Radiological and heavy metals analysis in soil and water at the former tin mining site in the urban area (Danau Kota Lake, Kuala Lumpur)

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Abstract. Former mining sites are known to be concentrated with enriched naturally occurring radioactive materials (NORM) and heavy metals, as a result of past mining activities. A number of the sites are reclaimed as an open area, which in turn raised concerns regarding public safety. Thus, it is crucial to evaluate the safety of the public engaging in activities around the former tin mining areas. A study is carried out to determine the concentrations of NORM and heavy metals in soil and water collected from Danau Kota Lake, Kuala Lumpur, known as a former mining site. Both NORM and heavy metals were analysed using gamma spectrometry and inductively coupled plasma mass spectrometry (ICP-MS), respectively. The average concentration of 226Ra and 232Th in water collected was 0.7 ± 0.2 Bq/L and 0.1 ± 0.03 Bq/L, respectively. 40K, however, was not detected in the water. The average activity concentration of 226Ra, 232Th, and 40K in soil was 60.8 ± 2.3 Bq/kg, 42.9 ± 1.4 Bq/kg, and 338.4 ± 11.7 Bq/kg, respectively. From the values obtained, it is observed that the activity concentrations for both soil and water are still within the range limit reported by WHO and UNSCEAR. In regards to heavy metals analysis, manganese concentration was the highest in both water and soil with a value of 1.18 µg/L and 147.7 mg/kg, respectively. To evaluate the radiological hazard, the radium equivalent activity index (Req), gamma index (Iγ), absorbed dose rate (D), effective dose rate (D eff) and external hazard index (H ex) are calculated and valued at 148 Bq/kg, 1.1 Bq/kg, 69 nGy/h, 0.1 mSv/year and 0.4, respectively. All radiological hazard indices are found to be below the safety limits. Therefore, the lake area is considered safe for public activities except for Iγ.

1. Introduction
Abandoned mining sites in Malaysia are actively reused or redeveloped into various land uses such as recreational parks, housing areas, and agricultural farms. The initiative of reusing those mining sites helps in restoring the land into a more economically usable state in this country. In spite of that, the soil disturbed throughout past mining activities contain enriched concentrations of naturally occurring radioactive materials (NORM) and heavy metals in the soil. The NORM and heavy metals in the soil arise through processes such as extraction of metals and soil smelting. The environmental degradation that occurs may pose detrimental impacts on the public’s health. According to Zalina et al., tin mine
sites contains a higher NORM concentration than other areas [1]. Additionally, people are at the risk of being exposed to hazardous gamma rays produced by NORM in soil, such as $^{238}\text{U}$ and its decaying products, $^{226}\text{Ra}$, $^{232}\text{Th}$ and $^{40}\text{K}$.

A lot of research regarding the impact of NORM and heavy metals on human health was conducted in the past, indicating how pressing the problems are when it comes to contamination of NORM and heavy metals towards the environment [2-5]. International bodies such as the World Health Organization (WHO), Environmental Protection Agency (EPA) and United Nations (UN) have developed many guidelines for environmental monitoring and assessment for NORM and heavy metals contamination that can threaten human health. The effects of heavy metal exposure such as lead, cadmium, mercury, and arsenic cause damages to the kidneys and bones and poses the risk of cancer [6]. The natural radionuclide and heavy metal pollution will then accumulate in aquatic life and subsequent plants to humans if taken as a source of nutrition [7].

Recreational lakes are more susceptible to the effect of urbanisation and anthropogenic activities due to their geographic areas, in which they are commonly located at the center of commercial areas [8]. In the case of recreational parks developed from mining lands, the human health risk towards hazards in soil and water via direct and indirect exposure are not be taken lightly. The pathway of toxic chemicals exposure changes depending on the type of actions performed and the degree of contact. Recreational activities can be categorised into two types, whole-body contact sports and non-body contact sports. Example of whole-body contact sports are swimming, surfing, and canoeing, whereas, non-contact sports are like fishing, walking, birdwatching, and picnicking (incidental contact). Generally, the exposure of skin and whole-body contact activities increases with the amount of probable water ingested. Most outcomes on matter regarding health problems arise due to activity exposure from swimming activities and the ingestion of water. Hence, WHO drinking water quality has been used as guidelines in screening-level risk assessment and monitoring recreational exposure [9].

It is evident how vital NORM and heavy metals studies are in ensuring the safety of the lake area for public uses. Therefore, the present work intends to determine the content of NORM and heavy metals in water and soil at Danau Kota Lake, Kuala Lumpur, which is a newly re-established recreational area from former tin mines that operated during the 1980s. Besides that, the radiological hazard assessment was conducted. To evaluate the safety of the lake area, the results obtained were further compared to the range limits reported by several credible guidelines.

2. Experimental

2.1. Materials and method

Water and soil samples were collected from six different stations represented as T1, T2, T3, T4, T5, and T6 as depicted in figure 1. The average concentration of NORM and heavy metals from each station represents the total concentrations of the lake area. The results obtained for concentration of NORM and heavy metals in both water and soil sample were compared with several guidelines such as National Lake Water Quality Criteria and Standards Malaysia (NLWQS), National Water Quality Standards Malaysia (NWQS), guidelines for Drinking Water Quality-World Health Organisation (WHO 2017), Alberta Soil Remediation guidelines, guidelines for safe recreational water environments (WHO 2003), Nuclear Energy Agency (NEA-OCED) Reports 1979, National Council on Radiation Protection and Measurements (NCRP) Reports 1999, Annex B- Exposures from natural radiation sources (UNSCEAR 2000) and Putrajaya Lake Water Quality Standards (PLWQS 2013) to evaluate the safety of the lake area.

2.2. Pre-treatment of samples

For soil samples, 2 kg of soil was taken from each station. The soil sample was taken in a diameter of 30 cm according to IAEA 2004 [10]. The physical parameters of water include pH, conductivity, dissolved oxygen, and temperature were determined using a pH meter (WITEG W 100), a conductivity meter (YSI SCT Model 33), and an oxygen meter (HANNA instruments HI 91942), respectively.
In NORM analysis, the water sample was filtered using a plasma membrane. 2000 mL of water was concentrated by heating until its volume decreases to 200 mL. For soil samples, it was weighed and dried in an oven before sieving it through 800 µm siever to obtain a uniform sample size. The water and soil samples were kept in polyethylene bottles (7 cm diameter × 9 cm height) for 30 days until a secular equilibrium state is achieved before it is further analysed by a Highly Pure Germanium (HPGe) detector [11].

For heavy metals analysis, 100 mL of water sample was filtered using filter paper, whereas, soil samples were digested by adding 6 mL of hydrochloric acid and 4 mL nitric acid and was further digested in Microwave Digestive System for two hours. The clear solution formed was kept in a bottle before being analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [12].

![Geographical map of Peninsular Malaysia, Selangor state, and location of the sampling site.](image)

**Figure 1.** Geographical map of (a) Peninsular Malaysia, (b) Selangor state, and (c) location of the sampling site.

### 2.3. Characterisation
The concentration of NORM in water and soil samples was measured using a High Purity Germanium (HPGe) detector (Canberra Model GC1018) with the efficiency of 30% at Nuclear Science Laboratory UKM. The concentration of NORM in the water sample can be calculated using Equation 1:

\[
A_s \left( \frac{Bq}{L} \right) = \frac{N}{\epsilon \times P_{\gamma} \times V} 
\]

where \( N \) is the corrected net peak area background (cps), \( \epsilon \) is the efficiency of the detector for a \( \gamma \)-ray interest (cps/Bq), \( P_{\gamma} \) is the branching ratio of elements (%), and \( V \) is the volume of the water sample (L). The concentration of NORM in the sample was determined from net count of the sample using...
multichannel analyser (Software Genie 2000) by referring to the peak energy for $^{226}$Ra (609 keV and 1764 keV) for soil and water, respectively, $^{232}$Th (2614 keV), and $^{40}$K (1460 keV) [13]. The NORM in soil sample can be calculated using the comparative method where the counts obtained by the sample are compared with the standard sample from IAEA. The concentration of the NORM in the sample can be calculated using Equation 2:

$$W_s \left( \frac{Bq}{kg} \right) = \frac{M_P}{M_s} \times \frac{A_s}{A_P} \times W_F,$$

where $W_s$ is the concentration of the radionuclide in the soil sample, $M_P$ is mass of the sample, $M_s$ is mass of the standard, $A_P$ is the activity of the sample, $A_s$ is the activity of the standard, and $W_F$ is the concentration of radionuclide in the standard sample. Heavy metals in water and soil samples were determined using the ICP-MS model (ELAN® DRC-E, Perkin Elmer Elan 9000) at Environmental Science Laboratory UKM. Five heavy metals were analysed which were Manganese (Mn), Arsenic (As), Copper (Cu), Nickel (Ni), and Lead (Pb).

2.4. Radiological hazard analysis

In the present study, six quantities were recognized as the parameters to assess the radiological safety of the lake site. First, the radium equivalent activity index ($Ra_{eq}$) was introduced to compare the specific activity of a sample with different concentrations of $^{232}$Th, $^{226}$Ra, and $^{40}$K. $Ra_{eq}$ is defined as the total activity of the three radionuclides based on the estimation that 370 Bq/kg of $^{226}$Ra, 259/kg of $^{232}$Th, and 4810 Bq/kg of $^{40}$K produce the same dose rates. The upper limit for $Ra_{eq}$ is 370 Bq/kg. $Ra_{eq}$ was determined using formula 3. Gamma Ray Index ($I_\gamma$) estimates that the value of gamma ray is correlated with the value of the natural radionuclide in soil-375 and can be calculated using formula 4. External Hazard Index ($H_{ex}$) is widely used to show external exposure. $H_{ex}$ can be calculated using formula 5. The safe value for $I_\gamma$ and $H_{ex}$ is $\leq 1$ [14-16].

Using Equation 6, Absorb dose ($D$) was measured using the conversion factor published by UNSCEAR 2000 with a height of 1 meter above the ground [17]. Next, Annual Effective dose ($D_{eff}$) was determined to consider the outdoor occupancy factor and coefficient of absorbed dose and can be calculated using Equation 7:

$$Ra_{eq}^{(Bq/kg)} = A_{Ra} + 1.43A_{Th} + 0.077A_K,$$

$$I_\gamma = \frac{A_{Ra}}{150} + \frac{A_{Th}}{100} + \frac{A_K}{1500} \leq 1,$$

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1,$$

$$D^{(ngy)}_{h} = 0.462A_{Ra} + 0.621A_{Th} + 0.0417A_K,$$

$$D_{eff} = D^{(ngy)}_{h} \times 8760 \times 0.2 \times 0.7 \times 10^{-6}$$

3. Results and discussion

3.1. Physical parameters of water

Physical parameters studied were pH values, water conductivity, temperature, and dissolved oxygen (DO). Results indicate that the lake water is alkaline with a pH of 8.8 ± 1.4. The average value for water conductivity, dissolved oxygen and the temperature of the lake water during the sampling is 38 ± 1, 4.13 ± 13 mg/L, and 32 ± 1 °C, respectively. The pH does not give a direct impact on recreational activities conducted there.

3.2. NORM and heavy metals concentration

The comparison between the concentration of NORM and heavy metals in soil and water samples in Danau Kota’s lake and other lakes in Malaysia are shown in Table 1. The concentration of NORM in water shows that the concentration of $^{226}$Ra (0.77 ± 0.22 Bq/L) was the highest, followed by $^{232}$Th (0.1 ± 0.03 Bq/L). Meanwhile, $^{40}$K was below detection reading where the value was almost similar to the
background reading. Guidelines from Putrajaya Lake Water Quality Standards (PLWQS) and National Lake Quality Water Standard (NLQWS) dictate that the concentration of radium in the lake water should be less than 0.1 Bq/L [18, 19]. The concentration of $^{226}$Ra is shown to be higher than the guidelines. Referring to the World Health Organization (WHO) guidelines, the concentration values of the samples are lower than the permitted value [20]. The value of NORM in water, excluding $^{40}$K, from this study was observed to be slightly higher than the study conducted at KUIS lake, which is also a former mining site [12]. Although fishing competitions are frequently conducted, no body contact activities such as swimming are conducted here. Thus, the dermal contact contributes very little exposure. For soil samples, the results show that all of the concentrations of NORM are below the average value stated by UNSCEAR 2000 except for $^{40}$K. $^{40}$K shows the highest concentration followed by $^{226}$Ra and $^{232}$Th. The high value of $^{40}$K might be due to the natural composition of $^{40}$K in the earth's crust and the use of NPK fertilizer in grass planting during the redevelopment of this recreational park. Alsaffar et al. (2016) explained that the increase of concentration of NORM in soil with the use of fertilizer enhance the soil properties for plant growth [21].

Five heavy metals that show significant concentration in both water and soil samples are shown in Table 1. Those five heavy metals are manganese (Mn), Arsenic (As), Nickel (Ni), Copper (Cu) and Lead (Pb). The concentration of heavy metals in both water and soil samples show similar trends where the concentrations are found in the order of Mn $>$ As $>$ Cu $>$ Ni $>$ Pb. The highest concentration is Mn, and the lowest is Pb. The concentration of Mn is still below the guidelines values from NLQWS and no health value guidelines made by WHO for Mn for drinking water as the concentration of Mn is not of health concerning levels. The high concentration of Mn presence in the water and soil samples was probably due to the natural abundance of existing Mn in the environment [22]. As, Ni, Cu, and Pb in water were found below the safe guidelines value provided by NLQWS and WHO.

All the heavy metals in soil samples except for As, do not exceed the values stated by Alberta Soil Remediation guidelines. The calculated heavy metal concentrations in this study also show a higher concentration of Mn and Ni when compared to that of Bestari Jaya, also a former mining area. The concentration for As obtained in this study and that of Bestari Jaya are almost similar and both concentrations exceed the Alberta Guidelines value. The concentration of As in this study is within the contamination level, thus poses a health risk to the lake users. Past mining activities can contribute to the high concentration of As in the collected soil samples. A study by Trajce Stafilov et al proved that mining activities increase the concentration of As in the soil [23].

Referring to National Lake Water Quality Criteria Standards (NLWQS) Malaysia 2015, taking physical parameters, NORM and heavy metals concentrations in the water into account, Danau Kota Lake can be classified into category D. This is due to its good preservation of aquatic life and effective integrated lake management strategies conducted. The guidelines from Interim National Quality Water Standard (INQWS) Malaysia states that lake water is classified into class III, where fishing activities are allowed. Extensive treatment is also needed if the lake is to be used as a source of water supply [18].
Table 1. Concentration of NORM and heavy metals in water and soil samples.

| Type of samples | Samples          | Concentration of NORM (Bq/L* or Bq/kg**) | Concentration of Heavy metals (µg/L* or mg/kg**) |
|-----------------|------------------|------------------------------------------|--------------------------------------------------|
|                 |                  | **226**Ra | **232**Th | **40**K | Mn | As | Ni | Cu | Pb |
| Water           | This study       | 0.77 ± 0.22 | 0.1 | bdl | 1.18 | 0.71 | 0.04 | 0.14 | 0.01 |
|                 | KUIS lake [12]   | 0.19 ± 0.10 | 0.04 ± 0.62± | bdl | 0.58 | - | 0.49 | - |
|                 | NLWQS [24]       | <1 | - | - | 100 | 400 | 50 | 20 | 50 |
|                 | WHO [20]         | 1 | 1 | - | - | 10 | 70 | 2000 | 10 |
| Soil            | This study       | 60.8 ± 42.9± | 338.4± | 147.7 | 66.3 | 9.9 | 13.5 | 0.2 |
|                 | Bestari Jaya [25]| - | - | - | 85 | 79 | 6.7 | 125 | 105 |
|                 | Alberta [26]     | 300 | 300 | 1700 | - | 17 | 45 | 63 | 140 |
|                 | UNSCEAR 2000 [17]| 67 | 82 | 310 | - | - | - | - | - |

* unit for water samples
** unit for soil sample
bdl below detection limit

3.3 Radiological hazard analysis

Radiological hazard analysis for the soil was further evaluated to study possible influence of NORM towards human upon direct contact with the soil while engaging in recreational activities. Table 2 presents that all radiological hazards analysis show safe values except for Iγ. The recorded Raeq was 225.5 Bq/kg, which is less than the recommended maximum levels by NEA-OCED (370 Bq/kg) [27]. Similar trend was observed for the Hext with values less than the unity [28]. In addition, the Deff value recorded in this study is lower than the range proposed by the UNSCEAR 2000 (1 mSv/y).

Value of D obtained in this study is lower than the Malaysian average (93 nGy/h) and slightly higher than the world average (59 nGy/h) as reported by UNSCEAR 2000 [17]. In comparison with a study conducted by Muneer Aziz et al. at eastern region peninsular Malaysia (172 ± 90 nGy/h), the value of D obtained in this study is lower [29]. However, Iγ was measured to be ≥ 1, with an average of 1.1 Bq/kg that exceeded the unity value as recommended by the European Commission which indicates that the soil is not safe to be used as building materials for construction [16]. All radiological hazard analysis in this study is seen to be lower than the results from KUIS lake study.

Table 2. Radiological Hazard Analysis.

| Location      | Raeq (Bq/kg) | Iγ | Hext (nGy/h) | D (mSv/y) |
|---------------|--------------|----|-------------|-----------|
| This study    | 148          | 1.1 | 0.4 | 69 | 0.08 |
| KUIS Lake [12]| 225          | 1.6 | 0.6 | 104.1 | 0.1 |
| Recommended   | 370          | ≤1 | ≤1 | 93 | 1-10 |
| value         | NEA-OCED [27]| EU [16] | NCRP [28] | UNSCEAR [17] |

4. Conclusion

Results from this study indicate that the lake site is safe for public use. Most of the concentration of NORM and heavy metals in water and soil samples are below the average values stated in the health guidelines. Despite the high concentration of 226Ra in water samples and As in soil samples, the site is still considered safe for public use due to the absence of direct contact activities. The soil sample is not suitable to be used as building materials based on the Iγ, which exceeded the safe value. For future studies, sediment inside the lake can be a good potential in determining the concentrations of NORM and heavy metals. This, in return, will help analyse the safety of the lake as most of the toxicants found...
in the water will deposit into the sediment. Moreover, studies on the aquatic life samples will provide useful information regarding the transfer factor of the NORM and heavy metals.

5. Reference

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