Comparison of Polycyclic Aromatic Hydrocarbons, Pahs Concentration Levels in Types of Beans and Maize from Markets in South East Nigeria

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Abstract: Polycyclic aromatic hydrocarbons, PAHs are carcinogenic, mutagenic and persistent organic compounds commonly generated from incomplete combustion of organic matters. Beans, *Phaseolus vulgaris* and maize, *Zea mays* form part of staple foods commonly consumed and are highly rich in protein and carbohydrate respectively. This study compared the concentration levels of the sixteen priority PAHs in different types of beans (Potasikum, white iron, brown iron, Gausau and Nija red) and maize (white, yellow and pop corn) obtained from various markets in south east Nigeria. The purchased beans and maize samples were picked, ground and extraction was by sonication with a solvent mixture of dichloromethane and hexane in the ratio of 3:1. The determination of PAHs was by gas chromatography coupled with flame ionization detector, GC-FID. The result showed that the PAHs concentration levels ($\times 10^{-2}$ µg/kg) of lower molecular weight PAHs, LMW detected in the analyzed beans samples ranged from 8.842±4.743 to 12.590±8.068 in white iron beans and brown iron beans respectively with percentages of 41.09% and 44.90% and 5.998±4.725 to 9.385±11.339 in pop and white corn respectively at 25.58% and 34.46%. While the high molecular weight, HMW PAHs concentration levels ($\times 10^{-2}$ µg/kg) varied from 12.673±5.554 in white iron beans to 16.998±3.129 in Nija red beans at 58.88% and 63.95% and from 17.84±11.768 in pop maize to 18.153±10.421 in yellow maize at 74.83% and 67.43% respectively. The probable carcinogenic PAH8 concentrations detected varied from (8.875±2.725 to 11.796±3.018) $\times 10^{-2}$ µg/kg in white iron beans and brown iron beans respectively and from (10.82±6.183 to 13.573±8.789) $\times 10^{-2}$ µg/kg in pop and yellow maize respectively.. Diagnostic ratio calculated showed fuel combustion to be the main source of emission. The sixteen priority PAHs were detected in all the analyzed samples at a very low concentration levels, lower than the permissible limit of 1.0 µg/kg established by EFSA for cereals and cereal based products. Hence these (PAHs) can at a long time accumulation in the body be very harmful. There is need to establish a permissible limit of PAHs in beans and other legume grains by either European Food Safety Authority, EFSA or other regulatory bodies.

Keywords: Beans, Corn, Food, Gas Chromatography, Polycyclic Aromatic Hydrocarbons

1. Introduction

Polycyclic aromatic hydrocarbons, PAHs are neutral, non polar molecules found in fossil fuels (oil and coal) and in tar deposits and are produced, generally when insufficient oxygen or other factors result in incomplete combustion of organic matter (e.g, in engines and incinerators, when biomass burns in forest fires, etc.) [1]. PAHs are lipophilic, most of them are not soluble in water and persist in the environment. Aqueous solubility of PAHs decreases approximately logarithmically as molecular mass increases

[2]. The lower molecular weight polycyclic aromatic hydrocarbons (LMW-PAHs) dissolve in water, making them more available for biological uptake and degradation [2]. While high molecular weight polycyclic aromatic hydrocarbons (HMW-PAHs) volatilize sufficiently to appear in the atmosphere predominantly in gaseous form, although the physical state of four-ring PAHs can depend on temperature [3]. In contrast, compounds with five or more rings have low solubility in water and low volatility; they are therefore predominantly in solid state, bound to particulate air pollution, soils, or sediments. In solid state, these compounds are less accessible for biological uptake or degradation, increasing their persistence in the environment [2, 4]. Because many PAHs are neither soluble in water nor volatile, they are found primarily in soil, sediment, oily substances and particulate matter suspended in air.

Several of these compounds are carcinogenic and/or mutagenic therefore, they may pose a human health threat [5]. However, the primary focus of the toxicological research on PAHs has been on genotoxicity and carcinogencity. Studies have shown that several PAHs damage DNA and cause mutations which in some cases may result to cancer [6].

It has been reported that PAHs are present in foods such as rice [7, 8] corn [9] soy bean oil [10] bread, meat, [11] fish, [12] fruits and vegetables, [13, 14] cereal products such as noodles, spaghetti and macaroni [15].

PAHs enter the environment mostly as releases to air from volcanoes, forest fires, residential wood burning, exhaust from automobiles and trucks. They can also enter water surface through discharges from industrial plants and waste water treatment plants, and they can be released to soils at hazardous waste sites if they escape from storage containers. They are present in air as vapours or stuck to the surfaces of small solid particles.

Beans, *Phaseolus vulgaris* are among the most versatile and commonly eaten foods throughout the world, and many varieties are grown in the U.S. and other countries because of their nutritional composition. Beans provide protein, fiber, folate, iron, potassium and magnesium and contain little or no total fat, trans-fat, sodium and cholesterol. The dietary fibre content of beans may play a role in reducing the risk of colorectal cancers [16]. Beans are high in natural antioxidants [17]. The colour of the bean coat appears to affect the antioxidant capacity because this correlates with total phenolic content of the bean. Coloured beans (red, brown or black) possess greater antioxidant activity than white beans [18]. Beans are naturally gluten-free food and they provide many vitamins and minerals often found in enriched grain products, including thiamin, riboflavin, folate, iron and fiber.

Maize, Zea mays is the most widely grown grain crop throughout Americas, with 332 million metric tons grown annually in the United States alone [19]. Maize was introduced into Africa in the 16th Century and has since become one of Africa's dominant food crops.

Maize is processed and prepared in various forms depending on the country. Ground maize is prepared into porridge in Eastern and Southern Africa, while maize flour is prepared into porridge in West Africa. In all parts of Africa, green (fresh) maize is boiled or roasted on its cob and served as a snack. Popcorn is also a popular snack. Maize is the most important cereal crop in sub-Saharan Africa (SSA) and an important staple food for more than 1.2 billion people in SSA and Latin America [20]. In industrialized countries, maize is largely used as livestock feed and as a raw material for industrial products.

According to US EPA [21] and IARC [22], PAHs are regarded as priority pollutants and exhibit properties such as persistency, bioaccumulation, mutagenicity, carcinogencity toxicity and potential for long-range environmental transportation to a certain extent. The bioaccumulating properties of the PAHs result in the magnification of the substances in the tropic level of food webs. These properties lead to increased concern for the toxic effects that they can exert, even at extremely low levels in the ambient environment. Therefore, there is great need of determining the PAHs concentration levels in these grains which forms major staple in Enugu and Anambra states and assess the safety and risk of consuming them.

The types of beans to be analyzed are Potiskum, white iron, brown iron, Gausau and Nija red and the types of maize are white, yellow and pop maize.

2. Materials and Methods

2.1. Materials and Reagents

All reagents were of analytical grade and included; hexane, dichloromethane, activated alumina. Four PAHs surrogate standard mixtures-acenaphthalene d_{10}, chrysene d_{12}, phenathrene d_{10} and perylene d_{12} were purchased from Sigma Aldrich U S A.

Different types of beans (Potiskum, white iron, brown iron, Gausua and Nija red) and maize (white, yellow and pop) were bought from some markets in Anambra and Enugu states, Nigeria.

2.2. Equipment and Instruments

Gas chromatography/flame ionization detector (HP 6890 Powered with HP ChemStation), rotary evaporator, borosilicate beaker, glass column, sonicator.

2.3. Sampling

Twenty-four grain samples which included different types of beans (Potiskum, white iron, brown iron, Gausau and Nija red) and corn (white, yellow and pop) were purchased from some major markets in Enugu and Anambra states of Nigeria. The markets included New market, Gariki market and Ogbete main market in Enugu East, Enugu South and Enugu North Local Government Areas of Enugu State respectively, Nsukka main market in Igboetiti Local Government Area, Awka central market in Awka South Local Government Area of Anambra State, Umunze main market in Orumba South L. G. A. of Anambra State. The samples were picked to remove sand and other impurities, ground and put in labeled amber

sample bottles ready for extraction.

2.4. Extraction of Samples

One sample was used to run recovery experiment to ensure the effectiveness of the method. A mixture of four deuterated PAHs (d-PAHs) which included, acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} were used. Three mixed standard solutions of concentrations 100, 500 and 1000 µg/mL were prepared using four deuterated PAHs (d-PAHs). These were used to spike three 5 g portions of ground grain samples which were extracted by sonication using mixed solvent- dichloromethane and hexane in the ratio of 3:1. The extracts were cleaned-up in alumina column using the same solvent mixture.

2.5. Determination of PAHs

All samples were each analyzed using a gas chromatography equipped with flame ionization detector, GC-FID, (HP 6890). Following recoveries of 94.0% to 99.2%, the grain samples were extracted and PAHs determined by the procedure.

2.6. Limit of Detection (LOD) and Limit of Quantitation (LOQ)

LOD was determined by continuous dilution and analysis of standard solution until the least concentration was obtained at the signal to noise ratio of 3. Likewise LOQ was determined by continuous dilution and analysis of standard solution until the least concentration was obtained at signal to noise ratio of 10.

2.7. Statistical Analysis

The statistical analysis of the data obtained in different samples was carried out using SPSS version 16.00 to calculate analysis of variance, level of significance at 95 % confidence and Pearson correlation coefficient.

2.8. Calculation of PAH Diagnostic Ratios

The sources of the PAHs detected in this study were calculated using PAH diagnostic ratios of Ant/(Phe+Ant), Fla/(Pyr+Fla), I[cd]P/(I[cd]P+B[ghi]P) and B[a]A/B[a]A+Chr. [23, 24]

3. Result and Discussion

3.1. Result

The average recoveries of PAHs ranged from 94% to 99%. Limit of detection and quantification varied from $(0.03 - 0.09) \times 10^{-3}$ µg/l and $(0.09 - 0.25) \times 10^{-3}$ µg/l. The mean concentration of individual PAH compounds in different types of beans were presented in Table 1. The mean concentration $(\times 10^{-2}$ µg/kg) of ∑16 PAHs in these bean types ranged from 21.516±7.429 to 28.04±11.10 in white iron and brown iron beans respectively and that of maize ranged from 23.84±16.493 in pop maize to 27.252±23.105 in white maize. The highest concentration of lower molecular weight, LMW PAHs was detected in brown iron beans constituting 44.9% of ∑16 PAHs and in white maize at 34.46% while the lowest concentration of LMW PAHs occurred in white iron beans constituting 41.1% of ∑16 PAHs and in pop maize at 25.58%. The highest concentration of higher molecular weight, HMW PAHs occurred in Nija red at 64% and in pop maize at 74.83% while the lowest concentration was obtained in white iron beans at 58.9% and in white maize at 65.57%. The mean concentrations of PAH2, PAH4 and PAH8 in the studied beans types varied from 5.569±1.237 to 7.964±2.450, 8.179±2.637 to 10.918±2.727 and 8.875±2.725 to 11.796±3.018 respectively and in the maize types from 5.739±3.589 to 7.57±7.276, 10.16±5.617 to 12.833±8.159, 10.82±6.183 to 13.573±8.793 respectively. The eight carcinogenic PAHs occurred highest in brown iron beans at the mean concentration of 11.796×10^{-2} µg/kg and in yellow maize at 13.573×10^{-2} µg/kg.

Table 1. Mean Concentration ($\times 10^{-2}$ µg/kg) levels of PAHs in the analyzed Beans types.

PAH	POTISKUM MEANS±SD	WHITE IRON BEANS MEANS±SD	BROWN IRON BEANS MEANS±SD	GAUSAU MEANS±SD	NIJA RED MEANS±SD
Naphthalene	0.031 ± 0.001	0.026 ± 0.008	0.0207 ± 0.012	0.024 ± 0.009	0.030 ± 0.006
Acenaphthylene	0.081 ± 0.057	0.095 ± 0.075	0.103 ± 0.047	0.154 ± 0.187	0.099 ± 0.059
Acenaphthene	1.314 ± 1.810	0.688 ± 0.711	2.661 ± 2.140	1.068 ± 1.630	0.602 ± 0.408
Fluroene	0.126 ± 0.183	0.107 ± 0.152	0.226 ± 0.214	0.171 ± 0.260	0.071 ± 0.087
Phenanthrene	4.889 ± 4.215	4.49 ± 3.020	5.097 ± 3.365	5.229 ± 3.823	3.945 ± 1.149
Anthracene	3.423 ± 2.885	3.437 ± 2.559	4.482 ± 3.095	4.415 ± 2.977	4.832 ± 1.185
Fluoranthene	0.713 ± 0.398	0.772 ± 0.439	1.194 ± 1.272	1.190 ± 1.067	0.954 ± 0.344
Pyrene	2.843 ± 2.836	3.026 ± 3.065	1.708 ± 0.348	3.022 ± 2.737	4.744 ± 1.781
Benzo[a]anthracene	2.611 ± 2.156	2.016 ±2.070	2.229 ± 0.619	2.870 ± 2.407	3.747 ± 1.458
Chrysene	1.106 ± 1.126	1.255 ± 1.354	3.918 ± 2.747	1.729 ± 2.184	1.100 ± 0.788
Benzo[b]fluoranthene	0.389 ± 0.113	0.421 ± 0.145	0.724 ± 0.406	0.514 ± 0.204	0.523 ± 0.051
Benzo[k]fluoranthene	0.435 ± 0.071	0.421 ± 0.044	0.390 ± 0.039	0.397 ± 0.093	0.398 ± 0.043
Benzo[a]pyrene	4.463 ± 2.362	4.486 ± 2.243	4.046 ± 0.591	4.798 ± 1.728	5.071 ± 1.242
Indeno[1,2,3-cd]pyrene	0.051 ± 0.043	0.049 ± 0.049	0.133 ± 0.098	0.066 ± 0.069	0.101 ± 0.088
Dibenzo[a,h]anthracene	0.032 ± 0.024	0.031 ± 0.020	0.051 ± 0.031	0.097 ± 0.107	0.062 ± 0.038
Benzo[g,h,i]perylene	0.228 ± 0.102	0.195 ± 0.092	0.305 ± 0.190	0.255 ± 0.124	0.297 ± 0.038
∑16 PAHs	22.735 ± 7.794	21.516 ± 7.429	28.04 ± 11.10	25.10 ± 9.845	26.576 ± 3.513
∑LMW PAHs	9.864 ± 6.694	8.842 ± 4.743	12.59 ± 8.068	11.061± 7.497	9.579 ± 1.486
∑HMW PAHs	12.871 ± 5.891	12.673 ± 5.554	15.45 ± 3.976	14.937± 5.095	16.998 ± 3.129

PAH	POTISKUM	WHITE IRON BEANS	BROWN IRON BEANS	GAUSAU	NIJA RED
	MEANS±SD	MEANS±SD	MEANS±SD	MEANS±SD	MEANS±SD
PAH2	5.569 ± 1.237	5.741 ± 0.903	7.964 ± 2.450	6.527 ± 0.721	6.172 ± 0.718
PAH4	8.568 ± 3.301	8.179 ± 2.637	10.918 ± 2.727	9.911 ± 2.518	10.442 ± 1.998
PAH8	9.315 ± 3.357	8.875 ± 2.725	11.796 ± 3.018	10.726± 2.779	11.300 ± 1.971

Table 3 presented PAHs diagnostic ratios. For the PAH ratio of Ant/Ant + Phe, the concentration ($\times 10^{-2}$ μg/kg) of the beans types ranged from 0.412 in Potiskum to 0.551 in Nija red and from 0.651 to 0.756 in yellow and white maize respectively: for Fla/Fla + Pyr, the concentration ranged from 0.201 in Potiskum to 0.533 in brown iron beans and from 0.0788 to 0.173 respectively in pop and yellow maize. In the case of PAH ratio of I[cd]P/I[cd]P + B[ghi]P, the concentration varied from 0.183 in Potiskum to 0.304 in brown iron beans, from 0.111 to 0.236 also in pop and yellowmaize respectively. The PAH ratio of B[a]A/B[a]A + Chr concentration ranged from 0.363 in brown iron beans to 0.773 in Nija red and from 0.370 to 0.723 in pop and yellow maize respectively.

Table 2. *Mean Concentration ($\times 10^{-2}$ μg/kg) levels of PAHs in the analyzed Corn types.*

PAHs	White Corn	Yellow Corn	Pop Corn
Naphthalene	0.029±0.021	0.028±0.0170	0.027±0.0191
Acenaphthylene	0.033±0.026	0.023±0.0189	0.032±0.0276
Acenaphthene	1.845±3.587	1.807±3.676	0.269±0.248
Fluorene	0.097±0.178	0.072±0.138	0.022±0.0184
Phenanthrene	1.854±1.684	2.388±1.656	1.182±0.370
Anthracene	5.56±5.842	4.457±5.704	4.467±4.0418
Fluoranthene	0.799±0.865	0.794±0.844	0.553±0.393
Pyrene	4.483±0.854	3.79±0.783	6.461±5.192
Benzo[a]anthracene	3.757±1.782	5.281±1.924	3.787±1.665
Chrysene	2.54±4.863	2.023±3.764	0.231±0.136
Benzo[b]fluoranthene	0.387±0.195	0.338±0.197	0.609±0.363
Benzo[k]fluoranthene	0.452±0.334	0.342±0.233	0.441±0.328
Benzo[a]pyrene	5.095±2.413	5.193±2.268	5.508±3.453
Indeno[1,2,3-cd]pyrene	0.073±0.119	0.072±0.115	0.021±0.0106
Dibenzo[a,h]anthracene	0.098±0.175	0.093±0.167	0.029±0.0247
Benzo[g,h,i]perylene	0.249±0.167	0.233±0.124	0.169±0.203
$\sum$16 PAHs	27.252±23.105	26.933±21.629	23.84±16.493
$\sum$LMW PAHs	9.385±11.339	8.7753±11.209	5.998±4.725
$\sum$HMW PAHs	17.867±11.766	18.153±10.421	17.84±11.768
PAH2	7.57±7.276	7.215±6.032	5.739±3.589
PAH4	11.713±9.253	12.833±8.153	10.16±5.617
PAH8	12.585±10.047	13.573±8.793	10.82±6.183

Table 3. *PAHs Diagnostic Ratios of the Analyzed Beans and Maize Types.*

PAHs RATIO	BEANS TYPES					MAIZE TYPE		
	POTISKUM	WHITE IRON BEAM	BROWN IRON BEANS	GUASAU	NUA RED	White	Yellow	Pop
ANT/ANT + PHE	0.412	0.434	0.468	0.458	0.551	0.756	0.651	0.791
FLA/FLA + PYR	0.201	0.203	0.533	0.283	0.167	0.151	0.173	0.079
I[cd]P/I[cd]P+B[ghi]P	0.183	0.201	0.304	0.206	0.254	0.227	0.236	0.111
B[a]A/B[a]A + CHR	0.702	0.616	0.363	0.624	0.773	0.597	0.723	0.037

3.2. Discussion

The average recovery of 96.5% indicated high efficiency of the extraction procedure. The values of limits of detection and quantification showed high efficiency of the determination procedure. The mean PAHs concentration levels of the beans and maize types were very low (although no regulatory body has established permissible limit for beans and other leguminous grains) compared to the permissible limit established by European Food Safety Authority, EFSA 1.0 μg/kg for cereal grains [25]. Among the analyzed beans types, brown iron recorded both the highest $\sum$16 PAHs concentration and PAH8 content with the values of 28.04 $\times 10^{-2}$ μg/kg and 11.796 $\times 10^{-2}$ μg/kg

respectively. While Nija red recorded the most abundance of HMW PAHs constituting 16.998 $\times 10^{-2}$ μg/kg detected with high $\sum$16 PAHs and PAH8 concentration ($\times 10^{-2}$ μg/kg) of 26.576 and 11.300 respectively. This may be attributed to their colour. Potiskum and white iron beans having similar colour recorded almost the same mean concentration levels of $\sum$16 PAHs with values of 22.516±7.794 and 21.516±7.429 respectively. They also recorded close mean concentration levels of HMW PAHs with the values of 12.871±5.891 for Potiskum and 12.673±5.554 for white iron beans. Their PAH8 concentration levels were 9.315±3.357 for Potiskum and 8.875±2.725 for white iron beans. Guasua beans recorded moderately high concentration levels of $\sum$16 PAHs, HMW-PAHs and PAH8. Although literature has not reported much

studies on bean grains, the total mean PAHs concentration levels obtained in this study compares very low to some reported studies on grains. The average total concentration of the PAHs in analyzed maize was 26.01 x 10^{-2} µg/kg with mean concentration of 1.63 ± 1.99. In this case, B[a]P was the dominant PAH with 5.158. The PAH concentrations of maize obtained in this study were far below that obtained by Embbey et al. [26] in analysis of imported canned maize. This might be as a result of contribution of more PAHs from preservatives added in the canned maize. Also Olabemiwo et al. [27] in their study on PAHs determination in three local snacks which included pop corn (guguru) collected from Ogbomoso in Nigeria, obtained the total 16 PAHs concentration levels in roasted pop corn as 3.835 µg/kg but in this study, the total 16 PAHs concentration obtained in pop corn was 0.024 µg/kg. This is comparably very low, probably because the pop corn analyzed in this present work were not exposed to a high temperature.

The total 16 PAHs detected in maize, 26.027×10^{-2} µg/kg in this study compared low to that reported by Olabemiwo [28] in roasted maize from road side vendor in Ogbomoso, Nigeria. This is because maize grains analyzed in this study were not exposed to a very high temperature.

It can be deduced from Table 3, based on the PAH diagnostic ratios for source identification complied by [24], that Ant/Ant + Phe being > 0.1 for the samples indicated fuel combustion source. Also B[a]A/B[a]A + Chr being > 0.35 for all the samples and I[cd]P/I[cd]P + B[ghi]P ratios recording between 0.2-0.5 (except for Potiskum) revealed the source of PAHs contamination to be fuel combustion. The Fla/Fla + Pyr ratios recorded < 0.4 for all the samples except Nija red, white and yellow maize indicating petrogenic emission source. Conclusively the sources of PAHs contamination in the beans and maize samples analyzed in this study were fuel combustion and petrogenic.. From the analysis of variance, p>0.05 proving no significant difference between the PAHs concentration of the analyzed grains.

4. Conclusion

The sixteen priority PAHs were all detected in analyzed beans and maize samples. The diagnostic ratio showed that the source of PAHs contamination of these samples was mainly fuel combustion and rarely petrogenic emission sources. However, these PAHs can get into human system by ingesting these contaminated beans and maize grains. Although the PAHs concentrations obtained in this study were five-fold low compared to the safety limit of 1.0 µg/kg established by EFSA for cereals and cereal based products, these PAHs at certain significant concentration level can be very dangerous to human health. This study has provided base values for future monitoring of contamination values of bean and maize grains. The regulatory bodies can use the values obtained in this study to establish the permissible limit for legume grains. It can also be ascertained the safety of consuming Nigerian bean and maize grains with respect to PAHs contamination levels. The environmental substances such as foods, soil, water and air should always be on regular analysis to ensure that they are not contaminated by PAHs beyond the safety limit.

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