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Natural radioactivity assessment of a phosphate fertilizer plant area

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ABSTRACT

Rock phosphate ore processing and disposal of phosphogypsum contribute to enhanced levels of natural radionuclides in the environment. The concentration of naturally occurring radionuclides in soil, rock phosphate and phosphogypsum samples collected around a phosphate fertilizer plant were determined. Also the external background gamma levels were surveyed. ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K activities in soil samples were 21–674 Bq/kg, 11–44 Bq/kg, 22–683 Bq/kg and 51–295 Bq/kg respectively. The external background gamma radiation levels in the plant premises were ranging from 48 to 133 nGy/h.

1. Introduction

Phosphate rocks of sedimentary origin contain Uranium (^{238}U), Thorium (^{232}Th) and its decay products in addition to phosphate minerals (Roesseler, 1990). Considerable variations are found in the chemical composition of rock phosphate from different mining areas. In general, sedimentary phosphate rocks, or phosphorites, originated in a marine environment, are characterized by activity concentrations of uranium much higher than those of volcanic and biological rocks. Reported values of ^{238}U in rock phosphate range from 1.0 to 5.7 Bq/g (Barisic, Lulic, & Miletic, 1992; Guimond & Hardin, 1989; Heijde, Klijn, & Passchier, 1988). These phosphates are largely used for the production of phosphoric acid, fertilizers and hence phosphate fertilizer industries are considered to be a potential source of natural radionuclide contamination. Their radioactivity leading to health problems from radiation at the level of the industrial processes which involves mining and transportation of phosphate ores and production of fertilizers. At the usage level, when fertilizers dispersed into the geo and biospheres, have a potential to transfer to living beings. Leaching of the minerals and wastes is another potential source of radioactivity dissemination which may contribute to enhanced exposure of workers, public and the environment to these radionuclides.

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Phosphogypsum is a waste by-product from the processing of phosphate rock by the "wet acid method" of fertilizer production, which currently accounts for over 90% of phosphoric acid production. The wet process is economic but generates a large amount of phosphogypsum (5 tons of phosphogypsum per ton of phosphoric acid produced) (USEPA, 2002). World phosphogypsum production is variously estimated to be around 100–280 mega tonnes per year (Parreira, Kobayashi, & Silvestre, 2003; Yang, Liu, Zhang, & Xiao, 2009). The nature and characteristics of the resulting phosphogypsum are strongly influenced by the phosphate ore composition and quality. Wet processing causes the selective separation and concentration of naturally occurring radium (Ra), uranium (U) and thorium (Th): about 80–90% of ^{226}Ra is concentrated in phosphogypsum while nearly 86% of U and 70% of Th end up in the phosphoric acid. Determining the types of impurities present can be very important when defining waste management processes and environmental policies. The discharge of phosphogypsum (PG) on earth surface deposits is a potential source of enhanced natural radiation and heavy metals, and the resulting environmental impact should be considered carefully to ensure safety and compliance with environmental regulations (Bolivar, Garcia-Tenorio, & Vaca, 2000; Shakhashiro et al., 2011).

Industrial processing of rock phosphate to manufacture phosphatic fertilizers involves the production of phosphoric acid according to the following chemical reaction (Haridasan, Paul, & Desai, 2001):

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot 2H_2O + 2HF$$

Only 15% of world phosphogypsum production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as a set controller in the manufacture of Portland cement. The remaining 85% is disposed of without any treatment. This byproduct is usually dumped in large stockpiles exposed to weathering processes, occupying considerable land areas and causing serious environmental damage (chemical and radioactive contamination), particularly in coastal regions. The radionuclide ^{226}Ra produces radon gas (^{222}Rn), which has a short half-life of 3.8 days, an intense radiation capacity, and causes significant damage to internal organs (USEPA, 2002). For this reason the USEPA has classified phosphogypsum and rock phosphate as "Technologically Enhanced Naturally Occurring Radioactive Materials" (TENORM) (USEPA, 2002) and phosphogypsum exceeding 370 Bq/kg of radioactivity has been banned from all uses by the EPA since 1992. Depending on the quality of the rock source, phosphogypsum can contain as much as 60 times the levels normally found prior to processing. The most important source of phosphogypsum radioactivity is reported to be ^{226}Ra (Rutherford, Dudas, & Samek, 1994). Due to the fact that this by-product accumulates a fraction of the natural radionuclides originally present in the minerals treated, it can be concluded that these industries through the phosphogypsum may produce a radioactive impact on their nearby environment (Bolivar, Garcia-Tenoriob, & Garcia-Leon, 1995).

The storage of phosphogypsum in large land areas without any prior treatment can cause serious environmental contamination of soils, water and the atmosphere. Negative atmospheric impacts can be caused by the erosion of phosphogypsum piles and the release of highly polluting substances, due to the presence of hazardous vapors containing heavy metals, sulphates, fluorosilicates, hydrogen fluorides, phosphorus, cadmium and ^{226}Ra (Marovic & Sencar, 1995). Atmospheric agents can transport the contamination to neighboring areas. Another matter of concern is the leachability of hazardous elements from phosphogypsum and thus the contamination of groundwater underlying phosphogypsum stacks (May & Sweeney, 1982, pp. 1–19, 1983, pp. 1–19). Since phosphogypsum waste is generally transported and disposed as aqueous slurry, phosphogypsum piles can be affected by tidal variations and dissolution/leaching of the elements naturally present in the phosphogypsum can occur. Dissolved elements may be deposited in nearby soils or transferred to waters and finally to living beings (Reijnders, 2007).

Hence, phosphogypsum disposal by piling the waste into open environment subjecting it to natural weathering processes without any treatment may lead to radioactive contamination. In this study, the distribution of ^{238}U, ^{232}Th, ^{226}Ra, and ^{40}K in soil was investigated in and around a phosphate fertilizer industry which stores and disposes its solid waste in the surrounding environment. The main goal is to evaluate the impact of such waste on soil and to identify the most influencing factors on contaminants distribution from a fertilizer plant producing about 25,000 MT phosphoric acid which results in an annual generation of more than 120,000 MT of phosphogypsum.

2. Materials and methods

2.1. *Sample preparation*

Soil samples were collected twice a month for a period of 3 months from 20 locations in and around a phosphate fertilizer plant (Fig. 1). Rock phosphate samples and gypsum were also collected from the location from their respective storage or disposal areas. Soil samples were crushed and cleaned to remove the clinker and other organic debris. The samples were dried for 24 h in an air-circulation oven at 110 °C. Samples were further ground, homogenized and about 100 g of each sample was filled in plastic containers of 6.5 cm diameter × 7.5 cm height and sealed to make them airtight. The containers kept undisturbed for 6 months so that to provide the longest-lived intermediary radionuclide ^{234}Th (24.1days) the opportunity to come to within 1% of secular equilibration with its parent ^{238}U. After attainment of secular equilibrium the samples were subjected to gamma-ray spectrometric analysis.

2.2. *Gamma spectrometric analysis*

The gamma-spectrometry system having an n-type coaxial HPGe detector (DSG, Germany) shielded with 7.5 cm thick lead having 100% relative efficiency and a resolution of 2.1 keV at 1.33 MeV gamma energy of ^{60}Co was used. The gamma spectra acquired for 60,000 s were analyzed using a 64K PC based multichannel analyzer and gamma spectrometry software.

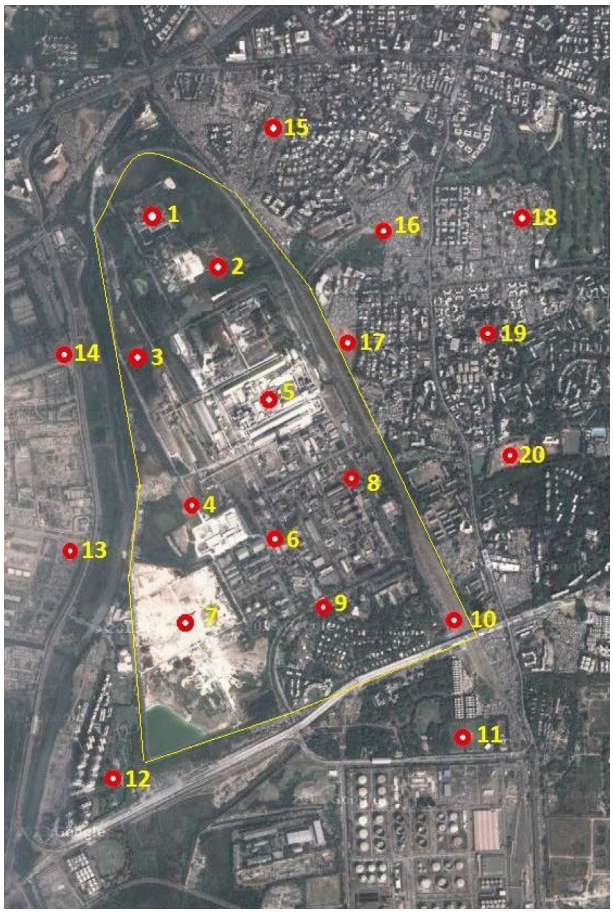

Fig. 1 – Sampling locations in the phosphate fertilizer plant.

Natural gamma background radiation levels were monitored by a NaI(Tl) based portable survey meter. The variation in external dose rate due to natural gamma background at various locations around the plant were measured using a NaI–Tl based handheld radiation survey meter (Fieldspec, Germany).

3. Results and discussion

The levels of naturally occurring radionuclides (^{238}U, ^{226}Ra, ^{232}Th and ^{40}K) in soil samples are given in Table 1. The ^{238}U activity in soil samples varied from 21.5 to 674.5 Bq/kg and that of ^{226}Ra was ranging from 22.8 to 683.7 Bq/kg. At location 7 (gypsum pond) ^{226}Ra values were found to be considerably higher than ^{238}U, which is consistent with the nature of elemental distribution during chemical processes resulting in the generation of phosphoric acid. During acid attack of rock phosphate to produce phosphoric acid, majority of uranium along with thorium get partitioned with phosphoric acid while the radium, which follows calcium chemistry, finds its way with phosphogypsum (Poole, Allington, Baxter, & Young, 1995). The levels of ^{238}U and ^{226}Ra in soils at the two locations (location 4 and 7) were about 10–30 times higher than the rest of the plant locations and the average Indian soil levels of 20 Bq/kg. The open storage of such high radioactivity material could affect the surrounding in various pathways like emanation of ^{222}Rn, atmospheric transport, leaching, dissolution and transport to aquatic environment (Bolivar et al., 1995). Activity concentration of all the nuclides except for ^{40}K, were found to be maximum at location 4, at the Rock Silo, where phosphate rock is stored in large quantities. This is due to the fact that raw materials containing phosphorus show low activity concentrations of ^{40}K but have significant activity concentrations of radionuclides belonging to ^{238}U chain (Serena, Patrizia, & Luigi, 2005).

Table 1 – The levels of naturally occurring radionuclides in soil samples.

	^{238}U (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)	^{40}K (Bq/kg)
Inside plant premises				
Location 1	68.9 ± 6.8	33.1 ± 19.0	11.5 ± 6.2	160.8 ± 35.0
Location 2	21.5 ± 9.0	31.4 ± 19.8	15.3 ± 4.0	204.6 ± 78.2
Location 3	23.7 ± 13.7	22.8 ± 8.5	18.5 ± 12.0	259.5 ± 38.8
Location 4	563.0 ± 59.4	537.7 ± 129.9	44.8 ± 10.7	130.5 ± 6.8
Location 5	132.2 ± 89.4	269.6 ± 68.9	21.6 ± 7.1	295.5 ± 86.9
Location 6	23.5 ± 14.5	28.4 ± 17.4	16.4 ± 0.3	216.9 ± 47.1
Location 7	674.5 ± 69.9	683.7 ± 83.4	33.6 ± 12.4	51.8 ± 11.5
Location 8	54.4 ± 11.3	34.1 ± 6.8	12.3 ± 4.2	145.6 ± 46.7
Location 9	24.3 ± 8.2	26.5 ± 3.4	13.6 ± 3.2	110.5 ± 26.4
Location 10	26.1 ± 5.9	24.4 ± 4.6	14.3 ± 2.1	143.7 ± 47.5
Outside plant premises				
Location 11	30.5 ± 3.4	28.6 ± 1.3	13.6 ± 1.2	220.0 ± 29.4
Location 12	53.1 ± 6.7	48.5 ± 5.4	12.4 ± 1.3	189.7 ± 34.4
Location 13	22.4 ± 1.8	23.6 ± 1.4	18.7 ± 0.8	234.0 ± 32.3
Location 14	44.6 ± 6.2	40.8 ± 3.9	20.0 ± 2.1	132.3 ± 19.4
Location 15	25.2 ± 2.6	26.4 ± 2.4	22.6 ± 1.8	217.1 ± 32.1
Location 16	31.3 ± 2.3	34.3 ± 3.3	20.5 ± 2.4	332.5 ± 39.6
Location 17	29.1 ± 2.1	36.4 ± 2.4	18.1 ± 1.4	211.6 ± 41.2
Location 18	36.6 ± 3.3	42.3 ± 3.5	23.8 ± 2.8	159.1 ± 21.2
Location 19	30.3 ± 2.7	39.4 ± 2.9	17.2 ± 1.2	225.2 ± 29.6
Location 20	28.8 ± 1.7	34.5 ± 1.4	14.6 ± 1.8	233.5 ± 24.3

Table 2 – Radioactivity (Bq/g) in phosphate rocks and phosphogypsum

Phosphate rock activity (Bq/g)						Phosphogypsum activity (Bq/g)					
Location	Reference	^{226}Ra	^{238}U	^{232}Th	^{40}K	Location	Reference	^{226}Ra	^{238}U	^{232}Th	^{40}K
Morocco	Guimond and Hardin (1989)	1.6	1.7	0.01	0.02	Florida	Olszewska (1995)	0.9	0.069	0.01	–
Taiba-Togo		1.1	1.3	0.03	0.004	Brazil	Mazzilli, Palmiro, Saueia, and Nisti (2000)	0.6	0.04	0.1	0.02
Bu-Craa (Western Sahara)		0.9	0.9	0.007	0.03	Brazil		0.2	0.04	0.1	0.01
Syria	Attar et al. (2011)	0.3	1.0	0.002	–	Syria	Attar et al. (2011)	0.3	0.03	0.002	–
Florida	Guimond (1990)	1.6	1.5	0.02	–	Egypt	Ahmed (2005)	0.1	–	0.04	0.5
Tunisia	Olszewska (1995)	0.8	1.0	0.02	0.03	Spain	José, Rafael, and Guillermo (2009)	0.8	0.08	–	–
India (Present Study)		1.29	1.34	0.09	0.01	India (Present Study)		0.3	0.03	0.01	0.005

The phosphogypsum and rock phosphate samples were analysed for the estimation of radioactivity in them along with the soil samples. The results for activity concentration of ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K in the samples were compared with other studies carried out worldwide. Table 2 shows the wide variation of activity concentrations of all the radionuclides observed by a number of researchers worldwide. Phosphate rock in present study showed high activity concentrations of ^{238}U and ^{226}Ra (1.34 Bq/g and 1.29 Bq/g), while the activity concentrations of ^{232}Th and ^{40}K were observed to be significantly low. This trend is consistent with the results from other studies on phosphate rocks. As it is learned that the radionuclides get partitioned between Phosphoric acid and the gypsum during to the chemical processes, the levels of these radionuclides were observed to be reduced in the solid residue i.e. phosphogypsum. The activity ^{238}U activity concentration which showed maximum reduction in gypsum was reduced to more than 1/40th of its activity concentration in rock phosphate. The activity concentrations of ^{232}Th and ^{226}Ra were reduced to 1/8th and 1/4th of their activity concentrations in rock phosphate, while the activity concentration of ^{40}K was minimum affected and was reduced only to half of its value in rock phosphate. The observed activity levels of ^{226}Ra in phosphogypsum were not as high as its chemistry would indicate, which favors more the gypsum root for ^{226}Ra than the phosphoric acid. This trend agrees with that reported by Awadalla and Thabashi (1985). The ^{226}Ra in the rock phosphate sample in present study were having activity

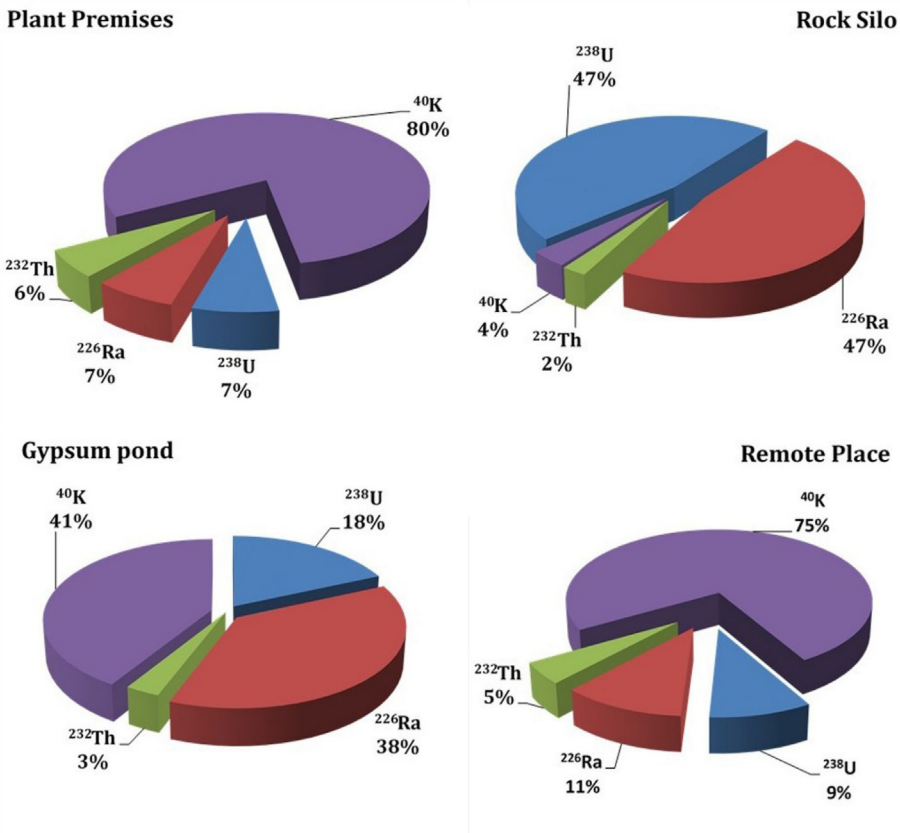

Fig. 2 – Percentage contribution of radionuclides in different soil samples.

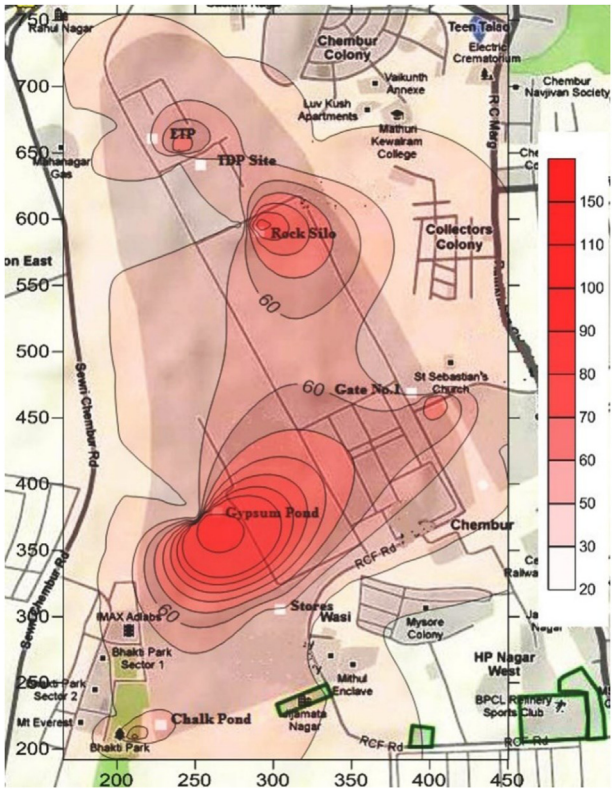

Fig. 3 – Variation in external dose rate due to natural gamma background at various locations around the plant. (Scale arbitrary).

concentrations above 1000 Bq/kg while in phosphogypsum it was slightly greater than 300 Bq/kg.

Fig. 2 shows percent distribution of the four radionuclides in soil samples collected from background locations in plant premises, from rock silo, gypsum pond and from a remote place outside the plant premises. The distribution in background soil within the plant and from the remote place were dominated by ^{40}K (75–80%) followed by ^{226}Ra, ^{238}U and ^{232}Th respectively. ^{232}Th had the minimum share in all soil samples. This result is consistent with the average activities of these radionuclides in the earth crust, showing no contamination of the plant premises and the surrounding area by the TENORM handled in plant. The percent distribution in soil from the rock silo was dominated by ^{238}U and ^{226}Ra with both contributing 47% each. This shows that the soil at rock silo contains large amounts of rock phosphate and thus both ^{238}U and ^{226}Ra are in secular equilibrium as is the case in most of the mineral deposits. The soil from gypsum pond showed maximum contribution from ^{40}K followed by ^{226}Ra. As the uranium concentrations are reduced significantly in the gypsum, ^{238}U shared nearly half the percentage of that of ^{40}K and ^{226}Ra in gypsum pond soil.

The background radiation survey carried out along with the soil sampling showed radiation levels varying between 48 and 133 nGy/h. As can be expected, higher background levels were observed at gypsum pond and rock silo. Other locations showed normal background radiation levels, indicating no contamination of the area away from gypsum pond and rock silo. Fig. 3 is a pictorial representation of the contours of variation in external dose rate due to natural gamma background at various locations around the plant, which also corresponds well with amount of natural radioactivity estimated in the soil samples at the respective locations. The hotspots at Rock Silo (location5) and Gypsum Pond (Location 7) can clearly be seen from the diagram except which, the external gamma radiation levels in the plant area were normal.

To assess the radiological hazard, the radium equivalent activity (Ra_{eq}) and external hazard index (H_{ex}) were calculated according to UNSCEAR (2000) as

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_K \quad (1)$$

$$H_{ex} = A_{Ra}/370 + A_{Th}/259 + A_K/4810 \quad (2)$$

Where A_{Ra}, A_{Th} and A_K are the activity concentrations of Ra^{226}, Th^{232} and K^{40} in Bq/kg respectively. Ra_{eq} is related to the external γ-dose and internal dose due to radon and its daughters. The maximum value of Ra_{eq} must be less than 370 Bq/kg. H_{ex} is obtained from the Ra_{eq} expression by assuming that its maximum value allowed (equal to unity) corresponds to the upper limit of Ra_{eq} (370 Bq/kg). The calculated average values of Ra_{eq} ranged from 54 to 735 Bq/kg with average of 211 Bq/kgin the plant premises (Fig. 4) while the same was 78 Bq/kg outside. The calculated values of H_{ex} ranged from 0.14 to 1.98 with an average of 0.57. It was

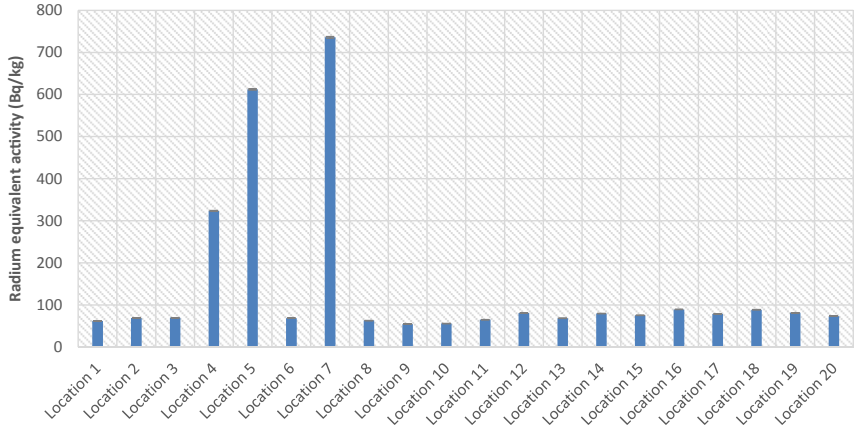

Fig. 4 – Radium equivalent activity (Ra_{eq}) of soil samples.

observed that the Ra_{eq} values were more at Gypsum pond (location 7) and Rock silo (location 5) than 370 Bq/kg and the H_{ex} values at the same locations were more than unity.

4. Conclusions

The phosphate fertilizer plant produces large amount of waste in the form of liquid and solid effluents. The soil from the solid waste disposal area i.e. gypsum pond and the soil from the rock silo which is the phosphate rock storage area showed higher levels of natural radionuclides than other locations in the plant premises. The ^{238}U levels in phosphogypsum sample were higher than those compared worldwide. The external gamma radiation survey didn't show any increased levels than the normal background except at gypsum pond and the rock silo area where the values though more than the background were not significantly high.

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