

## Pesticide Residues in Food Available for Human Consumption

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**Summary:** Organochlorine pesticides (DDT, DDE, Heptachlor, Aldrin, Dieldrin and BHC were detected in different food commodities like milk, fish, and vegetables supplied by water and sewerage board Karachi. Besides, few sample of shell fishes (shrimp, oyster and mussels) along with vegetables were purchased from market. The most interesting findings were the presence of DDT in milk. In vegetable, milk and fish concentration of DDT was higher than other pesticides reflecting its accelerated use. General concentration of each chlorinated pesticide in above mentioned food except fish, was DDT 1.02- 3.38, DDE 0.01-0.80, Heptachlor 0.53-2.35, Dieldrin 1.20 – 3.56 and alpha BHC traces – 1.52 ng/g.

The present study indicates that most of the food commodities sold in Karachi are not free from organochlorinated pesticide residues.

### Introduction

There has been tremendous use of chemicals in the industry and in agriculture during the last 50 years. The group that is extensively used is the chlorinated hydrocarbons and their derivatives like DDT & PCBs.

It is well documented that these chlorinated hydrocarbons and their metabolites are persistent pollutants and produce residual effects in the environment [1]. These pollutant get access to living biota via different routes. Accumulations of pesticides in living organisms cause adverse physiological effects, which has been observed by a number of scientists [5]. In marine environment, organochlorine pesticides influence hatching and settling mechanism of oyster larvae [2]. Similarly low levels of DDT effect the breeding process in birds [3]. Studies also have shown a number of health hazards in humans due to exposure of pesticide in environment. These hazards cause various diseases like impaired fertility, male reproductive disorders, hypertension, hyperlipidemia and hemorrhage cystitis etc [4]. Due to the harmful effects of DDT most of the developed countries have restricted or imposed a ban on the use of DDT. However, in the developing countries like Pakistan DDT is still extensively used in agriculture and for the eradication of insect born diseases like malaria [6] Karachi is a coastal city with a thick population having a large number of industries and agriculture land in the adjoining area. Extensive use of these chemicals in the industry and

in the fields has resulted in discharge of toxic waste in the environment including pesticides like chlorinated hydrocarbons, which is continuously polluting the environment and thus contaminating good stuff. It has been found that these chemicals leave residues, which are hazardous for human health [12]. Thus studies were carried out to analyze a group of pesticides (chlorinated hydrocarbons) and their residues in foodstuff like fish, milk and vegetables.

### Results and discussions

Chlorinated hydrocarbon residues detected in milk and vegetables and fish & shellfish are summarized in table 1&2 respectively. The results show a wide spread pollution of DDT and Heptachlor. The range being traces-60.37 ng/g for DDT & its metabolites like DDE traces-20.25 and traces-36.37 ng/g for heptachlor in fish and shell fish (table-2). These values are lower than to those reported earlier in mussels [8]. It can be observed that DDE concentration has a range of 0.35-0.80 ng/g in

(Table-1) Chlorinated Hydrocarbons in a variety of samples supplied by Water & Sewerage Board, Karachi. (Collected from Korangi Creak Area)

S. No	Sample	Chlorinated Hydrocarbons ng/g				
		DDT	DDE	Heptachlor	Dieldrin	$\alpha$ BHC
1.	Lucin	3.38	0.80	2.35	3.56	1.52
2.	Tomato	2.92	0.52	1.25	3.02	Traces
3.	Brinjal	1.87	0.35	0.98	2.37	1.25
4.	Milk	1.02	0.01	0.53	1.20	Traces

Table-2: Chlorinated Hydrocarbons found in tissues of some edible fish, shell fish and molluscs along Karachi Coast.

S.No	Location	Organization	Chlorinated Hydrocarbons (ng/g)				
			$\alpha$ -BHC	Aldrin	Heptachlor	DDT	DDE
1.	Korangi Creek	Oyster ( <i>C. revularis</i> )	Traces	ND	ND	24.50	20.25
		Fish (Mushka) Otolithis rubber)	15.30	26.20	36.37	60.37	1.87
2.	Monora Channel	Mullet ( <i>Liza SPP.</i> )	ND	ND	ND	ND	0-.80
3.	Cap. Monze	Sardines ( <i>Sardinella SSP.</i> )	0.0-12.26	Traces	Traces	ND	Trace
4.	Bhulaji	White Pomfret	23.24	ND	7.5	ND	ND
5.	Hawksbay	Shimp ( <i>P. monodon</i> )	Trace	23.56	-	Traces	ND
6.	Paradise Point	Mussel ( <i>P. viridis</i> )	ND	41.25-65.24	3.1-18.2	Trace	0-15.20

all samples except milk, which had more value, 0.01 ng/ml. The concentration of metabolites is not much higher than that found of DDT concentration in samples. The concentration of dieldrin is much higher than that of  $\alpha$ -BHC while the concentration of heptachlor in all samples is very similar to each other. High concentration of heptachlor was found in fish samples. The level of DDT & its metabolites found in fish & shellfish were on average much higher than milk samples table 1. Level of dieldrin has so far been relatively high in green vegetables as compared to milk samples. In vegetables variations in the concentration of pesticides was observed as compared to milk and fish. This difference may be due to type of sample, accumulation capacity and particle size [9].

The presence of pesticide residues in fish samples reflects marine pollution at Karachi. This may be due to vast quantities of industrial effluents, which are continuously being thrown in seawater. This is the reason more recently responsible legislative authorities have registered great apprehension and concern on pesticide pollution. The variation in concentration of pesticides in different samples particularly seafood is influenced by age and fat contents [10,11].

In the DDT family the concentration of the parent compound (p,p DDT) was considerably higher than their metabolites. The quantity varies with the type of products and area of sampling. Samples collected from coastal areas can receive appreciable amounts through oceanic waters.

Contamination of milk with these pesticides may be attributed to extensive spraying of these pesticides on crops and vegetables. Since the remains of these crops and fodder like lucin is widely used as

a food for ruminants and thus might become a route for secondary exposure to milk.

Organochlorine pesticide still contribute to the problem of human exposure. These pesticides are persistent and banned all over the world, but in Pakistan is still in used. Being cheaper these products some how found their way in the agricultural market thus creating a serious environmental problem. The food safety and inspection service (FSIS) 1990 annual residue plan(1) a residue monitoring programme for all domestic and imported animal food in the united states includes many of the chlorinated hydrocarbons pesticides currently and previously used in agriculture. These pesticides are of concern, because they persist in the environment and in animal tissue (2) and their significance to human health is not known [12].

Finally it is concluded in general, therefore a need to create awareness amongst the farming community to use pesticides prudently and in accordance with good and healthy food for our nation.

### Experimental

Samples of milk, fish and fin-fish, vegetables (Brinjals, Tomatoes, lucin) were supplied by water and sewerage board of Karachi. Different varieties of fish (*Mugil spp*, *Acanthopagarus*), oyster, shrimps & mussels were also collected from Karachi coast. Standard methods of AOAC were adopted for the preparation and determination of organochlorine pesticides.

#### Preparation of sample and fat from vegetables

Preparation of sample and fat from vegetables was according to AOAC 1984. Ref.29.012a. 100 gm

of washed and chopped vegetables were blended with 200ml CH<sub>3</sub>CN and 10gm Celite for 2 minutes at a high speed. The blended material was filtered through 12cm buchner funnel into 500 suction flask. The filtrate was transferred into a separator. 100 ml petroleum ether was poured in the separator and shaken for 2 minutes. To the solution 10ml saturated NaCl and 600 ml H<sub>2</sub>O was added, mixed and allowed to separate. The solvent layer was washed with water and transferred into an evaporator dish to obtain fat.

(ii) *Preparation of sample & fat extraction from milk*

Extraction of fat from milk was performed according to AOAC 1984 ref.29.012(c). 100 ml milk was mixed with 100 ml alcohol and 1gm Na or K Oxalate. 100 ml petroleum ether was added to the mixture, shaken for 2 minute, and centrifuged for 5 minutes at 15000rpm. The aqueous residue was extracted twice with petroleum ether and the solvent was blown into separator. Water was drained and discarded.

iii) *Preparation and fat extraction from animal tissue. (fish, shrimp oyster).*

This was done according to the AOAC 1984, ref.29.012(c) 50 gm of fish was blended with 100 gm anhydrous Na<sub>2</sub>SO<sub>4</sub>. 150 ml of petroleum ether was added and again blended for 2 minutes. Supernatant pet. ether was decanted using a buchner filled with shark skin into a 500 ml suction flask. The residue was reextracted twice in the blender jar with 100 ml petroleum ether. The ether layer from repeated blendings was decanted and combined with first extract.

iv). *Chemical analyses of Chlorinated Hydrocarbons of Prepared samples.*

*Column and Gas Chromatography of Prepared Samples.*

Chlorinated hydrocarbons trapped on Alumina Al<sub>2</sub>O<sub>3</sub> & Silica (Si<sub>2</sub>O<sub>3</sub>) resin were eluted with 150ml volume of hexane and then concentrated to 10ml. The

concentrated hexane was cleaned up by shaking with 5% fuming H<sub>2</sub>SO<sub>4</sub>. For the determination of chlorinated hydrocarbons, final hexane extract was further concentrated to 100 ml with micro concentration under blowing of purified nitrogen [5]. The determination of chlorinated hydrocarbons was performed on a gas chromatography equipped with electron capture detector (Shimadzu GC-9A). The column was 2 mm id/5m long and packed with purified 2% QF1+15% OV on 180-00 mesh chromosorb (WASHMDS). Acid washed chromosorb [6,7].

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