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Incidence of Persistent Organic Pollutants in Smoked-Dried Fish Samples and Their Public Health Implications in Benin City

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Abstract Persistent organic pollutants (POPs) are synthetic chemicals that have an intrinsic resistance to natural degradation processes, and are therefore environmentally persistent. The introduction of POPs into the environment from anthropogenic activities resulted in their widespread dispersal and accumulation in soils and water bodies, as well as in human and ecological food chains, where they are known to induce toxic effects. Due to their ubiquity in the environment and lipophilic properties, there is mounting concern over the potential risks of human exposure to POPs. POPs include organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), dioxins, polyaromatic hydrocarbons (PAHs) and short-chain chlorinated paraffins (SCCPs).Smoked fishes were obtained from three markets in Benin City.

The fishsamples were identified as *Oreochromis aureus* (Blue tilapia), *Scomber scombrus* (Atlantic mackerel) and *Gymnarchus niloticus* (Trunk fish). They were blended to obtain powdered samples and stored in ultra-freezer at 4 ºC. The powdered samples were extracted by Soxhlet extraction procedure using dichloromethane (200ml) POP residues were determined using Soxhlet extraction method and column chromatography for solvent elution. Eluate analysis was by Gas Chromatography (GC) tandem Mass Spectrophotometer (MS) technique.

Concentration of persistent organic pollutants such as lindane, aldrin, endosulfan, heptachlor, dioxins and polychlorinated biphenyls were not detected in the fishes. However, *Gymnarchus niloticus* from Oluku was found to contain oxirane (0.0362mg/L), tridecyl phthalates (0.0469mg/L) and naphthalene (0.0469mg/L) which are endocrine disruptor and polychlorinated aromatic hydrocarbon (PAH). Similarly, *Gymnarchus niloticus* and *Oreochromis aureus* from Aduwawa contained titanium dioxide, 1-chlorooctadecane (SCCP) (0.0214mg/L) and Bis(2-ethylhexyl) phthalate (0.0321mg/L) respectively. Although these levels of organic pollutants were low when compared with the maximum limit of Federal Environmental Protection Agency (FEPA), however, continuous exposure can be harmful if the trend is not checked.

Keywords Organochlorine, Persistent, Chromatography, Extraction, Pesticides

Introduction

Environmental xenobiotic are synthetic chemical compoundsthat are both persistent and bioaccumulative, with potential for long-range transportation across boundaries where they have never been used induce adverse effects on human health [1]. These organic pollutants are made up of complex molecules which do not breakdown easily in the environment; hence the name "persistent" [2]. The ecotoxicological effects of POPs in the aquatic environment are of great concern. POPs may be introduced into the environment from a variety of emission sources and anthropogenic activities. Point, area, and line sources include releases from industrial installations, domestic premises, traffic, waste disposal operations such as incinerators and landfills. In the last times emphasis has been focused in reducing or eliminating the discharges or emissions of an initial set of 12 persistent organic pollutants in the environment, as recommended by the UNEP and based in the guidelines proposed in the Stockholm convention in 2001 [3]. This ‘‘dirty dozen’’ include members of the organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), Polychlorinated aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and Short-chain chlorinated paraffins (SCCPs) [2, 4-5]. Fish harvested from polluted aquatic environments can contain chemical contaminants in levels deleterious to human health once consumed [6] One such toxic and persistent group of contaminants, which is of global interest, is pesticides [2]. Pesticides just like heavy metals are important group of chemical pollutants, whereby food is the main route for entry into our body. Pesticides are economic poisons used for controlling, preventing, destroying, repelling or mitigating any pest organism.Toxicity and persistence of pesticides are useful properties for killing their target organisms, but these qualities also cause problems for humans and the environment. Toxicological investigations found that several pesticides are carcinogenic in animals, thus raising concern over human exposure Dichlorodiphenyltrichloroethane (DDT) and its derivatives (DDD and DDE) have now been found in most environmental media, and constitute the dominant OCPs found in human tissues, most notably adipose tissue [7]. Organochlorines have been implicated in adverse human health effects including reproductive failures and birth defects, immune system malfunction, endocrine disruptions, and cancers [8].

Polycyclic aromatic hydrocarbons (PAHs) are group ofpops that are toxic, mutagenic, and suspected carcinogens in the environment. Traces of these substances have been found in various food products [9]. Numerous PAHs generating activities take place in Nigeria without much control. Wastes are either dumped directly into the water channels, or openly incinerated at different locations in the city. According to Guillen [10], emissions into air are of complex mixtures of different PAHs, which can adsorb on to air borne particles and eventually enter surface waters owing to precipitation of particles or to diffusion. There is a serious concern about a PAH compound like Benzo(a)Pyrene, which is mainly of pyrogenic source and a known carcinogen. As stated by Rose *et al.* [11], many PAHs such as Naphthalene and Phenanthrene are acutely toxic. The health effect resulting from PAH exposure has been extensively discussed. Some include growth retardation, low birth weight, small head circumference, low IQ, damaged DNA in unborn children and disruption of endocrine system [12].

Short-chain chlorinated paraffins Dioxins (PCDDs) and furans (PCDFs) are another group of organic pollutants also known as polychlorinated *n*-alkanes (PCAs) exerting high toxicity. They are a class of industrial chemicals comprising of chlorinated straight chain hydrocarbons [2]. They are produced with free radical chlorination and have a wide range of applications, but are mainly used as extreme pressure lubricant additives, plasticizers, flame-retardants and paint additives [13]. There are 210 different congeners: 75 dioxincongeners and 135 furan congeners, of which 17 are potentially toxic with dioxins and furans prevalent in air, water, and soil in almost all natural environments [14]. PCDD and furans are strongly bound to organic matter, where half-life in soil has been estimated at 10 to 20 years [15]. Waste incinerators were identified as one of the major sources in the urban environment, and others include uncontrolled combustion. Car exhaust emissions, especially from cars using leaded gasoline with halogenated scavengers. Following their widespread and diverse use, SCCPs can be found in a range of environmental samples, both biotic and abiotic. However, information on environmental levels is still scarce compared to other persistent organic chemicals (POPs) such as dioxins, PCBs and organochlorine pesticides [16]. SCCPs have been detected in marine wildlife, such as beluga (*Delphinapterus leucas*), ringed seal (*Phocahispida*) and walrus (*Odobenus rosmarus*) blubber in the Canadian arctic, in concentrations ranging from 0.095 to 0.626 mg kg^{-1} wet weight [17]. SCCPs have also been measured in the liver and muscle of seabirds from the European arctic in concentrations ranging from 0.005 to 0.088 mg kg^{-1} wet weight [18]. Although studies of concentrations in human tissues are very limited, a study from the United Kingdom has found SCCPs to be present in human breast milk at concentrations ranging from 49 and 820 ng g^{-1} fat (median 180 ng g^{-1} fat) [19]. Further research is needed in order to understand the mechanisms of toxicity of SCCPs. Toxicity studies in rodents and other animals indicate that chronic exposure to relatively low concentrations of SCCPs adversely affects their survival and development. Finally, more human biomonitoring data is needed, in order to understand the routes of uptake of these chemicals in the human body and the levels present in tissues. Given their persistence, bioaccumulative nature and potential to undergo long-range transport, The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of a commercial chlorinated paraffin product of average carbon chain length C_{10} and average degree of chlorination of 60 % in experimental animals and "possibly carcinogenic to humans" (Group 2B) [20].

The chemical stability of these compounds, their high lipid solubility and toxicity to human and animals, has led government and researchers to be concerned with their presence in the environment. Many ignorant farmers, fishermen and some other users have abused the use of organic compounds for agricultural and fishing purposes. Being persistent and toxic, they pose serious environmental and health hazards, not only in the areas of applications, but up the food chain as the receiving water body contains other edible zooplanktons that ingest these toxic chemicals which reside mostly in the fatty parts of their bodies. Considering that fishes share many physiological characteristics with mammals and are often the primary indicator of toxification of streams and rivers, hence the need for this research which is focused on investigating the incidence of persistent organic pollutants residues in some smoked fish samples sold in Aduuwawa, Oluku and Yanga markets in Benin metropolis in Edo State, and the potential health risk posed to consumers from the exposure to potential organic compounds through the regular ingestion of smoked fishes.

Materials and Method

Sample Collection

Samples were obtained randomly from three different markets in Benin-city using Ziploc freezer bags. A total of twenty-one (21) samples of three types of selected smoked fishes were collected, code-named and identified at the Department of Fisheries, Faculty of Agricultural Sciences, University of Benin, Benin City. The fishes include; *Oreochromis aureus* (Blue tilapia), *Scomber scombrus* (Atlantic mackerel) and *Gymnarchus niloticus* (Trunk fish). The fish samples were stored in refrigerator at 4 ºC.

Sample preparation and Laboratory analysis

Before use, the fish samples were blended to powdered form using an electric blender (Kenwood 1Litre Blender-BL335 350 Watts, China).

Chemicals and reagents: All chemicals and reagents used in this study were of high purity quality and were of analytical grade. Dichloromethane used for the extraction was obtained from Fischer Scientific, New Jersey. Silica gel used in the cleaning up of the extract was supplied by BDH Labs (UK) and anhydrous sodium sulphate was purchased from Sigma-Aldrich, Germany. Acetone (99.5%) was purchased from BDH, England. The individual reference pesticide standards (ISO 9001Certified) used for GC analysis of the organochlorines were purchased from Augsburg in Germany. A PAH standard mixture (NIST, Baltimore, MD, USA) containing naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylenedibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene was used in this study. A mixture containing four isotopically labeled PAHs (ChemService, West Chester, PA, USA), namely ($^{2}H_{10}$) acenaphthene (acenaphthene-d_{10}), ($^{2}H_{12}$) chrysene(chrysene-d_{12}), ($^{2}H_{10}$)phenanthrene (phenanthrene-d_{10}) and ($^{2}H_{12}$)perylene (perylene-d_{12}), was used as an internal standard.

Soxhlet extraction and Clean-up of Fish Samples

Prior to extraction, an aliquot of 10 g of blended fish was weighed using a whattman filter paper on a weighing balance and transferred into a semi-permeable membrane material and placed inside the Soxhlet extraction thimble for 3 h via a Soxhlet heating mantle. Extraction was carried out with dichloromethane (200 ml) in a cold extraction mode at temperature of 60 ºC. The extracted solvent was evaporated using a rotary evaporator under reduced pressure of 40 ºC [21-22]**.** Clean-up was carried out using a clean grease free beaker and a separating glass tube. Seven grams (7 g) analytical grade silica gel (160-200 mesh size) was packed unto a clean cotton wool with additional 1 cm of anhydrous sodium sulphate; Na_2SO_4 was added to the column. (to absorb water) and column chromatographic method (15 cm x 9 mm I.D film thickness) was used to elute solvents. The eluents were allowed to air-dry and 0.5 ml of dichloromethane was used to aid transfer into eppendorf tubes [22].

Preparation of Calibration Standards

Five standard solutions each containing 16 target compounds were prepared by diluting the standard mix (1647 mixfrom NIST) to desired concentrations with dichloromethane.

Quantification

Quantification of POPs was made on a GasChromatograph (Hewlett-Packard 5890 Series 11) tandem Mass Chromatography. 1 µL of sample solution wwas injected in the pulsed splitless mode onto a 330 m and 0.322 mm i.d. fused capillary column with a film thickness of 0.25 µm. Helium gas was used aas a carrier gas. An injectio temperatre was set at 300 ^{o}C. The colunm temperaature was initially 80 ^{o}C for 60 sec. and ramped to 320 ^{o}C at a rate of 20 ^{o}C /min and then 320 ^{o}C was held for 20 min. Identification of organic pollutants in the samples was based on comparison of the retention time with those in a standard solution and quantification on the corresponding areas of the respective chromatograms. Procedural blanks were also analyzed and quantified.Mass spectrometer mode was used was used and all spectra were acquired using a mass rangeof *m/z* 50–400 and automatic gain control (AGC).

Results

Organic compounds which are found in the fishes include polychlorinated aromatic hydrocarbons, 1-octadacanechloro, titanium dioxide and oxirane. Diethyl phthalates and Bis(2-ethylhexyl) phthalate which possess endocrine-disrupting activity on androgen and estrogen receptors were also identified

In **Table 1** is shown the acceptable maximum residue limit (MRL) of some persistent organic pollutant in fishes as analysed by Gas chromatography (GC). 1µl of 1ppb of octofluoronapthalene solution (OFN) was made and a signal to noise ratio of more than or equal to 200 was obtained for all organic pollutants tested. Organochlorine pesticides were not detected in the smoked fish samples. The concentration of naphthalene was 0.0469 mg/kg while Bis(2-ethylhexyl) phthalate was 0.0321 mg/kg. Further bombardment of molecules by Mass spectrometer (MS) gave off library of compounds contained in each smoked fish sample. Smoked fish samples from **Figure 1** and **Table 2** represents the gas chromatogram and library of compounds of *Gymnarchus niloticus* from Oluku market possessing oxirane (0.0362mg/L), naphthalene (0.0469mg/L) and tridecyl phthalate (0.0469mg/L).

Table 1: Persistent organic pollutants (POPs) in the fish samples and their acceptable maximum residue limit (MRL)

No.	POPs	Concentration (mg/Kg)	MRL (mg/Kg)
1	Lindane	N.D	0.01
2	Heptachlor	N.D	0.2
3	Aldrin	N.D	0.05
4	Endosulfan	N.D	0.5
5	DDT*	N.D	0.01
6	Bis(2-ethylhexyl) phthalate	0.0321	0.25
7	Naphthalene	0.0469	0.2
8	Permithrine	N.D	2
9	Cypermithrine	N.D	2

Key: N.D= Not Detected, DDT= Dichlorodiphenyltrichloroethane, MRL values = CODEX ALIMENTARIUS

Figure 2 and **Table 3** represent the gas chromatogram and library of compounds of *Gymarchus niloticus* from Aduwawa market possessing titanium dioxide.**Figure 3** and **Table 4** represents the gas chromatogram and library of compounds of *Oreochromis aureus* from Aduwawa market possessing 1- octachlorodecane (0.0214mg/L) known as short chain chlorinated parrafins-SCCPs (C_{10}-C_{13} with 60% chlorine).

In **Table 5** is shown the quantity of persistent organic pollutants recovered in some fish samples (mg/L). Concentrations of Bis(2-ethylhexyl)phthalate, tridecylphthalate, chlorinated paraffin, naphthalene and oxirane were 0.0321mg/L, 0.0469mg/L, 0.0214mg/L, 0.0469mg/L and 0.0362mg/L in that order.

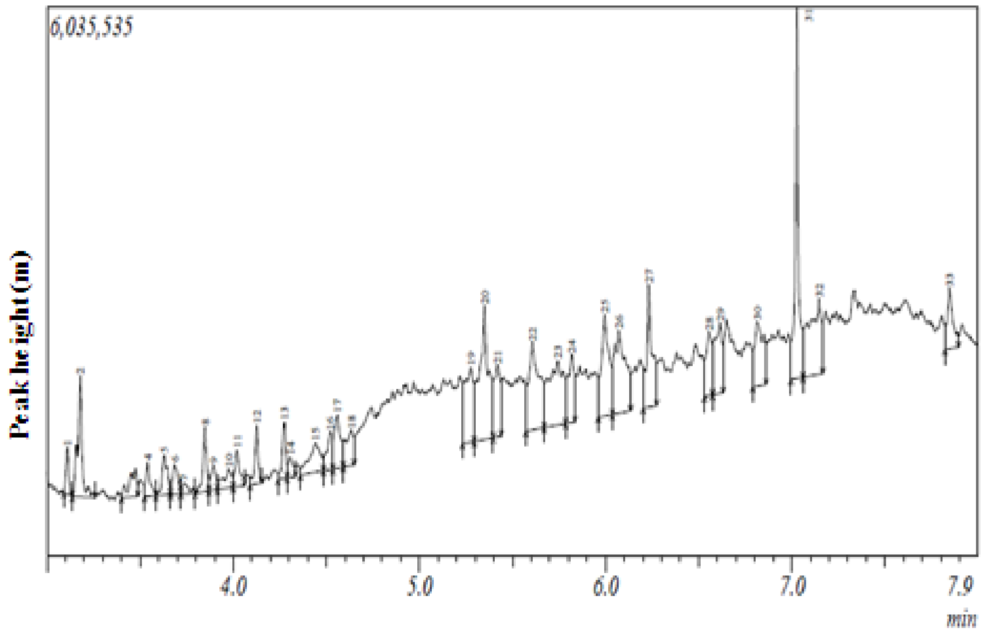

Figure 1: Gas chromatogram of Gymnarchus niloticus from Oluku market

Table 2: Library of compounds of *Gymnarchus niloticus* from Oluku market

Peak	Retention time (m)	Area (m^2)	Name
1.	3.109	502047	Tetradecane, 2, 6, 10-trimethyl-
2.	3.179	2220333	Oxirane, hexadecyl-
3.	3.460	902452	Cholestan-3-ol, 2-methylene-,
4.	3.541	530583	2-methyltetracosane
5.	3.627	939355	Cyclopropanebutanoic acid,
6.	3.686	622368	7-Hexadecenal, (Z)-
7.	3.735	286035	7-Hexadecenal, (Z)-
8.	3.848	1013608	Phthalic acid, butyl undecyl ester
9.	3.894	486629	Tetrapentacontane, 1,54-dibromo-
10.	3.976	645618	2-Bromotetradecanoic acid
11.	4.020	722997	7-Hexadecenal, (Z)-
12.	4.126	897797	Cyclopentadecanone, 2-hydroxy-
13.	4.273	864152	8,11,14-Eicosatrienoic acid,
14.	4.307	417850	7-Hexadecenal, (Z)-
15.	4.441	1436933	7-Hexadecenal, (Z)-
16.	4.520	863837	7-Hexadecenal, (Z)-
17.	4.559	1359979	7-Hexadecenal, (Z)-
18.	4.635	1130995	7-Hexadecenoic acid, methyl ester,
19.	5.277	2779050	7- Hexadecenal, (Z)-
20.	5.349	4951190	7-Hexadecenal, (Z)-
21.	5.419	1862502	7-Hexadecenal, (Z)-
22.	5.607	3875048	trans-2-Hexadecenoic acid
23.	5.744	914038	Tetrapentacontane, 1,54-dibromo-
24.	5.818	1765231	7-Hexadecenal, (Z)-
25.	5.995	3222344	7-Hexadecenal, (Z)-
26.	6.072	3820816	Hexadecenal, (Z)-
27.	6.232	2922097	Bis (tridecyl) phthalate, naphthalene

28.	6.557	1559324	Hexadecenal, (Z)-
29.	6.614	2107894	Cyclopentadecanone, 2-hydroxy-
30.	6.812	2324666	Pentadecenol
31.	7.027	5302697	Trimethyl-(3, 8, 12, 16-tetramethyl-heptadecanyl)
32.	7.145	3821441	i-Propyl 9-tetradecenoate
33.	7.846	1482726	Tetraallyl-1,3-disilacyclobutane

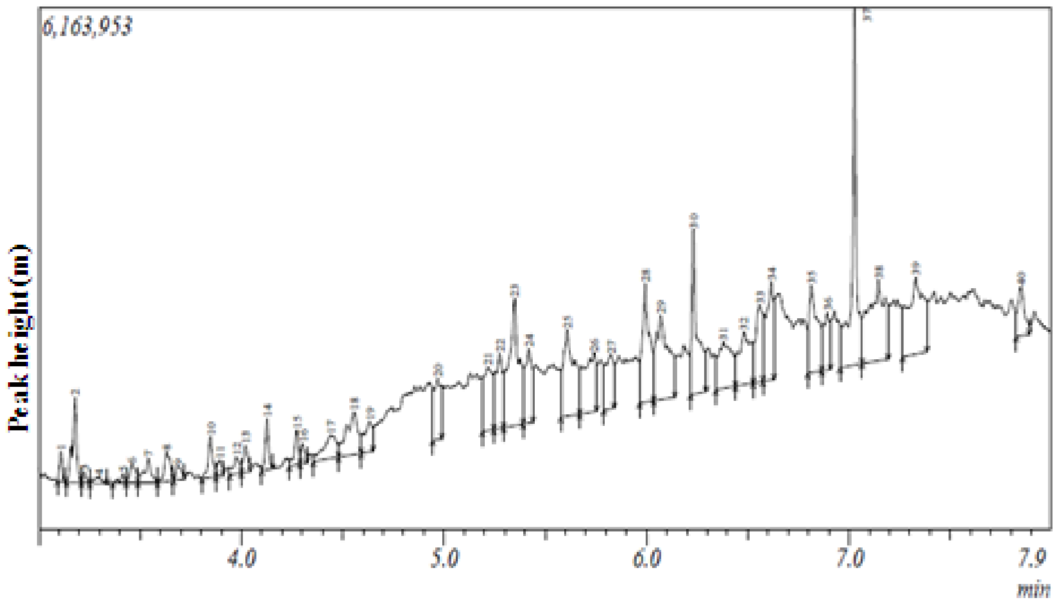

Figure 2: Gas chromatogram of Gymnarchus niloticus from Aduwawa market

Table 3: Library of compounds of *Gymnarchus niloticus* from Aduwawa market

Peak	Retention time (m)	Area (m^2)	Name
1.	3.108	350172	Tritetracontane
2.	3.180	1508853	Hexadecanal
3.	3.224	157922	Titanium dioxide, carbonylbis-cyclopentadien)
4.	3.295	211135	(2,2,6-Trimethyl-bicyclo[4.1.0]-methanol
5.	3.415	164395	9-(2',2')-3,6-dichloro-2,7-bis-[2(diethylamino)
6.	3.459	464318	Cholestan-3-ol, 2-methylene-,
7.	3.541	649243	Tetrapentacontane, 1,54-dibromo-
8.	3.630	719384	7-Hexadecenal, (Z)-
9.	3.687	345861	7-Hexadecenal, (Z)-
10.	3.848	752760	Phthalic acid, butyl undecyl ester
11.	3.893	287924	7-Hexadecenal, (Z)-
12.	3.976	424027	E-11-Hexadecenoic acid, ethyl ester
13.	4.021	492901	7-Hexadecenal, (Z)-
14.	4.125	729188	Cyclopentadecanone, 2-hydroxy-
15.	4.273	599052	8,11,14-Eicosatrienoic acid, (Z,Z,Z)-
16.	4.303	320589	Cholestan-3-ol,2-methylene-,(3.beta.,5.alpha)
17.	4.440	1266195	7-Hexadecenal, (Z)-
18.	4.556	1954247	Cyclopentadecanone, 2-hydroxy-
19.	4.634	976490	7-Hexadecenoic acid, methyl ester, (Z)-
20.	4.969	1739384	7-Hexadecenal, (Z)-
21.	5.216	2258627	Cyclopentadecanone, 2-hydroxy-
22.	5.276	2199145	7-Hexadecenal, (Z)-
23.	5.348	5017887	Oxacyclotridecan-2-one
24.	5.419	2199544	7-Hexadecenal, (Z)-

25.	5.609	3937246	trans-2-Hexadecenoic acid
26.	5.742	2985986	7-Hexadecenal, (Z)-
27.	5.824	1714216	7-Hexadecenal, (Z)-
28.	5.994	3500995	7-Hexadecenal, (Z)-
29.	6.072	4282710	7-Hexadecenal, (Z)-
30.	6.232	3910189	7-Hexadecenal, (Z)-
31.	6.379	2695643	7-Hexadecenal, (Z)-
32.	6.482	2454914	7-Hexadecenal, (Z)-
33.	6.558	2215663	7-Hexadecenal, (Z)-
34.	6.616	3012959	Cyclopentadecanone, 2-hydroxy-
35.	6.812	2971924	1,2-Oxathiane, 6-dodecyl-, 2,2-dioxide
36.	6.894	1574813	trans-2-Hexadecenoic acid
37.	7.027	6982917	2, 2, 4-Trimethyl-3
38.	7.145	5317683	Z-9-Pentadecenol
39.	7.329	4765936	i-Propyl 9-tetradecenoate
40.	7.849	1245810	i-Propyl 9-tetradecenoate

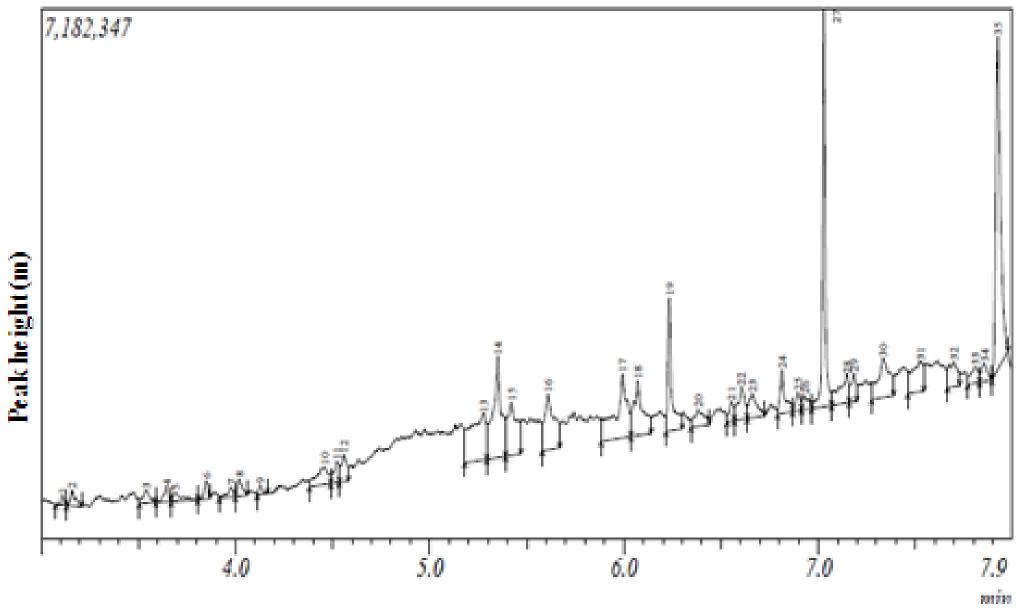

Figure 3: Gas chromatogram of Oreochromis niloticus from Aduwawa market

Table 4: Library of compounds of *Oreochromis aureus* from Aduwawa market

Peak	Retention time (m)	Area (m^2)	Name
1.	3.107	131533	Octadecane, 1-chloro-
2.	3.157	384586	2,2,6-Trimethyl-bicyclohept-1-yl-methanol
3.	3.541	397857	7-Hexadecenal, (Z)-
4.	3.647	371779	Cyclopropanebutanoic acid
5.	3.690	341348	7-Hexadecenal, (Z)-
6.	3.850	358519	Phthalic acid, butyl undecyl ester
7.	3.978	286801	Ethyl 9-hexadecenoate
8.	4.020	414862	7-Hexadecenal, (Z)-
9.	4.126	160998	7-Hexadecenal, (Z)-
10.	4.459	1048080	7-Hexadecenal, (Z)-
11.	4.522	552051	7-Hexadecenal, (Z)-
12.	4.559	712480	7-Hexadecenal, (Z)-

13.	5.277	3507838	Cyclopentadecanone, 2-hydroxy-
14.	5.350	3970357	Oxacyclotridecan-2-one
15.	5.421	2567748	7-Hexadecenal, (Z)-
16.	5.610	2573223	trans-2-Hexadecenoic acid
17.	5.994	3687469	7-Hexadecenal, (Z)-
18.	6.072	2466620	7-Hexadecenal, (Z)-
19.	6.233	2675220	Bis(2-ethylhexyl) phthalate
20.	6.382	810578	7-Hexadecenal, (Z)-
21.	6.555	444911	trans-2-Hexadecenoic acid
22.	6.606	1053328	Cyclopentadecanone, 2-hydroxy-
23.	6.661	931114	Palmitoleic acid
24.	6.813	1043198	1, 2-Oxathiane, 6-dodecyl-, 2,2-dioxide
25.	6.896	412317	trans-2-Hexadecenoic acid
26.	6.931	412755	trans-2-Hexadecenoic acid
27.	7.029	5761220	2,2,4-Trimethyl-3heptadecanyl)-
28.	7.147	1302342	n-Propyl 9-tetradecenoate
29.	7.183	691415	i-Propyl 9-tetradecenoate
30.	7.334	2257973	i-Propyl 9-tetradecenoate
31.	7.526	1729251	i-Propyl 9-tetradecenoate
32.	7.699	1016694	1, 1-Bicyclopropyl-2-octanoic acid
33.	7.809	568107	1, 1-Bicyclopropyl-,2-hexyl,methyl ester
34.	7.855	519491	i-Propyl 9-tetradecenoate
35.	7.924	7514817	Cholesterol

Table 5: Quantity of organic pollutants recovered in some smoked fish samples (mg/L) [23]

Fish Samples	DEHP	TDP	Chlorinated paraffin	Naphthalene	Oxirane
Scomber Scombrus	N.D	N.D	N.D	N.D	N.D
Gymnarchus niloticus	N.D	0.0469	N.D	0.0469	0.0362
Oreochromis aureus	0.0321	N.D	0.0214	N.D	N.D
FEPA Standard	0.81	0.81	3.00-5.00	2.00	0.10-1.00

Key: DEHP: Di (2-ethylhexyl) phthalate, TDP: Tridecylphthalate, N.D: Not Detected
Standard: FEPA, 1991

Discussion

The Gas Chromatography results showed that most of the compounds were organic, fatty acids and fatty acid derivatives, steroids (cholesterols), carboxylic acids, saturated alicyclic ketones, proteins, aldehydes, free amino acids (free in the sense that they are not found in the protein structure). Organochlorine pesticides were not detected in the fish samples

Phthalates are synthetic chemical esters of phthalic acid used to impact flexibility and elasticity to plastics and therefore known as plasticizers. Bis(2-ethylhexyl) phthalate (DEHP) is an organic compound used in rubber production [24]. It is an endocrine disruptor in males through its action as androgen antagonist which progresses with long-lasting effects on reproductive function in adolescents and adult males. Maternal exposure to DEHP disrupts placental growth and development in pregnant mice [25]. Frequent exposure to endocrine disruptors leads to delayed puberty, reduced testosterone production and impotency [26-27]. Even after delivery exposure to DEHP can occur through lactation causing hypertrophy of adrenal glands [25]. In another study, airborne concentrations of DEHP at a PVC plant were significantly associated with a reduction in sperm motility and chromatin DNA integrity [28]. The acute toxicity of DEHP is low in animal models: 30g/kg in rats (oral) and 24g/kg in rabbits [27].

Titanium dioxide was found in *Gymnarchus niloticus* from Aduwawa market. Titanium is a heavy metal and its exposure happens when added to cosmetics, sunscreens, dental implants, paints, food and confectionary such as chewing gum due to its crunchy coat [29]. It is the main content in food colouring. Although there is a permitted level in food and pharmaceutical products, it has been classified as a "possible carcinogens" to humans by International Agency for Research on Cancer and National Institute for Occupational Health and Safety. This form of titanium is used by various industries during production. It is slightly hazardous to the environment especially aquatic ecosystem. It is water insoluble and not excreted by the body because of its protective titanium oxide surface layer. Lethal dose LD_{50} is 7460mg/kg for rats [30]. Corrosion occurs only when it comes in contacts with the mucous membrane. Overexposure to titanium powder can lead to tightening of the chest and increase respiratory illness such as asthma [31]. In summary, titanium can induce relevant hypersensitivity in a subgroup of patients chronically exposed, (that is to say, it is highly dependent on dose).

Aromatic organic compounds, Bis(tridecyl) phthalate and naphthalene were detected in *Gymnarchus niloticus* from Oluku. Just like DEHP, they are also used as plasticizers to increase its flexibility, durability and transparency in plastics [27]. There is a frequent use as medical devices such as intravenous tubing and bags, dialysis bags, blood bags and intravenous catheters [32]. Those at high risk of developmental abnormalities are newborn in intensive care nursery settings, kidney dialysis patients, premature babies and sicklers [33]. Data on reproductive and developmental toxicity of Bis(tridecyl) phthalates (TBP), dibutyl phthalates (DBP) and diethyl phthalates (DEP) stated that they have an anti-androgenic effect in a human cell line as it inhibited the binding of dihydrotestosterone to the androgen receptor with an IC_{50} of 74µM and IC_{50} of 515µM respectively [34]. In concordance with this finding, a low binding affinity for the androgen receptor has been reported for DEP in a competitive binding assay (IC_{50} of 0.84mM) [35]. Due to the mutagenic and carcinogenic effects of PAH derivative(s), they have been included in several priority pollutant lists of the Agency of Toxic Substances and Disease Register (ATSDR), International Agency for Research on Cancer (IARC) and the Environmental Protection Agency (USEPA) [9]. Phthalates have also been included in the candidate list of endocrine disruptors and are classified as a category 1B reprotoxin and is now on the Annex XIV of the European union REACH legislation [6].

Oxirane (Ethylene oxide) is an organic compound produced in industries. Although it is used in the manufacture of detergents, continuous exposure is very hazardous, carcinogenic and mutagenic. The concentration value of 0.0362mg/L was low compared to 0.7362mg/L reported by Steenland *et al.* [36]. The International Agency for Research on Cancer classified oxirane into group 1 meaning that it is a proven carcinogen [20]. A study of 7,576 women exposed while at work in commercial sterilization facilities in the US suggested that oxirane is associated with breast cancer incidence [36]. An increased incidence of brain tumor, and mononuclear cell leukemia was found in rats that inhaled oxirane at concentrations of 10, 33 or 100 (mL/m^3) for two years. Results from human epidemiological studies differ. There is evidence from both human and animals studies that inhalation of oxirane can result in a wide range of carcinogenic effects.

Naphthalene is an organic pollutant which belongs to the class- polycyclic aromatic hydrocarbon (PAH). It is obtained from coal tar or distillation of petroleum. In industries, it is used as an insecticide, leather tanning agents, dyes, and pest repellent but also used in moth repellent. The concentration value of 0.0469mg/L was low compared to the result of Rose *et al.* [11] who suggested that low-molecular-weight PAHs, especially napthalenes and phenanthrene was indicative of runoff sources. The health effects resulting from PAH exposure include growth retardation, liver damage, cataract, low birth weight, small head circumference and the disruption of endocrine systems [9]. PAHs compounds are groups of potent carcinogens that are present in the environment. Hepatic tumors have been reported in wild fish exposed to sediment containing about 250mg/kg of PAH and traces of these substances have been found in various food products [11, 24]. Naphthalene enters the environment through fossil fuels, indiscriminate disposal of wastes by chemical industries and the home through insecticide and moth repellents. They are found in traceableamount in some fishes and shellfishes from polluted water [21]. Naphthalene has been classified as a group C "possible carcinogen" [20].

Another persistent organic pollutant detected among the tilapia (*Oreochromis aureus*) from Aduwawa is 1-chlorooctadecane. 1-chlorooctadecane is known as Short Chain Chlorinated Parrafins-SCCPs (C_{10}-C_{13} with 60%

chlorine) [20]. Chlorinated paraffins are used as secondary plasticizers for polyvinyl chloride (PVC) in applications such as electric cables when the inherent low inflammability of PVC would be impaired by primary plasticizers (e.g., dioctylphythalate) [13]. The concentration value of 0.0214mg/L was higher than the values of SCCPs obtained in the liver andmuscle of seabirds from the European Arctic in concentrations ranging from 0.005 to0.088 mg kg^{-1} wet weight [18]. This variation could be attributed to the fact that chlorinated compounds are lipophilic in nature and therefore dissolves readily in polyunsaturated oil in fish [21]. Chlorinated paraffins have also been isolated from human liver, kidney and breast milk [19]. They are toxic to small aquatic organisms and plants that fish feed on. The International Agency for Research on Cancer has classified this compound in Group 2B as "possibly carcinogenic to humans" [20]. This exposure circumstance entails exposures that are possibly carcinogenic to humans. This category is used for agents, mixtures and exposure circumstances for which there is limited evidence of carcinogenicity in humans but there is sufficient evidence of carcinogenicity in experimental animals [2, 13].

All the values obtained for the organic pollutants were very low when compared with the maximum limit of Federal Environmental Protection Agency [23]. Even though Naphthalene and Oxirane (ethylene oxide) were below the FEPA limit, these two compounds have been classified in GROUP 1 of extremely hazardous wastes (EHW) by IARC [20]. Continuous exposure can be harmful if the trend is not checked [21].

References

[1]. Amaral, M.J.J. (2002). The endocrine disruptors: A major medical challenge. *Food Chemistry and Toxicology* 40(6): 781-788.

[2]. UNEP, (2009). United Nations Environment Programme. Stockholm Convention on persistent organic pollutants (POPs) as amended in 2009, Geneva, Switzerland. Pp. 1-64. Ward, A. R. (1995). Fish smoking in the tropics: A review. *Tropical science* 35:103–112.

[3]. Li, Q.Q., Loganath, A., Chong, Y.S., Tan, J. and Obbard, J.P. (2006).Persistent organic pollutants and adverse health effects in humans. *Journal of Toxicology and Environmental Health* 69(21): 1987-2005.

[4]. Bordajandi, L.R., Gomez, G., Fernandez, M.A., Abad, E., Rivera, J. and Gonzalez M.J. (2003). Study on PCBs, PCDD/Fs, organochlorine pesticides, heavy metals and arsenic content in freshwater fish species from the River Turia (Spain). *Chemosphere 53: 163–171.*

[5]. Tsai, W.T. (2010). Current status and regulatory aspects of pesticides considered to be persistent organic pollutants (POPs) in Taiwan. *International Journal of Environmental Research and Public Health* 7: 3615-3627.

[6]. FAO/WHO, (2010). Food and Agriculture Organization of the United Nations. Report of the Joint FAO/WHO Expert Consultation on the Risks and Benefits of fish consumption. FAO Fisheries and Aquaculture Report No. 978. Rome. Pp.1-63.

[7]. Mussalo-Rauhamaa, H. (1991). Partitioning and levels of neutral organochlorine compounds in human serum, blood cells, and adipose and liver tissue. *Science of the Total Environ*ment 103:159–175.

[8]. Garabrant, D.H., Held, J., Langholz, B., Peter J.M. and Mark, T.M. (1992). DDT and related compounds and risks of pancreatic cancer. *Journal of National Cancer Institute* 84(10): 764-771.

[9]. Yusuf, K.A., Ezechukwu, L.N., Fakoya, K.A., Akintola, S.L., Agboola, J.I. and Omoleye, T.O. (2015). Influence of fish smoking methods on polycyclic aromatic hydrocarbons content and possible risks to human health. *African Journal of Food Science* 9(3):126-135.

[10]. Guillen, M.D. (1994). Polycyclic Aromatic Compounds: extraction and determination in food. Food Additives and Contaminants 11(6): 669-684.

[11]. Rose, A., Ken, D., Kehinde, O. and Babajide, A. (2012). Bioaccumulation of polycyclic aromatic hydrocarbons in fish and invertebrates of Lagos lagoon, Nigeria. *Journal of Emerging Trends in Engineering and Applied Sciences* (JETEAS) 3(2): 287-296.

[12]. Essumang, D.K., Doodoo, D.K. and Adjei, J.K. (2013). Effects of smoke generation sources and smoke curing during curation on the levels of polycyclic aromatic hydrocarbons (PAH) in different suites of fish. *Food and Chemical Toxicology* 58:56-94.

[13]. Kalanzi, O.I. and Alcock, R.A. (2011). Short-chain chlorinated paraffins in biota- levels and effects. *Proceedings of the 12th International Conference on Environmental Science and Technology* Rhodes, Greece 8(10): 790-795.

[14]. Pellizzato, F., Ricci, M., Held, A. and Emons, H. (2007). Analysis of short-chain chlorinated paraffins: a discussion paper. *Journal of Environmental Monitoring* 9: 924-30.

[15]. Ryan, J. J., Schecter, A., Masuda Y., and Kikuchi, M. 1987. Comparison of PCDDs and PCDFs in the tissues of Yusho patients with those from the general population in Japan and China. *Chemosphere* 16:2017–2025.

[16]. Ueberschär, K.H., Dänicke, S. and Matthes, S. (2007). Dose-response feeding study of short chain chlorinated paraffins (SCCPs) in laying hens: Effects on laying performance and tissue distribution, accumulation and elimination kinetics. *Molecular Nutrition* and *Food Research* 51: 248-254.

[17]. Tomy, G., Stern, G., Koczanski, K. and Halldorson, T. (1998). Polychloro-n-alkanes in beluga whales from the Arctic and the St. Lawrence River estuary. *Organohalogen Compounds*. 35: 399–401.

[18]. Reth, M., Ciric, A., Christensen, G.N., Heimstad, E.S. and Oehme, M. (2006). Short- and medium-chain chlorinated paraffins in biota from the European Arctic - differences in homologue group patterns. *Science of the Total Environment* 367 (1), 252-260.

[19]. Thomas, G.O., Farrar, D., Braekevelt, E., Stern, G., Kalantzi, O.I., Martin, F.L. and Jones, K.C. (2006). Short and medium chain length chlorinated paraffins in UK human milk fat. *Environment International* 32 (1): 34-40.

[20]. International Agency of Research on Cancer (IARC), (1990). IARC monographs on the evaluation of carcinogenic risks to humans. 48: 55-72.

[21]. Ize-Iyamu, O.K., Asia, I. O. and Egwakhide, P. A. (2007). Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State, Nigeria. *International Journal of Physical Sciences* 2(9): 237-241.

[22]. Adeyemi, D., Ukpo, G., Anyakora, C. and Unyimadu J.P. (2008). Organochlorine pesticide residues in fish samples from Lagos lagoon, Nigeria. *American Journal of Environmental Sciences* 4(6): 649-653.

[23]. Federal Environmental Protection Agency (FEPA). (1991). Guidelines and Standards lot. Environmental pollution control in Nigeria. *Ministry of Works, Housing and Environment Official Gazette,* Lagos, Nigeria. 560pp.

[24]. Guillen, M.D., Sopelena, P. and Partearroyo, M.A. (1997). Food as a source of polycyclic aromatic carcinogens. Reviews of Environmental Health 12:133-146.

[25]. Teng, Z., Lidan, L., Jia, H., Meijun, L., Mo, L., Zhang, L., Chengxue, Z., Bei, Y., Lei, W., Dalei, Z., Min, T. and Haibin, K. (2015). Maternal exposure to di(ethylhexyl)phthalate disrupts placental growth and development in pregnant mice. *Journal of Hazardous Materials* 297: 25-33.

[26]. Jonatan, A., Lars, R., Anna, R.H., Lindh, C.H., Jonasson, B.O.G. and Giwercman, A. (2015).Pre-natal phthalate exposure and reproductive function in young men. *Environmental research* 138: 264-270.

[27]. Noriega, N.C., Howdeshell, K.L., Furr, J., Lambright, C.R., Wilson, V.S. and Gray, L.E. (2009). Pubertal administration of DEHP delays puberty, suppresses testosterone production and inhibits reproductive tract development in male Sprague-Dawley and Long-Evans rats. *Toxological Sciences*111(1): 163-178.

[28]. Huang, L.P., Ching-Chang, L., Ping-Chi, H., Tung-Sheng, Shih. (2011). The association between semen quality in workers and the concentration of di(2-ethylhexyl) phthalate in PVC pellet plant air. *Fertility and Sterility* 96(1): 90-94.

[29]. Tomatis, L., Aitio, A., Wilbourn, J. and Shuker, L. (1989). Human carcinogens so far identified. *Japanese Journal of Cancer Research* 80:795-807.

[30]. Cogliano, V.J., Baan, R.A., Straif, K., Grosse, Y., Secretan, M.B., El-Ghissassi, F. and Kleihues, P. (2004). The Science and Practice of Carcinogen Identification and Evaluation. *Environmental Health Perspective* 112(13):1269-1274.

[31]. Jonasson, S., Gustafsson, A., Koch, B. and Bucht, A. (2013). Inhalation exposure of nano-scaled titanium dioxide (TiO_2) particles alters the inflammatory responses in asthmatic mice. *Inhalation Toxicology* 25(4):179-191.

[32]. Sampson, J. and De Korte, D. (2011). Diethylhexyl phthalates-Plasticized PVC: relevance to blood services. *Transfusion Medicine* 21(2): 73-83.

[33]. Shea, K.M. (2003). Paediatric exposure and potential toxicity of phthalates. *Paediatrics* 111(6): 1467-1474.

[34]. Christen, V., Crettaz, P., Oberli-Schrammli, A. and Fent, K. (2010). Some flame retardants and the antimicrobials triclosan and triclocarban enhance the androgenic activity *in vitro*. *Chemosphere* 81(10): 1245-1252.

[35]. Fang, H., Tong, W., Branham, W.S., Moland, C.L., Dial, S.L., Hong, H., Xie, Q., Perkins, R., Owens, W. and Sheehan, D.M. (2003). Study of 202 natural, synthetic and environmental chemicals for binding to the androgen receptor. *Chemical Research in Toxicology* 63(10) 1338-1358.

[36]. Steenland, K., Whelan, E., Deddens, J., Stayner, L. and Ward, E. (2003).Ethylene oxide and breast cancer incidence in a cohort study of 7576 women in United States. *Cancer Causes and Control* 14(6): 531-539.