

## SCREENING OF ORGANOCHLORINE INSECTICIDES (DDT AND HEPTACHLOR) IN DRY FISH COLLECTED FROM THE PROCESSING ZONE OF BANGLADESH

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### ABSTRACT

The concentrations of organochlorine insecticides DDT and Heptachlor were investigated to estimate the current status of insecticides used in dry fish during July 2007 to June 2008. The most popular dry fish; Bombay duck (*Loittya*), Ribbon fish (*Chhuri*), Chinese pomfret (*Rupchanda*) and Indian salmon (*Lakhua*) were selected for this study and these dry fishes were collected from different fish processing zone of Bangladesh namely Moheskali, Cox's Bazaar (COX-1); Nazirartek, Cox's Bazaar (COX-2); Dublarchor, Sundarban, Khulna (SUN-1) and Khajuria Shutki Para, Kuakata, Patuakhali (KUA-1). All the samples of dry fishes collected from four different fish processing zone contained DDT ranging minimum 2.057 ppb (Bombay duck, COX-2) to maximum 181.459 ppb (Indian salmon, COX-1). Heptachlor was not detected in some samples and the maximum value was 29.241 ppb (Indian salmon, COX-2).

**Keywords:** Dry fish, Conservation, Processing zone, Organochlorine insecticides, DDT and Heptachlor.

### INTRODUCTION

In Bangladesh, there are 260 freshwater fish species, 12 species of exotic fish, 475 species of marine fish and 60 species of prawn and shrimp available (Chandra, 2006). Fisheries sector contributes to GDP 5.24%, animal protein supply 63% and foreign exchange earning 4.76% for the nation (Chandra, 2006). Huge amount of fish catches from fresh and marine water during winter season. Such huge catch of fish cannot be sent to the towns or the metropolis on a daily basis either for shortage of transport or fish traders not willing to pay the right amount of money. As a result winter is considered to be the peak season for processing dry fish and continues till the onset of the rainy season.

For long conservation of fish by drying is common practice in Bangladesh. dry fish (Locally known as "Shutki") 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 either at the site or nearby coastal towns. In addition to this, the weather is humid particularly during the monsoon period. Due to high moisture content in the weather and dump condition of warehouse, the dry fishes absorbed moisture so rapidly that the fish becomes suitable for infestation by beetles and mites. Most unexpected cause of infestation is 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 insecticides whatever they are getting within their reach. Studies on dry fishes from four whole sell markets showed that a mixture of organochlorine (DDT and Heptachlor) is used in dry fish in Bangladesh (Bhuiyan *et al.*, 2008). These insecticides are health hazard both for users and consumers. There are many insecticides sold in the markets without names and insecticides are not true to the label. Unknown diluted varieties rarely contain any instructions on health hazards are sold to unaware users. Nobody can draw a statistic on insecticide causalities, although newspapers reports on deaths and sufferings or chronic effects are common in Bangladesh. DDT (Dichlorodiphenyltrichloroethane) and Heptachlor are banned in Bangladesh but there is no statistical figure about these organochlorine insecticides (UNEP, 2002). The organochlorine insecticides are their extreme lipophilic in nature and resistance to biodegradation, which results in their accumulation and concentration in fatty tissues and their extreme persistence in environment (Tannenbaum, 1979). 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). DDT and its by-products can persist in soil and sediments for more than 15 years and are known to bio accumulate in

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animal tissues. DDT was 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). Heptachlor is another organochlorine cyclodiene pesticide that has been used to control termites and as an insecticide on seed grains and food crops. Heptachlor epoxide, the main metabolite of heptachlor, is extremely persistent in soil. In some cases, trace amounts of heptachlor epoxide have been found in soil 14–16 years after application (Exttoxnet, 1996). Plants can draw heptachlor epoxide directly from the soil and the chemical bioaccumulates in animals. It has been banned or restricted in more than 60 countries (WHO, 1988). However, some of these countries still permit its use for termite and other pest control, and many developing nations still use for agricultural purposes (Noronha, 1998). Despite the imposition of a ban on use in the United States in 1988, U.S. customs data showed that it was exported in large quantities through 1994 (PANNA, 1997). A study showed that countries have restricted and banned heptachlor; levels detected in breast milk have dropped, often by more than 10-fold (Jensen and Slorach, 1991). But another studies showed that in the United States, levels in the Southeast were nearly double the levels in the rest of the country during the period when it was still used (Savage, 1981). The objectives of this study were to detect and determine the concentration level of insecticides (DDT and Heptachlor) used in dry fish processing.

## **MATERIALS AND METHODS**

**Sampling:** Sixteen samples of dry fish, Bombay duck (*Loitya*), Ribbon fish (*Chhuri*), Chinese pomfret (*Rupchanda*) and Indian salmon (*Lakhua*) were collected from four different fish processing zone of Bangladesh namely Moheskhali, Cox's Bazaar (COX-1); Nazirartek, Cox's Bazaar (COX-2); Dublarchor, Sundarban, Khulna (SUN-1) and Khajuria Shutki Para, Kuakata, Patuakhali (KUA-1) during October to December 2007 and March 2008. The control samples of four different fishes were collected from drying yards of Sonadia island that are known sample treated with no insecticides and taken into account as blank.

**Sample preparation:** Preparation, extraction and clean up was done according to Peter and Zeumer (1987). The final eluate was concentrated to 1 ml for analysis.

**Sample analyses:** The DDT and Heptachlor residues were analyzed by GC-14B, Shimadzu with an electron capture detector (ECD), a manual sampler and GC solution software. The temperature was fixed for the injector at 250°C, column at 280°C, detector at 280°C. The carrier gas was nitrogen with a 60 ml/min-flow rate. 1.0 ul sample was injected for each run and the running time was 25 min. The calibration was done at 3 points (25 ppb, 50 ppb and 100 ppb) by composite stock standard solution. GC system was calibrated using external standard technique.

**Analytical quality control:** Instrumental limit of detection for GC-ECD was 1.0 ug/l for organochlorine pesticides. The recoveries from untreated control samples of dry fish fortified with the analyzed compounds at level of 25 ppb were 96-100% for Heptachlor and 98-100% for DDT. The constancy and linearity of the ECD signal was checked by injecting serial dilutions of DDT and Heptachlor.

## **RESULTS AND DISCUSSION**

The results obtained from screening of dry fishes for DDT and Heptachlor are alarming for Bangladesh. All of the samples contained invariably health hazard organochlorine insecticides DDT and Heptachlor and the result are shown in table 1 and the chromatogram of all the samples (1-16) shown in fig. 1-16. In samples of dry fishes collected from Moheskhali (COX-1), DDT contents were varied from minimum 3.524 ppb in Chinese pomfret to maximum 181.459 ppb in Indian salmon and Heptachlor contents was found maximum 15.456 ppb in Chinese pomfret. In Ribbon fish and Indian salmon, Heptachlor was not detected. Although DDT (3.524 ppb) content was lower in Chinese pomfret than those of other species but Heptachlor content was the highest (15.456 ppb).

Table 1. Summary of DDT and Heptachlor concentrations in the dry fish samples of Bombay duck, Ribbon fish, Chinese pomfret and Indian salmon (The concentrations are in ppb unit).

Name of the sample	Name of insecticides	Name of the places			
		COX -1	COX -2	SUN -1)	KUA -1
Bombay duck	Heptachlor	1.300	*ND	*ND	*ND
(Loitty)	DDT	47.081	2.057	7.410	5.629
Ribbon fish	Heptachlor	*ND	*ND	*ND	*ND
(Chhuri)	DDT	26.927	12.125	21.760	61.969
Chinese pomfret	Heptachlor	15.456	1.613	8.995	*ND
(Rupchanda)	DDT	3.524	61.918	12.606	156.726
Indian salmon	Heptachlor	*ND	29.241	10.219	*ND
(Lakhua)	DDT	181.459	9.474	10.037	96.886

\*ND- Not detected

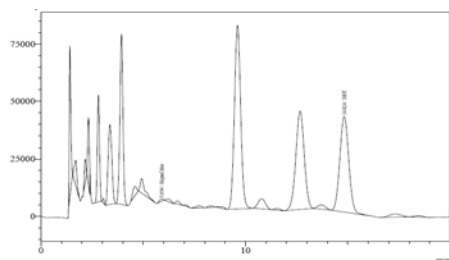


Fig. 1. Bombav duck. COX-1

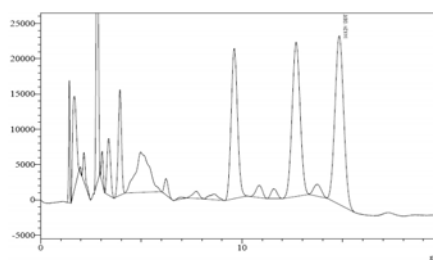


Fig. 2. Ribbon fish. COX-1

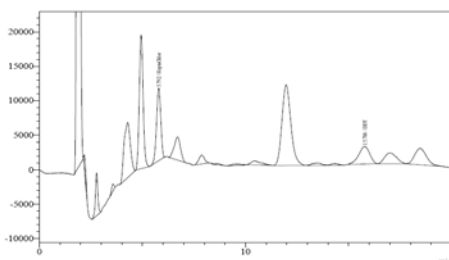


Fig. 3. Chinese pomfret, COX-1

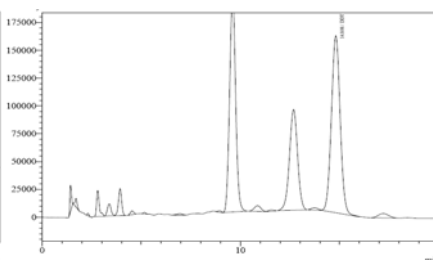


Fig. 4. Indian salmon, COX-1

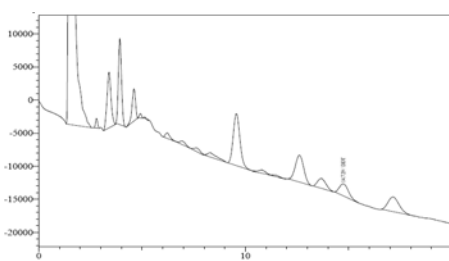


Fig. 5. Bombay duck, COX-2

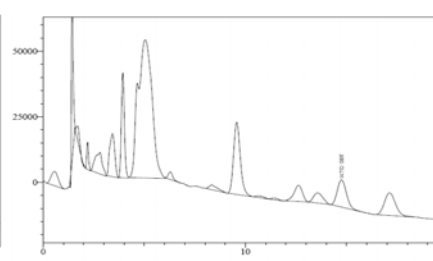


Fig. 6. Ribbon fish, COX-2

Fig. (1-6). Different chromatograms of DDT and Heptachlor for 16 samples of dry fishes.

One of the organochlorine insecticides, Heptachlor was not detected in the samples of dry fishes collected from Khajuria, Kuakata (KUA-1) but the average concentration of another organochlorine insecticides, DDT was comparatively higher than those of other places. The chromatograms of the almost all samples of all places (fig. 1 to fig. 16) showed some unexpected peaks which indicate the presence of other organochlorine rather than DDT and Heptachlor. Generally a mixture of organochlorine insecticides including DDT, Heptachlor and some other unexpected organochlorine insecticides (fig.1 to fig. 2) were used for the conservation of dry fish. Commonly higher concentrations of organochlorine insecticides were used in more costly fishes. If a particular sample contained relatively lower content of one organochlorine insecticide, than the other organochlorine insecticide was found higher for the same sample.

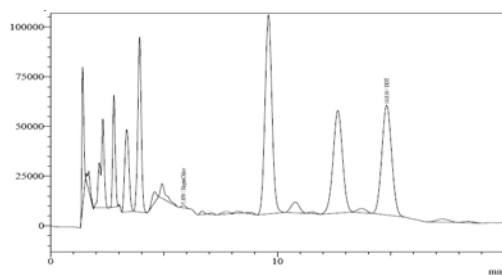


Fig. 7. Chinese pomfret, COX-2

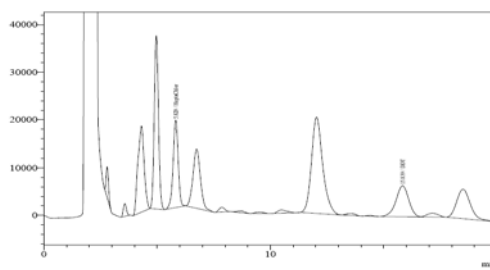


Fig. 8. Indian salmon, COX-2

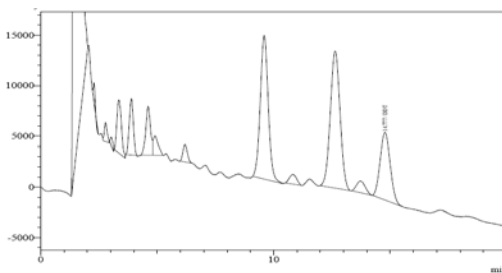


Fig. 9. Bombay duck, SUN-1

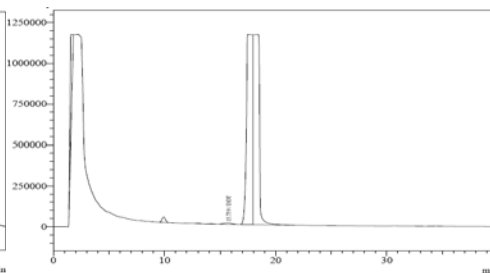


Fig. 10. Ribbon fish, SUN-1

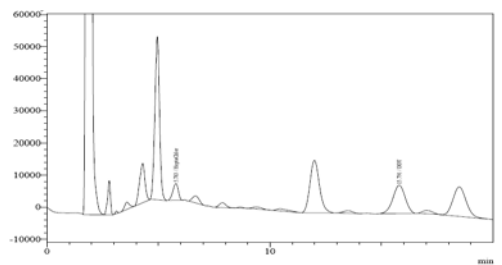


Fig. 11. Chinese pomfret, SUN-1

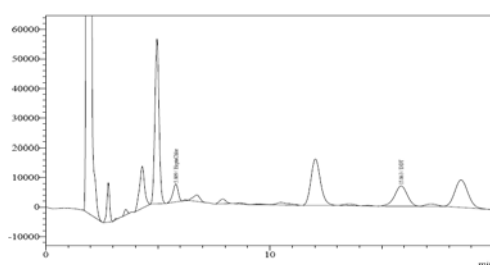


Fig. 12. Indian salmon, SUN-1

Fig. (7-12). Different chromatograms of DDT and Heptachlor for 16 samples of dry fishes.

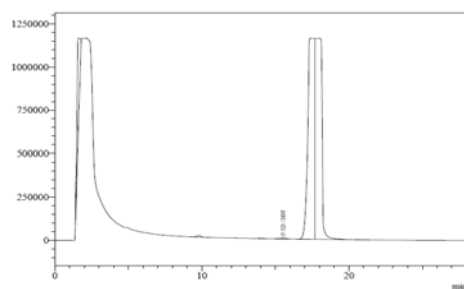


Fig. 13. Bombay duck, KUA-1

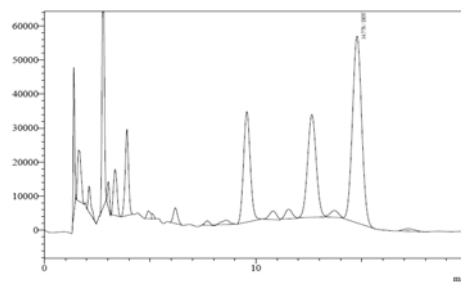


Fig. 14. Ribbon fish, KUA-1

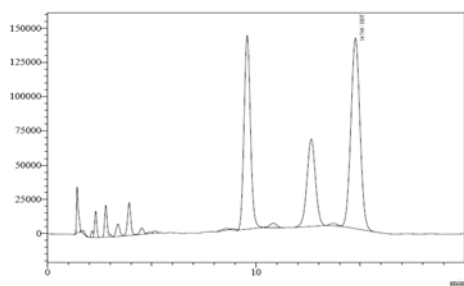


Fig. 15. Chinese pomfret, KUA-1

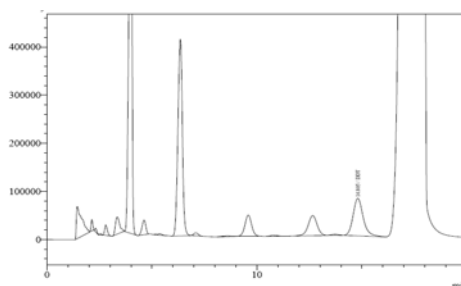


Fig. 16. Indian salmon, KUA-1

Fig. (13-16). Showed different chromatograms of DDT and Heptachlor for 16 samples of dry fishes.

The level of concentration of any organochlorine insecticide like as DDT and Heptachlor 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, a class B2 probable human carcinogen (US EPA, 1987), is a slow poisoning substance. It can transfer from generation to generation through breast milk (Solomon and Weiss, 2001). It is classified as "Moderately toxic" by the US National Toxicological Program and "moderately hazardous" by WHO, based on the rat oral LD50 of 113 mg/kg (WHO, 2005). In areas where it is used for malaria control, infants can be exposed via breast milk in levels that exceed the WHO's acceptable daily intake value for DDT (Bouwman *et al.*, 2006; Ntow *et al.*, 2008). Farmers exposed to DDT occupationally have an increased incidence of non-allergic asthma (Brow, 2007). Organochlorine compounds in general have been linked to diabetes (Jones *et al.*, 2008). A study of malaria workers who handled it occupationally found an elevated risk of cancers of the liver and biliary tract (Rogan and Chen, 2005). Exposure to it before puberty increases the risk of breast cancer later in life (Clapp *et al.*, 2008).

Heptachlor has been shown to bioaccumulates in fish and cattle. Most of the heptachlor that is swallowed is absorbed into blood. Heptachlor can pass directly from a mother's blood to an unborn baby through the placenta (LDWG, 2007). Animals fed heptachlor throughout their lifetime had more liver tumors than animals that ate food without heptachlor. EPA has classified heptachlor as a probable human carcinogen (B2) and established an oral cancer slope factor of 4.5 per mg/kg-day (LDWG, 2007). From the study, we can say that, there is an abundant use of insecticides in dry fish. They use DDT as a compulsory preserver of dry fish. Other insecticides are also used as a composite mixture of insecticides

to get good preservation as our chromatograms showed some unexpected peaks in every sample. It should take the necessary steps by the government regarding this problem.

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