DETERMINATION OF ^{210}Po IN FERTILIZERS BY ELECTROCHEMICAL DEPOSITION METHOD

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ABSTRACT

In this study, activities of radioactive polonium and natural radionuclide concentrations in fertilizer most consumed in agricultural lands in Turkey were measured.

Fertilizers containing phosphorus and potassium increase yield and quality. But, they contain some radionuclides. These radionuclides dissolve in water and first transport into plants and then transport from plants to humans. In the latest years, artificial fertilizing has replaced natural fertilizing in agriculture. Therefore, fruits and vegetables contain radionuclides those are found in artificial fertilizers. In this study, electrochemical deposition technique with alpha counting method was used for determining the radioactivity level of polonium in fertilizers. Radium, potassium and thorium concentrations were measured by gamma spectrometry. TSP, MAP, DSP,MKP, (15-15-15), (18-18-18), (20-20-20) compost fertilizers consumed at most has been analyzed and the results were evaluated with respect to human health.

INTRODUCTION

Nowadays nourishment problem is rising together with increasing population. The efforts for solving of problems that present agriculture and feed conditions are obtained high and quality yield occurs basic to solve these problems. The share of fertilizer for increasing yield and quality is 58 % and the share of other precautions is 42 %. In our country total fertilizer consumption was 2207000 ton according to data in 1993. The potassium and phosphate fertilizers constitute about 40 % of it (Özalp,1998).

Phosphate rock is the starting material for the production of all phosphate products and is the main source of phosphorus for fertilizers. The radioactivity in phosphate rocks is mainly caused by disintegration of radionuclides in ^{238}U series. Natural uranium can substitute for calcium in the phosphate rock structure and over a period of time , accumulate in the phosphate reserves. Thus, uranium present in fertilizers is manufactured from phosphate rocks (Bouwer et al. 1978).

Phosphate fertilizers are one of the end products from the phosphate industry. Phosphate and potassium are also found in multiple-nutrient fertilizers, which are available in different blends of nitrogen (N), phosphorus (P), and potassium (K).

Potash is another material used as a fertilizer that contains natural radioactivity, primarily ^{40}K. Potash is composed principally of the salts of potassium, of which potassium chloride and potassium sulfate are the major components.

Phosphate fertilizers are produced by mixing phosphoric acid directly with phosphate rocks. Ammonia and potassium salts are also added to produce a variety of fertilizers. Mined from sylvinite ore or produced by solar evaporation, potash can be used directly as a fertilizer without extensive chemical conversion. The continued widespread use of phosphate fertilizers may eventually result in a measurable increase in background radiation levels.

Radionuclide concentrations vary with the type of fertilizer and production process, with average concentrations ranging from 0.18 to 0.74 Bq/g (5 to 20 pCi/g) for ^{226}Ra, 0.74 to 2.22 Bq/g (20 to 60 pCi/g) for uranium, and 0.037 to 0.18 Bq/g (1 to 5 pCi/g) for thorium(Table 1). The activity of ^{40}K in potash depends of the quantity of potassium present, which is normally expressed as equivalent mass of K_2O. The equivalent concentration of ^{40}K in potash is about 25.75 Bq/g (696 pCi/g) K_2O. Since marketable potash contains about 60% K_2O, the concentration of ^{40}K in the final product calculates to approximately 15.5 Bq/g (420 pCi/g).

Radon fluxes for phosphate fertilizers in soil are expected to be similar to those for unfertilized soils. A typical flux for a fertilized soil is approximately 0.037 Bq/m^2 (1.0 pCi/m^2) per pCi/g of ^{226}Ra. The external gamma radiation attributable to fertilizer materials is only about 0.25% of that from unfertilized soil (EPA, 1993).

Table 1. Radionuclide Concentrations in the Average Fertilizer(EPA,1993)

	Phosphate Fertilizer Bq/g (pCi/g)
K-40	-
U-238	2.04 (55)
U-234	2.07 (56)
Th-230	1.96 (53)
Ra-226	0.31 (8.3)
Pb-210	0.22 (5.8)
Po-210	0.22 (5.8)
U-235	0.096 (2.6)
Pa-231	0.096 (2.6)
Ac-227	0.096 (2.6)
Th-232	0.037 (1.0)
Ra-228	0.037 (1.0)
Th-228	0.037 (1.0)

The concentrations of natural radionuclides in phosphate fertilizers were reviewed in the UNSCEAR 1977 and 1982 Reports. For a given radionuclide and type of fertilizer, the concentrations vary markedly from one country to another, depending on the origin of the components (UNSCEAR 1993). The radioactivity present in phosphate rocks can enter the environment and possibly pose radiation exposure concerns through several pathways. First, phosphatic fertilizers can enter agricultural lands during cultivation. Second, phosphogypsum may be used as agricultural gypsum (to deal with salinity). Third, phosphogypsum may be used as a building material (Hussein, 1994). The radioactivity in fertilizers may cause radiological hazards to human health by phosphatic fertilizer's entering to agricultural lands.

^{210}Po is a radioactive decay product of ^{226}Ra which is a long-lived member of ^{238}U chain. It radiates high energy alpha particles which are very dangerous especially by internal radiation. Because of polonium's being disintegration product of the ^{238}U series, it can enter the body with uranium and contained materials. A number of methods for determination of radioactivity content of fertilizers have been used but in few of them the radioactivity level of polonium were determined. Electrodeposition and electroplating techniques are widely used for the determination of α-emitting nuclides (Kathren, 1986). Santos et al.(1995) determined the ^{210}Po and ^{210}Pb concentrations in urine, hair and skin smear samples from individuals using phosphated fertilizers and compared with a control group of occupationally unexposed individuals. Urine and hair samples of the test group showed slightly higher concentrations of ^{210}Po and ^{210}Pb than those observed for the control group. These concentrations remained, however, lower than those for uranium mine workers. Skin smear values indicated contamination by direct contact with dust from fertilizers and this may contribute to skin cancer (Santos et al, 1995). In the Netherlands, all phosphogypsum produced by fertilizer plants is discharged into the Rhine; these annual discharges, which contain about 0.4 TBq of ^{238}U, 2TBq of ^{226}Ra, 0.7 TBq of ^{210}Pb and 2 TBq of ^{210}Po, were estimated to result in maximum annual individual effective doses of 150μSv and collective effective dose of 170 man Sv per year to the Dutch population via the ingestion of sea food, ^{210}Po being the main contributer to the dose (Köster et al. 1985).

The gamma decay of uranium atoms from fertilizers is investigated by gamma spectrometry. Gamma spectroscopy is used for determining the radionuclides whic radiate gamma rays from the environmental samples. In this method samples were prepared without applying chemical process. Radioactive elements were separeted and measured according to the energy of their gamma rays.

In this work, we have measured the polonium activity levels and radium and potassium concentrations in most consumed fertilizers in Turkey.

EXPERIMENTAL

Seven fertilizer samples containing phosphate and most consumed in Turkey were obtained from Toros Fertilizers Company. According to their main contents the samples separeted into two groups; phosphorus contained (TSP, MAP, DAP) and compost fertilizers (15-15-15, 18-18-18, 20-20-20, MKP).

For determining the radioactivity level of polonium, chemical deposition technique together alpha counting method was used. Radium, thorium and potassium concentrations were measured by gamma spectrometry.

To investigate chemical deposition of ^{210}Po on copper discs, ^{210}Pb standard solution which is in secular equilibrium with ^{210}Po and 2.1 cm diameter of copper discs have been used. Chemical deposition efficiency for different metal discs had been investigated by Karali et al. (1996). In this study copper was used for its being available and low cost.

Before chemical deposition, copper discs were cleaned by deionized water and pure acetone. Cleaned copper discs were put into 1M HNO_3 solution for a few minutes and were cleaned with deionized water and pure acetone again. A 3.0 g of fertilizer sample was dissolved in 150 ml 0.5 M HCl solution in beaker. This solution was waited overnight and then solution filtered through a filter paper. Freshly prepared 0.6 gr ascorbic acid solution was added. Copper discs were placed at the buttom of polyethylene deposition cell. The polyethlyene deposition cell was put into the beaker. The deposition was carried out for 5 hours at 65-70 °C. After the deposition, copper discs were taken carefully and let to dry at room temperature. Dry copper discs were counted for their α-activity with a ZnS(Ag) scintillation detector. Counting efficiency of the system was determined as 39.44%. The ^{210}Po activities of each sample are shown in Table 2.

The measurement of radium, potassium and thorium concentrations was carried out using gamma spectrometry. The gamma activities of the samples were calculated from the total counts under selected photopeaks. The samples were dried and transferred into per polyethylene cylinder boxes (2.5cmx6cm) as 100 grams. The containers were sealed and stored for 40 days to allow for % 99.9 secular equilibrium between ^{226}Ra and its decay products. Gamma spectroscopy measurements were carried out with a Tennelec “3x3” NaI(Tl) scintillation detector connected to a Tennelec PCA II 8192 multichannel analyzer.

The results are shown in Table 2.

RESULTS AND DISCUSSION

The polonium activity levels and equivalent radium, potassium and thorium concentrations of fertilizers studied have shown great differences.

The ^{210}Po activity in the fertilizers was observed to range from 1.76 to 120.75 Bq.kg^{-1} . The highest value was measured in DAP sample as 120.75 Bq.kg^{-1}.

Table 2. ^{210}Po activities of most consumed fertilizers in Turkey.

Samples	Chemical yield (%)	Count yield (%)	Total yield (%)	^{210}Po (Bq/kg)	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)
TSP	87.66	39.44	34.58	72.46	2889.11	15.32	1.076
DAP	69.29	39.44	27.33	120.75	LA	87.55	3.59
MAP	42.25	39.44	16.66	5.32	66.45	3.29	4.14
MKP	37.22	39.44	14.68	1.76	8834.42	1.72	LA
15-15-15	36.40	39.44	14.36	57.19	2479.66	LA	LA
18-18-18	45.57	39.44	17.97	8.65	7071.00	LA	LA
20-20-20	46.62	39.44	18.39	24.77	LA	17.66	1.97

LA:Low Activity

Radium was observed in TSP, DAP, MAP, MKP and 20-20-20; the potassium was observed in TSP, 15-15-15,18-18-18 and MKP.

Radium activities in fertilizers found to range from LA to 87.55 Bq.kg^{-1}. The highest value was measured in DAP sample as 87.55 Bq.kg^{-1}. Potassium activity in the fertilizers was found to range from LA to 8834.42 Bq.kg^{-1}. The highest value was measured in MKP sample as 8834.42 Bq.kg^{-1}.

Radium was not observed in 15-15-15 and 18-18-18 samples. In the production of phosphate-containing fertilizers, the phosphate rock is usually first converted to phosphoric acid to obtain readily soluble fertilizers. In the conversion of phosphate rock to phosphoric acid by reaction with sulfuric acid, phosphogypsum is formed as a waste product. To prevent enviromental concern alternative processes have been developed for attacting phosphate ores. These processes employ reagents other than sulfuric acid so that ^{226}Ra is dissolved along with ^{238}U, and solid wastes obtained thereafter contain very little ^{226}Ra and do not cause enviromental concerns(Nirdosh, 1987).

Chemical components of DAP and MAP samples do not include ^{40}K. That may be the reason for not observing potassium in gamma spectrometry.

In literature, there is hardly a few studies on ^{210}Po and ^{226}Ra contents of fertilizers. So the results of this study is compared with results given by EPA. From the Tables 1 and 2 it can be seen that ^{210}Po and ^{226}Ra contents of fertilizers investigated are lower than average values given by EPA.

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For a given radionuclide and type of fertilizer, the concentrations vary markedly from one country to another, depending on the origin of the components (UNSCEAR 1993). Niedergesaess et al. (1993) have reported uranium concentrations of phosphate fertilizers from different origins as follows; 400 Bq.kg^{-1} in Kola(USSR), 17060 Bq.kg^{-1} in USA, 4900 Bq.kg^{-1}in North Africa, 15510 Bq.kg^{-1} in Marocco (Hussein,1994) has reported ^{238}U concentrations of phosphate ore and superphosphate fertilizer as 523 and 473 Bq.kg^{-1}, respectively. Hussein (1994) has also reported ^{40}K concentrations of phosphate ore and superphosphate fertilizer as 19.3 and 16 Bq.kg^{-1}, respectively.

K_2SO_4	48.70	39.44	19.21	13.59	13147.59	LA	LA
KNO_3	58.42	39.44	23.04	10.61	11585.88	LA	LA