Correlation of natural radionuclides (Ra-226, Ra-228 and K-40) in catchment soil and river sediment from Middle Langat River Basin

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Abstract. Natural radionuclides Ra-226, Ra-228 and K-40 along three (3) stations in Middle Langat River Basin were collected over a 9-year period at 3 months interval. Variations of activity concentration in the catchment soil and river sediment samples were analysed using HPGe detector to identify temporal and spatial trend. Activity concentrations show indication of long-term fluctuation especially for K-40, but will require long data for further validations. Increased activity concentrations in the down-river direction suggests a couple catchment loss and river sediment relative gain based on analysis of the ratios between element pair. Correlation of Ra-226 and Ra-228 is very strong, but their correlation with K-40 varies considerably possibly due to the high potassium solubility.

1. Introduction
A significant quantity of natural radiation is attributed to naturally occurring radioactive material (NORM) which comprises long lived nuclides with decay half-lives comparable to the age of the earth. These include radioactive nuclei which are produced by the interaction of cosmic rays on the earth’s atmosphere, and ionising radiation from terrestrial radionuclides which exists in almost all geological materials and the earth’s surroundings. According to [1], over 85% of radiation exposure is due to natural radiation in the environment, which despite its low concentration, can still poses potential health risk to human being.

Natural radioactivity of soil and sediment depends on the soil and sediment formation and transport processes that were involved since soil and sediment formation; chemical and biochemical interactions influence the distribution patterns of uranium, thorium and their decay product [2]. Urban built-up surfaces are typically straight and impermeable, hence deposition of radionuclides, if any, is transient and is subjected to weathering, resuspension by wind into the atmosphere, or wash down by rainfall and surface runoff into drainage or sewer system, possibly ending up in wastewater collection and treatment facilities. Rural areas, on the other hand, consist of largely permeable surfaces that can function as effective long-term sink for radionuclides. Surface migration plays an important role in the dispersion and fate of these radionuclides. The rate of migration is dependent on the physiochemical properties of the radionuclides and the surface in which it resides. For instance, interception by foliar uptake is temporal, whereas biomass such as plant root uptake is highly effective in retaining radionuclides over extended time. In the latter, the radionuclides may only be remobilized in events such as a forest fire. Particle-reactive radionuclides are prone to be removed or scavenged by sinking...
particulates, such as sediment and organic matter. The extent of sorption of radionuclides by sediments depends upon characteristics of the radionuclide and the sediment, the available surface area, the concentration and types of the solute, time, and partly the temperature [3]. These particulates, as well as soluble radionuclides (e.g. Ra-226, 228, Rn-222, Sr-90, Cs-137 etc.), are easily transported by overland runoff and river flow into the fluvial network, thus causing the radionuclides to migrate or disperse to an original uncontaminated area, including downstream river bank, flood bank, in-stream or lateral storage, aquifer, the delta, the estuary and the coastal water.

According to [4], direct correlation between the activity concentrations of different radionuclides has been commonly reported but lack of detailed analysis. Furthermore, ratios of concentration of radionuclides from two different series has not been widely studied. The ratio of activity concentrations of two radionuclides for samples collected from the same locality is dependent on the sample origin, the mineral structure and related human activities. These values can be established to estimate whether there are increased concentrations of some radionuclides in soil or sediment.

In this study, the main objective is to evaluate the spatial and temporal variation of natural radioactivity attributed to Ra-226, Ra-228 and K-40 in Middle Langat River Basin (MLRB). The three radionuclides considered are from Uranium series, Thorium series and potassium respectively. The aim is to examine the correlation and the ratios of the above radionuclides in catchment soil and river sediment in order to identify the accumulation or dissipation of the respective radionuclides over time and space.

2. Study area

Langat river basin is located in the south of Selangor and north of Negeri Sembilan within the latitude 2° 40’N to 3° 20’N and longitude 101° 10’E to 102° 00’E, with a total area of approximately 2,394.38 km². The land use range from residential, industrial, urbanised township and agriculture land. For the area within 1 km buffer of Langat river, nearly half (47%) of the land use is dominated by commercial grown crops which includes rubber plantation and palm oil (183 km²) primarily on the downstream, 17% (66 km²) of the land use is municipal and residential, and 10% is mixed plantation like orchards, banana, coconuts etc. [5].

Fig. 1 shows Langat River Basin with its main and tributaries river network system. For this study, three (3) stations in the MLRB area are selected, namely S12 Semenyih (2° 57’ 8.2908”N 101° 50’ 49.0272”E), S2 Rinching Hilir (2° 54’ 17.946”N 101° 48’ 37.4688”E) and S3 Sungai Buah (2° 53’ 32.1576”N 101° 45’ 3.1968”E), which are located from upstream to downstream along Semenyih River. Natural radionuclide activity (Ra-226, Ra-228 and K-40) in samples taken from the catchment soil and river sediment for the three stations have been monitored regularly on quarterly basis annually since year 2010 under the program by Malaysian Nuclear Agency.
3. Method
Surface soil and river sediments samples were collected using auger at three (3) months interval every year from Station S12, S2 and S3. Each sample taken measured 1 kg in mass and is first air dry at the laboratory complex in Nuclear Malaysia, Bangi before drying in the oven at 105°C for 2 to 3 days to remove all water content. The dewatered samples were then crushed to powder with mortar and sieved with a 2-mm mesh to obtain homogenized sample. The prepared samples were weighted and sealed with standard electric tape in Marinelli beaker to avoid contact with the air, and stored for a minimum period of 21 days. The samples were tested on Ortec P-Type coaxial HPGe detector for radioactivity counting in the Radiochemistry and Environment Laboratory for a period of 15 hours to achieve equilibrium for U-238 and Th-232 with their respective progeny. The final reading of natural radionuclides Ra-226, Ra-228 and K-40 were then cross correlated and analysed for spatial and temporal variations between the three (3) stations over the monitoring period.

4. Results and discussion
Fig. 2 shows the mean activity concentration of Ra-226, Ra-228 and K-40 at each of the three (3) stations monitored. In Fig. 2a, the results of activity concentration in catchment soil sample shows no specific trend over the years from 2010 to 2018. On the other hand, Fig 2b shows that the activity concentrations tend to increase in the down-river direction S12-S2-S3 for all elements examined. This may be attributed to the mobility of sediment-attached radionuclides from the catchment into the fluvial system, hence gradual accumulation in the river water towards the downstream.
Fig. 3 and Fig. 4 show the activity concentration of Ra-226, Ra-228 and K-40 in catchment soil sample and river sediment, respectively, from year 2010 to 2018, averaged over all the three (3) stations considered. For catchment soil sample, it is interesting to note that the concentration of K-40 shows long term oscillation which peaked in year 2012 (525.667±113.993 Bq/kg) and 2018 (504.167±57.951 Bq/kg), with the lowest reading recorded in year 2015 (427.333±106.926 Bq/kg), hence suggestive of a 6-year periodic cycle. Meanwhile, K-40 in river sediment shows slightly different temporal trend with the highest observation in year 2010 (491±345.683 Bq/kg), and the lowest in year 2016 (353.865±201.672 Bq/kg). In both cases, the activity concentration of K-40 are evidently much higher than Ra-226 and Ra-228 by well over 3 times.
Figure 3. The mean activity concentration of radionuclides in catchment soil sample.

The activity concentration of Ra-226 and Ra-228 in catchment soil sample and river sediment also exhibit oscillation over the years within the observation window but are less pronounced compared to K-40. The cyclic pattern, if does exist, can only be analysed and verified provided there is sufficient long-term data. The highest and lowest mean activity concentrations of Ra-226 in soil sample occurs in year 2012 (112.667±21.008 Bq/kg) and 2018 (91.75±17.732 Bq/kg), respectively. For Ra-228 in soil sample, the highest activity concentration is recorded in year 2015 (119.5±48.267 Bq/kg) and the lowest in year 2010 (92.667±41.016 Bq/kg). For activity concentration in river sediment, Ra-226 range from 133±114.053 Bq/kg in year 2010 and 78.025±70.164 Bq/kg in year 2018, whereas Ra-228 range from 138.25±99.627 Bq/kg in year 2015 and 80.658±76.776 Bq/kg in year 2018.
Overall, the observed range of activity concentration is much higher for the river sediment compared to the catchment soil. It is worth noting that [4] also reported marked difference in the distributions of measured values in river, soil and irrigation channel for the case of the Danube. The consequence is that small increase of these natural radionuclides may not be easily detected. Here, the large variation of activity concentration in the river sediment is an indication of potential contribution from anthropogenic sources.

Next, the correlation between the radionuclide concentrations in catchment soil samples (Table 1) and river sediment (Table 2) samples are examined. In general, Ra-226 and Ra-228 shows good correlation of 0.6 or much higher (above 0.85) which can be attributed to their similarity in the environmental origin. [6] argued that K-40 concentrations might not be related to the presence of Ra-226 and Ra-228 and may be attributed to the high potassium solubility [7]. Nevertheless, the present data shows that reasonably good correlation between K-40 and radium in the range of 0.5 to 0.9 can be observed at Station S2 and S3 (Fig. 5), whereas for Station 12, the correlation is found to be excellent in river sediment (Table 2) but extremely poor for catchment soil sample (Table 1). The correlation of the observed activity concentrations of the same elements in the soil sample and the river sediment at the same station has also been inspected but is found to be very poor generally and omitted herein. Large deviation between correlation of the same radionuclide pair under different environment can be attributed to the varied chemical dynamics or indicative of industrial activities [4].

Table 1. The correlation between radionuclides in soil catchment sample.

| Stations | S12 | S2 | S3 |
|----------|-----|----|----|
| Radionuclide | Ra-226 | Ra-228 | K-40 | Ra-226 | Ra-228 | K-40 | Ra-226 | Ra-228 | K-40 |
Table 2. The correlation between radionuclides in river sediment sample.

| Radionuclide | S12 | S2 | S3 |
|--------------|-----|----|----|
| Ra-226/Ra-228 | 1.098 | 0.723 – 1.422 | 0.979 | 0.898 – 1.091 | 0.890 | 0.661 – 1.111 |
| Ra-226/K-40   | 0.234 | 0.193 – 0.297 | 0.183 | 0.153 – 0.297 | 0.184 | 0.090 – 0.258 |
| Ra-228/K-40   | 0.223 | 0.169 – 0.370 | 0.187 | 0.169 – 0.370 | 0.205 | 0.136 – 0.299 |

Table 3 and 4 summarise the mean and range of the ratios of the activity concentrations by station of different natural radionuclide-pairs in the catchment soil sample and river sediment, respectively. The mean ratio of Ra-226/Ra-228 is most closely related at around 1 in all cases. For Ra-226/K-40 and Ra-228/K-40, the ratios averaged between 0.168 to 0.294. It is interesting to note that in the downstream direction, the ratios of Ra-226/K-40 and Ra-228/K-40 tend to reduce for catchment soil sample, but tend to increase for the river sediment, suggesting of a coupled catchment activity depletion and river sediment activity relative gain.

Fig. 5 shows the frequency distribution of the ratios of the different elements in soil sample and catchment sediment. The ratio of Ra-226/Ra-228 in river sediment peak at 0.95 and distributed from 0.79 to 1.11; the ratio of Ra-226/Ra-228 in catchment soil sample has a large spread from 0.6 to 1.362. The ratios of Ra-226/K-40 and Ra-228/K-40 show considerable fluctuation in the order between 0.12 to just above 0.36.

Table 3. Ratio of radionuclides in catchment soil sample.

| Radionuclide | S12 | S2 | S3 |
|--------------|-----|----|----|
| Ra-226/Ra-228 | 1.170 | 0.939 – 1.406 | 1.099 | 0.977 – 1.235 | 1.000 | 0.955 – 1.111 |
| Ra-226/K-40   | 0.306 | 0.241 – 0.395 | 0.260 | 0.218 – 0.337 | 0.267 | 0.244 – 0.319 |
| Ra-228/K-40   | 0.261 | 0.221 – 0.293 | 0.237 | 0.207 – 0.273 | 0.268 | 0.240 – 0.329 |

Table 4. Ratio of radionuclides in river sediment sample.
5. Conclusion
In this study, the temporal and spatial trends in the observed activity concentration of three (3) natural radionuclides from different decay series, namely K-40, Ra-226 and Ra-228 in catchment soil samples and river sediment samples at three (3) stations along Semenyih River in Middle Langat River Basin have been reported. The data shows indication of long-term periodic fluctuation especially for K-40. Radioactivity correlation between activity concentration in catchment soil and river sediment sample for the same elements is very poor and omitted herein. Meanwhile, correlation between Ra-226 and Ra-228 is the strongest, whereas correlation between K-40 and radium range substantially from excellent to very poor. Activity concentration ratios show that K-40 is up to 3 times higher than both Ra-226 and Ra-228, which have almost identical values. Moving in the downstream direction, the ratios of Ra-226/K-40 tend to reduce for catchment soils sample, whereas the ratios of Ra-228/K-40 tend to increase for the river sediment. Increase in overall activity concentration in river sediment in the down-river direction may be attributed to catchment soil loss. Variation of the activity concentrations, the correlation and ratios for the three (3) radionuclides considered suggests possible sources from human activities other than the natural origin which will need to be appropriately identified especially in order to control the level of ambient radioactivity in long term.

6. References
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