

Determination of ^{40}K in Beach Sand and Seawater Samples at Sarımsaklı Beach of Aegean Sea (Turkey)

Şeyda TEZSEZER¹, Sevilay HACIYAKUPOĞLU^{1,♣}, Esra ORUCOĞLU²,

¹Istanbul Technical University, Energy Institute, TR-34469, Maslak, Istanbul, Turkey

²Istanbul Technical University, Faculty of Mines, TR-34469, Maslak, Istanbul, Turkey

Received: 28/10/2010, Accepted:28/03/2011

Abstract

This study dealt with analyzing of naturally occurring ^{40}K radioisotope in beach sand and seawater samples of Sarımsaklı beach at Aegean coastal region of Turkey and its contribution to natural radioactivity. By using gamma spectroscopy the mean radioactivity concentration was found as $1093.00 \pm 115.07 \text{ Bq kg}^{-1}$ for the beach sand and as $14.08 \pm 3.50 \text{ Bq kg}^{-1}$ for the seawater. The average external effective dose rate of beach sand was determined in air at 1 m above the ground as $45.58 \pm 4.80 \text{ nGy h}^{-1}$.

Keywords: Aegean Sea, Gamma Spectroscopy, ^{40}K ; Beach Sand, Seawater, Turkey

1. INTRODUCTION

Due to the fact that radionuclides can have harmful effects on the habitat and can also pose health hazard problems for human, the assessment of gamma radiation dose from natural sources is of particular importance as natural radiation is the largest contributor to the external dose of the world population [1, 2]. The dose rates vary depending upon the concentration of the natural radionuclides ^{238}U , ^{232}Th , their daughter products and ^{40}K present in soil, sands and rocks. There are growing environmental and national security needs for sensing the presence of radionuclides, to assess the various factors that may play a role in the functioning of the natural life. Also, the existence of these radionuclides can give information about the originated mineral deposits [3]. To determine radionuclide activities and to obtain average activity concentrations of these radionuclides, gamma spectroscopy and Kriging interpolation methodology has been used in various radioecological studies [4-5].

Potassium, the necessary element for living species, has three natural isotopes (^{39}K (93.2581 %), ^{40}K (0.0117 %) and ^{41}K (6.7302 %)) in which only ^{40}K is radioactive and can be taken into the body by drinking water, eating food, or breathing air [6]. The strong gamma radiation

associated with the electron-capture decay process by ^{40}K decay makes external exposure of this isotope important and the health hazard of ^{40}K with the general potential for subsequent cancer induction is associated with cell damage caused by this ionizing radiation [7, 8]. The objective of this paper is to make a contribution to studies of determining ^{40}K radioisotope radioactivity by gamma spectroscopy in beach sand and seawater and to evaluate and compare the results with the mean values given in UNSCEAR report and in the studies implemented in different parts of the world. Also it was aimed to point out the importance of measurement conditions by using different standards and the importance of determination of average effective dose rate by using Kriging interpolation method.

2. MATERIAL AND METHOD

2.1. Study site

The study site, Sarımsaklı beach is in the environs of Küçükköy sub-district that is located in Ayyalık district of Balıkesir city on Aegean Sea side where there are numerous beaches (Fig. 1). This region is famous with high oxygen levels of forests next to coasts and its beaches are constantly frequented by the general public [9].

♣Corresponding author, e-mail: haciyakup1@itu.edu.tr



Fig 1. Localization of the Sarımsaklı study site adapted from Google Earth.

Sarımsaklı beach with an approximated extension of 7 km possesses a shallow sea and fine sand; its surrounding had formed as a consequence of the volcanic activities during the Miocene Epoch. One of the products of these volcanic activities is the Sarımsak (garlic) stone, which is unofficially used as a building material by people living in the area. Additionally, Sarımsaklı beach formed from degradation and fragmentation of granitic rocks commonly found in near the region by a variety of wind and water driven physical factors [4, 10]. So, in order to evaluate the radioactivity on this beach that was not determined before, beach sand and seawater were sampled and analyzed.

2.2. Sample collection and preparation

Beach sand and seawater sample collection was carried out in October 2009 from the most used area of the beach with a length interval of 30 m to determine ^{40}K radioactivities. Beach sand samples were collected 2.5 m far from the coast and seawater samples were collected from the sea surface 15 m away from the coast line. Beach sand and seawater sampling was done manually with cylindrical plastic vials of 8 cm diameter and 10 cm height, including two representatives for each point.

Beach sand samples were bulked for measurement as a single sample and oven dried at 105°C . Seawater samples and beach sands were weighed as

approximately 500 ± 0.01 g (Sartorius L 2200 S Model) and sealed in cylindrical vials for gamma spectroscopy measurements.

2.3. Sample density

In order to determine the density of beach sand and seawater samples, which is important in gamma spectrometry measurements to specify absorption properties of compared standard materials, two representative samples from dried beach sand and seawater were added to Marinelli beakers with known dimensions and weighted.

2.4. Standards

In order to make the energy and efficiency calibration of the gamma spectroscopy system that are necessary for activity determination, two radionuclide standards were used. Firstly, certificated multiple gamma ray emitting large volume source standard was used; including ^{113}Sn , ^{137}Cs and ^{60}Co radioisotopes in the soil matrix in Marinelli geometry as 500 mL volume, with a density of 1.0 g cm^{-3} and an activity of $1 \mu\text{Ci}$ [11]. Secondly, for correction of counting deviations due to geometry of Marinelli standard to cylindrical sample vials, the IAEA-SOIL-6 soil standard reference material including ^{137}Cs radionuclide (53.65 Bq kg^{-1}) was used [12]. To indicate the attenuation coefficient for soil matrix standard and measured samples, the ^{60}Co

radioisotope point source with an activity 0.943 µCi was used [13].

2.5. Gamma spectroscopy

The measurements of ⁴⁰K activities were undertaken in Low Level Radioactivity Measurement Laboratory in the Istanbul Technical University Energy Institute by using copper lined lead shielding (10 cm) detector (GAMMA-X HPGe coaxial n-type germanium detector, 45.7 % efficiency and 1.84 keV full width at half maximum for 1.3 MeV of ⁶⁰Co) with the integrated digital gamma spectrometer (DSPEC jr. 2.0). Statistical confidence level and range were adjusted to 2σ and 8K, respectively. After measurements, standards and samples were corrected for decay time and mass. Peak areas were determined by using GAMMA VISION-32 software program [14]. Samples in cylindrical vials and standards in cylindrical vial and Marinelli beaker were counted at the top of the detector. Counting times were adjusted to 24 hours.

2.6. Statistical analysis

In order to acquire average value of ⁴⁰K activity concentration of beach sand and seawater samples for different sampling points, Kriging methodology that can predict values of a variable at locations, where data are not available, based on the spatial pattern of the available data, was applied by using Geostatistics for the Environmental Sciences GS+ Version 9 software [15].

3. RESULTS AND DISCUSSION

3.1. Gamma spectrometer calibration

Gamma spectroscopy system was calibrated for energy and efficiency considering nuclear properties of determined radionuclides (Table 1) by specifying effects of geometry and background radiation. Energy and efficiency calibration was performed by using the gamma-ray peaks of ¹¹³Sn, ¹³⁷Cs and ⁶⁰Co of the multiple gamma rays emitting large volume soil source standard according to standard procedures [17].

Table 1. Nuclear properties of used isotopes [16].

Radionuclide	Half-life (yr)	Energy (keV)	Intensity (%)
¹³⁷ Cs	30.17	661.66	85.1
¹¹³ Sn	0.3151	391.69	64.9
⁶⁰ Co	5.2714	1173.237	100
⁶⁰ Co	5.2714	1332.501	100
⁴⁰ K	1.277 10 ⁹	1460.859	10.67

The efficiencies of the detector ε_E at different energies (E) with the actual measurement geometry given in Table 2 were obtained using the equation (1):

$$\epsilon_E = \frac{(n_{Ns,E} / t_s)}{(A \cdot P_E)} \tag{1}$$

where A represents the activity of each radionuclide in the calibration source at the calibration time, n_{Ns,E} denotes number of counts in the net area of the peak at energy E in the calibration spectrum, t_s symbolizes calibration spectrum counting time and P_E probability of the emission of gamma radiation with energy E for each radionuclide.

Table 2. Calculated efficiencies of used radionuclides.

Radionuclide	Efficiency
¹¹³ Sn (392 keV)	0.04738
¹³⁷ Cs (662 keV)	0.02653
⁶⁰ Co (1173 keV)	0.01533
⁶⁰ Co (1333 keV)	0.01398

At least three data points above the knee and two below the knee are required for a quadratic fit corresponding to a quadratic function to the log (Energy) versus log (efficiency) curve and with only three points, the fit will be reported as exact for all data points above the knee [14]. Because of that, the fitting coefficients of quadratic logarithmic efficiency calibration equation can be calculated using ¹¹³Sn and ¹³⁷Cs peaks and two ⁶⁰Co peaks. By using the equation (2) for efficiency calibration, where E representing energy and ε denoting efficiency of gamma peak, with the fitting coefficients the efficiency of ⁴⁰K radionuclide at 1460.859 keV was calculated as 0.01317 as seen from the efficiency curve above the knee (Fig 2).

$$\epsilon = \exp(17.7656 - 5.44204(\ln E) + 0.3307(\ln E)^2) \tag{2}$$

3.2. Attenuation effect

By using the experimental results, the average densities of beach sand and seawater samples were calculated as 1.329 and 1.007 g cm⁻³, respectively. Since the density of beach sand is different from the density of used soil matrix standard; it is required to figure out the effect of the attenuation coefficient in samples in connection with density of the soil matrix. For this reason the direct transmission method was applied [18, 19]. Since the energies of ⁶⁰Co radioisotope's two gamma-ray peaks are close to the energy peak of ⁴⁰K radioisotope, the ⁶⁰Co point source was chosen to apply the method mentioned above. The ⁶⁰Co point source placed on the top of an empty Marinelli beaker and also on Marinelli beaker containers filled with soil matrix standard, beach sand and seawater respectively and counted for 1000 s.

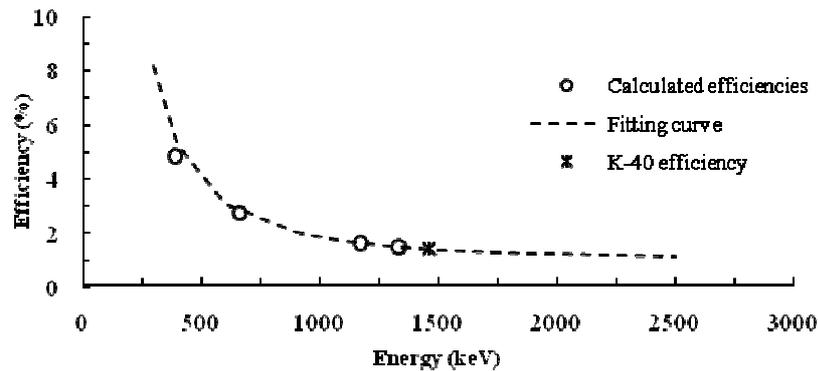


Fig 2. Efficiency as a function of the photopeak's energy above the knee.

The relative self-correction factor $f_{att,s, std}$ for a sample $f_{att,s}$ with respect to a standard sample $f_{att, std}$ was determined by the equation (3) adapted from Robu and Giovani [18]:

$$f_{att,s, std} = \frac{f_{att,s}}{f_{att, std}} = \frac{\left(\frac{\ln I/I_0}{(1-I/I_0)} \right)_{att,s}}{\left(\frac{\ln I/I_0}{(1-I/I_0)} \right)_{att, std}} \quad (3)$$

where I and I_0 are the peak count rates for the samples and empty Marinelli beakers with ^{60}Co point source. The calculated values for beach sand and seawater were 1.072 and 1.057 respectively.

3.3. Background effect

To eliminate the background effect in the samples, an empty cylindrical vial was measured by the gamma spectroscopy system under the same conditions as beach sand and seawater samples; the gamma peak area of ^{40}K was determined and subtracted from the measured gamma peak areas of ^{40}K in beach sand and seawater samples as given in ISO18589-3 [17].

3.4. Geometry effect

The shape of used standard is different from the shape of measured samples; to specify the geometry correction factor in connection with the shape, the IAEA-SOIL-6 standard was added in a cylindrical sample vial being in the same height with samples; positioned at the top of the detector and counted. Then the same amount of standard was added into the Marinelli beaker, placed over the detector and counted. Background correction was done in the results for ^{40}K . The change in activity concentrations of ^{40}K radionuclide for IAEA-SOIL-6 standard with different shaped containers was shown in Table 3.

Table 3. Activity concentrations of ^{40}K with different shaped containers.

IAEA SOIL-6	Activity concentration (Bq kg ⁻¹)	Uncertainty (%)
Marinelli beaker	467.43	0.91
Cylindrical vial	193.42	1.44

By dividing activity concentration in Marinelli beaker to the concentration in the cylindrical vial, geometry factor was calculated as 2.41 for ^{40}K .

3.5. Beach sand and seawater radioactivity

Radioactivity concentrations of ^{40}K radioisotope in beach sand and seawater samples given below in Table 4 were obtained from the equation (4):

$$a = \frac{(n_{N,E} / t_g)}{(P_E \cdot \epsilon_E \cdot m \cdot f_E \cdot f_{att,s, std})} \quad (4)$$

where a signifies the activity per unit of mass of each radionuclide present in the sample, $n_{N,E}$ denotes the number of counts in the net area of the peak at energy E in the sample spectrum with background correction, t_g symbolizes sample spectrum counting time, P_E corresponds to probability of the emission of gamma radiation with energy E for each radionuclide, m is a symbol of mass of the test portion, f_E characterizes the correction factor considering geometry and $f_{att,s, std}$ is the relative self-correction factor [17].

Table 4. ^{40}K radioactivity concentrations of beach sand and seawater samples

(S: beach sand; W: seawater; *: average of two counts).

Sample	Activity concentration (Bq kg ⁻¹)	Uncertainty (%)
1S	1007.49	0.90
2S	1001.04	0.67
3S	1066.30	0.74
4S	1250.22	0.65
5S	1176.46	0.73
6S	1095.72	0.68
7S	968.33	0.69
1W*	9.38	6.26
2W*	13.52	5.71
3W*	12.05	5.73
4W*	11.86	5.68
5W*	14.05	5.72
6W*	17.62	5.18
7W*	14.87	5.34

Average activity concentrations obtained by Kriging methodology for beach sand and seawater were found as 1093.00 ± 115.07 and 14.08 ± 3.50 Bq kg⁻¹ respectively and the minimum detectable activity based on the background value was calculated as 1.44 Bq according to the traditional ORTEC Method 1 [14].

3.6. Absorbed gamma dose rate in outdoor air

Utilizing the average activity concentration of ⁴⁰K for beach sand, the average absorbed gamma dose rate D_K of ⁴⁰K in air at 1 m above the ground was determined as 45.58 ± 4.80 nGy h⁻¹ by using the equation (5):

$$D_K \text{ (nGy h}^{-1}\text{)} = 0.0417 A_K \quad (5)$$

where A_K represents the average activity concentration [2].

4. CONCLUSION

With this study carried out in the selected area, the first data related with radioactivity at beach sand and seawater of Sarımsaklı beach on the Aegean Sea coast were obtained. Therefore extending the study for determination of all terrestrial radionuclides in this area and in its surroundings will make contribution to assessment of natural radioactivity indicators and to the radioactivity mapping works of this coastal region.

The results obtained in this study can be concluded as following:

- The experimentally determined geometry coefficient can be used in activity calculations, where sample geometry does not match the standard source geometry.
- Neglecting the effect of the attenuation coefficient for energies around 1333 keV for sand beach and seawater matrixes (densities 1.329 and 1.007 g cm⁻³) compared with soil matrix standard (density 1.0 g cm⁻³) will bring approximately 7 % error.
- The range of standard deviation of the average 40K radioactivity (14.08 ± 3.50 Bq kg⁻¹) in sea water obtained in this study is consistent with the world seawater 40K radioactivity level given as 11.84 Bq L⁻¹ by Preston and Chester [20].
- When the 40K activity concentration obtained in this study is compared with the worlds' values, it is seen that radioactivity of 40K radionuclide in Sarımsaklı beach sands in the studied site (1093.00 ± 115.07 Bq kg⁻¹) is higher than the population weighted average concentration of 40K in the soil for many countries given in UNSCEAR report in Table 5 [2] and higher than those studies implemented in some beaches of Brazil (13 to 888 Bq kg⁻¹), in a national park in Spain close to the Atlantic ocean (175 to 291 Bq kg⁻¹), in the Montenegrin Coast of Yugoslavia (150 Bq kg⁻¹), in beach sands of coastals at Red Sea in Egypt (548 to 930 Bq kg⁻¹) and in beach sands of coastal at Yellow Sea in China (1079.2 Bq kg⁻¹ [21-27].

Additionally, average external effective dose rate of 40K for beach sand determined in this study was higher than the dose rate which varies between 6-36 nGy h⁻¹ as given in UNSCEAR report [2].

- On the other hand, comparison with the values obtained from two other studies, which are close to the Sarımsaklı beach, radioactivity of 40K radionuclide in Sarımsaklı beach sands in the studied site (1093.00 ± 115.07 Bq kg⁻¹) is compatible with the average concentrations of 40K given by Örgün et al., (687.1 to 1421.2 Bq kg⁻¹) [3] and by Peev and Mitov [28] (150 to 1200 Bq kg⁻¹).

ACKNOWLEDGEMENTS

Part of this study includes results from MSc. Thesis of Şeyda Tezsezer. The authors thank to Prof. Dr. Yüksel Örgün for her valuable comments and M. Sahip Kızıltaş for help during study.

REFERENCES

- [1] Turner, J.E., "Atoms, Radiation and Radiation Protection", *J. Wiley*, New York, 1-13 (1995).
- [2] UNSCEAR, "Report to the General Assembly with Scientific Annexes". <http://www.unscear.org/docs/reports/annexb.pdf> (2000).
- [3] Örgün, Y., Altınsoy, N., Şahin, S.Y., Güngör, Y., Gültekin, A.H., Karahan, G., Karacık, Z., "Natural and anthropogenic radionuclides in rocks and beach sands from Ezine region (Canakkale), Western Anatolia, Turkey", *Appl. Radiat. Isot.*, 65 :739-747 (2007).
- [4] Tezsezer, Ş. "Ayrıvalık Sarımsaklı kumsalı deniz suyu ve kum örneklerinde K-40 radyoizotopunu tayini", MSc. Thesis (in Turkish), *Istanbul Technical University*, Istanbul, 1-47 (2010).
- [5] Alsamamra, H., Ruiz-Arias, J.A., Pozo-Vázquez, D., Tovar-Pescador, J., "A comparative study of ordinary and residual Kriging techniques for mapping global solar radiation over southern Spain", *Agric. For. Meteorol.*, 149 :1343-1357 (2009).
- [6] Pfennig, H., Klewe-Nebenius, H., Seelmann-Eggebert, W., "Karlsruher Nuklidkarte", 6. *Auflage* (1995).
- [7] Peterson, J.M., Mac Donell, M., Haroun, L., Monette, F., Hildebrand, R.D., Taboas, A., "Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas", *Human Health Fact Sheet*, Argonne, 38-39 (2007).
- [8] Farai, I.P., Obed, R.I., Jibiri, N.N., "Soil radioactivity and incidence of cancer in Nigeria", *J. Environ. Radioact.* 90:29-36 (2006).

- [9] Küçükköy Municipality. http://kucukkoy.com.tr/index.php?islem=paket/sayfaP/sayfa_-detay.php&anasayfa_id=5 (2010).
- [10] Oyman, T., "Geochemistry, mineralogy and genesis of the Ayazmant Fe-Cu skarn deposit in Ayvalık, (Balıkesir), Turkey", *Ore. Geol. Rev.* Doi: 10.1016/j.oregeorev.2010.03.002 (2010).
- [11] DKD-K-36901-000386, "Calibration certificate", *Isotope Products Laboratory*, Valencia, California (2006).
- [12] IAEA-Soil-6, "International Atomic Energy Agency Analytical Quality Control Services Report on the Intercomparison Run Catalogue", Vienna, Austria (1984).
- [13] D-116-21, "Certificate of Calibration", Canberra Industries Incorporation, Oak Ridge, Tennessee (2006).
- [14] ORTEC, "Gamma Vision-32 A66-B32 Software Users Manual" (2003).
- [15] Robertson GP, "GS+: Geostatistics for the Environmental Sciences", *Gamma Design Software*, Plainwell, Michigan USA (2008).
- [16] Firestone, R.B., Shirley, V.S., Baglin, C.M., Chu, S.Y.F., Zipkin, J., "Table of Isotopes 8th ed.", J. Wiley, New York 133, 277, Cs-137, Sn-113 (1996).
- [17] ISO 18589-3 "International Standard, Measurement of Radioactivity in the Environment Soil, Part 3: Measurement of Gamma-emitting Radionuclides", *ISO*, Geneva (2007).
- [18] Robu, E., Giovani, C., "Gamma-ray self-attenuation corrections in environmental samples", *Rom. Rep. Phys.*, 61:295–300 (2009).
- [19] Sima, O., Dovlete, C., "Matrix effects in the activity measurement of environmental samples: Implementation of specific corrections in a gamma-ray analysis program", *Appl. Radiat. Isot.* 48: 59–69 (1997).
- [20] Preston M.R., Chester R., "Chemistry and Pollution of the Marine Environment. In: Pollution: Causes, Effect and Control", Harrison, R.M (ed), *The Royal Society of Chemistry*, UK, 52-56 (2001).
- [21] Aquino, R.R., Pecequilo, B.R.S., " ²²⁶Ra, ²³²Th and ⁴⁰K analysis in sand samples from some beaches of Great Vitória, Espírito Santo, Brazil: Preliminary results", *International Nuclear Atlantic Conference - INAC 2009*, Rio de Janeiro, RJ, Brazil, 1-6 (2009).
- [22] Veiga, R., Sanches, N., Anjos, R.M., Macario, K., Bastos, J., Iguatemy, M., Aguiar, J.G., Santos, A.M.A., Mosquera, B., Carvalho, C., Baptista, F.M., Umisedo, N.K. "Measurement of natural radioactivity in Brazilian beach sands", *Radiat. Meas.*, 41:189-196 (2006).
- [23] Lu X., Zhang X., "Measurement of natural radioactivity in beach sands from Rizhao bathing beach, China", *Radiat. Prot. Dosim.* 130:385-388 (2008).
- [24] Gonzalez-Chornet G., Gonzalez-Labajo J., "Natural radioactivity in beach sands from Donana National Park and Mazagon (Spain)", *Radiat. Prot. Dosim.*, 112:307–310 (2004).
- [25] Harb, S., "Natural radioactivity and external gamma radiation exposure at the coastal Red Sea in Egypt", *Radiat. Prot. Dosim.*, 130:376-384 (2008).
- [26] Vukotic, P., Borisov, G.I., Kuzmic, V.V., Antovic, N., Dapcevic, S., Uvarov, V.V., Kulakov, V.M., "Radioactivity on the Montenegrin Coast, Yugoslavia", *J. Radioanal. Nucl. Chem.*, 235:151-157 (1998).
- [27] El-Arabi A.M., "Natural radioactivity in sand used in thermal therapy at the Red Sea Coast", *J Environ. Radioact.*, 81:11–19 (2005).
- [28] Peev T.M., Mitov I.G. "Some investigations of sea sands from the Black Sea coastline", *J Radioanal. Nucl. Chem.*, 241, 1:169-172 (1999).