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ORGANOCHLORINE PESTICIDES IN FISH MARKET

By

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ABSTRACT

Organochlorine pesticides, such as HCH (Hexachlorocyclohexane) and DDT (dichloro diphenyl tricolor ethane) and their metabolites were analysed in commercially important fishes, collected from fish (Cairo Nasr City, Obour Market, Suez Canal Area, General Market in Menoufia). In total HCH, the alpha isomer was recorded at very high level when compared with other isomers. Similarly was the dominant metabolic compound in total DDT in all the fish species. The residual concentration of the pesticides in fishes was well below the tolerance limits prescribed in this study, the levels of organochlorine (gamma-BCH, Alpha-BCH, Aldrin, o, and p'-DDE, endosulfan, dieldrin, p, p'- DDT, lindane, p, p'-DDD, o, p'-DDD and methoxychlor) pesticide residues were investigated using fish samples. Five fish species (Oreochromis Niloticus, Siluriformes, Mugil cephalus, Bagrus bajad and Alces piscis) were collected for this analysis. Fish samples of similar size were collected in order to avoid possible error due to size differences.The fish samples were labeled with unique identification number. Samples of fishes were transported to the laboratory on the same day then it were dissected to remove the flesh of each species of fish and stored pending extraction and analysis. The extractions, clean up and de-fattening of the fishes' organs were carried out using standard procedures. Endrin was the most abundant pesticide residue in the tissues of all the examined fish species. The present study revealed also that in all the examined fish samples all the pesticide residues were above the maximum residue limits (MRLs) and dietary intake (ADI) that is why it could be an important source of transferring pesticides to humans.

INTRODUCTION

Various activities such as farming, fishing, forestry, construction, mining, urban development and land pollution occurring in or near the watershed of a reservoir could bring about water quality problems and disruption in fish. Chlorinated organic pesticides are very stable in both fresh and salt water and are resistant to photo degradation .They will disappear from the water with secondary mechanisms such as, absorption on sediment, biological breakdown by

microflora and fauna, and absorption by fish through gills, skin and feeding. They are poorly hydrolyzed and slowly biodegrades in environment.Therefore, these compounds are persistent in food chains and accumulated in animal's tissues. Fish absorb those compounds directly via water or through ingesting contaminated food. In particular, organochlorine insecticides those are highly stable under different environmental conditions, persistent nature and chronic adverse effects on wildlife and humans.

Organochlorine herbicide/ pesticide pollution severely affects aquatic organisms at higher trophic levels including human beings **(Nwani *et al.,* 2010).** The effects of pesticides on fishes are of great concern **(Bagheri and Nezami, 2000 and Nwani *et al.,* 2010).** The effects of insecticides on fish are documented. Fishes are good bio-indicators of environmental pollution monitoring and can play significant roles in assessing potential risk associated with contamination in the aquatic environment. That is because they are directly exposed to chemicals resulting from agricultural production or indirectly through the food chain of an ecosystem **(Lakra and Nagpure, 2009).** Organochlorine pesticides have remained the major pollutants with numerous investigations reporting the continued and ubiquitous presence of Organochlorine pesticides in the globally **(Hung *et al.,* 2002**). Organochlorine pesticides are very stable compounds. For example, the degradation of dichlorodiphenyltrichloroethane (DDT) in soil ranges takes from four to thirty years. **(Afful *et al*., 2010).** Organochlorine pesticides have been reported also to cause human breast, liver cancer, testicular tumors moreover it lower sperm counts **(Davies and Barlow, 1995)**. Those chemicals are liposoluble compounds and are capable of bioaccumulating in fatty parts of the organs such as breast milk, blood and fatty tissues **(William *et al.,* 2008)**. Since the pesticides are lipophilic in nature, their cumulative accumulation at low concentrations in the fat tissues of mammal might pose potential hazards in the long run **(Metcaff,1997)**. India is a tropical country where persistent pesticides like HCH and DDT are used for control of pests in agriculture and public health importance. Moreover, India is the largest producer and consumer of pesticides in south Asia and a pesticide use has increased in the last three decades. The consumption of pesticides in India has moved from 2000 metric tons / year in the fifties to over 80,000 metric tons in recent years **(Karunagaran *et al.,* 1994)**. The human being in most developing countries is known to carry heavy burdens of pesticide residues. Fish are group of great importance for man as a major source of protein and vitamins. On the other hand, fish act as a main route for the accumulation of such toxic chemicals from pesticides to human bodies.

Industrial wastes are considered a serious pollutant of the aquatic environment. Pesticides have toxic effect in exposed organism. However, the presence of pesticides beyond permissible limits in water bodies has been reported worldwide. The present study focuses on the toxic effects of pesticides on fish. Most of seas are seriously polluted with industrial effluents. All the chemicals of industrial waste are toxic to animal and many cases of death or sub-lethal pathology of liver, kidney, reproductive system, nervous system of fishes has been reported. Pesticides are pollutants that affect seriously the aquatic fish. The presence of pesticides show alternation of behaviour, bioaccumulation of pesticides in the body of fish histopathological and biochemical alternations. **(Mukesh Kumar Napit, 2012).** The present investigation was carried out in order to know the concentration and distribution of these contaminants in fishes of various kinds (Planktonivorous and Carnivorous) from Mumbai coastal region. Mumbai is the Manchester of India, highly industrialized and densely populated metropolitan city. The vast development of industries, harbour activities and urbanization are the main sources for the different kinds of pollutants to the Mumbai coastal environment.

Therefore, the present work was conducted to study:

1- The most prevalent Organochlorine pesticides in fish market.

2-The effect of Pesticides on fish morphology through organoleptic examination.

3-The public health significance of the detected pesticides**.**

MATERIAL AND METHODS

Samples Collection:

Fish samples (Tilabia, Catfish, Mugil, Bayed and Moose) were collected from different markets. Fish samples of uniform size were collected to avoid the possible error due to size differences.The fish samples were labeled with an identification number.Samples of fish were transported to the laboratory on the same day, identified by an expert in the department of Fisheries then dissected to remove the flesh, liver, stomach and gills of each species of fish and stored.

Extraction of pesticides from fish samples:

The fish samples (20 g) were weighed into a conical flask 150 ml followed by the addition of 20 g and 5 g of anhydrous sodium sulfate and sodium hydrogen carbonate, respectively. Hundred ml of 1:1 (v/v) ethyl acetate/dichloromethane mixture were transferred into the 20 g

fish samples and thoroughly mixed by shaking the conical flask while corked. Then twenty grams of anhydrous sodium sulfate were then added to the content of the conical flask followed by 20 g of sodium hydrogen carbonate. Then the conical flask was corked tightly and shacked thoroughly for ten minutes. The contents were allowed to stand for three hours. The organic layer was decanted into a 200 mL round bottom flask then evaporated using the rotary evaporator at 40°C. The pesticide in the rotary flask was dissolved and collected with two mL of ethyl acetate then transferred into a two mL vial and ready for the cleanup.

Determination of pesticide residues by analytical estimation (Gas Chromatography):

The Shimadzu SHIMA DZU GC/MS (GC - 17A), equipped with fluorescence detector were used for the chromatographic separation and were achieve by using a 35% diphenyl/65percentage dimethyl polysiloxane column. The oven were programmed as follows: initial temperature 40°C, 1.5 min, to 150°C, 15.0 min, 5°C/min to 200°C, 7.5 min, 25°C/min to 290°C with a final hold time of 12 min and a constant column flow rate of 1 ml/min. The detection of pesticides were perform using the GC-ion trap MS with optional MSn mode. The scanning mode offer enhances selectivity over either full scan or selected ion monitoring (SIM). In SIM at the elution time of each pesticide, the ration of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decrease the accuracy at lower levels. The GC-ion trap MS were operate in MSn mode and perform tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the sample were compared with those of the standards for quantization.

Data handling:

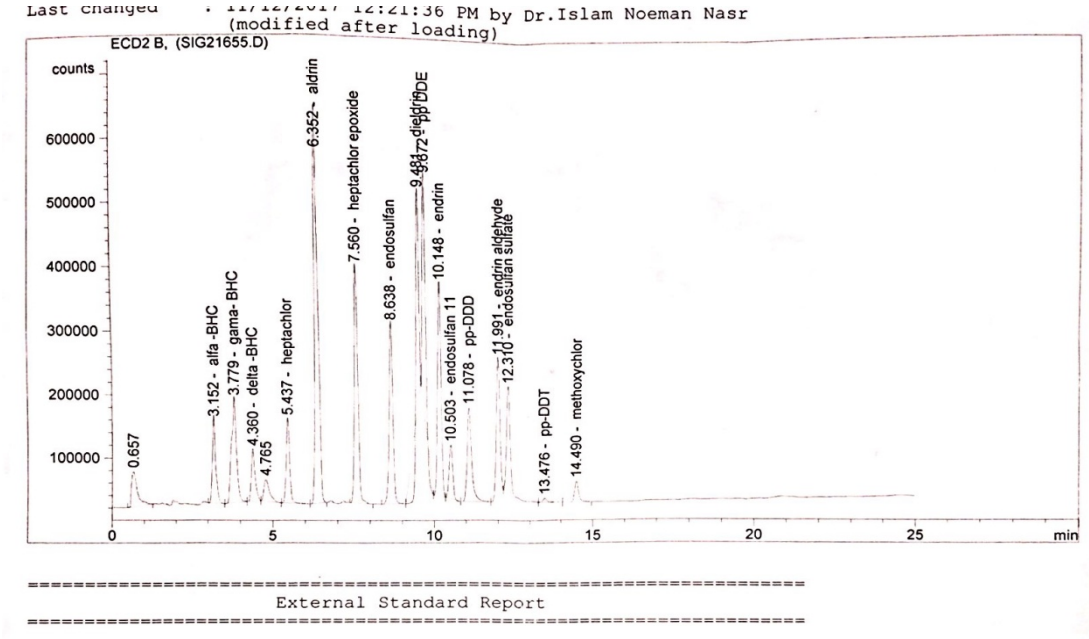
Data collected were subjected to one-way analysis of variance (ANOVA) were used to assess whether pesticide residues varied significantly between fish and tissues samples, possibilities less than 0.05 (p0.05) were considered statistically significant. All stastistical calculations were performed with SPSS 9.0 for windows.

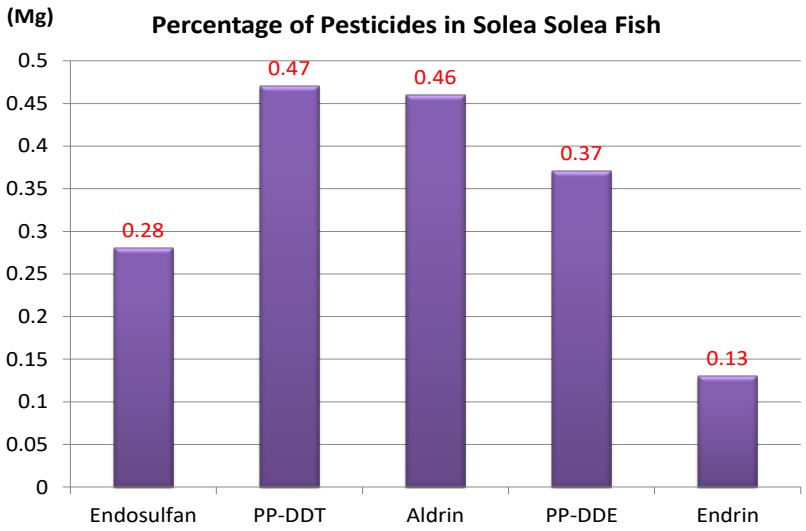
The concentration of measured pesticides was calculated according to the following equation: Concentration (C) of a certain pesticides in ng/g wet weight (ppb).

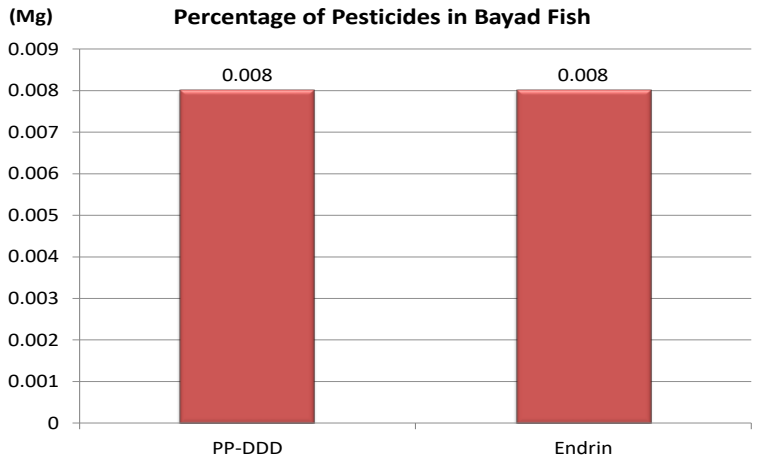
$$C = \frac{\text{peak area of (sample) X dilution (2 ml) X standard conc. (ng)}}{\text{Peak area of (standard) X injection volume (1µl) X sample weight}}$$

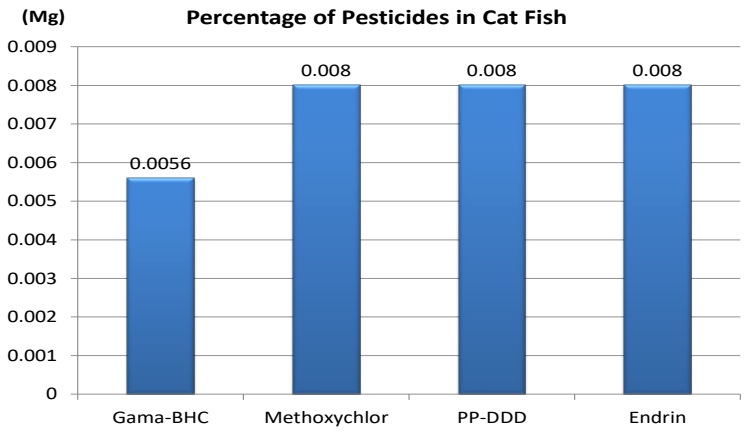
RESULTS AND DISCUSSION

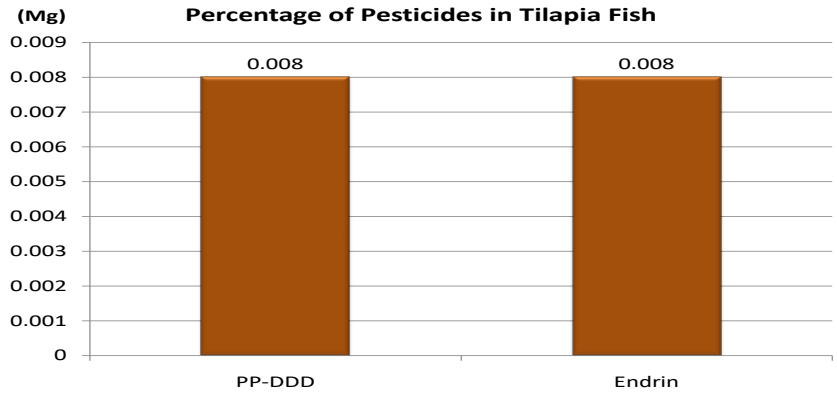
Fish are used extensively for environmental monitoring because they take contaminants directly from water and diet **(Lanfranchi *et al.,* 2006).** Generally, the ability of fish to metabolize organochlorines is moderate; therefore, contaminant loading in fish is reflective of the state of pollution in the surrounding environment **(Guo *et al.,* 2008)**. Organochlorine pesticides have become ubiquitous contaminants and implicated in a broad range of deleterious health effects in laboratory animals and man. The toxic effect includes reproductive failures and effect on human beings Immune system malfunction, endocrine disruption and breast cancers. **(Garabrant *et al.,* 1992; Kolpin *et al.,* 1998; Bouman, 2004; Ize *et al.,* 2007; Adeyemi and Ukpo, 2008)**. Many of these Organochlorine pesticides and their metabolites have also been implicated in a wide range of adverse human and environmentaleffects including reproduction andbirth defects **(Edwards,1987)**. Theconcentrations (ng.g-1) of total HCH and total DDT and their percentage compositions ,marine fishes from the Mumbai coast had relatively low levels of total DDT compared to the values reported by 0.86, -140 ng.g-1 **(Kannan *et al.,* 1992)**. In fishes from fish markets of some other metropolitan cities of India by **(Burns *et al.,* 1982)** in fishes from Oman coast the range was (15,-3200 ng.g-1). Of the 10 fish, samples of the present study the highest value of (19.1 and 58.30 ng.g-1) was recorded in the carnivorous fish Chirocentrus dorab for HCH and DDT respectively.

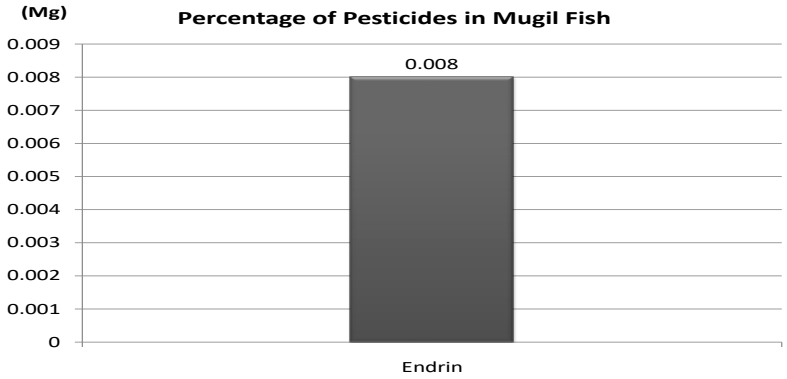



(Mg)
Percentage of Pesticides in Solea Solea Fish
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0.28
0.47
0.46
0.37
0.13
Endosulfan
PP-DDT
Aldrin
PP-DDE
Endrin


(Mg)
Percentage of Pesticides in Bayad Fish
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.008
0.008
PP-DDD
Endrin


(Mg)
Percentage of Pesticides in Cat Fish
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.0056
0.008
0.008
0.008
Gama-BHC
Methoxychlor
PP-DDD
Endrin





CONCLUSION

Pesticides have been recognized as serious pollution of aquatic environment. It affects fish directly through accumulation in their bodies. They also cause serious impairment in metabolic, physiological and structural systems. The accumulation of pesticides in the tissues of a fish can result in chronic illness and cause potential damage of population. Fish are able to accumulate and retain pesticides and other pollutants from their environment.

Accumulation of pesticides in the tissue of fish is dependent upon exposure concentration as well as other factors such as salinity, temperature, hardness and metabolism of fish.

Pesticides effect on specific vital organs such as liver, gill and kidney. Different degree of pesticides accumulation in various tissues depends upon the biochemical characteristic of pesticides. Fish may accumulate pesticides by absorption through gills, has been observed the concentration of pesticides in gill reflect the concentration of pesticides in water in which fish species live. The levels of most of the residues in fish were higher than those were found in

water. The presence of contaminants, which are usually carcinogenic in nature, in fish of the west coast may pose serious health hazards to the local population. Because I did very little work has been carried out in the Dadar fish market at Mumbai west coast of India. More detailed investigations, in terms of sampling network and sampling frequencies are required in view of increasing global concern for persistent organic pollutants and their hazardous impact on environmental and human health.

REFERENCES

Afful, S., A.K., Anim. and Serfor-Armah, Y. (2010): Spectrum of organochlorine pesticide residues in fish samples from the Densu Basin, J. Environ. Earth Sci., 2 (3): 133 - 138.

Adeyemi, D.,Ukpo,G., Anyakora, C. and Unyimandu,J. (2008): Organochlorine pesticides residues in fish samples from Lagos Lagoon, Nigeria. Am. J. Environ. Sci., 4: 649-653.

Bagheri, A. and Nezami, A. (2000): Effect of weed control and plant densities on yield and morphological characteristics of chickpea in dry farming of north khorasan. J. Agric. Sci. Ind. Iran., 14.

Bouman, H. (2004): South Africa and the Stockholm on persistent organic pollutants. Afr. J. Sci., 100: 323 - 328.

Burns, K.A., Villenevue, J.P., Aderlin, U.S. and Fowler, S.W. (1982): Survey of farm hydrocarbon and metal pollution in the coastal waters of Oman. Mar. Pollut. Bull., 13: 240-247.

Davies, D.L. and Barlow, H.L. (1995): Can environmental estrogens cause breast cancer Sci. Am., 144-147.

Edwards, C.A. (1987): The environmental impact of pesticides. Parasitis, 86: 309-329.

Garabrant, D.H., Held, J. Langholz, B., Peter, J.M. and Mark, T.M. (1992): DDT and related compounds and risk of pancreatic cancer, J. Natl. Cancer Inst., 84: 764 -771.

Guo, Y., Meng, X.Z., Tang, H.L. and Zeng, E.Y. (2008): Tissue distribution of organochlorine pesticides in fish collected from the Pearl River delta, China: Implications for fishery input source and bioaccumulation. Environ. Pollut, 155: 150-156.

Hung, H., Halsall, C.J.,Blanchard,P., Li H.H., Fellin, P. and Stern, G. (2002): Temporal trends of organochlorine pesticides in the Canadian Arctic Atmosphere. Environ. Sci. Technol., 36: 862-868.

Karunagaran,V.M.,Babu, S.,Babu Rajendran, R. and Subramanian, A.N. (1994): Organochlorine insecticide (HCH and p, p' - DDE) residues in fishes from Kanyakumari (80 04'N; 700 36'E). Indian J. Mar. Sci., 23: 182-183.

Kannan, K., Tanabe,S., Ramesh, A., Subramanian, A.N. and Tatsukawa, R. (1992): Persistent organochlorine residues in foodstuffs from India and their implications on human dietary exposure. J. Agri. Food. Chem., 40, 518-524.

Lakra, W.S, Nagpure,N.S. (2009): Genotoxicological studies in fishes: A review. Indian. J. Anim. Sci., 79: 93-98.

Lanfranchi, A.L., Miglioranza, M.L., Menone, K.S.B., Janiot, L.J., Aizpun, J.E. and Moreno, V.J. (2006): Striped weakfish (Cynoscion guatucupa): a bio monitor of organochlorine pesticides in estuarine and near-coastal zones. Mar. Pollut. Bull., 52: 74-80.

Mukesh Kumar, N. (2012): A review: the effect of pesticides on fish fauna of Bhopal upper lake (Madhya Pradesh), India. Biol. Forum Int. J., 4 (2):19 -21.

Nwani, C.D., W.S. Lakra, N.S. Nagpure, R. Kumar, B. Kushwaha and S.K. Srivastava (2010): Mutagenic and genotoxic effects of carbosulfan in freshwater fish *Channa punctatus* (Bloch) using micronucleus assay and alkaline single-cell gel electrophoresis. Food Chem. Toxicol., 48: 202-208.

William, J.,Tagoe, L., Drechsel, P.,Kelderman, P.,Gijzen, H. and Nyarko,E.(2008): Accumulation of persistence organochlorine contaminants in milk and serum of farmers from Ghana. Envrion, Res., 106: 17-26.