NATURAL RADIOACTIVITY IN CHEMICAL FERTILIZERS USED IN ALBANIA INVESTIGATED WITH A FULLY AUTOMATED GAMMA-RAY SPECTROMETER

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ABSTRACT

A fully automated gamma-ray spectrometer composed by two coupled HPGe detectors p-type with 60% relative efficiency was developed for monitoring the environmental radioactivity. Through fully automation of operational processes, up to 24 samples can be measured without any human attendance. The absolute efficiency of the MCA_Rad system is estimated by using two point sources ^{152}Eu and ^{56}Co, and validated at 5% relative uncertainty by measuring certified reference materials. The MCA_Rad system was employed in the measurement of the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th in different types of chemical fertilizers used in Albania. The results show a clear correlation between the content of K_2O measured and that labeled for chemical fertilizers. The presence of phosphorus in the chemical fertilizer is not clearly related to the activity concentration of ^{226}Ra and ^{232}Th. This is mainly due to the different origins of the phosphate ores and/or to the chemical processing of the ore during fertilizers manufacturing. The activity concentrations of ^{226}Ra and ^{232}Th in NPK samples are found to vary from MDA to 253±14 Bq/kg and MDA to 24±4 Bq/kg, respectively. The calculated radium equivalent activity was found to be comparable or higher than the threshold value of 370 Bq/kg varying from 362 Bq/kg to 967 Bq/kg, mainly due to the high concentration of ^{40}K and ^{226}Ra (especially for NPK-3, NPK-8 and NPK-9). Based on these results, no direct estimations on dose rate can be made, but we recommend to monitor the radiation exposure rate of workers in a storage warehouse

KEYWORDS

HPGe gamma-ray spectrometry; Chemical fertilizers; Natural radioactivity

INTRODUCTION

At the beginning of the XIXth century agriculture development in Europe and USA was faced with the problem of soil impoverishment and removal of nutrients due to increased crop production. In 1840, the German chemist Justus von Liebig initiated a revolution in soil science and agriculture. He proved that plants assimilate mineral nutrients from the soil and proposed the use of mineral fertilizers to increase nutrient supply of deficient soils promoting this way a tremendous increase in crop yields never seen before. The science of soil fertility and plant nutrition recognize the dominant importance of macro elements such as nitrogen (N), phosphorus (P) and potassium (K) and many other micronutrients crucially needed to maintain high yields but more importantly to sustain healthy plants. The NPK fertilizers are necessary to remediate depleted soils from the natural nutrients removed through farming and erosion. Phosphate rock is the raw material for the production of phosphate fertilizers due to the relatively high concentration of P_2O_5, at least 20%. These rocks contain together with other elements, also a relatively high concentration of uranium (^{238}U) normally between 370 and 2,470 Bq/kg (**Kratz and Schnug 2006** and references therein) and sometimes even higher than 12,350 Bq/kg, while thorium (^{232}Th) at relatively low concentrations less than 40 Bq/kg (**Menzel 1986**). In phosphate fertilizer industry, phosphate rocks are mainly processed through the so-called "wet-process", which includes chemical treatments, mostly by using sulfuric acid: the products are phosphoric acid (PA) and an insoluble calcium sulfate salt called phosphogypsum (PG), with a ratio PG/PA = 5. The PA and PG are usually separated by filtration and reactor off-gas and vapors: in this process the mixture of phosphoric acid and phosphogypsum constitute the product called normal or single super phosphate (SSP) containing the lowest grade of percentage of phosphorus, less than 20%. The utilization of the phosphoric acid in the "wet-process" is used to produce the triple superphosphate (TSP) and furthermore the combination with ammonia form various ammoniated phosphate fertilizers (e.g. mono-ammonium phosphate MAP and di-ammonium phosphate DAP). During these processes, the decay chains on ^{238}U and ^{232}Th suffer the disequilibrium, where approximately 80-90% of ^{226}Ra is concentrated in PG and 80-85% of ^{238}U and 70% of ^{232}Th is concentrated in PA (**Xhixha et al., 2013**), which ends up in chemical fertilizers. The presence of ^{40}K in NPK fertilizers is mainly due to the K content, which can be estimated knowing its isotopic ratio 0.0117%. On the other hand, the N content in NPK fertilizers generally doesn't contribute in the concentration of radioelements.

High-resolution gamma-ray spectrometry is a suitable technique for environmental radioactivity monitoring, since the decay chains of ^{238}U and ^{232}Th and the isotope of ^{40}K can be investigated simultaneously. However, the environmental radioactivity monitoring may require the measurement of a huge amount of samples. For this purpose we designed and built up a low-background high-resolution gamma-ray spectrometry system (**Xhixha et al., 2013**), which allows an autonomous investigation of the radioactivity content on a large amount of samples, without any human attendance. The absolute efficiency of MCA_Rad system is calibrated for a standard container volume of 180 cm^3 by using two point sources (^{152}Eu and ^{56}Co). We validated the calibration method by measuring certified International Atomic Energy Agency reference materials RGK-1, RGU-2 and RGTh-1 (**IAEA 1987**), containing some thousands of Bq/kg of ^{40}K, ^{238}U and ^{232}Th. The relative discrepancy between central values is found to be less than 5% within the reported uncertainty. The aim of this study was to check the applicability of such instrument in the characterization of natural radioelements in different chemical fertilizers and to draw the first conclusions on their radiological consequences for workers. For this purpose 11 different NPK fertilizers used in agriculture in Albania, are measured using the MCA_Rad system.

MATERIALS AND METHODS

MCA_Rad system: high-resolution gamma-ray spectrometry measurements

The natural radioactivity concentrations in chemical fertilizers were investigated using a fully automated high-resolution gamma-ray spectrometry system, called MCA_Rad system (**Figure 1**). This equipment is composed of two coaxial high-purity germanium (HPGe) p-type detectors with a 60 % relative efficiency, having an energy resolution of 1.9 keV at 1332.5 keV (^{60}Co). The HPGe detectors are accurately shielded with 10cm thick oxygen free copper and 10cm thick lead allowing to reach an environmental background reduction of two orders of magnitude. A severe lowering of manpower cost is obtained by a fully automated system which permits to measure up to 24 samples without any human attendance. Furthermore, a user-friendly software has been developed in order to analyze a high number of spectra, possibly with automatic procedure and customized output. The absolute photopeak efficiency of the MCA_Rad system has been determined by using two low activity standard point sources of ^{152}Eu (6.56 kBq in 1995) and a ^{56}Co home made source. The spectra obtained are corrected (as described in **Xhixha et al., 2013**) for: (1) coincidence summing on each individual detector, produced by the complex decay scheme of the sources, (2) differences between the geometry of the point sources and the sample shape and (3) self-attenuation of gamma-rays within the sample volume. The calibration process was validated by measuring three certified reference materials (95% confidence interval), prepared in a powder matrix (240 mesh) containing 4940±30 Bq/kg of ^{238}U (diluted uranium ore BL5), 3250±90 Bq/kg of ^{232}Th (diluted thorium ore OKA-2) in a secular equilibrium and 14000±400 Bq/kg of ^{40}K (high-purity K_2SO). As a result, this test achieved an overall relative discrepancy of 5 % among central values within the reported uncertainty.

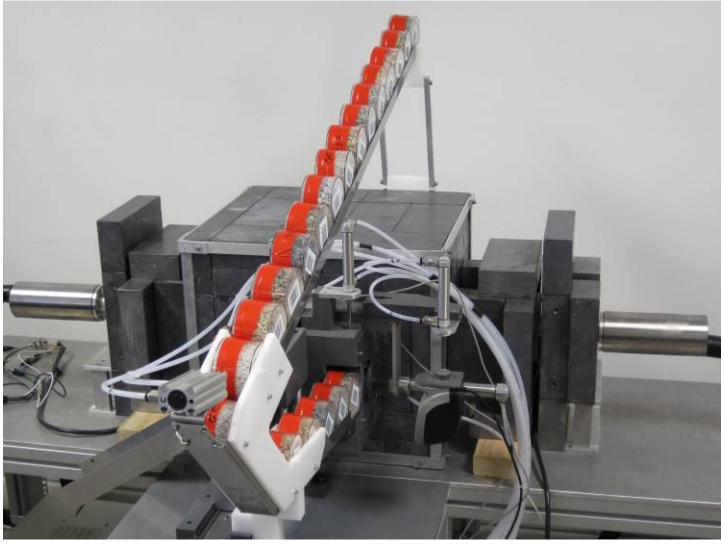

Figure 1. View of the MCA_Rad system.

The natural activity concentration of ^{226}Ra was determined through 351.9 keV (37.1%) of ^{214}Pb and 609.3 keV (46.1%) of ^{214}Bi. The activity of ^{232}Th was estimated as ^{228}Ra by measuring the gamma-ray of 911.1 keV (30.3%) of ^{228}Ac and 583.1 keV (33.2%) of ^{208}Tl. The activity concentration of ^{40}K was determined by measuring the 1460.8 keV gamma-ray. The minimum detectable activity (MDA) concentration was calculated for each energy of interest as described by **Currie (1986)**.

Sampling and sample preparation

Different brands of chemical fertilizers used in Albania are imported from countries worldwide. In this study, are investigated 11 types of chemical fertilizers, which differ from the N, P, K content. Samples, when needed, were crushed and milled into fine powders with the particle size of <2mm. To remove the moisture content, all of the samples were dried in a temperature-controlled furnace at 110°C for at least 24 h (or until constant weight). After cooling in a moisture-free atmosphere, each sample was transferred for measurement to a cylindrical PVC container (with the dimensions of diameter of 7.5 cm x 4.5 cm of height and an effective volume of 180 cm3) and was then weighted. The hermetically sealed containers were stored for at least 4 weeks prior to measurement to allow ^{226}Ra and its short-lived decay products to reach the secular equilibrium.

RESULTS AND DISCUSSION

Activity concentrations

The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in NPK samples were determined by measuring for 1 h using the MCA_Rad system (e.g. **Figure 2**) and the results of the activity concentrations are summarized in **Table 1**.

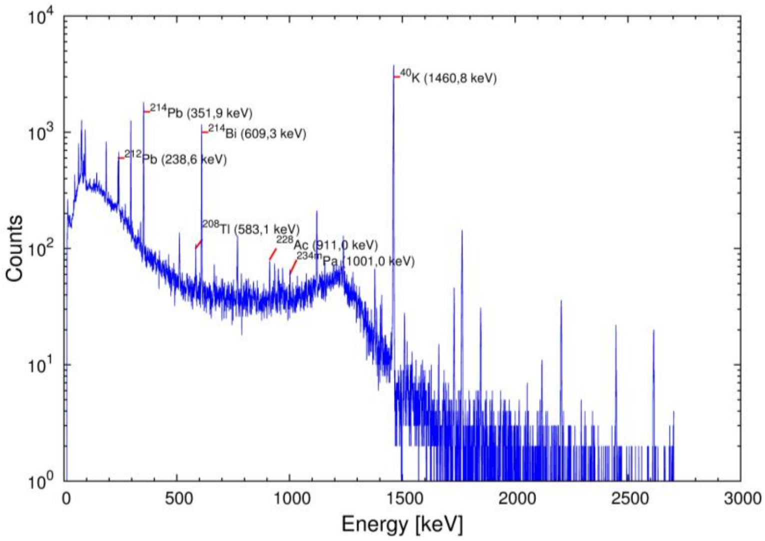

Figure 2. The gamma-ray spectra obtained for NPK-3 sample acquiring for 1h by using MCA_Rad system. The most intense gamma-ray energies for the isotopes investigated are indicated.

The radioisotope of ^{40}K was present in high concentrations in all the NPK varying from 3,927±202 Bq/kg to 12,557±633 Bq/kg. Taking to account that the activity concentrations of 1% K corresponds to 313 Bq/kg, the measured abundances of K are found to be comparable within 1σ with the labeled content of K_2O (calculated as $K_2O = K/0.83$) for each type of fertilizer (**Figure 3**). The activity concentrations of ^{226}Ra and ^{232}Th in NPK samples are found to be very variable from MDA to 253±14 Bq/kg and MDA to 24±4 Bq/kg respectively. Different studies (**Jibiri and Fasae 2012** and references therein) show also high variability in the activity concentrations of ^{226}Ra and ^{232}Th (^{228}Ra) ranging, respectively from MDA to 780 Bq/kg and MDA to 49 Bq/kg. We observe that the concentrations of phosphorus and the radioactivity concentration of ^{226}Ra and ^{232}Th are not correlated. This may be due to the different origins of the phosphate ores and/or on the chemical processing of the ore during fertilizers manufacture. Indeed, the phosphate rocks are found either in sedimentary or igneous deposits where the concentrations of ^{238}U(^{232}Th) vary from 20-11,000 Bq/kg (7-1,100 Bq/kg) to 70-200 Bq/kg (100-400 Bq/kg) respectively (**Falck and Wymer 2006** and references therein).

Table 1. In this table are shown the chemical fertilizers investigated and the respective N, P, K content as labeled (unlike N, the P and K represent the wt. % of respective oxides in the form of P_2O_5 and K_2O therefore for the mass fraction can be calculated by multiplying respectively with 0.436 and 0.83). The activity concentrations ($\pm 1\sigma$) for each chemical fertilizer is determined for ^{40}K, ^{226}Ra and ^{232}Th (in Bq/kg). Values reported as "<" show the minimum detectable activity (MDA).

Sample ID.	N-P-K (wt. %)	Country of origin	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (^{228}Ra) (Bq/kg)	Ra_{eq}
NPK_1	13.5-0-46.2	Israel	12557 ± 633	<3	<4	967
NPK_2	13-0-46	Italy	12458 ± 627	<3	<4	959
NPK-3	5-15-30	Italy	7646 ± 387	253 ± 14	20 ± 5	871
NPK-4	20-20-20	Italy	5471 ± 280	<2	10 ± 4	419
NPK-5	20-20-20	Italy	5851 ± 298	<2	<4	451
NPK-6	20-20-20	Belgium	5443 ± 278	<2	<3	435
NPK-7	18-18-18	Italy	4870 ± 249	<2	<3	375
NPK-8	12-12-17	Belgium	4316 ± 221	137 ± 8	11 ± 4	485
NPK-9	12-12-17	Italy	4051 ± 207	78 ± 5	8 ± 3	402
NPK-10	12-12-17	Italy	3927 ± 202	25 ± 3	24 ± 4	362
NPK-11	14-6-16	Italy	4443 ± 227	26 ± 3	<3	369

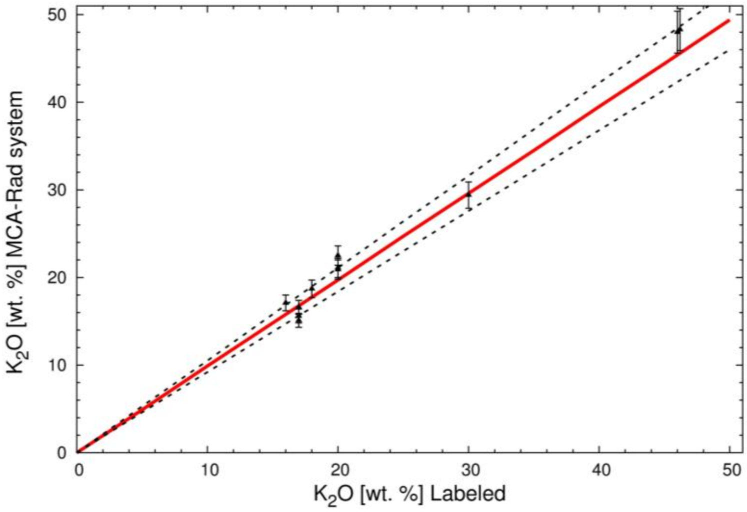

Figure 3. Comparison between labeled and measured K_2O in % wt. The relationship $K_{HPGe} = (0.99 \pm 0.07)\, K_{NPK}$ is obtained by fitting the data with a χ^2 of 1.9. Dashed lines represent ±1σ uncertainty interval.

Radiological characterization

From the radiation point of view, the storage of large quantities of chemical fertilizers in the warehouse may influence significantly the indoor radon concentration other than external gamma-ray exposure. The widely used radiation hazard index Ra_{eq} (radium equivalent activity) can be used to estimate the external gamma-ray exposure. The radiation equivalent activity is a weighted sum of activities of the three natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K based on the estimation that 370 Bq/kg of ^{226}Ra, 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma ray dose rate (**Beretka and Matthew 1985**). The radium equivalent activity was calculated by using the following relation.

$$Ra_{eq} = C_{Ra} + 1.43 C_{Th} + 0.077 C_K \qquad \text{(Eq. 1)}$$

where C_{Ra}, C_{Th} and C_K are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K in (Bq/kg) respectively.

In **Table 1** is shown that the radium equivalent activity calculated for NPK samples is comparable or higher than the reference value of 370 Bq/kg reaching the maximum value of 967 Bq/kg for NPK-1 sample. This indicates that the management of large quantities of stored chemical fertilizers can lead to an excess of the effective annual dose rate. However, we emphasize that this is mainly due to high concentrations of ^{40}K, with exception to NPK-3, NPK-8 and NPK-9, where the activity concentrations of ^{226}Ra are high and contribute to approximately 30%. This least may contribute to a radiological potential risk for workers due to indoor radon gas concentration. Based on these results, no direct estimations on dose rate can be made, but we recommend that controls should be made in order to monitor the radiation exposure rate of workers in a storage warehouse.

CONCLUSIONS

The MCA_Rad system was found to be a suitable technique used to characterize the natural radioactivity concentration in NPK fertilizers. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th were measured in different types of NPK fertilizers used in agriculture in Albania. All measured NKP fertilizers showed high activity concentration of ^{40}K varying from 3,927±202 Bq/kg to 12,557±633 Bq/kg. The results obtained by MCA_Rad system were found to be in excellent agreement with those labeled for chemical fertilizers under investigation. The presence of phosphorus in the chemical fertilizer is not clearly related to the activity concentration of ^{226}Ra and ^{232}Th in the chemical fertilizers mainly due to the different origins of the phosphate ores and/or on the chemical processing of the ore during fertilizers manufacture. The activity concentrations of ^{226}Ra and ^{232}Th vary between MDA to 253±14 Bq/kg and MDA to 24±4 Bq/kg respectively. Future studies are needed in order to investigate the transfer of radioelements from phosphate rocks to chemical fertilizers. The radium equivalent concentration was calculated in order to estimate the radiological implications of the storage and the management of NPK fertilizers. The calculated radium equivalent activity for all NPK fertilizers was found to be comparable or higher than the reference value of 370 Bq/kg varying from 362 Bq/kg to 967 Bq/kg. These high values are mainly due to high concentration of ^{40}K in all samples (65-100% of Ra_{eq}), while for NPK-3, NPK-8 and NPK-9 the contribution of ^{226}Ra accounts for 20-30% of Ra_{eq} concentration. Based on these results, the management of large quantities of stored chemical fertilizers can lead to an excess of the effective annual dose rate for workers and therefore we recommend that controls should be made in order to monitor the radiation exposure rate in storage warehouses. In this context the MCA_Rad system was shown to be an excellent tool for measuring the radioactivity in chemical fertilizers and to monitor huge amounts of samples.

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