RESEARCH ARTICLE Indian Journal of Animal Research, Volume 55 Issue 10: 1233-1239 (October 2021)

Occurrence of Pesticide Residues in Freshwater and Estuarine Fishes of Thamirabarani River

Manimekalai Durairaj, Srinivasan Arasan, Padmavathy Pandurengan, Jawahar Paulraj, Rosalind George

10.18805/IJAR.B-4498

ABSTRACT

Background: Studies pertaining to the presence of OCP residues in the freshwater and marine fishes caught from the Thamirabarani river basin region are not available to analyze the extent of bioaccumulation to assess their safety for human consumption. Hence, this study was undertaken as a maiden work to examine the OCP residues in the fishes collected from five sites spanning from the source to mouth region of the Thamirabarani river system, along with other related niches to examine the effect of environment pollution.

Methods: Pesticides from fish muscle and their organs were extracted as per AOAC 2007.01 using QuEChERS method. A Gas Chromatograph model Perkin Elmer - equipped with Ni Electron Capture Detector of activity 15 MCi was used for the analysis. A volume of 1.0 µl of the extracts was injected. The operating conditions were capillary column Elite-5 capillary column, 60 m × 0.25 mm, 1.00 µm temperature programme: 70°C (2 min) to 180°C (I min) 25°C/min to 300°C 5°C/min, Injection temperature: 270°C, Detector temperature: 300°C, Carrier gas: Nitrogen at 1.0 mL/min, Make up gas: Nitrogen at 29 mL/min.

Result: Among fishes, rohu accumulated maximum of 0.4014 to 0.605 ug/kg of DDT in station IV and V respectively. Dhananjayan and Muralidharan (2010) reported OCPs in 156 fishes sample from Kaveri river. The average concentration of DDT ranged between 0 and 0.605 ug/kg. Bhuvaneshwari and Babu rajendran (2012) also reported 2.8 ug/g of DDT in fishes from Kaveri river. The low occurrence of DDT in the presence study is mainly due to their rapid degradation with living organisms.

Key words: Gas chromatography-ECD, Organochlorine pesticides, QuEChERS method, Thamirabharani river.

INTRODUCTION

Pesticides are extremely used in developing countries for various purposes. It is estimated that about 25000 mt of chlorinated pesticides were used annually in India and DDT accounted for 40% of this group (Mathur, 1993). Thamirabharani is a perennial river situated in the Southern part of Tamil Nadu originating from Pothigai Hills of Western Ghats and discharging into the Gulf of Mannar region of Bay of Bengal (Kumarasamy *et al*., 2012).

Aquaculture activities are undertaken in areas originating from the upper reaches (Manimuthar) upto the mouth region (Punnakayal) by utilizing Thamirabharani river as the major water source. Freshwater aquaculture is widely practiced in Manimuthar, Ambasamudram, Kallidaikurichi, Tirunelveli, Srivaikuntam and Authoor regions, while the estuary region of Punnakayal is the home for migratory marine fishes. The main cropping pattern in the Thamirabharani river basin includes banana, coconut, groundnut and paddy which is regularly practiced in these areas. The cotton, sorghum, ragi, pulses and ginger are the important varieties cultivated in the rain-fed lands. However, only limited report was available on OCPs in Thamirabharani River.

MATERIALS AND METHODS

Chemicals

The present study was conducted from the period from October 2017 to October 2020 at Fisheries College and Research Institute, Thoothukudi.

Department of Aquatic Environment Management, Fisheries College and Research Institute, Tamil Nadu Dr. J. Jayalalithaa Fisheries University, Tuticorin-628 008, Tamil Nadu, India.

Corresponding Author: Srinivasan Arasan, Department of Aquatic Environment Management, Fisheries College and Research Institute, Tamil Nadu Dr. J. Jayalalithaa Fisheries University, Tuticorin-628 008, Tamil Nadu, India. Email: manimekalai@tnfu.ac.in

How to cite this article: Durairaj, M., Arasan, S., Pandurengan, P., Paulraj, J. and George, R. (2021). Occurrence of Pesticide Residues in Freshwater and Estuarine Fishes of Thamirabarani River. Indian Journal of Animal Research. 55(10): 1233-1239. DOI: 10.18805/IJAR.B-4498.

Submitted: 27-04-2021 **Accepted:** 11-06-2021 **Online:** 21-06-2021

Standard solutions of organochlorine pesticides (99% purity) containing α, β, γ, δ-BHC, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrinalde-hyde, endosulfan I, endosulfan II, endosulfan sulfate, p,p'-DDE, p,p'- DDT, p,p'-DDD, methoxychlor (M-8270-14-ASL) was obtained from AccuStandard, Inc. USA. Chemicals of QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) kit such as primary secondary amines (PSA), carbon-18 (C18), graphitized carbon black (GCB), magnesium sulfate ($MgSO_4$) and sodium acetate (NaOAc) were individually purchased from Sigma-Aldrich (Bangalore, Karnataka, India). All other solvents such as ethyl acetate, dichloromethane, acetone nitrile, n-hexane, methanol, acetic acid and petroleum ether used for sample analysis were of

HPLC grade obtained from Sigma-Aldrich and Rankem Chemicals (Gurugram, Haryana, India). The storage vials of 2 ml in capacity were purchased from Agilent Technologies, Germany.

Study area

Five sampling sites *viz*. Papanasam (Site 1), Cheranmadevi (Site 2), Vannarapettai (Site 3), Srivaikuntam (Site 4) and Punnakayal (Site 5) were chosen from the source to the mouth of the river and their locations are given in Plate 1 and 2.

A global position system (GPS, Leica G20, USA) was used to locate the sampling locations more precisely during the sampling. Fish samples were collected from the respective sites and brought to the laboratory in iced condition and held in deep-freezer at -20°C until analysis. Three freshwater fish *viz* catla (*Catla catla),* rohu (*Labeo rohita*) and tilapia (*Oreochromis mossambicus*) were collected from the first four sampling sites. Four marine and estuarine fishes such as Indian mackerel (*Rastrelliger kanagurta*), Milk fish (*Chanos chanos*), Indian oil sardine (*Sardinella longiceps*) and Mullet (*Mugil cephalus*). were collected from the station 5, which is an estuary region receiving influx of marine and freshwater.

Extraction and cleanup

Pesticides from fish muscle and their organs were extracted as per AOAC 2007.01 using QuEChERS method (Anastassiades *et al*., 2003a,b; Norli *et al*., 2011). For the analysis, 5g of each homogenized sample was mixed separately with 15 ml of 1% of acetic acid in acetonitrile in a centrifuge tube and vortexed well for 1min to maintain the pH between 5 to 7. From that, 4-5 ml of supernatant was taken in another centrifuge tube and kept at -20°C for 15 min to enable fat deposition. From which, 1.5 ml of upper layer was taken and 150 mg of MgSO4 and 100 mg of CaCl2 were added, vortexed well for 1 min and centrifuged again at 5000 rpm for 5 min to increase the solvent partitioning. Finally, 1 ml of supernatant was taken and added to QuEChERS clean up kit. The kit contained PSA - 25 mg (to remove the sugars, fatty acids and organic acids), C18 - 25 mg (to remove the long chain fatty compounds, sterols and non-polar interference), GCB- 7 mg (to remove the pigments, polyphenols and other polar compounds without loss of planar pesticides like HCB and Terbufos and MgSO4 -150 mg (to separate the solvent layer and improve the recovery of pesticides). The mixture was shaken vigorously and centrifuged at 9000 rpm for 5 min. After the clean-up process, 1 ml of supernatant was taken for GC-ECD analysis.

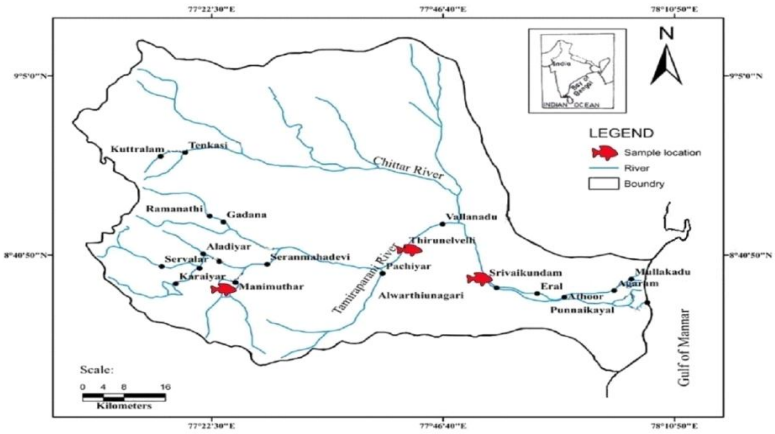

Plate 1: Sampling sites.

Plate 2: Study area.

Station I - Papanasam, Station II - Cheranmadevi, Station III - Vannarapettai, Station IV- Srivaikundam, Station V- Punnakayal.

RESULTS AND DISCUSSION

The occurrence of organochlorine pesticides in selected freshwater and estuarine fishes such as catla, rohu, tilapia, mullet, milk fish, sardine and mackerel ranged between 0 and 26.0521 µg/kg at different stations of Thamirabarani River and it was lower than the concentration observed in water samples.

BHC compounds

The seasonal variation of total BHC in fishes ranged from 0.0146 to 0.8686 µg/kg and the maximum concentration was observed in Station I during summer season. Among the fishes, tilapia (0.8686 µg/kg) accumulated more than rohu (0.3378 µg/kg) and catla (0.7148 µg/kg) during summer season. The concentration of alpha BHC in selected freshwater fishes ranged between 0.0146 and 0.4878 µg/kg. The range of beta and gamma BHC in catla, rohu and tilapia where found between 0.0219 and 0.3794 µg/kg, 0.0205 to 0.0908 µg/kg respectively. The concentration of beta and alpha BHC were higher in catla followed by rohu and tilapia during the monsoon season. Whereas Delta BHC and gamma BHC concentration were higher in tilapia followed by rohu and catla. Rohu showed the highest accumulation for beta BHC during pre monsoon and post monsoon seasons. In post monsoon season, delta BHC accumulation was observed high in Tilapia fish (0.1626 µg/kg).

The maximum of 0.1654 µg/kg and 0.0644 µg/kg of total heptachlor was observed in tilapia during monsoon season. Heptachlor was not found in catla in summer and post monsoon season. The accumulation of total BHC in fishes ranged from 0.0379 µg/kg to 0.9506 µg/kg and the high value was recorded in station V. The total BHC accumulation more in milk fish (0.9506 µg/kg) during premonsoon season. The concentration of alpha BHC was found very less in estuary region and the value observed was 0.0058 µg/kg. The maximum concentration of alpha BHC was observed as 0.4878 µg/kg in all the stations except Station V during monsoon season. The minimum concentration of beta BHC recorded as Station V and the value observed was 0.0117 µg/kg in post monsoon season. The range of beta BHC was observed from 0.0117 to 0.3784 µg/kg in all the stations. The lowest concentration was recorded in milk fish (0.117 µg/kg) during post monsoon season in Station V. the range of gamme BHC was observed from BDL to 1.245 µg/kg in all the stations. The seasonal variation of BHC compounds in fish samples of Thamirabharani river is given in Fig 1.

Heptachlor in fishes

The accumulation of total Heptachlor compounds in mackerel fishes ranged between BDL and 1.692 µg/kg. The highest concentration of heptachlor compound was found as 0.1758 µg/kg and it was observed in mackerel fishes during summer season in station V. The highest concentration of heptachlor epoxide was found in tilapia and the concentration observed was 1.6554 µg/kg during summer and monsoon seasons at station I, II, III and IV. The seasonal variation of Heptachlor compounds in fish samples of Thamirabharani river is given in Fig 2.

DDT compounds in fishes

The accumulation of total DDT compounds in all fishes varied between 0.020 to 26.1794 µg/kg at all stations. The concentration of DDE ranged from 0.0029 to 26.0521 µg/kg in all stations. The lowest concentration of DDE (0.0029 µg/kg) was observed in milkfishes and mackerel during post monsoon seasons at station V. The concentration of DDD ranged between 0.0014 to 1.1427 µg/kg in all stations. The lowest concentration of DDD (0.0014 µg/kg) was observed in mullet fishes at station V. The concentration of DDT ranged between 0 to 0.605 µg/kg in all stations. The maximum concentration of DDT (0.605 µg/kg) was observed in mullet fishes during summer seasons at station V. The lowest concentration of DDT was observed in catla fishes during summer monsoons at all stations except station V. The highest accumulation of total DDT compounds was found as 26.1794 µg/kg and it was observed in rohu fishes during summer seasons at all stations except in station V.

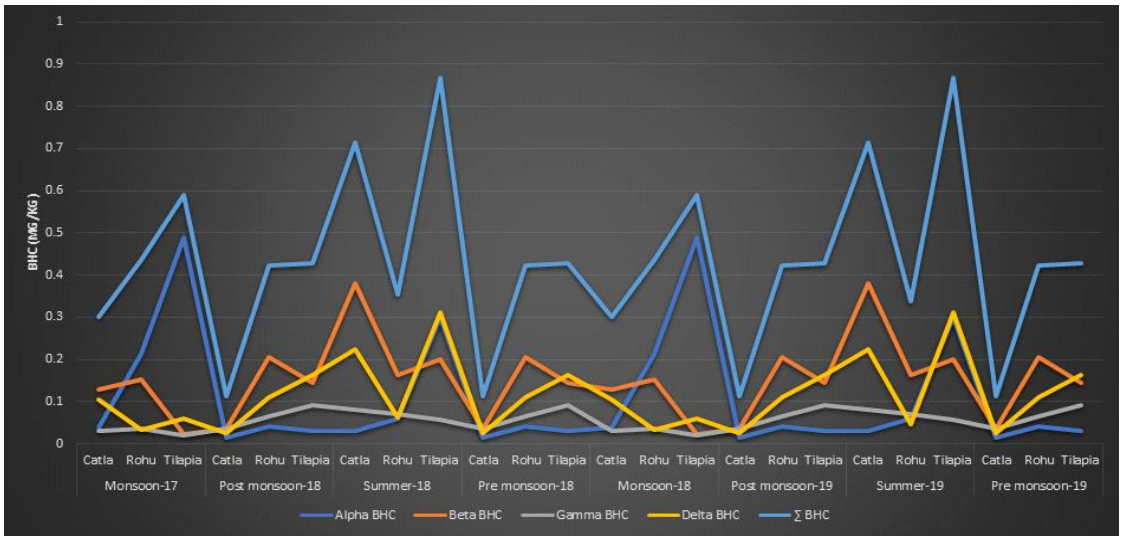

Fig 1: Seasonal variation Of BHC compounds in fish samples of Thamirabharani river.

The seasonal variation of DDT compounds in fish samples from station I to station V of Thamirabharani river is given in Fig 3.

Drin compounds in fishes

The accumulation of total Drin compounds in all fishes varied between 0.0526 to 31.7126 µg/kg. The concentration of Dieldrin ranges between 0.0014 to 5.6197 µg/kg in all stations. The maximum concentration of Dieldrin (5.6197 µg/kg) was observed in mullet fishes during monsoon fishes at station V. The lowest concentration of dieldrin (0.0014 µg/kg) was observed in catla fishes during monsoon seasons at all stations except in station V.

The accumulation of aldrin in all fishes varied between 0.0102 to 3.4486 µg/kg. The highest concentration of aldrin (3.4486 µg/kg) was observed in sardine fishes during premonsoon period at station V. The lowest concentration of aldrin (0.0102 µg/kg) was observed in catla during monsoon seasons at all stations except station V. The concentration of endrin in all fishes varied between BDL to 14.0508 µg/kg. The highest concentration of endrin (14.0508 µg/kg) was observed in milkfishes during monsoon season at station V. The seasonal variation of drin compounds in fish samples of Thamirabharani river is given in Fig 4.

Endosulfan in fishes

The accumulation of total endosulfan compounds in all fishes varied between 0.51568 to 65.1441 µg/kg. The concentration of endosulfan I ranged between 0.0117 to 64.1538 µg/kg in all stations. The maximum concentration of endosulfan I (64.1538 µg/kg) was observed in milkfishes during postmonsoon seasons at station V. The lowest concentration of endosulfan I (0.01172 µg/kg) was observed in mullet during postmonsoon seasons at station V. The \concentration of endosulfan II in all stations varied between BDL to 3.4486 µg/kg. The highest concentration of endosulfan II was observed in sardine fishes during premonsoon seasons at

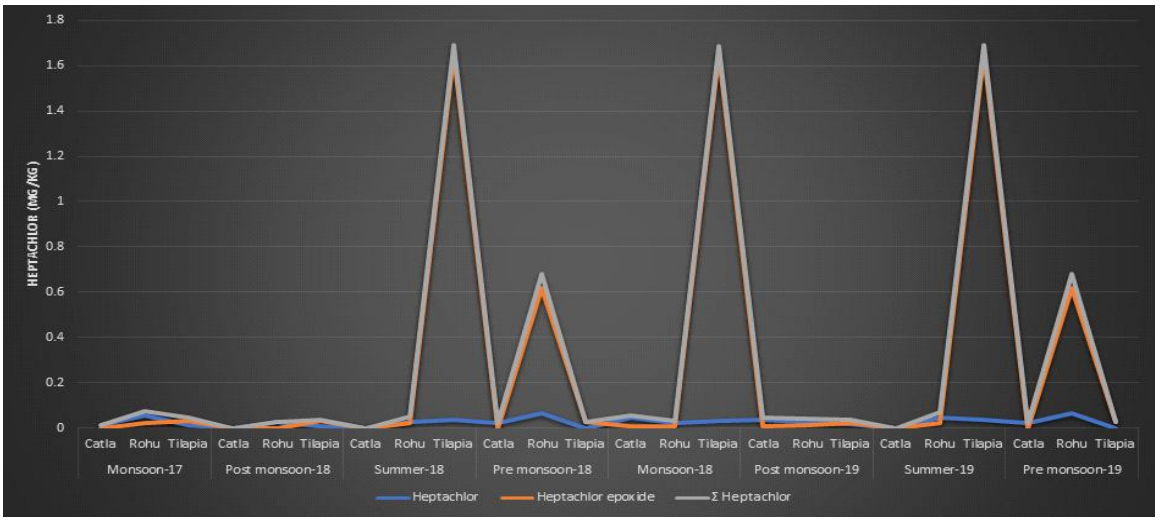

Fig 2: Seasonal variation of Heptachlor compounds in fish samples of Thamirabharani river.

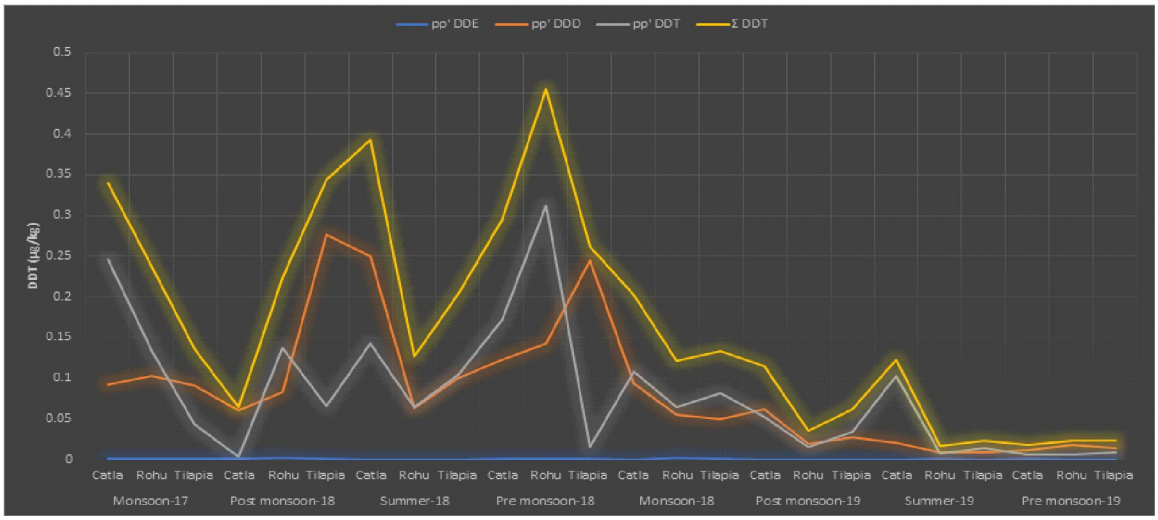

Fig 3: Seasonal variation of DDT compounds in fish samples of Thamirabharani river.

station V. The lowest concentration of endosulfan II (BDL) was observed in mullet fishes during post monsoon seasons at station V. The concentration of endosulfan sulphate varied between 0 to 1.484 µg/kg in all fishes. The maximum concentration of endosulfan sulphate (1.484 µg/kg) was observed in mullet fishes during post monsoon seasons at station V. The lowest concentration of endosulfan sulphate (0 µg/kg) was observed in catla and milkfishes during summer and monsoon seasons. Among all the endosulfan compounds, the concentration of endosulfan I was found to be higher and it was observed in milkfishes during post monsoon seasons at station V. The seasonal variation of endosulfan in fish samples of Thamirabharani river is given in Fig 5.

Total BHC, total heptachlor and total DDT compounds

The accumulation of total BHC in fishes ranged from 0.0379µg/kg and it was high in station V. The total BHC accumulation was more in sardine during premonsoon season. The concentration of total BHC was found very less in estuary region and the value observed was 0.0058 µg/kg. The maximum concentration of alpha BHC was observed as 0.4878 µg/kg in all stations except station V during monsoon season. The minimum concentration of beta BHC was recorded in station V and the value recorded was 0.0117 µg/kg during post monsoon season. The range of beta BHC was observed from 0.0117 to 0.3784 µg/kg in all the stations. The lowest concentration was recorded in milkfish (0.117 µg/kg) during post monsoon season in station V. The range of gamma BHC was observed from 0 to 1.245 µg/kg in all stations.

The maximum concentration of gamma BHC (1.245 µg/kg) was observed in milkfish and sardine during premonsoon seasons at station V. The lowest concentration of gamma BHC was observed in mullet and sardine fishes at station V.

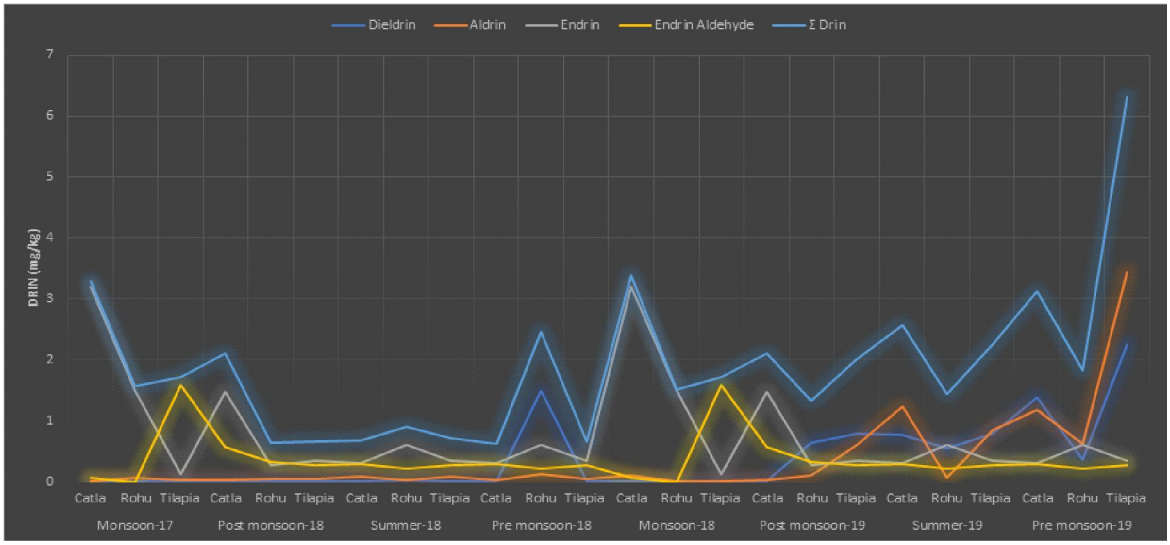

Fig 4: Seasonal variation of Drin compounds in fish samples of Thamirabharani river.

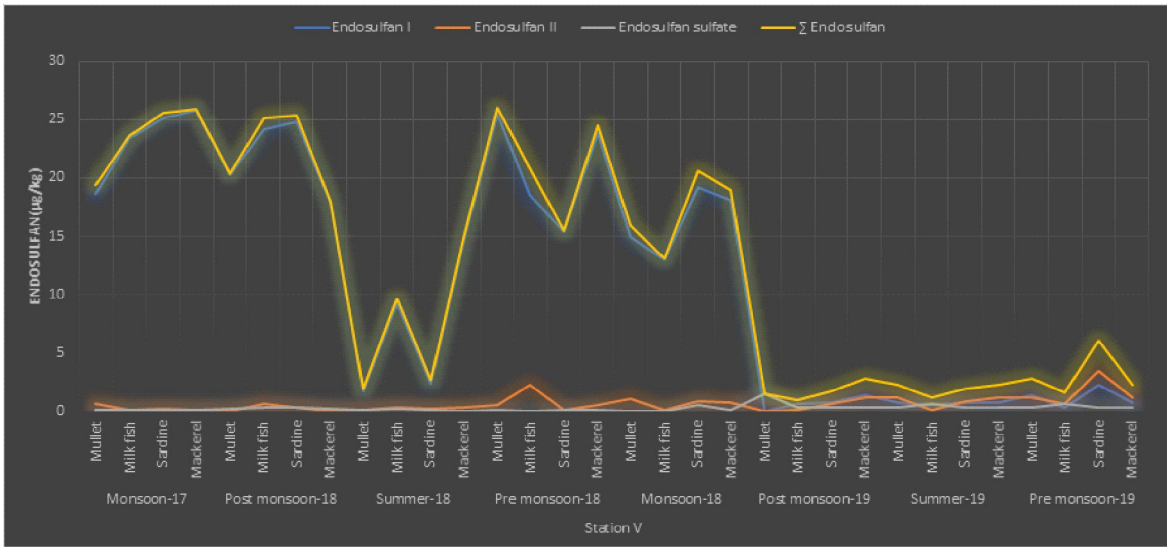

Fig 5: Seasonal variation of Endosulphan compounds in fish samples of thamirabharani river

Table 1: ANOVA table for OCPs in fishes in different stations of Thamirabharani river different seasonal period.

	OCPs	P > 0.05 level			
		Between compounds	Interpretation	Between seasons	Interpretation
Station I			**OCP in fish**		
1.	BHC	7.09E-05	Significant difference between compounds	7.63E-21	Significant difference between seasons
2.	Heptachlor	1.96E-05	Significant difference between compounds	0.010068	Significant difference between seasons
3.	Endosulfan	0.000165	Significant difference between compounds	2.4E-09	Significant difference between seasons
4.	DDT	0.001897	Significant difference between compounds	1.36E-11	Significant difference between seasons
5.	Drin	0.000183	Significant difference between compounds	8.06E-10	Significant difference between seasons
Station II					
6.	BHC	7.09E-05	Significant difference between compounds	7.63E-21	Significant difference between seasons
7.	Heptachlor	1.96E-05	Significant difference between compounds	0.010068	Significant difference between seasons
8.	Endosulfan	0.000195	Significant difference between compounds	8.01E-10	Significant difference between seasons
9.	DDT	1.07E-05	Significant difference between compounds	2E-11	Significant difference between seasons
10.	Drin	0.001897	Significant difference	1.36E-11	Significant difference between seasons
Station III					
11.	BHC	7.09E-05	Significant difference between compounds	7.63E-21	Significant difference between seasons
12.	Heptachlor	1.96E-05	Significant difference between compounds	0.010068	Significant difference between seasons
13.	Endosulfan	0.000165	Significant difference between compounds	2.4E-09	Significant difference between seasons
14.	DDT	0.000808	Significant difference between compounds	3.82E-11	Significant difference between seasons
15.	Drin	0.000243	Significant difference between compounds	2.68E-09	Significant difference between seasons
Station IV					
16.	BHC	7.09E-05	Significant difference between compounds	7.63E-21	Significant difference between seasons
17.	Heptachlor	1.96E-05	Significant difference between compounds	0.010068	Significant difference between seasons
18.	Endosulfan	0.000165	Significant difference between compounds	2.4E-09	Significant difference between seasons
19.	DDT	0.001897	Significant difference between compounds	1.36E-11	Significant difference between seasons
20.	Drin	0.000182	Significant difference between compounds	8.07E-10	Significant difference between seasons
Station V					
21.	BHC	2.28E-09	Significant difference between compounds	1.35E-12	Significant difference between seasons
22.	Heptachlor	8.03E-09	Significant difference between compounds	0.002151	Significant difference between seasons
23.	Endosulfan	5.31E-08	Significant difference between compounds	1.82E-14	Significant difference between seasons
24.	DDT	8.74E-11	Significant difference between compounds	2.8E-05	Significant difference between seasons
25.	Drin	3.72E-05	Significant difference between compounds	4.97E-12	Significant difference between seasons

The concentration of delta BHC ranged from 0.0058 to 0.6314 µg/kg in all the stations. The highest concentration of delta BHC (0.6314 µg/kg) was observed in mullet fishes during summer season in station V. The lowest concentration (0.0058 µg/kg) was recorded in sardine fishes during postmonsoon and summer seasons in station V.

Among fishes, tilapia accumulated more drin compound than rohu and catla at all station. Rohu accumulated 0.0526 ug/kg of endrin and rohu accumulated 0.346 ug/kg of endrin during monsoon. Bosnir *et al*. (2007) reported total endrin of 7.0 ug/kg in cyprinids in Sava river, Europe. Choudhury *et al*. (2013) indicated the presence of endrin similar to these findings. In this case of aldrin, maximum of 3.4486 ug/kg of aldrin was detected in Sardine fishes at Punnakayal estuary (Station V) during monsoon. Malik *et al*. (2009) also reported OCPs (2.58 to 22.56 ug/kg) with aldrin (0.3 to 7.84 ug/kg) as the predominant one in the Gomti river, Bhuvaneshwari and Babu Rajendran (2012) also reported maximum concentration of 128 ng/g of aldrin in fishes from Kaveri river. The accumulation of aldrin residues in fish tissues was largely dependent on fish species following a pattern, rohu> tilapia> catla because of its fat content. The presence of fat is a major factor for bioaccumulation of OCPs, due to their lipophillic nature (Zhao *et al*., 2009)

Among fishes, rohu accumulated maximum of 0.4014 to 0.605 ug/kg of DDT in station IV and V respectively. Dhananjayan and Muralidharan (2010) reported OCPs in 156 fishes sample from Kaveri river. The average concentration of DDT ranged between 0 and 0.605 ug/kg. Bhuvaneshwari and Babu rajendran (2012) also reported 2.8 ug/g of DDT in fishes from Kaveri river. The low occurrence of DDT in the presence study is mainly due to their rapid degradation with living organisms.

CONCLUSION

To conclude, relatively high levels of endosulfan in the Thamirabarani source water could certainly affect the safety of drinking water and in long term affect the aquaculture fishes and agriculture crops grown in this region. During the monsoon season, river runoff and other industrial pollution may increase the concentration of endosulfan, in the upper and lower reaches of the Thamirabarani river. The application of endosulfan in the tea estates and rubber plantations in the upper reaches of the Manimuthar was found to be the major cause for their presence and suitable action needs to be taken by the regulatory agencies.

REFERENCES

Anastassiades, M., Lehotay, S.J., Stajnbaher, D. and Schenck, F.J., (2003a). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. Journal of AOAC International. 86(2): 412-431.

Anastassiades, M., Mastovska, K. and Lehotay, S.J., (2003b). Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides. Journal of Chromatography A. 1015(1): 163-184.

Bosnir, J., Puntari, D., Klari, M., Matijana, G., Mirjana, L.K., (2007). Organochlorine pesticides in freshwater fish from the Zagreb area. Archives of Industrial Hygiene and Toxicology. 58: 187-193.

Buvanaeshwari, R., Rajendran, R.B., (2012). Induction of DNA damage and mutation in GADD45β gene due to environmentally relevant concentrations of organochloride pesticides and heavy metals using Zebra fish (*Danio rerio*). International Journal of Environmental Research. 7(1): 219-224.

Choudhury, B.H., Das, B.K. and Chutia, P. (2013). Evaluation of pesticide residues in fish tissue samples collected from different markets of Jorhat district of Assam, India. Inter. J. Sci. and Eng. Res. 4(12): 2286-2299.

Dhananjayan, V., Muralidharan, S., (2010). Organochlorine pesticide residues in inland wetland fishes of Karnataka, India and their implications on human dietary intake. Bulletin of Environmental Contamination Toxicology. 85: 619-623.

Kumarasamy, P., Govindaraj, S., Vignesh, S., Rajendran, R.B. and James, R.A. (2012). Anthropogenic nexus on organochlorine pesticide pollution: A case study with Tamiraparani river basin, South India. Environmental Monitoring and Assessment. 184(6): 3861-3873.

Malik, A., Ojha, P. and Singh, K. P. (2009). Levels and distribution of persistent organochlorine pesticide residues in water and sediments of Gomti river (India) - A tributary of the Ganges River, Environmental Monitoring and Assessment. 148: 421-435.

Mathur, S.C. (1993). Pesticides industry in India. Pesticide Information. 19: 7-15.

Norli, H.R., Christiansen, A. and Deribe, E. (2011). Application of QuEChERS method for extraction of selected persistent organic pollutants in fish tissue and analysis by gas chromatography mass spectrometry. Journal of Chromatography A. 1218 (41): 7234-7241.

Zhao, Z., Zhang, L., Wu, J. and Fan, C. (2009). Distribution and bioaccumulation of organochlorine pesticides in surface sediments and benthic organisms from Taihu Lake, China. Chemosphere: 77(9). 1191-1198.