

Article

Quality control analysis of imported fertilizers used in Ghana: the macronutrients perspective

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Abstract

The main objective of this environmental research was to validate specifications indicated by manufacturers on their fertilizer products. Selected fertilizers types were sampled from five major fertilizer importing companies in Ghana for macronutrient analysis to determine the fertilizer quality. Five analytical techniques including Instrumental Neutron Activation Analysis (INAA), flame photometry, Kjeldahl method for nitrogen analysis and UV-visible spectroscopy were employed to achieve this objective. Two reference materials (IAEA Soil-7 and SRM 1646a Estuarine Sediment) were used to validate the quantitative method employed in the INAA. There was generally good agreements (98% and above) between the measured values and the certified values for the primary macronutrients nitrogen, phosphorous and potassium (N, P and K). However, same could not be said for secondary macronutrients calcium, magnesium and sulphur (Ca, Mg and S). The secondary macronutrient values measured were compared to standard values from the Ministry of Food and Agriculture (MOFA) in cases where they were not certified by the manufacturer. Most of the manufacturers' claims for primary macronutrients were valid. However, most of them fell short of the requirements for secondary macronutrient concentration. There is therefore the need for a good quality control system to undertake periodic quality monitoring of the chemical compositions of fertilizers imported into the country since they may directly or indirectly have impacts on the environment.

Keywords fertilizer; macronutrient; quality control.

1 Introduction

More than 70% of African people live in rural areas and agriculture is by far Africa's most important economic sector (Camara and Heinemann, 2006). It is therefore clear that sustainable increases in agricultural productivity and rural incomes are the basis for broad-based economic growth (Zhang and Zhang, 2007). The central challenge however remains how best to create conditions under which farmers can intensify their production and increasingly link them to markets. Achieving this will help reduce food insecurity on the

continent (Ackah et al., 2011; Sayyed and Wagh, 2011; Tiwari, 2011). However, history shows that no region in the world achieved food security and substantial productivity increases without significantly expanding fertilizer use (FAO, 2006; Zhang and Zhang, 2007). Africa's soils are much depleted and poor compared to other continents and to produce on these soils, fertilizer is one of the major inputs that would be needed to replenish the soil (FAO, 2006).

Replenishing soil fertility is important because soil nutrient is the number-one natural resource in Africa currently being depleted and the nutrient capital of African soils is being mined just like mineral deposits of metals or fossil fuels (FAO, 2006). Smaling (1993) estimates the depletion rates of soil nutrients as 22 Kg/ha/yr for nitrogen (N), 2.5 Kg/ha/yr for phosphorus (P) and 15 Kg/ha/yr for potassium (K) in Africa. The challenges facing agriculture in Ghana are immense, with the large increase in population over the past several few decades, there has been increased pressure on land, and farmers can no longer fallow their fields to regain fertility like they used to. From 1988 to 1990, fertilizer use in Ghana averaged about 11,000 nutrient tons. However the nutrient requirements for the various crops for the same period were estimated to be 90,000 nutrient tons (Mwangi, 1996).

The implications for Ghana are clear: depletion of soil nutrients is becoming a serious constraint to soil fertility and crop productivity. Moreover, the level of depletion suggests that efficient and sustainable use of fertilizers would be required to maintain soil fertility (Mwangi, 1996). The Government of Ghana recognizes the critical role effective application of fertilizers is in increasing agricultural productivity and contributing to the achievement of national food security. Farmers throughout the country must therefore have access to good quality fertilizers at reasonable costs. The fertilizers should be appropriate for the local conditions, effective in use and according to the quality standards as per the label on the packaging. Ghana imports all of its fertilizers and in 2003, imported about 1.43×10^5 metric tons of fertilizer (FAO, 2005). These are mostly mineral or inorganic fertilizers that contain the macro nutrients required by plants.

Personal communications revealed that some Ghanaian farmers have raised concerns about the quality of some of these imported fertilizers they use on their farms. Thus, hinting on the fact that some of the imported fertilizers used in Ghana are not meeting quality standards. At the moment, there is no quality control system in the country dedicated to checking the quality of fertilizers that come into the country. Even though some work have already been done on fertilizers in Ghana (Addo et al., 2006; Appiah et al., 2000; Ofori-Frimpong et al., 1997), the problem of establishing the quality criteria for imported fertilizers has not been dealt with and Ghana is yet to have a quality data base for fertilizers against which any proper quality control work could be done. There is therefore the need for a system to regulate the quality of fertilizers that come into the country to ensure that the fertilizers and crop protection chemicals offered to the farmers are fit for the purpose stated, complies with required specifications and that adequate guidance is given to the farmer on their safe and effective application.

The fertility status of soils in the different regions of Ghana varies considerably due to the nature of soils that are found there (MOFA, 2003). The levels of organic carbon, nitrogen and available phosphorus are generally very low. Table 1 shows the average soil fertility status of some of the regions in Ghana.

Figures are not given for the levels of potassium in table 1 since it is mostly abundant in the soils of Ghana (MOFA, 2003). According to the fertilizer society of South Africa, the primary macronutrients are usually lacking from the soil first because plants use large amounts for their growth and survival. The secondary macronutrients are usually enough in the soil so the use of fertilizers is not always required to introduce them into the soils. Sulphur for instance is usually found in sufficient amounts in the slow decomposition of soil organic matter, hence a good reason for not throwing away grass clippings and leaves (Vlek 1985). Calcium

and magnesium are however associated with lime fertilizers and automatically find their way into the soil when lime fertilizers are applied to treat acidic soils (Vlek, 1985).

Table 1 Average soil fertility status of some regions in Ghana (MOFA, 2003)

Region	Organic Matter (%)	Total Nitrogen (%)	Available P (mg/kg soil)	Available Ca (mg/kg soil)
Ashanti	1.5 - 3.0	0.1 - 0.3	0.1 - 12.0	50 - 100
B-Ahafo	0.3 - 1.7	—	0.1 - 63.4	16 - 140
G. Accra	0.1 - 1.7	0.05 - 0.9	0.8 - 144.0	14 - 470
Northern	0.6 - 2.0	0.02 - 0.05	2.5 - 10.0	45 - 90
Upper East	1.1 - 2.5	0.06 - 0.14	1.8 - 14.8	44 - 152
Upper West	0.5 - 1.3	0.01 - 0.07	2.0 - 7.4	52 - 152
Western	1.0 - 5.7	0.06 - 5.4	0.4 - 11.3	28 - 420

The major importers of inorganic fertilizers into Ghana are private companies (Gerner, 1995). Imported fertilizers can be classified as straight (containing one of the primary nutrients N, P and K), or compound (containing at least two of the three primary nutrients) (Bonsu et al., 1996). The imports of compound fertilizers far exceed the imports of the other fertilizers in Ghana (FAO 2005). Regardless of the name, however, fertilizers are labeled according to the relative amounts of each of these three primary macronutrients by weight (i.e., mass fraction). Thus an NPK 18–51–20 fertilizer grade contains, by weight, 18% elemental nitrogen (N), 22% elemental phosphorus (P), and 16% elemental potassium (K).

Replenishing soil fertility with fertilizers does not just solve the problem. It is therefore important that, the right amount of nutrients are added to the soil since under application of nutrients may slow plant growth and excess fertilizer application may lead to situations such as fertilizer burns in crops resulting in a drying out of the roots and damage or even death of the plant, and further cause problems to the environment (Avoiding fertilizer burns 2010).

2 Materials and Method

2.1 Inclusion criteria for selecting companies for sampling

Fertilizer samples were obtained from five fertilizer importing companies in Accra and Tema metropolises. The criteria for selecting a company for sampling were based on the company being an importer of fertilizer and a major stake holder in the Ghana fertilizer industry. Visual surveys of the companies warehouses were made to make sure the warehouses were accessible for the sampling procedure that was intended to be used in this research. Five companies were thus identified and selected for this research. The companies were given code names A, C, D, G and Y.

2.2 Sample collection

Samples were collected under the authorisation from the Plant Protection and Regulatory Services Directorate (PPRSD) of the Ministry of Food and Agriculture (MOFA), the funding institution for this research. Standard procedures from the Guide to Laboratory Establishment for Plant Nutrient Analysis manual of the Food and Agriculture Organisation (FAO) (Motsara et al., 2008) was used in the sampling. The collection of a representative sample of a fertilizer was an important step in fertilizer analysis and quality control (Motsara et

al. 2008). The method of sample collection depended on the type and source of fertilizer. The sample collection methods can be classified broadly as concerning:

- ✓ Collection from bulk stock in warehouses;
- ✓ Collection from ship hatches or while the ship is being loaded/unloaded;
- ✓ Collection from bagged stock in warehouses of various types;
- ✓ Sample collection from damaged stock.

For this research, samples were collected from bulk stock in warehouses of the companies. The number of samples collected from a given stock will thus depend on the quantity of fertilizer available in stock. In the case of bagged material, stored in smaller quantities (e.g. at importers' warehouses), generally, 1 sample (minimum) is drawn from 10 bags; 2 samples from 100 bags, 6–7 samples from 1 000 bags; and 10 samples from 2000 bags (Motsara et al., 2008). There is no fixed number of samples that can be defined to represent a given quantity. However, it was necessary to ensure that the sample was truly representative of the lot it designates by taking as many samples as possible and at random. In all, twenty three fertilizer samples of five fertilizer types (NPK, Urea, Sulphate of Ammonia (SOA), Triple Super Phosphate (TSP) and Muriate of Potash (MOP)) were taken from the five companies.

About 2 kg each of the fertilizer samples were collected into polyethylene zip-lock bags and labelled (Table 2). The samples were stored under dry conditions under a constant temperature of 25°C. The samples were then taken to the laboratory for preparation and analysis using the various analytical techniques.

Table 2 Coding and Numbering for Fertilizer Samples

Company	Fertilizer Type	Sample Code	Sample number
A	NPK 15-05-30	A-15.05.30	3
	NPK 20-20-20	A-20.20.20	4
C	NPK 15-15-15	C-15.15.15	5
	TSP	C-TSP	9
	UREA	C-UREA	10
	MOP	C-MOP	11
	SOA	C-SOA	12
D	SOA	D-SOA	1
	NPK 15-15-15	D-15.15.15	2
	UREA	D-UREA	8
G	NPK 15-15-15	G-15.15.15	6
	NPK 23-10-05	G-23.10.05	7
	MOP	G-MOP(R)	13
	MOP	G-MOP(W)	15
	UREA	G-UREA	14
	SOA	G-SOA	16
	TSP	G-TSP	17
Y	MOP	Y-MOP	18
	NPK 15-15-15	Y-15.15.15	19
	UREA	Y-UREA	20
	NPK 23-10-05	Y-23.10.05	21
	TSP	Y-TSP	22
	SOA	Y-SOA	23

MOP (R) = Red coloured MOP fertilizer; MOP (W) = White coloured MOP fertilizer

2.3 Sample preparation and analysis

Each sample was thoroughly mix in the lab, and divided into two portions. One portion was sealed and stored away under dry conditions. The other half was pulverised using a mechanical pulveriser and sieved with a 1mm ISO 565 metric sieve to obtain a fine powder from which portions were taken for the various analysis.

2.3.1 Instrumental neutron activation analysis (INAA)

200 mg of each of the pulverised samples was weighed onto a dried polyethylene foil, wrapped, thermally sealed, labelled and placed in a 9.8 cm³ plastic (rabbit) capsule and heat-sealed. Two Reference Materials, IAEA Soil-7 supplied by the International Atomic Energy Agency, Vienna and NIST SRM 1646a Estuarine Sediment were prepared in the same way as the samples. The analytical samples and reference materials were prepared in triplicates. The reference materials were used as a comparator standard for gamma spectrum evaluation using the relative method of standardization for neutron activation analysis (NAA) and to check for the accuracy of the analytical method used. Preliminary studies were then carried out to obtain the right amount of sample to be taken for irradiation. This enabled the development of an irradiation scheme for fertilizers using the INAA technique.

The macronutrients analysed using this technique were Ca, Mg and S. These macronutrients are short-lived radionuclides (have very short half lives), hence samples were irradiated for 15 seconds, delayed for five minutes and counted for ten minutes. The irradiation process involved sending the samples into the Ghana Research Reactor-1 (GHARR-1) via the pneumatic transfer systems operating at 25.0 atmospheres. The samples and standards were then exposed to a neutron flux of $\sim 5.0 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$ at the inner irradiation sites of the Ghana research reactor-1 facility situated at the Ghana Atomic Energy Commission (GAEC). The GHARR-1 is a 30kw tank-in-pool miniature neutron source reactor. It uses 90.2% enriched uranium (U-235)-Aluminium alloy as fuel. It is cooled and moderated with light water and beryllium acts as reflectors (Akaho and Nyarko, 2002).

The samples and standards were placed on a high purity Germanium (HPGe) N-type coaxial detector (model GR 2518- 7500SL) with a resolution of 1.8 keV relative to the 1332.5keV γ - energy line of ⁶⁰Co; a relative efficiency of 25%; and a peak-to Compton ratio of 55. The measurements of the gamma ray spectral intensities were made using a spectroscopy system according to the nuclear data shown on Table 3. The output spectral intensities of the analytical samples and the reference materials were processed by a Multichannel Analyzer (MCA) software and card. The radioisotopes were identified by their peak energies. The area under the photo-peak of the elements was obtained by spectrum fitting. Quantitative analysis was carried out using the comparator method (Ehmann and Vance, 1991).

Table 3 Nuclear Data used to Determine Secondary Macronutrient Concentrations (Filby et al., 1970)

Element	Reaction	Half-life	Energy (KeV)
Ca	⁴⁸ Ca(n, γ) ⁴⁹ Ca	8.7 min	3084.4
Mg	²⁶ Mg(n, γ) ²⁷ Mg	2.58 hours	846.7, 1810.7, 2112
S	³⁷ S(n, γ) ³⁸ S	5.0 min	3102

2.3.2 Kjeldahl method for total nitrogen analysis

Total N includes all forms of inorganic N, such as NH₄⁺, NO₃⁻ and NH₂ (urea). Samples were first tested for

the presence of nitrates. 5grams of the sample was mixed with 25 ml hot water and then filtered using a whatmann's filter paper into a beaker. To one volume (5ml) of this solution, two volumes (10ml) of sulphuric acid free from HNO₃ and oxides of N were added and cooled in a test tube. Few drops (3-5 drops) of concentrated FeSO₄ solution were then added along the side of the test tube so the solutions do not mix. Samples which had nitrates (NO₃⁻) in them showed a purple colour at the junction and few seconds later turned brown.

0.1 gram of the samples containing NO₃⁻ was weighed into a kjeldahl digestion flask and 3grams of Devarda's alloy (consisting of 50% Cu, 45% Al and 5% Zn) added to samples that tested positive for nitrates (NO₃⁻) to reduce the NO₃⁻ into NH₃ in an alkaline condition. One tablet of a kjeldahl catalyst (containing CuSO₄ to accelerate digestion and K₂SO₄ to raise the boiling point of the acid so that loss of acid by volatilization is prevented) was added. 10ml of H₂SO₄ was then added to the sample in the flask and heated in the digestion unit for two hours at a temperature of 350°C till sample was totally digested to convert any organic nitrogen into (NH₄)₂SO₄. The digestion temperature and time is very important since at lower temperatures below 300°C, the digestion may not be complete, while at higher temperatures above 410°C, loss of NH₃ may occur. Distilled water was then added to the digested sample solution and transferred into a 50ml volumetric flask and made to volume. A 5ml aliquot was pipetted from the 50ml solution into a distillation flask and 10mls of 40% sodium hydroxide (NaOH) was added to the solution in the flask. The (NH₄)₂SO₄ in the solution was converted to NH₄OH.

5 ml of the resulting solution was distilled off into a receiving flask containing 5ml of 2% boric acid (H₃BO₃) using methylene blue - methyl red indicator until the purple colour of the boric acid changes to blue. At this stage, it is evidence that NH₃ has been trapped.

The blue boric acid- ammonia solution was then titrated against 0.01M HCl solution until the colour of the boric acid solution changes back to purple. The volume was recorded and the process repeated one more time. The mean titre was calculated and used to determine the total kjeldahl nitrogen (TKN) as follows:

$$\% N = \frac{N \times \text{titre} \times 0.014 \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot taken}}$$

where N= molarity of HCl = 0.01; Volume of extract = 50ml; Weight of sample = 0.1 grams; Aliquot taken = 5ml; 1ml of 0.01M HCl = 0.014 grams.

The reaction equations are as follows

Organic N + H₂SO₄ $\xrightarrow{\text{catalyst}}$ (NH₄)₂SO₄ + H₂O + CO₂ + other sample matrix by-products.

(NH₄)₂SO_{4(aq)} + 2NaOH_(aq) $\xrightarrow{\text{heat}}$ 2NH_{3(g)} + Na₂SO_{4(aq)} + 2H₂O_(l)

NH_{3(g)} + H₂O_(l) \longrightarrow NH₄OH_(aq)

4H₃BO_{3(aq)} + 2NH₄OH_(aq) \longrightarrow (NH₄)₂B₂O_{7(aq)} + 7H₂O_(l)

(NH₄)₂B₄O_{7(aq)} + 3H₂O_(l) \longleftrightarrow 2H₃BO_{3(aq)} + 2NH₄BO_{2(aq)}

2NH₄BO_{2(aq)} + 4H₂O_(l) \longleftrightarrow 2H₃BO_{3(aq)} + 2NH₄OH_(aq)

2.3.3 Determination of phosphorous (P₂O₅) using the UV-Visible spectrophotometer

This technique is based on the principle of colourimetry. Ultraviolet-visible spectroscopy refers to an absorption spectroscopy in the UV-Visible spectral region (Harris, 1982). This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The technique is base on the principle of the

Beer-Lambert law (Harris, 1982).

$$A = -\log_{10}(I/I_0) = \epsilon \cdot c \cdot L$$

$$A = -\log(\%T / 100\%)$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L is the path length through the sample, and C is the concentration of the absorbing species.

Stock solutions A and B were first prepared to be used later in the analysis. Their preparations were as follows:

Stock solution A; Prepared by diluting 140ml of conc. H_2SO_4 with distilled water to 1 litre; 12 grams of ammonium molybdate was weighed and dissolve in distilled water to 250ml in a 250ml volumetric flask; 0.2908gram of Antimony potassium tartrate was weighed and dissolved in 100ml of distilled water; the three solutions were then mixed together and made to a volume of 2 litres with distilled water to represent stock solution A.

Stock solution B; Prepared by dissolving 1.056grams of Ascorbic acid with the whole of stock solution A and mixed thoroughly.

0.1gram of the sample was weighed into a digestion tube, 20ml of HNO_3 and 30ml of perchloric acid were added to the sample in a ratio of 1:1.5. The resulting mixture was heated in a microwave oven at a temperature of $350^\circ C$ for two hours. The digested sample was allowed to cool and transferred to a 250ml volumetric flask and made to volume with distilled water. An aliquot of 2ml was taken from the 250ml solution into a 50 ml volumetric flask and 10 ml of distilled water was added. A drop of paranitrophenol solution was added and drops of NH_3 solution was added until the solution turned yellow; at this point a neutralization point had been reached.

8ml of stock solution B was then added for colour development which was read with a UV/visible spectrophotometer at a wavelength of 712nm.

A blank and a standard were prepared in the same way as the sample just that the blank did not contain the analyte of interest.

The reading from the blank was used to eliminate background readings.

The calculation for determining phosphorous (P) was:

$$\% P = \frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot} \times 10^6}$$

The above calculation gave the concentration of the phosphorous in its elemental form. In order to determine the value of phosphorous in the P_2O_5 form, a conversion factor of 2.29 was used, thus:

$$\% P_2O_5 = \left(\frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times \text{aliquot} \times 10^6} \right) \times 2.29$$

where Volume of extract = 250ml; Aliquot= 2ml; Weight of sample = 0.1gram; Reading = reading from the UV/Visible spectrophotometer.

2.3.4 Determination of potassium (K_2O) using the flame photometer

Flame photometry is an atomic emission method for the routine detection of metal salts, principally Na, K, Li,

Ca, and Ba (Willard et al., 1981).

0.1gram of the sample was weighed into a digestion tube. 20ml of conc. HNO_3 and 30ml of perchloric acid were added to the sample, covered and heated in the microwave oven for up to 2 hours at a temperature of 340°C . The solution was cooled after digestion and transferred into a 250ml volumetric flask and made up to volume with distilled water. A potassium standard and blank solution were prepared in the same way. The solutions were taken to the flame photometer lab of the crop science department laboratory to be read.

The readings were used to calculate the percent K_2O in the sample through the equation:

$$\% \text{ K} = \frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times 10^6}$$

The above calculation gave the concentration of potassium in it elemental K form. In order to calculate potassium in the oxide K_2O form, a conversion factor of 1.2 was used. Thus giving

$$\% \text{ K}_2\text{O} = \left(\frac{\text{Reading} \times \text{volume of extract} \times 100}{\text{Weight of sample} \times 10^6} \right) \times 1.2$$

3 Results and Discussions

3.1 Validation of analytical techniques

Method validation is a vital step in any analytical procedure. The methods used in this research were subjected to validation using standard reference materials. In order to evaluate the reliability of measurements in terms of accuracy and precision using the Instrumental Neutron Activation Analysis (INAA), three replicate analysis of the reference materials namely IAEA Soil-7 supplied by the International Atomic Energy Agency, Vienna and NIST SRM 1646a Estuarine Sediment were analysed. The mean concentrations of the secondary macronutrients Mg, Ca and S were compared with the certified concentrations (Fig. 1). The variations in the ratio of the measured concentrations to the certified concentrations are shown in Fig. 2. A variation in the ratios of 0.97, 0.98 and 1.01 for Mg, Ca and S therefore indicates favourable analytical results.

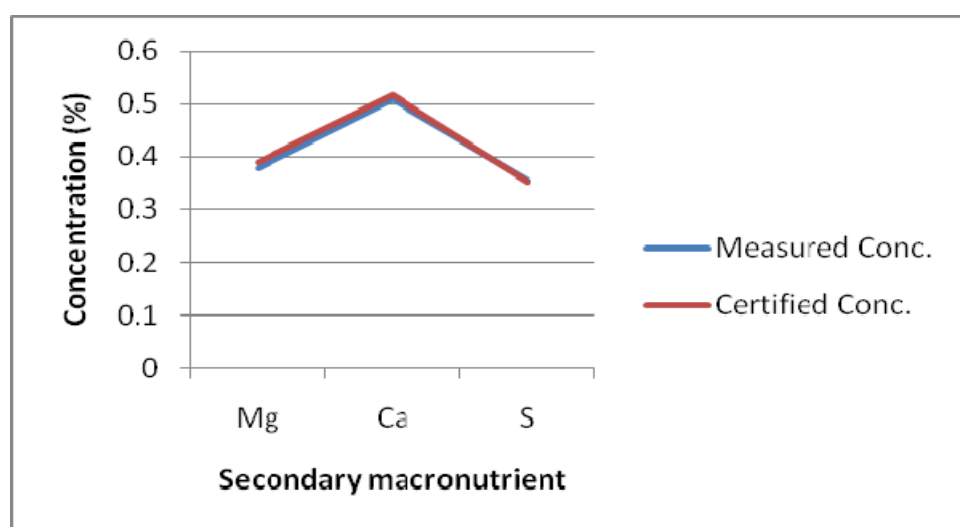


Fig. 1 Validation results of the INAA method using the NIST SRM 1646a Estuarine Sediment for Short lived radionuclides (secondary macronutrients)

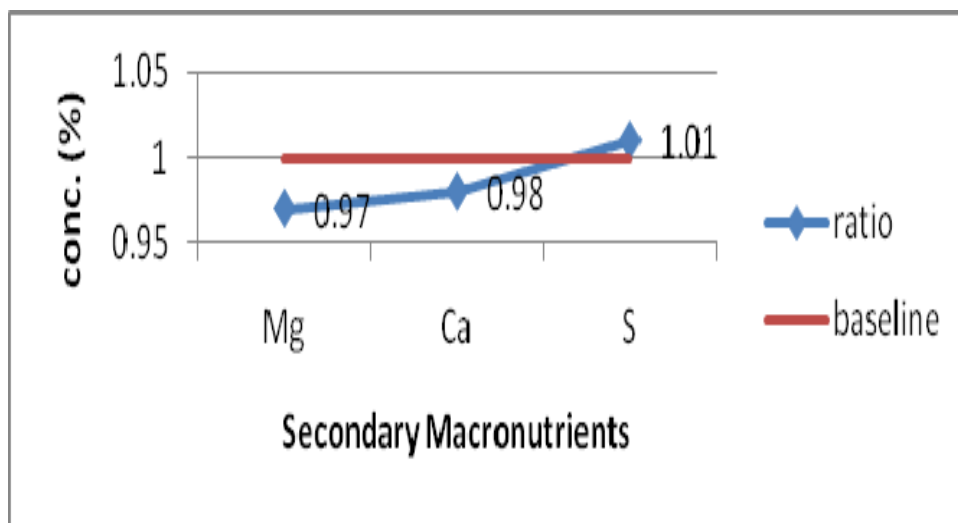


Fig. 2 Variation of measured values to the certified values (SRM 1646a Estuarine Sediment) for short-lived radionuclides (secondary macronutrients)

3.2 Macronutrients

The statistical summary of the results for the analysis for both primary and secondary macronutrients in the various types of fertilizers are shown in Tables 6,7,8,9 and 10 below. Table 4 presents the specification for macronutrients concentrations for the manufacture of fertilizers as indicated by Food and Agriculture Organization of the United Nations.

Table 4 Specification for the Manufacture of Fertilizers in terms of Macronutrients

Fertilizer Type	Specification
Urea	Total nitrogen content by weight: minimum 46%
SOA	Total nitrogen content by weight: minimum 20%
	Sulphur as S by weight : minimum 23%
TSP	Total Phosphates (as P ₂ O ₅) by weight : minimum 46%
MOP	Water soluble potash content (as K ₂ O) by weight: minimum 60%
NPK-15.15.15	Total nitrogen content by weight: minimum 15%
	Total Phosphates (as P ₂ O ₅) by weight : minimum 15%
	Water soluble potash content (as K ₂ O) by weight: minimum 15%
NPK-20.20.20	Total nitrogen content by weight: minimum 20%
	Total Phosphates (as P ₂ O ₅) by weight : minimum 20%
	Water soluble potash content (as K ₂ O) by weight: minimum 20%
NPK- 15.05.30	Total nitrogen content by weight: minimum 15%
	Total Phosphates (as P ₂ O ₅) by weight : minimum 05%
	Water soluble potash content (as K ₂ O) by weight: minimum 30%
NPK- 23.10.05	Total nitrogen content by weight: minimum 23%
	Total Phosphates (as P ₂ O ₅) by weight : minimum 10%
	Water soluble potash content (as K ₂ O) by weight: minimum 05%

The macronutrients N, P, K, Mg, Ca and S were detected in 100 % of the NPK fertilizer samples. The concentrations of N, P and K in the NPK fertilizers were within the certified limits indicated by the manufactures for each of the samples (Fig. 3).

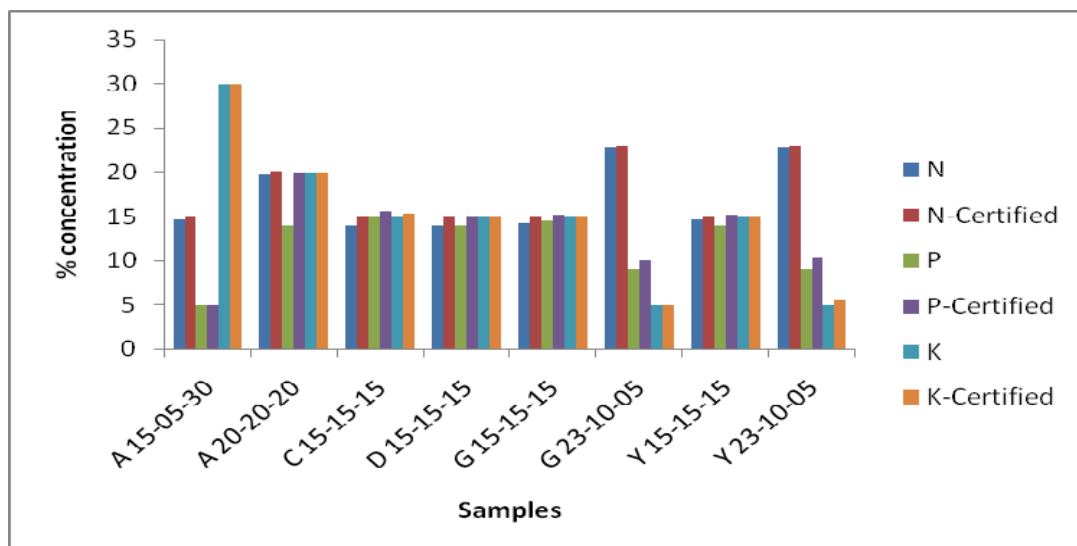


Fig. 3 Comparison of measured concentrations of primary macronutrients in NPK samples with certified concentrations

However, the concentrations of P in the NPK samples; G-23.10.05 and Y-23.10.05 were less than the certified concentrations by 10 % and 13.46 % respectively. The levels of Mg in all the NPK samples were marginally below the recommended minimum limit of 0.5 % set by the MOFA, Ghana. Table 5 below presents the minimum limits of secondary macro nutrients in fertilizers.

Table 5 Plant Nutrient Guaranteed Minimum of the Ministry of Food and Agriculture (MOFA 2009)

Element	Minimum Percent
Calcium (Ca)	1.0000
Magnesium (Mg)	0.5000
Sulfur (S)	1.0000

The concentrations of Ca in the NPK samples were extremely higher than the minimum limit of 1.0 %. Apart from A-15.05.30 and C-15.15.15 which measured favourable levels of Ca compared to the minimum recommended concentration, 75 % of the samples were far in excess. Notably, G-15.15.15 and G-23.10.05 measured Ca concentrations of 9.3 % and 14.2 % respectively. The concentrations of macronutrients in the NPK fertilizer types are shown on Table 6.

Only 37.5 % of the samples of NPK measured concentrations of Sulphur. The levels of Sulphur in 62.5% of the samples were thus below detection limit. Among the samples that measured concentrations of S, only G-15.15.15 measured a concentration of 0.056% which is below the minimum limit of 1.0 %. The concentrations

of S in the samples; G-23.10.05 and Y-23.10.05 were 3.2 % and 3.01 % respectively, far in excess of the minimum limit.

Table 6 Macronutrient Concentrations (%) in NPK Fertilizers

Sample code	Primary Macronutrients						Secondary Macronutrients					
	N	N-Certified	P	P-Certified	K	K-Certified	Mg	Mg-Minimum	Ca	Ca-Minimum	S	S-Minimum
A 15-05-30	14.6 ± 0.5	15	4.9 ± 0.2	5	30.0 ± 0.3	30	0.007 ± 0.002	0.5000	0.8 ± 0.4	1.0000	ND	1.0000
A 20-20-20	19.8 ± 0.3	20.1	14.0 ± 4.2	20	20.0 ± 1.0	20	0.001 ± 0.007	0.5000	3.3 ± 0.92	1.0000	ND	1.0000
C 15-15-15	14.0 ± 1.3	15	15.0 ± 0.8	15.6	15.0 ± 0.5	15.3	0.002 ± 0.009	0.5000	±0.02 ± 3.8	1.0000	ND	1.0000
D 15-15-15	14.0 ± 1.2	15	14.0 ± 1.2	15	15.0 ± 0.4	15	0.003 ± 0.007	0.5000	0.9 ± 9.3	1.0000	ND	1.0000
G 15-15-15	14.2 ± 1.1	15	14.5 ± 1.1	15.2	15.0 ± 0.5	15.1	0.002 ± 0.006	0.5000	2.2 ± 14.2	1.0000	0.002 ± 3.2	1.0000
G 23-10-05	22.8 ± 0.4	23	9.0 ± 0.9	10	5.0 ± 0.4	4.9	0.002 ± 0.006	0.5000	2.5 ± 3.8	1.0000	0.2 ± 3.8	1.0000
Y 15-15-15	14.6 ± 0.5	15	14.0 ± 1.3	15.2	15.0 ± 0.4	15.1	0.001 ± 0.006	0.5000	0.9 ± 0.9	1.0000	ND	1.0000
Y 23-10-05	22.8 ± 0.5	23	9.0 ± 1.2	10.4	5.0 ± 0.7	5.5	0.006 ± 0.001	0.5000	1.37 ± 0.02	1.0000	3.01 ± 0.02	1.0000

Table 7 Macronutrient Concentrations (%) in Triple Super Phosphate (TSP) Fertilizers

Sample code	Primary Macronutrient		Secondary Macronutrient					
	P	P-Certified	Mg	Mg-Minimum	Ca	Ca-Minimum	S	S-Minimum
C-TSP	46.0 ± 1.1	47	0.007 ± 0.002	0.5000	3.8 ± 0.9	1.0000	ND	1.0000
G-TSP	44.0 ± 1.8	46.4	0.005 ± 0.002	0.5000	2.6 ± 0.8	1.0000	0.21 ± 0.02	1.0000
Y-TSP	46.2 ± 0.9	47	0.006 ± 0.002	0.5000	2.95 ± 0.05	1.0000	ND	1.0000

Table 7 presents the macronutrient concentrations in samples of triple super phosphate (TSP) fertilizers. Concentrations of P, Mg and Ca were measured in all the TSP samples. The concentration of S was however measured in only G-TSP. The concentration of S, 0.21 % measured in G-TSP was far below the minimum limit of 1.0 % (MOFA 2009). Similar to the NPK samples, the concentration of P in all the TSP samples were favourable to the certified concentrations whiles the concentration of Mg in all the TSP samples fell marginally below the minimum limit of 1.0 %. The levels of Ca in the TSP samples were all in excess of the minimum limit of 1.0 %. The concentrations of Ca in the TSP samples ranged between 2.6-3.8 %.

The concentrations of N, Mg, Ca and S were measured in all the samples of Sulphate of ammonia (SOA). The concentrations of macronutrients in SOA fertilizer samples are shown in Table 8 below.

The samples measured concentrations of N within the respective certified limits (Table 8). The levels of Mg were however below the minimum limit of 0.5 %, ranging from 0.00008 % to 0.0003 %. Thus the concentrations of Mg in all the fertilizers analysed were lesser than the minimum limit. Levels of Ca and S in the SOA samples were all above the MOFA, Ghana minimum limits of 1.0 %. The concentrations of Ca and S in the SOA samples ranged from 1.9-10.1 % and 23.1-25.2 % respectively.

Table 8 Macronutrient Concentrations (%) in Sulphate of Ammonia (SOA) Fertilizers

Sample code	Primary Macronutrient		Secondary Macronutrient					
	N	N-Certified	Mg	Mg-Minimum	Ca	Ca-Minimum	S	S-Minimum
C-SOA	20.5 ±	21.2	0.0002 ±	0.5000	1.9 ± 0.6	1.0000	23.8 ±	1.0000
	0.6		0.0001				0.6	
D-SOA	20.6 ±	21	0.00008 ±	0.5000	5.3 ± 0.9	1.0000	24.6 ±	1.0000
	0.7		0.00001				1.1	
G-SOA	21.0 ±	21.02	0.0003 ±	0.5000	5.9 ± 1.0	1.0000	25.2 ±	1.0000
	0.1		0.0002				3.1	
Y-SOA	20.8 ±	21	0.0003 ±	0.5000	10.1 ±	1.0000	23.1 ±	1.0000
	0.5		0.0001		1.9		1.1	

In the Urea samples, the levels of S were below detection limit. Mg measured concentrations below the recommended minimum limit of 0.5 % while the concentrations of N were within the certified concentrations in all the urea samples. Only one urea sample, Y-urea measured a concentration, 0.82 % favourable to the minimum level of 1.0 % for Ca. The concentration of Ca in 75% of the urea samples were far in excess of the minimum limit, ranging between 5.1 % and 10.3 %. The concentrations of macronutrients in the urea samples are shown on Table 9.

Table 9 Macronutrient Concentrations (%) in Urea Fertilizers

Sample code	Primary Macronutrient		Secondary Macronutrient					
	N	N-Certified	Mg	Mg-Minimum	Ca	Ca-Minimum	S	S-Minimum
C-Urea	45.0 ±	46.7	0.0003 ±	0.5000	5.1 ± 0.7	1.0000	ND	1.0000
	2.0		0.0001					
D-Urea	45.6 ±	46	0.00006 ±	0.5000	2.8	1.0000	ND	1.0000
	0.6		0.00002					
G-Urea	45.8 ±	46.3	0.00006 ±	0.5000	1.1	1.0000	ND	1.0000
	0.6		0.00002					
Y-Urea	45.4 ±	46.3	0.0005 ±	0.5000	0.01	1.0000	ND	1.0000
	1.1		0.0002					

Table 10 Macronutrient Concentrations (%) in Potassium (MOP) Fertilizers

Sample code	Primary Macronutrient		Secondary Macronutrient					
	K	K-Certified	Mg	Mg-Minimum	Ca	Ca-Minimum	S	S-Minimum
C-MOP	59.0 ±	60.5	0.006 ±	0.5000	0.01	1.0000	ND	1.0000
	0.9		0.002					
G-MOP	60.2 ±	61.1	0.003 ±	0.5000	0.05	1.0000	ND	1.0000
	0.7		0.001					
Y-MOP	59.6 ±	60	0.003 ±	0.5000	0.07	1.0000	ND	1.0000
	0.6		0.001					

Table 10 presents the concentrations of macronutrients in potassium fertilizers (MOP). Concentrations of S in all the MOP samples were below detection limit while the concentrations of K, ranging from 59 % to 60.2 % were within the certified concentrations. Mg and Ca concentrations measured in the MOP samples were far below the MOFA recommended minimum limits.

4 Conclusions and Recommendations

4.1 Conclusions

The results of this study indicate that most of the fertilizer samples in the country have macronutrient concentrations within recommended limits. Interestingly, all the fertilizer samples measured primary macronutrients within their respective certified concentrations. Also, all the samples measured very low concentrations of Mg. For the secondary macronutrients, Ca measured low concentrations in MOP while extremely high concentrations were measured in NPK, TSP, SOA and Urea compared to the MOFA, Ghana minimum limit. The level of S was highest in SOA samples, ranging from 23.1 5% to 25.2 %. This was to be expected as specifications for SOA fertilizers indicate sulfur concentration by manufacturers to be a minimum of 23%. In the NPK samples, 25 % of the samples measured higher concentrations of S beyond the minimum limit.

4.2 Recommendations

Further investigations need to be carried out periodically to ensure strict compliance of label specifications and recommended limits in all the fertilizer samples. Investigations should be undertaken into imported fertilizers at retail points since most Ghanaian farmers obtain fertilizers at low quantities from the retailers. These shops could be an easy source of fertilizer adulteration by greedy business men.

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