KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF ENGINEERING

DEPARTMENT OF CHEMICAL AND MATERIALS ENGINEERING

IDENTIFICATION OF THE CRITICAL POINTS FOR POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATION ALONG THE COCOA PROCESSING AND STORAGE CHAIN IN GHANA

By

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(BSc Biochemistry)

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A Thesis Submitted to the Department of Materials Engineering, Kwame Nkrumah University of Science and Technology, in Partial Fulfillment of the Requirements for the award of Master of Science Degree in Environmental Resources Management

DECLARATION

I hereby declare that this thesis is my personal work and contains to the best of my knowledge, no materials previously published by another person or material which has been accepted for the award of any other degree, except where due acknowledgement has been made in the text.

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ABSTRACT

Cocoa, a natural resource has shouldered the socio-economic life of Ghana through generation of employment and foreign exchange since its introduction into the country in 1815 by the Dutch Missionaries. Nonetheless, the industry faces some challenges; Exported cocoa has come under strict scrutiny due to elevation of the levels of a carcinogenic, mutagenic and an endocrine-disrupting compound termed polycyclic aromatic hydrocarbon (PAH). Although the general post-harvest handling of cocoa has received some level of attention, how critical the contributions of the specific primary processing and storage stages along the chain are and the level of knowledge of farmers on the causes and effect of PAH contamination are not known. These situations shield areas that need intense focus and are assessed by this study to help in designing policies and strategies for quality improvement. The concentrations of PAH in cocoa sampled from Ashanti, Brong-Ahafo, Central, Eastern, Western-North, Western-South and Volta regions (cocoa-regions) of Ghana were analyzed using the Gas-Chromatography Mass Spectrometer. Also interview via questionnaires were used to ascertain knowledge of farmers and other handlers including purchasing officials with regards to PAH level. Results indicate that cocoa beans processing involves pods gathering and opening, bean fermentation and drying. It was followed by bagging and storage before shipment. PAH concentration was higher in the shell than the nib (although < EU's threshold limit of 2ppb) and occurred during drying (0.925 ppb), depot storage (1.486 ppb) and shipment (1.842 ppb). Inappropriate practices e. g drying near fire and vehicle roadside which promote contact of beans with smoke, petroleum products e. g. oil, diesel and petrol could account for this situation. Lack of knowledge by cocoa farmers due mainly to low level of education was also established as a critical factor that requires greater attention.

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DEDICATION

To the Almighty for all His love and my late grandparents Mame Yaa Atei and Okyeame Kwadwo Owusu.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Cocoa, the dried and fully fermented fatty seed of the *cacao tree*, described as the food of the gods, is much desired, appreciated and a great passion of people all over the world because of some characteristics which cannot be found in any other product (Rusconi and Conti, 2010). For instance chocolate in its many forms has for over 2,000 years been enjoyed and its effects have been exalted. It was believed that the Mexican god Quetzalcoatl left the cocoa tree for the people. The Aztec emperor Montezuma is reported to have consumed fifty (50) goblets of chocolate a day. It is called "the food of the gods," literally, as a translation of Theobroma Cacao, the cacao bean. Such a title must imply that chocolate has some naturally occurring superior quality. For many people, nothing can take the place of chocolate when a craving hits. The physics and chemistry of cocoa beans and cocoa products are very complex, changing throughout the life of the bean, depending on the processing it receives (Beckett, 1994). Among the most researched components of cocoa which are thought to have an effect on craving and addiction are fat, theobromine, caffeine, and salsolinol. Fat and sugar are substances naturally craved by the body, and thus although they may play a role in enhancing the attractive power of cocoa, they cannot be responsible for its appeal over other sweets. The caffeine in chocolate is sometimes regarded as part of its addictive properties. However, the amount of caffeine contained in one ounce of chocolate is about 5-35 milligrams, compared to the 140 milligrams found in a cup of brewed coffee (CNN, 1997). This does not dismiss the idea that caffeine plays a role in the appeal of chocolate. It is more likely to compounds the effect of other components. Theobromine, similar to caffeine but present in larger amounts in chocolate, is less potent than caffeine yet may retain stimulatory effects in large quantities of chocolate. Concentrations of theobromine vary in different chocolate products, and its effect on humans has not been consistently determined.

The economy of Ghana has been resting on natural resources, with cocoa as the mainstay through its hallmark of employment and foreign exchange generation cocoa is of world importance and has played a significant role in Ghana's economy since its introduction into the country several years ago. In fact Ghana is rated among the most important cocoa-producing nations in the world together with countries such as Cote d'lvoire, Brazil, Malaysia, Indonesia, Nigeria and the Cameroon. However, the industry is not without challenges which include diseases and pests infestation, lack of policy framework to sustain production, processing and consumption and promotion and intensification of cocoa extension all of which do not only limit production but also quality. One of the quality-related issues is the production of cocoa with moderate concentration of polycyclic aromatic hydrocarbons (PAHs) also termed polynuclear aromatic hydrocarbons, that is acceptable to both internal and external (especially the European Union countries (International board on the world cocoa economy, 2008).

PAHs is a very important compound in cocoa a group of organic contaminants with two or more benzene rings, formed from incomplete combustion of hydrocarbons, such as coal and gasoline (Kislov, 2013). They are usually byproducts of petroleum processing or combustion. Many of these compounds are highly carcinogenic at relatively low levels (Hansen, 1990). They range in appearance from colorless to white or pale yellow-green. Although they are useful in areas of research, manufacture of dyes, plastics, pesticides and medicines. They do not burn very easily and therefore they can stay in the environment for long periods of time. This persistent together with their ubiquity and persistence explain the cause of concern. At excess dose beyond the body requirement, PAH may cause health disorders such as infertility, foetal damage retarded growth, low birth weight and disruption of endocrine systems (Balabanič, 2011).

Sources of PAHs are both natural and anthropogenic. The latter are by far the major contributors. Natural sources include forest fires, volcanic eruptions (Neff, 1979), and degradation of biological materials, which has led to the formation of these compounds in various sediments and fossil fuels. Major anthropogenic sources include the burning of coal refuse banks, coke production, automobiles, commercial incinerators, and wood gasifers." (Lesage *et al*, 1992). Contamination by PAH is promoted through combustion of refined petroleum products (e. g. emission from train, vehicular traffic, industrial operations), natural and intentional burning of biomass fuels, uncontrolled and accidental input of unburned. PAH contamination of foods (e. g. cereals, smoked meat and fish, vegetable fats and oils) may occur through water & soil, deposition from the air, smoking and drying of the seed (Maryam, 2011).

1.2 Problem statement and Justification

The European Union countries form a major group of consumer of Ghana's cocoa. To protect public health the EU has set a maximum level for benzo[a]pyrene

(B(a)P), the most toxic and carcinogenic (ATSDR, 1995) in foods (EC Regulation 208/2005). This maximum is 2 ppb in vegetable oil and fats, for direct consumption (Moret, *at. al*., 2011) or used as an ingredient in food. The EU limit is not only applicable to EU produce but also to imports into the EU. The implication of this action by the EU is rejection of cocoa butter with PAH exceeding 2 ppb. Although the general post-harvest methods and practices that govern PAH concentration in cocoa have been receiving extensive attention, the contributions by the various stages of its handling are not known for the appropriate specific interventions to be made. Given the background that various stages namely collection of pods, breaking of pods, fermentation of beans, drying of beans, bagging and storage and transportation to the port for shipment cause various levels of contaminants into the products, it is essential to improve post-harvest practices to reduce PAH contamination and avoid a serious negative impact on the economies of the producing countries. This will contribute to improve the quality of produced cocoa consumed internally and externally. Determination of the most critical point(s) along the chain from processing to storage at where quality deterioration in terms of PAH occurs would be very helpful in designing policies and strategies for quality improvement including resources allocation.

1.3 Objectives

1. To identify the methods of primary processing and storage of cocoa beans from farm-gate to the point of shipment for export
2. To identify the critical points along the processing and storage chain of cocoa beans for PAH contamination.

3. To determine the part of the bean (shell and nib) that has the highest contamination of PAH.
4. To assess the level of understanding of Ghana's cocoa farmers and buyers of PAH contamination (causes, effects and prevention) along the processing and storage chain of cocoa beans.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 The History of Cocoa and its production in Ghana

Cocoa originated from around the headwaters of the Amazon in South America. Its cultivation and value spread in ancient times throughout central and Eastern Amazonian and northwards to Central America. Cocoa beans were used by the Native Americans to prepare a chocolate drink or chocolate and also as a form of currency for trading purposes and payment of tribute to the king (Delbourgo, 2011). After the conquest of Central America in 1521, Hernan Cortez and his Conquistadors took a small cargo of cocoa beans to Spain in 1528, together with utensils for making the chocolate drink.

It spread to the British, French and Dutch West Indies (Jamaica, Martinique and Surinarn) in the 17th century and to Brazil in the 18th century. From Brazil it was taken to SÃO Tome and Fernando Po (now part of Equatorial Guinea) in 1840; and from there to other parts of West Africa, notably the Gold Coast (now Ghana), Nigeria and the Ivory Coast(World cocoa foundation,2010). According to (Ministry Of Manpower, Youth and Employment, 2007) records indicate that Dutch missionaries planted cocoa in the coastal areas of the then Gold Coast as early as 1815, whilst in 1857 Basel missionaries also planted cocoa at Aburi.

However, these did not result in the spread of cocoa cultivation until Tetteh Quarshie, a native of Osu, Accra, who had travelled to Fernando Po and worked there as a blacksmith, returned in 1879 with Amelonado cocoa pods and established a farm at Akwapim Mampong in the Eastern Region. Farmers bought pods from his farm to plant and cultivation spread from the Akwapim area to other parts of the Eastern Region. In 1886, Sir William Bradford Griffith, the Governor, also arranged for cocoa pods to be brought in from Sao Tome, from which seedlings were raised at Aburi Botanical Garden and distributed to farmers. In recognition of the contribution of cocoa to the development of Ghana, the government in 1947 established the Ghana Cocoa Board (COCOBOD) as the main government agency responsible for the development of the industry. Currently there are six cocoa growing areas namely Ashanti, Brong Ahafo, Eastern, Volta, Central and Western regions.

Chocolate and cocoa are made from the beans of the cacao tree, which apparently originated in the foothills of the Andes in the Amazon and Orinoco basins of South America. The tree was introduced into Central America by the ancient Maya, and was cultivated in Mexico by the Toltecs and later by the Aztecs. Cacao' has been regarded as an 'elixir' by the Indians of Central America. Cocoa was an important commodity in Pre-Columbian Mesoamerica. Gold, silver and precious stones were not the only treasures brought back by the Spanish conquistadors led by Hernando Cortés in the early 1500's and became a popular beverage by 1700. They also introduced the cacao tree into the West Indies and the Philippines. It was used in alchemical processes, where it was known as Black Bean. They also discovered a small brown bean, which the Indians used to make a bitter but flavourful drink known as 'xocoatl' or 'chocolatl', whence the words cacao, cocoa and the chocolate of today. To the Aztec emperor Montezuma, this chocolate drink was for warriors and the élite, and it had great sacred and ceremonial importance as a drink fit for the gods. When Montezuma II, emperor of the Aztecs, dined he took no other beverage than chocolate, served in a golden goblet and eaten with a golden spoon. Flavored with vanilla and spices, his chocolate was whipped into a froth that dissolved in the mouth. No less than 50 pitchers of it were prepared for the emperor each day, and 2000 more for nobles of his court (Dunne, 1962).

Ensminger *et al*. (1995) recounted that the Swedish botanist Linnaeus, who was aware of cacao's reputation, assigned the plant species to a genus, which he named Theobroma cacao L.- the 'food of the gods'. Cacao reached the Old World in 1544, when the beans were presented to the future Philip II of Spain. The Spanish nobility were so entranced that they kept cacao secret from outsiders for nearly a hundred years. At that time, the drink must almost certainly have tasted like a medicine and it was consumed for its medicinal and even aphrodisiacal benefits! News of the drink, by now often flavoured with cinnamon and vanilla, gradually spread to the rest of Europe. In 1615, when the Spanish princess Anne married King Louis XIII of France, she brought along the recipe for chocolate as part of her dowry, and the first recorded chocolate drinker in France was Cardinal Richelieu, who enjoyed it as a food and as an aid to digestion. The English had to wait until around 1657 for cacao drinks to be sold in the London chocolate-drinking houses. Samuel Pepys, the famous diarist, frequented these fashionable meeting places, which became the precursors of many gentlemen's clubs, including the Garrick Club, which began life as 'The Cocoa Tree Chocolate House'.

In the seventeenth century, the Spaniards began growing cacao beans on the island of Fernando Po, off the coast of Africa. However, the major development of cocoa as a world commodity began around the 1880s, when the British introduced plantations in what is now Ghana. The west coast of Africa is still the largest cocoa-producing area of the world but cocoa is also a cash crop grown in Central America, small amount in South America, chiefly Brazil, the West Indies, and in parts of Asia such as Malaysia, Indonesia and the Philippines, where it is an important part of the national economies(World cocoa foundation,2010). The use of chocolate, cocoa and other products is world-wide. Belgium has the highest per capita consumption of cocoa at 5.5 kg, ten times the world-wide average. The history of cocoa and chocolate has seen them change from being expensive luxuries to products of mass consumption. Their wider availability reflects the changes in the nature and composition of the products, their move from being perceived as a bitter-tasting medicine to a delicious food, and the innovative technologies that make them more affordable. Today, chocolate, a divine product and a royal product, remains a world favourite.

2.2 Introduction of cocoa to Ghana

In 1859 the Basel mission successfully introduced cocoa to Ghana previously Gold Coast whilst Tetteh Quashie in 1879 also introduced the Amelonado variety from Fernado Po to Akwapim Mampong. By 1883 Tetteh Quashie has started selling cocoa pods to farmers at £1/pod or used them to raise seedlings. In 1885 the first cocoa export of 3 bags was made from Gold Coast to Germany. In 1887 the Governor of Gold Coast, Sir William Brandford Griffiths, brought Amelonado pods from Sao Tome to establish a plot of cocoa at Aburi for distribution of cocoa seedlings to local chiefs and the Basel Mission. From 1887 onwards Mampong and Aburi botanical gardens became a centre for cocoa distribution to the rest of the country. In 1900, 1,000 tonnes of cocoa was produced in Gold Coast for Export. In

1910/1911 Ghana became the world's leading producer of Cocoa until 1976/1977 and production peaked in 1964/1965 (580,869 tonnes)(World cocoa foundation, cocoa market update,2010)

2.3 World cocoa Production

About 3,000,000 tonnes of cocoa is produced each year (World Cocoa Foundation, *Cocoa market update, 2010*). The global production was over 30 years. Cocoa is produced primarily in Latin America (Belize, Mexico, Ecuador, Peru, Costa Rica and Brazil), West Africa (Cote d'Ivoire, Ghana, Cameroon, Nigeria, and Sao Tome), and Indonesia (Sulawesi, Central Sumatra). Most smallholder farmers use a variable system of production termed agroforestry by which forests are selectively thinned so that cocoa and other trees (e.g. fruit trees) can be planted beneath the remaining canopy (May *et al*. 1993, in Clay 2004). Greenberg *et al*, (2000) described a spectrum of cocoa producing strategies. At one end of this spectrum is ''rustic cacao'' where primary or secondary forests are thinned and cocoa is planted beneath the remaining canopy of native tree species. A similar system, cabruca, is used in Brazil and typically has native trees thinned to approximately ten percent of their original abundance. ''Planted shade'' is used to refer to systems where there is greater intercropping of cocoa trees with fruit, commercial timber, or fast-growing shade trees to various degrees. In contrast, full-sun cocoa production uses no shade trees and is becoming increasingly common in some cocoa growing regions.

Figure 1: Cocoa-producing countries of world

Source: UN Food and Agriculture organization (2011)

The western Amazon is the origin of cocoa (Clay, 2004) and the crop is presently grown in both Central and South America. Cocoa is grown using the traditional form of cocoa production, known as ‘‘rustic shade’’, or cabruca in Brazil as well as under ‘‘planted shade’’ canopy which is often composed of planted fruit trees rather than remnants of the native forest (Greenberg *et al*. 2000; Bentley *et al*., 2004). Cabruca production systems may become ‘‘planted shade’’ over time due to undergrowth clearing (to access the cocoa) which leads to native seedling loss, and the fact that as native shade species die they are typically replaced with non-native shade species (Saatchi *et al*. 2001).

Brazil and Ecuador are among the countries in Latin America with the greatest amount of land in cocoa production (Biodiversity Conservation, 2007). Brazil has an estimated 697,420 hectares in production while Ecuador has 287,300 hectares (Clay 2004). Cocoa production has contributed to the destruction of the Atlantic Rainforest in Brazil with deforestation resulting from increasing, decreasing, and stagnant cocoa prices (May *et al*. 1993, as cited in Clay 2004). Clay (2004) describes how it is presently the abandonment of cocoa and conversion of cocoa to other land uses such as pasture and annual crops that is causing the destruction of the remaining shade trees and forest patches. Since these alternative land uses maintain almost no biodiversity benefits, the shade-grown cocoa production system is now seen by many as the best alternative for preservation. However, the effectiveness of cabruca as a conservation tool is dependent on the presence of native forest in the surrounding landscape (Faria *et al*. 2006; Harvey *et al* . 2006).

West Africa is known for the production of higher quality cocoa, though yields tend to be lower than in Asia. Cote d'Ivoire and Ghana are the two countries with the greatest amount of land in cocoa production worldwide and they are also among the three largest cocoa producers. Cote d'Ivoire has an estimated 2.4 million hectares in cocoa and produces 1.4 million metric tons (as of 2000), and Ghana has an estimated 1.5 million hectares in production and produces 436,600 metric tons. However, both Cote d'Ivoire and Ghana have little remaining forest for the expansion of cocoa production, as the original forest remains only in patchy fragments. Other West African producer countries include Nigeria (966,000 hectares in production) and Cameroon (370,000 hectares in production) (Clay 2004).

In parts of Indonesia such as Sulawesi and Central Sumatra, cocoa is responsible for the opening up of primary forests and the establishment of settlements in these previously forested areas. The yields achieved by farmers in Asia tend to be higher than elsewhere and Indonesia produces the second largest amount of cocoa in the world (465,700 metric tons), following Cote d'Ivoire. It has an estimated 360,000 hectares in production (Clay 2004).

Akiyama and Nishio (1996) reported that Indonesian cocoa farmers have relatively low production costs, price transparency, and receive a large percentage of export price relative to other agricultural commodities. They suggested that some of the advantages experienced by Indonesian cocoa farmers were due to the government's free marketing and pricing system, and they attributed the boom in cocoa production in Indonesia to low transport costs facilitated by government investments in road infrastructure in rural areas. Full-sun cocoa, which increases the fragmentation of primary forests and is considered agriculturally unsustainable, is becoming common in Indonesia (Belsky and Siebert, 2003).

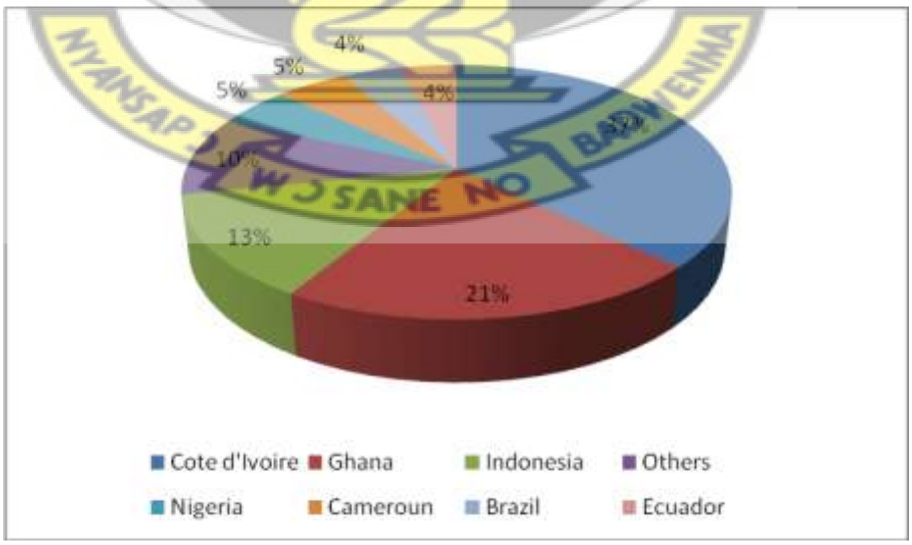


Figure 2: Distribution of Global Cocoa Production

Source: UN Food and Agriculture organization (2011)

2.4 Cocoa production in Ghana

Cocoa production occurs in the forested areas of the country- Ashanti, Brong-Ahafo, Central, Eastern, Western and Volta Regions where rainfall is 1,000 – 1,500 millimeters per year. The crop year begins in October, when purchases of the main crop begins, while the smaller mid-crop cycle starts in July. All cocoa, except that which is smuggled out of the country, is sold at fixed prices to Ghana Cocoa Board. Although most cocoa production is carried out by peasant farmers on plots of less than 3 hectares, a small number of farmers appear to dominate the trade. Indeed, some studies show that about one-fourth of all cocoa farmers receive just over half of total cocoa income (Clark, 1994).

Although Ghana was the world's largest cocoa producer in the early 1960s, by the early 1980s Ghanaian production had dwindled almost to the point of insignificance. The drop from an average of more than 450,000 tons per year to a low of 159,000 tons in 1983-1984 has been attributed to aging trees, widespread disease, bad weather, and low producer prices. In addition, bush fires in 1983 destroyed some 60,000 hectares of cocoa farms, so that the 1983-1984 crop was barely 28 percent of the 557,000 tons recorded in 1964-65. Output then recovered to 228,000 tons in 1986-1987. According to Clark (1994) revised figures show that production amounted to 301,000 tons in 1988-1989, 293,000 tons in 1990-1991, and 305,000 tons in 1992-1993. After declining to 255,000 tons in 1993-1994, the crop was projected to return to the 300,000 ton range in 1994-1995.

Figure 3: Cocoa-growing regions in Ghana

In 1979 the government initiated reform of the cocoa sector, focusing on the government's role in controlling the industry through the Cocoa Marketing Board. The board was dissolved and reconstituted as the Ghana Cocoa Board (Cocobod). In 1984 it underwent further institutional reform aimed at subjecting the cocoa sector to market forces. Cocobod's role was reduced, and 40 percent of its staff, or at least 35,000 employees, were dismissed. Furthermore, the government shifted responsibility for crop transport to the private sector. Subsidies for production inputs (fertilizers, insecticides, fungicides, and equipment) were removed, and there was a measure of privatization of the processing sector through at least one joint venture. In addition, a new payment system known as the Akuafo Check System was introduced in 1982 at the point of purchase of dried beans. Formerly, produce buying clerks had often held back cash payments, abused funds, and paid farmer with false checks. Under the Akuafo system, a farmer was given a check signed by the produce clerk and the treasurer that he could cash at a bank of his choice. Plantation divestiture proceeded slowly, however, with only seven of fifty-two plantations sold by the end of 1990 (Clark, 1994).

In the early 1990s, Cocobod continued to liberalize and to privatize cocoa marketing. The board raised prices to producers and introduced a new system providing greater incentives for private traders. In particular, Cocobod agreed to pay traders a minimum producer price as well as an additional fee to cover the buyers' operating and transportation costs and to provide some profit. Cocobod still handled overseas shipment and export of cocoa to ensure quality control.

In addition to instituting marketing reforms, the government also attempted to restructure cocoa production. In 1983 farmers were provided with seedlings to replace trees lost in the drought and trees more than thirty years old (about one-fourth of the total number of trees in 1984). Until the early 1990s, an estimated 40 hectares continued to be added to the total area of 800,000 hectares under cocoa production each year. In addition, a major program to upgrade existing roads and to construct 3,000 kilometers of new feeder roads was launched to ease the transportation and sale of cocoa from some of the more neglected but very fertile growing areas on the border with Cote d’Voire . Furthermore, the government tried to increase Ghana's productivity from 300 kilograms per hectare to compete with Southeast Asian productivity of almost 1,000 kilograms per hectare. New emphasis was placed on extension services, drought and disease research, and the use of fertilizers and insecticides. The results of these measures were to be seen in rising cocoa production in the early 1990s.(Clark,1994)

2.5 Cocoa Flowers

Tiny, intricate pink or whitish flowers grow along the trunk and main branches of the cocoa tree. The flower is pollinated before the tree can produce the pods that contain the seeds, or cocoa beans. Tiny flies are the main natural pollinators, but less than five percent of the flowers get pollinated. The cocoa farmer can also pollinate the flowers by hand.

Plate 1: Cocoa trees with mature pods

2.6 Varieties of Cocoa Trees

There are two main types of cocoa, with thousands of variations within these basic varieties, including some that have grown wild for thousands of years.

Criollo - Sometimes called the prince of cocoas because it is a very high quality grade of cocoa with exceptional flavor and aroma. Less than 15 percent of the world's cocoa is Criollo, grown mainly in Central America and the Caribbean.

Forastero - A much more plentiful variety of high quality cocoa, representing most of the cocoa grown in the world. Grown mainly in Brazil and Africa, it is hardier, more productive (higher yielding) and easier to cultivate than Criollo and is used in just about every blend of chocolate that is made.

A third type of cocoa, *Trinitario*, originated in Trinidad. It is a cross between strains of the other two types.

(a) ***(b)***

Plate 2 Trees of the Trinitario (a) and Forastero (b) varieties

2.7 Establishment of the cocoa farm

Cocoa should be cultivated in the areas where it thrives best, i.e. areas with hot, moist climate, with average rainfall of between 1150mm and 2500mm, and a temperature range of 18˚C to 32˚C. Such areas lie along the equator in West Africa, Central and South America, and in Asia/Oceania. It should be grown on land where there are no land tenure problems. Establishment of new cocoa farms on forest land should be avoided as far as practically possible. The soil for cocoa growing should be rich in nutrients and should have the appropriate physical and chemical properties, level of acidity, and organic matter content that are favourable to the development of the cocoa tree).

Depending on varietal requirements, adequate permanent shade trees should be provided in cocoa farms. Farmers shall keep records of the site history and field layouts. Land tillage practices that improve the soil structure should be encouraged. Land preparation for new cocoa farms should be done at least one year before cocoa seedlings are planted. Choice of planting materials and rootstocks should be based on characteristics such as high productivity, quality of the bean, consumer acceptability, resistance to pests and diseases, etc. Multiplication of seeds should be done in a seed garden using scientifically recommended practices. Farmers shall keep records of all the parent stocks. Each farm should have or be close to cocoa seeds and a seedling nursery that is properly maintained and shaded. Cocoa should be planted in the most suitable pattern and density according to the varietal requirements to ensure high productivity and easy management of the farms. The normal planting distance is 10 ft by 10 feet (3.08 m by 3.08 m).This give plant population of 441 per acre (1,090 per hecter).

2.8 Cocoa Farm Maintenance and Crop Husbandry

The length of time that a cocoa farm remains productive and financially viable is determined by the application of good maintenance practices, in particular pest and disease control. It is therefore important to maintain a high standard of farm management so that the cocoa tree is less susceptible to disease and insect attacks, as well as to ensure an appropriate response to specific outbreaks when they do occur. The following practices are recommended:

- Improvement and maintenance of soil organic matter through manure application; Adoption of field cultivation techniques that minimize soil erosion e.g. maintenance of soil cover.
- Encouragement of the most efficient use of farm resources (labour, inputs, etc,). Optimize the use of labour, in particular avoiding the worst forms of child labour.

- Use of management practices that minimize nutrient loss but maintain or improve the soil nutrient balance.
- Application of appropriate inorganic and organic fertilizers in accordance with scientific recommendations so as to maximize benefits and minimize losses.
- Use of efficient irrigation technologies and water management to minimize wastage and avoid leaching and salinization.

Adopt appropriate weed control measures to keep the ground around the cocoa tree and the shade tree free from weeds. In weed control, two different techniques can be distinguished: manual/mechanical and chemical control. Manual/mechanical control involves the use of grass knives or mechanical slashers. Chemical control involves the use of spraying machines to apply herbicides to the weeds that need to be controlled. Pruning is the removal of unwanted branches from a cocoa tree. It is an important operation and can affect yield for months, even years, as well as affecting the shape and structure of the tree for the rest of its life. Insects and diseases multiply more on un-pruned cocoa trees with dense canopies than on trees that have been opened up by pruning and display well-aired canopies.

Pruning can also stimulate flowering and pod production. Pruning can be carried out properly by using good tools such as a bow saw, a secateur, a chupon knife and a long-handle pruner. Shade has a very substantial effect on the growth and productivity of the cocoa tree throughout its development into a mature tree. Some degree of shade control is needed through pruning and thinning, to achieve the desired level of shade and maximize growth and production. The effect of shade on cocoa is very complex. Shade influences the microclimate of the cocoa block via its effect on the amount of solar radiation received by the cocoa trees, the wind, the relative humidity and through its effect on the metabolic rate of the cocoa trees, it indirectly affects the nutrient status of the soil. The micro-climate, in turn, influences the incidence of pests and diseases. Taken together, the above mentioned practices imply the application of appropriate integrated crop management to ensure sustainable productivity of cocoa farms.

2.9 Best Known Practices of Cocoa Cultivation

Cacao (Theobroma cacao) is a small (4-8 m tall) evergreen tree in the family Sterculiaceae (alternatively Malvaceae), native to tropical South America, but now cultivated throughout the tropics. Its seeds are used to make cocoa and chocolate.

The tree grows naturally in the low foothills of the Andes at elevations of around 200-400 m in the Amazon and Orinoco river basins; it is believed to have been introduced to Central America by the Maya people. Good climatic conditions should prevail (Bellis, 2008).

2.10 Cocoa crop protection

Disease is one of the major reasons for loss of cocoa production in the world. Controlling it is therefore a key part of efficient management of a cocoa farm. To be able to better control diseases on their farms, growers need to be able to recognize the symptoms, understand the causes of the diseases and know how the disease organisms operate. In controlling cocoa diseases, all trees should receive individual attention, as a single infected plant is likely to act as a source of infection for all the other trees on the farm. If left unattended, one sick tree will eventually lead to all the others also contracting the disease. There are four methods used to prevent diseases developing and/or controlling them if they do become established. These methods are: regulatory, cultural, biological and chemical.

In regulatory control, measures are taken, usually by law, to prevent material contaminated with a pathogen from being transported from one area that already has a particular disease to another area which does not yet have the disease. Cultural control is a broad approach that involves preventing the pathogen from coming into contact with and infecting the cocoa trees or eradicating the pathogen or significantly reducing its numbers in an individual plant or within an area. Biological control involves a range of measures that include directly introducing other micro-organisms that are enemies of the pathogen.

Chemical control usually seeks to remove the pathogen from the disease location. Chemicals that are toxic to the pathogen are applied to the cocoa or shade trees, either to prevent pathogen inoculum from establishing in a host, or to cure an infection that is already in progress. Utilization of pesticides should be m minimized as much as possible in order to protect the crop. More emphasis should be placed on resistant varieties, cultural and biological control of pests and diseases. Where possible, early warning mechanisms for pests and diseases i.e. pests and diseases forecasting techniques are observed. Adoption of Integrated Pest Management (IPM) regimes should be encouraged. Farmers should seek professional advice on IPM to control pests and diseases. The use of agrochemicals needs to be restricted to the officially registered ones and should be in accordance with legal, scientific and technical requirements. Only appropriate agrochemicals at the prescribed doses, timing and intervals of applications should be used. Use should be made of only pesticides that are target specific with minimal effect on the agro-ecosystem and minimal negative environmental implications. Agrochemicals should only be applied by adequately trained adults who are knowledgeable on the safe and proper use of the products. Equipment used for the handling and application of agrochemicals must comply with safety and maintenance standards. Routine application of broad spectrum insecticides to prevent pests from establishing themselves should not be carried out for the following reasons: Insecticides are expensive, and potentially dangerous/hazardous for the health of the person carrying out the spraying.

Furthermore, it can contaminate the local environment (soil and water streams) and the cocoa tree and pods with unacceptably high levels of chemical residues. In addition, excessive use of chemicals can create resistance in the target pests, and can reduce the population of useful predators. Over-used chemical control can lead to yet greater pest uncontrollable problems even with the recommended insecticide applications. Agrochemicals must be stored in accordance with local regulations and secured away from other materials in a well ventilated and well lit location.

2.11 West African Cocoa Farming

Estimated number of cocoa farms in West Africa as a sub-region is 1.2 - 1.5 Million which is 24% of the global figure. Average size of cocoa farms in West Africa is 10-15 Acres (2-6 hecters) (Cocoa Barometer, 2012). Average number of family members who live on a cocoa farm is 8-10. Ten million of people in West Africa live on cocoa farms. 70% of 3 million tons of cocoa produced worldwide each year comes from West Africa.(Cocoa Barometer, 2012)

Cocoa Pods

Cocoa trees begin to produce their first fruit at three to five years of age. Cocoa trees produce football-shaped pods that contain the seeds that will become cocoa beans. A shade-grown cocoa tree can produce fruit for 75 to 100 years or more.

2.12 Packaging and storage

Cocoa beans should be packaged in clean bags which are sufficiently strong and properly sewn or sealed. The bags should be made of non-toxic materials, preferably food grade vegetable oil treated jute bags. Once the drying and sorting out process has been completed, the cocoa beans must be put into appropriate bags and stored. Proper bagging and storage of the processed beans is just as important as proper fermentation and drying. Incorrect bagging and storage can lead to rejection of the beans, meaning that time and efforts as well as money have been wasted. The bagged cocoa beans must be placed in storage sheds that are weatherproof, well aired, free from damp and insect pests and away from smoke and other smells that would contaminate the cocoa. The bags must be kept above ground level and away from walls. The storage areas must be kept locked and clean at all times. Following proper fermentation, drying and bagging, the cocoa beans are ready to be sold.

2.13 Human welfare, health and safety of cocoa producers

Human welfare, health and safety are the principal components of sustainability, as the social and economic welfare of farmers, farm workers and their communities greatly depends upon it. Cocoa should be produced through practices that achieve an optimal balance between economic, social and environmental goals. Cocoa production should provide adequate household income and food security to producers. Cocoa producers must adhere to safe working procedures with acceptable working hours. Reasonable wages must be paid to hired labour, including women and children.

2.14 Farm record keeping

Farmers shall keep up-to-date records of all farming activities, including the use of inputs. A comprehensive record keeping system shall be established in which all the essential elements of cocoa production are captured. Records should be kept on the types and sources of planting materials; types of pesticides, fertilizers and usage; etc.

2.15 Cocoa Economics

Most of the world's cocoa is grown on small farms, not large plantations. According to the International Cocoa Organization, 2.5 million farmers produce almost 90 percent of the world's cocoa on 5-10 acre holdings. Typically, cocoa is the family's main source of cash. Cocoa provides important income for small farmers in developing economies all over the world. Number of cocoa farmers, worldwide is 5-6 million. Number of people who depend upon cocoa for their livelihood, worldwide is 40-50 million. Annual cocoa production, worldwide is 3 million M/t. Annual increase in demand for cocoa is 3 percent per year, for the past 100 years. Current global market value of annual cocoa crop is $5.1 billion. Length of time required for a cocoa tree to produce its first beans (pods) is five years. Duration of "peak growing period" for the average cocoa tree is 10 years. Cocoa has been the backbone of the Ghanaian economy throughout the century: It plays a major role in employment generation,

Table 1: Cocoa production and foreign Exchange Earnings

Crop Year	Cocoa Production (Mt)	FOB $/TONNE	ESTIMATED FOREIGN EXCHANGE ($)
2003/04		1650	
2004/05		1440	
2005/06	599,326	1450	869,022,700.00
2006/07	740,457	1500	1,110,685,500.00
2007/08	605,613		
2008/09	680,780		
2009/10*	524,034		

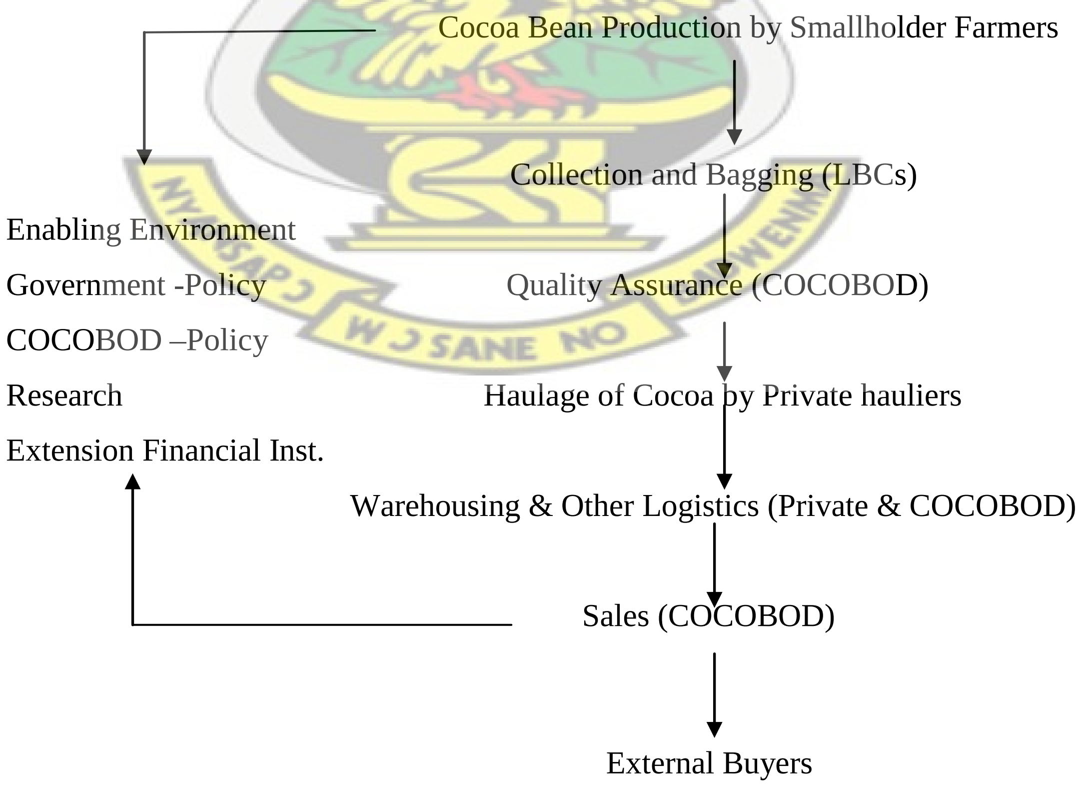
Source: cocobod Annual analysis,2010

* week 26 2010.It left with 7 weeks to close the season. It is left with estimated 21Mt as well as the mid crop produce which is to commence in June 2010.

In 2007, 35% of Ghana’s GDP and 60% of Total Employment were in agriculture. The Cocoa Industry is the single largest contributor to agricultural GDP (World cocoa foundation,2010). For cocoa to continue to earn Ghana such foreign exchange there is the need to maintain and improve on quality standards set by the international community or consumers of cocoa and cocoa products. There is also the need for Policy framework for sustainable production, economic viability,-social acceptability and environmental soundness. The Ghanaian National Policy Framework highlights efforts by the Government of Ghana and Ghana Cocoa Board towards making the cocoa industry a reference point of excellence. But there are challenges in the industry, some of which is the determination of the critical point of contamination of PAH if any, in the production and marketing chain.

2.15.1 THE COCOA INDUSTRY OF GHANA

(A MODEL PUBLIC/PRIVATE SECTOR RELATIONSHIP)



2.16 Products and Uses of Cocoa

Cocoa seeds are the source of commercial cocoa (cocoa beans), the four intermediate cocoa products (cocoa liquor, cocoa butter, cocoa cake and cocoa powder) and chocolate. Although the market for chocolate is the largest consumer of cocoa in terms of bean equivalent, intermediate products such as cocoa powder and cocoa butter are used in several areas. Cocoa powder is essentially used as flavor in biscuits, ice cream, dairy drinks and cakes. Apart its use as flavor it is also used in the manufacture of coatings for confectioners or frozen desserts. Cocoa powder is also consumed by the beverage industry for example for the preparation of chocolate milk. Besides the traditional uses in chocolate manufacture and confectionery, cocoa butter is also used in the manufacture of tobacco, soap and cosmetics. It is also a folk remedy for burns, cough, dry lips, fever, malaria, rheumatism, snakebite and wounds. It is reported to be antiseptic and diuretic (Hui *et al*,, 2006).

Table 2: Standard Specifications of the properties of cocoa butter

PROPERTIES OF COCOA BUTTER	SPECIFICATIONS
Colour	- Light Yellow
Odour	- cocoa and resembling chocolate
Free Fatty Acids	- 1.08%
Peroxide Value	- 1.28
Non-Saponifiables	- 0.2-0.4%
Saponification Value	- 197.7
Iodine Value	- 34.8
Aroma Indices	- 3.20
Total Saturated	- 56-72
Total Monounsaturated	- 20-40
Total Monounsaturated	- 20-40
Oleic	- 29-35%
Palmitic	- 20-30%
Linoleic	- 1-3%

Source: Handbook of food science, technology and engineering (2006)**.**

2.17 Uses of Cocoa Butter

Uses in Food

Cocoa butter is combined with different amounts of milk and sugar to make white chocolate, milk chocolate and dark chocolate. Without cocoa butter, many foods and liquids would no longer be on grocery store shelves. Some fried foods, such as french fries, are fried in cocoa butter. Recipes also list cocoa butter as a substitute for vegetable shortening, which is used in baking recipes.(The Cocoa Manual,1993)

Uses in medicine

A unique characteristic of cocoa butter is its low melting point. At room temperature it remains solid, but at body temperature it begins to melt. This attribute allows cocoa butter to be used to encase many types of medicine. Prescription of medication along with non-prescription of medication is stored inside capsules made with cocoa butter. Suppositories are also made with cocoa butter.(The Cocoa Manual,1993)

Uses in beauty products

Cocoa butter is used in many beauty products for its moisturizing effect. Many body washes, lotions and salves are all made with the butter. Since lips need moisture to keep from being chapped, cocoa butter is used in many lip salves, as well (The Cocoa Manual,1993).

Uses in Pregnancy

Although it has not been conclusively proven, many people believe cocoa butter has the ability to prevent stretch marks. Cocoa butter is now advertised as such and marketed toward pregnant women, as they are most likely to get stretch marks during pregnancy.

Cocoa butter as a source of antioxidants

Chocolate has been advertised a source of antioxidants. The antioxidants actually come from the cocoa butter. This is a highly important property since antioxidants remove free radicals, which can cause damage to cells.

Flavonoids in Chocolate

Of much greater interest in the context of health benefits is the rich flavonoid content of raw cocoa and the relatively rich flavonoid content of some chocolates and cocoas. Flavonoids are part of a large and diverse class of phyto-chemicals called polyphenols. Several thousand flavonoids exist in substantial amounts in common plant-based foods, such as tea, chocolate, cocoa, soybeans and wine. Epidemiological research, which studies the association between diet and health, in the last decade, has suggested that some flavonoids might protect against certain chronic diseases, especially cardiovascular disease (The Cocoa Manual, 1993).

2.18 Other Fun Facts

Chocolate's antioxidant potency roughly matches that of gallic acid, another potent antioxidant, and is even more effective at cutting oxidation of (LDLs) than those in red wine (consumption of which has been found to reduce significantly an individual's risk of heart attack (The Cocoa Manual,1993).

2.19 Chocolate and Dental Caries

Cocoa and chocolate have been shown to reduce the demineralization process-an activity which directly in the formation of dental caries. In a study conducted at the Eastman Dental Center in Rochester, New York. The researcher's report that: "Chocolate has a high content of protein, calcium, phosphate and other minerals, all of which have exhibited protective effects on tooth enamel.

Chocolate contains copper (0.8 mg per 100g) which enhances red blood cells' ability to carry oxygen. The average woman is deficient in copper. A good source of copper is liver but wouldn't you rather eat chocolate?

PEA (Phenylethylamine) is followed closely by theobroma as the chocolate chemical most responsible for lifting depressions. It is one of a group of plant-based stimulants called methylxanthines whose best known member is caffeine. Chocolate has straight caffeine, too, but in very small amounts (70 mg per100 g). The effects of theobroma are similar to, but milder than caffeine's, and include alertness and decreased fatigue.

Chocolate's high level of magnesium (131 mg per 100 g) is also credited for adding to the euphoria one gets from eating chocolate. Magnesium levels are found to be low during menstruation.

Serotonin (3 mg per 100 g) and tyramine (2 mg per100 g) are also present in chocolate and provide a mild calming, balancing effect.

2.20 Characteristics of Good Quality Cocoa

Among the set of regulations governing the international cocoa trade are the quality standards, standard delivery weights and the material for packaging (Wood and Lass, 1985). Ghana, as an origin of merchantable cocoa beans must conform to quality standards demanded by the trade. This implies that the buyer, the cocoa processor and the chocolate manufacturer must be satisfied of the quality of produce that is delivered on the international market. The required quality specifications of dry cocoa beans as stated in the sales contract include the following, among others:

(1) Superior Quality/Good Fermented: Cocoa should contain not more than 5% slaty beans and not more than 5% of all other defects.

(2) Fair Average Quality/Fair Fermented: Cocoa should contain not more than 10% of "all other defects." Mouldy, germinated, flat, insect attacked beans etc. are considered as "all other defects". In all cases, bean count (i.e. the number of beans per 100 gm wt.) should either be:

(i) Main Crop beans i.e. up to 100 beans/100 gms.

(ii) Light Crop beans i.e. 101 – 120 beans/100 gms.

Other quality parameters covered in the sale contract documents are:

i. Uniformly fermented cocoa

ii. Dry beans – moisture content of 7.5%

iii. Uniform in size

iv. Homogeneous in all other respects and the parcel shall be:

(a) Fit for the production of a foodstuff

(b) Virtually free from foreign matter and adulteration, contamination, live insects (including mites) rodents or other types of infestation.

(c) Reasonably free from flat beans, germinated beans and residue

2.21 Unique Characteristics of Cocoa

The characteristics of chocolate brown colour, flavour and aroma are unique to cocoa. These characteristics are not found in raw fresh cocoa seeds until the seeds are taking through certain post-harvest processes to develop them.

2.22 COCOA PRIMARY PROCESSING AND STORAGE CHAIN

To produce primary products with quality characteristics of chocolate brown colour, aroma and flavour unique to cocoa the underlisted processes must be adhered to.(Wood et al).

1. Harvesting of pods
2. Collection of pods
3. Storage of pods
4. Breaking of pods
5. Fermentation of beans
6. Drying of beans and
7. Storage of beans

Harvesting of Pods

Pods must be collected quickly and efficiently to prevent damage by rodents and other predators. Pods sorted out into healthy, diseased, damaged and mature classes. The time between pod harvesting and breaking of the pods influences bean quality. This period initiates rapid rise in temperature, initial germination and subsequent killing of the beans, reduce pulp sugars concentration, reduce cotyledon/ pulp ratio and improve aeration of the ferments Cocoa beans, which are the main ingredient in chocolate, are actually the seeds inside the fruit of the cocoa tree (Wood *et al*, 2001).

Matchets and wooden mallets are used for breaking of the pods. The latter is preferred and recommended since the use of matchets or any sharp tool can damage the seeds. Defective beans (germinated, flat, immature, insect damaged and diseased) should be discarded during the process.

The most important aspect of cocoa bean processing is fermentation because good quality bean is very much dependent on good fermentation.

This Process is Microbial fermentation in which the pulp is liquefied by microbial and enzyme activity to produce alcohol, acetic acid and lactic acid and rise in temperature, pH and seed death.

Fermentation Methods

Curing on drying mat

The various fermentation methods are:

1. Basket fermentation which is ideal for small quantities of cocoa beans.
2. Heap fermentation which is the normal methods used by Ghanaian farmers. This involves the spreading of banana leaves on the ground and heaping the beans on it and using the same banana leaves to cover the heap.
3. Box fermentation. In this situation wooding boxes are constructed and the beans are packed in it and covered.
4. Tray fermentation

In the fermentation process there is loss of moisture leading to Biochemical changes in which there is increase in Polyphenoloxidase activity, the astringent and the bitter taste is removed. Duration and temperature of drying have effects on the quality of the beans. Drying is done naturally or sun drying, artificial or mechanical drying. The duration and temperature of drying have effects on quality of dried beans. The drying of beans gives rise to lose of moisture content. There is also the enhancement of biochemical changes involving Polyphenoloxidase activity and removal of astringency and bitter taste. Natural sun drying (curing) is carried out when the beans are spread out on raised raffia mats in the sun to dry. While on the mat the beans are raked periodically to mix and expose fresh surfaces to the sun and also for better aeration. It takes about 10 to 12 days for the beans to dry to 6-8% moisture content (Lowor *et. al*., 2012).

Mechanical or Artificial dryers basically consists of long narrow platform constructed of perforated aluminium sheet or a similar material beneath in an enclosed chamber through which warm air is passed. The hot air is produced by a heat exchanger and electric fan. The drying efficiency is related to the depth of the layer of the beans combined with adequate mixing of the beans. The drying takes about 2-3 days to attain moisture content of 6-8 percent.

It has been demonstrated that beans from the same fermentation batch which were sun dried and properly controlled gave better results in terms of colour, flavour, and other sensory attributes. Sun-dried beans were less acidic than mechanically-dried beans. This is principally due to reduction in acetic acid levels. When mechanical dryers are employed , the quality of the cocoa can improved by reducing the drying rate to balance the speed of evaporation of liquid from the beans with its rate of diffusion from the cotyledons. Adequate drying is vital to the preservation of the good flavour of the beans, but care must be taken not to over dry the beans because this will make them brittle and cause them to break easily during handling and storage. Artificial drying if not properly done especially if the fuel source is allowed to come into contact with the beans could result in over drying, burning, charring and various forms of contamination leading to smoky beans and other off flavours.

Storage of Beans

This process is important in ensuring good quality beans and factors such as humidity, good ventilation and cleanliness of the storage facility are very necessary. During storage biochemical changes such as reduction in anthocyanins to further reduce the astringency and bitterness, reduction in intensity of purple colour and enhanced chocolate flavor and aroma. These processes are aimed at meeting international quality standards.

Quality control

Using the appropriate equipment (moisture meters, knives for cut-test, weighing machine, etc.), the quality of the cocoa beans in the bags must be checked before the cocoa is sold. This process is a crucial one as it can considerably affect the final price paid to the farmer. At this stage, the cocoa beans must fulfil certain criteria to the satisfaction of the buyer, including the following: the cocoa must be properly fermented and dried; the cocoa must be free from any foreign odours; the beans must comply with limits in contents of slaty, flat, double, broken, mouldy, insect-damage, foreign matter and germinated beans; the cocoa must conform to the required moisture level; and there have to be a number of cocoa beans per unit weight (100 or 1000 grammes).

While under the present circumstances, quality control is mostly carried out by officials from Quality Control Company (QCC) a subsidiary of COCOBOD, it is highly desirable that, in the context of sustainable and more modern cocoa production and marketing, farmers would play a larger role in the marketing of their cocoa. Eventually, they should take over quality control and carry it out at farm level before selling the cocoa beans, thus taking more responsibility for the quality of their cocoa and enabling them to command higher selling prices. In such an approach of closer involvement of farmers in the cocoa production and marketing process, current important issues such as traceability could also be addressed. Cocoa processing/storage chain in Ghana begins from the farmers end through the purchasing clerk, the district warehouse to either the transit depot in Kumasi or to the two ports at Tema and Takoradi.

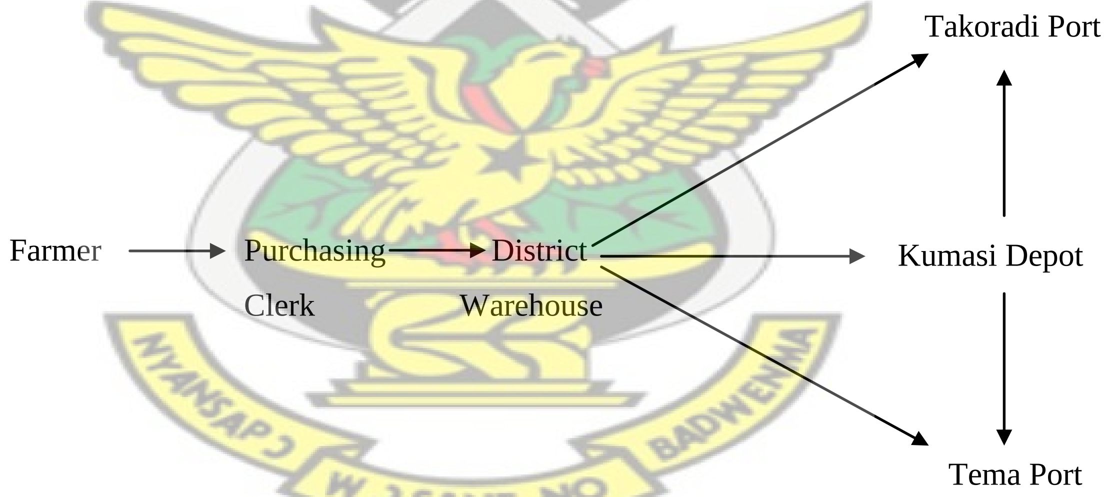


Figure 4: A model of Cocoa processing and storage chain

2.23 Occurrence and Distribution of Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are lipophilic, meaning they mix more easily with oil than water. The larger compounds are less water-soluble and less volatile (prone to evaporate). Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. However, they are also a component of concern in particulate matter suspended in air. Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils PAHs are one of the most widespread organic pollutants. In addition to their presence in fossil fuels they are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, or incense (Kislov, 2013).

Different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which isomers are produced. Thus coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as markers. Combustion of refined petroleum products as a result of Vehicular Traffic, Emission from Trains, Industrial Emissions, Fishing, Natural and Artificial Burning of Biomass, Fireplace, Woodfires, Natural Fires. Uncontrolled and accidental Input of Unburned Petroleum and its Refined Products, Asphalt and oil spills (e. g. crude oil). However, Hydrocarbon emissions from fossil fuel-burning engines are regulated in developed countries.

2.24 Human Health

PAHs toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being nontoxic to being extremely toxic. Thus, highly carcinogenic PAHs may be small or large. Compounds that are relevant in this context are in particular benzo(a) pyrene (BaP). The 15 other PAH considered by the United States Environmental Protection Agency (US EPA) . Benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke). Some of the 15 other PAH considered by EPA as probable human carcinogens are benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene in connection with the analysis of municipal and industrial waste waters. PAHs known for their carcinogenic, mutagenic and teratogenic properties are benz[a]anthracene and chrysene , benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene,benzo[a]pyrene, benzo[ghi]perylene, coronene, dibenz[a,h]anthracene ($C_{20}H_{14}$), indeno[1,2,3-cd]pyrene ($C_{22}H_{12}$) and ovalene.

2.25 Chemistry

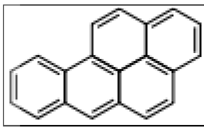
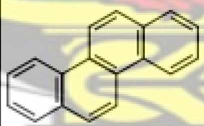
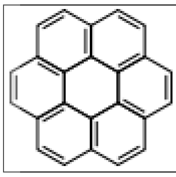
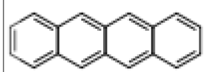
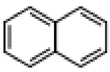
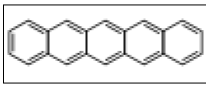
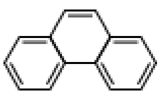
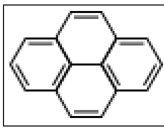
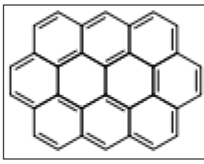
The simplest PAHs, as defined by the International Union on Pure and Applied Chemistry (IUPAC) {G.P Moss, IUPAC nomenclature for fused-ring systems), are phenanthrene and anthracene, which both contain three fused aromatic rings. Smaller molecules, such as benzene and naphthalene, are not PAHs. PAHs may contain four-, five-, six- or seven-member rings, but those with five or six are most common. PAHs composed only of six-membered rings are called **alternant** PAHs. Certain alternant PAHs are called "benzenoid" PAHs. The name comes from benzene, an aromatic hydrocarbon with a single, six-membered ring. These can be benzene rings interconnected with each other by single carbon-carbon bonds and with no rings remaining that do not contain a complete benzene ring. The set of alternant PAHs is closely related to a set of mathematical entities called polyhexes which are planar figures composed by conjoining regular hexagons of identical size.

PAHs containing up to six fused aromatic rings are often known as "small" PAHs and those containing more than six aromatic rings are called "large" PAHs. Due to the availability of samples of the various small PAHs, the bulk of research on them has been of those of up to six rings. The biological activity and occurrence of the large does appear to be a continuation of the small. They are found as combustion products, but at lower levels than the small due to the kinetic limitation of their production through addition of successive rings. Additionally, with many more isomers possible for larger, the occurrence of specific structures is much smaller.

PAHs possess very characteristic UV absorbance spectra. These often possess many absorbance bands and are unique for each ring structure. Thus, for a set of isomers, each isomer has a different UV absorbance spectrum than the others. This is particularly useful in the identification of PAHs. Most PAHs are also fluorescent, emitting characteristic wavelengths of light when they are excited (when the molecules absorb light). The extended pi-electron electronic structures of PAHs lead to these spectra, as well as to certain large PAHs also exhibiting semi-conducting and other behaviors. Naphthalene ($C_{10}H_8$ constituent of mothballs), consisting of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. By formal convention, it is not a true PAH, though is referred to as a bicyclic aromatic hydrocarbon. Aqueous solubility decreases approximately one order of magnitude for each additional ring. PAH form a class of diverse organic compounds ,each of them containing two or more aromatic rings .Compounds that are relevant in this context are in particular benzo[a]pyrene[BaP].

The 15 other PAH considered by the United States Environmental Protection Agency (US EPA). benzo[b]fluoranthene, benzo[k]fluoranthene, Acenaphthylene, acenaphthene, flourene, phnanthrene, anthracene, fluoranthene, indeno (1,2,3,e,c,d) pyrene, pyrene,benzo(a)anthracene, dibenz[a,h]anthracene, benzo[g,h,i]perylene. chysene, Because different investigators analyze different sets of PAH in foods benzo [a] pyrene, which almost always is included in analysis, as a marker for PAH in foods is used. Therefore, the pattern of PAH distributions (profiles) relative to benzo[a]pyrene in cocoa beans will be examined. Rapidly absorbed highest levels occurs in the thoracic lymph nodes after 3-4 hours of intake (Rees *et al.*, 1972).

Table 3: PAH compounds and chemical structures

Chemical compound		**Chemical compound**	
Anthracene		Benzo[a]pyrene	
Chrysene		Coronene	
Corannulene		Naphthacene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

The major routes of exposure to PAH are from food and inhaled air. PAH enter the environment via the atmosphere from variety of combustion processes and pyrolysis sources. Hundreds of individual PAH may be formed and released during incomplete combustion or pyrolysis of organic matter, during industrial processes and other human activities. PAH are also formed in natural processes, such as carbonization. For non-smokers, exposure to PAH occurs mainly by inhalation of air and by ingestion of food. Other ,possible minor ,exposure routes are ingestion of dust and soil, ingestion of drinking water, dermal absorption from soil and water, and the use of PAH-contaminated products such as preparations containing coal-tar.

PAH have been detected in a variety of foods, notably vegetables, as a result of deposition of airborne PAH, and in fish and mussels from contaminated waters. They have also been found in vegetable oils and margarine. PAH are also formed as a result of certain food preparation methods, such as grilling, roasting and smoking. Benzo[a]pyrene was last considered by IARC in 1987 (IARC, 1987), which concluded that it is a probable human carcinogen. Some other PAH compounds have also been identified as being carcinogenic, with possible genotoxic properties.

The contamination of food with environmental PAH depends on a number of physical and chemical properties of PAH such as their relative solubility in water and organic solvents, volatility, chemical reactivity, and biotic and abiotic degradability. PAH are lipophilic compounds having poor water solubility. Water solubility generally decreases with increasing molecular mass. They will not accumulate in plant tissues with high water content and transfer from contaminated soil to root vegetables will be limited. Because adsorption of PAH to the organic fraction of soil is strong they do not penetrate deeply in soils, other than sandy soils, and therefore leaching to groundwater and uptake by plants is low.

PAH are chemically stable and very poorly degraded by hydrolysis (Howard *et al,* 1991). In the presence of light, they are susceptible to oxidation and photo-degradation. Depending on various parameters e.g. type of adsorption onto particles, molecular mass etc. the half lives in air range from a few hours to days. In soil, PAH may be degraded by microbial activity. The estimated half lives in soils vary for individual PAH, from several months to several years. Degradation of PAH may lead to formation of oxidized reaction compounds, which have a great tendency to react with biological compounds such as those in foods. Although parent compounds cannot always be detected in PAH contaminated foods, degradation products or derivatives may be present.

2.26 Absorption, distribution, metabolism and excretion of PAH

Absorption

Following intragastric administration in rats benzo(a) pyrene is rapidly adsorbed with highest levels seen in the thoracic lymph nodes after 3-4hours (Rees *et al.*,1972). Kawumura *et al.* (1988) demonstrated that the composition of the diet influenced the absorption of c-benzo[a]pyrene in rats. The foods and components studied were triolein, soya bean oil, cellulose, bread, rice flakes, lignin, water, starch, katsuobushi (dried bonito), albumin, potato flake and spinach. The results suggested that the bioavailability of PAH from food will be in the range of 20-50% and that it increases with increasing content of lipophilic components in food.

Distribution in organisms

Distribution of PAH has been studied in rodents and detectable levels of PAH are found in almost all organs. The organs rich in adipose tissue act as depots from which material is slowly released. High levels are found in the gastrointerstinal tract irrespective of the route of administration.

Excretion

PAH metabolites are excreated in urine, bile and faeces. The bile was the major route of excreation ,in bile –duct cannulated rats in the initial 6 hours after intravenous administration of C labeled benzo(a) pyrene, biliary excreation accounting for 60% of the dose whist unrinary excreation was 3 %.

Metabolism

The general scheme of PAH metabolism ,using benzo(a) pyrene as e. g. involves oxidation to a range of primary (epoxides, phenols, dihydrodiols) and secondary (diols, epoxides, tetrahydrotetrols, phenol epoxides) phase 1 metabolites followed by conjugation to phase 2 metabolites with glutathione, glucuronic acid or sulphate.

Human BAP Metabolism

Benzo[a]pyrene (BAP) can enter the human body through dermal contact, inhalation, and ingestion. When this xenobiotic enters into the body it is acted upon first by monooxygenase, causing epoxidation of the BAP into simple epoxides such as benzo[a]pyrene-9,10-oxide, benzo[a]pyrene-7,8-oxide, benzo[a]pyrene-4,5-oxide (Wogan *et al*. 2004). These simple oxides are hydrated by the enzyme epoxide hydratase (epoxide hydrolase) to give dihyrodiols; this stage also produces the quinones and the phenols which result due to non enzymatic re-arrangement of the simple epoxides. The dihydrodiols are further hydrated by the monoxygenase enzyme to give the diol epoxides. The diol epoxides are the active carcinogen, but only in the bay-region configuration as explained above, in BAP metabolism the two active carcinogens that are known they include the 7,8 and 9,10 oxides (Yang *et al*., 1976; Yang *et al*., 1975). Stereoisomerism of the metabolites is of importance in the comparing the similarities of metabolism of a xenobiotic by different species. Mammalian Metabolism of PAHs always has metabolites predominantly in the Trans configuration; this is due to the action of the CYP450 enzyme complex. On the next page is the graphical representation of the stages in the metabolic activation of BAP adapted from Sims (Sims 1980).

Mechanism of Mutagenicity

The mechism of mutagenicity of PAH has been mainly investigated using benzo(a) pyrene and benzo[a] pyrene -7,8-diol-9,10-epoxide (BaPDE) as model compounds. The mutational spectrum induced by BaPDE In bacteria shows a prevalence of G>T TRANSVERSIONS. A similar spectrum of base-pair substitutions is induced by BaPDE IN mammalian cells in vitro (Yang *et al*., 1999). And by benzo[a] pyrene in vivo in transgenic mice (Kohler *et al*., 1991; Miller *et al*, 2000).

Receptor mediated biochemical and toxicological effects

Several of the effects of PAH, such as enzyme induction, immunosuppression, teratogenicity, and tumor promotion are believed to be mediated by sustained activation of arylhydrocarbon receptor (AhR) and subsequent disturbance of cellular homeostasis.

AhR and immunotoxicity of PAH

A functional Ah-receptor is required for proper function of the immune system. This has been demonstrated using transgenic mice lacking the AhR (Fernandes-Salguero *et al*., 2005). Furthermore; it has been shown that the AhR can influence PAH-mediated immune-suppression (Near *et al*., 1999). The spectrum of PAH immunotoxic outcomes suggests that PAH interfere with the lymphocyte programmed cell death/apoptosis machinery, eg induces pre-B cell apoptosis (Quadri *et al*., 2000). However, PAH can also induce non-AhR mediated apoptosis, e.g. fluoranthene induces apoatosis in murine.

CHAPTER THREE

METHODOLOGY

3.1.0 Farm sampling

3.2.1 The Conceptual Framework

The study was designed to provide empirical evidence that identifies the primary methods of cocoa beans processing and storage from farm-gate to the point of shipment for export, the points of contamination of cocoa beans by PAH, the part with the highest concentration of PAH and the level of understanding of Ghana's cocoa farmers and buyers of the causes, effects and prevention of PAH contamination. Ghana. The processes and procedures were organized in such a way that the most critical point(s) along the cocoa processing to storage chain where contamination of cocoa beans by Polycyclic Aromatic Hydrocarbon would be identified so as to be able to recommend remedial as well as preventive measures for them.

Farm Sample selection and Procedure

Sixty-seven cocoa districts in the country were identified. The sample frame for the survey followed a multi-stage sampling procedure in which specific major domains were distinguished for tabulation of important characteristics. The seven (7) cocoa regions in Ghana (Ashanti, Brong Ahafo, Central, Eastern, Western North, Western South and Volta) with each of their ecological designations were defined in terms of production levels as:

- high,

- medium, and
- low.

The target population in the study was the sample from the farm gate. Five (5) of these cocoa regions were purposively selected based on stratified sampling design to reflect high, medium and low cocoa producing areas in Ghana. Achieving a representative sample for the survey was critical for the study, and therefore the first sampling stage considered each of the regions as a cluster. Following the selection, the entire cocoa growing area in Ghana was stratified into five heterogeneous strata as follows:

Stratum 1 Western North

Stratum 2 Western South

Stratum 3 Ashanti

Stratum 4 Eastern

Stratum 5 Brong Ahafo

Subsequently, four (4) districts per cocoa region were then randomly sampled, followed by a random selection of four (4) depots for each of the districts for four licensed cocoa buyers (LBC) giving a total of forty (40) depots. Five (5) farmers for each LBC WHO deliver cocoa to each of the depots were also selected randomly. Cocoa growing districts defined by the Ghana Cocoa Board (COCOBOD) within each stratum formed the sampling frame of the Primary Sampling Units. The three warehouses mainly Kumasi, Takoradi and Tema also formed another sampling stratum.

In order to achieve the required precision, each sampling unit in the surveyed population had a known non-zero probability of selection. Non-probability methods represent a false economy and although they may yield reasonable estimates, they cannot provide the confidence that is necessary in the event of unexpected findings. If this occurs, the use of non-probability methods may lead to controversy and ultimately to criticism of the survey design. Every effort was therefore made to make the selection of farmers in the community, the LBCs, the depots, and the districts as random as possible.

Table 4: Strata and Cocoa-storage destinations in Ghana

Strata	No. Of Districts	No. of Depot Centers	No. of Depot in Kumasi	No. of Depot in Takoradi	No. of Depot in Tema
WESTERN NORTH	14	40	15	23	2
WESTERN SOUTH	14	32	0	32	0
ASHANTI	16	41	0	13	28
EASTERN	10	20	0	0	20
BRONG-AHAFO	8	16	0	0	16
Total	**62**	**149**	**15**	**68**	**66**

3.2.2 Farm sample size

In determining the sample size for a survey it is necessary to take into account both sampling error and non-sampling errors. Increasing the sample size has the desirable effect of decreasing the sampling errors. On the other hand, the non-sampling errors normally increase since it becomes more difficult to control the quality of the various survey activities especially the field operation. Cognizance of this, an operationally manageable sample size was taken for the study. A total sample of hundred (100) cocoa farming societies nationwide formed the actual study farm sample from 10 cocoa districts which were selected from the 5 cocoa regions of interest (Table 4).

In order to achieve acceptable precision, the distribution of the selected districts into each of the five regions of interest was based on proportionate allocation using the annual cocoa production levels for each region. This criterion was used with minor adjustments, based on the cocoa output of year 2004/2005 cocoa season. The adjustment was necessary to take into account the consideration that both Western North and Western South cocoa regions share similar characteristics.

Table 5: Selection of cocoa Producing districts and the number of districts per cocoa region

Cocoa Region	**Production (Mt)**	**Proportion**	**No. of Districts Allocated**	**No. of Depots Allocated**	**No. of Farmers Allocated**	**No. of samples at Take-over centers**
Western North	253,609	0.4	2	16(32)	40(40)	32(64)
Western South	166,040	0.3	2	16(32)	40(40)	16(32)
Ashanti	121,269	0.2	2	16(32)	40(40)	16(32)
Eastern	68,634	0.1	2	16(32)	40(40)	16(32)
Brong Ahafo			2	16(32)	40(40)	16(32)
TOTAL	**Total**	**62**	10	80 (160)	200 (200)	96 (192)

Source: Computed from data from COCOBOD, Accra.

3.2 IDENTIFICATION OF METHODS OF PRIMARY PROCESSING AND STORAGE OF COCOA BEANS

Primary methods of cocoa beans processing were investigated through study visit to cocoa farms and villages/communities and observation of processing methods adopted by farmers. Interview with farmers were also conducted through questionnaire and personal interviews and storage. Activities of interest included harvesting of cocoa pods, transport and gathering of the pods to a central location, removal of the cocoa beans, fermentation and drying of the cocoa beans.

3.2.1 Cocoa bean sampling

Again, to ensure adequate number of samples to permit analysis at the various domains of interest, the sample was designed to ensure that at least 100 cocoa farm households were selected from each cocoa district. The list of cocoa growing communities/societies from the Produce Buying Company (PBC), Kuapa Kooko(kuapa), Akuafo Adamfo Marketing company (AAMC) and Adwumapa Buyers (ABL) within the selected districts formed the sampling frame of the primary sampling units in each district. This constituted more than 95 percent of cocoa growing communities within the selected districts. The quantity of produce that the remaining societies sell to the other smaller companies was not significant. Samples of cocoa bean were collected as they arrive and leave the district depot, Kumasi depots and the Takoradi and Tema shipment ports for analysis of PAH concentration. At Kumasi, the frame in each district was arranged in alphabetical order and four depots were sampled using the Systematic Sampling procedure with equal probability allocated to each unit within the frame. A total of 552 cocoa bean samples were taken for analysis of PAH concentration. The use of probability proportional to the level of production, which results in a more representative sample, was not possible due to lack of information on the levels of production of each depot/society. Field data collection was conducted during the months of June to August for the mid-crop and October to December.

Table 6: Cocoa-buying districts and depots in Ghana

Cocoa Region	District	Depot	LBC
Western North	Sefwi Kaase	Kramokrom	PBC, FEDCO, AAMC, KUAPA
		Kaase	Same
	Bibiani-Anhwiaso	Bibiani	Same
		Anhwiaso	Same
Western South	Diaso	Diaso	Same
		Jameso Nkwanta	Same
	Dadieso	Dadieso	Same
		Dadieso Sonitra	Same
Ashanti	Tepa	Brosankro	Same
		Nyameadom	Same
	Nkawie	Nkawie	Same
		Toase	Same
Eastern	Akim Oda	Oda	PBC, ABL, AAMC, KUAPA
		Akroso	Same
	Ofoase	Ofoase	Same
		Nkwateng	Same
Brong Ahafo	Goaso	Nkasiem	Same
		Fawohoyeden	Same

3.3. IDENTIFICATION OF THE CRITICAL POINTS OF PAH CONTAMINATION OF COCOA BEANS (NIB AND SHELL)

3.3.1 Cocoa samples collection

Cocoa Samples were identified by the following:

1. Common name- Cocoa
2. Scientific name – Theobroma Cacao
3. Nature – Beans
4. Labelled on plastic sheets with permanent markers
5. The labeling was taken into consideration the origin of the sample.eg sealed cocoa sample from Akuafo Adamfo Company's Sefwi Kaase Depot at Sefwi Kaase District in the Western North Region for the coming mid-crop season will have the following labeling:
    a. Name of collector
    b. Name and number of QCC official grading the cocoa at the depot, and port.
    c. Seal number of the sampled cocoa beans.
    d. Graphical record of the sample will be taken. Photograph and weight.
    e. Storage material which in this case would be vegetable oil treated jute sacks.

3.3.2 Cocoa samples preparation and analysis for PAH concentrations.

Ten grammes (10 g) each of the samples cocoa beans were dehaulled to separate the shell from the nib and the weight of each established. Each was crushed separately dried, ground into small particles at low temperature and homogenized with Na_2SO_4

as drying argent. Soxhlet extraction method was used. In this method the samples were each placed in a porous cellulose thimble. The thimble is placed in an extraction chamber (2), which was suspended above a flask containing the solvent (1) and below a condenser (4). The flask was heated and the solvent evaporated and moved up into the condenser where it was converted into a liquid that trickles into the extraction chamber containing the sample. The extraction chamber is designed so that when the solvent surrounding the sample exceeded a certain level it overflows and trickles back down into the boiling flask. At the end of the extraction process, which lasted a few hours, the flask containing the solvent and lipid was removed. In this device a funnel (3) allowed to recover the solvent at the end of the extraction after closing a stopcock between the funnel and the extraction chamber. The solvent in the flask (1) was then evaporated and post extract cleaned with calcium gel. The extracts were concentrated using the rotary evaporator method and the mass of the remaining lipid was measured. The percentage of lipid in the initial samples was then calculated.

The method described by Soxhlet in 1879 is the most commonly used example of a semi-continuous method applied to extraction of lipids from foods. According to the Soxhlet's procedure, oil and fat from solid material are extracted by repeated washing (percolation) with an organic solvent, usually hexane or petroleum ether, under reflux in a special glassware.

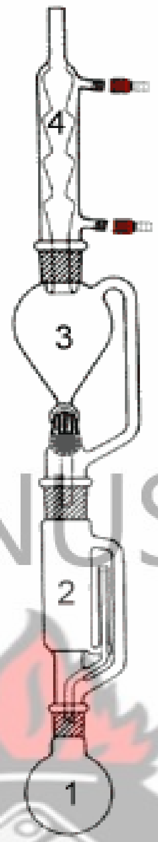


Figure 5. Soxhlet Extraction Apparatus

One hundred (100) samples were obtained and analyzed using the Gas-Chromatography-Mass Spectrometer (GC-MS). This involved two techniques: the gas chromatography which separated the components of the mixture and mass spectroscopy which characterizes the components individually. The technique enabled both qualitative and quantitative evaluation of the PAH in the cocoa samples.

3.4. ASSESSMENT OF FARMERS KNOWLEDGE OF PAH CONTAMINATION (CAUSES, EFFECTS AND PREVENTION)

Table 7: Distribution of categories of resrespondents

Category of Respondent	Number
Farmers	1000
Purchasing clerks	200
Depot keepers	40
Total	784
General Response rate	**63.23%**

Three main types of questionnaire aimed at soliciting information on level of understanding of Ghana's cocoa were farmers, depot keepers and buyers(purchasing clerks) of PAH contamination (causes, effects and prevention) along the processing and storage chain of cocoa beans were randomly selected from the three different categories of respondents. Farmers undertake the primary processing of the cocoa and sell to the purchasing clerk, Purchasing Clerks transfer cocoa from their sheds at he farming community to the Depots while Depot Keepers receive cocoa for onward transmission to the Ports of Delivery.

3.4.1 Data Analyses

The computer software programme, Statistical Package for Social Sciences (SPSS) was used to analyze the data collected of the study. The analysis carried out was simply the percentages of the best practices in the primary processing of cocoa as practiced by Farmers, Purchasing clerks and depot keepers with regards to the various items in the survey instrument which are meant to capture the best practices in the primary processes in cocoa. For each questionnaire, the Mean Rank Score (MRS) for Farmers, Purchasing clerks and Depot keepers was use to find out what the average practice for the individual items is. This was done by first assigning the following weights to the ordered categories:

- Poor = 1
- Satisfactory = 2
- Good = 3
- Very Good = 4
- Excellent = 5

The individual weights were used to multiply the frequency of each ordered category. These were aggregated and divided by the total number of respondents (frequency) for each item.

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CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

The results of the primary and secondary data obtained for the study are presented in this chapter. Results constitute an important component affecting the overall quality of a research (Yin, 2001).

In this chapter, the results of cocoa bean processing methods and laboratory analysis of concentrations of polycyclic Aromatic Hydrocarbon in samples of cocoa bean (shell and nib) along the cocoa processing ,storage from farm gate to the point of shipment and farmers are presented. The second section is related to assessment of the level of understanding of Ghana's cocoa farmers and buyers, of PAH contamination (causes, effects and prevention) along the processing and storage chain of cocoa beans The results have been presented in tables and figures namely pie charts and column to enable the data generated to be easily interpreted Therefore much care was taken in collection and recording of data generated during the study. In the study, it was observed that cocoa processing was initiated by farmers. It is the farmer who handles the raw cocoa, subject it to the drying methods before bagging and the subsequent transportation to storage centers by purchasing clerks.

4.1 IDENTIFIED METHODS OF PRIMARY PROCESSING AND STORAGE OF COCOA BEANS

The various stages and units of operations in the primary processing of the cocoa bean through which respondents (farmers) takes their cocoa, as identified in this study may be illustrated in a chain:

Harvesting of ripe pods ⟶ Gathering of pods ⟶ Storage of pods ⟶ Opening of pod ⟶ Fermentation of beans ⟶ Drying of beans ⟶ storage of beans in bags dispatch for export.

Firstly, the cocoa pods are harvested from the various cocoa trees, loaded in baskets transported and gathered at a central location. The gathered pods are opened to remove the wet cocoa beans and are stored or concentrated. This is to facilitate the next stage, fermentation which precedes drying of the cocoa beans. The beans are then packed into sacks sell to purchasing clerks of licensed cocoa buyers (LBC) and dispatched to the various destinations including abroad for use in manufacture of the various products.

4.1.1 Harvesting and Gathering of Cocoa Pods

Harvesting and processing of cocoa beans are very delicate and also labour intensive processes. Only pods that are ripe are harvested. They are identified by their yellow or red colour. Green pods indicate that they are not ripe and are therefore left on the trees. The harvested pods are immediately collected from the floor (to prevent damage by rodents and other animals) and are grouped into the following classes: healthy, diseased and damaged.

The methods of cocoa beans processing investigated through study visit to cocoa farms and villages/communities and observation of processing methods adopted by farmers and interview with farmers were also conducted through questionnaire and personal interviews revealed several activities. Activities of interest included harvesting of cocoa pods, transport and gathering of the pods to a central location.

Gathering of the cocoa pods at a central location usually facilitates easy access to the harvested cocoa for subsequent handling and management including de-husking, piling up for fermentation and drying of beans.

The gathering (Plate 3) was followed by removal of the cocoa beans, fermentation and drying of the cocoa beans. The whole cocoa beans in their pods are cut with large knives mostly with special knives attached to poles. Special precautions are taken that prevents possible damage to fruit-making flowers and buds that are close to the targeted pods. Flowers and pods of plants are delicate and easy to break or become bruised. The processes through which the cocoa bean from harvested pod is accessed begins with periodic (weekly during peak seasons) gathering of the pods into large baskets. Head-loads of cocoa are carried to a designated destination where they are piled up ready for splitting. This identified procedure is very labour-intensive requiring involvement of a whole family (including school children) together with friends and neighbours.

Plate 3: gathered Cocoa after harvesting

Although this is a profitable step, it may therefore promote child labour. There has been a report of enslaved children in the production of cocoa in Wes Africa (Raghavan and Chatterjee, 2001) and a widespread child slavery and child trafficking in the production of cocoa. The cocoa industry has been accused of profiting from child slavery and trafficking (Payson Center for International Development and Technology Transfer, 2010).

4.1.2 Splitting of Cocoa Pods

The gathered pods were opened to remove the wet cocoa beans (Plate 4). This is to facilitate the next stage, fermentation which precedes drying of the cocoa beans. This was done not later than the fourth day. The process involved hand-splitting using a thick piece of wood or a wooden mallet to expose the white pulp or mucilage covered beans (Plates 4 and 5).

Plate 4: Opening of harvested cocoa pods

The average number of seed or beans in each opened cocoa pod was 40 confirming the observation by The European Chocolate and Cocoa Industry that cocoa pods contain beans in the range of 30 to 50. The use of machetes and other sharp tool were avoided since they caused damage to the cocoa bean.

The beans (Plate 5) were then carried to the place where they are to be fermented. Several studies have shown the beneficial use of empty cocoa pods e. g. for preparation of composing for making fertilizers or substrates on which mushrooms may be grown (Owusu-Boateng and Dzogbefia, 2005) and for making potash used in soap manufacturing. This notwithstanding, most farmers left them on the farm. This may serve as suitable habitat for the microorganisms which attack the cocoa trees.

Plate 5: Cocoa pods with beans

Plate 6: Cocoa bean removed from pod for fermentation

Plate 7: Freshly removed cocoa beans

Plate 8: Cocoa bean removed from pod ready for fermentation

4.1.3 FERMENTATION

The cocoa beans in the study area consisted of seed coat, a kernel and a germ. Farmers may gather the fresh beans into heaps at a dry place and cover them mostly with banana leaves (Plates 7, 8 and 9) and left for 5 to 7 days depending on a number of factors including species. The beans ferment well if the heap is stirred from time to time e. g. every second or third day. During fermentation, micro-organisms mainly yeast transfer by insects such *as Drosophila melanogaster* or vinegar-fly grow on the pulp of the beans and convert the sugars in the pulp surrounding the beans to ethanol. Bacteria action causes temperature rise to 40^{o}C to 45^{o}C during the first two days. Acetic acid penetrates the husk to cause biochemical reactions in the bean. The elevated temperatures kill the cocoa bean to break cell walls or testa (shell) and kill the bean and disrupt internal cellular structure. This sets up a complex chemical changes in the bean to cause flavor (chocolate) and colour development. The content of water reduces from a range of 82-87 to 32-39). Longer period of fermentation results in well-developed aroma (Norman, *et. al.*, 2004).

Plate 9: Cocoa beans heaped to hasten fermentation (Heap fermentation)

According to Sukha and Butler (2006), fermentation is affected by factors including the type of cocoa and quantity of beans and pulp, degree of ripeness of the cocoa pods, storage practices, duration of fermentation, seasonality and climate. Five (5) or more days of fermentation result in lower acidity and lower acidity results in better bean quality.

4.1.4 DRYING OF COCOA BEAN

After fermentation, the cocoa beans were dried. Several methods of cocoa drying including natural and artificial methods such as fire under a tray, use of rustic artificial dryers (Samoa type) and use of industrial artificial dryers namely; static, vertical and rotary dryers have been adopted in various places but the study identified sun-drying, a natural method as the method adopted in Ghana.

The beans were spread on special woven mat of plant origin (raffia palm) mounted on a board at about 1 meter above the ground (Plates 9). Effectiveness of drying was found to be linked to the surface area exposed. Although the beans were stirred periodically, thicker depths reduced effectiveness. Arnold *et. al*. (1997) observed an optimum depth of 4 cm for effective drying. The listed available drying methods have varying degrees of success and output in terms of quality of product. The effectiveness and efficiency of the methods may be related to their respective abilities in drying the cocoa beans without introduction of potential contaminants mainly PAHs.

The number of days required for effective drying varied according to the climatic conditions of the area. In the forest regions moist climate posed a great challenge during drying. In the Western Region, six (6) days while in the Ashanti Region 4 to 5 days were enough for effective drying. Protection against rains, especially in the night, was a precautionary measure adopted by farmers. Although sun-drying, a method that decreases acidity, astringency and bitterness was the method employed by cocoa farmers, they occurred at different locations and distances from possible sources of cocoa bean contaminations. Examples of such locations were along the vehicular road side and kitchen vicinity (Plates 11 and 12). Drying of cocoa along roadside, near smoke, gases and open fires may increase build-up of PAH in the bean.

Plate 10: Drying of cocoa beans on a mat beans

Plate 11: Roadside drying of cocoa (a source of PAH contamination)

Plate 12: (a) and (b) Drying of cocoa beans near smoke, a source of PAH contamination

In an attempt to adequately dry the cocoa beans, special precautions were taken by farmers to ensure that they are not excessively dried. Over-drying of cocoa beans may cause easy breaking in the subsequent handling such as packing and storage of the beans.

4.1.5 BAGGING AND STORAGE OF COCOA BEAN

Storage of cocoa beans occurred at different stages of processing and marketing chain. It began from farmers' end through the purchasing clerk, the district warehouse to either the transit depot in Kumasi or to the two ports at Tema and Takoradi. These destinations along the chain may be illustrated in a model (Figure 4). Farmers, purchasing clerks and depot keepers/exporter packaged the beans in jute sacks, air-loose special arrangement (Plate 13) under moderate temperature.

Plate 13: bagged dry cocoa beans in stored in a depot

Bagging and storage (Plate 13) are processes through which cocoa beans contamination may occur. The type of bag and its state of hygiene and the sanitation of the storage environment including orientation for proper ventilation are some important sources of cocoa beans contamination. Proper ventilation is required to prevent contamination (FAO, 1969).

4.2 IDENTIFICATION OF THE CRITICAL POINTS ALONG THE PROCESSING AND STORAGE CHAIN OF COCOA BEANS FOR PAH CONTAMINATION

PAH can be present in very small quantities in various food products including cocoa. These small quantities are enough to be toxic to humans causing cancer and genetic dysfunctions in humans. Although PAHs may also form naturally, when released as a result of forest clearing or wood fires, for example, the largest proportion of PAHs as witnessed in recent times is caused by man-made activity. Food may be contaminated with PAHs in the process of smoking, heating or drying, if combustion residues such as smoke come into direct contact with the food. High PAH concentrations are known to occur in dried fruit.

Ghana intends to prevent PAH contamination of cocoa due to its harmful effect on humans and to comply with the new regulation in Europe about the standard limit of tolerance of PAH in cocoa in order to prevent economic loss. Analysis of the cocoa at all the destinations revealed the presence of sixteen (16) types of PAH compounds. Altogether, several PAH compounds are known, 16 of them are of serious health concern (US EPA, 2008.).

Variation in the concentrations of PAHs in the shell cocoa bean was observed in the study. Mean concentrations of PAH compounds as determined at the various destinations are presented (Table 8 and 9). Total of the mean concentrations was highest in cocoa samples before shipment (1.161 ppb) followed by cocoa sampled at the Port (1.013 ppb) and finally cocoa sampled at Farm Gate (0.585 ppb).

Table 8: Mean concentrations of various PAH components in the shell of cocoa bean from farm gate to shipment port

Serial No	PAH Compound	**Mean Concentration (ppb)**		
		Farm Gate-District Depot	District Depot To Port	Before shipment
1.	Naphthalene	0.132	0.113	0.132
2.	Acenaphthalene	0.016	0.002	0.022
3.	Acenaphthene	0.005	-	0.002
4.	Fluorene	0.003	0.005	0.040
5.	Phenanthrene	0.013	0.008	0.013
6.	Anthracene	0.013	0.008	0.003
7.	Fluorathene	0.069	0.026	0.054
8.	Pyrene	0.011	0.002	0.010
9.	Chrysene	0.012	0.050	0.090
10.	Benz[a]anthracene	0.007	0.050	0.090
11.	Benzo[b]Fluorthene	0.030	0.013	0.022
12.	Benzo[a]Pyrene	0.055	0.043	0.039
13.	Indno[1,2,3-c,d]Pyrene	0.056	0.035	-
14.	Benzo[g,h.i]Perylene	0.060	0.077	0.085
15.	Dibenzo[a,h]anthracene	0.044	0.174	0.099
16.	Benzo[g,h,i]Perylene	0.059	0.407	0.460
	Total	0.585	1.013	1.161

A similar trend was observed for PAHs concentrations in the nib of coca beans. Total of the mean concentrations was highest in cocoa samples before shipment (0.681 ppb) followed by cocoa sampled at the depot (0.473 ppb) and finally cocoa sampled at Farm Gate (0.367 ppb). Analysis of variance (at 5% level of significance indicated that the variation in the concentrations of PAH in cocoa beans at various sampling destinations were significant (Appendix II).

Table 9: Mean concentrations of various PAH components in the nib of cocoa bean from farm gate to shipment port

Serial No	PAH Compound	Mean Concentration (ppb)		
		Farm Gate-District Depot	District Depot To Port	Before shipment
1.	Naphthalene	0.049	0.076	0.155
2.	Acenaphthalene	0.002	0.013	0.007
3.	Acenaphthene	0.002	0.003	0.018
4.	Fluorene	0.000	0.005	0.010
5.	Phenanthrene	0.003	0.000	0.010
6.	Anthracene	0.003	0.000	0.013
7.	Fluorathene	0.000	0.000	0.009
8.	Pyrene	0.018	0.005	0.015
9.	Chrysene	0.029	0.020	0.007
10.	Benz[a]anthracene	0.029	0.020	0.007
11.	Benzo[b]Fluorthene	0.010	0.037	0.007
12.	Benzo[a]Pyrene	0.036	0.029	0.022
13.	Indno[1,2,3-c,d]Pyrene	0.023	0.021	0.043
14.	Benzo[g,h.i]Perylene	0.014	0.050	0.107
15.	Dibenzo[a,h]anthracene	0.015	0.044	0.032
16.	Benzo[g,h,i]Perylene	0.134	0.150	0.219
	Total	0.367	0.473	0.681

The trend of PAH concentration at the studied destinations may be linked to the trend of human contact with the cocoa beans. There was greater human contact at the 'Before Shipment' designation than 'District Depot to Port' and 'Farm Gate - District Depot designations. From the farm gate to the point of shipment the mean concentration increased in both the shell and nib (Figure 5). The observed trend might have occurred through various processing methods namely pod opening, fermentation and drying together with storage. According to Beckett (1994) the possible causes of cocoa contamination with PAH may include inappropriate production conditions (e.g. general cocoa bean drying, drying with smoke gases, open fireplaces/wood fires in the vicinity of the drying).

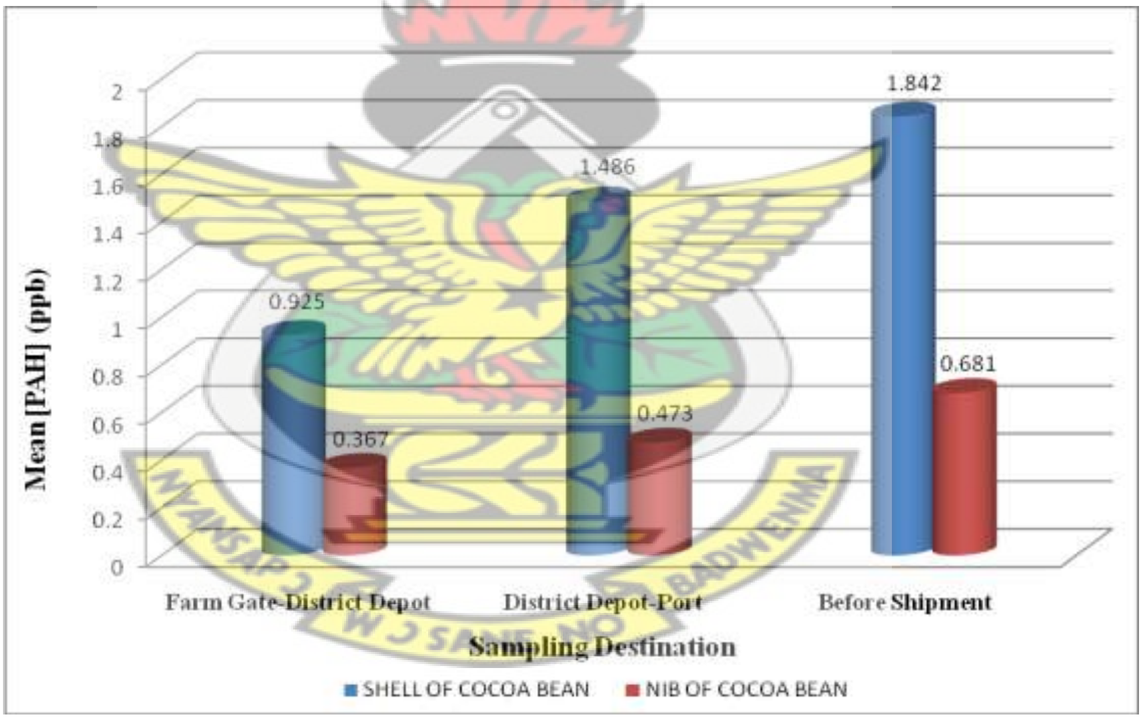

Figure 6: Mean concentrations of various PAH components in the shell and nib of cocoa bean from farm gate to shipment port

During drying, the beans may come into contact with PAH containing compounds such as fumes, smoke and hydrocarbons such as engine oil, kerosene, diesel, petrol, agrochemicals. Contact with fumes and smoke may result from artificial drying methods such the use of improperly designed artificial dryers. International board on the world cocoa economy, 2008) posited that the principal source for PAH in cocoa is smoke contamination of beans. Build-up of PAH in the beans may result from breakage of the bean, which may occur during pod opening and the periodic turning in fermentation (Adewumi and Fatusin, 2006).

Transportation and storage (in contaminated bags) may also promote build-up of PAH in cocoa beans. Improper handling and management practices including drying, transportation and storage are sources of PAH contamination. In some cocoa storage depots, insect infestation and rodents attacks are controlled by the use of PAH-Laden chemicals. This may cause increased level of PAH in cocoa beans.

Polycyclic aromatic hydrocarbons (PAH) are compounds made up of several condensed benzene rings with benzo[a]pyrene as the key component (Siddens, *et. al.*, 2012). The concentration of the most dangerous among the PAH compounds, benzo[a]pyrene occurred in greater concentration at the Farm-gate destination (0.055 and 0.036), followed by District Depot (0.043 and 0.029) with shipment (0.039 and 0.022) being the least for the shell and nib respectively. This may suggest exhibition of better handling methods as the cocoa bean progresses along the processing-storage chain and hence the need for extra attention at this stage. Although none of the PAH compounds exceeded the limit set by the European Union for cocoa producers, the possibility of the current practice driving the concentration to excess levels cannot be ruled out unless the current practices that lead to build up of PAH are held in check.

The part of cocoa bean (shell and nib) that has the highest PAH contamination

The main cause of PAH in cocoa was through smoke contamination of the beans during drying or storage when the beans came into direct contact with hydrocarbons. This leads to heavy contamination, but most of the contamination resided on the shell. Some contamination of the cocoa nibs, the edible part of the cocoa bean, however occurs through limited migration of the PAH. PAH contamination was higher in the shell (64%) than in the nib (36%) of the total concentration of PAH in the cocoa bean (Figure 6). This may suggest that the nib has a stronger mechanism of protection of cocoa against PAH contamination than the shell (Lowor *et. al*., 2012).

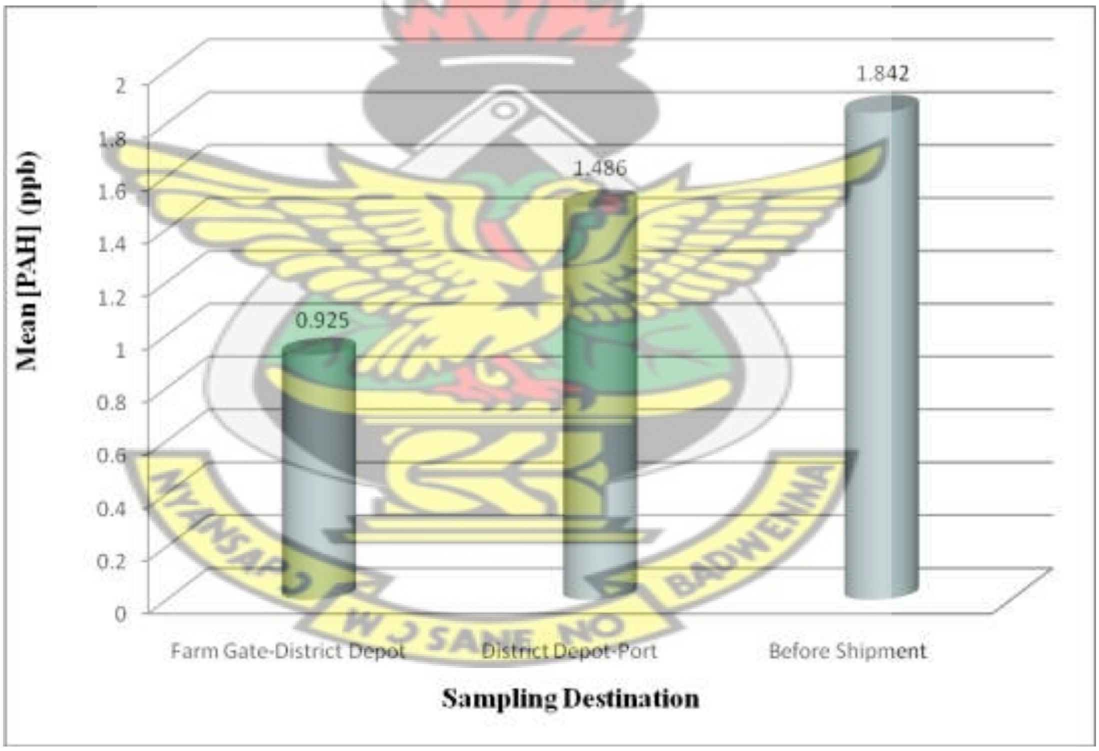

Figure 7: Total concentrations of various PAH components in the shell and nib of cocoa bean from farm gate to shipment port

4.4 ASSESSMENT OF THE LEVEL OF UNDERSTANDING OF COCOA FARMERS AND BUYERS OF CAUSES, EFFECTS AND PREVENTION OF PAH CONTAMINATION

4.5.1 Demographic Information

The appropriateness of a category of respondents (e. g. age and gender) to provide information related to exploitation and perception of resource is very important and needs to be ascertained. Demographic parameters including age, gender and education may exert varying effect on the quality of cocoa bean (Anger et *al*., 1997).

4.5.2 Gender

Out of the seven hundred and eighty four (784) people interviewed, 589 were males representing 75% of the total sample while 298 (i.e. 25%) were females. This variation may be due to the domination of males in the proportion of farmers which in turn promoted by culture of the communities. Males who are by culture the heads and leaders of families usually initiate cocoa farming and also undertake them as their main business while females in cocoa farming areas spend part of their time trading to support the family. Land ownership has also been following the same pattern since culture enjoins males to hold in trust for families. Also in the case of rented land males have usually fronted or initiated negotiations as observed in this study. This observation corroborates with that by Masterson (2007) who noted that in many parts of the world women have the least probability of owning land. Again, given the strength-driven requirement of the activities involved in cocoa farming, the relatively higher proportion of males than females who provided information for the study is not surprising. However, according to FAO (2013), women have considerable knowledge about water resources, including water quality and reliability and are key to the success of water resources development and protection.

Age of respondents

About 47% of respondents were between 35 and 54 years while cocoa-purchasing officials were dominated by those in the age group 24 -35 year. Relative to the percentage of farmers, 3% of officials were between 35 and 54 years (Table 10). This may be an energetic and active age category suggesting the effectiveness in execution of strength-driven activities involved in cocoa farming.

Table 10: Age of Respondents

	OFFICIALS		FARMERS	
AGES	**FREQUENCY**	**PERCENTAGE**	**FREQUENCY**	**PERCENTAGE**
25-34	80	33	36	5.70
35-44	40	17	96	15.20
45-54	60	25	205	32.55
55-64	20	8	110	17.46
65-74	-		63	10.00
75-84	-		16	2.54
85-94	-		16	2.54
Total	**240**	**100.0**	**630**	**100.0**

SOURCE: Survey Data Official $n = 240$ Farmers $n = 630$

It is well established that aging is associated with a significant decline in muscle strength (Doherty, 2001). The age of an individual is therefore a crucial factor in determining his or her ability to perform a job, suggesting therefore that there is the tendency for younger people to apply their virtues of eagerness, dedication, consciousness and motivation for successful achievement of their set target. According to Devendra and Shrestha (2009), economically active population comprises all persons of either sex, and above a certain age, who furnish the supply of labour for the productive activities (falling in the production boundary of the system), during a specified time-reference period. It includes all persons who fulfill the requirements for inclusion among the employed (employees or self employed) or the unemployed. Age is negatively related to output and that negative relation indicates that in advanced age, output decreases due to decline in the ability to do manual work.

Respondents have also been farming for not less than 10 years and maintained constant, their methods of farming, harvesting and processing. The longer the time in cocoa farming, the more experienced a farmer becomes and therefore more risk averse (Ajewole, 2010). This may explain the observed risk-aversion attitude of farmers in their farming and cocoa processing activities judging new technology.

4.5.4 Marital status

Out of the 630 farmers interviewed across the five cocoa regions, 42% were married, 37% unmarried, 11% widowed and 9% divorced. Cocoa farmers usually solicit assistance during cocoa harvesting, gathering fermentation and drying, packing and transportation to storage centers. Married respondents are likely to have more children, and are likely also to obtain the needed assistance from their children. According to Hoang and Yabe (2012), households with more members use more of their home labour to enhance their activities.

4.5.5 Education

Each of the cocoa-purchasing officials had formal education higher than the basic level. Only 164 (about 74%) out of the 630 respondents had formal education (from the basic education). Formal education generally provides sensitization to farmers on proper cocoa processing practices. Low level of educational attainment contributes to the less regard for these practices. Information about health effect and leaflets on cocoa contamination are usually transmitted in written form and so the ability to read and understand such information is very essential for the cocoa farmers to appreciate the consequences of poor handling and processing. The low level of educational attainment may therefore explain the use of unapproved methods for cocoa processing including drying along roadside, near smoke, gases and open fires and hydrocarbons such as engine oil, kerosene, diesel, petrol, agrochemicals and storage near these chemicals observed in this study. Ghimire and Mohai (2005) observed that the adjustments people make in their behaviour have profound influence on the delicate relationships that human beings exhibit with economic activities.

Plate 14: Researcher interviewing a cocoa farmer

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Cocoa farmers in Ghana adopt a scheduled pattern of primary processing activities for harvested cocoa. At the end of the processing activities begins the storage and shipment, tasks which are handled by cocoa purchasing officials. The various stages employed are presented schematically as:

Harvesting of ripe pods → Gathering of pods → Opening of pod → Fermentation → of beans → Drying of beans → Storage of beans in bags → Dispatch for export.

Although drying, a very effective means of arresting microbial deterioration in cocoa bean is the main method used by cocoa farmers in Ghana some drying processes cause elevated PAH levels, especially in the shell followed by the nib. This occurred at 0.925 ppb through contact of the bean with smoke from fires and fumes and petroleum products e. g. engine oil, kerosene, diesel, petrol due to inappropriate drying locations e. g. along vehicular roadside as well as contact with PAH-laden compounds during bagging and storage. This is followed by bagging and storage (0.925 ppb) and finally shipment (1.842 ppb) all of which were below the EU's threshold levels (2 ppb).

The study revealed that cocoa farmers seem to be unaware of or underestimate the risks associated with PAH probably due to low level of educational attainment by cocoa farmers.

There is therefore the possibility of further reducing the current level of PAH contamination in Ghanaian cocoa if issues related to low level of education, best processing and management practices as well as the apparently weak law enforcement on PAH contamination are addressed.

5.2 Recommendations

The seemingly lack of knowledge or awareness of the causes and effects of PAH contamination by cocoa farmers makes an urgent call on stakeholders, particularly the Ghana COCOBOD, Ghana Standards Authority standards and the Food Research Institute to intensify education to farmers and other handlers of cocoa. There should be greater involvement of cocoa farmers associations in the design of educational programmes aimed at prevention of PAH contamination of cocoa bean.

Workshops should be organized frequently for farmers and other handlers on the best practices for prevention of PAH contamination and general cocoa bean quality enhancement. The programmes for such workshops should have limited formal events and promote more informal interactions for a more effective sharing of knowledge.

Drying cocoa beans using or near open fires, sun-drying on tar on or near vehicular, road side and other inappropriate practices such as drying and storage of cocoa beans in the kitchen should be banned and enforced by law enforcement agencies. The use of modern day solar dryer should be promoted. Farmers associations should be encouraged to cooperate and support laws related to PAH contamination of cocoa bean.

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APPENDICES

Appendix 1

Sample Questionnaire Administered to Cocoa farmers

The researcher is a student of the Kwame Nkrumah University of Science and Technology, Kumasi conducting a research aimed at determination of the most critical point(s) along the chain, from processing to storage at where quality deterioration in terms of PAH occurs.

The information you provide will be treated as confidential and be used only for academic purposes. Thank you for your time and cooperation.

Demographic Information

1. Gender of respondent
(i) Male [ ] (ii) Female [ ]

2. Age
(i) 25 – 34 [ ] (ii) 35 – 44 [ ] (iii) 45 – 54 [ ] (iv) 54 – 64
(v) 65 - 74 [ ] (vi) 75 – 84 [ ] (vii) 85 – 94 [ ]

3. Educational attainment
(i) None [ ] (ii) Primary [ ] (iii) Secondary [ ] (iv) Tertiary [ ]

4. Marital status
(i) Married [ ] (ii) Unmarried [ ] (iii) Divorced [ ] (iv) Widowed [ ]

5. Number of years of farming
(i) Less than 4 years [ ] (ii) 4 – 6 years [ ] (iii) 7 – 10years [ ]
(iv) 10 year and above [ ]

6. Household
a. How many persons constitute your household? ……………………………
b. How many of them are:
(i) Children (Below 18 years)……….. (ii) Adults (Above 18 years)…………

7. What is your source of labour

(i) Self [ ] (ii) Family [ ] (iii) hired [ ]

COCOA PROCESSING METHOD EMPLOYED

8. **Cocoa gathering Method Employed**

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

9. Device/instrument for shell –opening

(i) Stick [ ] (ii) Wooden mallet [ ] (iii) Knife [ ]

10. Cocoa fermentation method employed

(i) Box fermentation [ ] (ii) Group fermentation [ ]

(iii) Others…………………………………………………………………………………

……………………………………………………………………………………….

11. Cocoa drying method employed

(i) Sun-drying [ ] (ii) Fire drying [ ] (iii) Solar drying [ ] (iv) Others…………………………………………………………………………………

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12. Location for cocoa drying

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13. Containers for dried cocoa

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PURCHASING AND PORT OFFICIAL

BAGGING AND STORAGE METHOD

14 Bagging method for dried cocoa

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…………………………………………………………………………………………………

15. Storage materials for dried cocoa

(i) Jute sack [ ] (ii) Plastic bags [ ]

(iii) Others (specify) ………...…………………………………………………………...

16. Storage houses

(i) Well-ventilated space [ ] (ii) Close space [ ]

(iii) Others (specify) ………...…………………………………………………………...

APPENDIX II

Analysis of variance (ANOVA)

Part of bean	F-value	P-value	Interpretation	Sample destinations showing variation (reference: LSD)
Nib	5.0.24	0.062	Significant variation	Farm gate and Depot
Shell	7.358	0.741	Significant variation	Depot and Shipment Centre

APPENDIX III

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL

NO.	PAH/sample	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10
1	Naphthalene	0	0	0	0	0	0	0.164	0	0.130	0.187
2	Acenaphthalene	0	0	0	0	0	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0.050	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0.156	0	0	0.119
6	Anthracene	0	0	0	0	0	0	0.156	0	0	0.119
7	Fluorathene	0	0	0	0	0	0	0	0	0	0.043
8	Pyrene	0	0	0	0	0	0	0	0	0	0
9	Chrysene	0	0	0	0	0	0	0	0	0	0
10	Benz[a]anthracene	0	0	0	0	0	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0	0	0	0	0	0	0	0.187
12	Benzo[a]Pyrene	0	0	0	0	0	0	0	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0	0	0.473	0	0.425	0
15	Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0	0	0	0	0	1.721	0.804	0	0

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL CONTINUED

NO.	PAH/sample	H11	H12	H13	H14	H15	H16	H17	H18	H19	H20
1	Naphthalene	0.082	0.116	0	0.123	0	0.221	0.114	0	0.253	0.063
2	Acenaphthalene	0	0	0	0	0.068	0	0	0.030	0	0
3	Acenaphthene	0	0	0.070	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0.045	0
6	Anthracene	0	0	0	0	0	0	0	0	0.045	0
7	Fluorathene	0.235	0	0	0	0	0.170	0	0	0	0.177
8	Pyrene	0	0	0.016	0	0	0	0	0.034	0	0
9	Chrysene	0	0	0.187	0	0	0.092	0	0	0	0
10	Benz[a]anthracene	0	0	0.104	0	0	0.092	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0.118	0	0.138	0	0	0	0	0
12	Benzo[a]Pyrene	0	0	0	0	0.200	0	0.224	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0	0	0	0	0	0
15	Dibenzo[a,h]anthracene	0	0	0	0	0	0.264	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0	0	0	0.794	0.496	0	2.345	0.490	0.554

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL CONTINUED

NO.	PAH/sample	H21	H22	H23	H24	H25	H26	H27	H28	H29	H30
1	Naphthalene	0.155	0.096	0.156	0.242	0.103	0.218	0.144	0.099	0.218	0.229
2	Acenaphthalene	0	0	0	0	0	0	0.136	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0.080	0	0	0	0	0	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0.099	0	0	0	0.330	0	0.158	0	0	0
8	Pyrene	0	0	0	0	0	0	0	0	0.147	0
9	Chrysene	0	0	0	0	0	00	0	0	0	0
10	Benz(a)anthracene	0	0	0	0	0	0	0	0	0	0
11	Benzo(b)Fluorthene	0	0	0	0	0	0	0.197	0	0	0
12	Benzo(a)Pyrene	0	0.207	0	0	0	0	0.242	0	0	0
13	Indno(1,2,3-c,d)Pyrene	0.301	0	0.538	0	0	0	0	0	0	0
14	Benzo(g,h.i)Perylene	0	0	0	1.158	0	0	0	0	0	0
15	Dibenzo(a,h)anthracene	0	0	0	0	0	0.693	0.660	0	0	1.651
16	Benzo(g,h,i)Perylene	3.102	0.852	0.672	0	0	1.056	0	0	0	0

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL CONTINUED

NO.	PAH/sample	H31	H32	H33	H34	H35	H36	H37	H38	H39	H40
1	Naphthalene	0.156	0.085	0.127	0	0.172	0.014	0.142	0.270	0.130	0.121
2	Acenaphthalene	0	0	0.030	0	0	0	0.082	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0		0	0	0.076	0.116
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0.382	0	0	0	0.084	0	0	0
8	Pyrene	0	0	0	0	0	0	0	0	0	0
9	Chrysene	0	0	0	0.652	0	0	0	0	0	0
10	Benz(a)anthracene	0	0	0	0.652	0	0	0	0	0	0
11	Benzo(b)Fluorthene	0	0	0	0	0	0	0	0	0	0
12	Benzo(a)Pyrene	0	0	0	0	0	0	0	0	0	0
13	Indno(1,2,3-c,d)Pyrene	0	0.969	0	0	0	0	0	0	0	0
14	Benzo(g,h.i)Perylene	0	0	0	0	0	0	0	0	0	0
15	Dibenzo(a,h)anthracene	0	0	0	0	0	0	0.930	0	0	0.354
16	Benzo(g,h,i)Perylene	0.950	0	0	0	1.123	0	0	0.846	1.025	0

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL CONTINUED

NO.	PAH/sample	H41	H42	H43	H44	H45	H46	H47	H48	H49	H50
1	Naphthalene	0.197	0.129	0.226	0.145	0	0.102	0.171	0.094	0	0.090
2	Acenaphthalene	0	0	0.079	0	0.021	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0.047	0	0	0	0
4	Fluorene	0	0.245	0	0.058	0	0	0.088	0.122	0	0.047
5	Phenanthrene	0	0	0	0	0	0	0	0.054	0	0
6	Anthracene	0	0	0	0	0	0	0	0.054	0	0
7	Fluorathene	0	0.172	0.177	0.050	0.015	0.140	0	0	0	0
8	Pyrene	0	0	0	0.073	0	0	0	0	0	0
9	Chrysene	0	0	0	0	0	0	0.584	0	0	0
10	Benz(a)anthracene	0	0	0	0	0	0	0.584	0	0	0
11	Benzo(b)Fluorthene	0	0.422	0	0	0	0	0	0	0	0
12	Benzo(a)Pyrene	0	0	0	0	0.264	0	0	0.253	0	0
13	Indno(1,2,3-c,d)Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo(g,h.i)Perylene	0	0.960	0	0	0	0	0	0	0	0
15	Dibenzo(a,h)anthracene	0	0	0.590	0	0	0	0	0	0	0
16	Benzo(g,h,i)Perylene	1.207	0	0.748	0.741	0	0.486	0	0	0	0.885

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA SHELL CONTINUED

NO.	PAH/sample	H51	H52	H53	H54	H55	H56	H57	H58	H59	H60
1	Naphthalene	0.168	0.049	0.147	0.164	0.167	0	0	0	0	0
2	Acenaphthalene	0.118	0	0	0.119	0	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0.122	0	0.080	0.182	0	0	0	0	0	0
8	Pyrene	0	0	0	0	0	0	0	0	0	0
9	Chrysene	0	0.197	0	0.923	0	0	0	0	0	0
10	Benz(a)anthracene	0	0.197	0	0.923	0	0	0	0	0	0
11	Benzo(b)Fluorthene	0	0	0	0	0	0	0	0	0	0
12	Benzo(a)Pyrene	0	0	0	0.520	0	0	0	0	0	0
13	Indno(1,2,3-c,d)Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo(g,h.i)Perylene	0	0	0.660	0	0	0	0	0	0	0
15	Dibenzo(a,h)anthracene	0	0	0	0	0	0	0	0	0	0
16	Benzo(g,h,i)Perylene	0	0	0.713	2.088	0	0	0	0	0	0

APPENDIX IV

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB

NO.	PAH/sample	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10
1	Naphthalene	1.129	0.067	0.065	0	0.076	0.068	0.056	0.052	0.147	0.111
2	Acenaphthalene	0	0	0	0	0	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0.167	0
5	Phenanthrene	0.089	0.038	0.014	0	0.045	0	0	0	0.028	0
6	Anthracene	0.086	0.038	0.014	0	0.045	0	0.066	0	0.028	0
7	Fluorathene	0	0	0	0	0	0	0.165	0	0	0
8	Pyrene	0	0.022	0	0.066	0.107	.076	0.165	0.020	0	0.048
9	Chrysene	0.047	0.356	0	0	0	0	0	0	0	0
10	Benz[a]anthracene	0.048	0.356	0	0	0	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0	0	0	0	0	0	0	0
12	Benzo[a]Pyrene	0	0	0	0	0	0	0	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0	0	0	0	.341	0
15	Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0	0.403	0	0	0	0.711	0	0.578	0.267

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB CONTINUED

NO.	PAH/sample	N11	N12	N13	N14	N15	N16	N17	N18	N19	N20
1	Naphthalene	0.199	0	0.067	0	0.730	0.073	0	0.140	0.084	0
2	Acenaphthalene	0	0	0.021	0	0	0	0	0	0	0.030
3	Acenaphthene	0	0	0	0	0	0	0.32	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0	0
5	Phenanthrene	0	0.013	0	0	0	0	0	0	0	0
6	Anthracene	0	0.013	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0	0	0	0	0	0	0	0
8	Pyrene	0	0.083	0	0	0	0	0	0	0	0
9	Chrysene	0	0	0	0	0	0	0	0	0	0.080
10	Benz[a]anthracene	0	0	0	0	0	0	0	0	0	0.080
11	Benzo[b]Fluorthene	0	0	0	0	0	0	0	0	0	0.177
12	Benzo[a]Pyrene	0	0	0	0	0	0	0	0.091	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0.124	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0.326	0	0	0	0.623	0
15	Dibenzo[a,h]anthracene	0	0	0	0	0	0.262	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0.333	0	0.320	0.478	0	0	0	0	0.827

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB CONTINUED

NO.	PAH/sample	N21	N22	N23	N24	N25	N26	N27	N28	N29	N30
1	Naphthalene	0.050	0	0	0.038	0.089	0.092	0	0.069	0	0
2	Acenaphthalene	0	0	0	0	0	0	0	0	0	0
3	Acenaphthene	0	0.038	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0.016	0	0	0	0	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0	0	0	0	0	0	0	0
8	Pyrene	0	0	0	0.012	0	0	0	0	0	0
9	Chrysene	0	0	0	0.081	0.024	0	0	0	0	0
10	Benz[a]anthracene	0	0	0	0.081	0.024	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0	0	0	0	0	0	0	0
12	Benzo[a]Pyrene	0	0	0	0	0	0	0	0.179	0	0.072
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0.243	0.251	0	0	0	0
15	Dibenzo[a,h]anthracene	0	0	0	0	0.247	0	0	0	0	0
16	Benzo[g,h,i]Perylene	1.529	0	0.250	0	0	0	0	0	0	0

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB CONTINUED

NO.	PAH/sample	N31	N32	N33	N34	N35	N36	N37	N38	N39	N40
1	Naphthalene	0	0.100	0.059	0	0.030	0.078	0	0	0.073	0.062
2	Acenaphthalene	0.11	0	0	0	0	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0	0.017
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0	0	0	0	0	0	0	0
8	Pyrene	0	0	0	0	0	0	0.018	0	0.019	0
9	Chrysene	0.046	0	0	0	0	0	0	0	0	0
10	Benz[a]anthracene	0.046	0	0	0	0	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0.126	0	0	0	0	0.215	0	0
12	Benzo[a]Pyrene	0	0	0.402	0	0	0.180	0	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0.261	0	0.386	0	0	0.535	0.269	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0.391	0	0	0	0	0	0	0.301
15	Dibenzo[a,h]anthracene	0.320	0	0	0	0	0	0.252	0	0.334	0
16	Benzo[g,h,i]Perylene	0	0.667	0	0	0	0	0.560	0	0	0

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB CONTINUED

NO.	PAH/sample	N41	N42	N43	N44	N45	N46	N47	N48	N49	N50
1	Naphthalene	0.058	0	0.033	0.064	0	0	0.090	0	0	.945
2	Acenaphthalene	0	0	0	0	0	0	0	0	0	0
3	Acenaphthene	0	0	0.048	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0.059	0	0.023	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0	0.007	0	0	0	0	0	0
8	Pyrene	0	0.017	0	0	0	0	0	0.041	0	0
9	Chrysene	0	0	0	0	0	0	0	0	0	0
10	Benz[a]anthracene	0	0	0	0	0	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0.354	0	0.129	0	0	0	0	0
12	Benzo[a]Pyrene	0	0.544	0	0	0.142	0	0	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0.302	0	0	0	0	0	0	0	0.350
15	Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0	0.864	0	0.356	0	0.652	0	0	0.412

CONCENTRATIONS OF PAH COMPOUNDS IN COCOA NIB CONTINUED

NO.	PAH/sample	N51	N52	N53	N54	N55	56	57	58	59	60
1	Naphthalene	0	0	0.036	0	0.074	0	0	0	0	0
2	Acenaphthalene	0	0	0.025	0.110	0.113	0	0	0	0	0
3	Acenaphthene	0	0	0	0	0	0	0	0	0	0
4	Fluorene	0	0	0	0	0	0	0	0	0	0
5	Phenanthrene	0	0	0	0	0	0	0	0	0	0
6	Anthracene	0	0	0	0	0	0	0	0	0	0
7	Fluorathene	0	0	0	0	0	0	0	0	0	0
8	Pyrene	0	0.007	0	0	0	0	0	0	0	0
9	Chrysene	0	0	0.274	0	0.108	0	0	0	0	0
10	Benz[a]anthracene	0	0	0.274	0	0.108	0	0	0	0	0
11	Benzo[b]Fluorthene	0	0	0	0	0	0	0	0	0	0
12	Benzo[a]Pyrene	0	0	0	0	0	0	0	0	0	0
13	Indno[1,2,3-c,d]Pyrene	0	0	0	0	0	0	0	0	0	0
14	Benzo[g,h.i]Perylene	0	0	0	0	0	0	0	0	0	0
15	Dibenzo[a,h]anthracene	0	0.255	0	0	0	0	0	0	0	0
16	Benzo[g,h,i]Perylene	0	0	0	0	0	0	0	0	0	0