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Analytical methodology for the determination of concentration of pollutants and radioactive elements in phosphate fertilizer used in Saudi Arabia

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ABSTRACT

In present work, we have reported the elemental analysis of phosphate fertilizer used in Saudi Arabia measured by means of different analytical methodology. The concentration of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K has been determined by gamma-ray spectrometer with NaI(Tl) detector. It was found that the average values of ^{226}Ra, ^{232}Th, ^{40}K ranged between 9±1.3 to 55±4.9 Bq kg^{-1}, 8.86±1.8 to 42±8 Bq kg^{-1} 45±8 to 2700±4.9 Bq kg^{-1}, respectively. The measured value of activity concentration of ^{40} K was estimated to be within the excepted world average range for NPK fertilizer (mean value 2700 Bq kg^{-1}). It was observed that the calculated radium equivalent (Raeq) in fertilizers are lower than the allowed maximum value of 370 Bq kg^{-1}, however, the calculated representative level index, Iγr, values for NPK and TSP phosphate fertilizers exceed the upper limit (Iγr ≅1). Furthermore, the concentration of the environmental pollutants (Cd, Cr, Ni, Pb, and Zn) and common elements (Mg, Mn, and Fe) was carried out using Atomic Absorption spectrometer (AAS). The obtained data are compared with available reported data from other countries in 'the literature.

KEYWORDS

Elemental analysis;
Heavy metals;
Natural radioactivity;
XRD.

INTRODUCTION

Beside the beneficial influence of the phosphate fertilizers on soil and agricultural plants, it is of utmost interest to estimate their hazard effect on the environment. The fertilizers are polluting the environment as they are major source of pollution in soil and water. Phosphate fertilizers contain varying amounts of heavy metals as contaminants from either phosphate rock ores or other ingredients used in the phosphate fertilizer industry. As some heavy metals are potentially harmful to human health, attention is being given to its avenues of entry into the human food chain. Uptake of such elements by plants consumed directly or indirectly by humans is one avenue of entry, so the effects of heavy metal contaminants in phosphate fertilizers are of concern[1]. Suppliers of fertilizers usually do not mention all contents and the reaction of these contents with soil and water. Only major contents are written on the bags of fertilizers[25]. Commercial fertilizers have been used for decades and will probably continue to be used for many decades to come. Hence, even low annual accumulations may finally build up undesired concentrations in soil, especially where fertilizers with high heavy element concentrations are used[33].

Phosphoric acid is the starting material for triple superphosphate (TSP), single superphosphate (SSP), ammonium phosphate fertilizers (DAP and MAP), NPK fertilizers. MAP and DAP are obtained by reacting directly phosphoric acid with different amounts of NH_3. TSP, SSP and NPK are obtained by reacting phosphoric acid with phosphate rock and NH_3. During the reaction of phosphate rock with sulphuric acid, the radioactive equilibrium between U, Th and their decay products is disrupted and the radionuclides migrate according to their solubility.

Several publications have been concerned about the natural radioactivity, rare earth and heavy elements in phosphate and phosphate fertilizers throughout the world[1,2,17,19,22,24,25,39,40,43,48,50,52,53].

Nuclear analytical techniques, with their broad band of applicability to almost all matrix types and their exceptional sensitivity to many elements, are an indispensable tool for environmental research. The aims of the present work were: 1) Measuring the concentrations of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K in phosphate fertilizers by gamma spectrometry using a NaI(Tl) detector, 2) Calculate the radiation doses and radiation hazards due to natural radionuclides in phosphate fertilizers to estimate their radio-ecological impacts. 3) Estimate the concentration of elements content in phosphate fertilizer using Atomic Absorption Spectrometry. For the sake of comparison the results of concentration levels and radiation equivalent activities are compared with similar studies carried out in other countries.

EXPERIMENTAL METHODS

Sample preparation for natural radioactivity

Samples of phosphate fertilizer were collected from local makets in Qassim region, Saudi Arabia. These materials represented most of the fertilizers marketed in the Kingdom of Saudi Arabia. The weighed samples were ground, homogenized and sieved to about 100 mesh by a crushing machine. Weighed samples were placed in polyethylene bottles, of 350 cm^3 volume, each. The bottles were completely sealed for more than one month to allow radioactive equilibrium to be reached. This step was necessary to ensure that radon gas is confined within the volume and that the daughters will also remain in the sample[18,20].

Instrumentation and calibration

Activity measurements were performed by gamma ray spectrometer, employing a NaI(Tl) crystal, coupled to PC Quantum MCA 2500R. To reduce gamma ray background, a cylindrical lead shield (100 mm thick) with a fixed bottom and movable cover shielded the detector. The lead shield contained an inner concentric cylinder of copper (0.3 mm thick) to absorb x-rays generated in the lead. In order to determine the background distribution in the environment around the detector, an empty sealed bottle was counted in the same manner and in the same geometry as the samples. The measurement time of activity or background was 12 h. The background spectra were used to correct the net peak area of gamma rays of measured isotopes[21]. A dedicated software program (Quantum) from Princeton Gamma Tech (PGT) has carried out the online analysis of each measured γ-ray spectrum.

Calculation of activity

Calculations of count rates for each detected photopeak and radiological concentrations (activity per mass unit or specific activity) of detected radionuclides depend on the establishment of secular equilibrium in the samples. ^{232}Th concentration was determined from the average concentrations of ^{212}Pb (238.6 keV) and ^{228}Ac (911.1keV), ^{226}Ra was determined from the average concentrations of the ^{214}Pb (351.9keV) and ^{214}Bi (609.3 and 1764.5 keV) decay products. ^{40}K radionuclide was identified by its single γ-line at energy of 1460 keV. It should be mentioned that no peak is appeared at energy of 661 keV in the spectrum due to decay of ^{137}Cs and it confims the artificial radioactivity in the investigated samples is below the detection limit[22,23].

Sample preparation for atomic absorption spectrometry (AAS)

Two grams of the sample were digested with aqua regia (21ml HCl conc +7ml HNO3 conc, both from

Merck p.a.) and refluxed for 2h. After cooling the aqua regia solution was transferred into a graduated 2500 ml flask, the flask was filled with water to the mark. Measurement to trace heavy metals was performed by atomic absorption analysis (Varian AA24OFS). The elements Pb, Cd, Mn, Zn, Fe, Ni Mg. Cr were determined with flame analysis, C2H2/Air. The details regarding quality assurance are given somewhere else[44].

The structure of the samples were checked at room temperature by means of X-ray powder diffraction (XRD) Shimadzu Diffractometer XRD 6000, Japan, with Cu-Kα_1 radiation (λ = 1.54056 Å). The data were collected by step-scan modes in a θ-2θ range between 10° and 80° with step-size of 0.02° and step time of 0.6 seconds. Pure Silicon~ Si 99.9999% was used as an internal standard.

RESULTS AND DISCUSSION

Heavy metals in phosphatic fertilizers used in Saudi Arabia

Heavy metal content is one of the deciding factors for the quality of phosphate fertilizers, which does not have any standard permissible limit because the maximum allowable content depend on soil characteristics, irrigation water quality, crop type, etc. Elemental analysis for four types of phosphate fertilizer used in Saudi Arabia was carried out to determine the concentration of heavy metals using Atomic Absorption Specrometry. The analytical results are summarized in TABLE 1. The elements analyzed in the present study have been classified as follows.

Environmental pollutants (toxic elements)

Chromium (Cr)

Toxicity of chromium (Cr) towards plants or animals depends on its oxidation state. For example Cr (III) is an essential nutrient that helps the body consume sugar, protein and fat, while Cr (VI) is considered to be carcinogen, so before making any conclusion, information about oxidation states must be known. By a rough comparison through Cr content, it was found that the average content of Cr in Saudi phosphate fertilizer was found to be ranged between 54-279 μg/g. The global range of Cr as given in TABLE 2 is 1-233 μg/g. The concentration determined in the present study is higher than the global range of Cr.

Lead (Pb)

Analysis of lead (Pb) shows that the average lead concentration found to be 12.6 μg/g in simple supper phosphate while lead under the detection limit in the other kinds of phosphate fertilizer. Still this situation in not alarming because uptake of lead in plants depends on soil pH, at higher pH soil, lead becomes immobilized[42].

Cadmium (Cd)

The average cadmium concentration in the present study was found to be from 12.5 to 28.2 μg/g while the global range of Cd concentration in phosphate rock as given in TABLE 2 is 0.1 - 60 μg/g. European countries implemented a limit of 10 μg/g of Cd on phosphate rock imports[11].

Zinc (Zn)

The global range of Zn concentrations in phosphate rock 6-515 μg/g while the average concentration determined in the present study is 17.5 to 634 μg/g that higher than the global range of Zn in phosphate rock. Zn do not present in simple supper phosphate.

Major elements

Manganese (Mn)

Manganese (Mn) is the basic macronutrient for plants. In the worldwide comparison given in TABLE 2, the global range in Mn concentration is 149-2235.5 μg/g while the average concentration determined in the present study ranged between 14.8- 510 μg/g far from the global range of Mn in phosphate rock.

Magnesium (Mg)

The amounts of magnesium (Mg) (secondary nutrient) in our phosphate fertilizer are comparable with those in phosphate rock given in TABLE 2 except for NPK fertilizer. The concentration of Mg in our samples varies between 240 - 16843 μg/g. This element not considered as pollutant or hazardous[38].

Nickel (Ni)

In case of nickel (Ni) content, the global range of Ni concentration in the worldwide comparison given in TABLE 2 is 2-116.5 μg/g while the average concentration determined in the present study ranged between 22.5- 66.6 μg/g and this is within the global range of Ni in phosphate rock. The highest Ni content was 66.6 μg/g which is far below than the tolerable limit as 100 μg/g or higher Ni content in plant is considered to cause toxicity[26].

TABLE 1 : The average content of heavy elements in phosphate fertilizer used in Saudi Arabia by using atomic absorption spectrometry.

Type of Fertilizer	Pb	Cd	Mn	Ni	Zn	Fe	Mg	Cr
MAP	< DL	< DL	14.8	< DL	17.5	52.3	240	< DL
MAP	< DL	12.5	54.7	51.8	634	2967	5235	279
NPK	< DL	< DL	273.7	22.5	103.8	10817	16834	64.1
SSP	12.6	28.2	510	66.6	< DL	7955	1374	54.2

TABLE 2 : Global pattern of toxic, major and minor elements in phosphate rock

Country	Cr	Pb	Cd	Zn	Mn	Mg	Ni	Ref.
Algeria	208	----	---	134	---	---	---	[39]
Brazil	70.5	44.5	4	299	---	12240	116	[15]
Egypt	NF	----	---	13.2	---	---	---	[1]
Israel	56	----	---	372	----	----	---	[39]
Middle East	129	4	9	315	----	---	29	[31]
Morrocco	291	7	30	345	----	---	26	[39]
Nigeria	28	---	---	59	5710	---	---	[37]
North Africa	105	6	60	420	----	----	33	[32]
Russia	23.3	3	0.1	19	---	---	2	[39]
Saudi Arabia	176	--	---	88	---	----	---	[5]
South Africa	1	35	2	6	---	---	35	[31]
Syria	136	---	---	269	----	----	---	[39]
Togo	75	---	---	143	149	---	---	[37]
Tunis	161	--	---	515	--	---	---	[39]
USA	142	12	11	403	2235	---	37	[11]
Pakistan	17	89	7.5	67.2	178	7410	28	[44]

Health hazards from trace elements in phosphate fertilizer

Metals such as iron, magnesium, manganese and zinc are essential metals, since they play an important role in biological systems. For instance, magnesium plays a role in the stability of all polyphosphate compounds in the cells, including those associated with DNA and RNA synthesis and manganese is also an essential trace nutrient in all forms of life. Nonessential metals, such as Ni, Pb and Cd are toxic even in trace amounts. Intake of cadmium above safe limit causes high blood pressure, liver disease and nerve or brain damage. The essential metals can also produce toxic effects at higher concentrations. They tend to bio-accumulate, cause toxicity to plants and contaminate the food chain[12,16,28]. Only a few metals of proven hazardous nature are to be completely excluded in food for human consumption. Thus, only three metals, namely lead, cadmium and mercury, have been included in the regulations of the European Union for hazardous metals[16]. While the US Food and Drug Administration (USFDA) has included further three elements, namely, chromium, arsenic and nickel in the list[47]. Heavy metals present in the fertilizer contaminate soil and the irrigated water. These contaminations transfer into the vegetables and accumulate there. Transfer factor of heavy metals from contaminated water to vegetables depends on the type of vegetable. For Pb, Ni, and Zn transfer factor is very high in many vegetables, for example ladyfinger cauliflower and cabbage whereas it is the highest for Cd as compared to Pb, Ni, and Zn[46]. Sale limits for Cd and Pb in agricultural product should be 0.2 and 0.3 μg/g, respectively, as reported in the literature[32].

Natural radionuclides, radiation hazard indexes in phosphatic fertilizers used in Saudi Arabia

The fertilizers are spread on land thus leading to a surface contamination which depends on the radionuclide concentration in the fertilizer and on the thickness of the layer on the land. The use of this land for agricultural production (vegetables, animal products) will then lead to an exposure of the public via the ingestion path. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K have been determined for the various phosphate fertilizers used in Saudi Arabia. The average values of activity measured as well as the respective standard deviations, of the above natural radionuclides are presented in TABLE 3. The use of fertilizers in large extent has affected radionuclides concentration, and especially for potassium, it is one of the causes for presence of high activity of ^{40}K in soil[3,4,9]. In the present study, the activity concentration of ^{40}K higher than that of ^{226}Ra and ^{232}Th for all types of fertilizers. The permissible activity levels for ^{226}Ra, ^{232}Th, and ^{40}K are 35, 35 and 400 Bq/kg respectively[51].

To represent the activity levels of ^{226}Ra, ^{232}Th and

TABLE 3 : Average activity concentrations of 226Ra, 232Th, 40K, Radium equivalent activity, representative level index, Iγr for phosphate fertilizers used in Saudi Arabia

Name	Ra-226	Th-232	K-40	Ra eq	Iγr
DAP	9.0 ± 1.3	36 ± 6	45±8	63	0.45
MAP	17 ± 2.1	42 ± 8	78 ± 9	83	0.58
NPK	70± 5.6	25±3.2	2700± 26	313	2.51
SSP	55.2 ± 4.9	8.86±1.8	553± 18	110	0.78

TABLE 4 : Comparison of natural radionuclides in phosphate fertilizers under investigation with those in other countries.

Country	Sample	^{226}Ra	^{232}Th	^{40}K	References
Egypt	SSP	8.2	61	627	[34]
Brazil	SSP	375	100	871	[45]
Pakistan	SSP	221	49.7	556	[30]
Bangladesh	SSP	143	-----	292	[6]
Lebanon	SSP	4.1	-----	1043	[13]
Saudi Arabia	SSP	55.2	8.86	553	Present work
Pakistan	NPK	386	38	885	[49]
Algeria	NPK	134.7	131.8	11644	[10]
Brazil	NPK	647.6	753.9	603	[7]
USA	NPK	780	49	200	[27]
Germany	NPK	520	15	720	[30]
Saudi Arabia	NPK	70	25	2700	Present work
Finland	NPK	54	11	3200	[35]
Nigeria	NPK	143	9	4729	[29]
Saudi Arabia	DAP	9	36	45	Present work
Saudi Arabia	MAP	17	42	78	Present work

^{40}K by a single quantity, a common radiological index has been introduced. This index is called radium equivalent (Raeq) activity. It can be calculated from the following relation[8].

$$Ra_{eq} = A_{Ra} + 1.43A_{Th} + 0.077A_{K} \quad (1)$$

Where: A_{Ra}, A_{Th} and A_{K} are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively expressed in Bq/kg. Another radiation hazard index called the representative level index, Iγr, is defined as follows[36].

$$I_{\gamma r} = \left(\frac{A_{Ra}}{150\ Bq/kg} + \frac{A_{Th}}{100\ Bq/kg} + \frac{A_{K}}{1500\ Bq/kg} \right) \quad (2)$$

Where: A_{Ra}, A_{Th} and A_{K} having the same meaning as in the Equation (1). The average results for the radium activity and representative level index Iγr are also presented in TABLE 3. It is observed that the calculated radium equivalent in fertilizers are lower than the allowed maximum value of 370 Bq/kg[8]. From TABLE 3, It is clear that the calculated Iγr values for NPK and TSP phosphate fertilizers exceed the upper limit for Iγr which is unity. The activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K for the investigated phosphate fertilizers were compared with similar investigations in other countries and the summary of results is given in TABLE 4. According to UNSCEAR report (2000), the world average value of activity concentration for ^{40}K is 140-850 Bq/kg (mean value 370 Bq/kg). The measured value of activity concentration of ^{40}K was within the world average range except for NPK fertilizer (mean value 2700 Bq/kg). As shown in TABLE 4, the radioactivity in fertilizers vary from one country to another. It is important to point out that these values are not representative values for countries mentioned but for the region from where the samples were collected. The use of phosphate fertilizers for growing crops and the resulting potential increase of background radiation doses give sufficient grounds for the justification of this kind of study. The ALARA-principle implies that reasonable measures must be taken not only to reduce radiation doses if necessary and also that costs have to be weighed against the averted radiation doses.

The X-ray diffraction patterns (XRD) of the various phosphate fertilizers used in Saudi Arabia are presented in Figure 1. The diffraction peaks of all the fertilizers can be well indexed on the basis of monoclinic hydrogen diammonium phosphate (JCPDS No. 29-0111) and tetragonal ammonium dihydrogen phosphate (JCPDS No. 37-1479) without additional diffraction peaks for individual metal or other detectable secondary phases.

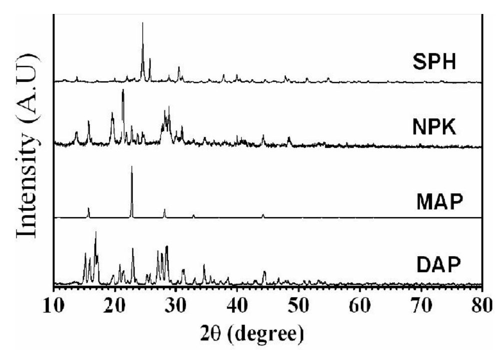

Figure 1 : X-ray diffraction patterns of phosphate fertilizer used in Saudi Arabia

CONCLUSION

Phosphate fertilizers used in Saudi Arabia were analyzed for some toxic, major and minor elements using the technique of atomic absorption spectrometry. The concentrations of the elements determined in the present study lay within the worldwide range of these elements. Furthermore, upper limit for a heavy metal (a pollutant) cannot be decided solely on the basis of the mass of that metal in phosphate rock and phosphate fertilizer made from that rock. Soil content is one of the deciding factors for setting up the upper limit of a heavy metal in the phosphate fertilizer. The concentration of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K were also determined by gamma-ray spectrometer. The average values of ^{226}Ra ranged between 9±1.3 to 55±4.9 Bq kg^{-1} and for ^{232}Th ranged between 8.86±1.8 to 42±8 Bq kg-1 and for ^{40}K ranged between 45±8 to 2700±4.9 Bq kg^{-1}. The measured value of activity concentration of ^{40}K was within the world average range except for NPK fertilizer (mean value 2700 Bq kg^{-1}). It is observed that the calculated radium equivalent in fertilizers are lower than the allowed maximum value of 370 Bq kg^{-1} and the calculated $I\gamma r$ values for NPK and TSP phosphate fertilizers exceed the upper limit for $I\gamma r$ which is unity.

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