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DDT residue and its metabolites in dried fishes of Dhaka city markets

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Abstract

A qualitative and quantitative study was carried out on DDT residue and its metabolites in commercially produced sun dried fresh water fish species of Dhaka city markets. Soxhlet method for extraction, Forisil Column Chromatographic method for clean-up and Gas Chromatograph with Electron Captured Detector (GC-ECD) for analysis were used in the present study. The results are alarming indicating that all the samples tested were found to be contaminated with DDT (Dichloro Diphenyl Trichloroethane) residue and its metabolites DDE (Dichlorodiphenylethane) and DDD (DichloroDiphenyl Dichloroethance). The concentration of total DDT in these fish samples ranged from 93.84 to11880.5 µg kg^{-1}. The concentration of total DDT in all the fish samples were within the permissible MRL level recommended by FAO/ IAEA/ WHO, except only one sample. As DDT is a long persistent and bioaccumulative substance in the environment, intake of significant amount of this slow poison with our diet is a matter of health concern.

Key words: Pesticides, organochlorine, DDT, DDD, DDE, GC-ECD, dried fish

Introduction

Fisheries and aquatic resources are economically, ecologically, culturally and aesthetically important to the nation. At present there are 260 freshwater fish species, 12 species of exotic fish, 475 species of marine fish and 60 species of prawn and shrimp available in Bangladesh (Chandra, 2006). In Bangladesh, fish is considered as one of the cheapest source of protein, fat and other nutrients and about 80% of the daily-required animal protein comes from fish source (Karim, 1987) of which a remarkable part comes from dried fishes. Fisheries sector contributes to GDP 5.24%, animal protein supply 63% and foreign exchange earning 4.76% for the nation (Chandra, 2006).

Being riverside country and the existence of the Bay of Bengal at the south of Bangladesh, it has a good natural production of fish. Distribution of these fishes to the consumers or at least to the fish markets is always troublesome due to communication problem. So the fishermen have to process all the excess fish with sun drying, the traditional and low cost procedure (Islam, 1999). The dry fish is properly known as “SHUTKI” (in Bangla). For long conservation of fish by drying is common practice in Bangladesh. This practice is usually made in the remote coastal isolated islands and in inland depressions where chilling and freezing facilities are lacking. The finally dried fish products are generally stored in a dump warehouse nearby coastal towns. In addition to this, the weather is humid particularly during the monsoon period and the dry fishes absorbed moisture rapidly that the fish becomes suitable for infestation by beetles and mites. Most unexpected causes of infestation are that the fishermen do not dry fishes properly due to loss of weight i.e., the fishermen want more profit selling the dry fishes in weight. For protection of dry fish from infestation they use a mixture of organochlorine (DDT and heptachlor) insecticides (Bhuiyan *et al.*, 2008). Some analyses in Bangladesh show alarming pollutants in fish like DDT and heptachlor (BCAS, 1990). In Kuakata (a fish processing zone in Bangladesh), high level of DDT powder (locally known as white powder) is used though Bangladesh banned the 'dirty dozen' in 1997 (Barua, 2007) and there is no statistical figure about these organochlorine insecticides in Bangladesh (UNEP, 2002).

Insecticides are health hazard both for users and consumers. In many countries of the world like Bangladesh, a great deal of indiscriminate and dangerous usage of insecticides because of the absence of clear recommendations for control of insects and lacks of training in the nature and correct uses of insecticides. There are many insecticides sold in the markets without names and insecticides are not true to the label (Bhuiyan *et al.*, 2008).

The present work was undertaken to find out the present status of DDT and its metabolites as well as to

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determine their residue level in dry fish procured from different markets of Dhaka, Bangladesh.

Materials and methods

Chemical Reagents

DDT, DDE, and DDD standards were purchased from Polyscience, Germany. Organic solvents (hexane, dichloromethane, acetone, ethyl alcohol and ethyl acetate) of analytical grade, Anhydrous sodium sulfate (Na_2SO_4), Aluminum oxide (Al_2O_3), Nitric acid (HNO_3), Silver nitrate ($AgNO_3$), Florisil (60-100 mesh size) and Silica gel.

Equipment

Sample Collection and Storage

The five big wholesale and retail markets chosen to collect dried fish samples in Dhaka City markets are Kawran bazar, New market, Kaptan bazar, Sham bazar, and Shah Ali bazar of Mirpur. Samples were collected in airtight polythene bag with tagging each sample and were brought to the Laboratory as early as possible and preserved at -20 ^{0}C (Amin Uddin *et al.*, 2007).

Sample preparations

Hundred grams dried fish sample was taken from storage and kept at the room temperature for thawing. Then, the samples were sliced, ground, sieved and prepared for extraction and clean up. Ten gram of each samples were then taken into mortar and pastel with 2-5 g of anhydrous sodium sulfate (Na_2SO_4). Then it took few minutes for equilibration and the samples became moisture free.

Extraction

A modification of Hans and Zeumer (1987) was used. The equilibrated samples taken into previously rinsed (by acetone and dichloromethane) thimble was placed into the siphoning part of the soxhlet with 250 mL of dichloromethane (DCM). Extraction was continued up to 10-12 cycles of siphoning. Concentrated just to dryness the extract solution by rotary vacuum evaporator up to volume 1-2 mL.

Clean-up

Florisil column chromatography was applied for the clean up of the extract (DFG Manual, 1987, Moasts, 1963). The top 1.5 cm of the florisil column was packed with anhydrous sodium sulphate. Elution was done by 2% diethyl ether in hexane (5 mL min^{-1}). Elute was concentrated on a rotary vacuum evaporator and transferred quantitatively to a glass-stopper test tube. Solvents were completely evaporated under mild flow of pure N_2. The evaporated sample was dissolved in double distilled hexane and made up to volume of 5 ml in a volumetric flask and used for the analysis.

Analysis

After cleaningup all the samples, sample volume was made as per required by adding double distilled hexane and was injected (1 µL) into the column of Gas Chromatography (PU- 4500, Phillips, Germany). The analysis was made in the following GC Conditions (ECD Mode) Table 1:

Table 1: Details of gas chromatographic conditions

Parameter	Condition
Column	*Packed Column* (1.6m length, 1.5 mm i.d., packed with 1.5% OV-17 +1.95% QF1 on 100-120-mesh chromosorb WHP and 3% OV-17 on 100-120-mesh chromosorb WHP
Oven temperature	200 ºC
Injector temperature	210 ºC
Detector temperature	255 ºC
Gas flow rate	Nitrogen as carrier, 25mL min^{-1}
Injection volume	1 µL

An aliquot was injected into the GC with a micro syringe. Tentative identification of the suspected insecticide was carried out in relation to retention times of the pure analytical standard(s): mixture of DDT, DDE and DDD (Poly Science, Germany). Quantification was made using a freshly drawn standard curve of DDT, DDE and DDD (Amin Uddin et al., 2007).

Results

Fifty samples of ten different fish species were analyzed to detect and determine the concentration of DDT and its metabolites in the dry fish and to elucidate their contamination level. Table 2 represents the concentration of pesticide residues (i.e., DDE, DDD & DDT) in the dried fish samples of Dhaka city markets. All the fish species tested were found contaminated with DDT residue and its metabolites DDE and DDD. The presence of total DDT in the *Laeo gonius* exceeded the FAO/ IAEA/ WHO recommended Maximum Residue Limit (MRL) level, but all the other samples remained below the MRL level. Figure 1 shows the relation between fat content and pesticide content, and DDT concentration in fat is more than that found in tissue. Table 3 represents the fat content of dry fish and it is found that different fish contained different concentrations of fat.

Figure 2 indicates the relation of moisture content with fat of dry fish samples. In dry fishes percent of moisture ranged from 187-303, 413-471, 389-522, 157-180, 163-238, 130-165, 113-262, 175-230, 103-267 and 181-254 g kg^{-1}, respectively, (Table 4).

Table 2. DDT and its metabolites in fresh water dry fishes of Dhaka city markets

Local name	Scientific name	DDT and its metabolites (µg kg^{-1})			
		DDE	DDD	DDT	∑DDT
Dry Puti	*Puntius sophore*	70.66	53.51	63.24	187.41
Chepa Sutki	*Puntius sophore*	82.43	82.47	78.11	243.01
Nona Illish	*Hilsa ilisha*	16.59	42.17	35.08	93.84
Baro Chingri	*Macrobrachium rosenbergii*	77.76	37.45	68.27	183.48
Gura Chingri	*Leander styliferus*	171.75	70.09	90.54	332.38
Kaski	*Corica soborna*	357.80	185.42	265.46	808.68
Chapila	*Gudusia chapra*	221.34	169.17	275.21	665.72
Shoal	*Channa striatus*	63.31	38.09	75.83	177.23
Deshi Chanda	*Chanda ranga*	105.35	87.67	361.76	554.78
Ghonia	*Labeo gonius*	1547.58	2364.66	7968.26	11880.5

Each data represents mean of 5 replications; FAO/ IAEA/ WHO recommended dose of DDT and its metabolites is 1000 MRL

Table 3: Fat content in fresh water dry fishes of Dhaka city markets

Local name	Scientific name	Fat weight (g kg^{-1})	Fat %	Fat range (g kg^{-1})
Dry Puti	*Puntius sophore*	153.70	15.37	96-230.3
Chepa Sutki	*Puntius sophore*	147.16	14.72	58.7-249.5
Nona Illish	*Hilsa ilisha*	161.48	16.15	58.2-327.5
Baro Chingri	*Macrobrachium rosenbergii*	113.88	11.39	78.9-182.1
Gura Chingri	*Leander styliferus*	119.50	11.95	47.7-202.3
Kaski	*Corica soborna*	179.22	17.92	119.9-321.9
Chapila	*Gudusia chapra*	211.28	21.13	130.5-417.1
Shoal	*Channa striatus*	47.32	4.73	11.5-87.3
Deshi Chanda	*Chanda ranga*	221.22	22.12	178-304.2
Ghonia	*Labeo gonius*	100.78	10.08	29.5-183.6

Each data represents mean of 5 replications;

Table 4. Moisture in fresh water dry fishes of Dhaka city markets

Local name	Scientific name	Moisture weight (g kg^{-1})	% Moisture	Moisture range (g kg^{-1})
Dry Puti	*Puntius sophore*	254.60	25.46	187-303
Chepa Sutki	*Puntius sophore*	442.20	44.22	413-471
Nona Illish	*Hilsa ilisha*	476.00	47.60	389-522
Baro Chingri	*Macrobrachium rosenbergii*	169.20	16.92	157-180
Gura Chingri	*Leander styliferus*	197.40	19.74	163-238
Kaski	*Corica soborna*	149.60	14.96	130-165
Chapila	*Gudusia chapra*	188.60	18.86	113-262
Shoal	*Channa striatus*	218.60	21.86	175-230
Deshi Chanda	*Chanda ranga*	174.60	17.46	103-267
Ghonia	*Labeo gonius*	226.60	22.66	181-254

Each data represents mean of 5 replications

Discussion

For protection of dry fish from infestation, the fishermen use insecticides whatever they are getting within their reach. Among the insecticides, DDT is a commercial organochlorine insecticide that has been widely used on agricultural crops as well as for vector control (ATSDR, 1995). These insecticides are health hazard both for users

and consumers. In many countries of the world like Bangladesh, a great deal of indiscriminate and dangerous usage of insecticides because of the absence of clear recommendations for control of insects and lacks of training in the nature and correct uses of insecticides. Nobody can draw a statistic on insecticide causalities, although newspapers reports on deaths and sufferings or chronic effects are common in Bangladesh.

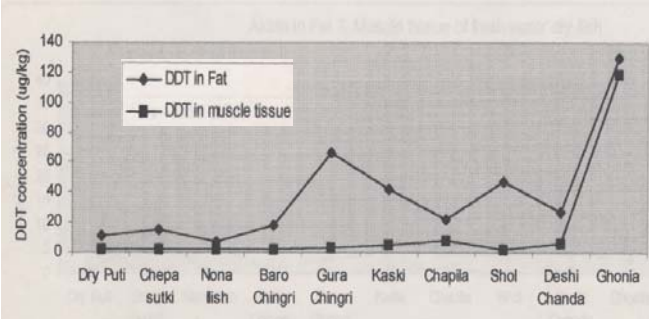


Figure 1: DDT in Fat & Muscle tissue of dry fish

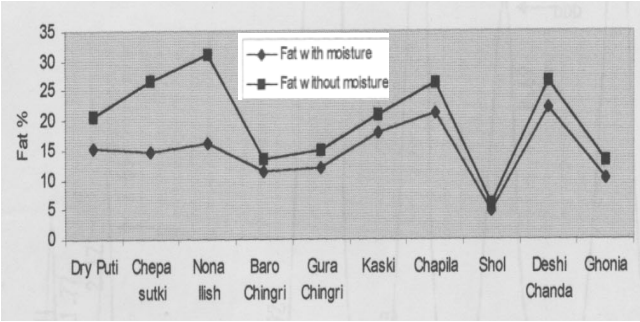


Figure 2: Fat in dry fishes in related with moisture

Though a few studies of DDT and its metabolites in the dry fish of Bangladesh have been carried out and some analyses in Bangladesh show alarming pollutants in fish like DDT and heptachlor (BCAS, 1990), there should run an extensive study to provide sufficient data on this issues The present study have been undertaken to provide the preliminary information on the concentration of DDT and its metabolites in the dry fish and to elucidate their contamination level. The results obtained are alarming. All the fish species tasted were found contaminated with DDT residue and its metabolites DDE and DDD. The presence of total DDT in the *Laeo gonius* exceeded the FAO/IAEA/WHO recommended MRL level, but all the other samples remained below the MRL level. Almost, similar findings were reported earlier (Amin Uddin *et al.,* 2007). The level of concentration of DDT in dry fish is a great concern but more concern is such a dangerous poison is still using in our some popular food items such as dry fish though it is banned in our country. DDT is a slow poisoning substance. It can transfer from generation to generation through breast milk (Solomon and Weiss, 2001).

Pesticides in dry fish as studied may be attributed to (i) accumulation from environment of the respective fish or/and (ii) due to use of pesticide while processing or stocking. DDT and its by-products can persist in soil and sediments for more than 15 years and are known to bioaccumulate in animal tissues. DDT had been banned for all uses in 49 countries and restricted to vector control in 23 (PANNA, 1995). The half-life of DDT in humans is approximately 4 years (Noren and Meironyte, 2000).

The most significant properties of the organochlorine insecticides are their extreme lipophilic nature and resistance to biodegradation, which results in their accumulation and concentration in fatty tissues and their extreme persistence in environment (Taqnnenbaum, 1979). In our study, an interesting relation has been found between fat content and pesticide content. DDT concentration in fat is more than that found in tissue of other parts of fish. It may be due to its lipophilic character. DDT is well soluble in fat. Fat acts as a storage depot of organic toxic compounds including DDT. Since DDT is toxic compound and it may cause many diseases or physical disorder (Doull *et al.,* 1975). Moisture content in most fish samples is also different. This variation of moisture content in dry fishes may be due to variation of processing, weather conditions, stocking condition etc. In fact, variation in moisture content in fish makes variation in fat and pesticide content i.e., variation of results.

Conclusions

Dried fish samples from Dhaka markets were found to be contaminated with different concentrations of DDT residues indicating unrestricted and unplanned use of DDT for controlling infestation during processing and storage. Data regarding pesticide residue levels, acceptable daily intake (ADI), maximum residue limits (MRLs) should be generated to make a massive awareness among people about health hazards concern. The government of Bangladesh should take all the necessary steps to combat the situation; it can be the steps to implement the legislation and improving the awareness of the related people through some program, public education campaigns and announcement of harmful role of these insecticides and make difficult the availability of these insecticides in market either its true pack or false pack.

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