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Assessment of Radioactivity in the Wastes Generated from the Diammonium Phosphate (DAP) Fertilizer Factory, Chittagong, Bangladesh

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Abstract
The activity concentration of ^{226}Ra, ^{232}Th and ^{40}K had been determined in solid and liquid samples collected from the DAP Fertilizer Factory, Chittagong, Bangladesh. Six different types of samples, namely, i) the liquid waste inside the factory ii) waste sample near the liquid waste disposal point of Karnaphuli river iii) solid waste iv) DAP dust v) the final product (DAP) and vi) normal soil adjacent to the factory had been analyzed by gamma spectrometric technique using a high purity germanium (HPGe) detector of 40% relative efficiency. The analysis of the liquid waste samples showed that the average activity concentrations of ^{226}Ra and ^{232}Th were 3.59 ± 1.05 and 37.08 ± 3.30 Bq/L, respectively and no ^{40}K was detected in any of the samples. In the solid waste samples the average value of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were 24.47 ± 4.15, 164.62 ± 11.08 and 191.52 ± 117.87 Bq/kg, respectively. Considering the stored wastes as a part of the ambient environment of the factory, radium equivalent activity, radiation hazard index and external annual effective dose to the worker and public due to these wastes had been calculated. The study provides a baseline radiological data on the wastes generated from the fertilizer industries of Bangladesh.

Keywords: Solid waste, radium equivalent, annual effective dose, DAP fertilizer.

Introduction
Various types of human practices and non-nuclear industries contribute to further concentrate some of the natural radionuclides that can be found in the earth's crust affecting the human and the environment. Fertilizer industries, specifically the phosphate fertilizer industries, are important sources of exposure to ionizing radiation of the people and possible contamination of the environment as phosphate fertilizers contains radionuclides of ^{238}U, ^{232}Th decay series as well as radioisotopes of ^{40}K. The production process of phosphate fertilizer redistributes radionuclides throughout the environment and introduces them into the final products and byproducts (Saueia et al., 2005).

Natural radioactivity in fertilizer plants is principally on account of dehydrated calcium sulphate (phosphogypsum) generated as by-product during production of phosphate fertilizer. Saueia et al. (2006). Phosphate fertilizers are used in huge amounts in Bangladesh since rapidly growing population must depend increasingly upon commercial fertilizers essential for food production. The natural resource from which agricultural phosphorus is obtained is phosphate rock, found in sedimentary formations, usually interbedded with marine shales or limestones. Saueia et al. (2006). The phosphate rock used as raw material presents in its composition radionuclides of the U and Th natural series. Mazzilli et al. (2000). Several types of phosphate fertilizers are produced, and these are usually blended for application in the field. The radium and uranium tend

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to separate in the process of producing phosphoric acid, an important step in fertilizer manufacture. Phosphoric acid is the starting material for triple superphosphate (TSP), single superphosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP),NPK fertilizer and di-calcium phosphate (DCP). Saueia et al. (2005). The environmental impact of fertilizer production depends on the raw materials, production processes and the status of the pollution control equipment. In addition, phosphate fertilizer plants cause environmental harm through emissions of process specific chemicals into the air, discharges into water and storage solid waste problems. Actions should be undertaken to minimize the emissions, to clean up spills and solid wastes.

Therefore, radioactivity released from the fertilizer plants could be produced an unambiguous radioactive impact in their surrounding environment through radionuclides from phosphogypsum wastes. The analyses of radionuclide concentrations and activity level would be provided us with interesting information to evaluate the extension, degree and routes of the radioactive impact, as well as for the knowledge of the different pathways followed for the radioactive contamination to disturb the natural system. Taking this into account, the main aim of the proposed study is to determine the content of radioactivity in waste generated from DAP fertilizer factory; to estimate the radiological impact due to release of this waste in the environment.

Materials and Methods

Sampling sites: The samples were collected from DAP Fertilizer Factory, Chitagong. The factory is located at the south east side of Bangladesh. The geographical coordinates of the study area as determined by a hand held GPS set are: latitude 24°39' N and longitude 91°56' E. Karnaphuli River flows by the side of the factory and it is the main source of local irrigation.

Sample collection and sample preparation: Six different types of samples, namely; liquid waste, water sample near the liquid waste disposal point of the Karnaphuli river, solid waste, DAP dust, final product (DAP), soil adjacent to the factory, were collected from the DAP fertilizer factory, Chittagong. Nineteen different types of samples were collected from the factory and its adjacent area. Standard methods were followed to process the samples for characterization (IAEA –TR 295-1989).

Processing of liquid samples: Marinelli type beakers (2 liter capacity) were used to process and measure the liquid samples. At the start of the sample processing steps, the beakers were made contamination-free cleaning those well by light hydrochloric acid solution and deionized water. The beakers were then dried using a temperature-controlled oven and empty weights of the beakers were noted. The beakers were then filled with liquid samples. The net weights of the samples were found from the difference of weights of sample-filled and empty beakers. The beakers filled with samples were then kept in the sun for several days. Finally, the beakers were closed by caps, sealed tightly and wrapped with thick vinyl tape about their caps and kept for 30 days for achieving the secular equilibrium between gaseous and non-gaseous decay products of naturally occurring radioactive series.

Processing of solid samples: The soil samples were dried in the sun for several days. The samples were then crushed into small pieces and dried again in a temperature controlled oven at 100°C for 24 hours in order to remove the moisture content in the samples. The dried samples were ground to fine powder and passed through a sieve of mesh size of 200 μm. The samples were then filled in cylindrical plastic containers of 6 cm diameter and 7 cm height with a volume of 180 ml. The weights of all the samples were taken by an electronic balance and the net weights of the samples were noted. Finally, the plastic containers were closed by caps and wrapped with thick vinyl tape about their necks to seal the containers tightly. The samples were then stored for about 30 days to assure secular equilibrium between the ^{238}U and ^{232}Th series and with their daughters. Tufail et al. (2000).

Sample Analysis: The detection and measurement of radionuclides in the samples were carried out by gamma spectrometry system using a vertical coaxial cylindrical HPGe detector of 172 cm^3 active volume and with 40% relative efficiency. The p-type HPGe detector supplied by CANBERRA (Model GC4020) had a resolution of 2 keV at 1332 keV of ^{60}Co. The detector was coupled to a 16 k-channel computer analyzer. The analysis was carried out using Genie 2000 spectra analysis software, which matched various gamma energy peaks to a library of possible radionuclides. The detector was enclosed in a cylindrical shielding container made of lead and iron with 11.3 cm thickness, 51 cm height and 28 cm internal diameter and with a fixed bottom and moving cover to reduce the external γ-ray background. Islam et al. (1990). All the samples were counted for 50 ks. Prior to the measurement of the samples, the environmental gamma background at laboratory site had been determined with an identical empty Marinelli beaker and plastic container used in the sample measurement. The energy regions selected for the corresponding radionuclides were 295 keV and 352 keV of ^{214}Pb and 609 keV, 1120 keV and 1764 keV of ^{214}Bi for ^{226}Ra, 583 keV and 2614 keV of ^{208}Tl, 911 keV and 969 keV of ^{228}Ac for ^{228}Th and 1460 keV for ^{40}K. Roessier et al. (1970).

Calibration of HPGe detector: In the present study the calibration for the efficiency of the detector was performed by standard sources of solid and liquid matrices prepared using ^{226}Ra standard solutions. Tahawy et al. (1992). The standard sources were prepared using identical containers used for the measurement of the samples, e.g., 2L Marinelli beakers for water and plastic container for soil. The preparation process of standard sources had been reported elsewhere. Harb et al. (2008). The detector efficiency calibration curves as a function of energy for both liquid and solid matrices have been shown in Fig.1. The energy calibration of the detector was performed by ^{137}Cs and ^{60}Co point sources.

Calculation of activity concentration

The net amount of a sample had been obtained by subtracting a linear background distribution of the pulse height spectra from the corresponding peak energy area. From the sample net counts activity of the samples were calculated using the formula (Usif and Taher 2008).

$$A = \frac{cps}{E \times I \times w} \text{ ---------- (1)}$$

Where, A = Activity of the sample in Bq.kg^{-1} or Bq.L^{-1}

cps = the net counts per second
= cps for the sample- cps for background value
E = the counting efficiency of the gamma energy
I = absolute intensity of the gamma ray and
w = samples net weight (in kg)

(a) **(b)**

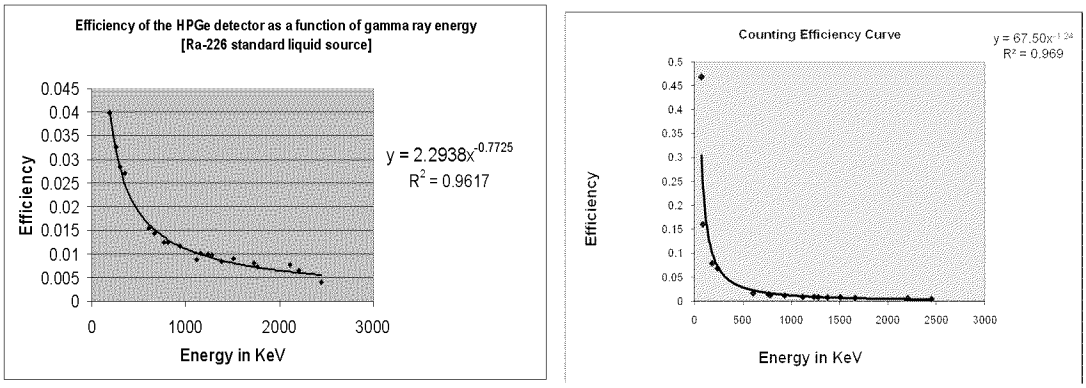

Figure 1: Efficiency calibration curve of HPGe detector for (a) liquid and (b) solid matrices.

The errors in the measurement had been expressed in terms of standard deviation ($\pm\sigma$), where σ is expressed as (Knoll, 1998).

$$\sigma = \left[\frac{N_s}{T_s^2} + \frac{N_b}{T_b^2}\right]^{1/2} \text{------(2)}$$

Where, N_s is the counts measured in time T_s and N_b is the background counts measured in time T_b. The standard deviation $\pm\sigma$ in cps was converted into activity in Bq.kg^{-1} according to equation (1).

Radium equivalent activity

A common index termed the radium equivalent activity (Ra_{eq}) is used for the comparing the radiological effect or activity of materials that contain ^{226}Ra, ^{232}Th and ^{40}K by a single quantity. This activity index provides a guideline in regulating the safety standards on radiation protection for the general public residing in the area under investigation. It can be measured by the following equation. Beretka et al. (1985).

$$Ra_{eq}\ (Bq/Kg) = A_{Ra} + 1.43A_{Th} + 0.07A_K \quad \text{.....(3)}$$

Where A_{Ra}, A_{Th} and A_K are the activity concentration in Bq/L or Bq/Kg of ^{226}Ra, ^{232}Th and ^{40}K respectively.

External hazard index

The external hazard index, H_{ex}, is defined as. Yu et al. (1992).

$$H_{ex} = A_{Ra} / 370 + A_{Th} / 259 + A_K / 4810 \quad \text{.................................(4)}$$

Where A_{Ra}, A_{Th} and A_K have the same meaning as in equation 3. The value of this index must be less than unity in order to keep the radiation hazard insignificant. The maximum value of H_{ex} equal to unity corresponds to the upper limit of radium equivalent activity (370 Bq/kg).

The absorbed dose rate

The absorbed gamma dose rate in air 1 m above the ground surface for the uniform distribution of radionuclides ^{226}Ra, ^{232}Th and $^{40}K$was computed using the following formula. Veiga et al. (2006).

$$D\ (nGy/h) = 0.462A_{Ra} + 0.604A_{Th} + 0.042A_K \quad \text{........................(5)}$$

Where A_{Ra}, A_{Th} and A_K have the same meaning as in equation 3.

The annual effective dose

To estimate the annual effective dose rates, the conversion coefficient from absorbed dose in air to effective dose (0.7 svGy−1) and outdoor occupancy factor (0.2) proposed by UNSCEAR (2000) were used. The effective dose rate in units of msv per year was calculated according to the following relation. Cevik et al. (2007).

$$E\ (Sv) = D \times 24 \times 365 \times 0.7 \times 0.2 \quad \text{......................................(6)}$$

Results and Discussions

The radionuclides detected and corresponding activity concentrations in different samples have been summarized in Table-1. The radionuclides found in the samples were ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{208}Tl (due to ^{238}U and ^{232}Th decay) and ^{40}K. There were only natural radionuclides present in the samples and no artificial radionuclide, such as ^{137}Cs, was found in any of the samples.

The average values of activity concentrations of ^{226}Ra, ^{232}Th in the liquid waste samples were found to be 3.59 ± 1.05 and 37.08 ± 3.30, respectively**.** It was also observed that no ^{40}K was found in any of the three samples, moreover, the amount of activity concentrations of other radionuclides (^{226}Ra and ^{232}Th) were also much less than the solid samples analyzed in this study. The radionuclides and their activity concentration found in the waste disposal point and normal water point of Karnaphuli river samples. It is seen that no ^{40}K has been seen in the waste samples but found in the normal water point.

The average concentration of solid waste samples of ^{232}Th is 164.62 ± 11.08 Bq/Kg which significantly a higher value. It is also found that activity concentrations of ^{232}Th in DAP dust samples are higher value, therefore, it has a similarity with solid waste samples. The activity concentrations of radionuclides in DAP fertilizer; it has been found a relationship with solid waste.

Table 1: Activity concentrations of the radionuclides in six different types of sample at different points in factory

Sample type	Samples ID	Activity concentrations of radionuclides (Bq/L)		
		^{226}Ra	^{232}Th	^{40}K
Liquid waste sample	Sample: 1	2.75 ± 1.16	35.31 ± 3.64	ND
	Sample: 2	4.64 ± 1.04	37.74 ± 3.26	ND
	Sample: 3	3.37 ± 0.94	38.19 ± 3.01	ND
	Average	**3.59 ± 1.05**	**37.08 ± 3.30**	**ND**
Waste disposal point of Karnaphuli river	Sample:4	3.91 ± 0.58	13.49 ± 1.70	ND
	Sample: 5	3.74 ± 0.63	17.79 ± 1.88	ND
	Average	**3.83 ± 0.61**	**15.64 ± 1.79**	**ND**
Normal water point of Karnaphuli river	Sample: 6	3.20 ± 0.58	10.22 ± 1.65	20.05 ± 9.97
	Sample: 7	2.52 ± 0.57	9.30 ± 1.64	15.70 ± 9.95
	Average	**2.86 ± 0.57**	**9.76 ± 1.64**	**17.88 ± 9.96**
		Activity concentrations of radionuclides (Bq/Kg)		
Solid waste sample	Sample: 8	25.28 ± 4.23	173.33 ± 11.26	144.24 ± 119.71
	Sample: 9	26.99 ± 4.14	168.44 ± 10.99	210.97 ± 117.02
	Sample: 10	21.13 ± 4.07	152.09 ± 10.99	219.34 ± 116.88
	Average	**24.47 ± 4.15**	**164.62 ± 11.08**	**191.52 ± 117.87**
DAP dust	Sample: 11	14.38 ± 5.74	141.42 ± 14.99	389.07 ± 168.23
	Sample: 12	14.58 ± 5.76	121.37 ± 14.84	317.41 ± 168.13
	Sample: 13	17.07 ± 5.15	130.94 ± 13.39	218.11 ± 149.23
	Average	**15.34 ± 5.55**	**131.24 ± 14.41**	**308.20 ± 161.86**
DAP fertilizer sample	Sample: 14	14.87 ± 3.91	66.30 ± 9.85	58.15 ± 25.26
	Sample: 15	18.46 ± 3.93	65.76 ± 9.84	19.38 ± 5.09
	Sample: 16	18.59 ± 3.94	77.17 ± 9.94	67.84 ± 21.30
	Average	**17.31 ± 3.92**	**69.74 ± 9.88**	**48.46 ± 17.22**
Normal soil sample adjacent to factory	Sample: 17	3.68 ± 2.98	33.91 ± 7.54	619.88 ± 90.02
	Sample: 18	12.55 ± 4.31	80.39 ± 11.02	840.91 ± 128.20
	Sample: 19	8.13 ± 3.02	39.84 ± 7.59	657.67 ± 90.17
	Average	**8.12 ± 3.44**	**51.38 ± 8.72**	**706.15 ± 102.80**

The average concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the normal soil samples were found to be 8.12 ± 3.44, 51.38 ± 8.72 and 706.15 ± 102.80 respectively. The activity concentration levels of the radionuclides in these two samples are comparable.

Table 2: Comparison of average concentrations of ^{226}Ra, ^{232}Th and ^{40}K with other published data on soil

Radionuclides concentrations in Bq/Kg			Region	Reference
^{226}Ra	^{232}Th	^{40}K		
77.10	146.00	370.00	Hong Kong	Yu et al. (1992)
16.60	18.10	316.00	Egypt	Ibrahiem et al. (1993)
38.80	41.00	653.00	Spain	Baeza et al. (1994)
114.60	43.20	274.60	India	Selvasekara et al. (1999)
25.00	25.00	370.00	World Average	(UNSCEAR 1988)
8.12	**51.38**	**706.15**	**Present Study**	

The wastes (liquid waste and solid waste) generated from the production process of the DAP fertilizer had been stored in the open environment; therefore, these wastes with natural radionuclides had become a constituent of the ambient environment of the factory complex. Therefore, these wastes could be treated as the part of environment contributing to the exposure to the workers of the factory and to the general public. Therefore, the radium equivalent activity (Ra_{eq}), external radiation hazard index (H_{ex}), absorbed gamma dose rate (D) and annual effective dose (E) were calculated for the three types of samples.

The calculated values of radium equivalent activity (Ra_{eq}), external hazard index (H_{ex}), external gamma absorbed dose rate (D) and annual effective dose (E) have been calculated and have been summarized in Table -3. The maximum value of radium equivalent activity (Ra_{eq}), external hazard index (H_{ex}), external gamma absorbed dose rate (D), the annual effective dose have been found to be 283.24 Bq/Kg, 0.78, 123.07 nGy/h and 0.15 mSv/y, respectively.

The world quoted value for Ra_{eq}, H_{ex}, D and annual effective dose are 370 Bq/Kg, 1.0, 55 nGy/h and 0.115 mSv/y, respectively (ICRP 1990). The calculated value of radium equivalent activity and dose for present study compared with world average which is shown graphically in fig. 2. It is seen that the average value of dose are higher than the world average. The value of radiological indices in the solid waste and normal soil samples are not significantly higher than standard value set by ICRP for the general public (ICRP 1990).

Therefore, the study shows that the factory complex of DAP Fertilizer factory and its adjacent surrounding area is normal natural background radiation area and no excess radionuclide concentration was found in the investigated samples collected from this factory. This study could be useful as a baseline data for the radiological impact of the fertilizer industry on the public and the environment of Bangladesh.

Table 3: Radium equivalent activity, external radiation hazard index, absorbed dose rate and annual effective dose for solid waste, phosphate rock and normal soil

	Sample ID	Ra_{eq} (Bq/Kg)	H_{ex}	D (nGy/h)	E (mSv/y)
Solid waste	Sample: 8	283.24	0.78	122.43	0.15
	Sample: 9	282.62	0.77	123.07	0.15
	Sample: 10	253.97	0.70	110.83	0.14
	Average	**273.28**	**0.75**	**118.78**	**0.15**
DAP dust	Sample: 11	243.85	0.67	108.40	0.14
	Sample: 12	210.35	0.57	93.37	0.11
	Sample: 13	219.58	0.60	96.13	0.12
	Average	**224.59**	**0.61**	**99.30**	**0.12**
Normal soil	Sample: 17	95.56	0.27	48.21	0.06
	Sample: 18	186.36	0.52	89.67	0.11
	Sample: 19	111.13	0.31	55.44	0.07
	Average	**131.02**	**0.37**	**64.44**	**0.08**

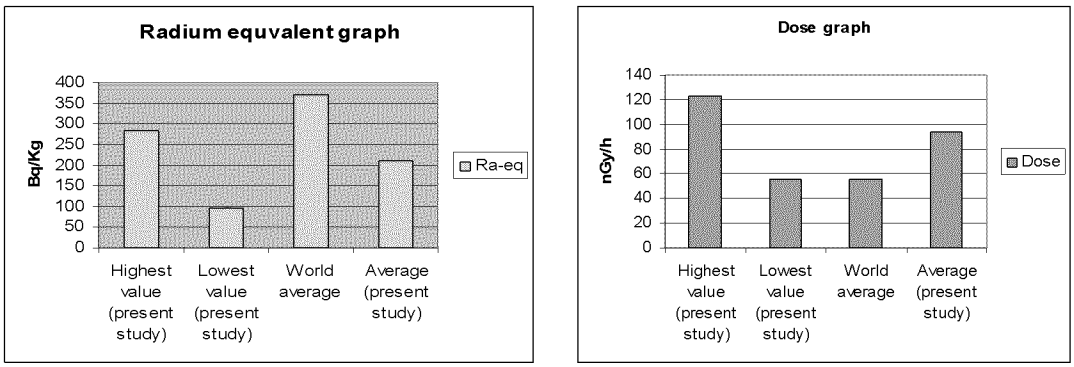

Figure. 2: The graphical representation of radium equivalent activity and dose of present study with that of world average value.

Conclusion

Radionuclide concentration and associated radiological risk have been investigated in and around the DAP Fertilizer factory in Chitagong, Bangladesh as a case study of the radiological impact assess work of the fertilizer industries of Bangladesh. The radionuclides detected in the samples are all natural and no artificial radionuclide was found in the study. The results found in the present study were compared with that of the world average values. The annual effective doses from these samples were found within the acceptable limit set by ICRP.

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Reference

Baeza, A., Del Rio, M., Miro, C., Paniagua, J., 1994. Natural Radionuclide Distribution in Soils of Caceres (Spain), Dosimetry Implications, Journal of Environmental Radioactivity. 23, 19-37.

Beretka, J., Mathew, P.J., 1985. Natural radioactivity of Australian building materials, industrial wastes and products. Health Phys. 48, 87-95.

Cevik, U., Damla, N., Nezir, S., 2007. Radiological characterization of cayirhan coat-fired power plant in Turkey. Fuel. 86, 2509-2513.

Harb, S., Din, K.S. Abbady, A., 2008. Study of efficiency calibrations of HPGe detectors for radioactivity measurement of environmental samples. Proceedings of the 3rd Environmental Physics Conference, Aswan, Egypt 19-23 Feb.

IAEA Technical Report No. 295, 1989. Measurement of Radionuclides in Food and the Environment, Vienna, IAEA.

Ibrahiem, N.M., Ghani, Abd El A.H., Shawky, S.M., Ashraf, E.M., Farouk, M.A., 1993. Measurement of Radioactivity Levels in Soil in the Nile Delta and Middle Egypt, Health Physics 64, 620-627.

ICRP 1990. Recommendations of the ICRP, Publication 60.

Islam, M. N., Alam, M.N., Mustafa, M.N., Siddique, N.,Miah, M.M.H., Shaha, S.L., Chowdhury, M.I., Kamal, M., Ali, L., Roy, P.K., 1990. Characteristics of a shielding arrangement for a HPGe detector designed and fabricated locally. Chittagong University studies, Part II, Sci. 14(2), 105-111.

Knoll, G.F., 1998. Radiation Detection and Measurement. Third edn. New York.

Mazzilli B., Palmiro, V., Saucia, C., Nisti, M.B., 2000. Radiochemical characterization of Brazilian phosphogypsum. J. Environ. Radioact. 49, 113-122.

Roessier, C. E., Smith, Z.A., Bolch, W.E., Prince, R.J., 1970. Uranium and radium in Floride phosphate materials. Health Phys. 37, 269-277.

Saueia, C.H., Mazzilli, B.P., Favaro, D.I.T., 2005. Natural radioactivity in phosphate rock, phosphogypsum and phosphate fertilizers in Brazil. Journal of Radioanalytical and Nuclear Chemistry. 264, 445-448.

Saueia C.H.R., Mazzilli, B.P., 2006. Distribution of natural radionuclides in the production and use of phosphate fertilizers in Brazil. J. Environ. Radioact. 89, 229-239.

Selvasekarapandian, S., Manikandan, N.M., Sivakumar, R., Balasubramanian, S., Venkatesan, T., 1999. Gamma Radiation Dose from Radionuclides in Soil Samples of Udagamandalam (OOTY) in India, Radiation Protection Dosimetry. 82, 225-228.

Tahawy, M.S.,Rarouk, M.A., Hammad, F.H. and Ibrahiem, N.M., 1992. Natural potassium as a standard source for the absolute efficiency calibration of Ge detectors. Journal of Nuclear Science. 29, 361-363.

Tufail, M, Iqbal,M., Mirza, S.M., 2000. Radiation doses due to natural radioactivity in Pakistan marble. Radioprotection 34, 355-359.

UNSCEAR, United Nations Scientific Committee on the Effects of Atomic Radiation. 1988. Source, Effects and Risk of Ionizing Radiation, Report to the General Assembly, United Nations, New York.

Usif, M.A., Taher, A.E., 2008. Radiological assessment of Abu-Tartur phosphate, western desert Egypt. Radiation Protection Dosimetry. 130, 228-235.

Veiga,R., Sanches,N., Anjos, R.M., Macariok, J. Bastos, M. Iguatemy, Aguiar, J.G., Santos, A.M.A., Mosquera,B., Carvalho,C., Baptista, F.M., Unisedo, N.K. 2006. Radiat, Meas. 41, 189-196.

Yu, K.N., Guan, Z.J., Stokes, M.J. and Young, E.C.M., 1992. The assessment of natural radiation dose committed to the Hong Kong people. J.Environm.Radioact. 17(1), 17-31.