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POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN FOREIGN AND LOCAL RICE SAMPLES FROM ENUGU MARKETS, NIGERIA

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Abstract

Concentration levels of sixteen polycyclic aromatic hydrocarbons, PAHs were determined in the Foreign and Local rice from markets in Enugu state Nigeria. Samples of various types of Foreign rice (Indian, Royal stallion, Thailland and Peoples' choice) and Local rice (Abakaliki, Nzam, Lafia and Adani) were purchased from various markets in Enugu. The samples were extracted by sonication using 3:1 dichloromethane –hexane mixture as solvent followed by clean – up with activated alumina. The measurement of the concentration levels of PAHs was carried out using a gas chromatograph coupled with flame ionization detector (GC- FID). The mean concentrations ($\times 10^{-2}$ *µg/kg) of different types of Foreign rice ranged from 25.01 to 28.72 and from 20.01 - 32.66 in Local rice. Anthracene showed the highest concentration in the analyzed Foreign rice at the average of 5.10 while naphthalene showed the lowest concentration at the average of 0.035. Benzo[a]pyrene showed highest concentration in the analyzed Local rice at the average of 4.83 and naphthalene also showed the lowest concentration at 0.08. The PAHs concentrations detected in this study were much lower than 1.0 µg/kg which is the permissible limit established by European Food Safety Authority. This indicates that both the Foreign and Local rice sold in Enugu markets are free from PAHs contamination.*

Keywords: Rice, Foreign, Gas Chromatography, Local, Polycyclic aromatic hydrocarbons.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of toxic xenobiotic fused-ring aromatic compounds consisting of hydrocarbon molecules of two or more fused benzene and/or pentacyclic rings in linear, angular or cluster formation [1]. Polycyclic Aromatic Hydrocarbons (PAHs), are produced as a result of incomplete combustion of organic matter, emission sources, automobile exhaust, coal-fired electricity, generating power-plants, domestic matter, forest fires, waste incineration, road traffic and volcanic eruption [2-3]. PAHs are sparely soluble in water and highly lipophilic, almost non-biodegradeable and can undergo long distance atmospheric transportation and deposition. Due to these characteristics, PAHs are likely to cause adverse human health or environmental effects near to and distance from their source [2- 4].

PAHs occur in foodstuff such as meat, grains, bread, flour, vegetables and fruits [5, 6, 7, 8], as a consequence of environmental contamination and the thermal processes to which the foods are subjected to during processing and manufacturing. PAHs can enter the food chain by deposition from air or by deposition and transfer from soil and water. In most cases, ingestion of contaminated foods is the main source of human exposure to these pollutants. The occurrence of PAHs in variety of plants has been demonstrated [9].

Cereals especially rice grains constitute the main staple food for most developing countries and serve as major source of energy, protein, vitamin B and some mineral elements for world population [10]. Cereals and cereals products, milk, vegetables and fruits are the highest contributors to total PAHs intake. These contaminants may enter and accumulate in agriculture soil and crops through irrigation and atmospheric sink and will directly threaten food safety [11].

PAHs are detrimental to public health due to their carcinogenic properties and bioaccumulation and this have been a worldwide concern [12]. The United State Environmental Protection Agency, USEPA lists sixteen PAHs as priority pollutants present in the air, water and soil [13]. This study therefore proposed to determine the levels of PAHs in rice grains from markets in Enugu State Nigeria.

Materials and Methods

Reagents

All reagents and solvents were of analytical grade and were purchased from Sigma Aldrich U S A. These included hexane, dichloromethane, activated alumina as well as four deuterated (surrogate) standard namely acenaphthalene d_{10}, chrysene $d_{12,}$ phenathrene d_{10} and perylene d_{12}.

The analysis was carried out in Multi Environmental Management Consultants Ltd, Plot 4/5 Laara Sownmade Rd, off Igbe Rd, Ijede Ikorodu, Lagos, Nigeria.

Equipment and Instruments

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

Sampling

Twenty – four (24) samples which included different types of rice, foreign rice (Peoples' choice , Indian rice, Royal Stallion, Thailand rice) : local rice (Abakaliki, Lafia , Adani, Nzam) 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.

Extraction of Samples:

Recovery experiments to optimize PAH extraction from grain samples were carried out. 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 3:1 dichloromethane-hexane mixture as solvent. The extracts were cleaned-up in an alumina column using the same solvent mixture [14].

Determination of PAHs

PAHs concentrations were determined with 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 same procedure [14].

Statistical Analysis

Analysis of variance and Pearson Correlation Coefficient at 95% confidence level were carried out using SPSS version 16.00 on the data obtained.

Calculation of PAH Diagnostic Ratios

The diagnostic ratios were calculated using the expression, Ant/(Phe + Ant) for LMW PAHs, B[a]A/(B[a]A + Chr) and Fla/(Pyr + Fla) for MMW PAHs then I[cd]P/(I[cd]P + B[ghi]P) for HMW PAHs. The PAHs involved in each ratio have close molar mass, so it is assumed they have similar physicochemical properties based on the PAH isomer ratios in source identification compiled by Yunker et al [15].

Results and Discussion

Result

The analyzed Foreign rice were Indian, Royal Stallion,Thailland, Peoples' choice and Local rice were Abakaliki, Lafia, Adani and Nzam. The average PAH concentration levels of these grains are given in Tables 1.0 and 2.0 respectively.

Table 1.0: Average PAH Concentrations (× 10^{-2} µg/kg) in the Foreign Rice.

PAH	Indian	Royal Stallion	Thailand	Peoples Choice
Naphthalene	0.034	0.031	0.038	0.032
Acenaphthylene	0.054	0.051	0.140	0.038
Acenaphthene	2.606	2.916	1.905	0.339
Fluorene	0.261	0.322	0.197	0.017
Phenanthrene	1.778	2.150	5.574	3.190
Anthracene	4.649	5.083	4.594	6.059
Fluoranthene	1.890	2.117	1.221	0.502
Pyrene	1.634	1.863	3.287	5.720
Benzo[a]anthracene	3.648	2.956	3.001	5.066
Chrysene	3.008	3.660	1.512	0.218
Benzo[b]fluoranthene	0.606	0.713	0.465	0.400
Benzo[k]fluoranthene	0.577	0.666	0.446	0.499
Benzo[a]pyrene	3.266	3.746	4.031	6.299
Indeno[1,2,3-ed]pyrene	0.118	0.135	0.053	0.030
Dibenzo[a,h]anthracene	0.070	0.079	0.027	0.025
Benzo[g,h,i]perylene	0.811	0.444	0.195	0.282
TOTAL	25.009	26.93	26.686	28.716
AVERAGE	1.563	1.683	1.668	1.795
STDEV	1.487	1.613	1.856	2.508

EFSA Permissible limit for cereals and cereal products = 1.0µg/kg

Table 2.0: Average PAH Concentrations (× 10^{-2} µg/kg) in the Analyzed Local Rice.

PAH	Abakaliki	Lafia	Adani	Nzam
Naphthalene	0.019	0.048	0.041	0.039
Acenaphthylene	0.077	0.051	0.052	0.029
Acenaphthene	3.958	0.694	1.029	0.33
Fluorene	0.601	0.044	0.0560	0.023
Phenanthrene	5.641	2.957	3.004	3.833
Anthracene	6.327	3.546	3.303	3.022
Fluoranthene	2.813	0.689	0.862	0.648
Pyrene	1.508	3.573	1.925	5.779
Benzo[a]anthracene	2.168	3.974	2.486	5.403
Chrysene	5.230	0.826	0.606	0.306
Benzo[b]fluoranthene	0.932	0.368	0.273	0.425
Benzo[k]fluoranthene	0.783	0.447	0.412	0.447
Benzo[a]pyrene	1.845	5.767	5.581	6.123
Indeno[1,2,3-cd]pyrene	0.190	0.047	0.053	0.034
Dibenzo[a,h]anthracene	0.103	0.030	0.032	0.028
Benzo[g,h,i]perylene	0.465	0.612	0.293	0.285
TOTAL	32.662	23.672	20.011	26.754
AVERAGE	2.041	1.479	1.251	1.672
STDEV	2.139	1.834	1.601	2.313

EFSA Permissible limit for cereals and cereal products = 1.0µg/kg

From Table 1.0, the average total PAH concentrations (× 10^{-2} µg/kg) in the studied Foreign rice were Indian- 25.009, Royal Stallion - 26.93, Thailland - 26.69, Peoples' choice - 28.72 with the total of a 107.34 and mean concentrations of 1.56 ± 1.49, 1.68 ± 1.61, 1.67 ± 1.86, 1.80 ± 2.51 respectively. While those of Local rice were Abakaliki - 32.66, Lafia - 23.67, Adani - 20.01, Nzam - 26.75 with the grand total of 103.10 and mean concentration of 2.04 ± 2.14, 1.48 ± 1.83, 1.25 ± 1.60, 1.67 ± 2.31 respectively. From the total obtained, the PAH concentrations in Foreign rice was greater than that of Local rice. The PAH concentrations in both Foreign and Local rice arranged in decreasing order was Abakaliki > Peoples' choice > Royal Stallion > Nzam > Thailland > Indian > Lafia > Adani. In other words, Abakaliki rice analyzed contained the highest PAH concentrations while Adani rice analyzed contained the lowest PAH concentrations.

Discussion

The average PAH concentration of rice obtained was lower than what was reported in some reviewed studies. In a reported work on dynamics analysis for distribution of PAHs in polished and unpolished rice by Xiaoxing Liu et al. (2001) [16], using GC/MS after solid phase microextraction, SPME, nine targeted EPA prioity PAHs (acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene and perylene) were detected at the total concentration levels of 58±9.5 µg/kg for unpolished rice and 19±2.6µg/kg dry weight for polished rice. In this study, the total concentrations of the same nine EPA priority PAHs was 22.77µg/kg which was a bit higher than total concentration of polished rice. According to Xiaoxing Liu et al. (2001) [16], the PAH concentrations in the polished rice was far lower than the unpolished rice which they attributed to the purification stages. Escarrone et al. (2014) [17], also reported detection of some PAHs in rice grain dried by different processes using quick, easy, cheap, effective, rugged and safe extraction method, QUECHERS and GC-MS for analyzing 17 PAHs. Essumang, (2011) [18], reported the determination level of 18 PAHs introduced into cooked rice through some common cooking methods in Ghana using GC-FID analysis. According to Essumang, the rice used as a control in the research showed various levels of PAHs, notably among them were pyrene (0.24 mg/kg), benzo[b]fluoranthene (0.66), dibenzo[a,h]anthracene (2.54 mg/kg), 2-methyl naphthalene (0.16 mg/kg). The values were too high in comparison with the values obtained in this study and this might be due to the cookintemperature. Also the study by Akan et al. (2018) [19], on polycyclic aromatic hydrocarbons in different varieties of rice from Yobe state revealed detection of 16 PAHs but in a very low concentrations. The authors reported the predominant of the lower molecular weight PAHs over the higher molecular weight PAHs in the studied rice samples, naphthalene, fluorine and pyrene having the highest values of 2.25 × 10^5, 4.26 × 10^5 and 3.23 × 10^5mg/kg respectively. From the PAHs diagnostic ratios calculated, the values showed that the emission sources of PAH concentration in rice analyzed were combustion and petrogenic. This may be attributed to absorption from contaminated soil and deposition from fuel combustion during transportation and processing. The higher PAHs concentration in foreign rice than local rice might be attributed to PAH emission source from fuel combustion as a result of transportation. However, the PAH concentrations obtained in this study were below the permissible limit which is 1.0 µg/kg established by EFSA for cereals and cereals products.

Conclusion

All the sixteen priority PAHs were detected in the analyzed grain samples. Most of the PAHs get into them either through plant absorption of contaminated soil during food processing or even through vehicle emission and fuel combustion during transportation. The diagnostic ratio showed that the source in addition. However these PAHs can get into human system by ingesting contaminated food, inhaling contaminated air dermal contact with contamination soil.

Although the PAHs concentrations obtained in this study were below the safety limit recommended by EFSA for cereals and cereal based products, these PAHs at certain significant concentration levels can be very dangerous to human health. This study has provided base values for future monitoring of contamination values of the grains. Also there is assurance of high quality and safety of Nigerian grains with respect to PAHs contamination levels. All 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 safety limit.

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