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Full Length Research Paper

Evaluation of metal composition of phosphate fertilizers in Ghana

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The elemental composition and possible sources of metals in phosphate chemical fertilizers used in Ghana were determined. The fertilizers used in this include Rock Phosphate (RP), Triple Super Phosphate (TSP), Mono Ammonium Phosphate (MAP), Diammonium Phosphate (DAP), and NPKs in varying proportions. Analysis of these metals of interest was carried out with Flame Atomic Absorption spectrometer (FAAS). Metals such as Cr, Co, Cu, Cd, Mg, Mn, Pb and Zn were possibly generated by the dry milling process of phosphate rocks in the fertilizer manufacturing factories. The chemical reactions within the factories probably participated in the metal loads. Triple Super Phosphate (TSP) had relatively high levels of metals in the fertilizers.

Keywords: Phosphate, Rock, Fertilizer, Metal

INTRODUCTION

Phosphorus is one of the most essential plant nutrients; its deficiency in soils severely affects the growth of crops production. Soils deficient in phosphorus can be amended with phosphate-containing fertilizers produced from phosphate rocks. Cadmium and other heavy metals, as well as radionuclide contaminants are present in phosphate rocks. Different quantities of these elements are transferred into phosphorous fertilizers. The heavy metals in phosphate fertilizers depend on the phosphate ore from which the fertilizer was produced and the chemical processing of the ore.

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 and Bonotto, 2006).

Heavy metals occur naturally in all soils in minute quantities, but can accumulate in agricultural soils from various sources, such as fertilizers, organic supplements, atmospheric deposition and urban and industrial activities. Some of these metals are essential nutrients for plants and animals. However, sufficiently high concentrations can become toxic and constitute serious health problems

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Table 1. Analytical characteristics of AAS 240FS

Metal	lamp current (nA)	wavelength (nm)	slit width(nm)	fuel /gas	oxidant	working range (ug/ml)
Cd	4	228.8	0.5	acetylene	air	0.02-3
Co	7	240.7	0.2	acetylene	air	0.05-15
Cr	7	357.9	0.2	acetylene	air	0.06-15
Mn	5	279.5	0.2	acetylene	air	0.02-5
Cu	4	324.7	0.5	acetylene	air	0.03-10
Zn	5	213.9	1.0	acetylene	air	0.01-2
Pb	5	217.0	1.0	acetylene	air	0.1-30
Mg	4	285.2	0.5	acetylene	air	0.003-1

whenever they enter into the human food chain (Oliver, 1997). Kongshaug et al. (1992) gave a comprehensive account of some heavy metal concentrations found in various phosphate rock deposits. It is known that these heavy metals, present as impurities in phosphate rocks, are transferred to the fertilizers during processing.

As trace elements, Cu, Mn and Zn are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metals are dangerous because they tend to bio-accumulate. Accumulation of heavy metals in soil has potential to restrict the soil function, cause toxicity to plants, and contaminate the food chain. Heavy metals are associated with a myriad of adverse health effects, including allergic reactions (e.g. Cr), neurotoxicity (e.g. Pb), anemia, stomach and intestinal irritation (e.g. Cu), and cancer (e.g. Cr-VI) (Goyer, 1996). Increased concern about the contamination of soil and water resources with heavy metals has been shown in recent years. Adverse health effects consequent upon consumption of contaminated feeds have also received much attention (Singh, 1991; 1994). Analysis of fertilizers commercially marketed in India, Italy, Australia, New Zealand, England and USA indicated that all phosphate fertilizers contained significant and varying amounts of heavy metals (Williams and David, 1973; Arora et al., 1975; Pezzarossa et al., 1990).

In Ghana, fertilizer use is on the increase, mainly to restore soil fertility in order to increase agricultural productivity. However, this does not come without adverse effect of inorganic fertilizer application. The aim of this work is to determine composition and possible sources of metals in the phosphate inorganic fertilizer used in Ghana.

MATERIALS AND METHODS

Samples of some of the various types of phosphate fertilizers, commonly used by Ghanaian farmers, were obtained. These include: Rock Phosphate (RPL), Triple Super Phosphate (TSP), Mono Ammonium Phosphate (MAP), Diammonium Phosphate (DAP), and NPK in varying proportions.

The samples were ground into powdered form using a mortar grinder (FRISCH Pulverisette 2) and dried in an oven (Memmert) at 104 ºC. An amount of 0.50g of each dried powdered sample was taken and digested with the combined solutions of 6ml of 65% HNO_3 and 2.5 ml of 37% H_2SO_4 in a microwave oven (ETHOS 900 Microwave Labstation). The chemicals used were analytical grade chemicals obtained from Sigma Aldrich. Reagent blanks and standards were subjected to the same digestion procedure as the samples. The solutions obtained after digestion were each diluted to 20 ml with de-ionized water.

The concentrations of the elements; Cd, Co Cr, Cu, Mg, Mn, Pb and Zn were then determined by flame atomic absorption spectrometry (FAAS) using Varian AAS 240FS.The analytical conditions for the operation of the AAS equipment are shown in Table 1.

RESULTS AND DISCUSSION

The analytical results obtained for elemental analysis of nine phosphatic fertilizer samples are summarized in Table 2.

Total concentration of Cr was measured in this work. The highest level of total Cr (i.e. 23.52 µg/g) was found in RPL whilst the lowest of 0.36 µg/g was in NPK 21:10:10. The concentration of elements in the other remaining samples, µg/g, was of the order; RP > TSP > PKA > PKL > NPK 23.10. 5 > MAP > NPK 15.15.15 > DAP > NPK 21:10:10. Chromium concentration measured in this work falls within ranges reported in similar work under taken in other countries (Table 3). The toxicity of chromium (Cr) to plants or animals depends on its oxidation state. Chromium (III),for instance, is an essential nutrient that helps the body consume sugar, protein, and fat while Cr (VI) is considered to be a carcinogen. Information about oxidation states must, therefore, be known to make conclusions on toxicity or health benefit.

Table 2. Concentration (in µg/g) of some toxic and potentially toxic elements in phosphate fertilizers

Sample ID	Cr (µg/g)	Pb (µg/g)	Cd (µg/g)	Zn (µg/g)	Mn (µg/g)	Mg (µg/g)	Co (µg/g)	Cu (µg/g)	Metal load (µg/g)
DAP	0.56	<0.001	0.88	0.88	45.04	<0.001	1.52	3.4	52.28
MAP	4.66	<0.001	0.62	8.12	1.58	1.11	3.82	2.62	22.53
TSP	10.54	1.92	1.72	12.52	91.18	1.52	2.16	5.8	127.36
PKA	8.88	<0.001	0.64	8.12	2.6	1.25	2.76	4.04	28.29
PKL	7.28	<0.001	0.88	8	2.36	1.31	3.36	3.84	27.03
RPL	23.52	<0.001	1.72	16.6	58.76	0.84	3.28	17.08	121.8
NPK-15.15.15	0.62	<0.001	0.68	0.44	16.8	<0.001	0.7	2.06	21.3
NPK- 21.10.10	0.36	<0.001	<0.002	0.36	10.28	0.44	<0.005	2.8	14.24
NPK-23.10.5	7.08	<0.001	2.36	0.38	4.52	2.08	0.32	2.36	19.1

The concentration of lead in TSP was 1.92µg/g. The rest of the samples had concentrations below detection limit (0.001µg/g). During the manufacturing process of phosphate fertilizers, the application of sulphuric acid either separates Pb in phosphogypsum or immobilizes it as insoluble lead sulfate (C.J. Rosen 2002).The concentration of lead in TSP cannot be said to be alarming with regard to plant nutrition owing to the fact that plants do not take-up Pb below 300µg/g in soil.

From the analysis, the concentration of Cd in NPK-21:10:10 was below the detection limit of 0.002µg/g. However, NPK-23:10:5 recorded the highest concentration of 2.36µg/g with MAP recording the lowest concentration of 0.62µg/g. Cadmium is a health issue, its content in food has to be controlled and limited.

The concentration of Zn, in µg/g, in the phosphate-containing fertilizer samples in increasing order was; NPK 21:10:10 (0.36) < NPK 23.10. 5 (0.38) < NPK 15.15.15(0.68) < DAP (0.88) < PKL (8.00) < PKA = MAP (8.12) <TSP (12.52) < RPL (16.60). According to Pantelica et al 1997, a concentration range of 25–200 µg/g for zinc is considered as adequate for most field-grown crops.

The analysis shows that the levels of Cu in phosphatic fertilizer samples were highest in RPL (i.e 17.08 µg/g) and lowest in NPK 15.15.15 (i.e 2.06 µg/g).Copper is a micronutrient and is required in very small quantities for the proper growth of plants. Its content in plants must be at least above 3µg/g for their proper growth while the maximum normal concentration of Cu in plant must be below 50 µg/g (Pantelica *et al,* 1997). The concentration of Cu determined in the various samples ranges between 2.06µg/g for NPK 15.15.15 and 17.08µg/g for RPL. The concentrations of Mn in the samples were profound in TSP, DAP NPK 15.15.15 and NPK 21.10.10 (> 50% of analyzed trace metal composition of the samples). Manganese is known to be a basic macronutrient for plants. The concentration range of <0.001-2.08 µg/g recorded for Mg was far lower than that of 12240 µg/g recorded in Brazil by K. Edgell in 1988.

The increasing order of Co concentration (in µg/g) in the various phosphatic fertilizers were NPK 23:10:5(0.32) < NPK 23:10:5(0.70) < DAP (1.52) < TSP (2.16) < PKA (2.76) < RPL (3.28) <PKL (3.36) < MAP (3.82). This indicates that MAP recorded the highest concentration of Co whereas the lowest was observed in NPK 23:10:5. Cobalt showed varying concentrations among the nine phosphate-containing fertilizers. The concentration of Co in NPK 21:10:10 was however below detection limit (0.005µg/g).

The load of elements in fertilizers varies depending on the geographic location of the phosphate rocks from which the fertilizers were manufactured. The metal load in this case is simple arithmetic addition of the concentration of elements analyzed in the study. The TSP had the highest load (127.36µg/g) with Mn and Cr contributing 72% and 8% respectively (Figure 1). It was only TSP that had 1.92µg/g of lead; the rest had levels below detection limit. Generally the NPKs contained relatively lower levels of metals though cadmium level in NPK 23.10.5 was highest (2.36µg/g).The staggering concentration of metals in the samples indicate that source of elements in the fertilizers is phosphate rocks from which they were manufactured. It is in record that phosphate rocks from Togo contain high levels of cadmium and so likely that fertilizer processed from such mineral would have high levels if good separation methods were not employed.

Most of the metals determined in the fertilizers are micronutrient for plant nutrition. The levels of the elements

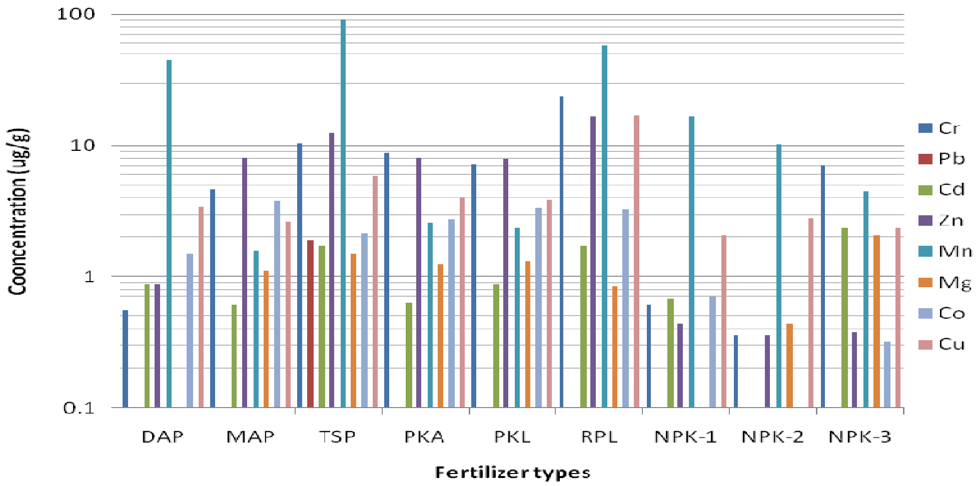

Figure 1. Metal composition in phosphate fertilizer samples from Ghana (*NPK-1, NPK-2, and NPK-3 are NPK 15.15.15, NPK 21:10:10, and NPK 23.10. 5 respectively*).

Table 3. Concentration (μg/g) of some metals in phosphate fertilizers in some countries

Country	Cr	Pb	Cd	Zn	Mn	Mg	Co	Cu	Reference
Brazil	70.5	44.5	4	299		12240		97	Edgell (1988)
Egypt				13.2			385		Abdel-Haleem *et al* (2001)
Israel	56			372			0.37		Pantelica *et al* (1997)
Morocco	291	7	30	345			0.48	22	Pantelica *et al* (1997)
Nigeria	28			59	5716		19.8		Edgell (1988)
North Africa	105	6	60	420				45	Kongshaug *et al* (1992)
Russia	23.3	3	0.1	19			2.05	30	Pantelica *et al* (1997)
Saudi Arabia	176			88				130	Kongshaug *et al* (1992)
Syria	136			269			0.4		Pantelica *et al* (1997)
Tunisia	161			515			0.67		Pantelica *et al* (1997)
Togo	75			143	149		1.2		Edgell (1988)
USA	142	12	11	403	2235		0.44	23	Conceicao *et al* (2006)

in the phosphate fertilizers were within limits required for most field crops. However, one cannot say their application to crops will not cause devastating effects to plant growth. This is because the mineral composition of the soils on which the fertilizers will be applied is not known. Analysis of fertilizers commercially marketed in India, Italy, Australia, New Zealand, England and USA indicated that all Phosphate fertilizers contained significant and varying amounts of heavy metals (Williams and David, 1973; Arora *et al*., 1975; Pezzarossa *et al*., 1990). The elemental concentration range as reported in similar works in other countries is also shown in Table 3.Application of these fertilizers on such soils may aggravate the situation and cause deleterious effects to plants.

Fertilizers are water soluble and easily get contaminated with surface water, groundwater and food. Levels of metals determined in the fertilizer samples (Table 2) exceeded maximum limits of WHO (2004) guideline for potable water. This suggests that fertilizers are potential sources of pollutants in water resources. Kaka et.al (2012), Kortatsi (2003), Pelig-Ba (1991, 2009) reported high levels of some trace metals in groundwater attributable to, among others, agricultural activities such as fertilizer and pesticide/herbicide applications.

The heavy metals in the phosphate fertilizers were not intended for and hence their presence is a nuisance.

The level of the metals in the fertilizers raises concern for also investigating presence of naturally occurring radioactive materials in these phosphate fertilizers. Martin el al. (1999), Al-Masri et al. (2004), Mourad et al. (2009)show that radioactive matter may concentrate in phosphogypsum; a by-product emanating from the fertilizer production reactions.

CONCLUSION

This study aimed at determining the composition and possible sources of metals in the phosphate inorganic fertilizer used in Ghana. When compared to other studies, the inorganic chemical analysis of the sampled fertilizers showed moderate levels of metals. Elements such as Cr, Co, Cu, Cd, Mg, Mn, Pb and Zn were possibly generated by the dry milling process of phosphate rocks in the factories from which the fertilizers were manufactured. The chemical processes within the factory probably participated in the metal loads. Triple Super Phosphate (TSP) had high levels of metals in the fertilizers whilst the NPKs generally had low metal loads. The metals in the fertilizers are impurities since they were not intended for though their concentrations were below maximum limits required for most field crops. The fertilizers are water soluble and therefore are potential sources of metallic pollutants in water resources. We recommend measurement of radioactive materials in these phosphate fertilizers which are sold on markets in Ghana.

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