Impact of phosphate fertilizers on the uranium and thorium of cultivated soils profiles, Kamphaeng Phet, Thailand

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Abstract. Phosphate fertilizers contain uranium and thorium isotopes due to impurities in the phosphate rock used for fertilizer manufacture. Long term application can significantly accumulate and reach undesirable concentrations in agricultural soils. The presented study determined the $^{238}$U and $^{232}$Th in the four cultivated fields, one forest reference site and five phosphate fertilizers collected from Kanu Woraksaburi district, Kamphaeng Phet province. The uranium and thorium isotopes were measured by using radiochemical analysis and alpha spectrometry. The radionuclides in four arable soils revealed that the in more clayey soils were higher than in more sandy soils and dramatically decreased along the depth of both soil profiles. The cultivated soils were significantly higher than the reference site where no fertilizers were applied. The values were compared with available reported data from other countries in literature.

1. Introduction
The growth of population and the degradation of cultivated soil are resulting in increasing rate of fertilizer application in order to obtain high crop yields. However, the long term of fertilization applications may cause severe degradation of soil structure and contamination of uranium and thorium in soil. Phosphate rocks, raw material of phosphate fertilizer are source of naturally occurring radionuclides, such as radioisotopes of uranium $^{238}$U and thorium $^{232}$Th decay products [1, 2]. As a significant amount of uranium and thorium in phosphate fertilizers, the inappropriate application of fertilizer could be increase the uranium and thorium levels in agriculture soils.

Presently, soil degradation due to contaminated with fertilizer derived uranium and thorium are worldwide considered on public health problem. High uranium concentrations (up to hundreds of ppm) have been reported in the literature in fertilizers containing phosphate [1-5]. Uranium is mobile in surface soils as uranyl complex; therefore soluble fertilizer-derived uranium from agricultural soils could be uptake by plants or mobile into ground and surface waters which led to the spread in all the area [3]. Soluble uranium salts are toxic and are readily excreted in the urine, although some accumulation in the kidneys does occur in the case of chronic exposure. World Health Organization has established a daily "tolerated intake" of soluble uranium salts for the general public of 0.5 µg/kg body weight (or 35 µg for a 70 kg adult) [6]. Thorium is more abundant in the Earth's crust, being almost three times more abundant than uranium. Thorium is radioactive and can accumulate in the bones. Thus, it can cause bone cancer many years after exposure has taken place [7].
The aims of this study are to determine the uranium-238 and thorium-232 in the surface soils of Kamphaeng Phet province, Thailand. The soil samples were obtained from cultivated land of paddy field, maize, sugar cane, and cassava including natural forest where no application of any phosphate fertilizer (control site). The soil samples were collected for 2 years during 2015-2016 in totally 15 plots. In addition, five phosphate fertilizers available and used in the study area were collected and evaluate the uranium-238 and thorium-232 content.

2. Method

2.1 Soil sampling

Samples of surface soils from Khanu Woralaksaburi district, Kamphaeng Phet province were collected as per the protocols of International Atomic Energy Agency [8]. The fifteen cores each of 0-10, 10-20, 20-30, and 30-40 cm were separated into group. Group of each depth layers soil was mixed and homogenized in field to be a composite sample before analysis. Soil samples were sealed in plastic bags and were air dried, grounded to pass through a 2.0 m.m. sieve and stored for chemical analysis.

2.2 Analytical method

In each plot and soil depth, 5 g of dried finely grounded soil sample was processed. Sample was acid digested on hot plate with HNO₃ to near dryness. The residue was treated with HClO₄ to remove any remaining organics. Residue was further digested with 3 times HF to near dryness and digested repeatedly with 3 times concentrated HCl. Uranium-238 present in the sample was purified for 2 steps, firstly by solvent extraction using di-isopropyl ether and secondly by ion exchange using AG1x8, 100-200 mesh, Chloride form resin. U⁵⁸ was eluted with 50 cm³ of 0.2 M HCl, collected into 50 cm³ beaker and evaporated to dryness.

The dry residue was dissolved in 0.1 M HNO₃, saturated ammonium oxalate and (NH₄)₂SO₄ buffer with pH 2. The solution was transferred to an electrodeposition cell containing a platinum electrode. U⁵⁸ was electrodeposited on a stainless steel disc for 2 h at 0.95 A. At 1 min prior to the end of this stage, 1 cm³ of concentrated ammonia solution was added to the cell before switching off the current. The cell was disassembled and the disc was then rinsed and allowed to dry. The electrodeposited uranium was measured using implant ultra-pure silicon detector (450 mm² active area ORTEC EG&G) equipped with high resolution alpha spectrometry (ORTEC Model Octete Plus).

The accuracy and precision of the radiochemical method were evaluated using IAEA reference material.

3. Results and Discussion

3.1 U²³⁸ and Th²³² in soil

The range concentration of U²³⁸ and Th²³² in four cultivated soils and one forest reference site were shown in Table 1 and 2.

### Table 1. Concentrations of U²³⁸ in different agricultural soils and control sites

| Sites          | Number of plot | U²³⁸ Bq.kg⁻¹   | U²³⁸ µg.g⁻¹   |
|---------------|----------------|---------------|--------------|
| Paddy field   | 3              | 15.688 – 239.151 | 0.194 – 2.952 |
| Maize         | 3              | 14.022 – 92.805  | 0.173 – 1.146  |
| Sugar cane    | 3              | 40.814 – 199.302 | 0.504 – 2.461  |
| Cassava       | 3              | 39.746 – 213.731 | 0.491 – 2.639  |
| Forest (control site) | 3 | 8.613 – 25.411  | 0.106 – 0.314  |
Table 2. Concentrations of $^{232}$Th in different agricultural soils and control sites

| Sites              | Number of plot | $^{232}$Th Bq kg$^{-1}$ | $^{232}$Th μg g$^{-1}$ |
|--------------------|----------------|-------------------------|------------------------|
| Paddy field        | 3              | 11.206 – 159.434        | 2.726 – 38.792         |
| Maize              | 3              | 10.000 – 66.289         | 2.433 – 16.129         |
| Sugar cane         | 3              | 36.332 – 142.359        | 8.840 – 34.637         |
| Cassava            | 3              | 28.390 – 152.665        | 6.908 – 37.145         |
| Forest (control site) | 3            | 6.152 – 18.151         | 1.497 – 4.416          |

The results shown that both $^{238}$U and $^{232}$Th were relatively constant along the vertical section in forest soil samples which no fertilizer application and thus were considered as a control site. Therefore, concentrations of $^{238}$U and $^{232}$Th in forest soil samples were used to be a baseline values. The amounts of $^{238}$U and $^{232}$Th elevated in the cassava > paddy field > maize > sugar cane > natural forest. It was found that the concentrations of both radionuclides were decreased dramatically from surface soil down to the bottom depth (40 cm) which eventually were closed to the control site’s values. The most plausible reasons are the right amount of phosphate fertilizers were applied to the soils and crops have significant effects on $^{238}$U and $^{232}$Th uptake from soil. The observations in this study are agreed with the distribution pattern in China [5]. The values of $^{238}$U and $^{232}$Th in this study found to be much less than the United States Nuclear Regulatory Commission residual contamination criteria of 30 and 45 μg/g, respectively [9].

3.2 $^{238}$U and $^{223}$Th in Phosphate fertilizer
Levels of $^{238}$U and $^{232}$Th in Phosphate fertilizer measured in this study were low when compared with reported in literatures. Therefore, the rate of $^{238}$U and $^{232}$Th accumulation in the soil samples are likely to be slow and take several years. Summary of $^{238}$U and $^{232}$Th in phosphate fertilizer samples are shown in Table 3.

Table 3. Mean concentrations of $^{238}$U and $^{232}$Th in phosphate fertilizers

| Fertilizer | Number of samples | $^{238}$U Bq kg$^{-1}$ | $^{232}$Th Bq kg$^{-1}$ |
|------------|-------------------|------------------------|------------------------|
| F1         | 5                 | 16.54                  | 4.02                   |
| F2         | 5                 | 17.52                  | 5.18                   |
| F3         | 5                 | 20.16                  | 5.53                   |
| F4         | 5                 | 23.71                  | 5.59                   |
| F5         | 5                 | 25.72                  | 7.31                   |

4. Conclusion
The $^{238}$U and $^{232}$Th in cultivated soils elevated in the cassava > paddy field > maize > sugar cane > natural forest. It was observed that $^{238}$U and $^{232}$Th concentration decreased dramatically along soil depth of 40 cm in all cultivated soil. Eventually both levels of $^{238}$U and $^{232}$Th in all cultivated soil samples were closed to the values in forest soil at the depth of 40 cm (bottom layer). As compare with the control site, it indicated that both radionuclides were increased due to the long term of the phosphate fertilizer. However, the levels of $^{238}$U and $^{232}$Th in phosphate fertilizer were much lower.
than that were found in the cultivated soil profile. This can explain that most of the $^{238}\text{U}$ and $^{232}\text{Th}$ in the soils were derived from the source-rock of the area. In addition, the right amount of phosphate fertilizers were applied to the soils and crops have significant effects on $^{238}\text{U}$ and $^{232}\text{Th}$ uptake from soil. It suggested that the rate of fertilizer derived $^{238}\text{U}$ and $^{232}\text{Th}$ accumulation in the soil samples are likely to be slow and take several years. The values of $^{238}\text{U}$ and $^{232}\text{Th}$ in this study found to be much less than the United States Nuclear Regulatory Commission residual contamination criteria of 30 and 45 $\mu$g/g, respectively [9]. At the present, there were no causes for environmental alarm concerning the $^{238}\text{U}$ and $^{232}\text{Th}$ contents detected in the soils studied in this work.

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