The effects of various types of phosphate fertilizers on the environment and their natural activity

1Yasmyn S. Khalf , 2Kareem K. Mohammad
1Al-Nahrain University, College of Science, Physics Department, Baghdad, Iraq
2Al-Nahrain University, Al-Nahrain Nano-renewable Energy Research Center, Baghdad, Iraq

Corresponding author E-mail: yassaminphy@gmail.com

Abstract. In this study, the effect of various types of fertilizers on natural radioactivity levels in agricultural soil was investigated in this research. The activity concentration of 226Ra, 232Th, and 40K in fertilizer samples were determined by using gamma-ray spectroscopy and a high-purity germanium (HPGe) detector to determine the activity concentrations 226Ra, 232Th, and 40K. The activity concentrations for 226Ra, 232Th, and 40K in fertilizers and phosphate raw were (2300-5400) Bq/kg, (9-53) Bq/kg, and (56-3000) Bq/kg, respectively. This research could serve as a baseline data for understanding the effects of fertilizer radiation on human health.

Keyword: Natural radioactive, fertilizer, spectroscopy

1. Introduction

Superphosphate are extremely common and contaminate agricultural soils through the use of fertilizer. Residues of phosphates include the naturally occurring radioisotopes 232Th and 238U with their daughter isotopes (230Th, 234U, 226Ra, 222Rn, and 210Pb). Once phosphate fertilizers are derived from phosphate rocks, containing 238U with other radionuclides.222Rn, as an inert gas, is not harmful on its own; however it allows for the dispersion of other radionuclides over field crop. Fertilizer has been used to create a vegetative cover for infertile and poorly eroded soils, thus minimizing the transport of surface runoff water, soil and nutrients. Fertilizers usually contain the following ingredients in varying proportion there are three major macronutrients. Nitrogen (N) that is necessary for leaf development, Phosphorus (P) is required for the development of roots, flowers, seeds and Potassium (K) promotes strong stem growth, water movement in plants, and flowering and fruiting [1-2].

Phosphoric acid is the primary raw material for many types of phosphate fertilizers such as potassium sulfate (K), di ammonium phosphate (DAP), mono ammonium phosphate (MAP), Nitrogen, Phosphorous and Potassium (NPK), urea ammonium phosphate (NP), and single superphosphate (SSP). NPK are obtained by reacting phosphoric acid with NH3. the radioactive equilibrium between U, Th and their decay products is disrupted during the phosphate rock reaction with sulphuric acid and the radionuclides migrate according to their solubility. Uranium isotopes form highly soluble phosphate ion compounds, while isotopes, 210Pb and 210Po concentrate in phosphogypsum [3].
There is a risk here. Fertilizer elements, as well as their derivatives, have the potential to reach (plant, animal, human, food chain components). It is cumulatively concentrated in consecutive trophic levels, with urban densities and towns posing a higher risk excessively crowded. It is important to assess the human and environmental health risks associated with fertilizer pollutants. Attempts have been made to create upper limits in fertilizers for trace elements, thus restricting the inadvertent transfer to consumers of potentially harmful substances [4].

2. Materials and method

2.1 Preparation of samples

The aim of using the phosphate fertilizers is soil and the plant supply with phosphorus element that is considered one of the most important chemical elements to fertilize the soil. There are many sources to get the phosphorus of which phosphate rock and roth [5].

The fertilizer was collected from a variety of sources and varieties of fertilizers, including 17 samples of widely used fertilizer (potassium sulfate, Urea ,NP,Bitmos,NPK,MAP, and DAP). The samples were put it in a small, airtight containers, which is kept for a month in (hood) to reach the nuclear equilibrium state between radium and its daughter products before being taken for gamma spectrometric analysis. A month later we put the samples in marinelli beaker (one-kilogram weight) washed with plain water, and then distilled water. Then dry up the samples in an oven dried at 80°C until they reached a constant weight, each sample was place in 1kg plastic container (marineli).

3. System initialized

The present study used high pure germanium detector supplied by accompany (BSI Baltic scientific instruments) consisting of germanium crystal (2*2 (HPGe ) using (spectral line Gp) computer software. The detector was inside lead shield of thickness (4.5 cm) to reduce the back ground radiation in order to reduce the contribution of x-ray fluorescence the inner surfaces of lead shield are provided graded lining with Copper sheet (0.8mm thick). The system is linked to primary amplifier, amplifier and power supply. Because of cosmic radiation that constantly strikes the earth's atmosphere and the presence of natural radioactivity in the environment, all radiation detectors record some background signals. The existence of this context varies greatly depending on the detector type and scale, as well as the layers of shielding that may be used around it [6].

The measured back ground for (2hr) to counting. The detector was calibrated using standard sources type (CBSS 2) 241Am (59.3)kev, 60Co (1173.1, 1332.3)kev, 137Cs (661.6)kev show in Table(1). We put each sample over the detector for (2hr) to counting, after calibrations the activity concentration of samples were calculated.

| Radionuclide | Half-life (days) | Activity(Bq/kg) | Combined standard uncertainty | Energy(kev) |
|--------------|-----------------|----------------|-------------------------------|-------------|
| Am-241       | 157800          | 4.433          | 1.1                           | 59.3        |
| Cd-109       | 4626            | 16.17          | 1.5                           | 88.1        |
| Ce-139       | 137.5           | 0.740          | 1.1                           | 165         |
| Co-57        | 271.26          | 0.855          | 1.1                           | 122.1,136   |
| Co-60        | 1925.4          | 2.659          | 1.1                           | 1173.1,1332.3 |
4. Calculations

4.1. Activity concentration $A$:

The activity concentrations ($A$) of isotopes in the sample as in the results shown in the table (2) were calculated by using the following formula: [8]

$$A = \frac{\text{Net count}}{(\varepsilon \times I_\gamma \times T \times M)} \pm \frac{\text{SD}}{(\varepsilon \times I_\gamma \times T \times M)}$$  

(1)

Where $\varepsilon$ the absolute gamma peak efficiency of the detector for a given gamma ray energy, $I_\gamma$ is gamma index, $T$ is the counting time for the measurement in seconds, SD is the standard deviation of the net count rate per second and $M$ is the mass of the sample in kg [8]. The figure (1) show one for the spectrum of phosphate raw.
Table 2. the activity concentration of 226Ra, 232Th and 40K, *ND: not detection limited.

| Sample code | Sample ID | Origin       | Activity of $^{226}$Ra (Bq/kg) | Activity of $^{232}$Th (Bq/kg) | Activity of $^{40}$K (Bq/kg) |
|-------------|-----------|--------------|---------------------------------|---------------------------------|-------------------------------|
| Y1          | Potassium sulfate (K) | Iraq         | ND                              | ND                              | 2100                          |
| Y2          | Urea (N)  | Iraq         | ND                              | ND                              | 130                           |
| Y3          | Nitrogen phosphorous and potassium (NPK) | Jordan       | ND                              | ND                              | 4900                          |
| Y4          | Mono ammonium phosphate (MAP) | Saudi       | ND                              | 9                               | 56                            |
| Y5          | Urea ammonium phosphate (NP) | Iraq         | 2300                            | ND                              | ND                            |
| Y6          | Potassium sulfate (K) | Italia       | ND                              | ND                              | 1200                          |
| Y7          | Di ammonium phosphate (DAP) | Saudi       | 12                              | ND                              | ND                            |
| Y8          | Bitmous (B) | Spain        | ND                              | ND                              | ND                            |
| Y9          | Mono ammonium phosphate (MAP) | Jordan   | ND                              | 12                              | ND                            |
| Y11         | Potassium sulfate | Holland     | ND                              | ND                              | 3000                          |
| Y12         | NPK        | United state | ND                              | 6.2                             | 460                           |
| Y13         | Bitmous    | Turkish      | ND                              | 11                              | ND                            |
| Y14         | Potassium sulfate | France     | ND                              | ND                              | 2600                          |
| Y15         | NPK        | Holland      | ND                              | ND                              | 660                           |
| Y17         | NPK        | Russia       | ND                              | 53                              | 170                           |
| Y18         | Phosphate raw | Iraq        | 5400                            | ND                              | ND                            |
5. Results and Discussion

The spectra of 17 fertilizer samples of different types of original from random markets in Iraq and one phosphate raw sample from phosphate quarries in Al-Qaim city in Iraq were analyzed. The activity concentration of natural radioactive nuclides 226Ra, 232Th and 40K are showed in table (1). The highest concentration of 226Ra was observed in Np type Iraqi phosphate fertilizer with 2300 (Bq/kg), the other samples appear not detection sensitivity while the phosphate raw showed 5400 (Bq/kg) specific activity, which is a high value as compared to the ICRP recommended value.

The highest concentration of 232Th was measured in NPK Russian phosphate fertilizer with 53 (Bq/kg). While the lowest concentration of 232Th observed in NPK American fertilizer with 6.2 (Bq/kg).

The highest activity concentration of 40K was observed in NPK Jordanian fertilizer with 4900 (Bq/kg), the lowest concentration of 40K was measured in MAP Saudi fertilizer with 56 (Bq/kg), while no activity was found for the other two Urea samples (y10 and y16) because their ores had no naturally occurring radionuclides. We notice that the activity concentration of 226Ra of Np and of phosphate raw were higher than the world average, while the activity concentration of 232Th in MAP, DAP, Potassium sulfate and Bitmous were less than the world average unless the NPK Russian Type that high the world average. The activity concentrations of 40K of all samples were less than the average world (IAEA) [11].

The highest concentration of 226Ra is higher than the concentration of other countries, while the highest concentration of 232Th is lower than the other countries. The concentration of 40K is higher than the other countries as show in table (3).

The results indicate a wide range of gamma activity in the fertilizers and this may be due to the following factors:

1. The differences between produced fertilizer factories.
2. The different locations from which the raw minerals for fertilizer manufacturing were sourced.
3. Radioactive elements in raw materials had different properties depending on where they were found [13].

Table 3. Activity concentration of phosphate fertilizers from different countries.

| Country | Sample ID | 226Ra | 232Th | 40K | Reference |
|---------|----------|-------|-------|-----|-----------|

Figure 1. The spectrum of phosphate raw relation between count and channel
Conclusions

By analyzing the fertilizers in the local markets. As some of it is imported and the other part is locally produced, the conclusions are as following:

1- There are high concentrations compared to other countries as well as the international agency.

2- It requires monitoring the markets as well as queries in industrialized countries.

3- It is clear that fertilizers have role in increasing the radioactivity of the environment, agriculture, animals and human, thus it requires setting parameters for each country in terms of the use of industrial fertilizers.

4- It is preferable to use plant and animal fertilizers.

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