Global Journal of Science Frontier Research: B Chemistry
Volume 18 Issue 2 Version 1.0 Year 2018
Type: Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Metabolic Effects of Sulphur Derivative Pesticides in Fish Samples of Fresh Water in Bangladesh

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GJSFR-B Classification: *FOR Code: 039999*

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Abstract- In Bangladesh, there are lots of fishes in abundance. Fifteen fresh water fish samples namely *Puntius sarana* (Shawrputi), *Channa punctatus* (Taki), *Wallogonia attu* (Boal), *Macrognathus aculiatus* (Baim), *Ailia coila* (Kajoli), *Mystus cavasisus* (Gulsa), *Ompok pabda* (Pabda), *Corica soborna* (Kachki), *Mystu svittatus* (Tengra), *Glossogobius giuris* (Baila), *Macrobrachium malcolmsli* (Chingri), *Amblypharyngodon microlepis* (Mola), *Anabas testudineus* (Koi), *Channa striatus* (Shol), *Heteropnueste fossilis* (Shing). These fish samples were collected from two rivers and a cultured fish pond. The samples were extracted by QuEChERS method, cleaned up with conc. H_2SO_4 and cleaned extracts were analyzed by GC-ECD. Small size cultured Koi fish sample which did show detectable amount of sulphur containing pesticides and its metabolites was used for the recovery experiments. Percent recovery was found to be in the range of 80%-123%. Amount of total pesticides were found to be 54.34, 48.81, 62.09, 54.72, 78.81, 60.07, 47.0, 42.7, 26.31, 10.36, 25.32, 12.96, 20.10, 12.78, 17.65, and 4.71, 8.58, 11.3 and 19.01 ng/g in shawrputi, taki, boal, baim, Kajoli, gulsha, pabda, kachki, tengra, baila, chingri, mola, koi, shol, shing fish samples, respectively. However, the residual amounts of pesticides in all the fish samples were below maximum residue limit according to Codex Alimentarius Commission.

Keywords: OSPs, biomagnification, gas chromatography, fresh water fish and food chain.

I. Introduction

Organosulpher Pesticides (OSPs) which are highly stable and bio-accumulative compounds identified as hazardous environmental contaminants for decades [1, 2]. As Bangladesh is an agricultural country, these compounds are used in the country from the middle of the twenty first century in agriculture to increase crop production and other purposes including controlling vector diseases [3]. It is long persistence in the environment and transport long distances via air, water and sediment. The major exposure of the persistent OSPs to humans is via contaminated food, drinking water, inhalation and dermal uptake [2, 4]. OSPs including Fenitrothion, Endosulfan, Thiobencarb, Thiocyclam have been banned in Bangladesh after signing Stockholm Convention [4, 5]. Aquatic ecosystems in Bangladesh are very much susceptible for being contaminated with pesticides and other pollutants. Pesticides enter into the aquatic systems either by direct discharge or transported by evaporation and/or run-off processes [4]. OSPs and its metabolites are not soluble in water but can be present as suspended materials associated with the phytoplankton, algae or through adsorption on soil or sediment [2, 3]. Fish and other aquatic organism can easily be contaminated by taking these suspended materials as their food [1]. Fish is one of the important bio-indicator of bioaccumulation of organic pollutants in fatty tissues and it is one of the sources for accumulation of OSPs to human blood through food chain. Presence of OSPs and its metabolites were reported by our research group in fresh & dry fish, chicken meat and human blood samples [7-11]. In continuation of our work on chemical contaminants in food and environment, we are now reporting the presence of OSPs in fifteen fresh water fish samples from two different rivers and cultured water pond.

II. Materials and Methods

a) Sample Collection

Fifteen live fish samples were collected from Madaripur (Padma river) and Barishal (Arial Kha river and cultured fish pond). The collected fish samples were kept in jip-locked plastic bag with label in chill-box then transported to the laboratory and stored in the freezer at -20°C until extraction carried out. Name sizes, place of collection are given Table 1.

b) Chemicals, Reagents and Solvents

The certified standards; Fenitrothion, Endosulfan, Thiobencarb, Thiocyclam (99% purity) were purchased from Merck, Germany. Analytical grade anhydrous magnesium sulfate and sodium sulfate were purchased from Scharlau, Spain. Analytical grade solvent such as hexane and acetone were purchased from Sigma Aldrich. Sulfuric acid (98%) and sodium chloride were purchase from Merck, Germany.

c) Apparatus and Equipment

All evaporations were carried out by rotary vacuum evaporator at water bath temperature not exceeding 50°C. The residual solvent of the dried mass

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was removed by a freeze dryer (Adward, RV12). Anhydrous sodium and magnesium sulphate were heated at 300°C in a furnace (Carbolite, GSM 11/8 Hope valley, S336 RB, England). For 4 hours and dried materials were kept in a vacuum desiccators.

Calibrated balance, volumetric flasks and pipettes (calibrated by BSTI) were used for the analysis. Gas Chromatography (Shimadzu 2010) coupled with Electron Captured Detector (GC-ECD) used for analysis was calibrated by local agent of the company (AQC).

Table 1: Fish samples collected from Madaripur and Barishal

Fish samples from Padma river

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Channa punctatus*	Taki	27.0-28.0
02	*Wallogonia attu*	Boal	46.0
03	*Macrognathus aculiatus*	Baim	16.0-17.7
04	*Ailia coila*	Kajoli	11.0-12.0
05	*Mystus cavasisus*	Gulsa	12.0-13.2
06	*Ompok pabda*	Pabda	12.0-12.5
07	*Corica soborna*	Kachki	2.9

Fish sample of Arial Kha river

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Mystus vittatus*	Tengra	8.0-8.4
02	*Channa punctatus*	Taki	17.0-17.8
03	*Glossogobius giuris*	Baila	11.0-12.5
04	*Macrobrachium malcolmsli*	Chingri	3.9
05	*Amblypharyngodon microlepis*	Mola	3.7
06	*Anabas testudineus*	Koi	11.0-11.5
07	*Macrognathus aculiatus*	Baim	11.0-12.5
08	*Channa striatus*	Shol	34.0
09	*Heteropnueste fossilis*	Shing	14.4-15.0

Fish sample from cultured pond in Barishal

Serial No.	Scientific Name	Local Name	Size (cm)
01	*Puntius sarana*	Shawrputi	21.2-22.0

Gas Chromatograph (GC-2010 Shimadzu) coupled with Electron Capture detector, (GC-ECD) was used for analysis. Separations were performed on HP-5 quartz capillary column (30 m long 250 μm i.d: 0.25 μm film thickness), nitrogen was used as carrier (column flow 1.92 mL/min.) as well as make up gas. The injector and detector temperatures were set 300°C and 350°C, respectively and the oven temperature was programmed as 100°C (2 min hold) to 200°C (4 min hold) and 20°C rise per min. All the injections (1 μL) were done in split less/spit mode. Identifications of the analyte samples were done by comparing retention time of corresponding certified standard samples and quantification by using external calibration curves of the corresponding reference samples.

d) Extractions and Clean-up

Large fish samples were divided into head, abdominal and dorsal parts and small fish whole samples were taken for analysis. Each of the fish sample was homogenized by a kitchen blender 50-60 g in each jip lock bag was kept in a freezer until analysis carried out. Freeze dried fish samples (10g) were refluxed with n-hexane (60 mL 3; 30 min each time). The combined n-hexane extract was evaporated to dryness and percent fat content was determined and expressed on fresh weight basis (Tables 2 and 3).

Fish sample (10 g 3 for replicate study was taken out from the freezer, thawed and extracted by QuEChERS (Quick, Easy, C0heap, Effective, Rugged and Safe) method [12]. The extract was cleaned with sulphuric acid treatment [13]. The cleaned extract was analysed by GC-ECD. Standard deviations were calculated from three replicate analyses (Tables 2 and 3).

Table 2: Residual amounts of OSPs in the fish samples collected from Padma river

Fish sample	Amount of OSPs and its metabolites (ng/g) in fresh weight basis				Fat (%)
	Fenitrothion	Endosulfan	Thiobencarb	Thiocyclam	
Taki abdominal	4.36 ± 0.17	4.32 ± 0.24	2.99 ± 0.48	3.36 ± 0.46	15.03
Taki dorsal	4.91 ± 0.64	4.47 ± 0.73	1.30 ± 0.09	1.88 ± 0.14	12.56
Taki head	2.86 ± 0.14	3.01 ± 0.09	0.85 ± 0.03	1.81 ± 0.04	8.53
Gulsha	7.01 ± 0.91	9.13 ± 0.79	14.15 ± 1.17	24.03 ± 1.30	54.32
Kachki	4.05 ± 0.26	4.15 ± 0.30	8.55 ± 0.59	9.56 ± 0.37	26.31
Pabdha	9.71 ± 0.69	5.69 ± 0.35	16.33 ± 4.68	17.08 ± 0.60	48.81
Boal abdominal	6.18 ± 0.30	1.76 ± 0.03	0.86 ± 0.04	1.21 ± 0.02	11.01
Boal dorsal	9.71 ± 0.69	1.21 ± 0.03	0.66 ± 0.04	0.64 ± 0.09	10.22
Boal head	4.69 ± 0.07	2.82 ± 0.21	1.05 ± 0.05	1.80 ± 0.25	12.36
Kajoli	2.26 ± 0.32	20.53 ± 0.83	2.51 ± 0.11	6.71 ± 0.21	32.01
Baila	9.75 ± 0.48	14.38 ± 0.66	12.61 ± 0.42	25.35 ± 0.56	62.09

Table 3: Residual amounts of OSPs in the fish samples collected from Arial Kha river

Fish sample	Amount of OSPs and its metabolites (ng/g) in fresh weight basis				Fat (%)
	Fenitrothion	Endosulfan	Thiobencarb	Thiocyclam	
Taki	6.26 ± 0.31	8.79 ± 0.19	0.18 ± 0.00	10.09 ± 0.46	25.32
Baila	4.70 ± 0.11	4.82 ± 0.35	0.31 ± 0.00	0.55 ± 0.05	10.38
Chingri	4.63 ± 0.47	4.18 ± 0.24	1.92 ± 0.04	2.23 ± 0.06	12.96
Mola	12.06 ± 0.75	6.20 ± 0.29	0.65 ± 0.03	1.19 ± 0.04	20.10
Koi	1.55 ± 0.04	1.71 ± 0.04	0.2 ± 40.03	1.21 ± 0.05	4.710
Baim	33.92 ± 1.37	37.25 ± 3.35	4.73 ± 0.33	2.91 ± 0.04	78.81
Shol	3.57 ± 0.41	3.98 ± 0.41	0.17 ± 0.04	5.06 ± 0.49	12.78
Tenra	19.93 ± 1.40	22.16 ± 1.40	0.49 ± 0.03	4.41 ± 0.33	46.99
Shing	7.81 ± 0.48	7.84 ± 0.48	0.31 ± 0.00	1.69 ± 0,07	17.65
Swarputi	2.82 ± 0.23	2.73 ± 0.06	1.42 ± 0.05	1.61 ± 0.05	8.58

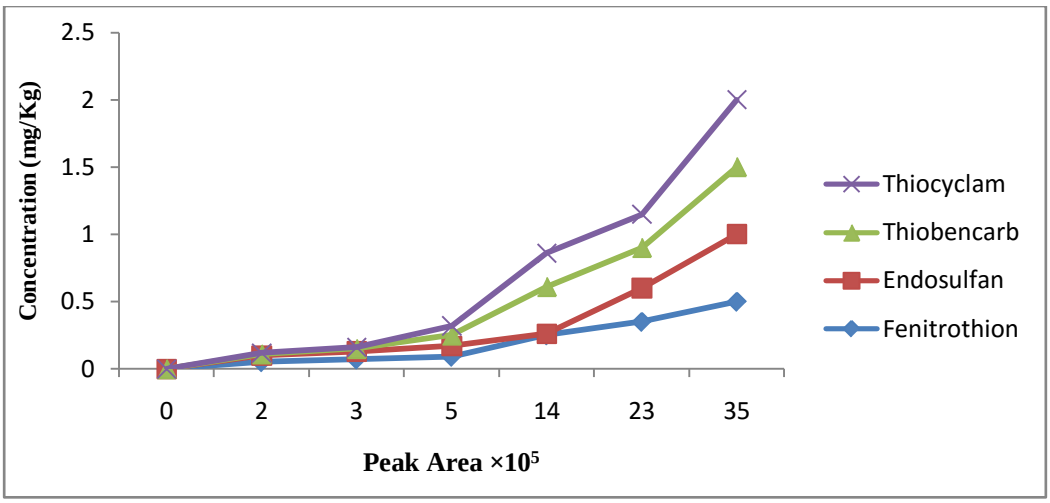

Figure: Calibration curves for standard OSP solutions

To get recovery experiments, we have collected two Rui fish *(Labeo rohita)* from local market as a blank fish matrix. We blended bone free fish and took 5gm for use. We spiked OSPs solution to the fish tissue and allowed stand for 2 hr to let the pesticides to be absorbed into the samples. The samples were extracted freed and cleaned-up by following the same procedure as described above and made final volume 1.0mL. The recovery of the each analyte was calculated according to the following formula:

$$R = \frac{A_m \times C_{st} \times 100}{A_{st} \times C_m \times M_{st}}$$

Where *R* is the recovery (%), A_m is the peak area of the analyte in the matrix, A_{st} is the peak area of the analyte in the standard, C_m is the concentration of the analyte in the matrix, C_{st} is the concentration of the analyte in the standard, and M_{st} is the spiking level (mg/kg). The percentage recoveries for fish samples were found to be 90%-98%, 101%-123%, 80%-104% and

75%-95% for Fenitrothion, Endosulfan, Thiobencarb and Thiocyclam, respectively.

III. Results and Discussion

Fourteen fish samples from two rivers Padma (Madaripur) and Arial Kha (Barishal) were selected to find out overview of environmental contaminants in two different areas. One fish sample cultured in fish pond was taken to evaluate contaminants which get fish feed and grow faster than naturally live fishes. Most of the small indigenous fishes were adult in their size and size of two large fish samples, boal and shol were also adult size.

Boneless flesh part of large fish and cultured fish samples were studied for sulphur derivatives and metabolites whereas in case of small indigenous fish samples total edible parts including head were taken.

By Calibrating all the apparatus, balance and the GC-ECD were used during the experiments. Three replicate analyses were done for each of the analysis and standard deviation was calculated are satisfactory level. Regression coefficient, r^2 were 0.996 for Fenitrothion, Endosulfan, Thiobencarband 0.999 for Thiocyclam. Percent recovery of the standards were 80% - 123%, which were in the range 75% - 130% and acceptable for fish samples according to standard methodology.

Sulphur derivatives and its metabolites varied from sample to sample. Small fish adult samples showed the presence of higher amount OSPs than other fish samples. The OSPs accumulation depends on mainly on fat content as they deposit in fatty tissue of fishes. Other factors like food habit, lipid content, digestion metabolism rate, excretion rate and habitat etc. also contribute to OSPs accumulation in fish species [6]. In the herbivorous mola fishes, higher amount of fat content is responsible for higher amount of OSPs. Furthermore, the mola fish was found extensively in rivers, canals, beels and ponds throughout the country [7]. The baila is a carnivorous [6]. As we know that OSPs are biomagnified sometimes 7,000 times greater in the top consumer to first consumer. This fish is on the top position in the food chain and contained the higher value. The lowest value of OSPs is found in shole, taki and boal, these three are highly carnivorous. As we mentioned previous OSPs accumulation depends on not only food habit but also on metabolism rate, excretion rate and fat content. In these three fishes their metabolism and excretion rate is higher [6] and fat content also too low. Therefore, although these are carnivorous, they have lower amount of OSPs. The swarputi is a cultured fish and it contains comparatively lower amount of OSPs (Table 3) although it is omnivorous and contained higher amount of fat. Thus in cultured fishes OSPs residue is comparatively low than that of marine and river fishes. The amounts of OSPs content were varied in different part of the same fish. In taki and boal fish samples, the abdominal part contained higher amount of OSPs than their dorsal and head parts (Table 2).Thus in cultured fishes OSPs residue is comparatively low than that of marine and river fishes. However, the residual OSPs in all the fish samples were below maximum residue limit (MRL) of OSPs in fish, but continuous consumption of such fishes may cause a threat to human health as a result of biomagnifications. As OSPs are 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.

IV. Conclusions

From the present study, the residual amount of OSPs and its metabolites were found in cultured fishes lower than river fish samples. Furthermore, the overall results of OSPs are lower than previous studies. Thus, extensive and indiscriminate uses of organosulphur pesticides especially Fenitrothion, Endosulfan, Thiobencarb and Thiocyclam are decreasing day by day. This study was area-specific giving a holistic picture of the floodplains of our country. The further work is required to determine the overall picture of the pollutants in aquatic environment of Bangladesh.

Acknowledgement

The authors are very grateful to Bangladesh Council of Scientific and Industrial Research (BCSIR), Bangladesh Standard and Testing Institute (BSTI) and Jahangirnagar University (JU) for their valuable support.

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