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RISK ASSESSMENT OF PESTICIDE RESIDUES IN FISH SAMPLES FROM NWANIBA RIVER, AKWA IBOM STATE, NIGERIA

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ABSTRACT

This study was conducted to determine the levels of contamination of organochlorine pesticide residues in fish from Nwaniba River in Uruan Local Government Area of Akwa Ibom State. A total of 18 samples of different species of fish were obtained at two stations within Nwaniba River. The analysis of residual pesticides was carried out using Gas Chromatography coupled with electron capture detector (GC-ECD). The obtained results revealed the predominance of Dieldrin in the different samples of fish analysed from Ufak Effiong in the southern District (station 1) and Akani Obio in Uruan Central District (station 2) of Uruan. Pesticide levels were found to be significantly higher than the World Health Organization/Food and Agricultural Association (WHO/FAO) Maximum Residue Limits (MRL). The levels of organochlorine pesticides (OCPs) ranged from Below detection limit (BDL) to 8.53×10^{-2} ng/µL for fish samples. Carcinogenic risk values for gamma - BHC, delta - BHC, Dieldrin, Endosulfan I and Heptachlor epoxide in the fish samples were found to be less than 1.0×10^{-5}, thus posing no potentially serious cancer risk to consumers. The values of cancer risk obtained in this study were lower (6.448×10^{-11} and 7.208×10^{-11}) than the established maximum limit. This study also revealed that hazard index (HI) of OCPs in fish were higher in children than adults except silver catfish in adults from Akani Obio (0.78807), showing no potential risk since HI is less than or equal to 1. The hazard index of OCPs in other fish species (Nile tilapia and Upside-down catfish) exceeded the threshold value of 1, which is evidence that daily exposure could pose potential ecological and public Health concern.

Keywords: Organochlorine pesticides, gas chromatography, residual pesticides, risk assessment

Introduction

Agricultural pesticides are mainly of organochlorine and organophosphorous compounds. These pesticides are considered to be dangerous not only to the environment but also to human beings as well (Itah and Akpan, 2005). Most farmers, in order to increase their yields, use agrochemicals, which penetrate both surface and ground waters through runoff from treated soils, leaching processes, aerial drift and inappropriate disposal methods thus altering the water chemistry (Olanike, 2003; Joseph *et al*., 2013). On entering into water bodies (lakes and rivers), pesticides have immediate toxic effects on aquatic life (flora and fauna). Pesticides in river system and estuary not only pose threats to human health through water and food consumption, but also to aquatic organisms (Zheng *et al*., 2016). Fish samples are one of the most important indicators of pollution in aquatic systems and are therefore useful for the evaluation of pesticides pollution level (Okonkwo *et al*., 2017).

The contamination of lagoons is a major concern since it is the habitat for fish and other aquatic organisms such as mussels, oysters, prawns and lobsters which are major sources of protein for most people in Nigeria. Poisoning from pesticides is a global public health problem and accounts for nearly 300,000 deaths worldwide every year (Sabarwal *et al*., 2018. The use of pesticides in modern agriculture has not only significantly increased productivity, but has also significantly increased the concentration of pesticides in food and in our environment, with associated negative effects on human health (Zou *et al*., 2016). Misuse of pesticides by individuals, and lack of and/ or weak national policy are behind the outbreak of adverse effects in developing countries (Elbialy *et al*., 2015). During the last decades, it was realised that agrochemical residues did spread in the environment, causing significant contamination of terrestrial ecosystems and poisoning human foods (Carvalho, 2017; Joseph *et al*., 2013; Sabin *et al*., 2009).

The harmful effects of pesticide residues in fish include acute and persistent injury to the nervous system, injury to the reproductive organs, dysfunction of the immune and endocrine systems (Ernst *et al*., 2018). Organochlorines have a high tendency to be attracted to the fatty tissues of humans, animals and plants. Most of them can build up in fatty tissues and organs, and are accumulated significantly in animals such as fish (Idowu *et al*., 2013). Annually, there are dozens of million cases of pesticide poisonings worldwide (Richter, 2002). Moreover, it is now better understood that pesticides have significant chronic health effects, including cancer, neurological effects, diabetes, respiratory diseases, fetal diseases, and genetic disorders (Fang *et al*., 2015; Nuruzzaman *et al*., 2016). Pesticide residues in food have been responsible for several cases of food poisoning and death in Nigeria. This is due to high levels of pesticide residue arising from improper applications and multiple sprays of sub-lethal doses upon food (Oyeyiola *et al*., 2017; Bundschuh *et al*., 2018; Agarwal and Joshi, 2010; Patil *et al*., 2016).

Akoto *et al*. (2016) evaluated the levels of organochlorine (OC) and organophosphorus (OP) pesticide residues in fish, sediments and water and the health risk associated with the consumption of the fish from the Tono Reservoir, Ghana. They analyzed a total of 29 pesticides comprising 16 OCs and 13 OPs, out of which aldrin, pp′-DDE and pp′-DDD were detected in fish and sediment samples. Mean concentrations of organ chlorine pesticide (OCP) residues in fish ranged from 0.017 to 0.17, 0.043 to 0.30, 0.027 to 0.243 and 0.097 to 0.263 µg/g in *Sarotherodon galilaeus, Clarias anguillaris, Schilbe intermedius* and *Marcusenius senegalensis* respectively. Mean concentrations of organophosphates pesticides ranged from 0.080 to 0.090, 0.080 to 0.087 and 0.050 to 0.063 µg/g in C.anguillaris, S. intermedius and M. senegalensis respectively. The results revealed that all the residues in water had their concentrations below detection limit. Mean concentrations of OCP residue in sediments ranged from 0.047 to 0.090 µg/g. Aldrin recorded the highest level while pp′-DDD recorded the lowest level. The mean concentrations for all the detected residues were below the WHO/FAO maximum residue limits. Paul *et al*. (2017) measured the organochlorine pesticide residues in three species of fish: *Tilapia zilli* (Red belly tilapia), *Ethmalosa fimbriata* (Bonga Shad) and *Chrysichthys nigrodigitatus* (silver catfish). Their results revealed that the concentrations of DDT, DDD, DDE, HCB, dieldrin and transnonachlor in fish samples were below the extraneous residue limit of 5 ppm set by the Codex Alimentarious Commission of FAO-WHO (1997).

Determining the levels of pesticide residues in Nile tilapia (*Oreochromis niloticus*), silver catfish (*Chrysichthys nigrodigitatus*) and upside-down catfish (*Synodontis nigriventris*) is essential in order to ensure that the exposure of humans to these contaminants particularly through dietary consumption, does not pose health challenges. Subsequently, the study shall aid the evaluation of the potential health risk of pesticide residues detected in specific fish species on the human population in Akwa Ibom State.
Thus, the aim of this study was to determine the levels of contamination of organochlorine pesticide residues in commonly consumed fish species from Nwaniba River in Uruan Local Government Area of Akwa Ibom State and the public health implications.

MATERIALS AND METHODS

Study Area

Uruan Local Government Area occupies a large landmass (449 Km^2). It situates between latitude 6°40´N and longitude 7°20´ E (Figure 1). It is bounded in the East by Odukpani Local Government Area in Cross River State, in the South by Okobo Local Government Area, in the West by Nsit Atai and Ibesikpo Asutan Local Government Areas and in the North by Itu Local Government Area. The study area was divided into two sampling stations. These were Ufak Effiong in Southern district and Akani Obio in Uruan Central district here known as station I (ST1) and station II (ST2) respectively.

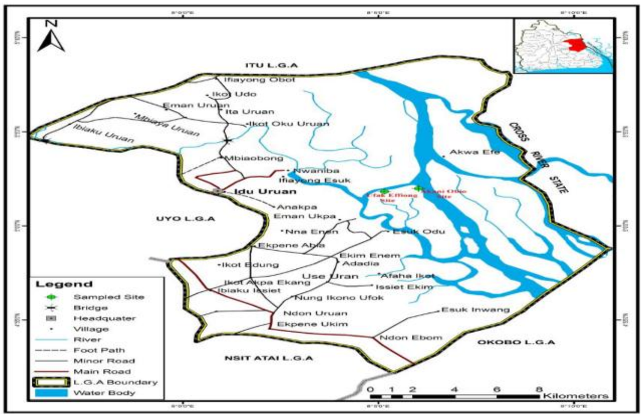

Figure 1: Location of Sampling Stations on the Map of Uruan Local Government Area. Inset: Map of Akwa Ibom State showing location of Uruan Local Government Area

Sample Collection and Preparation

Sample collection and preparation were based on EPA Method 1699 of 2007. The glasswares were rinsed with tap water and then scrubbed with a brush and warm water containing a liquid detergent. They were then rinsed with distilled water and finally with acetone before drying in an oven at 110°C overnight.

The fish species sampled were Nile tilapia (*Oreochromis niloticus*), silver catfish (*Chrysichthys nigrodigitatus*) and upside - down catfish (*Synodontis nigriventris*). Species are among the commonly consumed fishes from the river. These samples were collected in September 2018 during a fishing tour. Each sample consists of a composite of pooled tissues from three individual fish, depending on the size. Composite sample provides a more cost-efficient estimate of mean concentrations than one single fish sample. The fish samples were collected by hook and line and only market size was taken. Each fish was given a unique identifying number. The fish samples were individually wrapped in aluminum foil, put in plastic bags, labelled with species names and placed on ice for transport to chemistry postgraduate laboratory, University of Uyo, where the samples were frozen pending extraction. The fish samples were thawed enough to remove the foil wrapper, scaled and rinsed with tap water and then with de-ionised water. The entire fillets from one or both sides were removed with stainless steel knife. A total of 18 fish samples comprising 3 of each species from the two sampling sites were used for this study.

Extraction of Fish Samples

Fish samples were extracted and cleaned up according to the method described by Nag *et al*. (2016). Ten grams of muscle tissues of the fish samples were homogenized with 10 g of anhydrous granulated sodium tetraoxosulphate (VI) (Na_2SO_4). Cold solvent extraction was performed. Petroleum ether/acetone (1:1 v/v) mixture (50 cm^3) was introduced into a bottle containing the homogenized fish sample. The mixture was shaken and allowed to stand for 30 minutes and then filtered. The solvent extracts were concentrated to 1 cm^3 using a rotary evaporator and clean-up using solid phase extraction (SPE). Sample clean-up was performed by C18 SPE cartridges before being analysed by GC-ECD. The cartridge was conditioned with 6 mL (1:1, v/v) hexane and petroleum ether. Then, 2 mL of concentrated extract was transferred to the SPE cartridge, followed by 6 mL (1:1 v/v) hexane and petroleum ether. The final eluate was then concentrated to exactly 1 mL before being analyzed by GC-ECD.

Quantification of the Pesticide Residues

The extracts and the working standards were removed from the deep freezer and thawed at room temperature. Each extract (1 µL) was injected into the GC column using 5 µL hypodermic syringes with a 7 cm long needle. The syringe was rinsed several times with redistilled n- hexane before and after use. The detector response was observed for 20 minutes. Identification was done by comparing the retention times of the sample peaks on the chromatograph to the ones of the standard chromatograph. Quantification was done by comparing the peak heights of the sample components with that of the corresponding components in standards of known concentrations. The amount of each compound in 1µL of sample was calculated by considering the final volume of the extract and correcting for the dilution using equation 1.

$$P = \frac{h \times Cs \times V}{hs \times m} \qquad 1$$

where p = concentration (ng/µL) of pesticide residues in sample, h = peak height of the residue in chromatograph of the sample, hs = peak height of the pesticide in standard chromatograph, m = weight (g) of the sample used in the analysis, v = Volume of n-hexane used to dissolve the extract, and Cs = Concentration of the standard in ng/µL.

Risk Assessments

A human health risk assessment is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media now or in the future (Aven, 2016). The essence of conducting risk assessment to human health is to define the nature of the risk and to provide a measure of the likelihood and the magnitude of the risk associated with a defined exposure (SPN, 2000). The risk levels of analytes were assessed using the average daily dose (ADD), reference dose (RFD), hazard quotient (HQ) and cancer risk (CR). Values were evaluated from equations 2 – 3.

For the calculation of the risk assessment:

$$ADD = \frac{C \times FI \times IR \times EF \times ED}{BW \times AT} \qquad 2$$

where ADD = Average daily dose (mg/kg/day), C = Contamination concentration of the analytes during monitoring period (ng/µL), FI = Fraction ingested (an absolute number with 0 – 1, specifying the contribution of the particular pollution sources to the pollutant intake by people, but in this study estimated FI for water =0.65), IR = Daily water intake based on age group; age 0 – 6 years = 0.3 L/day, age 7 – 17 years = 1 L/day and adults = 1.4 L/day, EF = Exposure frequency = 365 days/year, ED = Exposure duration based on age group; age 0- 6 years = 6, age 7 – 17 years = 11 and adults = 30, and BW = Body weight in kg (16kg for children and 70kg for adults). Hazard quotients for humans were computed as ratios between average daily dose (ADD) and the reference dose (RfD) which are considered to be harmless levels of exposure over the lifetime.

$$HQ = \frac{ADD}{RfD} \qquad 3$$

where ADD = average daily dose (mg/kg/day), and RfD = reference dose (mg/kg/day).

When HQ is >1, the implication is tha lifetime consumption of pesticides containing the measured level of OCP residues could pose health risks, when HQ < 1, the implication is that a relative low risk i.e adverse effects are not likely to occur. A large HQ implies a greater ecological risk (Wang *et al.*, 2011).

$$\text{Cancer risk (CR)} = \frac{C \times DI \times ED \times CSF \times CF}{BW \times AT} \qquad 4$$

where C is the concentration of the analytes during monitoring period, DI is the daily intake of water ($Lday^{-1}$): 1.4 $Lday^{-1}$, ED is the exposure duration (year): 30 years for adults and 6 years for children, BW is the body weight (kg): 70 kg for adults and 16 kg for children, AT is the average life span (year):70 years × 365 = 25550 days (for all ages), CSF is the cancer slope factor (mg/kg/day), and CF is the conversion factor: 10^{-6}. CR > 1.0×10^{-5} indicate potential carcinogenic risk and CR =10^{-3} requires protective measures (Yahaya *et al*., 2017).

RESULTS AND DISCUSSION

The occurrence of organochlorine pesticides was studied in the selected districts of Uruan local Government Area of Akwa Ibom State, Nigeria and the detected pesticides were heptachlor, gamma-BHC, delta-BHC, heptachlor epoxide, endosulfan I, dieldrin and endosulfan sulfate while the selected fish species were Nile tilapia (*Oreochromis niloticus*), Silver catfish (*Chrysichthys nigrodigitatus*) and upside - down catfish (*Synodontis nigriventris).*

As shown in Table 1, it is indicated that dieldrin was predominant in the three fish species obtained from Ufak Effiong station with silver catfish (*Chrysichthys nigrodigitatus*) having the lowest pesticide residues, upside down catfish (*Synodontis nigriventris*) has the highest level followed by Nile tilapia (*Oreochromis niloticus*) while delta-BHC was detected in *Oreochromis niloticus* and *Synodontis nigriventris* only due to their high fat contents. The levels of organochlorine pesticides in fish species obtained from Ufak Effiong ranges from BDL to 8.13×10^{-2} ng/µL. The levels of dieldrin detected in *Oreochromis niloticus* and *Synodontis nigriventris* are higher than that of *Chrysichthys nigrodigitatus* due to the fact that they have high affinity for fat which accounts for their retention in animal fat (WHO 2004) and a high level of heptachlor epoxide detected in *Chrysichthys nigrodigitatus* is due to its high solubility in water. The high level of dieldrin in *Synodontis nigriventris* is because the fish is an omnivore and also lives more in the sediment than the water surface. Since dieldrin and delta-BHC accumulate and bind to the sediment, *Synodontis nigriventris* absorbs more of them than *Chrysichthys nigrodigitatus* which lives in the water surface. The highest total level of OCPs is found in *Synodontis nigriventris* while the lowest is in *Chrysichthys nigrodigitatus*. The levels of pesticide residues observed in *Oreochromis niloticus* and *Synodontis nigriventris* may be attributed to the habitation and mode of feeding. Pesticide accumulation in fish is dependent on their lipid content (Ezemonye *et al.*, 2015).

Table 1: Levels of organochlorine pesticides (OCPs) in fish species from Ufak Effiong sampling station

Pesticide	Nile tilapia (ng/µL)	Silver Catfish (ng/µL)	Upside-down Catfish (ng/µL)
α-BHC	BDL	BDL	BDL
β-BHC	BDL	BDL	BDL
Heptachlor	BDL	BDL	BDL
Aldrin	BDL	BDL	BDL
γ-BHC	BDL	BDL	BDL
Delta-BHC	5.01×10^{-2}	BDL	6.34×10^{-2}
Heptachlor epoxide	7.90×10^{-3}	2.53×10^{-2}	BDL
Endosulfan I	BDL	BDL	BDL
p,p′-DDE	BDL	BDL	BDL
Dieldrin	4.33×10^{-2}	1.01×10^{-3}	8.13×10^{-2}
Endrin	BDL	BDL	BDL
p,p′-DDD	BDL	BDL	BDL
Endosulfan II	BDL	BDL	BDL
p,p′-DDT	BDL	BDL	BDL
Endrin aldehyde	BDL	BDL	BDL
Endosulfan sulfate	BDL	BDL	BDL
Methoxychlor	BDL	BDL	BDL
ΣOCPs	1.013×10^{-1}	2.631×10^{-2}	1.447×10^{-1}

BDL = Below detection limit, ΣOCPs = summation of the concentration of organochlorine pesticides

In the same vein, Table 2 showed that heptachlor, gamma-BHC, endosulfan I, dieldrin and endosulfan sulfate were present in fish species obtained from Akani Obio with varying amounts. The levels of OCPs detected in fish species from Akani Obio ranges from BDL to 8.34×10^{-2} ng/µL. Among the three fish species analysed for the presence of organochlorine pesticides, *Oreochromis niloticus* has the lowest total OCP residues followed by *Chrysichthys nigrodigitatus* while *Synodontis nigriventris* has the highest. *Chrysichthys nigrodigitatus* from Ufak Effiong has the lowest total OCPs compared to that of Akani Obio. Average levels of OCPs in *Oreochromis niloticus* in this study agree with those of Shinggu *et al.* (2015) while the average levels of OCPs in *Chrysichthys nigrodigitatus* in this study is lower compared to the average levels of OCPs in *Chrysichthys nigrodigitatus* from Shinggu *et al.* (2015). The levels of OCPs detected in fish from both locations exceed the maximum residue levels set by WHO/FAO (2009).

Hazard quotient helps in the evaluation of the magnitude of toxic harm posed to the consumers of fish species contaminated with pesticides while hazard index is a tool for long term risk assessment (Nkpaa *et al.,2016*).

Table 2: Levels of organochlorine pesticides (OCPs) in fish species from Akani Obio sampling station

Pesticide	Nile tilapia (ng/µL)	Silver Catfish (ng/µL)	Upside-down catfish (ng/µL)
α-BHC	BDL	BDL	BDL
β-BHC	BDL	BDL	BDL
Heptachlor	2.20×10^{-2}	8.68×10^{-3}	3.74×10^{-2}
Aldrin	BDL	BDL	BDL
γ-BHC	4.78×10^{-3}	6.23×10^{-2}	8.02×10^{-3}
Delta-BHC	BDL	BDL	BDL
Heptachlor epoxide	BDL	BDL	BDL
Endosulfan I	5.66×10^{-3}	2.86×10^{-2}	2.36×10^{-3}
p,p′-DDE	BDL	BDL	BDL
Dieldrin	3.02×10^{-2}	BDL	8.34×10^{-2}
Endrin	BDL	BDL	BDL
p,p′-DDD	BDL	BDL	BDL
Endosulfan II	BDL	BDL	BDL
p,p′-DDT	BDL	BDL	BDL
Endrin aldehyde	BDL	BDL	BDL
Endosulfan sulfate	3.50×10^{-3}	3.08×10^{-2}	2.58×10^{-3}
Methoxychlor	BDL	BDL	BDL
ΣOCPs	6.61×10^{-2}	1.30×10^{-1}	1.34×10^{-1}

BDL = Below detection limit, ΣOCPs = summation of the concentration of organochlorine pesticides

The human health risk associated with the consumption of fish species from Ufak Effiong and Akani Obio is presented in Table 3. Children have greater HI values than adults implying that they are mostly affected when consuming contaminated fish from both locations because of their weak immune systems. Generally, HI values for fish species are all above unity. However, the HI for OCPs in the silver catfish is lower for adults of Akani Obio, implying no potential health risk through the consumption of silver catfish from Akani Obio. The results of Human Health Risk estimations obtained from this study, conform with those obtained by Ezemonye *et al*. (2015) who reported that the life time consumption of fish species could pose some health risk because HI > 1.

Table 3: Human health risk associated with the consumption of fish from Ufak Effiong (ST1) and Akani Obio (ST2) Hazard Quotient of Fish Samples (Ingestion)

SST	R	FS	Heptachlor	ϒ-HCH	Delta HCH	Heptaclor Epoxide	Endosulfan I	Dieldrin	Endosulfan sulfate	Hazard index
UE	C	Nile Tilapia	-	-	-	4.177	-	5.96	-	10.137
	C	Silver Catfish	-	-	-	13.385	-	0.1388	-	13.5238
	C	Upside down catfish	-	-	-	-	-	11.18	-	11.18
UE	A	Nile Tilapia	-	-	-	2.038	-	2.9	-	4.938
	A	Silver Catfish	-	-	-	6.53	-	0.0678	-	6.53678
	A	Upside down catfish	-	-	-	-	-	5.46	-	5.46
AO	C	Nile Tilapia	0.302	0.1097	-	-	0.00648	4.16	0.00402	4.5822
	C	Silver Catfish	0.1194	1.4270	-	-	0.0328	-	0.0353	1.6145
	C	Upside down catfish	0.514	0.1837	-	-	0.0027	11.46	0.00295	12.16335
AO	A	Nile Tilapia	0.1478	0.107	-	-	0.003167	2.02	0.001967	2.3087
	A	Silver Catfish	0.0582	0.6967	-	-	0.016	-	0.01717	0.78807
	A	Upside down catfish	0.252	0.0897	-	-	0.00132	5.6	0.00143	5.9445

R= Receptor, SST = Sampling Station, UE = Ufak Effiong, AO = Akani Obio, C = children, A = Adults, FS = Fish Species

The cancer risk (CR) of fish species from Ufak Effiong and Akani Obio is shown on Table 4. The total cancer risk of fish ranges from 1.5×10^{-13} to 7.8×10^{-12} with Nile tilapia having the highest total cancer risk followed by silver catfish and *Synodontis nigriventris* from Ufak Effiong. The total cancer risk of fish from Akani Obio are in the order: *Synodontis nigriventris*>*Oreochromis niloticus*>*Chrysichthys nigrodigitatus*. Despites all these values, none exceeds the cancer risk value of 1.00×10^{-5} indicating that there is no potential carcinogenic risk of fish consumption from Ufak Effiong and Akani Obio.

Table 4: Cancer risk of consuming fish from Ufak Effiong and Akani Obio

SST	FS	Heptachlor	ϒ-HCH	Delta HCH	Heptaclor Epoxide	Endosulfan I	Dieldrin	Endosulfan sulfate	Total Cancer Risk
UE	Nile Tilapia	-	-	-	5.7×10^{-12}	-	2.4×10^{-12}	-	7.8×10^{-12}
	Silver Catfish	-	-	-	1.8×10^{-12}	-	5.6×10^{-14}	-	1.9×10^{-12}
	Upside down Catfish	-		-		-	1.5×10^{-13}	-	1.5×10^{-13}
AO	Nile Tilapia	7.8×10^{-13}	-		-	-	1.7×10^{-12}	-	2.4×10^{-12}
	Silver Catfish	3.1×10^{-13}	-		-	-	-	-	3.1×10^{-13}
	Upside down catfish	1.3×10^{-12}	-		-	-	4.6×10^{-12}	-	5.9×10^{-12}

R = Receptor, SST = Sampling Station, UE = Ufak Effiong, AO = Akani obio, FS = Fish Species

CONCLUSION

This study showed that the fish samples from Akani Obio have higher levels of pesticides than those from Ufak Effiong. The levels of organochlorine pesticides in fish species obtained from Ufak Effiong and Akani Obio were below the internationally acceptable standard though there is a potential risk due to pesticide contaminants in fish from both stations. The cancer risk value from both locations of all the samples indicates that there is no potential carcinogenic risk of fish consumption from Ufak Effiong and Akani Obio.

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