RADIOACTIVE CONTAMINATION OF SOIL CLOSE TO PHOSPHOGYPSUM DISPOSAL POND

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Abstract
Natural radioactivity is a part of our natural surrounding and concentrations of natural radionuclides in the environment increase with the development of technologies. It has become clear that the rapidly growing world population must depend increasingly upon commercial fertilizers for its food and fiber. Phosphate materials used for production of phosphate fertilizers contain a minor quantity of radioactive material, mainly various members of the uranium and thorium series, and radiopotassium. In Republic of Croatia, the annual use of phosphate fertilizers is low. Specific activity of uranium is from 600 to 1400 $Bqkg^{-1}$, of potassium about 3000 $Bqkg^{-1}$. Thorium content is neglected. The basic phosphate material used to produce phosphate fertilizers unfortunately is very insoluble. For that reason, drastic chemical treatment with strong acid is necessary to produce soluble phosphate products. The result of classical process is precipitation of gypsum (termed phosphogypsum).

The aim of the present work was to define the level of some natural radionuclides in soil samples collected from uncultivated surfaces close to phosphogypsum disposal pond at phosphate fertilizer plant in Republic of Croatia. The specific activities of uranium (^{238}U) and thorium (^{232}Th) decay series, as well as radiopotassium (^{40}K) have been determined gammaspectrometrically.

Key words
Radioactivity, phosphogypsum, soil, phosphate fertilizers.

Introduction

The data presented in this work will try to elucidate a long time existing situation at the site of a gypsum (termed phosphogypsum) disposal pond. The phosphogypsum disposal pond is a part of the Fertilizer factory, which is situated in the central part of Republic of Croatia, close to banks of river Sava.

The basic phosphate materials used to produce phosphate fertilizers contain minor quantities of radioactive material. The primordial radionuclides include those belonging to the ^{235}U, ^{238}U and ^{232}Th series and ^{40}K, which is the major naturally occurring radionuclide(1). This phosphate material, unfortunately is very insoluble, and therefore, in its original state is practically unavailable as a plant phosphorus source(2). For that reason, drastic chemical treatment is necessary to produce soluble phosphate products. To produce phosphoric acid, the phosphate rock is treated with sulphuric acid. The by-product, gypsum (termed phosphogypsum) is filtered from the acid. The chemical reaction occurring during acidulation is as follows:

$$[Ca_3(PO_4)_2]_3CaF_2 + 10H_2SO_4 + 2H_2O \longrightarrow 6H_3PO_4 + \mathbf{10CaSO_4} \times \mathbf{2H_2O}\downarrow + 2HF$$

This fertilizer factory, at the production of phosphoric acid by the wet dehydrate process, with it′s 1.5 million tones of mineral fertilizer per year design capacity, generate around five tons of phosphogypsum per one ton of P_2O_5(3). Radium (^{226}Ra), contained in phosphate rocks is mostly incorporated into phosphogypsum, replacing calcium in chemical structure of gypsum. One of the biggest problems is safe phosphogypsum disposal, until used as secondary raw material.

In the Fertilizer factory waste phosphogypsum generated in the production is mixed with water and hydraulically transported from the Phosphoric acid plant to the land disposal site by a special pipeline. Water from the pool surface is pumped back into production, which makes the system closed. The excess quantity of pond water is treated with lime before discharging into the waste channel. Disposal site is situated about five kilometers southward from the factory. The phosphogypsum disposal pond is divided in five basins and covers total area of about 1.6 km^2. The deposit capacity is about ten million cubic meters at the level of earthen dams. At present situation, there is deposited about four million tons of phosphogypsum with about one million cubic meters pond water(3).

Sampling and Measurement Procedure

Soil samples were collected once a year, from uncultivated surfaces, close to phosphogypsum disposal pond. Three layers of soil, taken from the depths of 0-5 cm, 5-10 cm and 10-15 cm, collected over period of four years were analyzed. Samples were taken with coring tool of known diameter (φ = 10 cm). Ten cores from a total surface area of one cubic meter were taken and composed to make a single sample. At laboratory, samples were speread on plastic sheets, and allowed to dry at room temperature for several days. Stones and roots were discarded, samples were ground to pass a mesh size of 2 mm, dried at 105 °C for three days, and calcinated at 450 °C(4).

The specific activities of ^{238}U and ^{232}Th decay series, as well as ^{40}K have been determined gammaspectrometrically. Gammaspectrometry was carried out by use of Ge(Li) detector (resolution 1.78 keV on 1.33 MeV ^{60}Co, relative efficiency 16.8 %) jointed to 4K channel analyzing system and connected on line with the computer. The measuring time was 80000 seconds. All samples were measured in Marinelli beaker, volume one litre.

Results and Discussion

From our gammaspectrometric data, for this study, we have chosen four naturally occurring radionuclides: ^{238}U and ^{226}Ra from uranium decay series, ^{232}Th from thorium decay series, and ^{40}K. Figure 1 shows the activities in soil samples close to phosphogypsum disposal pond, presented as mean values of four years analysis.

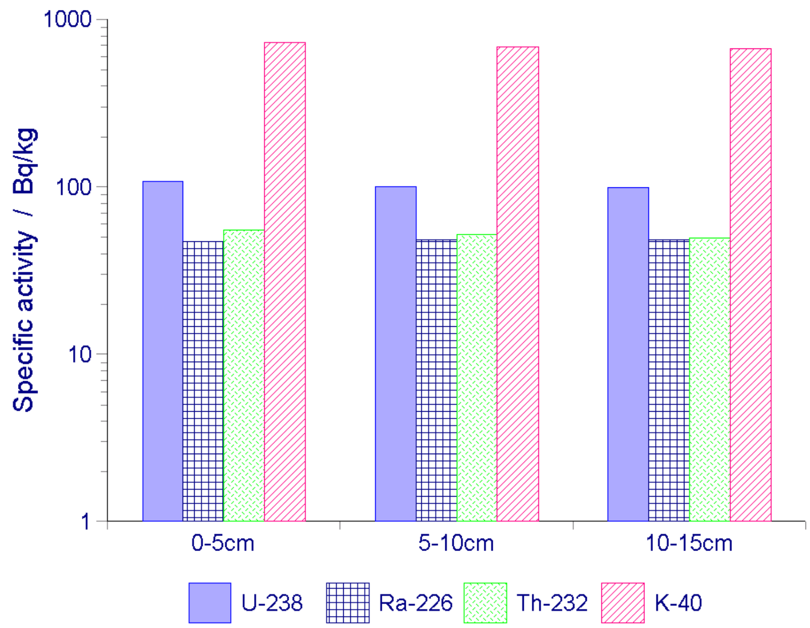

Figure 1. **Mean specific activities in soil close to phosphogypsum disposal pond (Bqkg^{-1})**

The data shows that natural radioactivity in samples of uncultivated soils collected close to the phosphogypsum disposal pond is constant up to the investigated depth.

For the comparison, the phosphogypsum sample collected as a grab sample, and the soil samples taken from uncultivated area on location in vicinity of Zagreb, were analyzed the same way as soil the samples. The results of both measurements are presented at Figures 2 and 3.

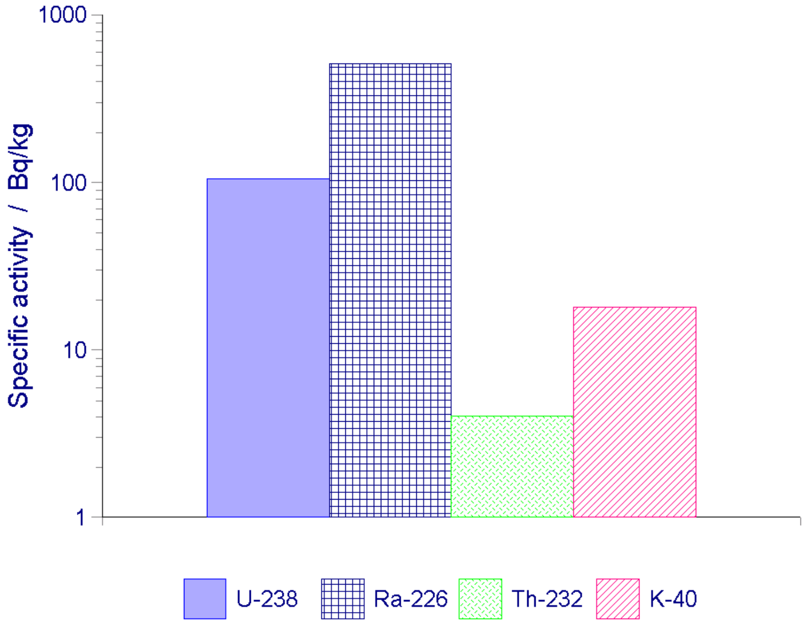

Figure 2. **Specific activities in phosphogypsum (Bqkg^{-1})**

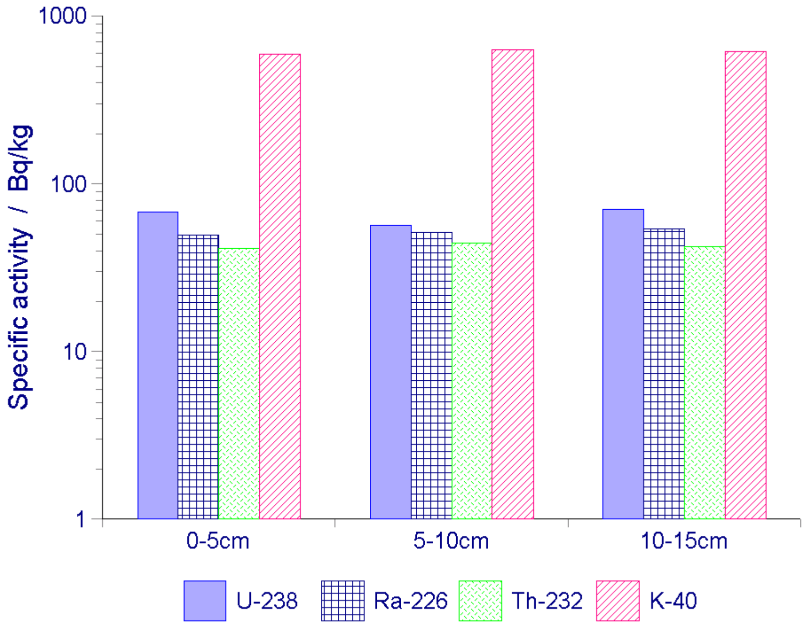

Figure 3. **Specific activities in soil from vicinity of Zagreb (Bqkg^{-1})**

∗ The specific activities of ^{238}U in phosphogypsum are of the same order of magnitude as in uncultivated soils close to the phosphogypsum disposal pond, but lower than in soil from Zagreb vicinity(6).
∗ Specific activities of ^{226}Ra in both soil samples are of the same order of magnitude. In phosphogypsum sample radium activity is about ten times higher than in soils samples. It is well known that, during the technological process radium tends to be concentrated in phosphogypsum. Since the chemical properties of radium are equivalent to those of calcium, practically all radium gets into the phosphogypsum(7).
∗ Due to the technological process, specific activity of ^{40}K is about thirty times lower in phosphogypsum, when compared with activity in soil samples, wherever the soil samples were collected.
∗ The specific activities of ^{232}Th are even ten times higher in soil, than in phosphogypsum sample.

Conclusion

The results of this study show that at the present time there is no increasing of specific activities in soil samples close to the phosphogypsum disposal pond, compared with the soil samples taken from uncultivated area on location in vicinity of Zagreb. This is a proof that there is no evidence for an impact to the environment of the area due to permeability of phosphogypsum disposal pond.

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