Uranium and heavy metals in Phosphate Fertilizers

Ashraf E. M. Khater[1&2]

[1]National Center for Nuclear Safety and Radiation Control, Atomic Energy Authority, Cairo, Egypt,
[2]Physics Department, College of Sciences, King Saud University, Riyadh, Kingdom of Saudi Arabia

ABSTRACT

Agricultural applications of chemical fertilizers are a world wide practice. The specific activity of uranium-238 and heavy metals in phosphate fertilizers depends on the phosphate ore from which the fertilizer produced and on the chemical processing of the ore. Composite phosphate fertilizers samples where collected and the uranium-238 specific activity, in Bq/kg, and As, Cd, Cu, Pb, Se concentration, in ppm, were measured. The annual addition of these elements in soil due to fertilization were calculated and discussed.

INTRODUCTION

Since the 1950s, the application of plant nutrients, including phosphate fertilizers, has increased substantially. More than 30 million metric tons of phosphate fertilizers are annually consumed worldwide, which increase crop production and land reclamation (Lambert et al., 2007). The long-continued application of phosphate fertilizers can redistribute and elevate uranium and toxic heavy metals, such as As, Cd and Pb, in soil profiles and consequently their transfer to the food chain, mainly in acid soils. It can also raise these elements concentrations in irrigation runoff/drainage waters (da Conceicao, Bonotto, 2006). This work aims at estimating the concentration of uranium and heavy metals (As,Cd, Cu, Pb and Se) in phosphate fertilizers used in Saudi Arabia and to investigate the possible environmental hazards.

MATERIAL AND METHODS

Sampling and sample preparation

Thirteen phosphate fertilizer samples of ten different brands were collected from the local market of Riyadh City. Five of those brands were of granular form, while the other five were leafy (water soluble) phosphate fertilizers. Samples were pulverized and homogenized.

Analytical Techniques

Gamma spectrometric analysis; the dried samples were transferred to polyethylene containers of 100 cm^3 capacity Uranium-238 specific activity was measured using well calibrated gamma spectrometry based on hyper-pure germanium (HpGe) detectors. The HpGe detector had a relative efficiency of 40% and full width at half maximum (FWHM) of 1.95 keV for ^{60}Co gamma energy line at 1332 keV. The gamma line transition 1001 keV was used for ^{238}U specific activity calculation and the spectrometer was calibrated using reference uranium ore sample (IAEA-RG-U).

Inductively Coupled Plasma- Mass Spectrometer (ICP-MS); the concentration of As, Cd, Cu, Pb and Se were measured using ICP-MS after chemical dissolution and dilution. Standard solutions were used for calibration and quality control measures.

RESULTS AND CONCLUSIONS

Specific activity of ^{238}U in Bq/kg and concentration of As, Cd, Cu, Pb and Se in ppm in phosphate fertilizers in Saudi Arabia and their statistical summary are given in table 1 and 2 respectively. The granule fertilizers are applied directly to the soil and dissolved slowly in the irrigation water. The leafy fertilizers (powder form) are dissolved in water that is spraying onto plants' leaves. The average activities (range) of ^{238}U was 1017 (173.8-2234) Bq/kg and <20 Bq/kg in granule and leafy phosphate fertilizers, respectively. In the locally produced fertilizer samples, the ^{238}U, average (range) 1791 (1273 – 2234) Bq/kg, are much higher than

that in imported fertilizer samples, 242 (174 – 368) Bq/kg, and vice versa for ^{226}Ra, 3.7 (2.7 – 4.9) and 145 (35.0 – 283) Bq/kg, respectively. Moreover, the specific activities of ^{238}U and ^{226}Ra in imported granule fertilizers are comparable with ^{226}Ra/^{238}U activity ratios in the range of 0.2-0.8 and in the range 0.6-0.8 after excluding one imported phosphate sample (PH8). Also, their activities are strongly correlated with correlation coefficient (R^2) value of 0.95 (Khater et al., 2008).

Table 1: Specific activity of 238U in Bq/kg and concentration of As, Cd, Cu, Pb and Se in ppm in phosphate fertilizers in Saudi Arabia

Type	Sample	U-238±EP[&P]	As	Cd	Cu	Pb	Se	$PB_{2B}OB_{5B}$ %	Ra 226I U-2
Granule fertilizers	PH 1*	1774±3	7.6	7.6	20	<DL	29.15	46	0.0
	PH 2*	2234±5	-	-	-	-	-	46	0.0
	PH 3*	1884±2	7.5	7.51	22	<DL	28.04	46	0.0
	PH 4*	1273±1	-	-	-	-	-	23	0.0
	PH 5P[+P]	193±0.34	0.49	0.50	17	0.67	-0.82	17	0.6
	PH 6P[+P]	233±0.32	0.51	0.50	14	0.66		17	0.5
	PH 7P[+P]	368±0.42	1.0	1.0	11	1.6	23.92	18	0.7
	PH 8P[+P]	174±0.23	4	4.1	111	0.63	0.79	17	0.2
Leafy Fertilizers	PH 9	< 20	0.01	0.10	63	0.09	2.21	20	-
	PH 10	< 20	0.21	0.21	9.2	0.11	1.71	44	-
	PH 11	< 20	0.26		29	0.06	3.60	30	-
	PH 12	< 20		0.02	26	<DL	0.14	20	-
	PH 13	< 20	0.04	0.04	<DL	<DL	3.61	52	-

[P&P] Error * locally produced + imported

Generally, the specific activities of natural ^{238}U series radionuclides in phosphate fertilizers depend on their levels in the used raw phosphate ore material. Radioactivity levels in phosphate ores are varied according to their geological origin (sedimentary, volcanic or biological origin) where ^{238}U and its decay products tend to be elevated in phosphate deposits of sedimentary origin due to the accumulation of dissolved uranium, in the form of uranyl complex, in the sea water during geological formation of the phosphate rocks. A typical concentration of ^{238}U in sedimentary phosphate deposit is 1500 Bq/kg (UNCEAR, 1993; Khalifa and El-Arabi, 2005). During phosphate fertilizers manufacture the phosphate ore is firstly attacked by sulfuric acid to produce the phosphoric acid (green acid) where uranium will be mainly concentrated in the phosphoric acid while radium, polonium, thorium and other insoluble radionuclides will be precipitated as sulfate salts and concentrated in the phosphgypsum by product. That could explain the high

Table 2: statistical summary of P[238P]U specific activity in Bq/kg and As, Cd, Cu, Pb and Se concentrations in phosphate fertilizers used in Saudi Arabia.

	Granule			Leafy	All
	Local	Import	All		
U-238	1791 ± 199, 397* (1273-2234), 4	242 ± 44, 88 (174-368),4	1017 ± 308, 870 (174-2234), 8	< 20	1017 ± 308, 870 (174-2234), 8
As	7.6 ± 0.03,0.05 (7.5-7.6), 2	1.5 ± 0.86, 1.71 (0.49-4.1), 4	3.5 ± 1.4, 3.4 (0.49-7.6),6	0.11 ± 0.05, 0.12 (< dl-0.26), 5	2 ± 0.9, 3 (< dl-7.6), 11
Cd	7.5 ± 0.03,0.04 (7.5-7.6), 2	1.5 ± 0.85, 1.7 (0.5-4.1), 4	3.5 ± 1.4, 3.4 (0.5-7.6), 6	0.09 ± 0.04, 0.08 (0.02-0.21), 4	2.2 ± 0.97, 3.1 (0.02-7.6), 10
Cu	20.8± 0.88,1.25 (22-42), 2	38 ± 24, 49 (11-111), 4	32 ± 16, 39 (10.5-111),6	32 ± 11, 23 (9-63), 4	32 ± 10, 32 (9.2-111), 10
Pb	< DL	0.89 ± 0.23, 0.46 (0.63-1.58),4	0.71 ± 0.25, 0.57 (< dl-1.58), 5	0.07 ± 0.02, 0.05 (< dl - 0.11), 4	0.42 ± 0.17, 0.52 (< dl - 1.6), 9
Se	28.6 ± 0.56, 0.79 (28-29),2	12.4 ± 11.6, 16.4 (0.79-24), 2	21 ± 6.7, 13 (0.79-29), 4	2.3 ± 0.65, 2.2 (0.14-3.6), 5	10.3 ± 4.2, 13 (0.14-29), 9
$PB_{2B}OB_{5B}$ %	40 (23 - 46)	17 (17-18)	29 (17 - 46)	33 (20 - 52)	30 (17 - 52)

* Mean± Standard error, standard deviation (range), number of samples

concentration of ^{238}U in locally produced phosphate fertilizers. Mazzilli et al. (2000) found that 90% of ^{226}Ra and 80 % of ^{232}Th fractionate into phosphogypsum, while ^{238}U is being predominantly incorporated in phosphoric acid. The ^{238}U in phosphoric acid occurs as $[(UO_2)SO_4]$ and $[U(SO_4)_2]$ that as water soluble (Rothbaum et al., 1979). ^{226}Ra is more enriched in phosphogypsum and has a chemical behavior similar to calcium and may occur substituted in $CaSO_4.nH_2O$ or (Ba, Sr) SO_4 (radiobarite). $^{226}Ra/^{238}U$ activity ratios in phosphate fertilizers, table 1, indicate the occurrence of chemical fractionation and their concentrations are deviated from the secular equilibrium conditions. The variations of these ratios depend on the origin of the phosphate ore and/or on the chemical processing of the ore during fertilizers manufacture. The relatively low ^{238}U concentration in imported granule fertilizers could be explained due to the low content in the phosphate ore that used as row material. For the leafy fertilizer samples, the specific activity of U-238 was less than the lower limit of detection, 20 Bq/kg.

Table 3: The annual addition$P^{\#P}$ of $P^{238P}U$, As, Cd, Cu, Pb and Se due to the phosphate fertilizers application

Type	Sample	U-238		As	Cd	Cu	Pb	Se
		Bq/mP^{2P}	Bq/kg	g/ha				
Granule fertilizers	PH 1	106	1419	4.6	4.5	12	-	18
	PH 2	134	1787	-	-	-	-	-
	PH 3	113	1507	4.5	4.5	13	-	17
	PH 4	76	1018	-	-	-	-	-
	PH 5	12	154	0.29	0.30	10	0.40	-
	PH 6	14	186	0.31	0.30	9	0.40	-
	PH 7	22	294	0.60	0.62	6	0.95	14
	PH 8	10	139	2.4	2.4	66	0.38	0.47
Leafy Fertilizers	PH 9	-	-	0.01	0.06	38	0.05	1.3
	PH 10	-	-	0.12	0.12	6	0.07	1.0
	PH 11	-	-	0.16	-	18	0.04	2.2
	PH 12	-	-	-	0.01	15	-	0.08
	PH 13	-	-	0.03	0.02	-	-	2.2

Annual application rate is 600 kg/hectare (10000 mP^{2P})
* locally produced + imported

By comparing uranium concentration intervals in phosphate fertilizers from different countries, the highest uranium concentration were found, in ascending order, in phosphate fertilizers from USA (221 ppm), Germany (186 ppm), and Saudi Arabia (180 ppm) but the ranges of uranium concentration in these fertilizers are wide, 8.9-221 ppm (116-2470 Bq/kg ^{238}U), 3.2-186 ppm (45-2300 Bq/kg ^{238}U) and 14-180 ppm (174-2234 Bq/kg ^{238}U), respectively(Hamamo et al., 1995; Pfister et al., 1976; Al-Shawi and Dahl, 1995; Lal et al., 1985; Barisic et al., 1992; Vucic and Ilic, 1989; Yamazaki and Geraldo, 2003). Uranium concentration is correlated with the phosphorus percentage (P_2O_5%) in phosphate rock and fertilizers. Since the natural uranium can substitute calcium in the phosphate rock structure due to the similarity in ionic size between U^{4+} and Ca^{2+} the correlation between ^{238}U and phosphorus percentages (P_2O_5%) in granule phosphate fertilizers is very strong with correlation coefficients (R^2) of 0.9 (Guzman, 1992 from da Conceicao, Bonotto, 2006).

Most fertilizers contain trace amounts of trace elements. Several studies have shown that heavy metals in phosphoric fertilizers can accumulate in soil and become readily available to plants. In term of fertilizer use, As, Cd, Cr, F, Sr, Th, U and Zn are the elements that have a potential risk of accumulation in soil (Sauerbeck,1992, from Modaihsh et al. 2004) McLaughlin et a. (1996) assessed the potential for contamination by phosphate fertilizers and concluded that Cd and F would accumulate at faster rates than As,Pb or Hg (Modaihsh et al. 2004). Table 2 shows the average concentrations, it is clear that there are variations in heavy metals concentrations in local produced and imported, and generally in granule and leafy fertilizers. For U, As, Cd and Se, their concentrations in local fertilizer are relatively higher than that in imported and Except for Cu, concentrations of U, As, Cd, Pb and Se in granule fertilizer are relatively much higher than that in leafy fertilizers.

The calculated annual addition of ^{238}U, As, Cd, Cu, Pb and Se due to the phosphate fertilizers application are given in table 3. Generally, if we consider the UK annual allowable limit for Cd and Pb, 0.166 and 33 Kg/ha, and assuming the complete accumulation of both element in soil tope surface, it will need at least 35 up to thousands of year to reach these limits (da Conceicao, Bonotto, 2006).

CONCLUSIONS

This study represents preliminary results of ^{238}U, As, Cd, Cu, Pb and Se concentrations in phosphate fertilizers in Saudi Arabia. Uranium concentration is fall in the lower range of uranium concentrations in phosphate fertilizers from different countries. The annual addition of ^{238}U, As, Cd, Cu, Pb and Se and their accumulation in top soil were calculated. To reach the annual allowable limit (for As, Cd, Cu, Pb and Se) it will take tens or thousands of years. These calculations are theoretically correct but practically the situation is different, if we consider the excess application of fertilizers and the other environmental pathways of these elements such as water and food-chain.

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