



## Research Article

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## EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBON IN SUYA AND SMOKE FISH FROM BAYELSA STATE

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**Abstract:** This study was carried out to investigate some ubiquitous group of environmentally persistent organic compound of varied toxicity. This study investigated grilled meat samples popularly called "suya" and species of smoked catfish samples were purchase from an open market in "Tombia, Swali, Amassoma," all located at the Niger Delta region of Bayelsa State. Dual samples were made from the purchased items and a part were soaked in boiled water for ten minutes. The soaked samples was sun dried in the laboratory. The samples were analyzed for sixteen Polycyclic Aromatic Hydrocarbons content namely Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenz (a,h) anthracene, Indeno (1, 2, 3 - c, d) pyrene, Benzo (g,h,i) perylene. Gas Chromatography – Mass Spectrometric analysis was performed on a Thermo Scientific TRACE GC ultra - system. Results from this study revealed that the highest mean levels of the individual PAHs were observed in samples of smoked fish with Phenanthrene, Naphthalene, Fluorene, Fluoranthene and Pyrene concentration of  $16.22 \pm 1.10 \mu\text{g/kg}$ ,  $9.42 \pm 0.14 \mu\text{g/kg}$ ,  $4.46 \pm 0.10 \mu\text{g/kg}$ ,  $2.14 \pm 0.06 \mu\text{g/kg}$  and  $1.14 \pm 0.02 \mu\text{g/kg}$  for the smoked fish species and  $5.23 \pm 0.09 \mu\text{g/kg}$ ,  $4.89 \pm 0.09 \mu\text{g/kg}$ ,  $1.18 \pm 0.03 \mu\text{g/kg}$ ,  $0.57 \pm 0.05 \mu\text{g/kg}$ , and  $0.07 \pm 0.02 \mu\text{g/kg}$  for the smoked fish soaked in hot water. The results further reveals that the PAHs values for grilled meat/smoked fish are far higher than those obtained with those soaked in boiled water. Hence, it is recommended that consumers of these food produce should be educated on a modern technique of preparing them in order to limit the release of these toxic material into the food items before they are consumed.

**Keywords:** Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Smoke,

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## INTRODUCTION

The human race holds a special place in the animal kingdom. Her successful blending of substances for consumption, which gives her nutritional assistance mostly obtained through hunting, gathering, and agriculture, is a result of her cerebral competence. There is no doubt that this millennium has seen noticeable change in the fields of science, technology, life expectancy, and lifestyle, as well as in the foods we consume. Some of these changes were not adequately handled, and as a result, in later decades, we saw an increase in the incidence of diet-related illnesses like obesity, heart disease, diabetes, cancer, and dementia. (FAO,2010). The successful combination of substances on consumption, has a growing body of evidence that indicates that omega-3 fatty acids has a number of nutritional qualities that help maintain proper functioning of the heart, by playing a role in the regulation of blood clotting and vessel constriction, as well as in the neurological development before and after childbirth; it reduces tissue inflammation and the symptoms of rheumatoid arthritis; it has a positive impact on the cardiac arrhythmias. A common example of a dietary item that has this substance that prolongs life is fish. Fish is a high-protein, low-fat food with a number of health advantages. (Ezomoh and Madukosiri,2016). They have a lower fat content and are rich in omega-3 fatty acids, popularly known as "the good fat." According to a

general review, fish is nutritionally low in omega-6 fatty acids, the so-called "bad" fats frequently present in red meat.

The polycyclic aromatic hydrocarbons (PAHs), often referred to as the poly nuclear aromatic hydrocarbons, are one of the pervasive groups of molecules that are abundant in the environment. With two or more fused aromatic rings consisting of carbon and hydrogen atoms, PAHs make up a sizable family of organic molecules. Figure 1 depicts several PAHs' chemical structures. A source of PAH is food (Guillen *et al.*, 1997). When food is smoked, roasted, barbecued, or grilled, especially meat, meat products, and fish, PAHs are created as a result of incomplete combustion or thermal degradation of the organic ingredients (WHO, 2006). The PAH produced by the pyrolysis of the lipids in the meat or fish are deposited on the food. The amount of fat in the meat or fish and the distance of the food from the heat source both affect how much PAH is produced when food is cooked over charcoal (barbecued, grilled) (Phillips, 1999; Kazerouni *et al.*, 2001).

This study is aimed to determine the PAH concentrations in smoked fish (catfish) and grilled meat (suya), sold in the Niger Delta area of Nigeria and the results compared with those obtained when this food items is processed with hot water for minutes before

being used for food and the possible health effect analyzed on consumption.

## MATERIALS AND METHODS

### Study Area

The study was carried out in Amassoma and Yenagoa, all in Bayelsa State, Nigeria.

### Sample Preparation

Grilled meat popularly called suya were purchased from vendors in an open market located at the Swali and the Tombia market situated in the Yenagoa region and two different samples of smoked fish species of mud fish frequently consumed in Bayelsa, were purchased from the Tombia market, the Swali market and the Amassoma market, all located at the Niger Delta region of Bayelsa State. Dual samples of these items were prepared and triplicated. Triplicate of one part of the samples to be investigated in this study were soaked in boiled water for 5 minutes while the other sample were prepared for analysis. The samples were brought out of the hot water and air dried in the laboratory. The samples under investigation were grounded by a blender and stored in a freezer at -20°C in tightly sealed bottles prior to analysis for sixteen PAHs, namely Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz (a)anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenz (a,h) anthracene, Indeno (1, 2, 3 - c, d) pyrene, Benzo (g,h,i) perylene.

### Principle

The homogenized smoked fish and grilled meat (suya) samples are fortified with appropriate labeled internal standards and saponified with methanolic KOH. After repeated extraction in hexane, further cleanup was carried out on a silica – SPE cartridge. The concentrated extract was analyzed by GC – MS/MS using a Thermo Scientific TSQ Quantum XLS gas chromatography triple quadrupole mass spectrometer system. The PAHs of the smoked fish and grilled meat sample were quantified and compared with those from existing standards.

### Saponification

2g of the homogenized meat and fish samples was weighed into a different 250 mL Duran bottle and 50 µL of PAH internal standard solution was added to the samples. The mixture was vortexed for 10 sec and was allowed to stand for 10 min to attain equilibrium. 200 mL of MeOH/KOH solution was added and the samples introduced into an ultrasonic bath for 30 min at 60°C for saponification and then was allowed to cool.

### Extraction

2g of the saponified fish and meat samples was filtered through a glass wool into a 500 mL separating funnel. 100 mL of hexane samples was added and the resulting mixture was shaken for 3 min. The hexane layer from each sample was transferred into a 100 mL Erlenmeyer flask. The hexane layer of each sample was

combined in a separator funnel and the layer washed by shaking with a 50mL of MeOH/H<sub>2</sub>O solution for 1 min. The resulting solutions were evaporated to 1 mL under vacuum at 220 mbar / 50°C.

### Clean up

The SPE cartridge were conditioned with a 3 mL hexane solution. The extract were applied to the cartridge. This were eluted into an evaporator glass tube with 50 mL of hexane. The resulting solution was evaporated at 40°C to dryness using a blow down apparatus under a gentle stream of nitrogen before finally reconstituting in 180 µL of cyclohexane plus 20 µL of injection standard.

### GC – MS Analysis

GC – MS analysis was performed on a Thermo Scientific TRACE GC ultra - system at a column of Thermo Scientific TR – 50MS 30 m and a split time of 1 min at an oven temperature of 60°C for 1 min. The system were reprogrammed at 12°C/min to 210°C and then 80°C/min to 340°C with 5 min hold time. Mass Spectrometry were carried out using a TSQ Quantum XLS triple quadrupole mass spectrometer at an emission current of 50µA and an ion source temperature of 250°C.

### Identification and quantification of PAHs.

The identification of individual PAH was performed by comparison of the substance retention time of the peak and the retention time of the peak of those obtained with true standards of PAHs. A careful inspection of the standard reference materials chromatogram was carried out to check interference. The measured peak area ratio of precursor to quantifier ion was in close agreement with those of the standard. To obtain standard calibration curves, PAH standard solutions relative to the two internal standard compounds were determined at five PAHs concentrations (1, 2, 5, 10, and 20 µg/g).

**Table 1.** Analysis conditions of Gas Chromatography-Mass Spectroscopy for the sixteen polycyclic aromatic hydrocarbons

<b>Instruments</b>	Thermo Scientific TRACE GC ultra – system
<b>Column</b>	Thermo Scientific TR – 50MS 30 m
<b>Column ID</b>	0.25mm, 0.25 µm film capillary column
<b>Injection Mode</b>	Split less with a 5mm injection port liner
<b>Injection port temperature</b>	270°C
<b>Flow rate</b>	1.2mL/min
<b>Split Flow</b>	“On” with 1.2mL/min
<b>Split Time</b>	1min

Method validation and analytical quality assurance.

Method was validated for accuracy, precision, and linearity, limit of detection (LOD) and limit of quantification (LOQ). Validation proceeded on 2 matrices including spiced meat (suya) and catfish samples. All standard mixtures were injected at a volume

of 1 µL in triplicate to construct calibration curves. Accuracy (%) and precision (%) were evaluated by repeating the spiked samples run. The spiked samples were analyzed in 3 different times during the same day and in three different day.

## RESULT

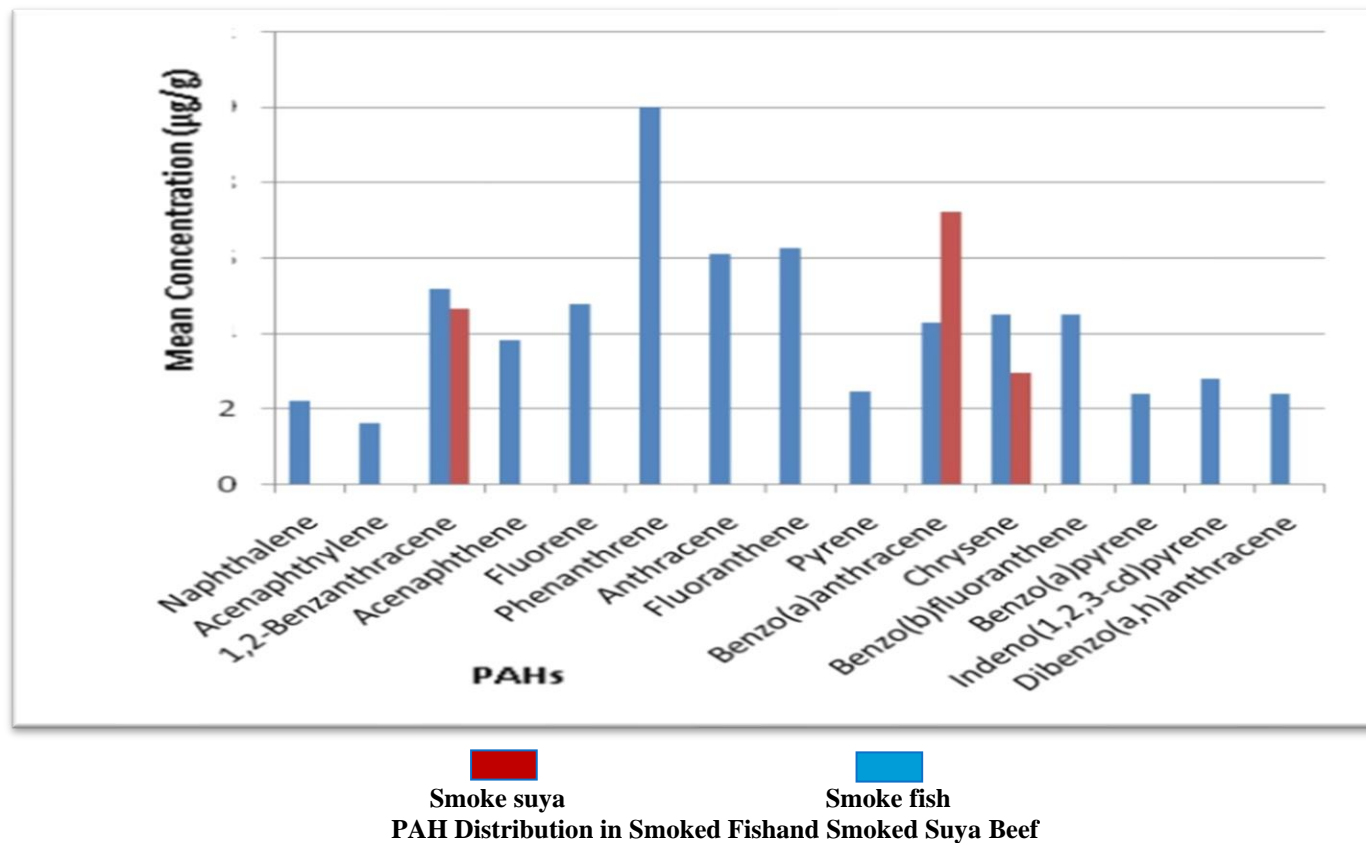
**Table 1.** Summary of PAH Concentrations in Food Samples in µg/kg

PAH	Smoked Catfish	Smoked Catfish Soaked in Hot Water	Smoked/Spice Meat (Suya)	Smoked/Spice Meat (Suya) Soaked in Hot Water
	Mean	Mean	Mean	Mean
Naphthalene	9.42 ± 0.14	4.89 ± 0.09	ND	ND
Acenaphthylene	0.37 ± 0.08	0.12 ± 0.01	0.07 ± 0.02	ND
Acenaphthene	1.28 ± 0.04	0.04 ± 0.06	ND	ND
Fluorene	4.46 ± 0.10	1.18 ± 0.03	ND	ND
Phenanthrene	16.22 ± 1.10	5.23 ± 0.09	0.24 ± 0.02	ND
Anthracene	1.99 ± 0.08	0.02 ± 0.03	ND	ND
Fluoranthene	2.14 ± 0.06	0.57 ± 0.05	ND	ND
Pyrene	1.14 ± 0.02	0.07 ± 0.02	ND	ND
Benz(a) antracene	0.32 ± 0.02	0.02 ± 0.04	7.38 ± 0.02	1.01 ± 0.02
Chrysene	ND	ND	3.27 ± 0.03	0.03 ± 0.01
Benzo(b) Fluoranthene	0.10 ± 0.01	ND	ND	ND
Benzo(k)Fluoranthene	ND	ND	ND	ND
Benzo(a)Pyrene	ND	ND	ND	ND
Dibenzo(a,h)antracene	ND	ND	ND	ND
Indeno(1, 2, 3 - c, d)pyrene	ND	ND	ND	ND
Benzo(g, h, i)perylene	0.22 ± 0.01	0.06 ± 0.02	ND	ND
Total	37.66 ± 1.57	12.20 ± 0.44	10.96 ± 0.09	1.04 ± 0.03

ND= Not Detected

The highest mean levels of individual PAHs were observed in samples of smoked fish with Phenanthrene, Naphthalene, Fluorene, Fluoranthene and Pyrene concentration of 16.22 ± 1.10 µg/kg, 9.42 ± 0.14 µg/kg, 4.46 ± 0.10 µg/kg, 2.14 ± 0.06 µg/kg and 1.14 ± 0.02 µg/kg for the smoked fish species and 5.23 ± 0.09 µg/kg, 4.89 ± 0.09 µg/kg,

1.18 ± 0.03 µg/kg, 0.57 ± 0.05 µg/kg, and 0.07 ± 0.02 µg/kg for the smoked fish soaked in hot water. The individual PAH of lower molecular weight found in high concentration could be attributed to the lower temperature obtained from the burning wood used in the smoking process. See table 3.



## DISCUSSION

Table 3.1 displays the findings of the examination of the PAH content for samples of smoked fish, suya, and both smoked fish and suya treated in boiling water. The Scientific Committee on Food (SCF) advised that the PAH concentrations in smoked meat products should be as low as is technically feasible after considering the properties of the PAH chemicals examined in this study.

According to data from table 1, smoked fish species contained detectable amounts of eleven of the sixteen PAHs that were the subject of this investigation. Ten of the sixteen PAHs evaluated in this study with the smoked catfish soaked in hot water were detected in substantial amounts and have concentrations of  $12.20 \pm 0.44$  g/kg, compared to the smoked fish species, which has a concentration of PAH of  $37.66 \pm 1.57$  g/kg. The fact that the PAH component in the smoked fish is dissolved in the hot water may be the cause of the increased PAHs concentration in those fish species as compared to those soaked in hot water. The distinctive color and smell of the ensuing hot water allowed one to see this. According to a general poll, newly produced smoked fish has a distinctively sweet flavor when consumed, but this flavor disappears when the fish is bathed in hot water for a few minutes before consumption. The smoked spiced meat known as "suya" followed the same pattern.

Only two of the sixteen PAHs that were the subject of this study's investigation—four of them—were found in the spiced pork (suya) that had been bathed in hot water. The

elevated fatty content of the fish in comparison to the beef may be responsible for the study's findings. There are more factors that might have an impact on these findings. Factors including the types of beef used in this study, some of which have significant levels of retained fat. The methods used to prepare the suya could also have an impact on the results because oil poured on hot spice meat drops onto hot coal, which enhances the compound's production. Since PAH molecules are retained in fatty fish tissue, researchers have observed a link between fish lipids and PAH compounds in their study. Stated in their study that the conditions of smoking play a major role in determining the amount of PAHs produced during the processing of smoked fish. In the old-fashioned method of smoking, smoke is produced in the bottom of the oven, and the food is placed right on top of it.

## CONCLUSION

The Nigerian Niger Delta population uses traditional smoking techniques to preserve fish and other food, such as beef. When compared to those that were soaked in hot water, it can be shown that smoked catfish and the flesh often referred to as suya have higher concentrations of PAHs. Findings from this study show that the skin or outer layer of the species under investigation could be peeled off or discarded when consumed because the mentioned portion of the fish under investigation serves as a sink for PAHs and may also play a significant role in PAH bioaccumulation. Despite the fact that the researcher was unable to compare the concentration loads

of PAHs compounds in the fish's primary canal between "smoked" and "unsmoked" samples or to estimate the PAHs concentration from the residual brackish smoky water obtained from the soaked smoked fish, the research still intends to proceed in order to overcome this limitation. Therefore, the general public should be made aware of the health risk posed by the bioaccumulation of these dangerous compounds. They should be informed about the importance of using current preservation techniques for these things because doing so could limit the discharge of harmful materials into them. This study has demonstrated that the Niger Delta market's smoked fish and grilled meat, such as suya, are polluted with high concentrations of PAHs. When these foods are prepared by first soaking in hot water for a short period of time before ingestion, this could be controlled.

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