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Polycyclic Hydrocarbons (Pahs) in Ghana Cocoa Beans

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Abstract

The concentration of polycyclic aromatic hydrocarbons (PAHs) in cocoa beans from six regions of Ghana was investigated. Thirty-six (36) samples of cocoa beans were randomly collected from farming communities in each of the six regions during the lean and major seasons. The samples were air-dried for two days to prevent hydrolysis and degradation and stored in amber glass bottles. The PAHs were extracted using the Soxhlet extraction method and analysed using gas chromatography (GC). With PAH_S, even though cocoa farmers in these regions were not found drying the beans with heat generated from locally manufactured ovens, some levels of polycyclic aromatic hydrocarbons were detected in all the thirty-six farms visited. The regions from which the cocoa bean samples were obtained include: Western, Ashanti, Eastern, Central, Volta and Brong-Ahafo regions. Only one farm in the Western Region recorded two carcinogenic polycyclic aromatic hydrocarbons, Benzo[a]Flourenthene, and Dibenzo[a]anthracene at low levels (BDL - 4.80 ± 10.00 ng/kg) and (BDL - 15.50 ± 40.00 ng/kg) respectively. Pyrene (49.90 ± 90.00 - 578.90 ± 650.00 ng/kg) and Flourenthene (113.60 ±180.00 - 620.80 ± 390.00 ng/kg) were however present in all the cocoa samples collected from the 36 farms. The presence of these polycyclic aromatic hydrocarbons was thought to have originated from vehicular emissions, as that particular cocoa bean samples were found being dried in close proximity to roads within their communities. The results obtained for the PAHs in the cocoa beans were compared with the WHO/FAO permissible levels. The results obtained were for four PAHs, namely: pyrene, fluoranthene, benzo[k]fluoranthene and dibenz[a,h]anthracene, in the cocoa beans from all the six regions were found to be lower than the WHO/FAO permissible levels. However, benzo[k]fluoranthene and dibenz[a,h]anthracene were not detected in the cocoa beans from five of the regions.

Keywords

Cocoa Beans, Polycyclic Aromatic Hydrocarbons, Carcinogenicity, Pyrene, Fluoranthene, Benzo[k]fluoranthene and Dibenz[a,h]anthracene

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are harmful chemicals that humans have released into the world. PAHs are hydrophobic chemicals that have two or more benzene rings that are joined together. They are mostly made when organic material combustion occurs, geothermal heat is released, and plants are burned [1]. They are mostly found in developed countries, where people burn things, which is where most PAHs in soils come from. PAHs are very common and can be found in many natural samples. Industrial operations, such as the processing, burning, and dumping of fossil fuels, are linked with the presence of PAHs in highly polluted areas [2]. PAHs make up a big part of creosote and anthracene oil, which are used to treat wood infested with pests. They move through the air, where they are usually found in small amounts (a few nanograms per cubic meter). There are more than 600 known PAHs. The most important ones are those that affect public health. PAHs have low air pressure, high freezing and boiling points, and a low ability to dissolve in water. Over time, they build up in fatty tissue. People can easily be exposed to PAHs in many ways.

Pollution, described as the entrance of chemicals or energy into the environment by people or animals, can cause dangers to human health, living resources, and natural damage.

Ghana's cocoa business, employing around 800,000 farm families in 10 of its 16 areas, is a major addition to the country's GDP, giving food, jobs, tax income, and foreign exchange gains [3]. However, the quality of cocoa beans is affected by production, processing, and handling, which can introduce pollutants like herbicides and polycyclic aromatic hydrocarbons (PAHs), which are dangerous environmental toxins. PAHs are formed by imperfect burning of organic molecules and natural processes, and their deadly potential is a worry. Cocoa production also includes drying the beans, which can be soiled by asphalt, bitumen, or direct fire drying models. Polycyclic hydrocarbons can also be affected during storage and shipping.

Cocoa, a natural plant native to central and southern America, was rare and expensive, only given to the rulers of Ica or Aztec. It was used to cover chickens and was banned by commoners. The Portuguese and Spanish stole seeds for sale. Cocoa seeds and goods were expensive in Europe, only available to the rich. Ghanaian history links cocoa to Tetteh Quarshie's visit to Soa Palme [4].

Historically, Ghana was the world's largest cocoa producer. Ghana is the second-largest producer and exporter of cocoa beans of worldwide production [5].

Cocoa is widely used in sweets, drinks and beauty care items worldwide.

The global desire for cocoa seeds has grown over time, with Europe taking 50% of global cocoa production, followed by the Americas, Asia, and Africa. Cocoa, long used for treating illnesses like heart diseases, has seen a drop in healing use, but modern studies are reviving its medical importance. Cocoa is rich in antioxidants, including polyphenols and flavonoids, which constitute about 8% of the dry weight of the beans. Flavonoids, such as flavonols, can possibly lower the chance of coronary heart diseases [1]. Ghana's cocoa business is important for foreign exchange creation, with its first production hitting one million tonnes in 2010. Only 5% is made into candies, while the rest is shipped, earning $2 billion. This adds to almost half of Ghana's GDP and funds building growth and social services. Cocoa is referred to as Ghana's black gold due to its major economic impact. Polycyclic aromatic hydrocarbons (PAHs) are the most poisonous component of petroleum products, made of two or more joined benzene rings. PAHs can be grouped into low-molecular-weight and high-molecular-weight groups based on their physical and chemical features [6]. PAHs can appear naturally or be made for study reasons. They typically appear as clear, white, or pale yellow-green masses with a slight, nice smell. PAHs are found in crude oil, used motor oil, smoke, and complex mixes of toxic chemicals. Diesel engines, gasoline cars, metal smelters, and coal-fired power plants are major sources of PAHs in urban settings. They can also be found in coal tar production plants, coking plants, bitumen and asphalt production plants, coal-gasification sites, smoke houses, aluminium production plants, coal tarring facilities, and city trash incinerators. PAHs can be transformed and degraded in the atmosphere through the process of pyrolysis and reaction with ozone, nitrogen oxides, dinitrogen oxide, hydroxide, peroxyacetyl nitrate and sulfur dioxide to produce oxy-, hydroxyl-, diones, nitro-, sulfonic acids, dinitro-and hydroxynitro-polycyclic aromatic hydrocarbon derivatives [7]. PAHs are a major amount of harmful components found in polluted soils or sediments, mainly found in soil, sediment, and oily substances, rather than water or air [8].

Some studies believe that the formation of polycyclic aromatic hydrocarbons (PAHs) may be helped by free radical reaction, although the exact process remains unclear.

Polycyclic aromatic hydrocarbons (PAHs) have different degrees of aromaticity based on their resonance structure. Phenanthrene has two sextets at the ends, while anthracene has one and spreads its aromaticity out. The difference in sextets is mirrored in UV absorption spectra, with phenanthrene having the highest absorption wavelength around 290 nm and anthracene having the highest wavelength bands around 380 nm. Chrysene has three Clar structures with two sextets. PAHs are neutral and steady chemicals with low solubilities in water and low volatilities. They are highly lipophilic, resulting in low amounts of water and long half-lives in natural media. In aerobic sediments, half-lives range from three weeks for naphthalene to 300 weeks for benzo[a] pyrene. PAHs are known as persistent organic pollutants (POPs), and their longevity increases with ring number and

condensation depth [9]. PAHs can enter the body through the lungs through smoke from cigarettes, wood, coal, and industrial places [10]. People living near dangerous trash areas can also be exposed to PAHs. PAHs are changed into different chemicals by all organs, some more dangerous than others. Animal studies indicate that PAHs do not stay in the body for long, leaving within a few days through faeces and urine. Most PAHs enter the body through faeces and urine [11]. Polycyclic aromatic hydrocarbons (PAHs) are taken through the lungs and enter organs with fat, with most held in kidneys, liver, and fat tissues. They are listed as Group 1 human carcinogens by the International Agency for Research on Cancer (IARC), with various individual PAHs as Group 2A or 2B carcinogens. PAHs can be processed by different enzymes to reactive products capable of damaging DNA. Some PAHs link to the aryl hydrocarbon receptor, causing both genotoxic and non-genotoxic effects. Other processes involve interaction with gap junction intracellular signalling and disruption of cell signals. PAH exposure can cause non-cancer toxins such as immunotoxicity, reproductive toxicity, developmental toxicity, neurotoxicity, and developmental toxicity. Risk studies are performed to predict possible health effects from polluted garbage areas, air pollution, and certain meals. Most studies have focused on a few PAHs, with carcinogenicity being the most commonly studied outcome [12].

2. Materials and Methods

2.1. Study Area

The study collected dry cocoa bean samples from six Ghanaian cocoa-growing areas, selected due to their proximity to roads. The farms were selected for the study since they are about approximately 50 meters from road source. A total of six samples were collected randomly from each farming community in the regions during the two crop seasons. The major season was in October/November while the lean season was in July/August.

The regions from which the cocoa bean samples were obtained include: Western, Ashanti, Eastern, Central, Volta and Brong-Ahafo regions.

2.2. Collection of Samples

Cocoa bean samples were collected late in the day (2 pm - 5 pm) to prevent airborne exposure to PAHs and vehicular fumes. The cocoa beans were also air-dried on the next day of collection for two days to avoid hydrolysis and degradation of the PAHs. The fact that PAHs can be adsorbed onto plastic materials, samples were collected and kept in amber glass bottles. The samples were kept in a dark place at room temperature to prevent degradation of PAHs by sunlight prior to treatment. Cocoa bean samples were collected late in the day to prevent airborne exposure to PAHs and vehicular releases. They were air-dried for two days to prevent hydrolysis and degradation. Samples were stored in amber glass bottles and kept at room temperature to prevent sun exposure before treatment.

2.3. Quality Control

The study involved washing and drying glassware with laboratory detergents (TEEPOL), distilled water, and drying at 130˚C to prevent contamination. Hexane was rinsed before analysis. Quality control procedures included using analytical-grade reagents and distilling non-academic-grade reagents in glass. Two PAH recovery studies were conducted using PAH-certified reference material with the code CRM 1941B from NIST. Ten grams of the CRM 1941B sample were subjected to the same extraction procedures as cocoa bean samples.

2.4. Calibration

A calibration graph of the ratio of PAH concentration to that of the certified reference material (CRM 1941B) peak area against mass of PAH in sample injected was constructed via the data handling system. The original sample concentration was calculated from the sample volume extracted, sample volume injected and dilution factor.

2.5. Reagents/Chemicals

The study utilized analytical quality reagents and chemicals from BDH Chemical Limited in the UK, including dichlomethane, ethyl acetate, cyclohexane, sodium sulphate, sodium chloride, methanol, and potassium hydroxide.

2.6. Preparation of 50% Potassium Hydroxide

The potassium hydroxide solution was prepared by dissolving 250 g of potassium hydroxide pellets in distilled water, cooling, and then transferring to a 500 ml volumetric flask to obtain 50% KOH.

2.7. Preparation of Methanolic-KOH Solution

The cocoa sample was saponified by mixing 200 ml of methanol with 25 ml of an alkaline solution, enhancing the extraction of lipophilic PAH by making the fat water-soluble.

2.8. Sample Preparation

The samples were packaged in metal foils and put into black polyethene and sent to the laboratory. In the laboratory, the samples were freed from foreign materials such as pebbles and air dried for five hours at room temperature. The cocoa beans were pulverized into paste. (using a laboratory multipurpose blender Polymix KCH-Universalmühle M 20). Ten grams wet weight samples were placed in amber glass bottles and kept overnight in a dark locker at room temperature. Approximately 10.0 g of anhydrous Na_2SO_4 was added to the wet sample, mixed and the mixture allowed to stand for twenty-four hours in a desiccator containing silica gel activated overnight at 105˚C in an electric oven to dry. The dried mixture was reweighed and the dry mass of the cocoa beans calculated in order to determine the moisture content.

2.9. Extraction of PAHs from Cocoa Samples

The Chen & Lin (1997) method for extracting PAHs in fatty food crops involved adding methanolic-KOH to a sample and allowing it to stand for 3 minutes. The sample was then transferred to a thimble for the Soxhlet extraction, and 250 ml of dichloromethane was extracted for 16 hours. The crude extracts were concentrated using a rotary evaporator and stored at room temperature before saponification.

2.10. Saponification Procedure for PAH

The crude extract was prepared by adding a 50 ml methanolic-potassium hydroxide solution and 30 ml of 30% brine to the crude concentrate. The mixture was then transferred to a separating funnel containing distilled water, cyclohexane, dichloromethane, and cyclohexane. The funnel was shaken and allowed to stand for two hours. The organic layer was then drained into dichloromethane. Anhydrous sodium sulphate, dried at 105˚C for 24 hours, was added to the organic layer and allowed to stand for 50 minutes. The dried extract was filtered using a Buchner funnel and concentrated to 2 ml. The procedure was repeated for all samples, and the 2 ml crude extract was kept in desiccators before cleanup.

2.11. Clean up for PAHs

The process of gas chromatographic analysis involves purifying crude concentrate extracts by cleaning them up. A chromatographic column is packed with 30 g of florisil and activated in an oven for 2 hours. The column is then loaded with a 1:1 dichloromethane-cyclohexane mixture, and the extracts are dissolved in 5 ml of dichloromethane. The elution is repeated with 2 × 25 ml of the mixture. The eluates are collected and quantitatively transferred to a flask. The final extract is concentrated to 1 ml at 30˚C using a rotary evaporator. The final extract is stored in a desiccator for gas chromatographic analysis.

2.12. GC Analysis

The GC-MS parameters were optimized before sample analysis, using a glass liner with glass wool to prevent contamination. The injection port temperature was set at 280˚C, and several temperature programs were experimented on to obtain the best resolution for PAHs in cocoa bean analysis. The standard was analysed in scan mode to see the fragmentation pattern of each PAH. If the standard is not in good condition, decomposition products appear in SCAN mode. After scanning, the standard target and qualifier ions were determined for each PAH. SIM mode improved sensitivity by limiting the mass of the ions detected to one or more specific fragment ions of known mass. The most popular method of spectral interpretation and identification is the comparison of sample spectra with collections of reference spectra. The presence of a target compound is established when two criteria are met: retention time and ion ratios. Mass software performs automatic integration of peaks, but visual inspection is essential for accurate results. The

surrogate standard mixture used for the analyses contained acenapthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12. Monitored ions for PAHs were used for the analyses.

2.13. Calibration of Instrument for Sample Analysis

A calibration curve is prepared by running at least four standards. There are two methods: the external standard calibration method and the internal standard calibration method. The external method plots the area or height response against concentrations, while the internal standard method is more reliable. Both methods involve adding equal amounts of internal standards to equal volumes of sample extracts and calibration standards.

3. Results and Discussions

Dry cocoa beans from thirty-six farming communities in six regions were analysed for polycyclic aromatic hydrocarbons, including pyrene and fluoranthene. However, only one farm in the western region detected two additional carcinogenic polycyclic aromatic hydrocarbons: benzo[k]fluoranthene and dibenz[a,h]anthrancene. The levels of these hydrocarbons were found to be lower than the WHO/FAO recommended levels worldwide (2008). The mean levels of some polycyclic aromatic hydrocarbons were also compared to those detected by (Takrama *et al.* 2012). For example, benzo[k]fluorenthene was detected at 4.80 µg/kg, below the recommended levels (20.00 - 270.00 ng/kg) and dibenz[a,h]anthrancene at 15.5 ng/kg, similar to the recommended levels (10.00 - 120.00 ng/kg).

Two PAH recovery studies were conducted using certified reference material (CRM 1941B) from the National Institute of Standards and Technology (NIST) to ensure quality results. Ten grams of CRM 1941B sample were subjected to the same extraction procedures as cocoa bean samples. A calibration graph was constructed to calculate the ratio of PAH concentration to the reference material peak area against mass of PAH in the sample injected. The results indicated that recovery of mixed standard PAHs of pyrene, fluoranthene, benzo[k]fluor, and dibenz[a,h]an at 0.1ng/kg was within an acceptable range of 80.0% - 150.0% (Table 1 and Figure 1).

Table 1. Mean levels of PAHs in samples from all the six cocoa growing regions in Ghana (ng/kg).

PAH	Pyrene	Fluoranthene	Benzo[k]fluor	Dibenz[a,h]an
Eastern	175.8 ± 150	155.0 ± 120	BDL	BDL
Western	227.6 ± 270	620.8 ± 390	4.8 ± 10	15.5 ± 40
Ashanti	469.3 ± 420	418.8 ± 350	BDL	BDL
Central	578.9 ± 650	501.8 ± 490	BDL	BDL
Volta	375.8 ± 580	256.9 ± 160	BDL	BDL
BA	49.9 ± 90	113.6 ± 180	BDL	BDL
WHO	3500.0	2500.0	250.0	100.0

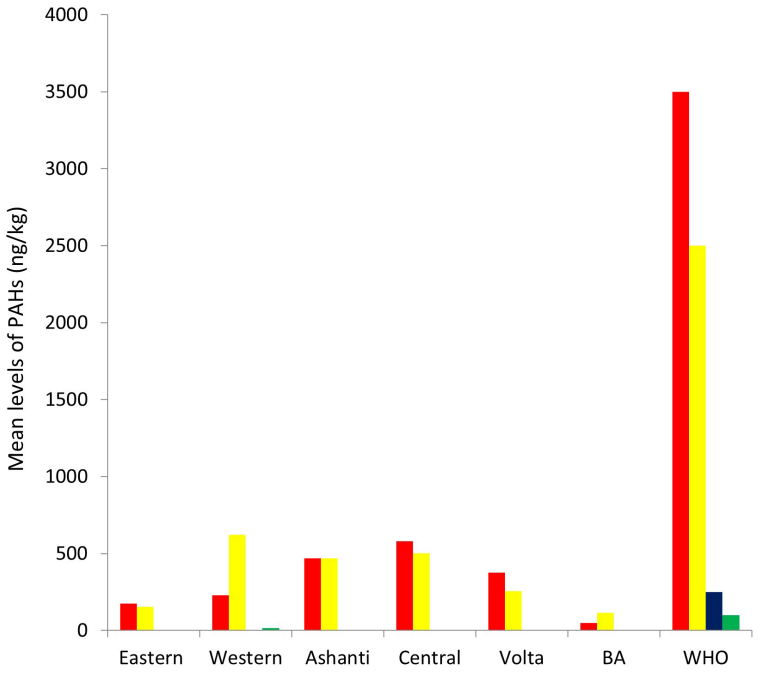

Figure 1. A comparison of PAHs in Cocoa with WHO/FAO levels. Key: pyrene (Red), fluoranthene (Yellow), benzo[k]fluoranthene (Blue), dibenz[a,h]anthracene (Green).

4. Conclusions

The results of this study provide important insights into the presence of polycyclic aromatic hydrocarbons (PAHs) in Ghana's cocoa beans and their possible effects on public health and trade. Despite the lack of direct contamination from traditional drying methods such as firewood and oven drying, the study found varied amounts of PAHs across all tested areas. Notably, cocoa beans dried near roads showed higher amounts, showing vehicle fumes as a main pollution source. However, the discovered PAH levels, including key carcinogenic compounds like benzo[k]fluoranthene and dibenz[a,h]anthracene, stayed well below the WHO/FAO acceptable limits, confirming the safety of Ghanaian cocoa for both local usage and foreign markets.

The study stresses the importance of keeping strict post-harvest handling practices to reduce pollution risks. Strengthening tracking systems, ensuring proper drying methods away from pollution sources, and enhancing quality control measures will be essential for keeping Ghana's image as a top cocoa producer. Further study is suggested to explore long-term environmental risks and prevention methods. By effectively handling these concerns, Ghana can protect its cocoa industry while ensuring the continued production of high-quality, safe cocoa beans for global consumers.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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