PHYSICAL DEVICES FOR ECOLOGY, MEDICINE, BIOLOGY

Investigation of Some Properties of Chemical Fertilizers Using Gamma-ray Spectrometry and Energy Dispersive X-ray Fluorescence Spectrometry

Canel Eke*

Department of Mathematics and Science Education, Faculty of Education, Akdeniz University, Antalya, 07058 Turkey *e-mail: caneleke@hotmail.com, ceke@akdeniz.edu.tr

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Abstract—The purpose of this study is to investigate chemical fertilizers using gamma-ray spectrometry and energy dispersive X-ray fluorescence spectrometry (EDXRF). Eight different types of chemical fertilizers were examined. Samples were counted using high purity germanium (HPGe) spectrometry for counting periods of one day. Spectra were analysed using computer software. After this process, radioactivity concentration of radionuclides, radium equivalent activity, internal hazard index, external hazard index and activity concentration index were calculated and compared with reported values in the scientific literature. Macro, minor and micronutrients were investigated using EDXRF. Size and shape of the chemical fertilizers were studied by scanning electron microscope (SEM) micrographs. ²²⁶Ra was detected only in sample 1 whilst ⁴⁰K was detected in all chemical fertilizers. ²³²Th and ¹³⁷Cs were not detected in any fertilizer. Except for sample 2 and sample 3, the radioactivity concentration of ⁴⁰K and dose values are higher than the world average and limit values reported in the respective literature.

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1. INTRODUCTION

Chemical fertilizers are used predominantly in agriculture area to enhance the efficient growth of the nutrients [1]. The fertilizers usually contain three fundamental and many minor essential chemical components. The fundamental components are nitrogen (N), phosphorus pentoxide (P_2O_5) and potassium oxide (K_2O), minor components are sodium (Na), calcium (Ca), sulfur (S), magnesium (Mg) and trace components, e.g., iron (Fe), sulfur (S), manganese (Mn), zinc (Zn), molybdenum (Mo), and copper (Cu) [2–4].

Nitrogen has been utilized in the form of ammonium salts, nitrates, and organic nitrogenous materials. These components alert the vegetative growth in plant, through nitrogen-containing proteins and chlorophyll. Upon lack of nitrogen the color of plant leaves turns yellow, if nitrogen exceedes it gives rise to grade growth and impeding ripeness [4, 5].

The ground material of phosphorus fertililizers is phosphate rock (Fluoroapatite). The chemical formula is $3Ca_3(PO_4)_2 \cdot CaF_2$ (calcium fluorophosphate). If the phosphate rock is separated by using sulphuric acid, superphospate which contains 18-20%phosphorus pentoxide (P₂O₅) is obtained. If phosphate rock is dissociated by phosphoric acid, triple superphosphate which incorporates 48% phosphorus pentoxide (P_2O_5) is acquired. The phosphates stimulate plant growth, provide resistance to disease, generate stronger seedlings and accelerate crop ripeness [4, 5]. However, phosphate fertilizers are considerable sources of radon gas which is a decay product of ²³⁸U [6].

Potassium is widely incorporated in blended fertilizers. It is involved in the entire metabolic processes, thus is a significant element for all growing plants. If some crops contain undesirably high chloride concentrations, potassium sulphate or potassium nitrate are efficacious remedies. When agriculture areas lie fallow, potassium minerals slowly dissociate and release significant amounts of potash to the plants from year to year. Some of the potash which is abosorbed by the plants stays in the vegetal areas [4, 5].

The acvitivity concentration of the natural radionuclides in the soil changes from one area to another, because of the largescale use of chemical fertilizer which is the dominant source of radioactivity on soil rather than its natural origin [7, 8]. Due to the significantly higher radioactivity concentration level in soils and can rise the amount of ingestion by human population owing to exposure ways such as underground water, drinking water and the food chain [9, 10]. If the radioactivity released from chemical fertilizers (plus the ambient natural one) exceed the allowed humans' exposure level, this might give rise to cancers and other health problems. Therefore, tracing the radioactivity concentration of natural radionuclides is relevant in terms of radiation protection [11].

Many researchers have investigated natural radionuclides (first and foremost ⁴⁰K and the decay chains of ²³⁸U, ²³²Th, respectively) in chemical fertilizers using gamma-ray spectrometry [6, 7, 11-15], and also using atomic and nuclear techniques to determine major, minor, trace and toxic elements. As examples: contents of 35 elements in six different imported nitrogen/phosphorus/potassium (NPK), nitrogen/phosphorus (NP) and potassium (K) fertilizers were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in two different laboratories. Furthermore, by instrumental neutron activation analysis (INAA) [1]. Fertilizer phosphates of natural and industrial origin including three standard reference materials (NBS-SRM 120b, BCR-SRM nos. 32 and 33) were studied using INAA [3]. The concentration of major components (Al₂O₃, SiO₂, P₂O₅, SO₃, Cl, K_2O_1 , Fe_2O_3) of fertilizers were determined by X-ray fluorescence (XRF) also X-ray diffraction (XRD) was applied to examine the compound of fertilizers [14, 161. Potassium silicate fertilizers were studied using X-ray powder diffraction and energy dispersive X-ray flourescence (EDXRF) spectroscopy [17]. Chemical characterization of a diammonium phosphate (DAP) fertilizer was carried out using laser induced breakdown spectroscopy (LIBS), and Mg, Al, P, Ti, Cr, Mn, Fe, Co, Ni, Mo, Pb and traces of U were detected [18]. Multi-element analyses of fertilizer samples were applied using a combination of LIBS and partial least squares (PLS) [19]. Potassium fertilizers were studied using LIBS [20], phosphorus in commercial fertilizers were determined by atomic absorption spectroscopy (AAS) [21]. Last but not least, concentration of K, Na, and Zn as major elements, Ni and Co as minor elements, and Pb, Cd, Cr, and Cu as environmental pollutants or toxic elements were investigated in 14 commercial phosphate fertilizers from Iraqi market by AAS [22].

The aim of this study is to: 1) obtain the activity concentrations of natural radionuclides 2) give an information of the radiation hazard values, 3) carry out elemental analysis of chemical fertilizers using energy dispersive X-ray fluorescence (EDXRF) spectrometry. For this purpose, the natural radioactivity concentration of ²³⁸U, ²³²Th, and ⁴⁰K, in extensively used chemical fertilizers in Antalya, also radium equivalent activity (Ra_{eq}), internal and external hazard index (H_{in} , H_{ex} , respectively) hazard indexes were calculated and compared with literature-reported values. In the following, materials and methodology will be described, and the results will be presented of this study.

2. MATERIALS AND METHODS

Eight different types of chemical fertilizers which were collected from a fertilizer market in Antalva. Turkey, were studied using gamma-ray spectroscopy and EDXRF spectroscopy. To measure the radioactivity concentration of natural radionuclides, samples were transferred into 100 mL plastic cups, labeled, and sealed. The masses of the samples were weighed. The diameter and height of cups are 61 and 53 mm, respectively. The sample masses varied between 104 to 148 g. The samples were stored 5 weeks to achieve the equilibrium of radium and radon (²³⁸U and its daughter nuclei) to calculate radioactivity concentration of the natural radionuclides (²³⁸U and ²³²Th) [13, 14]. The activity concentration of ⁴⁰K can be calculated directly without waiting because this nuclide does not produce a decay chain like ²³⁸U and ²³²Th.

To calculate the radioactivity concentration of the natural radionuclides each sample was counted for 86400 s (1 day) using a high purity germanium detector (HPGe, 40% relavite efficiency, *p* type, electrically cooled; resolution: 1.85 keV at 1332 keV, 768 eV at 122 keV). The HPGe dedector is located in Department of Physics in Akdeniz University. The energy calibration was checked using point γ -sources.

Before counting the samples, the background radiation was counted for 86400 s to substract the background from the fertilizer spectra. Each samples were counted 86400 s, and the spectra were collected using the Maestro-32 [23] computer software. The collected fertilizer spectra and the background spectrum were analyzed automatically by the Gamma-W [24] computer software.

The minimum detectable activity (MDA) was calculated according to Currie [25, 26] as shown in equation (1):

$$MDA = \frac{2.71 + 4.65\sigma}{t\varepsilon I_{\gamma}m},\tag{1}$$

where σ , *t*, ϵ , I_{γ} , and *m* are standard deviation of counts of background spectrum, counting time, efficiency, probability of gamma-ray emission, and mass of sample, respectively. The MDAs of [²¹⁴Pb (351.93 keV), ²¹⁴Bi (609.32 keV), ²²⁸Ac (911.20 keV), ⁴⁰K (1460.82 keV), and ¹³⁷Cs (661.66 keV)] for 1-kg sample size and 50398 s live counting time were calculated using the background spectrum. MDA of ²²⁶Ra was determined using mean value of ²¹⁴Pb and ²¹⁴Bi.

The radioactivity concentration of the natural radionuclides A (Bq/kg) in the chemical fertilizers were calculated by the well-known following equation [27]:

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$$A = \frac{N}{mt\varepsilon I_{\gamma}},\tag{2}$$

where N is the net peak counts after substracted bacground, m (kg) is the mass of the sample, t(s) is the counting time of the sample, ε is the efficiency of the dedector, I_{γ} is the gamma-ray emission probability taken from literature sources. The dead time of our experimental setup was neglected because it is lower than 5% [27]. Also, to calculate the activity concentration of the radionuclides, the self attenuation effect correction factors of the samples were considered. The self attenuation correction factor (SACF) of the chemical fertilizers were calculated using the Cutshall transmission method [28]. Details can be found in [29].

The uncertainty of the natural radionuclides' radioactivity concentration was calculated using the following equation [30]:

$$\Delta A = A \sqrt{\left(\frac{\Delta N}{N}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta \varepsilon}{\varepsilon}\right)^2 + \left(\frac{\Delta I_{\gamma}}{I_{\gamma}}\right)^2 + \left(\frac{\Delta m}{m}\right)^2 + \left(\frac{\Delta f}{f}\right)^2},\tag{3}$$

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where ΔN , Δt , $\Delta \varepsilon$, ΔI_{γ} , Δm , and Δf represent the uncertainties of count, counting time, detector efficiency at the gamma-ray energy, emission probability of the gamma radiation, mass of the sample and the selfattenuation correction factor.

The activity concentrations of the natural radionuclides were used to also estimate radiological hazard indices as radium equivalent activity, internal hazard index and external hazard index of the chemical fertilizers.

The radium equivalent activity $(Ra_{eq})(Bq kg^{-1})$ is a term to estimate the external exposure due to the presence of gamma-rays from ²²⁶Ra, ²³²Th and ⁴⁰K. The equivalent is calculated using following equation [31]:

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_{K},$$
(4)

where A_{Ra} , A_{Th} , and A_{K} are the radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K, respectively.

The external hazard index (H_{ex}) and the internal hazard index (H_{in}) are calculated using following equations [31, 32] to estimate the hazard index of the natural gamma radiation emitted by ²²⁶Ra, ²³²Th, and ⁴⁰K:

$$H_{\rm ex} = \frac{A_{\rm Ra}}{370} + \frac{A_{\rm Th}}{259} + \frac{A_{\rm K}}{4810},\tag{5}$$

$$H_{\rm in} = \frac{A_{\rm Ra}}{185} + \frac{A_{\rm Th}}{259} + \frac{A_{\rm K}}{4810}.$$
 (6)

The activity concentration index (I) which is one of the hazard indices, is calculated using the following equation [33]:

$$I = \frac{A_{\rm Ra}}{300} + \frac{A_{\rm Th}}{200} + \frac{A_{\rm K}}{3000},\tag{7}$$

where A_{Ra} , A_{Th} , and A_{K} are the radioactivity concentrations of ²²⁶Ra, ²³²Th, and ⁴⁰K, respectively.

The contents of components were defined using EDXRF spectrometry at Basic Sciences Application and Research Center in Erzincan Binali Yildirim University.

3. RESULTS AND DISCUSSION

The MDA is 1.10 Bq kg⁻¹ for 226 Ra, 1.23 Bq kg⁻¹ for 214 Pb, 0.97 Bq kg $^{-1}$ for 214 Bi, 3.12 Bq kg $^{-1}$ for 228 Ac (^{232}Th) , 0.94 Bq kg⁻¹ for ^{137}Cs , and 8.91 Bq kg⁻¹ for ⁴⁰K. As shown in Table 1, the activity concentrations of ²²⁶Ra and ⁴⁰K are higher than indicated by the MDA of the radionuclides. ²²⁶Ra (except for sample 1) was not detected in the chemical fertilizers. ¹³⁷Cs which is an artificial radionuclide, and ²³²Th were not detected in the chemical fertilizers. ⁴⁰K was detected in all chemical fertilizers. The radium activity concentration $(180 \pm 19 \text{ Bq kg}^{-1})$ is higher than the reported world average value (33 Bq kg⁻¹) according to UNSCEAR [34]. The activity concentration of 40 K varies from 34 \pm 8 Bq to 28065 \pm 2705 Bq kg⁻¹. The samples 2 and 3 except, the mean value of the ⁴⁰K radioactivity concentration is 17294 Bq kg⁻¹ which is significantly higher than the world average value reported by UNSCEAR [34] (420 Bq kg⁻¹). In contrast, the average specific 40 K activity of samples 2 and 3 (35 Bg kg⁻¹) is lower than the UNSCEAR [34] limit value by about one order of magnitude, thus negligible (see Table 1).

Table 1. Radioactivity concentration of chemical fertilizers 226 Ra and 40 K (232 Th and 137 Cs were not detected)

		,
Sample No	226 Ra, Bq kg $^{-1}$	40 K, Bq kg ⁻¹
Sample 1	180 ± 19	9028 ± 897
Sample 4	N.d	18595 ± 1791
Sample 5	N.d	28065 ± 2705
Sample 6	N.d	25350 ± 2459
Sample 7	N.d	13010 ± 1296
Sample 8	N.d	9713 ± 970
Mean1	—	17294 ± 1686
Sample 2	N.d	36 ± 5
Sample 3	N.d	34 ± 8
Mean2	—	35 ± 7

N.d. not detected.

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Sample No	Ra _{eq} , Bq kg ⁻¹	$H_{\rm in}$	H _{ex}	Ι
Sample 1	874.94	2.85	2.36	3.61
Sample 4	1431.82	3.87	3.87	6.20
Sample 5	2160.97	5.83	5.83	9.35
Sample 6	1951.97	5.27	5.27	8.45
Sample 7	1001.76	2.70	2.70	4.34
Sample 8	747.94	2.02	2.02	3.24
Mean1	1361.57	3.76	3.68	5.88
Sample 2	2.73	0.01	0.01	0.01
Sample 3	2.62	0.01	0.01	0.01
Mean2	2.68	0.01	0.01	0.01

Table 2. Dose assessment of chemical fertilizers

The results of radium equivalent activity (Ra_{eq}) , internal hazard index (H_{in}) , external hazard index (H_{ex}) and activity concentration index (*I*) for chemical fertilizers are presented in Table 2.

As shown in Table 2,

- The Ra_{eq} values of the samples 1, 4, 5, 6, 7, 8 are greater than 370 Bq kg⁻¹ which is the permissible limit value [31].

- The H_{in} and H_{ex} values, respectively, of the samples 1, 4, 5, 6, 7, 8 are greater than 1, but should be beneath unity [31].

- The *I* values of samples 1, 2, 3, 7, and 8 are lower than 6 (which is permissible limit value [33]). but the values of samples 4, 5, and 6 are higher than 6.

Analytical results of the chemical fertilizers using EDXRF are given Table 3 and EDXRF spectra and scanning electron microscope (SEM) micrographs of chemical fertilizers are shown in Fig. 1. *N*, *P*, and *K* are major nutrients, Ca, Mg, and S are minor nutrients,

Fe, Mn, Cu, Zn, B, and Mo are micro nutrients for plants in the soil besides their function as nutrients. Ca and Mg are significant in setting the pH of the soil [1].

Chemical fertilizers are classified in three categories, namely: single nutrient fertilizers (N, P, or K), binary nutrients fertilizers (NP, NK, or PK) and multi-nutrient fertilizers (NPK or NPK + S) according to their components [35]. Sample 2 is an N fertilizer, sample 3 is an NP fertilizer, sample 4 and sample 6 are PK fertilizers, sample 5 is a K fertilizer, sample 7 is an NK fertilizer, sample 8 is an NPK fertilizer. Sample 1 and sample 5 are single nutrient fertilizers, sample 3, sample 4, sample 6, and sample 7 are binary nutrient fertilizers, only sample 8 is a multinutrient fertilizer.

There are 16 elements stimulating growth and survival of plants. These are categorized as mineral and non-mineral nutrients. Thirteen mineral nutrients are found in soil, but non-mineral nutrients are H and C which are found in air and/or water, whilst O is ubiquitous. Moreover, mineral nutrients are separated additionally into two categories as macronutrients and micronutrients, according to their intake by plant, mandatory for its growth. Potassium and calcium are macronutrients required for growth and ameliorating of plants.

Sample 1 and sample 8 contain aluminum and iron which act as minor and trace components. The oxides of these elements play a significant role in soil aggregates [36] since they have a positive impact upon the physical features of the soil, boosting the aggregate uniformity, permeability, fragility, porosity and hydraulic conductance and decreasing puffing, clay disintegration, bulk density and modules of fracture [37].

Silicon (Si) was detected only in sample-1 as a micro nutrient. Silicon is present in form of silicon dioxide in the earth crust as a second most abundant element after oxygen. Silicon is considered one of the

Table 3. Analytical results of chemical fertilizers using EDXRF

Ele-	Concentrations, wt% (relative uncertainty, %)							
ment	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6	sample 7	sample 8
0	57.61 (10.10)	49.36 (10.26)	54.69 (9.53)	49.64 (8.67)	40.28 (10.93)	55.50 (10.24)	47.99 (10.19)	56.11 (9.67)
Al	2.57 (8.74)	N.d	N.d	N.d	N.d	N.d	N.d	0.74 (8.91)
Si	2.68 (7.12)	N.d	N.d	N.d	N.d	N.d	N.d	N.d
Ca	35.27 (1.10)	N.d	N.d	N.d	N.d	N.d	7.30 (3.25)	N.d
Fe	1.86 (6.35)	N.d	N.d	N.d	N.d	N.d	N.d	N.d
S	N.d	27.15 (2.12)	N.d	N.d	20.33 (2.56)	N.d	14.17 (2.57)	0.87 (3.65)
Na	N.d	N.d	N.d	22.95 (8.69)	N.d	N.d	1.15 (13.12)	1.85 (11.02)
Ν	N.d	23.49 (10.74)	16.40 (11.16)	N.d	N.d	N.d	14.96 (11.79)	34.57 (7.73)
Р	N.d	N.d	28.90 (3.09)	18.02 (4.74)	N.d	3.57 (5.15)	N.d	0.39 (7.68)
Κ	N.d	N.d	N.d	9.39 (2.88)	39.39 (2.54)	40.93 (1.22)	14.43 (2.25)	5.46 (1.22)

N.d. not detected.



Fig. 1. EDXRF spectra and SEM micrographs of chemical fertilizers.

essential nutrients for plant life [38]. It exerts positive influence on the plant growth and development. It creates an outer safety layer composed of silica deposits. It enhances the reactivity of the absorbed silicon with the heavy metals ions and other components therein. Thus, the metabolic functions of silicon in stressed plants are strenthened [39]. Calcium (Ca) was detected in sample 1 as major element and as minor element in sample 7. Calcium plays a significant role in producing crops of high quality. Calcium supplement enhances cell wall strength and thickness [40].

Iron (Fe) was detected only in sample 1 as micro element. Iron is a necessary micronutrient for all living





organisms because it plays substantial role in biological processes such as respiration, photosynthesis, deoxyribonucleic acid (DNA) synthesis, nitrogen fixaxion and assimilation [41, 42]. Furthermore, it plays a significant role in chlorophyll synthesis and it is necessary for chloroplasts structuring and function. If the amount of iron is low in plants, harvest and nutritional quality are poor. Thus, lack of iron prevents healthy growing of plants [42]. Sulfur (S) was detected in sample 2, sample 5, and sample 7 as macronutrients and in sample 8 as micronutrient. Sulfur is a component of methionine, cysteine and cystine, three of the 21 amino acids that are the main building blocks of proteins. Generally, methionine and cystine are found in plants [43, 44]. Also, sulfur is constituent of vitamin synthesis and enzymes reactions and metal binding in the plant, and it is required for the formation of chlorophyll. Sulfur is

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No. 3

absorbed by the plant roots in the form of sulfate (SO_4^{2-}) or as thiosulfate $(S_2O_3^{2-})$; leaves absorb small amounts of SO₂ [45].

Sodium (Na) was detected as a macronutrient in sample 4 whilst it is as a micronutrient in sample 7 and sample 8. Sodium is defined as functional nutrient for plants. However, it is only essential for a restricted number of C_4 plants to adjust concentration of carbon dioxide. The functions of sodium for plants are: (1) Support of chlorophyll synthesis, (2) Replacing potassium functions, (3) Adjusting internal osmosis (4) Support stomatal functions, (5) Providing ion balance, (6) Enzyme activation and (7) Improving the plant growth [46, 47]. The deficiency of sodium is observed only in C_4 plants because sodium is essential for these plants [46].

Nitrogen (N) was detected as macronutrient in sample 2, sample 3, sample 7, and sample 8. Nitrogen is an indispensable element for whole organisms that constitutes proteins, nucleic acids (DNA, ribonucleic acid (RNA)), membrane lipids, adenosine triphosphate (ATP), NADH, NADPH, co-enzymes, photosynthetic pigments, secondary metabolites and other different compounds. Inorganic nitrogen compounds are obtained by the mineralization of organic material, separation of organic waste or chemical fertilizers. The nitrogen is taken from soil as ammonium (NH_4^+) and

nitrate (NO_3^-) which are the major forms of nitrogen, but organic nitrogen is absorbed like amino acids [48].

Phosphorus (P) was detected as macronutrient in sample 3 and in sample 4, as minor nutrient in sample 6 and as micronutrient in sample 8. Phosphorus is an essential element for growth and ripeness of plants and finally is required for the entire life cycle of plants.

Phosphorus is absorbed as $H_2PO_4^-$ and $H_2PO_4^{2-}$ forms by the roots of plants from the soil. The functions of phosphorus are: to play a role in photosynthesis, respiration, energy storage and transfer like ADP (adenosine diphosphate), ATP, DPN (diphosphopyridine) and TPN (triphosphopyridine), genetic information (DNA and RNA), cell division, root development, flower initiation, seed and fruit development, resistance against plant diseases, development of the quality of crops and several other processes in plants [49].

Potassium (K) was detected as macronutrient in sample 5 sample 6, and sample 7; it is a minor nutrient in sample 4 and sample 8. Potassium is an indispensable element for plants. It is essential for nearly all plants. Potassium is an enzyme activator for metabolism functions, aids to plants' use of the water for stomatatal regulations, maintains the equilibrium of the electrical charges at the location of ATP generation in photosynthesis, regulates the transport of sugar in photosynthesis for growth of plants or storage in fruit or roots, provides protein, starches and cellulose synthesis to promote ATP production, develops resistance against plants' diseases, enhances the size of grains and seeds, and the quality of fruits and vegetables [49, 50].

4. CONCLUSIONS AND OUTLOOK

Natural radionuclides (decay chain nuclides of 226 Ra and 232 Th, respectively, and 40 K), and the artificial radionuclide ¹³⁷Cs, contents of components of eight different chemical fertilizers were studied using gamma-ray spectrometry and EDXRF (see Fig. 1). Except for sample 1, 226 Ra was not detected in the chemical fertilizers. 232 Th and 137 Cs were not detected in any chemical fertilzier whilst ⁴⁰K was detected in all samples. The radium equivalent activity, internal hazard index, external hazard index and activity concentration index for the chemical fertilizers were calculated and compared with reported limit value of literature. Except for sample 2 and sample 3, these values are higher than reported by literature. The size and outer structure of the chemical fertilizers' components are shown in SEM micrographs (see Fig. 1). There are differences between the contents of components defined by the producer and EDXRF results. Some expected trace elements were not detected by EDXRF, thus further experimental work is necessary using other nuclear and atomic techniques such as neutron activation analysis (NAA), photon activation analysis (PAA), atomic absorption spectrometry (AAS), etc. Nonetheless, gamma-ray spectrometry and EDXRF can be used for environmental radioactivity applications and elemental analysis of samples, respectively. This study gives preliminary information about indicative environmental contamination from chemical fertilizers. Because of the nutrition chain: Fertilizer-Plant-Animal-Human this study is particularly important.

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CONFLICT OF INTEREST

The author declares that she has no conflicts of interest.

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