1.00						
As	0.20	−0.25	0.11	0.22	0.43	1.00					
Pb	0.02	0.11	−0.23	0.12	0.31	**0.65**[a]	1.00				
Ni	**0.51**[a]	−0.23	−0.44	−0.13	0.38	0.14	0.12	1.00			
Zn	−0.17	−0.48	**0.63**[a]	**0.90**[a]	−0.02	0.23	0.23	−0.40	1.00		
Cu	−0.37	−0.42	−0.07	**0.53**[a]	−0.27	0.19	−0.08	0.43	0.36	1.00	
Fe	−0.29	−0.11	**−0.51***	0.12	−0.10	0.20	0.36	**0.72**[a]	−0.02	**0.66**[a]	1.00

[a] Correlation is significant at the 0.05 level.

value approaching −1 indicates the opposite. Values above or below 0.5 and −0.5 respectively, were considered to have significant relations.

The results presented in Table 4 indicate strong relations between pairs ^{226}Ra with ^{232}Th and ^{40}K, the cytotoxic heavy metals (specifically Cd, As, and Pb) as well as Cu and Fe with most of the heavy metals for soil samples. However a different result could be seen for sediment samples of the study as the only significantly correlated pairs were ^{226}Ra/^{232}Th (r = 0.90), ^{232}Th/^{40}K (r = −0.63), ^{226}Ra/Ni (r = −0.51), ^{40}K/Cd (r = 0.61), ^{40}K/Zn (r = 0.63), ^{40}K/Fe (r = −0.51), Cd/Zn (r = 0.90), ^{40}K/Cu (r = 0.52), As/Pb (r = 0.65), Ni/Fe (r = 0.72) and Cu/Fe (r = 0.66). Positive correlations indicates that both elements were observed to increase in relation with each other while negative correlation values denotes the opposite. The study discovered that the could be a plausible positive correlation between ^{226}Ra/^{232}Th, ^{40}K/Cd, ^{40}K/Zn, Cd/Zn, ^{40}K/Cu, As/Pb, Ni/Fe and Cu/Fe where the increase of one has the potential the other while a plausible negative correlation between ^{232}Th/^{40}K, ^{226}Ra/Ni, and ^{40}K/Fe could be present where the increase of could cause a decrease of the other. This could be attributed to the presence of other minerals present in the samples that was not able to be detected using the XRD phrase indetification analysis.

In essence, a quantification of correlation has been established between the studied pollutants which signifies a substantial association between one another. Though no clear distinctions could be made by this test alone, the findings do suggest that correlations between the pairs could be a result of the pollutants of the study site coming from a singular or similar source, that being the processing and mineral extraction activities in the areas. In the efforts of maintaining environmental sustainability by developing a more comprehensive regulation, this indication of possible contaminant source is vital as it could lay the foundation of for the local government to plan the proper course of action to remedy to problem.

3.4. Geo-accumulation index (I_{geo}) and enrichment factor (EF)

To gauge the level of heavy metal accumulation, the Geo-accumulation index (I_{geo}) was calculated by taking into account the elemental concentration of heavy metal in samples with the concentration in the control samples by using equation (8) [50,53]:

$$I_{geo} = Log_2 \frac{C_s}{1.5 \times C_b} \tag{8}$$

where C_s represents the concentration of heavy metal in samples taken while C_b represents the concentration of the same element in the control sample. An estimation of how polluted the samples were classified between 0 and 6 where class 0 ($I_{geo} < 0$) being unpolluted, class 3 ($2 < I_{geo} < 3$) being moderately polluted, and class 6 ($I_{geo} > 5$) extremely polluted [14,50].

The rise of heavy metal concentration in the environment as a result of anthropogenic activities conducted in the vicinity was gauged via the enrichment factor by using the ratio of metals in the samples against the ones in the control. The EF was calculated using equation (9) [50,51,53]:

$$EF = \frac{\frac{C}{R}\ Sample}{\frac{C}{R}\ Control} \tag{9}$$

where C/R sample refers to the concentration ratio of the element of interest over the reference element in the samples while the C/R control is the concentration ratio of the element of interest over the reference element from the control sample. For this study, the reference element used was Fe. The range of pollutant concentration severity is gauged by different ranges of EF values where EF < 2 is considered to have none to low levels of pollution, 2 < EF < 5 shows moderately polluted, 5 < EF < 40 shows considerable to highly polluted and EF > 40 is considered extremely polluted [14,50].

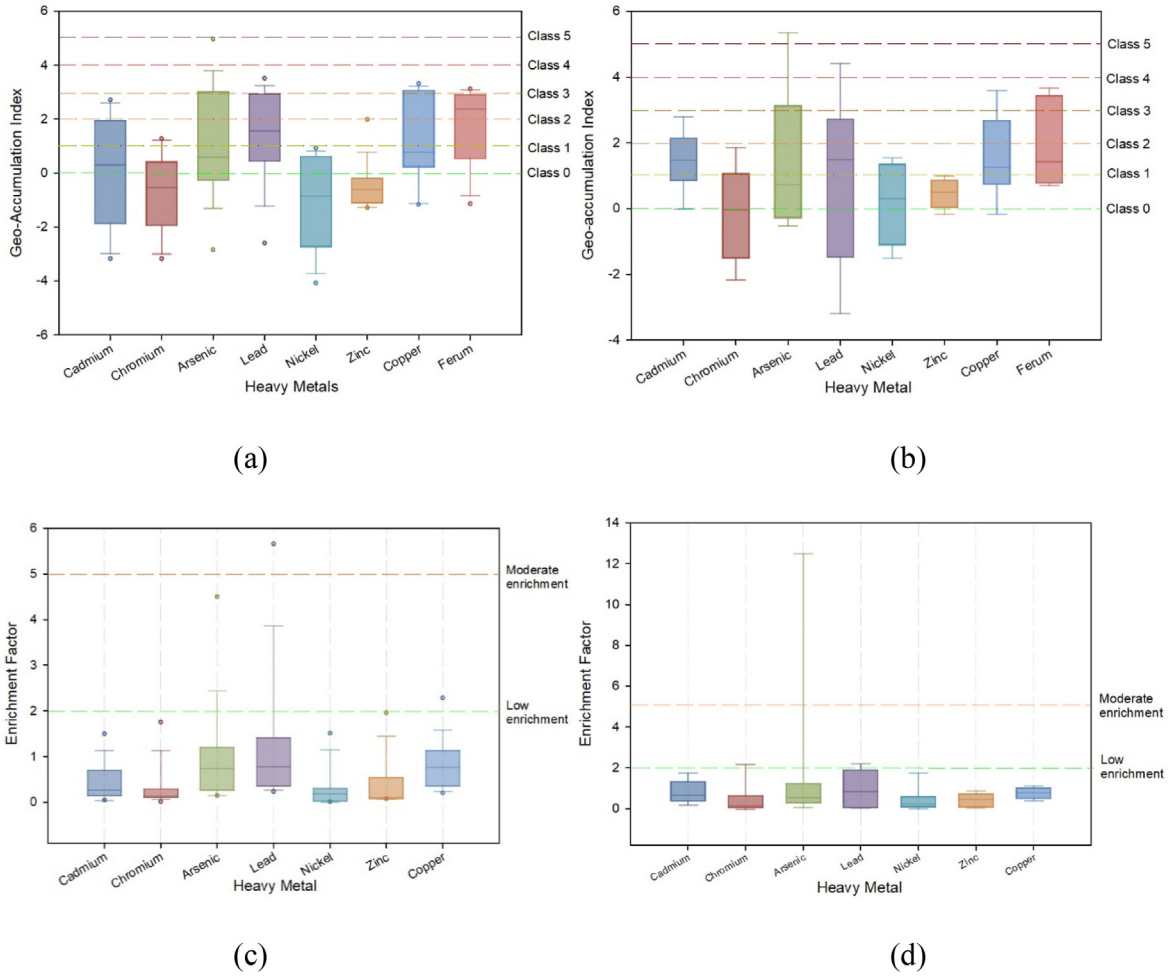


Fig. 3. Distribution of geo-accumulation index for (a) soil samples, (b) sediment samples and distribution of enrichment factor for (c) soil samples, (d) sediment samples.

Fig. 3 shows the range of the Geo-accumulation index of soil and sediment samples collected. Based on the I_{geo} index, the pollution levels of Ni, Cr, and Zn in both soil and sediments in the processing plants show low levels (Class 0 and 1) with only 14.89% of the total sample being considerably polluted (Class 2). However, As, Pb, Cd, Cu, and Fe showed higher states of pollution. where 25.53% of the samples were shown to be moderately polluted (Class 2–3) with Cd. For Pb, 36.17% of the total samples were found to be moderately polluted (Class 2–3) while another 25.53% of the samples were considerably more polluted (Class 4–5). The I_{geo} of As also shows concerning results with 21.28% of the samples being moderately polluted (Class 2–3), 12.27% samples were shown to be relatively highly polluted (Class 4–5) and 4.26% were extremely polluted (Class 5). For Cu and Fe, a total of 17.02% and 18.29% were moderately polluted (Class 2–3) while 17.02% and 19.15% were considerably more polluted (Class 4–5).

A large contribution to the number of polluted samples polluted with Cd, As, Cu, and Fe originated from a processing plant that is no longer actively operational. Despite the status of the said processing plant, the level of contamination is significant due to years of operation with little regard for safety and environmental awareness.

Fig. 3 also shows the distribution of the enrichment factor for each element in soil and sediment samples. The enrichment factor found in the study is relatively low as most samples collected were found to be in the region of low enrichment with only 6.39% samples were moderately enriched with As, 12.77% were moderately enriched with Fe and Pb and only 2.13% were enriched with Ni and Cr respectively. Additionally, only 10.64% and 14.89% of collected samples were significantly enriched by As and Pb respectively.

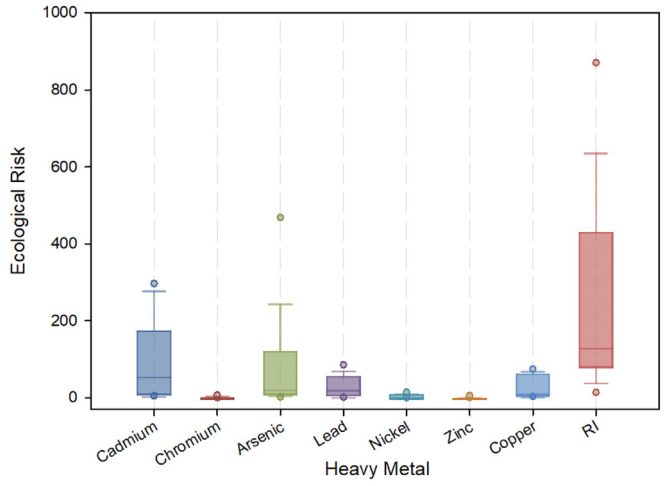
Soil sample indicates a higher enrichment of heavy metals comparative to sediment samples however both do not show a need for concern in terms of environmental pollution.

3.5. Single (ER) and total ecological risk assessment (RI)

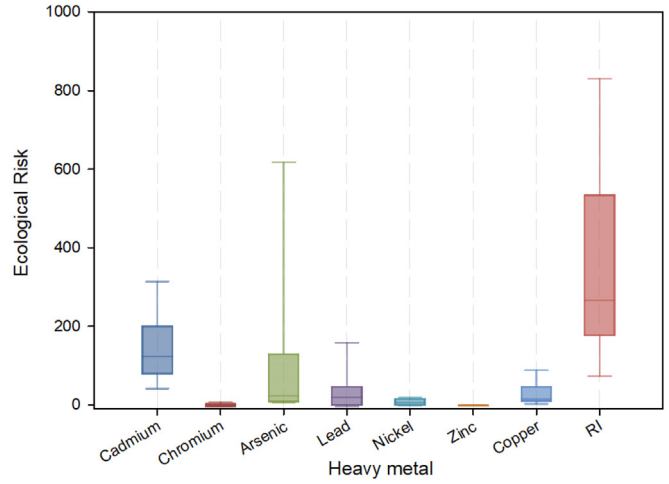
Additionally, the contamination factor was collated to calculate the risk factor of each heavy metal and subsequently the risk index.

$$Er = Tr \times CF \tag{10}$$

The singular ecological risk factor could be calculated using equation (10) where CF refers to the contamination factor and Tr denotes the toxic response factor of an element where the toxic response for As, Cd, Cr, Pb, Ni, Zn, and Cu are 10, 30, 2, 5, 5, 1 and 5 respectively [50,51,52,54]. Ecological risk values are quantified as to below for Er values < 40, moderate for 40≤Er < 80, significant for 80≤Er < 160, high risk for 160≤Er < 320, and very high ecological risk for values above 320.



(a)



(b)

Fig. 4. Er and RI of samples collected from all processing plants with (a) being soil samples and (b) being sediment samples.

Once calculated, The potential ecological damage due to heavy metal contamination was assessed by calculating the risk index using equation (11) with the classifications of RI being low for RI < 150, moderate ecological risk for 150 < RI < 300, high for 300 < RI < 600 and significantly severe ecological for RI values above 600 [50,54,53,55],:

$$RI = \sum Er \tag{11}$$

Fig. 4 shows a visual representation of Er and RI values in soil and sediment samples. The potential ecological risk puts the hazard of the industry towards the environment into perspective. The calculated Er values for Cr, Ni, Pb, Cu, and Zn indicate that the ecological risk posed by these heavy metals is low. For Cd, and As, the potential ecological risk posed ranged from low to very high risk, especially for As where soil and sediment from a sampling site both indicated to be between high and very high risk.

Taking all these values into account, the risk index was determined and revealed that 21.13% and 19.14% of the total samples face moderate and high ecological risk respectively while another 4.26% face severe ecological risk from exposure to heavy metals. It must be noted that each sample was taken as a composite, representing a larger area thus, despite the number of samples in the moderate, high, and severe ecological risks are relatively small, the repercussions it introduces to the ecology of the study sites is cause for concern.

3.6. Worker exposure and risk assessment

Using the concentration of heavy metals acquired, an estimation of heavy metal was determined via Average Daily Intake (ADI) (mg/kg-day) depending on which exposure pathway was to be assessed. Because the study was done in an industrial site, only exposure via soil ingestion and dermal contact were assessed using equations (12) and (13) respectively [13,56] as exposure via other pathways are not probable:

$$ADI_{SI} = \frac{C \times IR \times ED \times EF}{BW \times AT} \tag{12}$$

and

$$ADI_{DC} = \frac{C \times CF \times AF \times ABS \times SA \times EV \times ED \times EF}{BW \times AT} \tag{13}$$

where C denotes the concentration of heavy metals in the samples, IR denoting intake rate via soil ingestion (100 mg/day), ED being the Duration of exposure (10 years), EF represents the frequency of exposure (300 days/year), AT denotes average time (70 × 365 days/year) CF the conversion factor and AF representing the adherence factor on the skin (0.07 mg/cm^2). For BW being the average body weight, the average weight of adult male Malaysian workers between the age of 18–59 (62.25 kg) [57], while surface area exposed, SA are the estimated surface area of adult hands (284 cm^2) [58] and the being the dermal absorption factor ABS value used was 0.001 [13,60,61].

The impact of heavy metals on humans occurs primarily from exposure to polluted environments through several different pathways such as via dermal contact and soil ingestion. The USEPA reported that soil ingestion in adults occur subconsciously as dust and soil particles adhere to surfaces such as food, cigarettes, and exposed skin, especially when engaged with outdoor or industrial work [56]. Exposure to toxic heavy metals introduces two main risks that could be gauged in terms of carcinogenic and non-carcinogenic risks.

The assessment of human exposure to toxic heavy metals is first done by estimating the average daily intake both via ingestion and dermal contact as shown in Table C.1. On average, the amount of heavy metal intake via soil ingestion for Cd and Ni shows the least value with an average of 2.47 × 10^{-7} mg/kg-day and 7.01 × 10^{-6} mg/kg-day respectively. The most ingested amongst metals studied were Fe and As with an average intake rate of 4.61 × 10^{-3} and1.44 × 10^{-4} mg/kg-day respectively. The same could be said for exposure via dermal contact where the average daily intake for Cd and Ni being the lowest at 3.62 × 10^{-8} mg/kg-day and 1.03 × 10^{-6} mg/kg-day respectively while As and Fe is the highest at 5.59 × 10^{-4} and 5.98 × 10^{-4}.

3.7. Non-carcinogenic risk assessment

Using the ADI values calculated, the non-carcinogenic risk of exposure was estimated by calculating the Hazard Quotient (HQ) for each element and pathway. The HQ is an estimation of non-carcinogenic effects risk posed when exposed to a single chemical proposed by the USEPA while the Hazard Index (HI) does the same for multiple chemicals [62,63]. Any values HI below one would have little to no observable adverse effects while a value above one has a

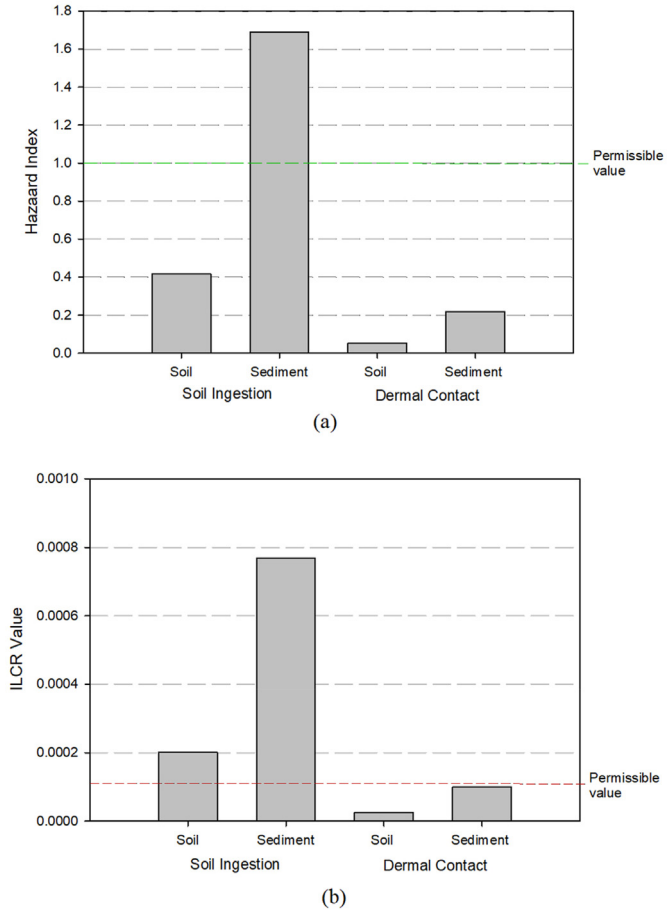


Fig. 5. Shows the human exposure assessment distribution where (a) is the non-carcinogenic effect hazard index and (b) is the carcinogenic incremental lifetime cancer risk.

higher probability of exhibiting adverse health effects [64]. The HQ and HI are calculated using equation (14)

$$HI = \sum HQ = \sum \frac{\mathrm{ADI}}{\mathrm{RfD}} \tag{14}$$

where the RfD refers to the reference dose for each heavy metal which is 0.001, 0.003, 0.0003, 0.0035, 0.02, 0.3, 0.0371, and 0.7 for Cd, Cr, As, Pb, Ni, Zn, Cu, and Fe respectively [13,14,60].

Table D.1 shows the non-carcinogenic risk posed by heavy metal exposure. Referencing the RfD values from the USEPA, the average HQ values for all the heavy metals in terms of soil ingestion are found to follow the order of As > Pb > Fe > Cr > Ni > Cu > Cd > Zn for soil samples while for sediment samples followed the order of As > Pb > Fe > Cr > Cd > Ni > Cu > Zn with the highest, being As having an HQ value of above 1. For exposure via skin contact with the samples, the HQ values follow the same order as soil ingestion for both soil and sediment samples with all the HQ values were found to be below 1.

This of course contributes to the mean hazard index where the HI values calculated for exposure to sediment samples via both soil ingestion and dermal contact were 1.69 and 0.22 respectively. Additionally, exposure via skin contact with soil samples was also found to be at 0.42 and 0.05. These values indicate that only exposure to sediment produced by tailing processing activities via soil ingestion with these daily exposure rates has the potential to cause adverse health effects [14,65]. On top of that, from the calculations done, the study could pinpoint the main contributor to such high values where the large estimated amount of As intake daily. Fig. 5(a) shows the distribution of the hazard index. A study done by Li in 2014 reported the same result noting that As was the second-highest heavy metal pollutant found in the mines of China [63].

3.8. Carcinogenic risk assessment

Since certain heavy metals are proven to be carcinogens, a probabilistic estimation was done to assess the likelihood of an individual developing cancer throughout a lifetime known as the Incremental Lifetime Cancer Risk (ILCR). This probability was achieved by multiplying the intake rate with the appropriate cancer slope factor (CSF) for each heavy metal as stated in equation (15):

$$\mathrm{ILCR} = \mathrm{ADI} \times \mathrm{CSF} \tag{15}$$

The acceptable range for the ILCR value is between 1×10^{-6} to 1×10^{-4} where risks below this range are said to pose no significant risks to the health of an exposed individual. Values above 1×10^{-4} are deemed unacceptable and pose significant health risks. The CSF values used in this study references multiple previous studies and could be seen in Table B.1.

Table E.1 shows the average and the sum of ILCR values calculated for the study. Taking into account the cancer slope factors, it was found that the ILCR value is within the range of 2.09×10^{-7} to 7.43×10^{-4} for soil ingestion and 2.71×10^{-8} to 9.65×10^{-5} with the highest in terms of cancer risk coming from the exposure to sediment samples via soil ingestion as shown in Fig. 5(b). In terms of highest to lowest, the order of ILCR values for soil ingestion of soil follows the order As > Cr > Ni > Cd > Pb while the for sediment follows the trend. Additionally, the trend follows for dermal contact as well with As being the highest and Pb being the lowest.

It is found that the $\mathrm{ILCR_{sum}}$ values have exceeded the acceptable value of 1×10^{-4} when gauging the risk of exposure via soil ingestion. Both soil and sediment levels produced an average of 2.01×10^{-4} and 7.69×10^{-4} respectively which indicates the presence of carcinogenic risk to humans when exposed to these polluted environmental media via soil ingestion. Exposure via skin contact however shows to be within the acceptable range of $1.00\mathrm{E}^{-6}$ to $1.00\ \mathrm{E}^{-4}$ indicating low carcinogenic risks from exposure. It is worth noting that the highest contributor to this elevation is As, contributing from 92.04% to 96.69% of the total value. The findings of this study are parallel to the study done by Li where the carcinogenic risk assessment was done in mines in China and showed that the carcinogenic risk was within the range of 1×10^{-5} to 1×10^{-6} [63].

At present (2020) the atomic agency licensing board has taken it upon itself to revisit the regulations that govern the conduct of this industry in terms of radiation safety. This is due to the growing concern that these processing plants do not practice very strict radiation safety protocol which includes the absence of proper storage facility, the providence of PPEs, and lack of supervision and monitoring with regards to the workers as well as the environment from radiation material contamination [1,66]. Though the main focus of the regulation revisiting leans heavily towards radiation protection and safety, it could not be dismissed the two issues (radiation safety to workers and environment as well as toxic metal pollution) are interrelated where changes and modifications

applied to existing radiation regulations could potentially affect the industry positively in terms of environmental sustainability as well.

4. Conclusion

Operation of the tin tailing processing industry in Malaysia has been conducted for years and has since caused a significant impact on the environment in the vicinity of the processing plants. The study has shown that in terms of radiological impact, workers in the industry are at risk of facing overexposure from TENORM produced by the industry, specifically up to an absorbed dose between 2.6×10^2–8.9×10^3 nGy/y and annual effective dose between 0.3 and 11.0 mSv which exceeds the recommended threshold proposed by UNSCEAR. Gauging exposure levels via the radium equivalent revealed that the samples collected pose a significant threat to human health both via gamma-ray exposure. Calculation of ELCR showed values within the range of 4.0×10^{-4} to 9.3×10^{-2} with most exceeding the global average however relatively does not pose concerning elevation to cancer risks. In terms of heavy metal pollution, the study has shown that there is significant heavy metal environmental contamination which has reached concerning levels and indicates probable subsurface impact in both soil and sediments. Pollution indices calculated in this study shows significant pollution levels with the main pollutants following in the order of As > Pb > Cu > Fe > Cd > Cr > Ni > Zn with the highest impact was caused by As. Geo-accumulation index shows environmental pollution levels in sediments reaching severe degrees with the two main concerns being As and Pb. Enrichment factors similar trends indicating that processing activities have caused significant pollutant enrichment in environmental soil and sediment. Assessment of human exposure via soil ingestion and dermal contact also shows concerning values since the concentration of heavy metals in the workspace environment is showing moderate to high levels of pollution. The estimated intake rate of heavy metals via soil ingestion of sediments in processing sites poses non-carcinogenic adverse health effects as indicated by the hazard index value. Furthermore, carcinogenic risk also shows a more concerning trend as the risk posed by ingesting even small amounts of soil or sediment or even having them cling on the skin of workers over years introduces carcinogenic risks if not supervised and taken care of. The study shows that the working environment in these tin tailing plants are not conducive for worker and poses several hazards that must be addressed to ensure worker safety and environmental sustainability. Correlation analysis shows the presents of a possible relationship between the concentration of pollutants and their possible point of origin.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDICES

Appendix A

Table A.1
Minerals found in tailing samples collected

Processing Plant	Minerals	Chemical Formula
P1	Xenotime	$Y(PO_4)$
	Rutile	TiO_2
	Columbite	$(FeMn)(Nb_2O_6)$
	Ilmenite	$FeTiO_3$
	Petalite	$Li(AlSi_4O_{10})$
	Zircon	$ZrSiO_4$
	Monazite	$(Ce,La,Y,Th)PO_4$
	Cassetirite	SnO_2
	Gadolinite	$Y_2FeBe_2Si_2O_{10}$.
	Schorl	$NaFe_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$
P2	Rutile	TiO_2
	Ilmemorutile	$(Ti,Nb,Fe)O_2$
	Schorl	$NaFe_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$
	SelenoSpinel	$CdTm_2Se_4$
	Wulfingite	Zn(OH)2
	Graphite	C
	Chromceladonite	$KMgCr(Si_4O_{10})(OH)_2$
	Zircon	$ZrSiO_4$
	Pyrite	FeS_2
	Monazite	$(Ce,La,Y,Th)PO_4$
	Scorodite	$FeAsO_4.2H_2O$
	Zirconia	ZrO_2
	Quartz	SiO_2
	Bustamite	$CaMn(Si_2O_6)_2$
	Sodalite	$Na_8Al_6Si_6O_{24}Cl_2$
P3	Rutile	TiO_2
	Graphite	C
	Anatase	TiO_2
	Wustite	FeO
	Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$
	Wakefieldnite	$LaVO_4$
	Spinel Group	$MgAl_2O_4$
	Magnetite	Fe_3O_4
	Pyrite	FeS_2
	Quartz	SiO_2
	Zircon	$ZrSiO_4$
	Chromite	$FeCr_2O_4$
	Xenotime	YPO_4
	Ilmenite	$FeTiO_3$
	Zirconolite	CaZrTi2O7
	Columbite	$(FeMn)(Nb_2O_6)$
P4	Cassiterite	SnO
	Zircon	$ZrSiO_4$
	Pyrhotite	FeS
	Hematite	Fe2O3
	Ilmenite	FeTiO3
	Rutile	TiO2
	Muscovite	H2KAl3Si3O12
	Quartz	SiO2
	Cornwallite	$Cu_5(AsO_4)_2(OH)_4$

Appendix B

Table B.1
Cancer slope values used in the study referenced by past studies.

Heavy Metal	CSF	Reference
Cd	6.3	[14,61,65]
Cr	0.5	[13,14,67]
As	1.5	[13,14,67]
Pb	0.0085	[13,14,61,65]
Ni	0.91	[14,61,65]

Appendix C

Table C.1
Average Dose intake for via Soil ingestion and Dermal contact

Heavy Metal	ADI (Soil ingestion)			ADI (Dermal contact)		
	Soil	Tailing	Sediment	Soil	Tailing	Sediment
Cd	2.04E-07 ± 1.99E-07	1.08E-07 ± 1.07E-07	5.24E-07 ± 2.85E-07	2.64E-08 ± 2.58E-08	1.40E-08 ± 1.39E-08	6.80E-08 ± 3.70E-08
Cr	1.45E-05 ± 1.21E-05	4.57E-06 ± 3.71E-06	2.54E-05 ± 2.54E-05	1.89E-06 ± 1.57E-06	5.93E-07 ± 4.82E-07	3.30E-06 ± 3.30E-06
As	1.19E-04 ± 1.65E-04	5.97E-05 ± 8.53E-05	4.96E-04 ± 1.10E-03	1.54E-05 ± 2.14E-05	7.75E-06 ± 1.11E-05	6.43E-05 ± 1.43E-04
Pb	2.77E-05 ± 2.03E-05	2.45E-05 ± 9.90E-06	4.98E-05 ± 4.43E-05	3.59E-06 ± 2.64E-06	3.18E-06 ± 1.28E-06	6.47E-06 ± 5.74E-06
Ni	7.26E-06 ± 7.21E-06	6.24E-06 ± 7.97E-06	1.03E-05 ± 8.91E-06	9.42E-07 ± 9.36E-07	8.10E-07 ± 1.03E-06	1.34E-06 ± 1.16E-06
Zn	2.83E-05 ± 1.44E-05	1.76E-05 ± 1.09E-05	6.15E-05 ± 2.41E-05	3.67E-06 ± 1.86E-06	2.29E-06 ± 1.42E-06	7.98E-06 ± 3.13E-06
Cu	1.06E-05 ± 8.88E-06	6.20E-06 ± 6.52E-06	1.81E-05 ± 7.73E-06	1.38E-06 ± 1.15E-06	8.05E-07 ± 8.46E-07	2.35E-06 ± 1.00E-06
Fe	4.24E-03 ± 3.16E-03	3.01E-03 ± 4.05E-03	6.58E-03 ± 3.69E-03	5.50E-04 ± 4.10E-04	3.91E-04 ± 5.26E-04	8.53E-04 ± 4.79E-04

Appendix D

Table D.1
Average Hazard Quotient and Hazard Index for based on exposure via Soil ingestion and Dermal contact

Heavy Metal	HQ(Soil ingestion)			HQ (Dermal contact)		
	Soil	Tailing	Sediment	Soil	Tailing	Sediment
Cd	2.04E-04 ± 1.99E-04	1.08E-04 ± 1.07E-04	5.24E-04 ± 2.85E-04	2.64E-05 ± 2.58E-05	1.40E-05 ± 1.39E-05	6.80E-05 ± 3.70E-05
Cr	4.85E-03 ± 4.02E-03	1.52E-03 ± 1.24E-03	8.48E-03 ± 8.47E-03	6.29E-04 ± 5.22E-04	1.98E-04 ± 1.61E-04	1.10E-03 ± 1.10E-03
As	3.96E-01 ± 5.48E-01	1.99E-01 ± 2.84E-01	1.65E+00 ± 3.66E+00	5.14E-02 ± 7.12E-02	2.58E-02 ± 3.69E-02	2.14E-01 ± 4.75E-01
Pb	7.91E-03 ± 5.80E-03	7.01E-03 ± 2.83E-03	1.42E-02 ± 1.26E-02	1.03E-03 ± 7.53E-04	9.10E-04 ± 3.67E-04	1.85E-03 ± 1.64E-03
Ni	3.63E-04 ± 3.60E-04	3.12E-04 ± 3.98E-04	5.17E-04 ± 4.46E-04	4.71E-05 ± 4.68E-05	4.05E-05 ± 5.17E-05	6.72E-05 ± 5.78E-05
Zn	9.43E-05 ± 4.79E-05	5.88E-05 ± 3.64E-05	2.05E-04 ± 8.05E-05	1.22E-05 ± 6.21E-06	7.63E-06 ± 4.73E-06	2.66E-05 ± 1.04E-05
Cu	2.87E-04 ± 2.40E-04	1.68E-04 ± 1.76E-04	4.90E-04 ± 2.09E-04	3.73E-05 ± 3.11E-05	2.18E-05 ± 2.29E-05	6.36E-05 ± 2.71E-05
Fe	6.05E-03 ± 4.52E-03	4.31E-03 ± 5.79E-03	9.39E-03 ± 5.27E-03	7.85E-04 ± 5.86E-04	5.59E-04 ± 7.52E-04	1.22E-03 ± 6.84E-04
HI	4.16E-01 ± 5.49E-01	2.13E-01 ± 2.84E-01	1.69E+00 ± 3.66E+00	4.16E-01 ± 5.49E-01	2.13E-01 ± 2.84E-01	1.69E+00 ± 3.66E+00

Appendix E

Table E.1
Average Incremental lifetime cancer risks for each heavy metal and sample type based on exposure via Soil ingestion and Dermal contact

Heavy Metal	ILCR (Soil ingestion)			ILCR (Dermal contact)		
	Soil	Tailing	Sediment	Soil	Tailing	Sediment
Cd	1.27E-06 ± 1.29E-06	6.80E-07 ± 6.73E-07	3.30E-06 ± 1.80E-06	1.64E-07 ± 1.68E-07	8.82E-08 ± 8.73E-08	4.28E-07 ± 2.33E-07
Cr	7.36E-06 ± 6.23E-06	2.29E-06 ± 1.86E-06	1.27E-05 ± 1.27E-05	9.55E-07 ± 8.09E-07	2.97E-07 ± 2.41E-07	1.65E-06 ± 1.65E-06
As	1.85E-04 ± 2.54E-04	8.96E-05 ± 1.28E-04	7.43E-04 ± 1.65E-03	2.40E-05 ± 3.30E-05	1.16E-05 ± 1.66E-05	9.65E-05 ± 2.14E-04
Pb	2.42E-07 ± 1.77E-07	2.09E-07 ± 8.41E-08	4.23E-07 ± 3.76E-07	3.14E-08 ± 2.29E-08	2.71E-08 ± 1.09E-08	5.50E-08 ± 4.88E-08
Ni	6.90E-06 ± 6.68E-06	5.68E-06 ± 7.25E-06	9.42E-06 ± 8.11E-06	8.95E-07 ± 8.67E-07	7.37E-07 ± 9.41E-07	1.22E-06 ± 1.05E-06
$ILCR_{sum}$	2.01E-04 ± 2.54E-04	9.84E-05 ± 1.28E-04	7.69E-04 ± 1.65E-03	2.61E-05 ± 3.30E-05	1.28E-05 ± 1.66E-05	9.98E-05 ± 2.14E-04

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