Influence of Smoking on the Volatiles Profile of *Arius parkii*, *Cyprinus carpio* and Three Selected Sciaenidae Family Fish Species

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Abstract

The impact of smoking on the volatile components of five fish species via a two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOF-MS) was studied. Among these, *C. carpio* was found to be the most susceptible to deterioration. The experimental results affirmed that: fresh fish flavors are delicate, aroma/odor production via smoking depends on the fish specie involved and that industrial processes with heat application may affect fresh fish odor-active components. It further indicated the possibility of smoking to bring about the contribution of volatile compounds from wood smoke, production of off-flavors and/or increase the levels of some harmful compounds in fish.

Keywords: *Arius parkii*; *Cyprinus carpio*; fish smoking; *pseudotolithus*; volatile compounds

Introduction

For decades, fish has been a key part of human diet and source of livelihood for many individuals in developing countries (Adeyeye & Oyewole, 2016; Odukoya et al., 2020). Despite its high nutritional value as noted in literature, it's also subject to high level of deterioration (Odukoya et al., 2020) which starts from when caught (Martinsdottir, 2002). The biochemical, physical, enzymatic and bacterial effects lead to changes in the composition as well as state of the fish (Martinsdottir, 2002). Leduc et al. (2012) indicated fish freshness and odor as key quality indicators as the smell changes rapidly in relation to the level of freshness. Notwithstanding, according to Ganguly, Mahanty, Mitra, Raman, and Mohanty (2017), safety of fishery products is the chief quality parameter while consumer acceptance/rejection depends on their sensory attributes such as odor, flavor and palatability.

Several authors, including Leduc et al. (2012), indicated that fish spoilage during storage leads to the production of volatile compounds with different odors. Ganguly, Mahanty, Mitra, Raman, and Mohanty (2017) also reported a link between fish flavors and the volatile compounds in fish. These fresh fish flavors are very unstable and under unfavorable conditions, they give rise to unwanted flavor compounds associated with deterioration. With respect to Lindsay (1994), fish flavor deterioration is as a result of microbial and endogeneous enzymic activities which lead to destruction of some compounds as well as the generation of others. This author (*i.e*., Lindsay, 1994), added that chemical changes of volatile compounds in fish during storage and processing also give rise to various fish flavors.

On the other hand, different traditional methods such as drying, frying, salting, smoking, fermentation and their combinations, have been used in the preservation/processing of fish for consumption as well as storage (Adeyeye & Oyewole, 2016). Among these, smoking, which involves the use of smoke generated via the pyrolysis of wood (Varlet, Prost, & Serot, 2007), is the most commonly employed method in many African countries (Adeyeye & Oyewole, 2016). According to these latter authors, compounds in the smoke, like phenols, destroy bacteria while the fish is also cooked in the process due to the high temperature involved. Generally, as stated in Adeyeye and Oyewole (2016), wood smoke is made up of different complex chemical product gases, vapor and volatile substances in which the latter become absorbed on the fish wet surfaces to produce the characteristic aroma. Some of the recorded benefits of smoking include: increase in shelf life, flavor enhancement (Adeyeye & Oyewole, 2016; Adeyeye et al., 2017; Arvanitoyannis & Kotsanopoulos, 2012; Visciano, Perugini, Conte, & Amorena, 2008), inhibition of toxins formation (Adeyeye et al., 2017), reduction of microbial growth (Adeyeye et al., 2017; Arvanitoyannis & Kotsanopoulos, 2012), minimization of waste during the period of bountiful harvest and storage potential for lean season (Adeyeye & Oyewole, 2016), among others. Nevertheless, it was pointed out in Durnford and Shahidi (1998) that the main purpose for smoking fish is for flavor improvement.

Arius parkii is a specie of marine catfish (Conand, Camara, & Domain, 1995) of the Ariidae family (Ecoutin, Albaret, & Trape, 2005; Golani, 2002; Jayaprakash et al., 2015). As reported by Jayaprakash et al. (2015), it feeds on smaller fishes and shrimps. Meannwhile, *Cyprinus carpio*, of the Cyprinidae family (Zhang et al., 2008) and commonly referred to as common carp, is one of the key fish species in the global aquaculture production (Crexi, Monte, Soares, & Pinto, 2010; Xu et al., 2014; Zhang et al., 2011). In addition to its importance as a food source, in line with Xu et al. (2014), *C. carpio* is a valued ornamental fish specie. On the other hand, *Pseudotolithus* (ray-finned fish) is a genus of croaker belonging to the Sciaenidae family (Abimbola, 2016). This family, Sciaenidae, also comprises drums, meagres and weak fishes (Edwards, Gill, & Abohweyere, 2001) while Anyanwu (1983) identified *Pseudotolithus elongatus*, *Pseudotolithus senegalensis* and *Pseudotolithus typus* as the most economic important species of this family.

As aromas of fish are known to be very perishable and fish processing has been indicated to possibly results to the production of desirable aroma/flavor (Durnford & Shahidi, 1998), this research was designed to evaluate the impact of smoking on the volatile compounds from *A. parkii*, *C. carpio* and three members of the Sciaenidae family (*P. elongatus, P. senegalensis* and *P. typus*) using two dimensional (2D) gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOF-MS). To date, the volatile compounds in the smoked samples of these five selected fish species have not been comprehensively studied while Odukoya et al. (2020) noted improved separation/efficiency, increased sensitivity as well as “purity” of mass spectra as some of the important advantages of GC×GC-TOF-MS over the one-dimensional (conventional) GC systems. The current study seeks to address the following research questions:

i. Is smoking a suitable means of preserving/processing the selected fish species for storage and human consumption?
ii. To what extent/degree is the quality, volatile attributes and consumer acceptance of the investigated fish species influenced by smoking?

Materials and methods

Samples collection and preparation

Fresh samples of the five fish species (*A. parkii*, *C. carpio*, *P. elongatus*, *P. senegalensis*, and *P. typus*) were bought immediately after arriving the Doula fishing seaport and transferred in their fresh form to the laboratoy in an icebox [fish/ice ratio = 1:2 (w/w)]. Prior to evisceration, the fresh fish samples were carefully cleaned to remove slime and blood. Preparation for smoke-drying was done following the procedure as explained in Ahmed, Dodo, Bouba, Clement, and Dzudie (2011) with some modifications. This involved pre-drying of the appropriate fish to be smoked while an improved Altona-type smoking oven, with mangrove roots and trunks as fuel, was utilized for the final smoking-drying step. Clean materials and work surfaces were used in transferring the smoked fish samples. Extraction of lipids from the fresh and smoked fish samples was achieved via a soxhlet apparatus. Figure 1 highlights the steps followed before the volatiles analysis.

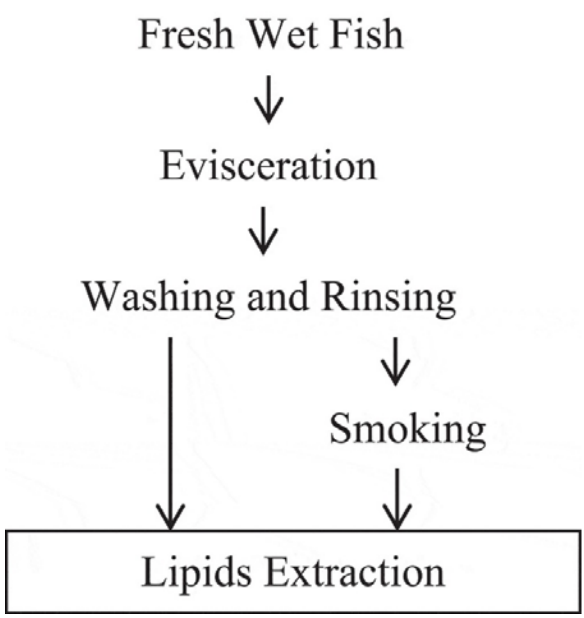

Figure 1. Summary of the steps involved in the extraction of lipid from the fresh and smoked fish samples prior to volatiles’ analysis.

Volatiles analysis

For the volatiles analysis of the fish samples, the previously described procedure of Odukoya et al. (2020; 2021) was employed. After the lipids' extraction, saponification was achieved by refluxing with KOH/EtOH, 2 M for 2 h. This was followed by conversion of the fatty acids obtained to methyl esters via the reaction with methanolic hydrogen chloride (3%) under reflux for 45 min, dissolved in hexane. Purification using silica gel chromatography was done while hexane/diethyl ether (10:1, v/v) was employed as eluent.

The volatile components and fatty acid methyl esters (FAMEs) of the fish (fresh and smoked) samples were then analyzed using the GC×GC-TOF-MS (LECO Corporation, USA) which operating conditions have been explained in Odukoya et al. (2020). Briefly, this involved the use of a GC×GC modulator, secondary oven (LECO Corporation, USA), modified Agilent 7890A gas chromatograph as well as helium, the carrier gas. Necessary retention time alignment and peak matching were achieved using ChromaTOF software (LECO, USA) while the NIST, Adams and EO libraries were employed for identification based on mass spectral database comparison.

Data and statistical analyses

Estimation of the percentage of eluted volatile compounds from the fresh and smoked fish samples was achieved using their peak areas. Where appropriate, line (with markers), clustered column, pie and clustered bar charts were used to statistically summarize the data obtained.

Results and discussion

Application of stress on the processes (physical, chemical and biological) that bring about spoilage has been indicated as a means of preserving freshly caught fish when there is no cold means (Doe, 2002) while Tylewicz, Inchingolo, and Rodriguez-Estrada (2017) pointed out that lipid oxidation and thermal reactions are parts of the ways food aroma compounds are produced. These latter authors, *i.e*., Tylewicz, Inchingolo, and Rodriguez-Estrada (2017), added that heat-generated flavors are the most abundant group of volatile compounds in food and identified: acids, alcohols, amines and other nitrogen compounds, carbonyl compounds, esters, lactones, oxygen-containing heterocyclic compounds, pyrazines, sulfur compounds as well as terpenes, as the chief aroma compound classes.

Earlier studies have also reported a link between volatile compounds, fish flavor (Ganguly, Mahanty, Mitra, Raman, & Mohanty, 2017) and odor (Aprea et al., 2012; Odukoya et al., 2020). Meanwhile, in the use of fish smoking as a form of processing, according to Varlet, Knockaert, Prost, and Serot (2006), odorant compounds can be from three sources: (1) lipid oxidation in unsmoked fish flesh, (2) lipid oxidation arising from the conditions of the smoking process, and (3) from the wood smoke. In the current study, analysis of the five fish species' fresh and smoked samples showed that the detected volatile compounds were: alkenes, alkynes, alcohols, aldehydes, a ketone (2-pentyl-3-methyl-2-cyclopenten-1-one), acids, esters, amines, and other miscellaneous compounds (Table 1). The detection of some of these compounds in the smoked fish samples supports the view of Arvanitoyannis and

Kotsanopoulos (2012) that smoking brings about the deposition of hydrocarbons, alcohols, aldehydes, ketones, esters, *etc*., on the surface of the smoked product which gradually enters the inner flesh.

Several authors, such as Lindsay (1994), Durnford and Shahidi (1998) and Leduc et al. (2012), have reported that fresh fish have mild, green, sweet, pleasant, delicate flavors and plant-like aroma which are contributed by C_6-, C_8- and C_9- carbonyls and alcohols from the action of endogeneous enzymes on long chain polyunsaturated fatty acids. The experimental results showing absence of these compounds in fresh samples of the five selected fish species indicate the tendency of harvested fish to deteriorate prior to processing, even when stored. Whereas, in agreement with Di Natale et al. (2001) as well as Dini et al. (2010), the absence/less amount of short chain alcohol and carbonyls, amines, sulfur compounds, aromatics, *N*-cyclic compounds and some acids, in some of the analyzed fresh fish samples suggests that these fish samples, at the point of analysis, are void of microbial spoilage odor. The varied composition of the volatiles recorded from the different fresh fish samples is also in consonance with the former authors that the odor of fresh fish is a function of the fish specie involved.

As shown in Figure 2, the effect of smoking was more predominant in the three fish species of the genus *Pseudotolithus* as it resulted to greater number of volatile compounds in the smoked fish samples than the fresh fish. This corroborates Adeyeye et al. (2017) who noted that fish smoking brings about change of flavor. It also further agrees with Durnford and Shahidi (1998) that the main essence of smoking fish is to improve flavor.

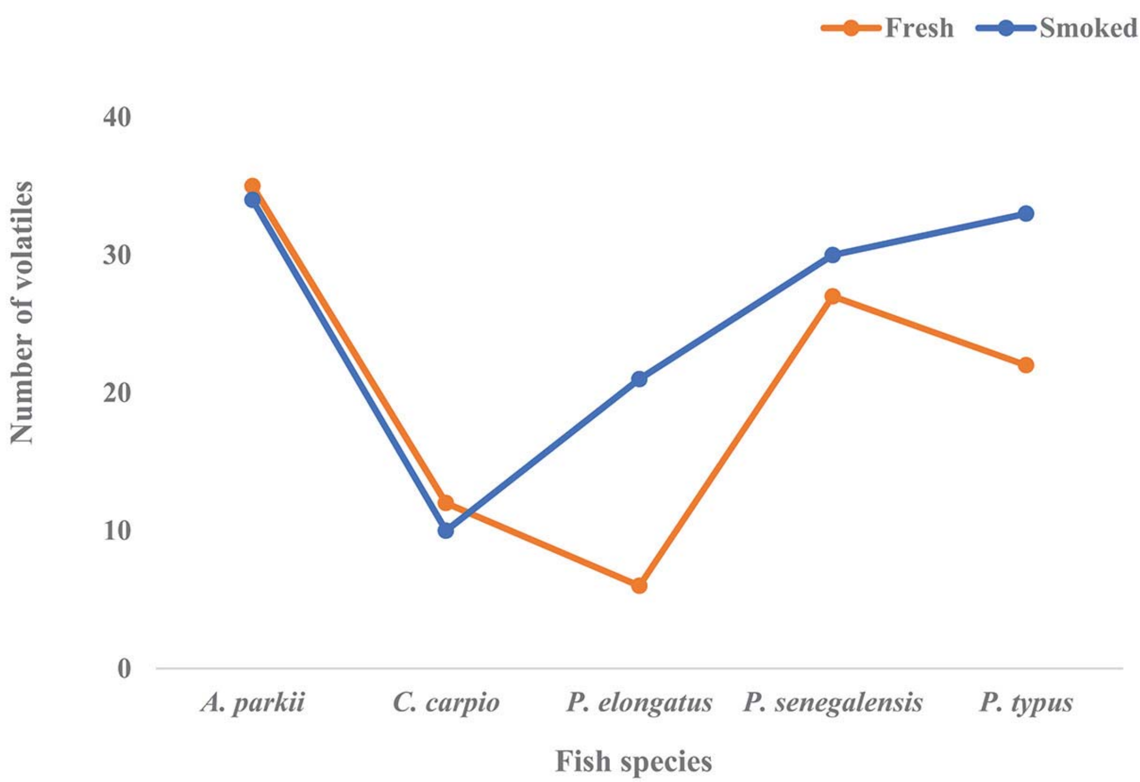

Figure 2. Line graph showing the distribution of volatiles in the five fish species.

Table 1. Detected volatile compounds in the fresh and smoked fish samples.

Name	Molecular formula	A. parkii		C. carpio		P. elongatus		P. senegalensis		P. typus		Odour descriptor	References
		F	S	F	S	F	S	F	S	F	S		
Alkenes													
2,5-Dimethyl-3-vinyl-1,4-hexadiene	$C_{10}H_{16}$									√			
1,4,8-Cycloundecatriene, 2,6,6,9-tetramethyl-	$C_{15}H_{24}$								√				
Alkynes													
1-Undecen-3-yne	$C_{11}H_{18}$									√			
1,11-Dodecadiyne	$C_{12}H_{18}$	√											
Oxacyclotetradeca-4,11-diyne	$C_{13}H_{18}O$										√		
1,11-Hexadecadiyne	$C_{16}H_{26}$									√			
Alcohols													
2-Methylpropan-1-ol	$C_4H_{10}O$		√	√	√							Solvent like, malty, pungent	(Giri, Osako, & Ohshima, 2010; Mohamed, Man, Mustafa, & Manap, 2012)
Myrtenol	$C_{10}H_{16}O$										√		
Cyclododecanol	$C_{12}H_{24}O$										√		
1-Heptatriacontanol	$C_{37}H_{76}O$										√		
Aldehydes													
Tetradecanal	$C_{14}H_{28}O$	√										Wet wood, marine, plastic	(Varlet, Knockaert, Prost, & Serot, 2006)
Pentadecanal	$C_{15}H_{30}O$							√				Fresh, waxy	(Queiroga et al., 2019)
Hexadecanal	$C_{16}H_{32}O$								√			Chemical, fecal	(Zabaleta, Gourrat, Barron, Albisu, & Guichard, 2016)
2-Heptadecenal	$C_{17}H_{32}O$							√					
9,12-Octadecadienal	$C_{18}H_{32}O$		√										
Ketone													
2-Pentyl-3-methyl-2-cyclopenten-1-one	$C_{11}H_{18}O$										√		
Acids													
2-Methylpentanoic acid	$C_6H_{12}O_2$			√	√								
9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$								√		√		
Docosahexaenoic acid (Doconexent)	$C_{22}H_{32}O_2$						√						
Esters													
Hex-5-ynoic acid, methyl ester	$C_7H_{10}O_2$										√		
Hexanoic acid, methyl ester	$C_7H_{14}O_2$		√	√	√			√			√	Fruity, sweet	(Queiroga et al., 2019)
Ethanol, 2,2′-oxybis-, diacetate	$C_8H_{14}O_5$			√	√								

(*Continued*)

Table 1. (Continued).

Name	Molecular formula	A. parkii		C. carpio		P. elongatus		P. senegalensis		P. typus		Odour descriptor	References
		F	S	F	S	F	S	F	S	F	S		
7-Nonenoic acid, methyl ester	$C_{10}H_{18}O_2$		√										
Octanoic acid, 2-methyl-, methyl ester	$C_{10}H_{20}O_2$	√											
Nonanoic acid, methyl ester	$C_{10}H_{20}O_2$			√	√							Fruity, sweet	(Queiroga et al., 2019)
Decanoic acid, methyl ester	$C_{11}H_{22}O_2$			√	√							Fresh	(Angerosa et al., 2004)
Undecanoic acid, methyl ester	$C_{12}H_{24}O_2$					√							
Methyl 10-Deuterio-10-(Trideuteriomethyl) Undecanoate	$C_{13}H_{22}D_4O_2$			√	√								
Tridecanoic acid, 3-methyl-, methyl ester	$C_{15}H_{30}O_2$						√						
Tetradecanoic acid, methyl ester (Methyl myristate)	$C_{15}H_{30}O_2$	√	√				√	√	√		√	Fatty, balsamic	(Queiroga et al., 2019)
1,2-Benzenedicarboxylic acid, mono (2-ethylhexyl) ester	$C_{16}H_{22}O_4$					√							
Z-10-Tetradecen-1-ol acetate	$C_{16}H_{30}O_2$		√										
Pentadecanoic acid, methyl ester	$C_{16}H_{32}O_2$	√	√				√	√	√		√		
Hexadecatrienoic acid, methyl ester	$C_{17}H_{28}O_2$	√							√		√		
Hexadecadienoic acid, methyl ester	$C_{17}H_{30}O_2$	√	√										
7-Hexadecenoic acid, methyl ester, (Z)-	$C_{17}H_{32}O_2$						√	√	√	√	√		
9-Hexadecenoic acid, methyl ester, (Z)- (Methyl palmitoleate)	$C_{17}H_{32}O_2$	√	√					√			√		
Hexadecanoic acid, methyl ester (Methyl palmitate)	$C_{17}H_{34}O_2$	√	√			√	√	√	√	√	√	Waxy, fatty, oily	(Queiroga et al., 2019)
Methyl 8,11,14-heptadecatrienoate	$C_{18}H_{30}O_2$									√	√		
Methyl 9-cis,11-trans-octadecadienoate	$C_{18}H_{31}O_2$		√										
cis-10-Heptadecenoic acid, methyl ester	$C_{18}H_{34}O_2$	√	√					√					
6-Hexadecenoic acid, 7-methyl, methyl ester	$C_{18}H_{34}O_2$						√	√	√	√			
Heptadecanoic acid, methyl ester	$C_{18}H_{36}O_2$	√	√				√	√	√	√	√		
Cis-6,9,12,15-Octadecatetraenoic acid methyl ester (Methyl stearidonate)	$C_{19}H_{30}O_2$	√							√	√	√		
9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)- (Methyl linolenate)	$C_{19}H_{32}O_2$	√					√	√			√		
8-Octadecynoic acid, methyl ester	$C_{19}H_{34}O_2$		√										

(*Continued*)

Table 1. (Continued).

Name	Molecular formula	A. parkii		C. carpio		P. elongatus		P. senegalensis		P. typus		Odour descriptor	References
		F	S	F	S	F	S	F	S	F	S		
9,12-Octadecadienoic acid, methyl ester (Methyl linoleate)	$C_{19}H_{34}O_2$	√	√					√	√		√		
9-Octadecenoic acid (Z)-, methyl ester (Methyl Oleate)	$C_{19}H_{36}O_2$	√	√				√	√	√	√	√		
Octadecanoic acid, methyl ester (Methyl stearate)	$C_{19}H_{38}O_2$	√	√			√	√	√	√	√	√	Oily, waxy	(Queiroga et al., 2019)
7,10,13-Eicosatrienoic acid, methyl ester	$C_{20}H_{34}O_2$		√										
Ethyl (9z,12z)-9,12-octadecadienoate (Ethyl linoleate)	$C_{20}H_{36}O_2$		√										
Methyl 9,10-methylene-octadecanoate	$C_{20}H_{38}O_2$		√										
Nonadecanoic acid, methyl ester	$C_{20}H_{40}O_2$	√	√				√	√	√				
cis-5,8,11,14,17-Eicosapentaenoic acid, methyl ester	$C_{21}H_{32}O_2$	√	√			√	√	√	√	√	√		
5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	$C_{21}H_{34}O_2$	√	√			√	√	√	√	√	√		
Methyl 8,11,14-eicosatrienoate	$C_{21}H_{36}O_2$		√										
11-(3,4-Dimethyl-5-propyl-2-furyl)-undecanoic acid, methyl ester	$C_{21}H_{36}O_3$										√		
11,14-Eicosadienoic acid, methyl ester	$C_{21}H_{38}O_2$	√	√					√	√	√			
cis-11-Eicosenoic acid, methyl ester	$C_{21}H_{40}O_2$	√	√					√	√				
Hexadecanoic acid, 3,7,11,15-tetramethyl-, methyl ester (Methyl phytanate)	$C_{21}H_{42}O_2$	√							√				
Eicosanoic acid, methyl ester (Methyl arachidate)	$C_{21}H_{42}O_2$	√	√				√	√	√		√		
Methyl 6,9,12,15,18-heneicosapentaenoate	$C_{22}H_{34}O_2$								√		√		
4,7,10,13,16,19-Docosahexaenoic acid, methyl ester, (all-Z)-	$C_{23}H_{34}O_2$	√	√				√	√	√	√	√		
Methyl 4,7,10,13,16-docosapentaenoate	$C_{23}H_{36}O_2$	√	√				√	√	√	√	√		
cis-7,10,13,16-Docosatetraenoic acid, methyl ester	$C_{23}H_{38}O_2$		√							√			
cis-13,16-Docosadienoic acid, methyl ester	$C_{23}H_{42}O_2$		√										
13-Docosenoic acid, methyl ester, (Z)- (Methyl erucate)	$C_{23}H_{44}O_2$	√	√								√		

(*Continued*)

Table 1. (Continued).

Name	Molecular formula	A. parkii F	A. parkii S	C. carpio F	C. carpio S	P. elongatus F	P. elongatus S	P. senegalensis F	P. senegalensis S	P. typus F	P. typus S	Odour descriptor	References
Docosanoic acid, methyl ester	$C_{23}H_{46}O_2$	√	√				√	√	√	√	√		
1,2-Benzenedicarboxylic acid, diisooctyl ester (Diisooctyl phthalate)	$C_{24}H_{38}O_4$	√								√			
Cyclopropanedodecanoic acid, 2-octyl-, methyl ester	$C_{24}H_{46}O_2$						√						
15-Tetracosenoic acid, methyl ester, (Z)-	$C_{25}H_{48}O_2$	√						√	√		√		
Tetracosanoic acid, methyl ester	$C_{25}H_{50}O_2$	√						√	√	√	√		
Cholest-5-en-3-yl benzoate	$C_{34}H_{50}O_2$	√							√				
Amines													
N-Nitrosodimethylamine	$C_2H_6N_2O$			√	√								
Neopentylamine	$C_5H_{13}N$			√									
1-Pentanamine	$C_5H_{13}N$			√									
Miscellaneous compounds													
2-Pyrrolidinone-5, 5-D2	$C_4H_5D_2NO$			√	√								
(2RS, 4S)-[5-C(13)]-Leucine	$C_6H_{13}NO_2$			√	√								
Decyl 2-methylacrylate	$C_{14}H_{26}O_2$	√											
Citronellyl tiglate	$C_{15}H_{26}O_2$									√			
2-(Aminomethyl) cyclohexanemethanol	$C_{18}H_{17}NO$	√											
Cholesta-3,5-diene	$C_{27}H_{44}$	√	√					√	√		√		
3-Bromocholest-5-ene	$C_{27}H_{45}Br$	√					√		√				
Hematoporphyrin	$C_{34}H_{38}N_4O_6$						√						
Astaxanthin	$C_{40}H_{52}O_4$									√			

Note: F = Fresh fish sample; S = Smoked fish sample.

As presented in Table 1, smoking removed 2,5-dimethyl-3-vinyl-1,4-hexadiene detected in the fresh fish sample of *P. typus* but added 1,4,8-cycloundecatriene, 2,6,6,9-tetramethyl- to *P. senegalensis*. It also led to the removal of 1,11-dodecadyine detected in fresh *A. parkii* as well as 1-undecen-3-yne and 1,11-hexadecadiyne in fresh *P. typus*. It, however, contributed to the presence of oxacyclotetradeca-4,11-diyne in smoked *P. typus*.

Tylewicz, Inchingolo, and Rodriguez-Estrada (2017) indicated that primary and secondary alcohols contribute to food aroma and can be from the reduction of carbonyl group as well as oxidation of long-chain polyunsaturated fatty acid. But Di Natale et al. (2001), Dini et al. (2010) and Odukoya et al. (2020), reported that fish odor from the detection of short-chain alcohols and carbonyls is one of the indicators of microbial spoilage. In this study, the absence of 2-methyl propan-1-ol in fresh *A. parkii* which was later detected in the smoked sample (Figure 5b) clearly indicated that it was from the wood smoke which agrees with Maga (1987) that this compound is among the volatiles identified from wood smoke. Smoking also led to the detection of myrtenol, cyclododecanol and 1-heptatriacontanol in *P. typus* (Table 1).

On the other hand, carbonyl compounds, more accountable for “fishy” odor (Varlet, Knockaert, Prost, & Serot, 2006), particularly aldehydes, are important group of volatile compounds found in smoked fishes’ aroma recorded in previous studies (Varlet, Prost, & Serot, 2007). These aldehydes, saturated and unsaturated, according to Varlet, Prost, and Serot (2007), in fish flesh are from the degradation of fatty acids and triglycerides by autoxidation. Based on their concentration, they can lead to the production of off-flavors and reduce the fish shelf life. Some of the aldehydes found in smoked fishes can be potentially harmful while many of them generated from wood smoke or during lipid peroxidation are also carcinogenic and can bring about diseases in the mouth, stomach or esophagus (Varlet, Prost, & Serot, 2007).

In *P. senegalensis*, smoking led to the loss of pentadecanal and 2-heptadecenal. But contributed to the production of hexadecanal (Table 1; Figure 8b). With respect to Varlet, Prost, and Serot (2007), the aliphatic aldehydes in smoked *A. parkii* (9,12-octadecadienal) and smoked *P. senegalensis* (hexadecanal) recorded in this experiment are from the fish flesh through lipid oxidation. The 2-heptadecenal, though a long-chain unsaturated aldehyde, detected in the fresh fish sample of *P. senegalensis*, in a way, supports the report of Varlet, Prost, and Serot (2007) that 2-alkenals are present in many seafood products. This carbonyl, *i.e.*, 2-heptadecenal, would give an unpleasant odor to fresh *P. senegalensis* as a result of the increased size of the carbonated skeleton (Varlet, Knockaert, Prost, & Serot, 2006).

Lipid oxidation is also one of the major ways for the production of ketones (Tylewicz, Inchingolo, & Rodriguez-Estrada, 2017). The detection of 2-pentyl-3-methyl-2-cyclopenten-1-one (the only ketone recorded in this research) in smoked *P. typus* suggests the contribution of volatile compounds in wood smoke to the smoked fish sample as Maga (1987) and Varlet, Knockaert, Prost, and Serot (2006) indicated derivatives of cycylopentenone as possible contributions from wood smoke. These cyclopentenone derivatives, according to these authors, *i.e.*, Maga (1987) and Varlet, Knockaert, Prost, and Serot (2006), give somewhat sweet and grassy odor. Meanwhile, Tylewicz, Inchingolo, and Rodriguez-Estrada (2017) stated that ketones with a 5–13 carbon atom structure most times give fruity or musty notes.

Furthermore, these latter authors pinpointed organic acids as part of the major classes of odor compounds. Fraser and Sumar (1998) noted that short-chain fatty acids, which contribute to the odor of spoiled fish, may be produced from the microbial degradation of fish. Although 2-methyl pentanoic acid was one of the compounds Maga (1987) identified to be present in wood smoke, the experimental outcome as shown in Figure 6b revealed that the higher level of 2-methyl pentanoic acid in fresh fish sample of *C. carpio* is an indication of microbial degradation of the fish. Smoking led to the detection of 9,12-octadecadienoic acid in *P. senegalensis* and *P. typus* which is in line with the view of Di Natale et al. (2001) that fish processing can be a contributor to fish odor. Interestingly, however, smoking brought about the detection of docosahexaenoic acid (*n*-3 PUFA), an important fish component (Varlet, Prost, & Serot, 2007), in *P. elongatus* (Figure 7b).

Esters, according to Tao, Wu, Zhou, Gu, and Wu (2014), may be generated via the esterification reaction between alcohols and carboxylic acids formed from lipids' microbial degradation. In line with Giri, Osako, and Ohshima (2010), acetates of higher alcohols and ethyl esters of fatty acids can enhance the aroma of finished products. Like the research findings of Odukoya et al. (2020), esters were the most occurring class of compounds in the analyzed fish (fresh and smoked) samples and as indicated in Tylewicz, Inchingolo, and Rodriguez-Estrada (2017), esters are most times linked with fruity or floral notes. In all the fish samples, with the exception of *C. carpio*, smoking led to the production of higher number of esters than those found in the fresh fish samples (Figure 3).

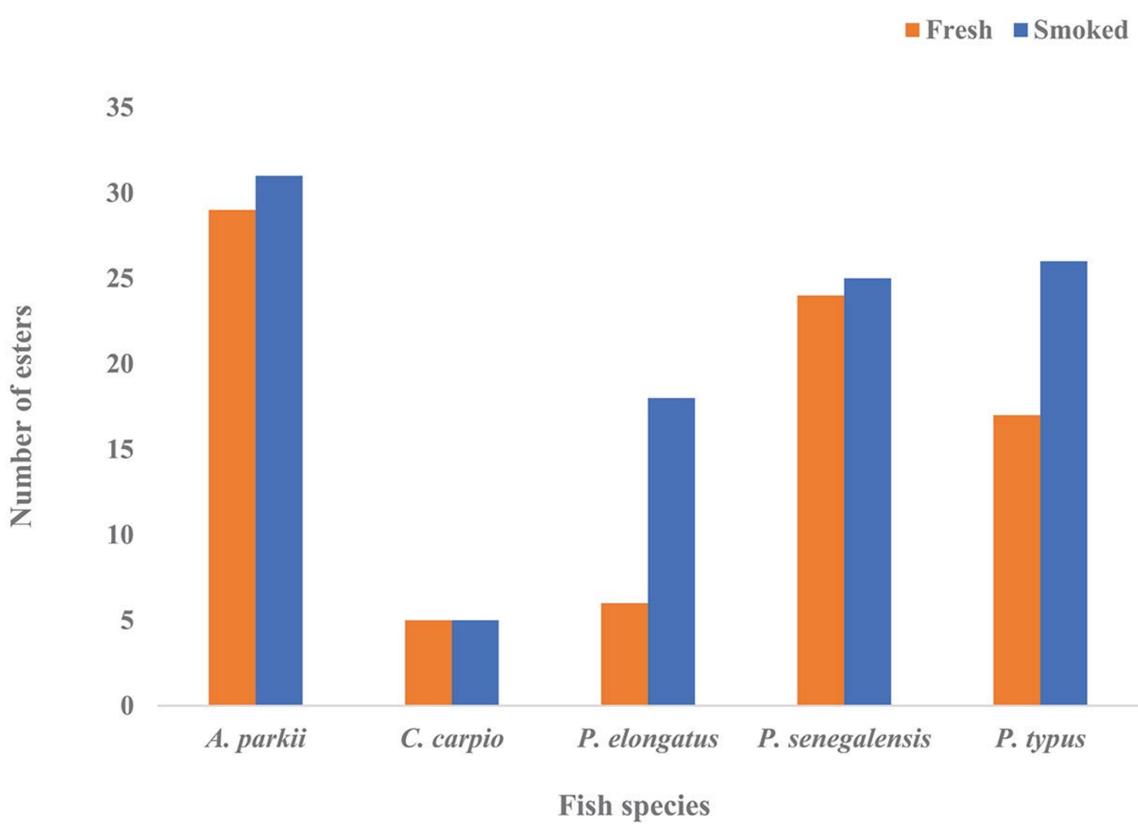

Figure 3. Distribution of the number of esters in each fish sample.

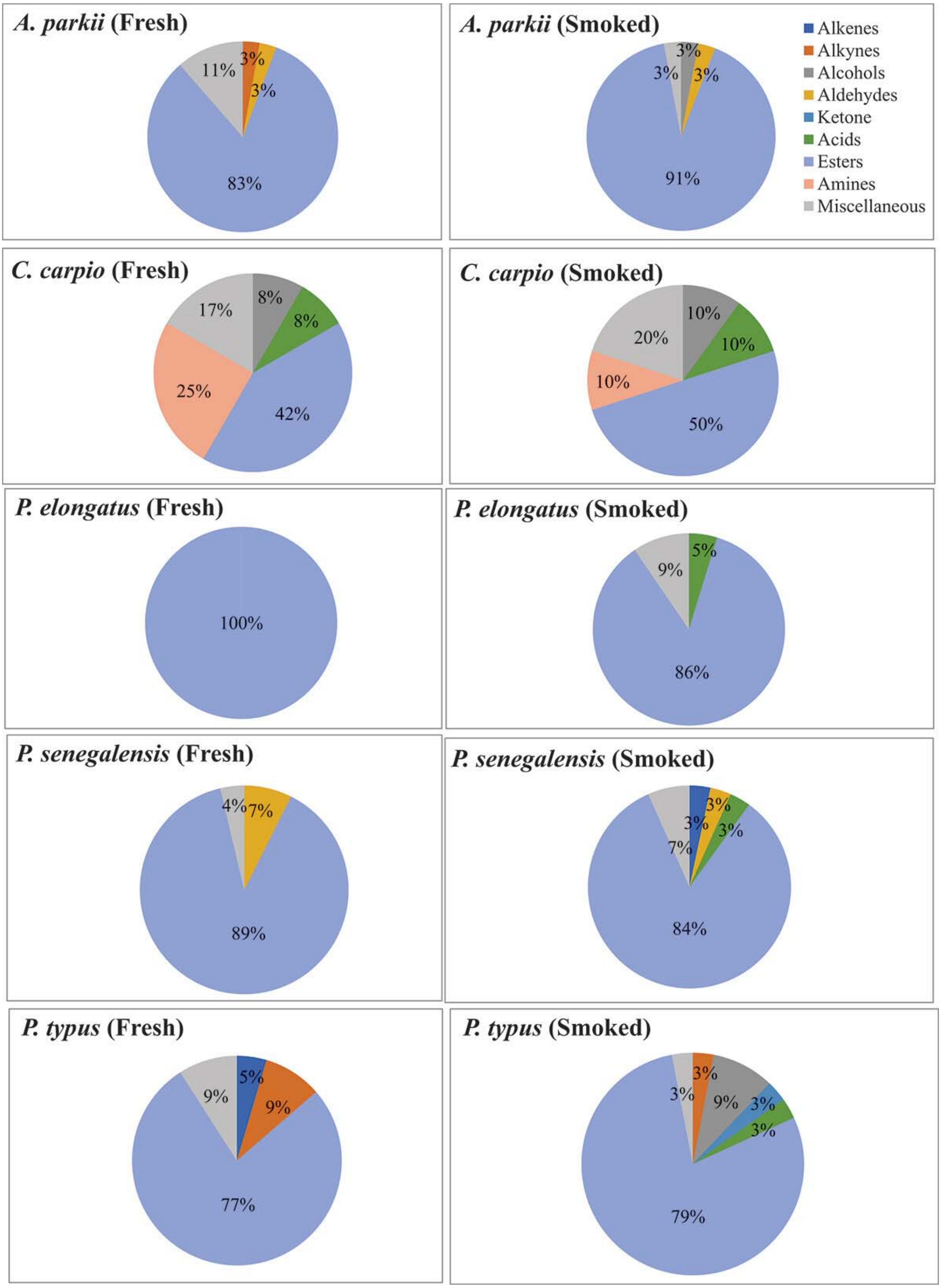

Figure 4. Percentage of each class of volatile compounds obtained from the five fish species' fresh and smoked samples.

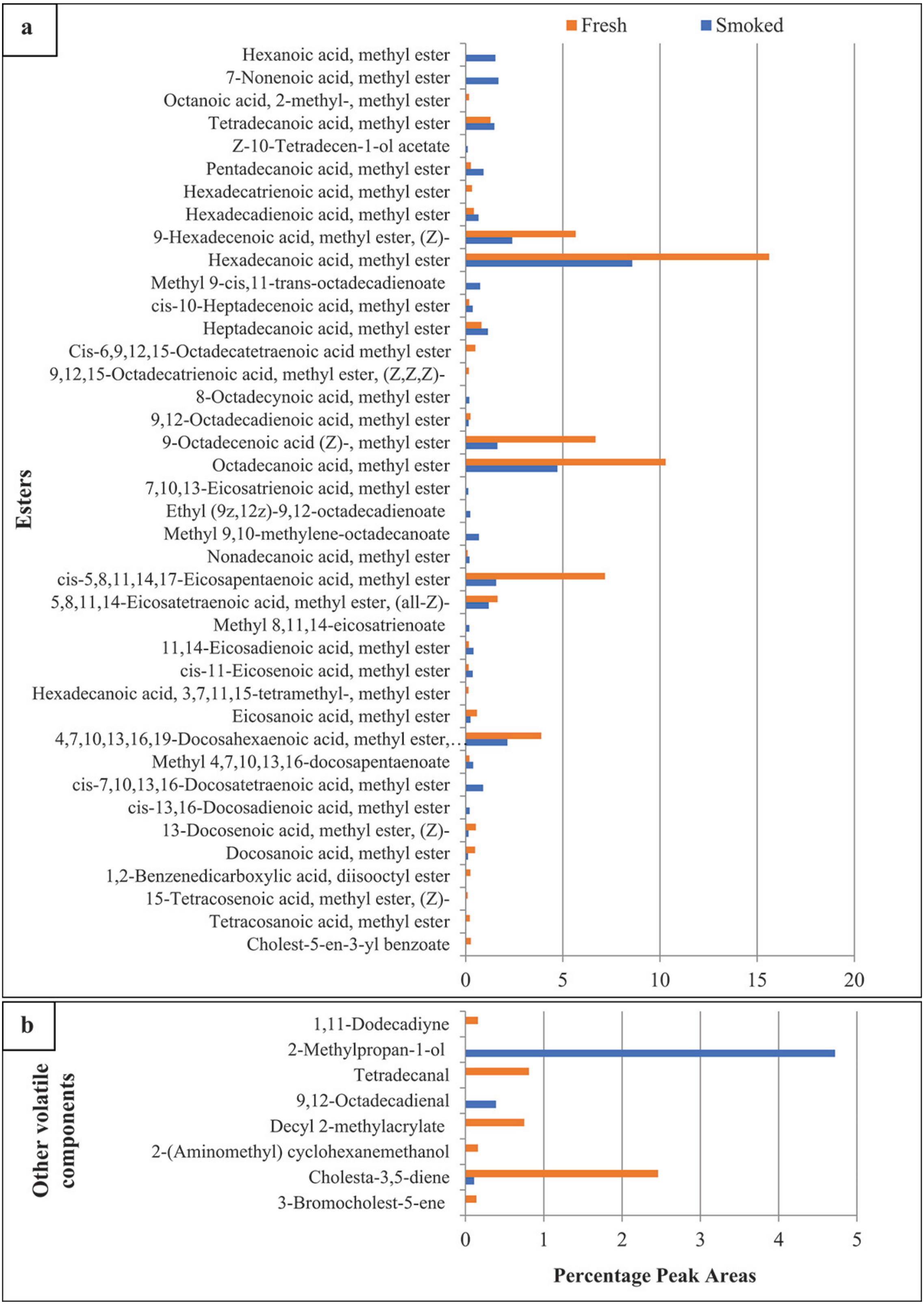

Figure 5. Relative abundance with respect to peak area of [A] esters, and [B] other volatile components in fresh and smoked *A. parkii*.

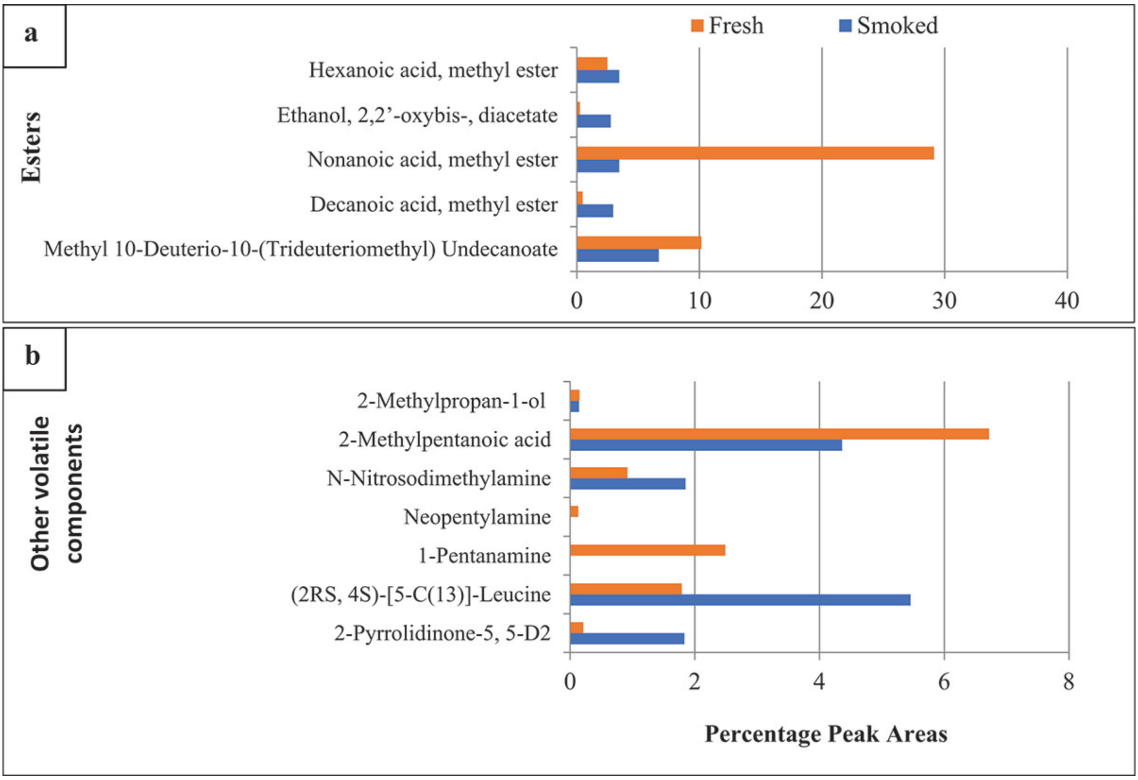

Figure 6. Relative abundance with respect to peak area of [A] esters, and [B] other volatile components in fresh and smoked *C. carpio*.

In terms of percentage composition, smoking led to lower percentage of esters in *P. elongatus* and *P. senegalensis* as it led to the production of other volatile compounds in these fish species (Figure 4). Meanwhile, the most significant effect of smoking on esters in the fresh fish samples was recorded in *P. elongatus* (Figure 3); to a very large extent, it brought about the detection of more esters in the fish (Figure 7a). Smoking, in most cases, was also found to reduce the level of some esters in *A. parkii, C. carpio and P. typus* as well as led to generation of some others in these fish species (Figures 5a, 6a and 9a). This was in contrast to the impact of smoking on *P. senegalensis*' esters as it led to higher levels of most of them (). Notwithstanding, in line with Maga (1987), the sole detection of tetradecanoic acid, methyl ester (methyl myristate) in smoked *P. elongatus* (Figure 7a) and smoked *P. typus* (Figure 9a) as well as the higher level of hexadecanoic acid methyl ester (methyl palmitate) in smoked *P. elongatus* (Figure 7a) and smoked *P. senegalensis* (Figure 8a), affirms the introduction of these compounds from wood smoke.

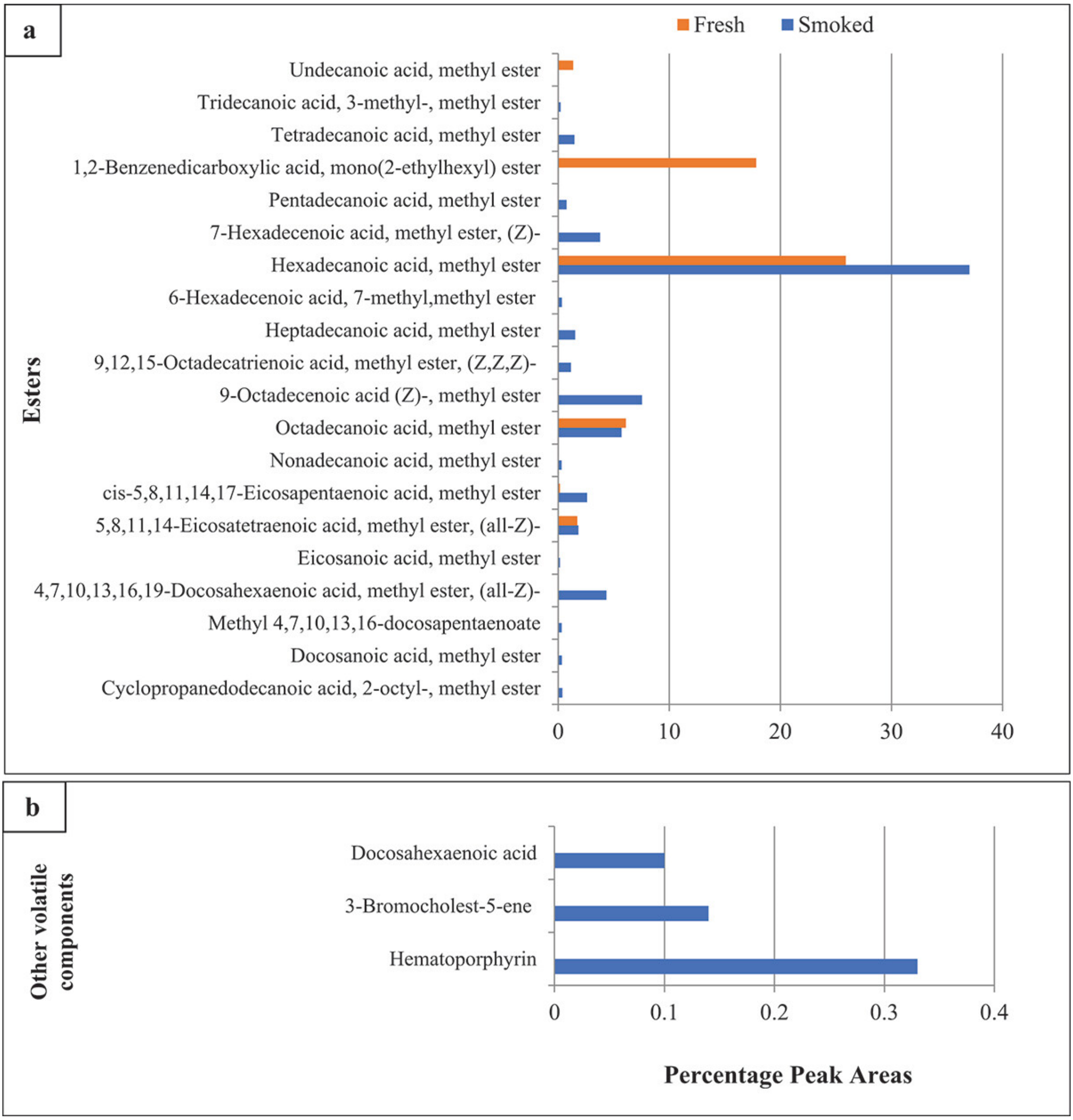

Figure 7. Relative abundance with respect to peak area of [A] esters, and [B] other volatile components in fresh and smoked *P. elongatus*.

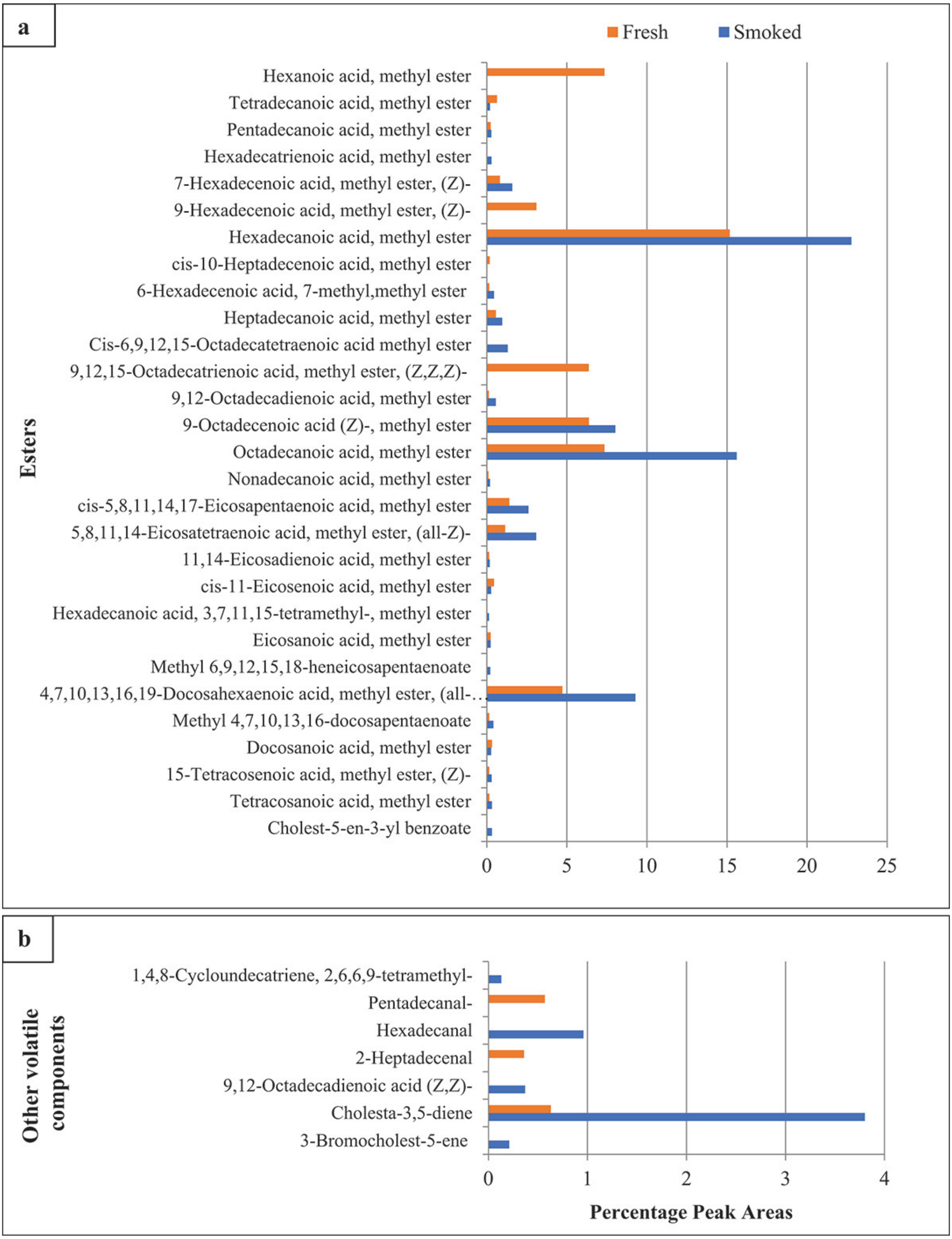

Figure 8. Relative abundance with respect to peak area of [A] esters, and [B] other volatile components in fresh and smoked *P. senegalensis*.

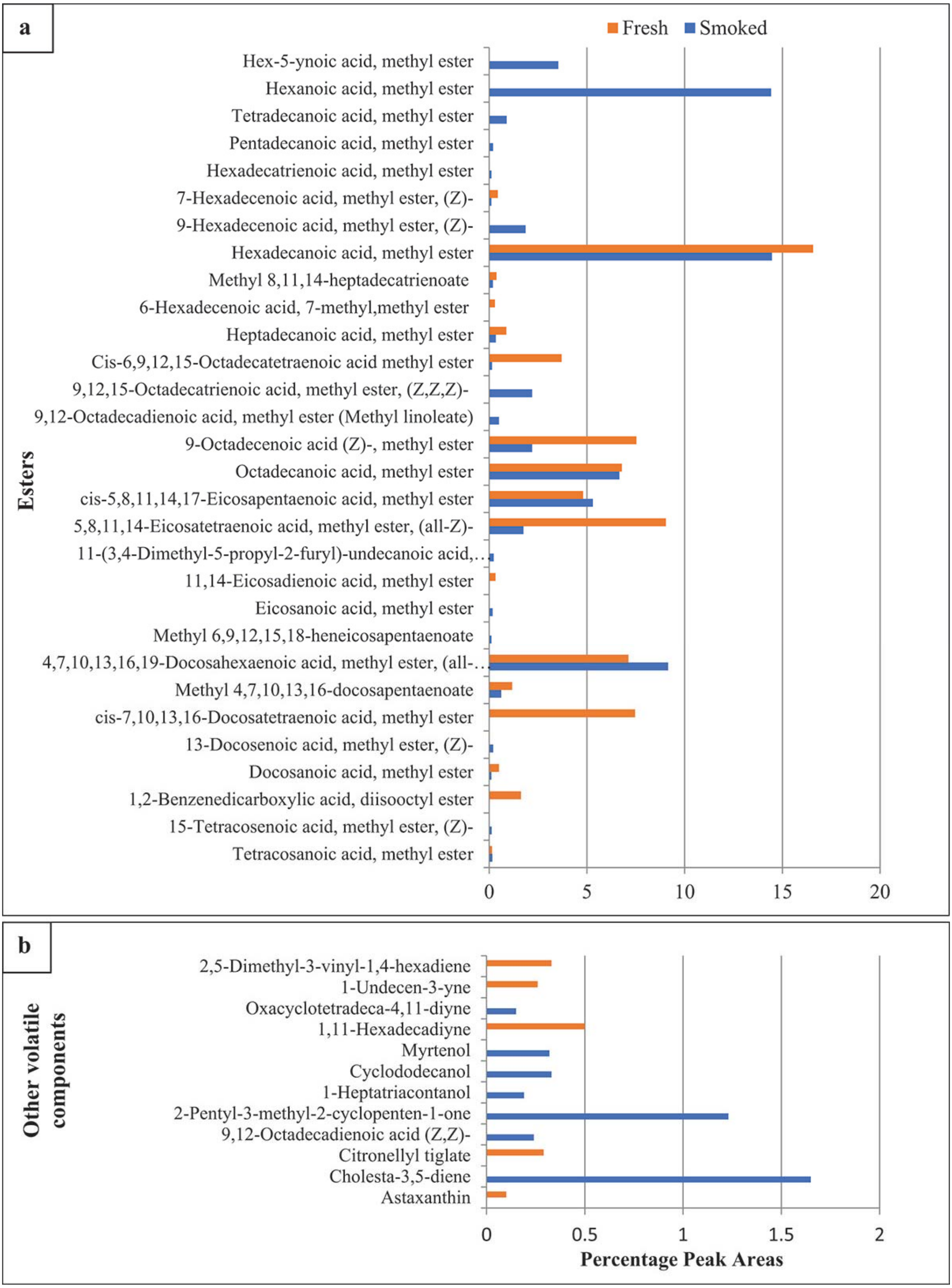

Figure 9. Relative abundance with respect to peak area of [A] esters, and [B] other volatile components in fresh and smoked *P. typus*.

On amines distribution in the studied samples, Tylewicz, Inchingolo, and Rodriguez-Estrada (2017) recorded that some of the odor of volatile amines can be linked with food degradation giving rise to fishy or putrid notes. Amines were only detected in the fresh sample of *C. carpio* suggesting that, among the five selected fish species, this fish is the most prone to spoilage as Dini et al. (2010) identified amines as distinct markers in the determination of fish freshness. Smoking removed neopentylamine and 1-pentanamine detected in the fresh *C. carpio* samples (Table 1), but contributed more to the generation of *N*-nitrosodimethylamine (a carcinogen) and some other volatiles (Figure 6b). Figures 5-9 give a summary of the relative abundance of esters and other detected volatile compounds in the fresh and smoked fish samples based on their peak areas.

Among the detected miscellaneous volatile compounds, smoking was effective in reducing the level of cholesta-3,5-diene in *A. parkii* (Figure 5b) but a reverse of this was found in *P. senegalensis* (Figure 8b). It also led to the removal of decyl 2-methylacrylate, 2-(aminomethyl)cyclohexanemethanol, 3-bromocholest-5-ene (in *A. parkii*) (Figure 5b) as well as citronelly tiglate and astaxanthin in *P. typus* (figure 9b). Smoking, however, contributed to the detection of 3-bromocholest-5-ene and hematoporphyrin in smoked *P. elongatus*, 3-bromocholest-5-ene in smoked *P. senegalensis* and cholesta-3,5-diene in smoked *P. typus*. It also gave rise to higher level of 2-pyrrolidinone-5,5-D2 and (2RS, 4S)-[5-C(13)]-leucine in smoked *C. carpio* (Figure 6b).

Conclusion

This study provides a clear understanding on the impact of smoking, a common traditional practice, on the volatile components of the five selected fish species. Although the aroma of very fresh fish may vary, the experimental outcome revealing less/no amount of C_6-, C_8- and C_9- carbonyls and alcohols in the fresh fish samples of the different five species investigated confirmed that fresh fish flavors are very delicate. The experimental results also affirmed that aroma/odor production via smoking depends on the fish specie involved and that industrial processes involving the application of heat may affect the odor-active components of the studied fresh fish samples. It indicated that: (1) some of the volatile compounds like 2-methyl propan-1-ol, tetradecanoic acid, methyl ester (methyl myristate) and hexadecanoic acid methyl ester (methyl palmitate) detected in some of the smoked fish samples were from wood smoke, (2) the overall odor of smoked fish samples are complex combination of odor from components of the fresh fish under the smoking condition and that of the smoked fish, and (3) fish smoking can lead to the production of off-flavors and/or increase the levels of some harmful compounds in fish for human consumption. Among the studied five fish species, *C. carpio* was the most susceptible to deterioration as amines were only detected in the fresh sample of this fish specie.

Future work is required to assess the human health risk arising from the consumption of 9,12-octadecadienal and hexadecanal in smoked *A. parkii* and *P. senegalensis*, respectively. In addition, the contribution of smoking to the accumulation of polycyclic aromatic hydrocarbons, a possible source of human carcinogens, in the studied fish species needs to be investigated. With respect to management, the numerous benefits of fish smoking necessitates collaboration between fish farmers/stakeholders and research institutes/universities to further improve fish smoking technology which would enhance the availability and safety of smoked fish. Appropriate legislations and policies are also required to guide fish postharvest operations after necessary biological, environmental, technological, economic, social, and cultural considerations.

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References

Abimbola, A. O. (2016). Proximate and mineral composition of Pseudotolithus senegalensis and Pseudotolithus typus from Lagos Lagoon, Nigeria. *Food and Applied Bioscience Journal*, 4(1), 35–40.

Adeyeye, S. A. O., & Oyewole, O. B. (2016). An overview of traditional fish smoking in Africa. *Journal of Culinary Science & Technology*, 14(3), 198–215. doi:10.1080/15428052.2015.1102785

Adeyeye, S. A. O., Oyewole, O. B., Obadina, O. A., Omemu, A. M., Adeniran, O. E., Oyedele, H. A. … Omoniyi, S. A. (2017). Effect of smoking methods on quality and safety of traditional smoked fish from Lagos State, Nigeria. *Journal of Culinary Science & Technology*, 15(1), 17–35. doi:10.1080/15428052.2016.1185072

Ahmed, A., Dodo, A., Bouba, A. M., Clement, S., & Dzudie, T. (2011). Influence of traditional drying and smoke-drying on the quality of three fish species (Tilapia nilotica, Silurus glanis and Arius parkii) from Lagdo Lake, Cameroon. *Journal of Animal and Veterinary Advances*, 10(3), 301–306. doi:10.3923/javaa.2011.301.306

Angerosa, F., Servili, M., Selvaggini, R., Taticchi, A., Esposto, S., & Montedoro, G. (2004). Volatile compounds in virgin olive oil: Occurrence and their relationship with the quality. *Journal of Chromatography: A*, 1054(1–2), 17–31. doi:10.1016/S0021-9673(04)01298-1

Anyanwu, A. O. (1983). Parasitic infestations of Pseudotolithus spp. off the coast of Lagos, Nigeria. *Journal of Fish Biology*, 22(1), 29–33. doi:10.1111/j.1095-8649.1983.tb04723.x

Aprea, E., Corollaro, M. L., Betta, E., Endrizzi, I., Demattè, M. L., Biasioli, F., & Gasperi, F. (2012). Sensory and instrumental profiling of 18 apple cultivars to investigate the relation between perceived quality and odour and flavour. *Food Research International*, 49(2), 677–686. doi:10.1016/j.foodres.2012.09.023

Arvanitoyannis, I. S., & Kotsanopoulos, K. V. (2012). Smoking of fish and seafood: History, methods and effects on physical, nutritional and microbiological properties. *Food and Bioprocess Technology*, 5(3), 831–853. doi:10.1007/s11947-011-0690-8

Conand, F., Camara, S. B., & Domain, F. (1995). Age and growth of three species of Ariidae (Siluriformes) in coastal waters of Guinea. *Bulletin of Marine Science*, 56(1), 58–67.

Crexi, V. T., Monte, M. L., Soares, L. A. D. S., & Pinto, L. A. A. (2010). Production and refinement of oil from carp (Cyprinus carpio) viscera. *Food Chemistry*, 119(3), 945–950. doi:10.1016/j.foodchem.2009.07.050

Di Natale, C. D., Olafsdottir, G., Einarsson, S., Martinelli, E., Paolesse, R., & D'Amico, A. (2001). Comparison and integration of different electronic noses for freshness evaluation of cod-fish fillets. *Sensors and Actuators: B, Chemical*, 77(1–2), 572–578. doi:10.1016/S0925-4005(01)00692-X

Dini, F., Paolesse, R., Filippini, D., D'Amico, A., Lundström, I., & Di Natale, C. (2010). Fish freshness decay measurement with a colorimetric artificial olfactory system. *Procedia Engineering*, 5, 1228–1231. doi:10.1016/j.proeng.2010.09.334

Doe, P. E. (2002). Fish drying. In H. A. Bremner (Ed.), *Safety and quality issues in fish processing* (p. 350). Cambridge: Woodhead Publishing Limited.

Durnford, E., & Shahidi, F. (1998). Flavour of fish meat. In F. Shahidi (Ed.), *Flavor of meat, meat products, and seafoods* (p. 131). London: Blackie Academic & Professional.

Ecoutin, J. M., Albaret, J. J., & Trape, S. (2005). Length–weight relationships for fish populations of a relatively undisturbed tropical estuary: The Gambia. *Fisheries Research*, 72(2–3), 347–351. doi:10.1016/j.fishres.2004.10.007

Edwards, A. J., Gill, A. C., & Abohweyere, P. O. (2001). *A revision of Irvine's marine fishes of tropical West Africa*. Darwin Initiative.

Fraser, O. P., & Sumar, S. (1998). Compositional changes and spoilage in fish (part II) - microbiological induced deterioration. *Nutrition & Food Science*, 98(6), 325–329. doi:10.1108/00346659810235242

Ganguly, S., Mahanty, A., Mitra, T., Raman, R. K., & Mohanty, B. P. (2017). Volatile compounds in hilsa (Tenualosa ilisha, Hamilton) as detected by static headspace gas chromatography and mass spectrometry. *Journal of Food Processing and Preservation*, 41(6), e13212. doi:10.1111/jfpp.13212

Giri, A., Osako, K., & Ohshima, T. (2010). Identification and characterisation of headspace volatiles of fish miso, a Japanese fish meat based fermented paste, with special emphasis on effect of fish species and meat washing. *Food Chemistry*, 120(2), 621–631. doi:10.1016/j.foodchem.2009.10.036

Golani, D. (2002). The Indo-Pacific striped eel catfish, Plotosus lineatus (Thunberg, 1787), (Osteichtyes: Siluriformes) a new record from the Mediterranean. *Scientia Marina*, 66(3), 321–323. doi:10.3989/scimar.2002.66n3321

Jayaprakash, M., Kumar, R. S., Giridharan, L., Sujitha, S. B., Sarkar, S. K., & Jonathan, M. P. (2015). Bioaccumulation of metals in fish species from water and sediments in macrotidal Ennore creek, Chennai, SE coast of India: A metropolitan city effect. *Ecotoxicology and Environmental Safety*, 120, 243–255. doi:10.1016/j.ecoenv.2015.05.042

Leduc, F., Tournayre, P., Kondjoyan, N., Mercier, F., Malle, P., Kol, O. … Duflos, G. (2012). Evolution of volatile odorous compounds during the storage of European seabass (Dicentrarchus labrax). *Food Chemistry*, 131(4), 1304–1311. doi:10.1016/j.foodchem.2011.09.123

Lindsay, R. C. (1994). Flavour of fish. In F. Shahidi & J. R. Botta (Eds.), *Seafoods: Chemistry, processing technology and quality* (pp. 75–84). Springer US. doi:10.1007/978-1-4615-2181-5_6

Maga, J. A. (1987). The flavor chemistry of wood smoke. *Food Reviews International*, 3(1–2), 139–183. doi:10.1080/87559128709540810

Martinsdottir, E. (2002). Quality management of stored fish. In H. A. Bremner (Ed.), *Safety and quality issues in fish processing* (p. 360). Cambridge: Woodhead Publishing Limited.

Mohamed, H. N., Man, Y. C., Mustafa, S., & Manap, Y. A. (2012). Tentative identification of volatile flavor compounds in commercial Budu, a Malaysian fish sauce, using GC-MS. *Molecules*, 17(5), 5062–5080. doi:10.3390/molecules17055062

Odukoya, J. O., Kayitesi, E., Mphahlele, M. P., Tata, C. M., Njinkoue, J. M., Gouado, I. … Ndinteh, D. T. (2020). Effect of processing methods on the volatile components of Ethmalosa fimbriata using a two-dimensional gas chromatography-time-of-flight mass spectrometry (GC×GC-TOF-MS) technique. *Journal of Food Processing and Preservation*, 45(2), 1–11. doi:10.1111/jfpp.15110

Odukoya, J. O., Kayitesi, E., Mphahlele, M. P., Tata, C. M., Njinkoue, J. M., Gouado, I. … Ndinteh, D. T. (2021). Contribution of the volatile components from fresh egg, adult female and male of Pestarella tyrrhena to odour production. *Physical Sciences Review*. doi:10.1515/psr-2020-0144

Queiroga, R. D. C. R. E., Leite Neta, M. T. S., Dutra Sandes, R. D., Narain, N., Sousa Galvão, M. D., Madruga, M. S., & Germano Costa, R. (2019). An insight in key volatile compounds in goat milk based on their odor active values. *Journal of Food Science and Nutrition Research*, 02(01). doi:10.26502/jfsnr.2642-1100008

Tao, N.-P., Wu, R., Zhou, P.-G., Gu, S.-Q., & Wu, W. (2014). Characterization of odor-active compounds in cooked meat of farmed obscure puffer (Takifugu obscurus) using gas chromatography–mass spectrometry–olfactometry. *Journal of Food and Drug Analysis*, 22(4), 431–438. doi:10.1016/j.jfda.2014.02.005

Tylewicz, U., Inchingolo, R., & Rodriguez-Estrada, M. T. (2017). Food aroma compounds. In C. M. Galanakis (Ed.), *Nutraceutical and functional food components* (pp. 297–334). Elsevier. doi:10.1016/B978-0-12-805257-0.00009-0

Varlet, V., Knockaert, C., Prost, C., & Serot, T. (2006). Comparison of odor-active volatile compounds of fresh and smoked salmon. *Journal of Agricultural and Food Chemistry*, 54(9), 3391–3401. doi:10.1021/jf053001p

Varlet, V., Prost, C., & Serot, T. (2007). Volatile aldehydes in smoked fish: Analysis methods, occurrence and mechanisms of formation. *Food Chemistry*, 105(4), 1536–1556. doi:10.1016/j.foodchem.2007.03.041

Visciano, P., Perugini, M., Conte, F., & Amorena, M. (2008). Polycyclic aromatic hydrocarbons in farmed rainbow trout (Oncorhynchus mykiss) processed by traditional flue gas smoking and by liquid smoke flavourings. *Food and Chemical Toxicology*, 46(5), 1409–1413. doi:10.1016/j.fct.2008.01.001

Xu, P., Zhang, X., Wang, X., Li, J., Liu, G., Kuang, Y. … Sun, X. (2014). Genome sequence and genetic diversity of the common carp, Cyprinus carpio. *Nature Genetics*, 46(11), 1212–1219. doi:10.1038/ng.3098

Zabaleta, L., Gourrat, K., Barron, L. J. R., Albisu, M., & Guichard, E. (2016). Identification of odour-active compounds in ewes' raw milk commercial cheeses with sensory defects. *International Dairy Journal*, 58, 23–30. doi:10.1016/j.idairyj.2016.01.018

Zhang, Y., Liang, L., Jiang, P., Li, D., Lu, C., & Sun, X. (2008). Genome evolution trend of common carp (Cyprinus carpio L.) as revealed by the analysis of microsatellite loci in a gynogentic family. *Journal of Genetics and Genomics*, 35(2), 97–103. doi:10.1016/S1673-8527(08)60015-6

Zhang, Y., Xu, P., Lu, C., Kuang, Y., Zhang, X., Cao, D. … Sun, X. (2011). Genetic linkage mapping and analysis of muscle fiber-related QTLs in common carp (Cyprinus carpio L.). *Marine Biotechnology*, 13(3), 376–392. doi:10.1007/s10126-010-9307-x