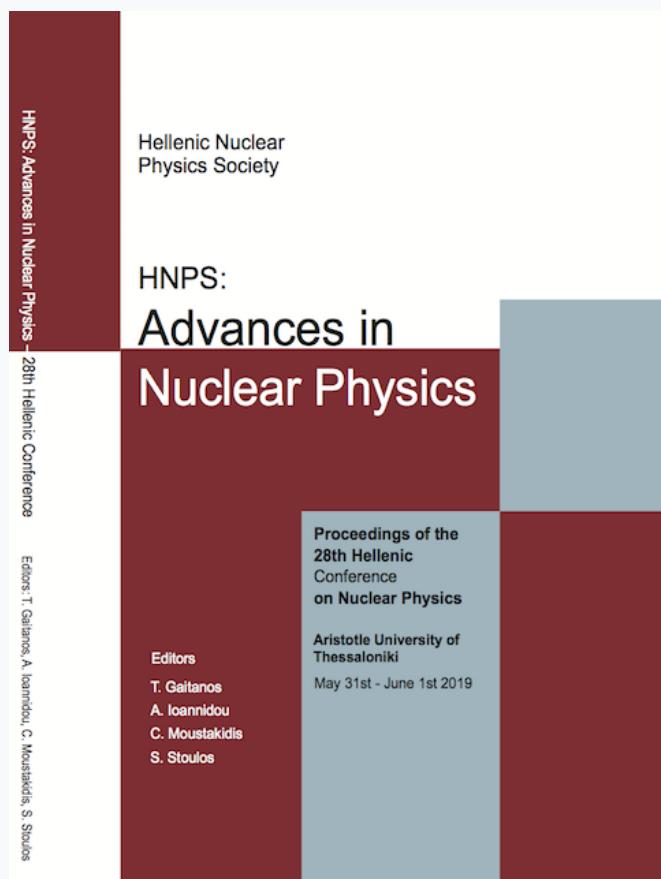


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*Filothei K. Pappa, Christos Tsabaris, Dionisis Patiris, Georgios Eleftheriou, Effrossini G. Androulakaki, Michael Kokkoris, Roza Vlastou*

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# Inter-comparison exercise utilizing x- and $\gamma$ -ray spectrometry

F.K. Pappa<sup>1,2</sup>, C. Tsabarlis<sup>1</sup>, D.L. Patiris<sup>1</sup>, G. Eleftheriou<sup>1</sup>, E.G. Androulakaki<sup>1</sup>,  
M. Kokkoris<sup>2</sup>, R. Vlastou<sup>2</sup>

<sup>1</sup>*Institute of Oceanography, Hellenic Centre of Marine Research, Anavyssos, Attiki, 19013, Greece.*

<sup>2</sup>*Department of Physics, National Technical University of Athens, Zografou, Athens, 15780, Greece.*

**Abstract** Radionuclides are characterized by their nuclear and chemical behavior. Additionally, the geochemical characteristics of radionuclides result in their accumulation in the sediments via sorption processes. In this work the radionuclide activity concentrations obtained by gamma-ray spectrometry (HPGe detector) were converted to metal concentrations as described in [1]. The results were compared with the measured metal concentrations obtained by atomic spectrometry (X-ray fluorescence system-XRF). The samples originate from the coastal environment of two Greek areas, characterized by elevated values of natural radionuclides (e.g.  $^{226}\text{Ra}$ ) and metals. The preliminary study revealed a good agreement among the concentrations of potassium calculated via activity concentrations of  $^{40}\text{K}$  and those of XRF measurement, while a great divergence was observed for the thorium case. These differences can be attributed to the low statistics, as well as to the calibration set-up of Th XRF measurement.

**Keywords:** gamma-ray spectrometry, x-ray spectrometry, metal concentrations

Corresponding author: F.K. Pappa (fkpappa@hcmr.gr) | Published online: May 1st, 2020

## INTRODUCTION

The X-ray fluorescence (XRF) is a well-established technique for the determination of low trace element concentrations, such as uranium and lead, without destroying the sample and with low detection limits in the orders of parts per million. The main advantage of this technique is the small required amount of mass for the measurement, as well as the rapid and multi-element determination with minimal sample preparation. Additionally,  $\gamma$ -ray spectrometry as a non-destructive method can be also applied for the determination of low elemental concentrations utilizing the radioactive nature of some elements. However,  $\gamma$ -ray spectrometry requires great amount of masses (usually 10 times more than the XRF), enough sample preparation time so as to be obtained the secular equilibrium among the parent nuclides and their progenies and at least 24 h measurement time to achieve good statistics. Both techniques can be applied for determining elemental concentrations and the one can be indicative of the other in cases of monazite exploitation (rich in  $^{232}\text{Th}$ ) [2,3], exploration for uranium and thorium [4] and environmental monitoring [5]. Thus, in this work the association of the elemental concentrations obtained via these methodologies in two metal mining areas of Greece (Ierissos Gulf-Stratoni and Lavrio) was studied to support the use of in-situ XRF for locating minerals of high natural radioactivity (such as uranium, feldspars rich in  $^{40}\text{K}$ ) or vice versa and propose the utilization of in-situ  $\gamma$ -spectrometry to identify minerals (such as rare earths, monazite etc).

## EXPERIMENTAL DETAILS

The experimental details regarding sampling, sample preparation and radionuclide measurements are described in detail elsewhere [6]. A total of 87 sediment samples were collected from Ierissos Gulf (Stratoni) and Lavrio (Oxygono Bay). After the sample preparation  $\gamma$ -ray and x-ray measurements were performed so as to determine the activity concentrations of natural radionuclides and metal



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concentrations, respectively. The  $\gamma$ -ray measurements were performed with the HPGe detectors of (a) the Marine Environmental Radioactivity Laboratory (MERL) of Hellenic Center for Marine Research (HCMR), (b) the Nuclear Laboratory of Physics Department of National Technical University of Athens (NTUA) and (c) the Institute of Nuclear and Particle Physics of National Center for Scientific Research (NCSR) “Demokritos”. Additionally, the appropriate calibrations of the detection systems and corrections (e.g., True Coincidence Summing effects) were taken into account. The majority of radionuclide measurements were held in Marine Environmental Radioactivity Laboratory (MERL) of Hellenic Center for Marine Research (HCMR). Similarly the metal concentrations were realized via WDXRF system in the X-ray fluorescence laboratory of HCMR. More information regarding the applied methodologies mentioned above are included in [6].

### *Elemental concentration determination*

The activity concentrations ( $\text{Bq kg}^{-1}$ ) of  $^{40}\text{K}$  and  $^{232}\text{Th}$  were converted to metal concentrations (in  $\mu\text{g g}^{-1}$ ) of potassium and thorium, respectively. The  $^{40}\text{K}$  activity concentration was determined via 1460.8 keV photopeak, while  $^{232}\text{Th}$  was calculated via  $^{228}\text{Ac}$  (911.1, 964.6, 968.9 keV photopeaks) assuming secular equilibrium. Moreover,  $^{232}\text{Th}$  represents the total thorium as it is found in 99.98% natural abundance. The activity concentration of radionuclide of interest (e.g.  $^{40}\text{K}$ ) is estimated from the metal concentration and vice versa according to equation (1):

$$A = \lambda NC_E = \frac{\ln 2}{t_{1/2}} \frac{N_A H_E}{M_E} C_E \quad (1)$$

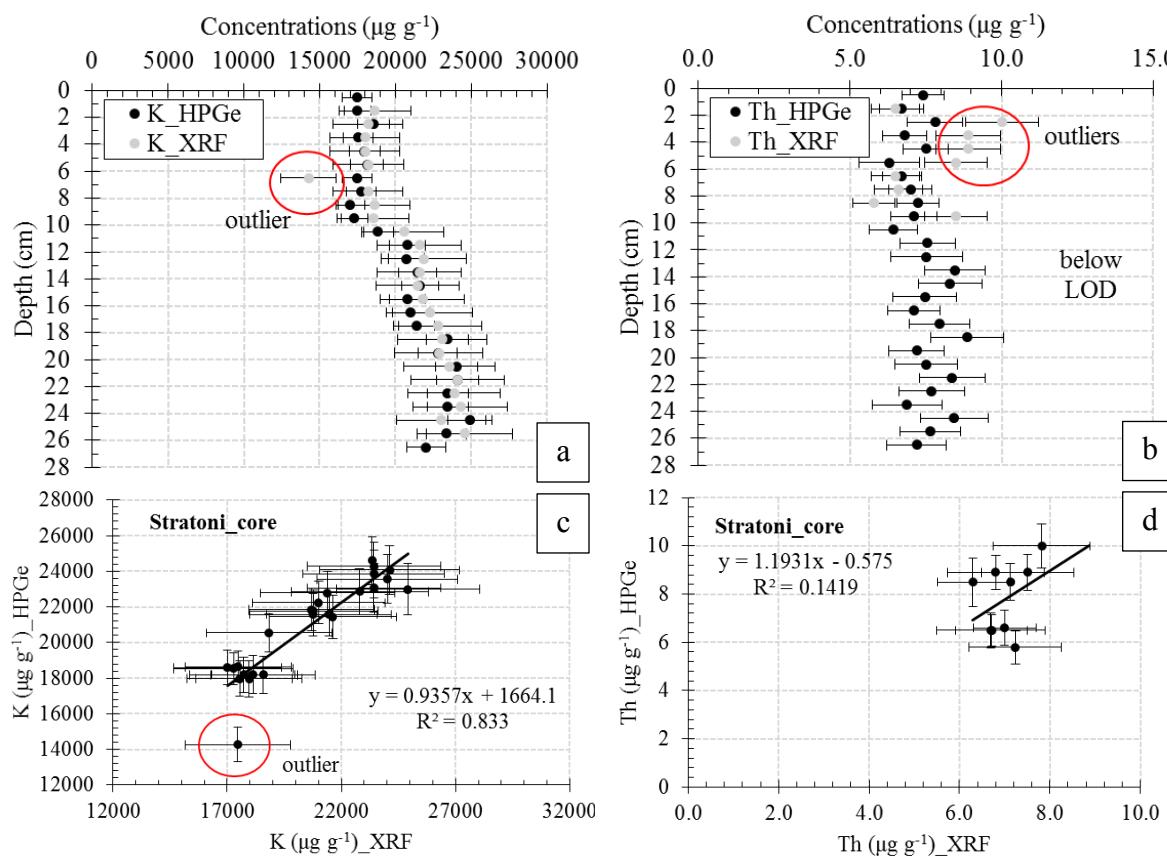
where,  $\lambda$  is the decay constant of the radionuclide ( $\text{s}^{-1}$ ),  $N$  is the number of atoms of the radionuclide in 1g of the corresponding element,  $t_{1/2}$  is the half-life of the radionuclide (s),  $N_A$  is Avocadro constant ( $6.022 \cdot 10^{23}$  atoms per mol),  $H_E$  is the isotopic abundance of the radionuclide in the element content (%),  $M_E$  is the atomic mass of the element (amu),  $C_E$  is the elemental composition in the sample ( $\mu\text{g g}^{-1}$ ).

## RESULTS AND DISCUSSION

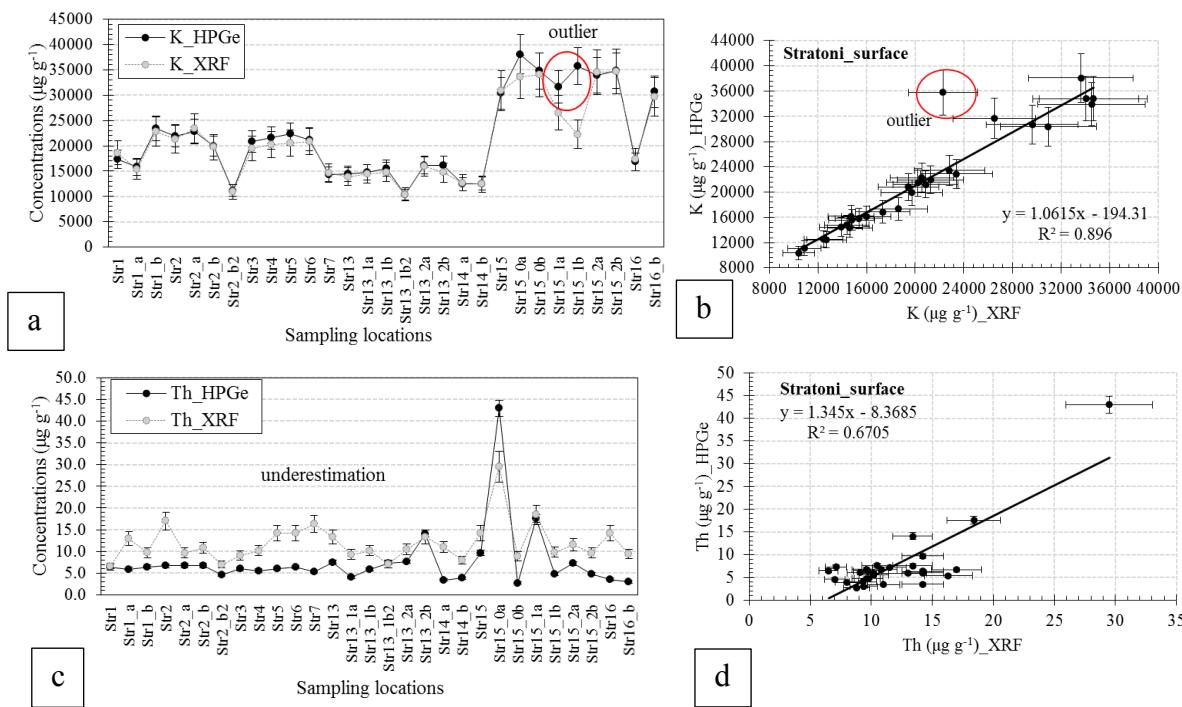
The concentrations of K and Th estimated via HPGe and measured via XRF are depicted in Fig. 1 and 2 for Stratoni and Fig. 3 and 4 for Lavrio, organized in surface and core sediments. The uncertainties of  $^{40}\text{K}$  and  $^{232}\text{Th}$  were found 10% and 5–14%, respectively and these are the uncertainties of the elemental concentrations of K and Th estimated via radionuclide measurements. Additionally, the uncertainties of K and Th were found 12.8% and 12% for measurements utilizing XRF system.

### *Ierissos Gulf*

The two methodologies were in good agreement, within uncertainties, especially in the case of potassium (Fig. 1a) for the core sediment samples. Additionally, the elemental concentrations of potassium determined via  $\gamma$ -spectrometry (K\_HPGe) were positively strongly linearly associated ( $R^2=0.83$ ) with those measured via XRF, a fact that was also verified by a simpler type of association (Spearman,  $R^2=0.88$ ). It should be noted that possible divergence (above 10%, see outliers in Fig. 1a and c) of the elemental concentrations of potassium observed between the two methodologies may be attributed to the sample preparation (fusion) for the x-ray fluorescent measurement. Nevertheless, the low concentrations of thorium, near the limit of detection of the XRF method, limited the observation of a possible association between the two methodologies (Fig. 1d), while many outliers were found (Fig. 1b).



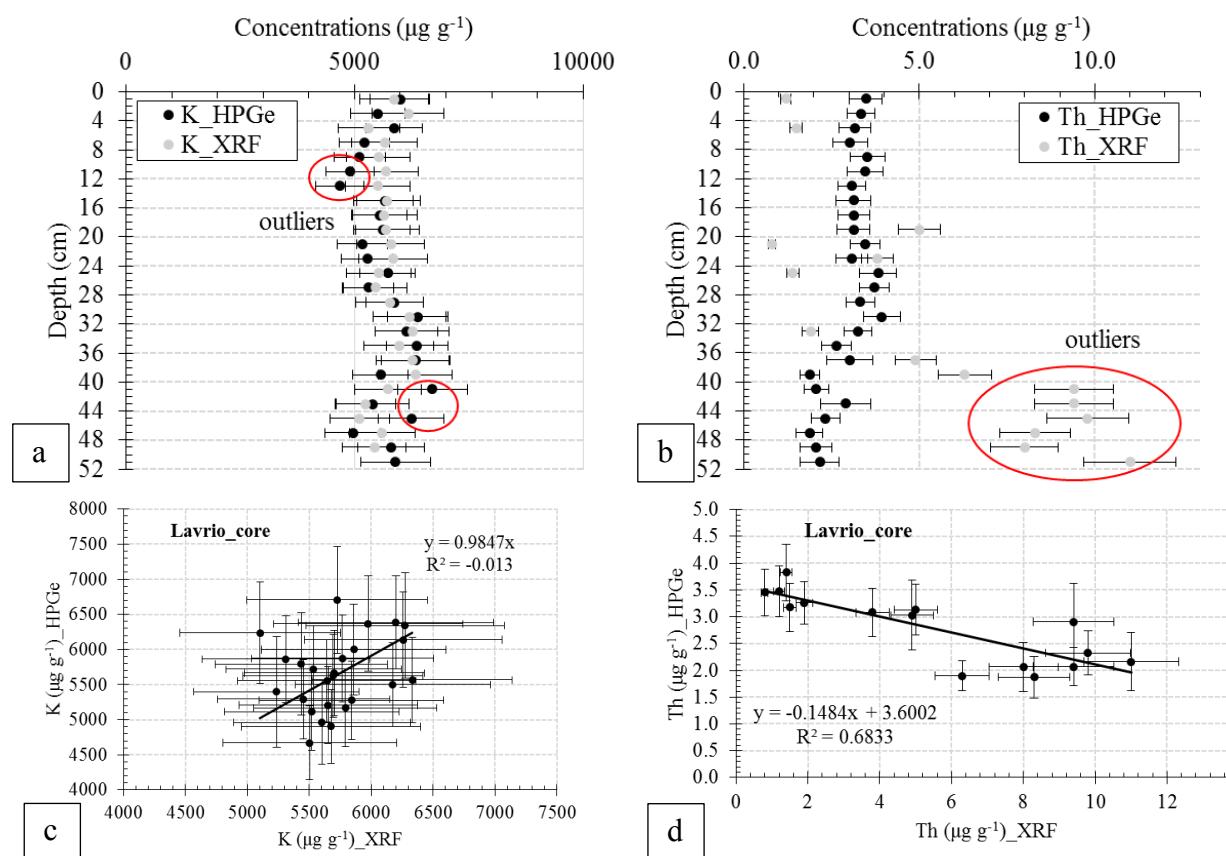
**Figure 1.** The vertical metallic profiles of potassium (K) and thorium (Th) obtained via  $\gamma$ - (HPGE) and x- (XRF) spectrometry (Fig. a and c, respectively) in the sediment cores of Ierissos Gulf (Stratoni) and the association between the two methodologies (Fig. b and d, respectively).



**Figure 2.** The surficial metal concentrations of potassium (K) and thorium (Th) obtained via  $\gamma$ - (HPGE) and x- (XRF) spectrometry (Fig. a and b, respectively) at Ierissos Gulf and the association between the two methodologies (Fig. c and d, respectively).

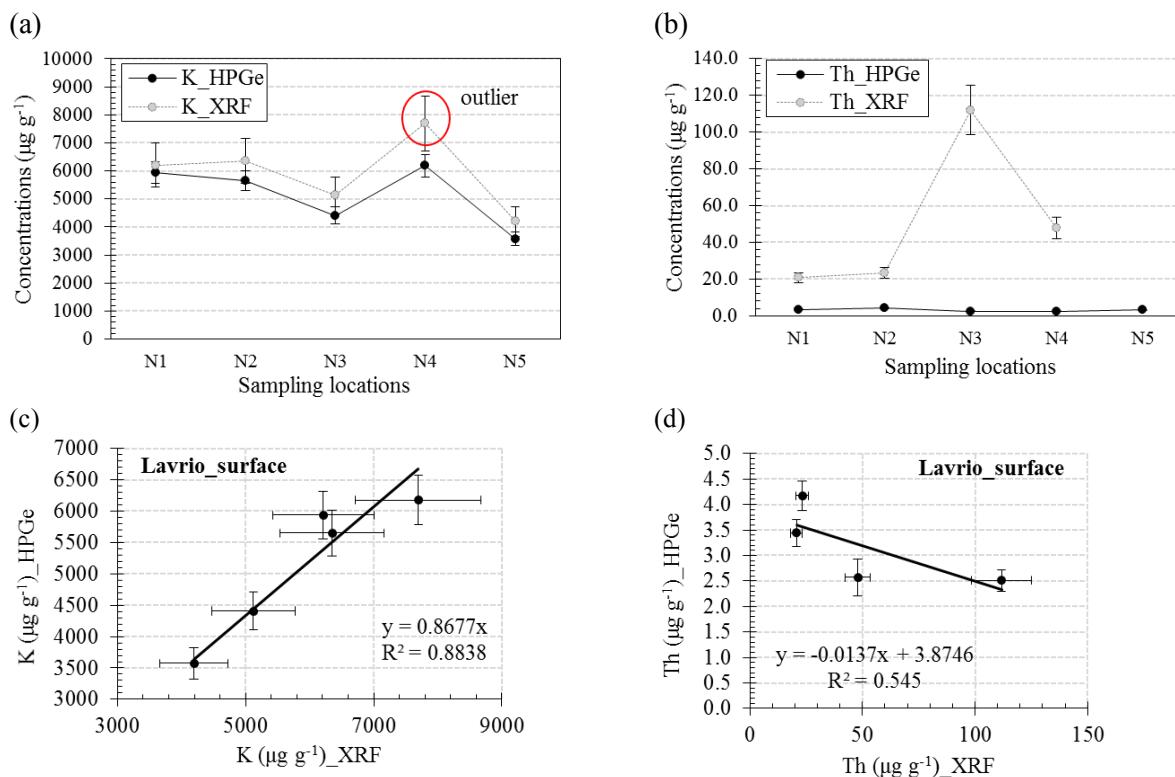
Similarly, the two methodologies were in good agreement, within uncertainties, especially in the case of potassium (Fig. 2a) for the surficial sediment samples, where they were found positively strongly linearly associated ( $R^2=0.89$ ) (Fig. 2b). Again, possible divergence (above 10%, see outliers in Fig. 2a and b) of the elemental concentrations of potassium can be attributed to the fusion sample preparation process for the x-ray fluorescent measurement. Nevertheless, the concentrations of thorium in the surficial samples were found systematically higher for almost all sampling points than those obtained via  $\gamma$ -ray spectrometry (Fig. 2c), indicating a systematic uncertainty during the measurements. Moreover, the associations between the two methods were found positively weak either linearly ( $R^2=0.67$ ) (Fig. 4d) or non-linearly ( $R^2=0.43$ , Spearman) maybe due to the small range of concentrations around  $8\text{--}18 \mu\text{g}\cdot\text{g}^{-1}$ .

### Lavrio



**Figure 3.** The vertical metallic profiles of potassium (K) and thorium (Th) obtained via  $\gamma$ - (HPGe) and x-ray spectrometry (Fig. a and b, respectively) in the sediment cores of Lavrio and the association between the two methodologies (Fig. c and d, respectively).

In the case of the core sediment collected at Oxygono Bay of Lavrio the  $\gamma$ - and x-ray measurements gave similar, within uncertainties, elemental concentrations for potassium (Fig. 3a). However, possible associations were not observed due to the small range of the metal concentrations (Fig. 3c). The thorium elemental concentrations measured via XRF varied greatly and were not in agreement with those obtained via  $\gamma$ -spectrometry, revealing the limitations of XRF methodology for really low concentrations, below  $10 \mu\text{g}\cdot\text{g}^{-1}$  (Fig. 3b). Additionally, a weak negative linear association ( $R^2=0.68$ ) was observed between the two methodologies (Fig. 3d), strengthening the observation of XRF limitations.



**Figure 4.** The surficial metal concentrations of potassium (K) and thorium (Th) obtained via  $\gamma$ - (HPGe) and x- (XRF) spectrometry (Fig. a and b, respectively) at Lavrio and the association between the two methodologies (Fig. c and d, respectively).

Regarding the elemental concentrations of potassium and thorium measured in the surficial samples of Lavrio (Oxygono Bay), they were found higher with the XRF method, especially thorium case (Figs. 4a and 4b). This, may be attributed to the calibration set-up of the XRF system for the thorium case, as in really low concentrations (below  $5 \mu\text{g}\cdot\text{g}^{-1}$ , according to the  $\gamma$ -ray measurement) the obtained thorium values cannot be accepted (see great variation in Fig. 4b and negative associations in Fig. 4d). Nevertheless, for the potassium case a strong positive linear association ( $R^2=0.88$ ) was observed among the two methodologies (Fig. 4c), while the differences in the concentrations (Fig. 4a) can be slightly accepted within uncertainties.

## CONCLUSIONS

The preliminary study revealed a good agreement among the concentrations of potassium calculated via activity concentrations of  $^{40}\text{K}$  and those of XRF measurement, while a great divergence was observed for the thorium case. These differences can be attributed to the low statistics, as well as to the calibration set-up for Th at XRF system. It is worth noting that in order for the XRF measurement held in HCMR to be in agreement with the  $\gamma$ -ray spectrometry, high concentrations ( $>10\text{--}15 \mu\text{g}\cdot\text{g}^{-1}$ ) are required.

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