

**ASSESSMENT OF RADIOLOGICAL SIGNIFICANCE OF THE WASTES
GENERATED FROM THE TRIPLE SUPER PHOSPHATE (TSP)
FERTILIZER FACTORY, CHITTAGONG, BANGLADESH**

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ABSTRACT

The activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K was determined in solid and liquid samples collected from the TSP Fertilizer Factory, Chittagong, Bangladesh. A total of 18 samples of seven different kinds (including liquid and solid wastes) were collected and analyzed by gamma ray spectrometry 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 ²²⁶Ra and ²³²Th were 6.26 ± 0.63 and 10.01 ± 1.39 Bq/L, respectively and no ⁴⁰K was detected in any of the liquid samples. In the solid waste samples the average value of activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K were 187.49 ± 4.88 , 70.06 ± 11.76 and 655.94 ± 110.24 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 were also calculated and compared with world average values.

Key words: Activity concentration, Radioactive waste, Gamma ray spectrometry, TSP fertilizer, Radium equivalent activity, Annual effective dose

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 contain radionuclides of ²³⁸U, ²³²Th decay series as well as radioisotopes of ⁴⁰K. The production process of phosphate fertilizer redistributes radionuclides throughout the environment and introduces them into the final products and byproducts (Saeuia *et al.* 2005).

In general, the major source of natural radioactivity in phosphate fertilizer plants is the dehydrated calcium sulphate (phosphogypsum) generated as a by-product during production of phosphate fertilizer (Saeuia *et al.* 2006). Phosphate fertilizers are used in

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huge amounts in Bangladesh since rapidly growing population must depend increasingly upon commercial fertilizers essential for increasing the 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 (Saeuiea *et al.* 2006). The phosphate rock used as raw materials for the production of phosphate fertilizer contains radionuclides of the ^{238}U and ^{232}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 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) (Saeuiea *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. Attempts should be made to minimize the emissions, to clean up spills and solid wastes. Therefore, radioactivity released from the fertilizer plants could produce an unambiguous radioactive impact in their surrounding environment through radionuclides from phosphogypsum wastes.

Analyses of radionuclide concentration and activity level in the wastes generated from the phosphate fertilizer production would provide us with interesting information to evaluate the extension, degree and routes of the radiological impact, as well as for the knowledge of the different pathways followed for the radioactive contamination to disrupt the natural system. Considering all the above mentioned points, the objective of the present study was to determine the contents of radioactivity in the wastes generated from TSP fertilizer factory under study and to estimate the radiological impact due to release of these wastes in the environment.

MATERIALS AND METHODS

The samples were collected from TSP Fertilizer Factory, Chitagong. The factory is located at the south-east region of Bangladesh with the geographical coordinates: latitude $24^{\circ}39'$ N and longitude $91^{\circ}56'$ E. The factory is situated on the bank of Karnaphuli River which is the main source of water for local irrigation also. The location of the factory is depicted in Fig. 1.

A total of 18 samples of seven different kinds, namely (i) liquid waste, (ii) water sample from the liquid waste disposal point of the factory in the Karnaphuli river, (iii) normal water sample, (iv) raw materials, (v) final product (TSP), (vi) solid waste, and (vii) normal soil adjacent to the factory were collected from the factory complex and its

surrounding areas. Standard methods were followed to process the samples for characterization (IAEA-TR 295-1989).

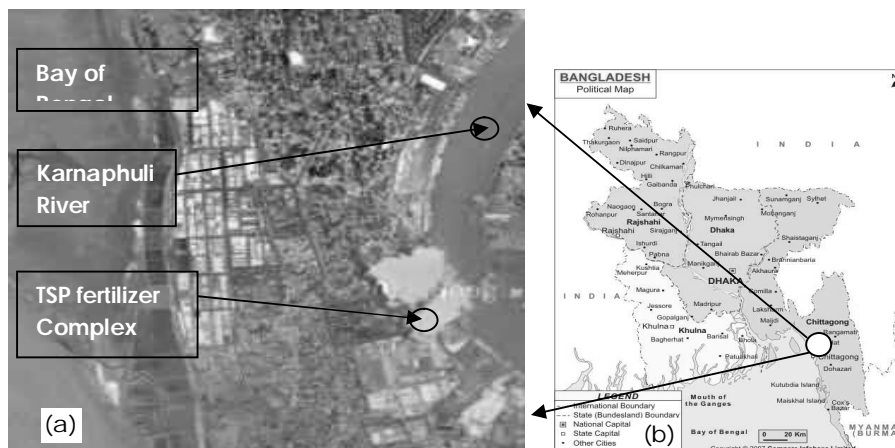


Fig. 1. Sampling location: (a) satellite map, (b) Position of the factory in the map of Bangladesh.

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 by cleaning those well using very dilute 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. Finally, the beakers were closed by caps, 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.

The solid samples were dried in the sun for several days after removing the stones, pebbles, grass roots etc. from the samples. 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. To obtain the representative samples, the dried samples were thoroughly mixed, 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).

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 cm³ 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 ⁶⁰Co gamma ray line. The detector was coupled to a 16 k-channel analyzer. The spectra of all samples were perfectly analyzed using Genie-2000 spectra analysis software (which matched various gamma energy peaks to a library of all probable radionuclides) to calculate the concentrations of ²³⁸U, ²³²Th and ⁴⁰K. 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 10 ks. Prior to the measurement of the samples, the environmental gamma background at laboratory site was 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 ²¹⁴Pb and 609 keV, 1120 keV and 1764 keV of ²¹⁴Bi for ²²⁶Ra, 583 keV and 2614 keV of ²⁰⁸Tl, 911 keV and 969 keV of ²²⁸Ac for ²³²Th and 1460 keV for ⁴⁰K (Roessier *et al.* 1970).

The efficiency calibration of the detector was performed by standard sources of solid and liquid matrices prepared using ²²⁶Ra 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 liquid and plastic container for solid samples.

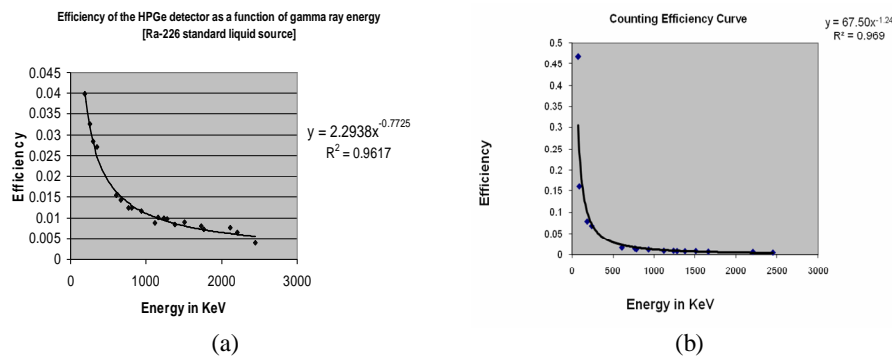


Fig. 2. Efficiency calibration curve of HPGe detector for (a) liquid and (b) solid matrix.

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 presented in Fig. 2. The energy calibration of the detector was performed by ¹³⁷Cs and ⁶⁰Co point sources.

RESULTS AND DISCUSSIONS

Following the spectrum analysis, count rates for each detected photopeak and activity per mass unit (specific activity or radiological concentration) for each of the detected nuclides were calculated. Calculations of count rates for each detected radionuclide depend on the establishment of secular equilibrium between ^{238}U , ^{232}Th and their decay products. Since the detection system gives only the count rate that is proportional to the amount of radioactivity in the samples, the radioactivity concentration in the environmental samples was obtained using the following formula (Usif and Taher 2008):

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

Where, A = Activity of the sample in Bq./kg or Bq./l,

cps = The net counts per second,

= Cps for the sample-cps for background,

E = The counting efficiency of the gamma energy,

I = Absolute intensity of the gamma ray and

w = The net weight of the sample (in kg).

The errors in the measurement were expressed in terms of standard deviation ($\pm \sigma$), where σ is expressed as (Knoll *et al.* 1998):

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

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 according to equation (1).

The radionuclides detected and their corresponding activity concentrations in different samples are summarized in Tables 1 and 2. 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 . Only natural radionuclides were found in the investigation and no trace of artificial radionuclide, such as ^{137}Cs , was found in any of the samples.

The activity concentrations of the radionuclides ^{226}Ra , ^{232}Th and ^{40}K detected in the three liquid waste samples are presented in Table 1. The average values of activity concentrations of ^{226}Ra , ^{232}Th in these samples were found to be 6.26 ± 0.63 and 10.01 ± 1.39 , respectively. No ^{40}K was observed in any of these 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.

Table 1. Activity concentrations of the different types of liquid samples collected from the TSP fertilizer factory complex and its adjacent areas.

Sample nature	Samples ID	Activity concentrations of radionuclides (Bq/l)		
		²²⁶ Ra	²³² Th	⁴⁰ K
Liquid waste samples	Sample: 1	7.67 ± 0.75	10.33 ± 1.70	ND
	Sample: 2	4.82 ± 0.54	12.78 ± 2.97	ND
	Sample: 3	6.28 ± 0.61	6.93 ± 0.98	ND
	Average	6.26 ± 0.63	10.01 ± 1.39	ND
Water samples of the waste disposal point of Karnaphuli river	Sample:4	3.26 ± 0.55	6.44 ± 1.28	ND
	Sample: 5	4.16 ± 0.58	3.77 ± 1.24	ND
	Average	3.71 ± 0.57	5.11 ± 1.26	ND
Normal water samples of the Karnaphuli river	Sample: 6	1.92 ± 0.48	3.64 ± 1.28	16.20 ± 9.24
	Sample: 7	2.26 ± 0.52	3.01 ± 1.14	20.06 ± 9.97
	Average	2.09 ± 0.50	3.33 ± 1.21	18.13 ± 9.61

ND: Not detected.

The radionuclides detected and their activity concentrations observed in the samples collected from the liquid waste disposal point of the factory in the Karnaphuli River and the normal water samples of the Karnaphuli River are also presented in Table 1. Again no ⁴⁰K was detected in the samples collected from waste disposal point, however, it was found in the normal water samples collected from the river. The activity concentrations of ²²⁶Ra and ²³²Th found in these samples are comparable as are seen in the table. However, the reason of non-detection of ⁴⁰K in the samples other than normal river water requires further study.

The activity concentrations of radionuclides in different types of solid samples investigated in the current study are presented in Table 2. The average concentration of ²²⁶Ra in the raw materials (phosphate rock) was found as 851.27 ± 7.10 Bq/kg which is significantly higher than all other samples analyzed in the present study. However, this value is consistent with other studies conducted on phosphate rock (Taher and Makhluf 2010).

Comparable activity concentrations of ²²⁶Ra were found in solid waste (187.49 ± 4.88 Bq/kg) and phosphate fertilizer samples (211.90 ± 4.74 Bq/kg). However, the activity concentration of ²²⁶Ra in waste samples was observed in between raw materials and final product. The average activity concentrations of ²²⁶Ra in all other solid samples were significantly higher than those of the normal soil samples (9.23 ± 3.35 Bq/kg).

Among all the four kinds of solid samples presented in Table 2, the highest value of average ²³²Th concentration was found in solid waste sample (70.06 ± 11.76 Bq/kg) and the lowest value was found in the raw materials (19.63 ± 6.57 Bq/kg). The value of average ²³²Th concentration in normal soil sample was 53.52 ± 10.84 Bq/kg and in the fertilizer sample it was 42.48 ± 10.56 Bq/kg.

The analysis of the samples also revealed that the normal soil samples contained the highest average concentration values of ^{40}K which was 723.77 ± 101.04 Bq/kg. However, no ^{40}K was detected in the fertilizer samples. The activity concentration of ^{40}K in raw material samples were rather lower (54.06 ± 5.93 Bq/kg) than the solid waste (655.94 ± 110.24 Bq/kg) and normal soil samples.

Table 2. Activity concentrations of radionuclides in different kinds of solid samples collected from the TSP fertilizer factory and its adjacent areas.

Sample nature	Samples ID	Activity concentrations of radionuclides (Bq/kg)		
		^{226}Ra	^{232}Th	^{40}K
Raw material (Phosphate rock) samples	Sample: 8	906.60 ± 7.15	36.13 ± 9.27	99.79 ± 8.62
	Sample: 9	874.44 ± 7.04	17.91 ± 9.08	29.60 ± 4.27
	Sample: 10	772.78 ± 7.12	4.85 ± 1.35	32.79 ± 4.89
	Average	851.27 ± 7.10	19.63 ± 6.57	54.06 ± 5.93
Solid waste (Phosphogypsum) samples	Sample: 11	206.03 ± 4.85	45.09 ± 11.02	677.08 ± 104.53
	Sample: 12	177.26 ± 4.67	70.36 ± 11.10	641.90 ± 104.38
	Sample: 13	179.19 ± 5.11	94.74 ± 13.15	648.83 ± 121.82
	Average	187.49 ± 4.88	70.06 ± 11.76	655.94 ± 110.24
Phosphate fertilizer samples	Sample: 14	216.47 ± 4.86	44.90 ± 10.90	ND
	Sample: 15	207.32 ± 4.61	40.05 ± 10.22	ND
	Average	211.90 ± 4.74	42.48 ± 10.56	ND
Normal soil samples	Sample: 16	10.68 ± 2.85	46.86 ± 8.97	764.44 ± 85.06
	Sample: 17	12.55 ± 4.25	75.09 ± 14.06	787.00 ± 127.97
	Sample: 18	4.45 ± 2.96	38.60 ± 9.48	619.88 ± 90.08
	Average	9.23 ± 3.35	53.52 ± 10.84	723.77 ± 101.04

ND: Not detected.

The raw materials and also the wastes (both liquid and solid) generated from the production process of the TSP fertilizer were stored in the open environment in the factory; therefore, these raw materials and wastes had become a constituent of the ambient environment of the factory complex. Therefore, these wastes could be treated as the part of the ambient environment of the factory contributing to the radiation exposure of the workers of the factory and 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) for these stored items as well as the normal soil samples (for the purpose of comparison) were calculated using the following equations (Kessaratikoon and Awaekuchi 2008):

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

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.

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

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

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

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

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

In order 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 calculated values of Ra_{eq} , H_{ex} , D and E are summarized in Table 3. The maximum values of these parameters were found to be 965.24 Bq/Kg , 2.61 , 444.86 nGy/h and 0.546 mSv/y , respectively. The highest average annual effective dose of 0.5 mSv was found in phosphate rock sample (raw material) and the value was 0.192 mSv in the solid waste sample.

Table 3. Radium equivalent activity, external radiation hazard index, absorbed dose rate and annual effective dose calculated for the raw materials, solid wastes and normal soil samples.

Sample nature	Sample ID	Ra_{eq} (Bq/Kg)	H_{ex}	D (nGy/h)	E (mSv/y)
Solid waste	Sample: 11	317.91	0.872	150.86	0.185
	Sample: 12	322.80	0.884	151.35	0.186
	Sample: 13	360.08	0.985	167.26	0.205
	Average	333.60	0.914	156.49	0.192
Phosphate rock (Raw material)	Sample: 8	965.24	2.61	444.86	0.546
	Sample: 9	902.12	2.44	416.05	0.510
	Sample: 10	782.00	2.11	361.33	0.443
	Average	883.12	2.39	407.41	0.500
Normal soil	Sample: 16	131.20	0.368	65.34	0.080
	Sample: 17	175.02	0.487	84.21	0.103
	Sample: 18	103.04	0.289	51.41	0.063
	Average	136.42	0.381	66.99	0.082

The world quoted values for Ra_{eq} , H_{ex} , D and E are 370 Bq/kg , 1.0 , 55 nGy/h and 0.115 mSv/y , respectively (ICRP 1990). It is seen that the calculated values for raw materials and waste samples are higher than the world average but lower in the normal soil samples except for absorbed dose. However, as per ICRP (ICRP 1990) the permissible limit of the annual effective dose for public is 1 mSv . Therefore, the annual effective dose from the ambient environment of the factory complex is below the permissible limit and is safe from any immediate health effect. However, the workers working for the longer time with raw materials may face chronic health effect.

CONCLUSION

Detection and calculation of activity concentrations of natural radionuclides in seven different types of samples collected from in and around the TSP Fertilizer Complex, Chittagong, Bangladesh was performed as a case study of the radiological impact assessment work of the fertilizer industries of Bangladesh. The radionuclides detected in the samples were all natural and no artificial radionuclide was found in the study. Activity concentrations of the detected radionuclides and the doses from these samples were found within the acceptable limit. 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.

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