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Estimation of some metal and quality profile of Cocoa beans in Ghana

Lowor S. T[1],* and Osae Shiloh[2]
[1]Cocoa Research Institute of Ghana, P.O Box 8, Tafo–Akim, Ghana.
[2]National Nuclear Research Institute, Ghana Atomic Energy Commission, Kwabenya.

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ABSTRACT

Toxic heavy metal monitoring in the environment and food is a key requirement for protection against the hazards of metal toxicity. The concentrations of heavy metals (Mercury, Copper and Cadmium) and other elements (Vanadium, Magnesium, Manganese, Calcium and Chloride) in cocoa beans from 73 district representing six of the seven cocoa regions for the 2011/2012 light crop year were analyzed using Neutron Activation procedures to look at the distribution of metals, especially heavy metals in the beans meant for export. Certain basic quality parameters such as pH, moisture and percentage fat content were also measured. Analysis of cocoa beans yielded the following results; Calcium (Ca; 2155 -5863, average 3443.20 mg kg^{-1}) showed the highest concentration, followed by Magnesium (Mg; 2147 to 4601 mg kg^{-1}, average 3227.02 mg kg^{-1}) and Aluminium (Al; 32.86 -147.40, average 54.32 mg kg^{-1}). Manganese (Mn) was also found to range between 19.66 -50.01; average 35.40 mg kg^{-1}. Vanadium and chloride were on the average 0.20 and 82.37 mg kg^{-1} respectively. Amongst the heavy metals analysed, Cadmium (Cd) was in the range of <0.01 and 48.30 µg kg^{-1}, well below the proposed MRL of 0.6 mg Kg^{-1} whereas mercury was below 0.01µg kg^{-1}, the detection limit of the NAA method used. Copper (Cu) was in the range of 10.04–26.76 mg kg^{-1} in the beans analysed. Fat content of the beans were higher than 52.63% with a pH range of 4.52-5.58, typical of Ghana's cocoa. The results showed that heavy metal concentrations in the beans are generally low with accompanying high quality indicators. Although levels of these heavy metals are very low, a potential danger may emerge in the future depending on the management of soil pollution since soil-to-plant transfer of heavy metals is a major pathway to product pollution.

Introduction

Cocoa (*Theobroma cacao*) from Cameroon, Côte d'Ivoire, Ghana, Nigeria and Togo accounts for approximately 74% of the world's production. In Ghana, it contributes approximately 28% of the foreign exchange earnings and is the main source of income to millions of farmers in Ghana. Chocolates and other candies are widely consumed as products obtained from roasted seeds, commonly called cocoa beans, of the cocoa plant. The popularity of cocoa processed into chocolates and other beverages is ever increasing because of the recent acclaimed good health benefits derived from the antioxidants and other chemicals helping in reducing Blood pressure and Cholesterol levels (Keen *et al*., 2005; Manach *et al*., 2004; Hollenberg, 2009).

Consumption of cocoa and its products however is highest in Europe, the leading importer, followed by NAFTA countries, Asia and the Pacific. Cocoa is appreciated not only for its flavor but the resulting higher dietary flavonoids content per serving compared to teas or red wine (Lee *et al*. 2003). Post harvest processing of cocoa to a large extent influences the final unique quality of the beans which constitutes the raw material of importance to industries manufacturing semi-finished products (e.g. cocoa mass) and finished products intended directly for consumption such as chocolate powder, chocolate bar and chocolate confectionery. Unfortunately a lot of contaminants and off flavour notes are also likely to be introduced into the cocoa during the pre and post harvesting/ primary processing stage.

Cocoa beans are expected to meet sanitary and Phytosanitary standards to ensure consumer safety. In this direction, more stringent international standards are being set to regulate the levels of heavy metal contaminants such as cadmium in cocoa beans. Ghana has an obligation to meet such standards if it is to maintain market access with its cocoa beans. Elements like Fe, Zn and Cu play significant roles in health (EU 2007) for which maximum permitted levels of 0.2-25 mg kg^{-1}, 2-50 mg kg^{-1} and 15mg kg^{-1} respectively exists for various foods. Human health is threatened by heavy metals associated with exposure to lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) and some trace elements (Srogi, 2006) with Permissible tolerable weekly intakes (PTWI) of Pb, Cd and Hg set at 25, 7 and 1.6 µg kg^{-1} of body weight, respectively (WHO 1989; 1993). The maximum permitted level of Arsenic in foods is 1 mg kg^{-1} (WHO, 1989). The presence of trace elements in foods can depend on plant variety, storage and processing conditions, added ingredients composition, environmental pollution, fertilizer and pesticide application and climatic conditions (Torelm and Danielsson, 1998; DosSantos *et al* 2005; Pedro *et al*, 2006). Cocoa production has been recognized as an effective tool to alleviate the poverty that is prevailing in the producing countries. However, the new regulations by the EU, the USA and Japan have the potential, if not properly adhered to, of affecting cocoa trade and consequently depriving cocoa

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Tele:
E-mail addresses: slowor2@yahoo.co.uk

smallholder farmers and governments of the producing countries, of the much needed revenues. This will harm the welfare of the farmers and affect the countries' poverty alleviation programmes.

This fact together with the necessity of more data related to the safety of cocoa beans, in particular, of heavy metal profile, such as Cadmium, led to this study to determine the content of cadmium and copper in whole beans of cocoa produced in the 2012 light crop season in order to understand the impact of the cocoa growing soils on the levels of cadmium and other elements in cocoa.

Materials and methods

Samples

A total of 162 cocoa bean samples were analyzed. These samples were taken from the six cocoa growing regions which are further divided into 73 cocoa districts. Variation in number of samples taken from a cocoa region was based on the number of districts and licensed buying companies in the region.

Neutron Activation Analysis

Sample preparations for NAA

Each sample was blended into smooth powder using Waring 8011ES blender model HGB2WTS3. 200mg of each sample was weighed (4 replicate each) and wrapped in a transparent polyethylene film. The samples were further encapsulated into irradiation capsules and heat sealed for neutron activation (irradiation).

Sample irradiation and counting

The samples and the Certified References Materials (for both calibrations and validations) were irradiated in the Ghana Research Reactor-1 (GHARR-1) at the National Nuclear Research Center (NNRC), Ghana Atomic Energy Commission.

GHARR-1 is operated at a half full power of 15KW which generate a thermal flux of $5\text{x}10^{11}\text{n-cm}^{-2}\text{s}^{-1}$. Two separate irradiations were performed based on the element of interest and the half life of the radionuclide; two minutes and 1 hour irradiation times were chosen for short lived radionuclide(s) and relatively medium lived radionuclide(s) respectively. The activated samples (short irradiation) were delayed within a period of 2-5 minutes and counted for 10 minutes in order to identify the short lived radionuclide (elements). In order to identify the Medium lived radionuclide(s), the activated samples were delayed within 24hours and counted for 10 minutes. Radioactivity measurement of induced radionuclide was performed by a PC-based γ-ray spectrometry set-up which consisted of an N-type HpGe detector (coaxial type) coupled to a computer based multi-channel analyzer (MCA) via electronic modules. The relative efficiency of the detector is 40%. Its energy resolution is 1.8keV at a γ-ray energy of 1332keV of ^{60}Co. The data acquisition and identification of γ-rays of product radionuclide were identified by their γ-ray energy (ies) via ORTEC MAESTRO-32. Quantitative analysis was done via relative comparator method. The peak area determinations, processing and concentration calculation were done by multipurpose γ-ray spectrum analysis software; winSPAN-2010 version 2.10.

winSPAN (spectrum evaluation software) calibration

Application of the relative comparator method requires Standard Reference Materials (SRM's) or Certified Reference Materials (CRM's) for element(s) of interest. NIST standard reference material 1547 (peach leaves) and NBS standard reference materials 1572 (citrus leaves) were used alternatively for calibration and validations where appropriate. The purpose of this alternate calibrations and validations was to ensure that, only high photo peaks (well defined peaks and of good statistics) were used for calibrations in order to obtain good results (calibration factors).

However, because of low concentration of As, Cd and Hg, sensitivity method was used for quantification. This required a separate standard solution of As, Cd and Mercury. The net counts under the full energy peak of both samples and standards were integrated manually from the Ortec Maestro software. The principle for elemental quantification based on sensitivity method is as shown below;

Definition of terms:

X (µg) - Mass of irradiated pure standard element

W (g) - Mass of irradiated Sample

Y Counts - Net Counts under the full peak of the Standard

Z Counts - Net Counts of the EOI under the full peak in the sample.

EOI - Element Of Interest

Note µg g⁻¹ = mg kg⁻¹ = ppm= 1000ug kg⁻¹

$$\text{Sensitivity} = \frac{Y\ Counts}{X\mu g} \quad (1)$$

$$\text{Amount of EOI of Interest} = \frac{z\ counts}{Sensitivity} \quad (2)$$

$$= \frac{ZCounts}{\frac{\text{Y Counts}}{X\mu\text{g}}}$$

$$= \frac{ZCounts \times X\mu\text{g}}{\text{Y Counts}}$$

$$\text{Concentration} = \frac{Amount\ of\ EOI\ of\ interest}{Mass\ of\ sample\ W\ g}\ \text{(ppm)} \quad (3)$$

$$= \frac{ZCounts \times X\mu\text{g}}{\text{Y Counts} \times W\text{g}}\ (\mu\text{g g}^{-1})$$

Acidity (pH)

Ground nibs (10g) were homogenised in 90 mL of hot distilled water. The mixture was filtered withWhatmanNo.4 filter paper and cooled to 25 ◦C. The pH of the resulting filtrate was measured using a pH meter (SevenEasy mettler-Toledo AG, Schwerzenbach, Switzerland) that had been calibrated with buffers at pH 4 and 7. This measurement was performed in triplicate (Jinap *et al* 1994).

Titratable acidity (TA)

The nib titratable acidity was determined according to the AOAC. 25mL of the aliquot collected for pH determination was titrated against 0.1 M NaOH to pH 8.1 using a pH meter (SevenEasy mettler-Toledo AG, Schwerzenbach, Switzerland). Measurements were performed in triplicate.

Fat content

Weighed amounts (10g) of ground seeds were placed in a cellulose extraction thimble and oil soxhlet-extracted with petroleum ether (40-60°C) for 8 h (AOAC, 2005). The residues were ground to a fine powder and extracted for 4 h with fresh solvent. Petroleum ether was removed in a rotary evaporator (Büchi rotavapor EL 131, Switzerland) at 30°C and the oils dried to constant weight at 100°C. The results were expressed as a percentage of dry matter (% DM).

Table 1. Cadmium and Mercury contents ($\mu g\ Kg^{-1}$) of dried cocoa beans from six cocoa regions in the 2011/2012 cocoa season. Sample size varied from 9 to 62 depending on the size of the cocoa region

	Cd levels ($\mu g\ Kg^{-1}$) in beans by Cocoa Regions						Hg levels ($\mu g\ Kg^{-1}$) in cocoa beans by Cocoa Regions					
Districts	W/ S	W/ N	ASH	CENT	EST	B/A	W/ S	W/ N	ASH	CENT	EST	B/A
1	11.40	<0.01	<0.01	17.89	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2	9.41	<0.01	4.24	9.77	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
3	13.09	<0.01	8.86	11.25	19.41	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
4	<0.01	28.39	8.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
5	2.79	24.27	<0.01	7.93	14.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
6	3.51	<0.01	8.30	2.18	6.55	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
7	12.37	<0.01	13.47	7.23	24.38	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
8	14.81	37.80	9.59	<0.01	19.90	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
9	21.84	<0.01	18.08	<0.01	14.07	40.96	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
10	7.04	9.51	2.02	4.61	23.09	-	<0.01	<0.01	<0.01	<0.01	<0.01	-
11	32.04	6.82	17.89	3.15	<0.01	-	<0.01	<0.01	<0.01	<0.01	<0.01	-
12	48.30	3.13	<0.01	3.39	-	-	<0.01	<0.01	<0.01	<0.01	-	-
13	24.15	19.00	<0.01	<0.01	-	-	<0.01	<0.01	<0.01	<0.01	-	-
14	12.86	<0.01	<0.01	<0.01	-	-	<0.01	<0.01	<0.01	<0.01	-	-
15	6.27	2.95	-	-	-	-	<0.01	<0.01	-	-	-	-
16	6.82	4.98	-	-	-	-	<0.01	<0.01	-	-	-	-
17	5.53	<0.01	-	-	-	-	<0.01	<0.01	-	-	-	-
18	5.54	<0.01	-	-	-	-	<0.01	<0.01	-	-	-	-
19	<0.01	-	-	-	-	-	<0.01	-	-	-	-	-
20	<0.01	-	-	-	-	-	<0.01	-	-	-	-	-
21	<0.01	-	-	-	-	-	<0.01	-	-	-	-	-
22	<0.01	-	-	-	-	-	<0.01	-	-	-	-	-
Range	<0.01- 48.30	<0.01-37.80	<0.01 -18.08	<0.01-17.89	<0.01 – 24.38	<0.01 – 40.96	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

< and - represents values below detection limit of NAA and no districts for sampling respectively. W/S-Western South, W/N- Western North, ASH-Ashanti, CENT- Central, EST- Eastern, B/A- Brong Ahafo Region

Table 2: Mean Copper and Magnesium concentration in cocoa beans ($mg\ kg^{-1}$) from six cocoa growing regions in Ghana determined by INAA method

REGION	**Cu**	**Range**	**Mg**	**Range**
Ashanti	19.41	11.22 - 26.76	3115.30	2147 – 3728
Brong Ahafo	18.49	15.69 - 24.21	3178.20	2786 – 3481
Central	18.87	13.28 - 23.30	3167.40	2471 – 3464
Eastern	15.21	12.17 - 18.96	3255.90	2960 – 3495
Western North	18.14	4.57 - 25.93	3387.90	2519 – 4601
Western South	17.11	10.04 - 22.87	3257.40	2220 – 4405
Mean	19.37		3227.02	
Lsd	ns		ns	

ns – not significantly different at $p< 0.05$

Table 3: Mean Calcium, Aluminium and Chloride concentration in cocoa beans ($mg\ kg^{-1}$) from six cocoa growing regions in Ghana determined by INAA method

REGION	**Ca**	**Range**	**Cl**	**Range**	**Al**	**Range**
Ashanti	3207.40	2399 - 5031	76.64	53.17- 106.90	53.98	34.29 -85.86
Brong Ahafo	3837.20	3382 - 4523	84.67	33.79 - 135.80	63.90	35.48 -144.60
Central	3391.00	2155 - 5863	97.14	58.10 - 183.30	45.85	32.86 - 62.83
Eastern	3585.00	2470 - 4788	79.05	55.03 -113.60	54.45	35.03 -105.50
Western North	3461.50	2234 - 4823	79.23	34.15 -157.80	56.77	35.05 - 95.12
Western South	3177.10	2178 - 5805	77.51	19.30 - 230.30	50.98	30.36 -147.40
Mean	3443.20		82.37		54.32	
Lsd	n.s		n.s		ns	

ns – not significantly different at $p< 0.05$

Table 4: Mean manganese and vanadium concentration in cocoa beans (mg kg^{-1}) from six cocoa growing regions in Ghana determined by INAA method

REGION	Mn	Range	V	Range
Ashanti	34.13	19.66 - 48.66	0.20	0.05 - 0.25
Brong Ahafo	32.60	26.33 - 39.90	0.23	0.12 - 0.39
Central	35.70	25.66 - 50.01	0.18	0.09 - 0.27
Eastern	32.94	27.01 - 40.01	0.21	0.13 - 0.27
Western North	38.29	23.75 - 45.09	0.19	0.01 - 0.45
Western South	38.71	21.90 - 56.98	0.20	0.05 - 0.54
Mean value	35.40		0.20	
Lsd	n.s		n.s	

ns – not significantly different at $p < 0.05$

Table 5: Percentage fat, pH, titratable acidity and moisture content of cocoa beans from six cocoa growing regions in Ghana as quality parameters

REGION	n	pH	Range	Titratable acidity Meq NaOH/10g	Range	% Fat	% Moisture
Ashanti	22	5.15	4.61 -5.69	1.16	0.62 - 1.51	52.86	6.59
Brong Ahafo	10	5.32	5.18 - 5.70	1.06	0.86 - 1.42	52.63	6.82
Central	19	5.29	4.87 -5.74	0.98	0.71 -1.50	53.91	7.39
Eastern	11	5.56	5.24 -5.88	0.94	0.59 - 1.18	55.08	6.56
Western North	24	5.48	4.92 - 5.87	0.91	0.48 -1.33	55.50	7.25
Western South	76	5.46	4.83 - 6.25	0.92	0.47 -1.23	55.74	7.27
Lsd		0.21		0.17		2.91	n.s

n - sample size, ns – not significantly different at $p < 0.05$

Results and discussion

Cadmium concentrations in cocoa beans across the six cocoa regions ranged between <0.01 and 48.30µg kg^{-1} (Table 1). All the regions had samples that were very low in cadmium and most of the time below the detection limit of NAA. Individual samples from Western North and South and Brong Ahafo regions had values above 37 µg kg^{-1}, even though far below the proposed MRL of 0.6 mg kg^{-1} for cocoa. On the average there were no significant differences in the cadmium levels of the beans across the cocoa regions ($P>0.05$). In Malaysia, high concentrations of Cd in cocoa (*Theobroma cacao*) has been attributed to input from phosphate fertilizers (Zarcinas *et al.*, 2004). The High-Tech programme in Ghana which began about 6 years ago encourages farmers to apply fertilizers for increased yield. Values of cadmium recorded suggest that the application of fertilizers is not resulting in increased cadmium in the soils and subsequent bioaccumulation by the cocoa plants, as has been observed elsewhere. The levels present are likely to be emanating from natural cadmium present in low levels in the soils on which the cocoa is grown as cadmium is found in the earth's crust. Even though cocoa powder, mushrooms, liver, shellfish, mussels and dried seaweed have been found to be significant source of cadmium for uptake in humans, cocoa powder made from Ghana's cocoa can be regarded as safe since the cadmium levels are very low. Large amounts of cadmium (25,000 tons a year) are known to be released into the environment, about half of which is released into rivers through weathering of rocks and through forest fires and volcanoes (LennTech, 2012). The regular monitoring of cadmium therefore is very important to ascertain possible build up in Ghana's cocoa beans.

The Small scale mining activities, both legal and illegal has become very common in most cocoa growing areas of Ghana and mercury is often used in the process of refining. Results of the analysis however indicated that mercury was not detected in any of the cocoa samples from all the cocoa districts, all being below the detection limit (<0.01µg Kg^{-1}) of the Neutron Activation Analysis method used (Table 1). The development of new mining sites in the cocoa growing zones however needs to be examined to prevent pollution of the soil that could result in bioaccumulation by the cocoa plant.

Copper occurs naturally in the environment and its application in industry and agriculture has resulted in lifted production and increased quantities in the environment. Cocoa production in Ghana uses copper based fungicides as key pesticides to control the Black pod disease. In Nigeria, it has been reported that about 15% of applied copper fungicides on cocoa gets to the target while the remaining 85% end up in the soil (Aikpokpodion *et al.*, 2009). Though application on farmers farm's in Ghana is much more efficient, accidents and misapplications could occasionally occur. Cocoa plants derive nutrients from the soil via the roots, suggesting a high tendency for soil accumulated copper to be transported to the vegetative part of the plant which includes the beans. Wide variation occurred in the level of copper in the cocoa beans, but there was no significant difference between the regions in terms of the level of copper in the cocoa beans (Table 2). The highest amount obtained in samples was 26.76 mg kg^{-1}, well below the MRL level of 50mg kg^{-1}. On the average, levels present in the beans were less than 20 mg kg^{-1}. The concentrations reported here are quite high compared to other recently collected data from Ghana (Agyen, 2011; Dankyi *et al.*, 2009; Takrama 2012 (unpublished). The differences may be due to hulls (shells) that were included in this particular analysis involving the whole beans. Concentrations of 37.8 mg kg^{-1} have been reported from hulls of cocoa in Japan (Chung *et al.*, 2003). Ghanaian soils for cocoa cultivation, though reported to contain low levels of copper (Agyen, 2011) could have contributed to the levels found in the whole beans. Threat to human health usually comes from water soluble copper compounds which are released through agricultural application. Copper is a trace element and essential for human health. Excesses however cause health problems. Since copper concentrations in air are usually low, copper is usually obtained by humans through food or water. Copper breakdown in the environment does not occur and hence can accumulate in plants and animals when present in soils. It binds strongly to organic matter and minerals in the soil and hence does not travel far from point of release and gets accumulated by the plants. The results of the study show that cocoa beans could contribute to copper intake in finished products. The levels however are within acceptable limits and the application of copper based fungicides may have to be monitored to determine possible bioaccumulation by the cocoa plant.

Plant mineral composition most of the time depends on the minerals present on the soil in which it is grown. Magnesium in the cocoa beans was found to vary but did not significantly differ ($P > 0.05$) across the cocoa growing regions (Table 2). The range was between 2147 and 4601 mg kg^{-1}. This high level of magnesium could have come from the soil since it is the third most abundant element in the earth crust. The hulls of the beans have been reported to have a magnesium concentration of 4835 mg kg^{-1} (Chung *et al.*, 2003) and could contribute to a significant portion of the amount determined in the whole beans. Beans from Nigeria have been reported to contain as high as 5200mg kg^{-1} (Olaefe, 1987). Humans have been reported to need at least 200 mg of magnesium per day even though between 250 and 350 mg is consumed daily. The result of the study indicates that cocoa beans when used in finished products could act as a significant source of magnesium required in the diet.

Among the elements analysed, calcium was found to be the most abundant in the beans (Table 3). No significant differences ($p > 0.05$) were found across the regions even though the concentration ranged from 2155 – 5863mg kg^{-1}. The values reported here are relatively higher than the 21.7mg/100g cocoa reported by Olaefe, (1987) in Nigeria. Calcium is the third most abundant metal in the earth and essential to plant and animal life. Essential for plant growth, it is always present in every plant. In the human body it is the most abundant, being part of bones and teeth with important metabolic functions. It has been reported that calcium together with magnesium create new osseous mass and should be taken together in a ratio of 2:1 (Lenntech, 2012). The presence of calcium and magnesium together at quite high levels as determined in this study may make whole cocoa beans a very good source of these minerals compared to seafood, whole grains, nuts beans and green vegetables.

Aluminium is one of the metals with no known beneficial effect in the human diet. Levels found in the cocoa samples ranged from 30.36 – 147.40 mg kg^{-1} across the cocoa regions with a mean of 54.32 mg kg^{-1} (Table 3). This concentration is for the whole beans and may be lower in the nibs, the part of commercial value to processors. Values compare favourably with 165 mg kg^{-1} found in cocoa powders (Stahl *et al.*, 2011) and between 50 and 150 mg kg^{-1} in cocoa and chocolate samples (Schlegel and Richter, 1977). These reports suggest cocoa and cocoa powders as having the highest levels of aluminium among a total of 1,431 food samples analysed. Aluminium is mainly bioaccumulated by the plant and is usually sourced from the soil. Chloride content was low and ranged from 76.64 -97.14 mg kg^{-1}.

Recorded uptake of manganese, a toxic essential trace element in humans is mainly through foods such spinach, tea and herbs. Grains, rice, soya beans, nuts, olive oil, green beans, oysters and eggs are traditionally known foodstuffs containing high manganese concentrations. The cocoa beans analysed contained on the average about 35.40mg Kg^{-1} with a range of 19.66 to 56.98 mg Kg^{-1} (Table 4). There were however no significant differences ($P > 0.05$) in the levels across the various regions. Hulls contain about 45.3 mg kg^{-1} (Chung *et al.*, 2003) and could have contributed to this level found in the whole beans. Burning of fossil fuels and other industrial activities enhance manganese concentration in the air and could also contribute to the uptake by the plant.

Vanadium in the human diet mainly comes from foodstuffs such as buckwheat, soya beans, olive oil, sunflower oil, apples and eggs. In variable amounts, it is abundant in most soils and is taken up by plants at levels that reflect its availability. Since vanadium is also associated with bauxite deposits, expectations were that the levels in beans from those regions where bauxite was mined would show some high levels but levels in the cocoa beans were not significantly different across the cocoa regions with a range of 0.01 – 0.45 mg kg^{-1} (Table 4). Reported levels of vanadium concentration in food range between 1-30 μg kg^{-1} fresh weight. Fats and oils, fruits and vegetables have been reported to contain the least vanadium, ranging from 1-5 μg kg^{-1} while whole grains, seafood, meats and dairy products generally contain 5-30 μg kg^{-1}. Dillseeds and black pepper contain the most vanadium, 431 and 987 μg kg^{-1}, respectively (Myron *et al.*, 1977). The range of values obtained for whole cocoa bean (shell + nib) puts cocoa in the whole grains and Dillseeds and blackpeper groups. The daily dietary intake for vanadium in humans is very low (WHO, 1996) and estimated to be 13μg/day in the UK (Evans *et al.*, 1985).

The moisture, pH, Titratable acidity and percentage fat content are presented in Table 5. Storage conditions play a vital role in the quality of a produce especially, oilseeds (Cassels *et. al.*, 2003). High moisture and temperature can be detrimental, causing loss in seed viability, increase in free fatty acid and products of oxidation in the oil (Reuss and Cassels, 2003). Dry cocoa beans are hygroscopic and therefore tend to absorb moisture from the environment when the environment contains more moisture than it does and vice versa. The results of the test however indicated that all the beans had been properly dried and stored in well maintained warehouses with the moisture content range of 6.82 -7.27, values within the acceptable limits for Ghana's cocoa. Cocoa in Ghana is usually dried to about 6% moisture content before being graded and sealed. Storage and transportation however in the high humidity environment sometimes causes the levels to rise. The average fat content of the beans ranged from 52.63 – 55.74%. Fat content of beans from the Ashanti and Brong Ahafo cocoa districts were found to be significantly ($P < 0.05$) lower than the other four cocoa districts, namely Western North and South, Eastern and Central. The Brong Ahafo and Ashanti districts seems to share the same environmental conditions and would have experienced on the average the same amount of rainfall and probably less than the other districts as there has been changes in the weather pattern for this particular cropping year. The values however are within the standards set for Ghana's cocoa and compares favourably with others from elsewhere (Wood and Lass, 1987). pH is a parameter that indicates the strength of an acid condition. Two acids commonly found in properly fermented and dried cocoa beans are acetic and lactic acid. Their presence lowers the pH and thought to affect chocolate flavour if the pH is less than 5. The pH of the dried beans ranged from 4.83 – 6.25 but showed no significant differences within cocoa districts. The pH values below 5 probably points to under-fermentation from those four cocoa regions that recorded those pHs. The beans from the Ashanti region were significantly ($P < 0.05$) more acidic compared to those from Western south, Western north and Eastern regions. A similar trend was observed in the titratable acidity of the dried beans. Titratable acidity however measures total acidity and therefore the beans from the Western south, Western north and Eastern regions had significantly less acidity compared to those from the Ashanti region.

Conclusions

This paper provides a quantitative data of both heavy and essential metals in cocoa. Results suggest cocoa from Ghana does not contain any appreciable amount of Cd, Zn, Cu and Hg as toxic elements with corresponding high fat and other quality parameters. Continuous monitoring of these parameters however is necessary as a result of the fertilizer application and possible pollution problems that may arise, resulting in an increase of toxic metals in the crop soil, taken up by the cocoa plants, and passed on in the beans.

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