

# Natural Radionuclide Contents in Ceramic Clays in Southern Thailand and their Radiation Hazard Indices

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## ABSTRACT

The present study aimed to: 1) measure the natural radioactivity due to the presence of radionuclides in natural clay, used widely as raw material in the ceramics industry; and 2) assess the possible radiological hazard associated with the ceramic products made with them. Natural clays from 17 localities in southern Thailand and commercial clay used in ceramics and pottery factories were studied. The activity concentrations of natural radionuclides, Th-232, Ra-226 and K-40, were measured by means of low background gamma-ray spectroscopy with a high purity germanium detector. The measured activity concentrations of Th-232, Ra-226 and K-40 of all clay samples ranged from 83 to 476, 67 to 576 and 161 to 1200 Bq/kg, respectively. These levels were comparable to those of other clays globally. The calculated radium equivalents varied from 327 to 1226 Bq/kg, with the average value (662 Bq/kg) being significantly higher than the standard criterion of 370 Bq/kg. The external hazard indices varied from 0.88 to 3.31, with an average of 1.79, which was higher than the standard criterion (1). The gamma radiation hazard indices of all samples studied ranged from 1.14 to 4.22, which were below the criterion limit (<6) corresponding to a dose rate <1 mSv/y for superficial use and use with other materials with restricted use, but were higher than the criterion limit (1) when used in bulk amounts. Therefore, the hazard indices should be reduced by choosing carefully among the clays studied and other mixing ingredients.

**Keywords:** natural radionuclide, clays, southern Thailand, gamma-ray spectrometer

## INTRODUCTION

Clays have been used as raw materials in many industrial fields (including ceramics, paper, paint and petroleum, among others). Two types of clay are generally used, which are often termed as China clay and ball clay. China clay is one of the most useful industrial minerals, with a

wide range of application. Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is the main mineral in both clays and is made up of alternate octahedral gibbsite and tetrahedral silica layers giving a platy structure. In kaolin, minor quantities of quartz and transition elements, such as iron, titanium and manganese, are generally present in additive minerals (Chandrasekhar and Ramaswamy, 2007). Ball

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clays are finer than China clay and are often referred to as plastic clay, as they provide greater plasticity in ceramic products (Das *et al.*, 2005).

Among the naturally occurring radioactive materials (NORMs), the most important radionuclides are Ra-226 and Th-232, including their radioactive decay products, and K-40. Potassium is the most abundant of these and is found in the earth's crust on average up to 2.6%, while uranium and thorium are present in levels of parts per million. The radioisotope K-40 comprises only 0.012% of all natural potassium. However, the radioactivity from potassium often dominates the natural activity of sediment because of its high potassium content (Ayres and Theilen, 2001). Clays in southern Thailand originated from the hydrothermal alteration of granitic rocks of both primary and secondary deposits. Some of the southern Thailand granites contain abundant natural radionuclides, namely, nuclides in the uranium series, thorium series and potassium. Furthermore, the highly cationic adsorption capacity of clay minerals (such as montmorillonite) is another reason why NORM can be present in a high concentration in clay raw materials. The content of natural radionuclides in clay contributes to radiation exposure for people mainly the external exposure, which is caused by direct gamma rays emitted from the clay or ceramic products. Knowledge of the level of radioactivity is important to assess the possible radiological hazard to human health and to develop guidelines for the use and management of these materials (Somlia *et al.*, 2008; Turhan, 2009).

In the present study, 17 samples of clay were analyzed using gamma-ray spectrometry to determine the activity concentrations of Ra-226, Th-232 and K-40. The results were used to assess the potential radiological hazards associated with these materials by the radium equivalent activity, the external gamma hazard index and gamma index values.

## MATERIALS AND METHODS

All samples were collected from southern Thailand (about latitude: 6°N to 11°N, longitude: 98°E to 102°E) at 17 localities where clay mining was active (Table 1 and Figure 1). The samples were collected from stock ready for sale to industries. Each sample (200 g) was crushed using a ball mill and then ground in an agate mortar. Each sample was homogenized and sieved (50 mesh), dried in an oven at 110°C for 24 h and then the samples were packed into cylindrical plastic boxes. The boxes were sealed and kept for 4 w, in order to establish the secular radioactive equilibrium of Ra-226 and Th-232, along with their decay daughter products (Papaefthymiou, 2008).

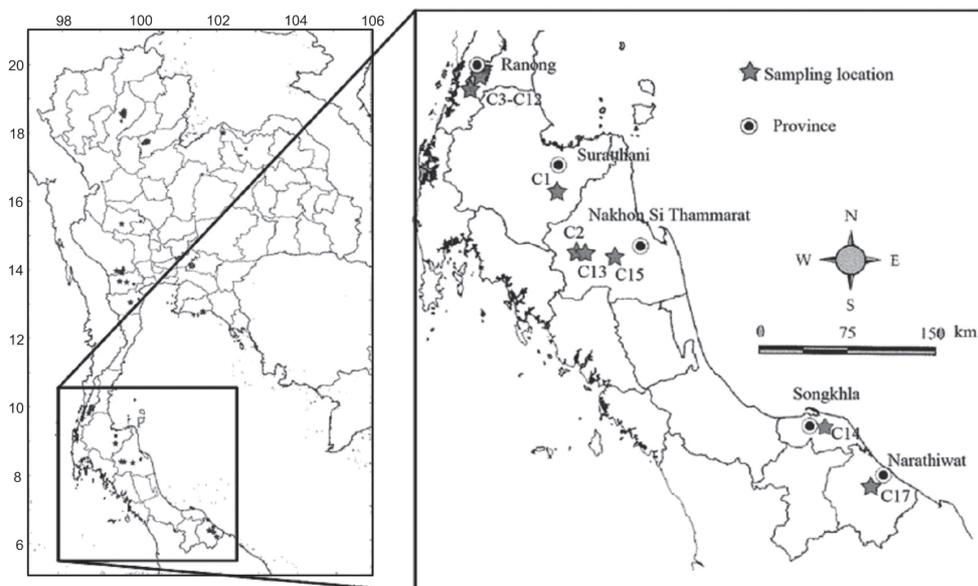
A gamma-ray spectrometric system with a Canberra coaxial high purity germanium detector (HPGe, Canberra, GC1319, USA) with an active volume of 59.9 cm<sup>3</sup> was used to measure the gamma rays emitted from samples. The detector gave a relative efficiency of 13.9% and a gamma ray energy resolution of 1.75 keV full-width at half maximum (FWHM) at 1,332.5 keV gamma-ray energy. A low background lead shield (Canberra Model 747, USA) was used to reduce background gamma-ray in the detector chamber. After attaining secular equilibrium, each of the prepared samples was analyzed for the Ra-226, Th-232 and K-40 contents using the gamma spectrometric system.

The specific activities of the radionuclides studied were averaged from gamma-ray photo-peaks at several energies. Since U-238 and Th-232 are not gamma-emitters, they were analyzed indirectly through the gamma-rays emitted from their decay products of Ra-226 and Th-232 after their secular equilibrium. Gamma-rays from Pb-214 and Bi-214 were used to determine the activity of Ra-226 (also known as the U-238 equivalent). Gamma-rays emitted from Ac-228, Pb-212 and Bi-212 were used to determine the average activity of Th-232, whereas

**Table 1** Clay sample code, name and source of the clay samples.

| Code | name                | Mining company; locality   |
|------|---------------------|--|
| C1   | Kaolin -325mesh     | Sakonsamrath Co. Ltd.; T. KunTalay, A. Muang, C. Suratthani                      |
| C2   | Ball Clay           | Siam Fine Clay Co. Ltd.; T. Thangphun, A. Chaloeiphra-kiat, C. Nakhonsithammarat |
| C3   | Kaolin-325mesh      | Kaolin Mine Hinpung Co. Ltd.; T. Haadsompan, A. Muang C. Ranong                  |
| C4   | Kaolin-325mesh      | Kaolin Mine Co. Ltd.; T. Haadsompan, A. Muang, C. Ranong                         |
| C5   | Kaolin-325mesh      | Thungchaina Clay Chvala Mine Co. Ltd.; T. Haadsompan, A. Muang, C. Ranong        |
| C6   | Kaolin-325mesh      | PaimRai Co. Ltd.; T. Haadsompan, A. Muang, C. Ranong                             |
| C7   | Kaolin-325mesh(1)   | Rathnarathon and Bood Co. Ltd.; T. Haadsompan,                                   |
| C8   | Kaolin-325mesh(2)   | A. Muang, C. Ranong  |
| C9   | Kaolin-325mesh(3)   |  |
| C10  | Kaolin MRD-White    | Minerals Resource Development Co. Ltd. (MRD Mine);                               |
| C11  | Kaolin MRD-Plus     | T. Haadsompan, A. Muang, C. Ranong   |
| C12  | Kaolin MRD-Standard |  |
| C13  | Kaolin              | Barakath Mine; T. Thungyai, A. Lansaka, C. Nakhonsithammarat                     |
| C14  | Brick clay          | Ban Dinlan; A. Bangkam, C. Songkhla  |
| C15  | Ball clay           | Barakath Mine; T. Thungyai, A. Lansaka, C. Nakhonsithammarat                     |
| C16  | Compound Clay       | Compound Clay Co. Ltd.; Khlongsamwa, Bangkok                                     |
| C17  | Kaolin              | Nara Industry Co. Ltd., A. Sungi Padi, C. Narathiwat                             |

**Note** C16 is the commercial compound clay used in the ceramic/pottery industry.



**Figure 1** Map showing the sampling locations of clay sources in Southern Thailand, modified from DMR (2002).

potassium was measured directly by the K-40 isotope. Gamma-ray energies used in this analysis are shown in Table 2. The radiometric analysis for the radionuclides studied was carried out through the selected energy regions of interest (ROIs). The spectra were analyzed using the Genie2k computer software (Canberra, USA). An empty bottle with the same geometry as the samples was used for background gamma subtraction.

The minerals present in each sample were examined using an X-Ray powder diffraction system (Phillips X'Pert MPD diffractometer, The Netherlands), which was operated with Cu K<sub>α</sub> X-rays and a scanning 2θ ranged from 5° to 90° with a step size of 0.02, time per step = 2 s, current = 30 mA and high voltage = 40 kV. The minerals were identified by reference to the ICDD (International Centre for Diffraction Data) powder diffraction database (available from: <http://www.gly.uga.edu>). The semi-quantitative analysis was performed using the X'Pert HighScore Plus computer software, on the basis of the reference intensity ratio (RIR) values (often called I/I<sub>c</sub>), which determines the estimated mass fraction of the mineral identified. The normalization used in this method assumes that the sum of all identified

phases is 100%. This means that only the crystalline phase would be identified with no amorphous phase present in the sample. Under these conditions, a semi-quantitative result was calculated by equation (X'Pert HighScore Plus, version 2.1), as described by Chung (1974a; 1974b; 1975). Equation 1 was used to evaluate X<sub>α</sub>, the concentration of phase α:

$$X_{\alpha} = \frac{I_{(hkl)\alpha}}{RIR_{\alpha} I_{(hkl)\alpha}^{rel}} \left[ \frac{1}{\sum_{j=1}^n (I_{(hkl)j} / RIR_j I_{(hkl)j}^{rel})} \right] \quad (1)$$

Where:

$I_{(hkl)}$  and  $I_{(hkl)}^{rel}$  are intensities of the selected Bragg reflection  $hkl$ , for phase α in the measurement and ICDD, respectively,

$I_{(hkl)j}$  and  $I_{(hkl)j}^{rel}$  are intensities of the selected Bragg reflection  $hkl$ , for mixture in the measurement and ICDD, respectively,

$RIR_{\alpha}$  and  $RIR_j$  are RIR values of phase α and the mixture, respectively.

The analysis of the semi-quantitative results is shown in Table 3.

Radium equivalent activity (Ra<sub>eq</sub>) is a common index used to represent the specific activity of Ra-226, Th-232 and K-40 by a single

**Table 2** Gamma-ray energies used to analyze radiated isotopes.

| Radiated Isotope | Energy (keV) | Analyzed isotope |
|------------------|--------------|------------------|
| Pb-214           | 295.2        | Ra-226           |
|                  | 351.9        |                  |
| Bi-214           | 609.3        |                  |
|                  | 1,120.3      |                  |
|                  | 1,764.5      |                  |
| Ac-228           | 209.3        | Th-232           |
|                  | 270.2        |                  |
|                  | 338.3        |                  |
|                  | 463.0        |                  |
|                  | 911.2        |                  |
|                  | 969.0        |                  |
| Pb-212           | 238.6        |                  |
| Bi-212           | 727.3        |                  |
| K-40             | 1,460.8      | K-40             |

quantity which takes into account the radiation hazards associated with them. The  $Ra_{eq}$  is a weighted sum of activities of the above three radionuclides, based on the estimation that 370 Bq/kg of Ra-226, 259 Bq/kg of Th-232 and 4,810 Bq/kg of K-40 produce the same gamma-ray dose. It is defined by Equation 2 (Turhan, 2009):

$$Ra_{eq} = A_{Ra} + \left[ \frac{10}{7} \right] A_{Th} + \left[ \frac{10}{130} \right] A_K \quad (2)$$

Where:  $A_{Ra}$ ,  $A_{Th}$  and  $A_K$  are the activity concentrations in Bq/kg of Ra-226, Th-232 and K-40, respectively.

The external hazard index ( $H_{ex}$ ) due to the emitted gamma rays of the samples is calculated by Equation 3 (Somlia *et al.*, 2008):

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \leq 1 \quad (3)$$

Where:  $A_{Ra}$ ,  $A_{Th}$  and  $A_K$  are the activity concentrations in Bq/kg of Ra-226, Th-232 and K-40, respectively.

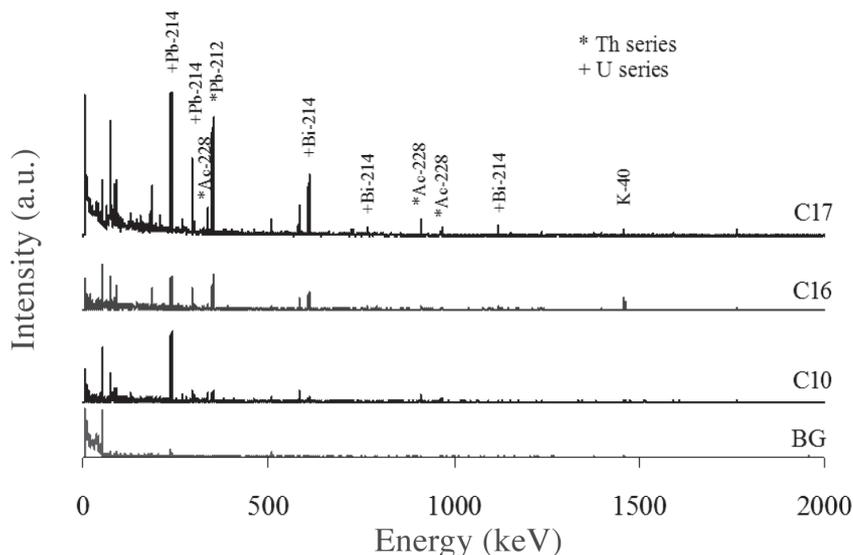
In the present study, the gamma radiation hazard index was calculated using Equation 4 (NEA-OECD, 1979):

$$I_\gamma = \frac{A_{Ra}}{300} + \frac{A_{Th}}{200} + \frac{A_K}{3000} \quad (4)$$

Where:  $A_{Ra}$ ,  $A_{Th}$  and  $A_K$  are the activity concentrations (Bq/kg) of Ra-226, Th-232 and K-40, respectively.

## RESULTS AND DISCUSSION

There were numerous rare elements in the clay samples due to their mineral composition and adsorbing features. The main radionuclides of clays were Ra-226 and Th-232 which are in radioactive equilibrium with their daughter products, such as Pb-214, Bi-214, Ac-228, Pb-212 and Bi-212 (Dodona, 2000). Figure 2 shows the typical gamma-ray spectra of samples, coded C17, C16, C10 and BG (empty bottle used for background gamma subtraction). Radioactivity levels of Ra-226, Th-232 and K-40 measured in clays from different collection areas in the present study are presented in Table 3, which shows that the activity concentrations of Ra-226, Th-232 and K-40 ranged from 67 to 576, 83 to 476 and 161 to 1200 Bq/kg, respectively. The activity



**Figure 2** Gamma-ray spectra of the clay samples C10, C16, C17 and BG (empty bottle used for background subtraction).

concentration of K-40 was expected to have a higher concentration at all locations studied as the clay minerals usually contain large amounts of potassium.

Radiation hazard indices were used to assess the radiation hazard associated with the clay samples due to the content of radionuclides in the clay samples studied. Indices used were: activity concentration, the radium equivalent activity, the external hazard index and the gamma radiation hazard index.

### Activity concentration

The Safety Guide No.Rs-G-1.7 (IAEA, 2004) recommends values of activity concentration for radionuclides of natural origin. The values were derived using the exclusion concept, with 10,000 Bq/kg for K-40, and 1,000 Bq/kg for U-238, Ra-226 and Th-232. Annual doses to individuals as a consequence of these

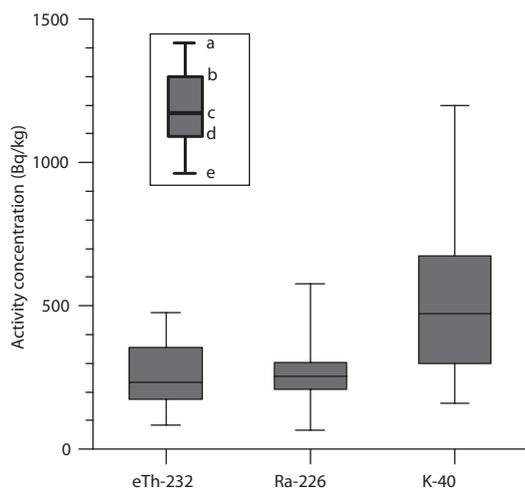
levels of concentrations would be unlikely to exceed about 1 mSv. This means that it is usually unnecessary to regulate the content of radionuclides, when their activity concentrations are lower than these values (Chang *et al.*, 2008). The activity concentrations of Ra-226, Th-232 and K-40 measured in Bq/kg in the samples studied are presented in Table 3 and Figure 4. The results show that the activity concentrations of Ra-226, Th-232 and K-40 in all the clay samples studied were lower than the recommended values, ranging from 83 to 476 Bq/kg for Th-232, 67 to 576 Bq/kg for Ra-226 and 161 to 1200 Bq/kg for K-40. The concentrations of Ra-226 and Th-232 were not significantly ( $\alpha=0.05$ ) different by an independent t-test, while the K-40 concentration was significantly ( $\alpha=0.05$ ) higher than that of Ra-226 and Th-232 (Figure 3).

The graphs in Figures 5(a), 5(b) and 5(c) show the correlation between the activity

**Table 3** Activity concentrations of eTh-232, Ra-226, K-40 in Bq/kg, thorium equivalent mass concentration eTh in mg/kg and Ra-226 in ng/kg, K-40 and clay content. (Where applicable, mean  $\pm$  standard deviation values are shown.)

| Source | eTh-232<br>(Bq/kg) | eTh<br>(mg/kg) | Ra-226<br>(Bq/kg) | Ra-226<br>(ng/kg) | K-40<br>(Bq/kg) | K-40<br>( $\times 10^{-4}$ ) % | Clay<br>(%) |
|--------|--------------------|----------------|-------------------|-------------------|-----------------|--------------------------------|-------------|
| C1     | 173 $\pm$ 14       | 43             | 99 $\pm$ 9        | 3                 | 290 $\pm$ 61    | 1.09                           | 49          |
| C2     | 149 $\pm$ 13       | 37             | 302 $\pm$ 15      | 8                 | 675 $\pm$ 88    | 2.55                           | 61          |
| C3     | 363 $\pm$ 23       | 89             | 243 $\pm$ 15      | 7                 | 582 $\pm$ 84    | 2.20                           | 82          |
| C4     | 225 $\pm$ 16       | 55             | 255 $\pm$ 18      | 7                 | 413 $\pm$ 63    | 1.56                           | 79          |
| C5     | 354 $\pm$ 23       | 87             | 208 $\pm$ 10      | 6                 | 474 $\pm$ 76    | 1.79                           | 91          |
| C6     | 476 $\pm$ 26       | 117            | 280 $\pm$ 17      | 8                 | 572 $\pm$ 86    | 2.16                           | 83          |
| C7     | 305 $\pm$ 17       | 75             | 195 $\pm$ 13      | 5                 | 472 $\pm$ 78    | 1.78                           | 98          |
| C8     | 277 $\pm$ 20       | 68             | 480 $\pm$ 30      | 13                | 1031 $\pm$ 100  | 3.89                           | 80          |
| C9     | 232 $\pm$ 20       | 57             | 291 $\pm$ 15      | 8                 | 663 $\pm$ 83    | 2.50                           | 92          |
| C10    | 173 $\pm$ 14       | 43             | 67 $\pm$ 8        | 2                 | 161 $\pm$ 45    | 0.61                           | 95          |
| C11    | 245 $\pm$ 18       | 60             | 223 $\pm$ 16      | 6                 | 282 $\pm$ 60    | 1.06                           | 95          |
| C12    | 321 $\pm$ 20       | 79             | 254 $\pm$ 18      | 7                 | 440 $\pm$ 74    | 1.66                           | 92          |
| C13    | 177 $\pm$ 16       | 44             | 260 $\pm$ 13      | 7                 | 163 $\pm$ 56    | 0.62                           | 76          |
| C14    | 150 $\pm$ 15       | 37             | 235 $\pm$ 14      | 6                 | 421 $\pm$ 63    | 1.59                           | 12          |
| C15    | 113 $\pm$ 12       | 28             | 338 $\pm$ 15      | 9                 | 694 $\pm$ 87    | 2.62                           | 54          |
| C16    | 83 $\pm$ 11        | 20             | 189 $\pm$ 10      | 5                 | 1200 $\pm$ 111  | 4.53                           | 29          |
| C17    | 439 $\pm$ 25       | 108            | 576 $\pm$ 21      | 16                | 299 $\pm$ 79    | 1.13                           | 98          |

concentration of Ra-226 and Th-232, K-40 and Ra-226, and K-40 and Th-232, respectively, with a trend line drawn through the data points using a linear regression technique. The correlation coefficient between Ra-226 and Th-232 was 0.39, whereas the correlation coefficients between K-

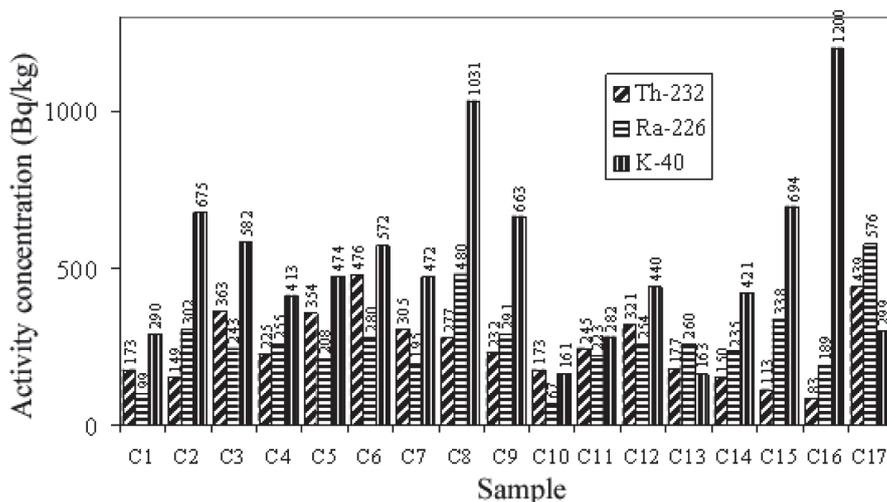


**Figure 3** Box plot of the activity concentration of eTh-232, Ra-226 and K-40 of the studied clays. (inset letters a, b, c, d and e mean maximum, third quartile, median, first quartile and minimum value respectively.)

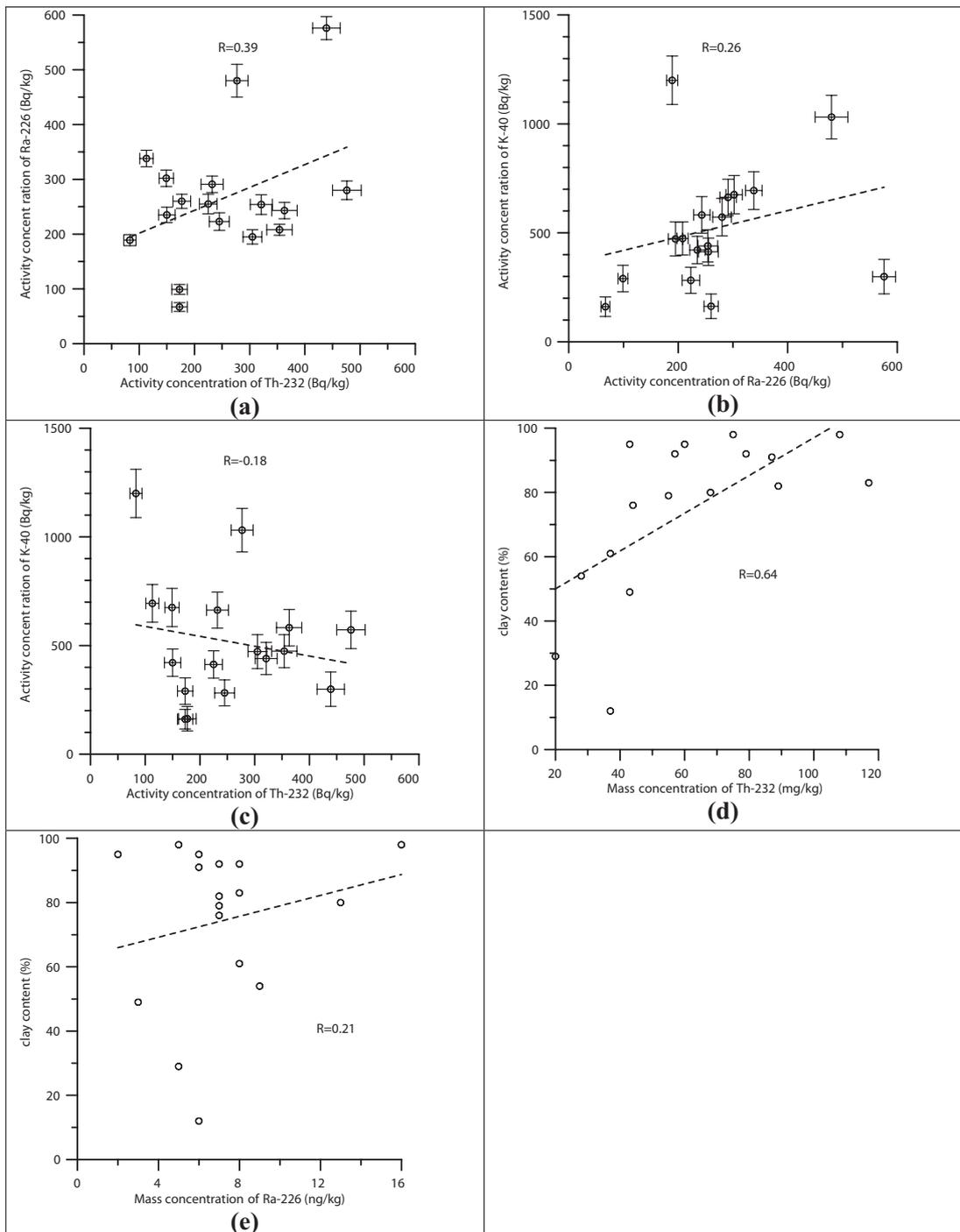
40 and Ra-226, and K-40 and Th-232 were rather low (0.26 and -0.18). This was not unexpected, since Ra-226 and Th-232 originated from the natural decay series of U-238 and Th-232, respectively, whereas K-40, although a naturally occurring radionuclide, was not a part of any such decay series.

Figure 5d shows a medium correlation ( $r=0.64$ ) was obtained from the relationship between the clay content and the thorium-equivalent concentration (eTh). A high thorium activity level reflects a high clay content, while a poor correlation was observed between clay content and the Ra-226 concentration ( $r=0.21$ ), which indicated that Ra-226 was probably not related to the presence of clay (Figure 5e), probably because of the difference in mobility of the two metallic ions in the oxidizing environment. Radium is more mobile and can escape, resulting in a reduction of radium in the clay body, whereas thorium remains attached to the clay body.

A poor correlation ( $r=0.39$ , Figure 5a) was observed for the plot of Th-232 and Ra-226 activity concentrations in the clay samples, while a good correlation ( $r=0.87$ ) was reported for a monazite sample (El Afifi *et al.*, 2006). The monazite crystal grains can certainly retain the



**Figure 4** Activity concentrations of eTh-232, Ra-226 and K-40 of the clay samples (C1-C17).



**Figure 5** Graphs of the linear correlation between: (a) activity concentration of Ra-226 and Th-232; (b) activity concentration of K-40 and Ra-226; (c) activity concentration of K-40 and Th-232; (d) % clay and eTh (mg/kg); and (e) % clay and Ra-226 (ng/kg) in the studied clay samples. (In graphs 5(a), 5(b) and 5(c), the values plotted are mean values  $\pm$  standard deviation.)

Th-232 and Ra-226, including radon and decay products, whereas radium can escape the clay body due to its high mobility.

#### Radium equivalent activity ( $Ra_{eq}$ )

This index is useful to compare the activity concentrations of the materials containing different concentrations of Ra-226, Th-232 and K-40. The maximum value of  $Ra_{eq}$  must be less than 370 Bq/kg for safe use (NEA-OECD, 1979). The radium equivalent activities (Table 5) in the clay samples studied from Southern Thailand ranged from 327 to 1226 Bq/kg, with most of them being significantly higher than the recommended maximum value of 370 Bq/kg. This highlighted the good adsorbent characteristics of the clays

studied, especially as clays colloids. There were two exceptions, namely the clay sample coded C1 from Suratthani ( $368 \pm 22$  Bq/kg) and the sample coded C10 from Ranong ( $327 \pm 22$  Bq/kg). Nevertheless, it is important to note that this recommended value is proposed for materials used in bulk amounts, and it is not appropriate for superficial use or for use with other materials with restricted use, such as boards and tiles.

#### External hazard index ( $H_{ex}$ )

A number of indices related to the assessment of excess gamma radiation have been proposed for outdoors (outside a dwelling). In the present study, the gamma-index was calculated as proposed by the European Commission (1999),

**Table 4** Limits of the activity concentration index (European Commission, 1999).

| Dose criterion   | 0.3 mSv/y    | 1 mSv/y    |
|--|--------------|------------|
| Materials used in bulk amounts                               | $I \leq 0.5$ | $I \leq 1$ |
| Materials used for superficial purposes, boards, tiles, etc. | $I \leq 2$   | $I \leq 6$ |

**Table 5** Radium equivalent ( $Ra_{eq}$ ), the external hazard index ( $H_{ex}$ ) and the gamma radiation hazard index ( $I_g$ ) of the studied clays. (Values are mean  $\pm$  standard deviation.)

| Sample | $Ra_{eq}$ (Bq/kg) | $H_{ex}$        | $I_g$           |
|--------|-------------------|-----------------|-----------------|
| C1     | 368 $\pm$ 22      | 1.00 $\pm$ 0.06 | 1.29 $\pm$ 0.08 |
| C2     | 568 $\pm$ 26      | 1.53 $\pm$ 0.07 | 1.98 $\pm$ 0.09 |
| C3     | 806 $\pm$ 36      | 2.18 $\pm$ 0.10 | 2.82 $\pm$ 0.13 |
| C4     | 608 $\pm$ 30      | 1.64 $\pm$ 0.08 | 2.11 $\pm$ 0.10 |
| C5     | 750 $\pm$ 35      | 2.03 $\pm$ 0.10 | 2.62 $\pm$ 0.12 |
| C6     | 1003 $\pm$ 41     | 2.71 $\pm$ 0.11 | 3.50 $\pm$ 0.14 |
| C7     | 666 $\pm$ 29      | 1.80 $\pm$ 0.08 | 2.33 $\pm$ 0.10 |
| C8     | 954 $\pm$ 42      | 2.58 $\pm$ 0.11 | 3.33 $\pm$ 0.15 |
| C9     | 674 $\pm$ 33      | 1.82 $\pm$ 0.09 | 2.35 $\pm$ 0.11 |
| C10    | 327 $\pm$ 22      | 0.88 $\pm$ 0.06 | 1.14 $\pm$ 0.08 |
| C11    | 594 $\pm$ 31      | 1.61 $\pm$ 0.08 | 2.06 $\pm$ 0.11 |
| C12    | 747 $\pm$ 34      | 2.02 $\pm$ 0.09 | 2.60 $\pm$ 0.12 |
| C13    | 525 $\pm$ 27      | 1.42 $\pm$ 0.07 | 1.81 $\pm$ 0.09 |
| C14    | 482 $\pm$ 26      | 1.30 $\pm$ 0.07 | 1.68 $\pm$ 0.09 |
| C15    | 552 $\pm$ 24      | 1.49 $\pm$ 0.06 | 1.92 $\pm$ 0.08 |
| C16    | 399 $\pm$ 20      | 1.08 $\pm$ 0.06 | 1.44 $\pm$ 0.07 |
| C17    | 1226 $\pm$ 43     | 3.31 $\pm$ 0.11 | 4.22 $\pm$ 0.15 |

who suggested a dose criterion that was recommended to be less than or equal to 1.

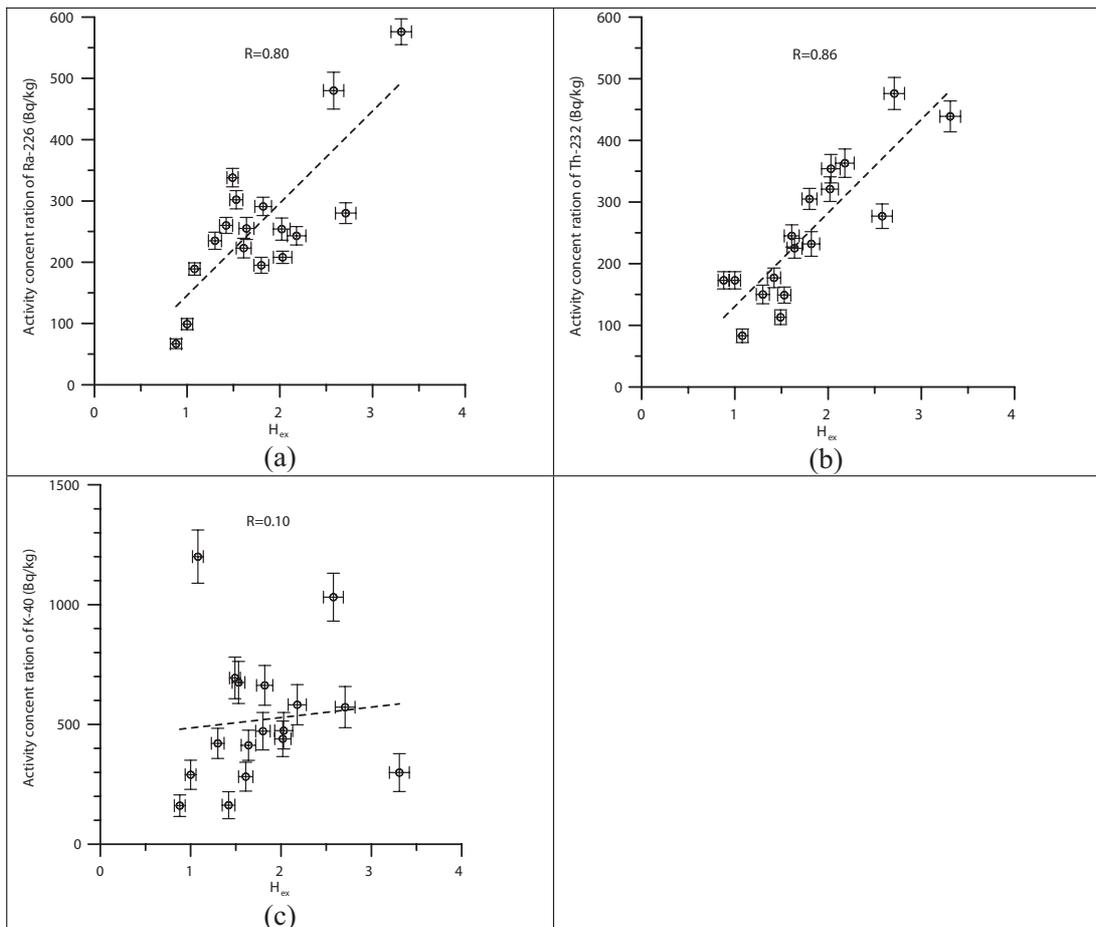
The study results are summarized in Table 5. The  $H_{ex}$  of the studied clays ranged from 0.88 to 3.31. The  $H_{ex}$  average value was highly (99% confidence interval;  $\alpha=0.01$ ) significant and higher than the recommended maximum value of 1, except for sample C10. Furthermore, the annual effective dose due to radioactivity in the material studied was more than 1.5 mSv/y (Ngachin *et al.*, 2008), so that the radiation hazard could be classed as high. A good correlation ( $r=0.80$ , Figure 6a) was observed between Ra-226 and  $H_{ex}$ , and also between Th-232 and  $H_{ex}$  ( $r=0.86$ , Figure 6b).

These results indicate that the high activity concentration values in the clay samples resulted from high levels of Ra-226 and Th-232 impurities when compared to other clays. A poor correlation ( $r=0.10$ , Figure 6c) was observed between K-40 and  $H_{ex}$ , which indicates that the gamma rays emitted from K-40 activity were not a major contributor to  $H_{ex}$ .

### Gamma radiation hazard index ( $I_g$ )

The gamma radiation hazard index should not exceed the upper limit dependent on the dose criterion (Table 5).

The recommended dose limit for



**Figure 6** Correlations between the  $H_{ex}$  and activity concentration of: (a) Ra-226; (b) Th-232; and (c) K-40.

individual members of the public is 1 mSv/y (ICRP, 1991). The gamma radiation hazard index values are presented in Table 5 and ranged from  $1.14 \pm 0.08$  to  $4.22 \pm 0.15$  with a mean value of 2.31. They were significantly ( $\alpha = 0.01$ ) higher than the criterion value for an effective dose of 1 mSv/y for materials used in bulk amounts. However, the mean value of  $I_\gamma$  was highly significantly ( $\alpha = 0.01$ ) smaller than the criterion of  $I_\gamma = 6$  (European Commission, 1999), which corresponds to an effective dose of less than 1 mSv/y when using clays superficially or in other materials with restricted use.

### CONCLUSIONS

The activity concentrations of all clays sampled from Southern Thailand were within the criterion limit set by the IAEA (2004) and the radium equivalent activities of the clays were higher than the criterion limit (NEA-OECD, 1979) except for C1 and C10.

The natural radionuclides content, activity concentrations, the radium equivalent activity and the gamma index were determined to assess the radiological hazard from clay samples commonly used as ceramic raw materials in Thailand. The results showed that the radiation hazard index values of the measured clays were higher than the recommended safety limit for radiation hazard. With reference to the dose limit of 1 mSv/y for the public, it was concluded that the calculated mean values of the gamma radiation hazard index of the studied clays indicate there should be restrictions on using the study clays in bulk amounts. However, ceramic products do not usually use clay in bulk amounts, but mix the clay with other ingredients, such as quartz and feldspar. By using a properly selected mixture of radioactive clay with other low radioactive ingredients, the dose received from ceramic products can comply with the safe dose limit of 1 mSv/y.

All clay samples studied had gamma

radiation hazard index values below the criterion limit of  $I_\gamma = 6$ , indicating the clays were safe for superficial use or with other materials with restricted use. With such proper uses of the clays, the corresponding dose rate would be well below 1 mSv/y.

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