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Contamination profile of organophosphorus pesticides (OPPs) residues in water, sediments and fish tissues of the Thamirabarani river system, South India

U. Arisekar, Robinson Jeya Shakila*, Geevaretnam Jeyasekaran, R. Shalini and S. Sundhar
Department of Fish Quality Assurance and Management, Fisheries College and Research Institute, Tamil Nadu Fisheries University, Tuticorin 628 008, Tamil Nadu, India
jeyashakila@gmail.com

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Abstract

This study was undertaken to examine the extent of organophosphorus pesticides (OPPs) contamination in water, sediments and fish samples collected from the five sampling sites of Thamirabarani river viz. Manimuthar (site 1), Tirunelveli (site 2), Srivaikuntam (site 3), Authoor (site 4) and Punnakayal (site 5) following the standard protocol EPA 525.5 and AOAC 2007.01 QuEChERS using GC-MS. The concentration of OPPs in surface waters ranged from 0.01 to 13.74µg l^{-1}; sediments from 0.81 to 19.05µg kg^{-1}; and muscle of catla, rohu and tilapia from 0.01 to 1.89µg kg^{-1}.Disulfoton, methyl parathion, phorate and parathion were the predominant OPPs found in Thamirabarani river system. Disulfoton (2.41µg l^{-1}) and phorate (1.69µg l^{-1}) were detected nearly the MRLs of 3µg l^{-1} and 2µg l^{-1}, respectively in the water at site 4 is a concern of safety. The levels of OPP residues found in the muscles were below the maximum residual limits set by Joint committee on Food and Agriculture Organization and World Health Organization. A positive correlation existed between fat content and OPPs levels in fish muscle tissues. The results indicated that OPPs contamination is not prevalent in the Thamirabarani river basin, phorate and disulfoton levels need to be tested routinely to have a check on threshold levels. Accumulation of OPPs in sediments was relatively high and in accordance with the organic matter, except site 5, which have saline alkaline soil.

Keywords: OPPs, Thamirabarani river, QuEChERS kit, GC-MS, Fishes, Bioaccumulation, Methyl parathion, MRLs.

Introduction

Non-point pollution of shallow water, groundwater and sediments is an important environmental problem worldwide. Pesticide is one among the non-point sources, which are used by farmers to protect the crops from microbes, insects, rodents and molds. There are several classes of pesticides that include organophosphorus (OPPs), organochlorine (OCPs), carbamates and Synthetic pyrethroid (SPP). OPPs are extensively used in agriculture and in aquaculture sector to control the protozoan and metazoan parasites. In India, OPPs and OCPs are used extensively used in agriculture sector[1]and about 50% of the insecticides used in India comes under this chemical group[2]. But, OCPs are now-a-days prohibited due to their persistence nature in the environment, biomagnification effects and toxicity to living organisms. OCPs are now replaced by OPPs[1,3].

They are used indiscriminately by farmers due to the lack of awareness about their ill effects on the environment. They enter the aquatic environment through the rainfall runoff from agriculture fields[4,5,6], direct entry from spray operation, industrial effluent[7], atmospheric deposition[7], leaching process, soil erosion, inappropriate disposal methods[1] and sewage treatment plant[8,9]. They accumulate in sediment, surface and underground waters. They also have the potential for bioaccumulation in animal and plant tissues[6]. Their wide spread application has led to their accumulation[10,11]. In the aquatic system, the presence of particulate organic matter easily absorbs the pesticides due to their octanol-water partition co-efficient (K_{ow})[6].

OPPs mainly inhibit cholinesterase activity that causes functional disturbance in central nervous system (CNS)[6]. The ill effects of OPPs include short term implication like abdominal cramps, fatigue, headaches, diplopia, nausea, ocular disturbances, dermatopathies, while long term effects include respiratory failed, depression, nerve defects, prostate cancer, leukemia and infertility[10]. One of the major source of human exposure to environmental contaminants is through fish consumption[11]. The most striking effect of some of the pesticides is their ability to concentrate in the fatty portion of fish tissues[10]. Many international standard regulatory organizations such as the United States Food and Drug Administration (USFDA), Codex Alimentarius Commission (CAC), World Health Organization/ Food and Agriculture Organization) (WHO/FAO), and European Union (EU) as well as many countries have issued their own pesticide maximum residual limits (MRLs) in the international trade[13]. In India, Food Safety Standard Authority of India (FSSAI) has issued the guidelines for the maximum residual limit for OCPs and OPPs in water, fruits and vegetables but not specifically for fish and fishery products.

Few monitoring data are available on the presence of OCP residues in water and sediments of Tamil Nadu, India[3,4,14,16,17]. Thamirabarani is a perennial river situated in the Southern part of Tamil Nadu originating from Pothigai Hills of Western Ghats and being discharged into the Bay of Bengal in the Gulf of Mannar region[3]. It is the main source of drinking water in Tirunelveli and Thoothukudi of Tamil Nadu. Besides, it provides water supply to irrigation and other industrial units of these districts. There are reports on the use of pesticides in this region by the farmers to protect the crops, which account for about 82 tons in 2013-14[18]; and the presence of OCP residues in the surface water of the Thamirabarani river system[3,14].As, there was no report on the presence of OPP residues in water, sediments and fish muscle of Thamirabarani river system, this study was aimed at assess the occurrence of OPP residues in sediments, surface water and fish obtained from different sites and to discuss their contamination profile in system.

Materials and methods

Chemicals and reagents: A mixture of nine OPPs standard solution containing disulfoton, methyl parathion, parathion, sulfotep, phorate, dimethoate, thionazin, o,o,o-triethyl phosphorothioate and famphur was obtained from Accu Standard, Inc. USA. Chemicals of QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) clean-up kit such as primary secondary amines (PSA), carbon-18 (C_{18}), graphitized carbon black (GCB) and magnesium sulfate ($MgSO_4$) were individually purchased from Sigma-Aldrich, Bangalore, Karnataka, India. Chemicals of extraction kit contains sodium acetate (NaOAc) and calcium chloride ($CaCl_2$) were purchased from Sigma-Aldrich (Bangalore, Karnataka, India). C_{18} cartridge column was obtained from Varian Pvt., Ltd. USA. 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).

Study area: Thamirabarani is a perennial river situated in the southern peninsular part of India in the geographical location between 8°30' and 9°15'N latitude and 77°10' and 78°10'E longitude. The river receives large quantities of agriculture run-off and urban and rural sewage effluents throughout the year. Five sampling sites, *viz.* Manimuthar (site 1), Tirunelveli (site 2), Srivaikuntam (site 3), Authoor (site 4), and Punnakayal (site 5), were chosen within the catchment right from the origin to the mouth of the river and their geographical locations are given in Table-1. First four sampling sites were freshwater regions; while site 5, was an estuarine region.

Samples: Water samples were collected in pre-cleaned sterilized glass screw-cap bottles to avoid microbial degradation of some of the OPPs. Sediment samples were collected using Peterson Grab sampler from the river bed and placed in sterile polyethylene bags. Water and sediments samples were brought to the laboratory in iced condition and kept 4°C in a chilled cabinet until further analysis.

Table-1: Sampling sites chosen in Thamirabarani river basin and their geographical location.

Sites	Name of the Place	Latitude and longitude
1	Manimuthar	8.6535° N, 77.4134° E
2	Tirunelveli	8.7139° N, 77.7567° E
3	Srivaikuntam	8.6312° N, 77.9125° E
4	Authoor	8.6227° N, 78.0695° E
5	Punnakayal	8.4955°N, 78.1191° E

Freshwater fish, *viz*. catla (*Catla catla),* rohu *(Labeo rohita*) and tilapia (*Oreochromis mossambicus)* were collected from the first four sampling sites and marine fishes*viz.* Indian mackerel (*Rastrelliger kanagurta*), emperor bream (*Lethrinus nebulosus*), barracuda *(Sphyraena barracuda)* and Indian oil sardine (*Sardinella longiceps*) were collected from site 5, in sterile polyethylene bags.Uniform sizefish samples were collected to avoid the possible error by reason of the size variation. In the laboratory they were washed in potable water and dissected to remove the flesh separately and kept frozen at - 20°C in the deep freezer until further analysis.

Extraction of pesticides from surface water: Pesticides from surface water samples were extracted by standard liquid-liquid partition method EPA 525.2[19]. For the analysis, 1L water was filtered through the Whatman filter paper (No. 1) to remove debris and suspended materials. To the filtrate, 40-50mg Na_2SO_4 crystals were added and using 6N HCl to adjust pH < 2.0 for reducing the microbial degradation of some pesticides. Then, 10ml methanol was added and the entire content was passed through the C_{18} cartridge column (Varian Pvt. Ltd., USA) under vacuum. The pesticides adsorbed by C_{18} resins were eluted with 5ml ethyl acetate followed by 5ml dichloromethane from the column and collected in a test tube. From that, upper ethyl acetate layer was carefully removed using a micropipette and filtered through sodium sulfite (Na_2SO_3) crystals and concentrated to 1ml in a nitrogen gas evaporator before analysis by gas chromatography-mass spectrometry (GC-MS).

Extraction of pesticide from sediments and fish muscles: Pesticides from sediment and fish muscle were extracted as per AOAC 2007.01 using QuEChERS method[20,21]. For the analysis, 5g of homogenized sample was mixed individually with 15ml of 1% of acetic acid in acetonitrile in a centrifuge tube and vortexed well for 1min to maintain the pH between 5 and 7. To the content, 2ml hexane was added to separate the fatty layer to reduce the interference. Then, 6g $MgSO_4$ and 1.5g NaOAc were added, shaken vigorously for 1 min, and centrifuged at 3000xg

for 5min in a refrigerated centrifuge (Eppendorf 5804R, Hamburg, Germany) to facilitate the solvent partitioning and to improve the recovery of pesticides. From that, 4-5ml supernatant was taken in another centrifuge tube and kept at -20°C for 15min to enable fat deposition. 1.5ml of upper layer was taken, and to which, 150mg $MgSO_4$ and 100mg $CaCl_2$ were added, vortexed well for 1 min, and centrifuged again at 5000xg for 5min to increase the solvent partitioning. Finally, 1ml supernatant was taken and added to QuEChERS clean-up kit, which contained 25mg PSA (to remove the sugars, fatty acids, and organic acids), 25mg C_{18} (to remove long-chain fatty compounds, sterols, and non-polar interference), 7mg GCB (to remove pigments, polyphenols, and other polar compounds without loss of planar pesticides such as HCB and terbufos) and 150mg $MgSO_4$ (to separate the solvent layer and improve the recovery of pesticides). The mixture was taken aback centrifuged at 9000xg for 5min. After the clean-up process, 1ml supernatant was taken for GC-MS analysis.

Gas chromatographic – mass spectrometry analysis: Pesticides were then analyzed by a GC-MS system (Trace 1300 and ISQ LT Single Quadrupole Mass Spectrometer; Thermo Fisher, Inc., Waltham, MA, USA) fitted with a TG-5MS column (30m×0.25mm×0.25µm). The injector temperature was set at 290°C. Gradient temperature programming was followed. The initial oven temperature was maintained at 90°C for 0.5min, which was then increased to 280°C at a rate of 8°C min^{-1} and again to 300°C at a rate of 15°C min^{-1} for 2.5min. The split flow and carrier gas flow were 50 and 1ml/min, respectively. The temperatures of transfer line and ion source were set at 290 and 250°C, respectively. Helium (99.995% purity) was used as a carrier gas. The mass spectrometry was used for identification and quantification of compounds and their isomers. The compounds were detected with four fragment ions from each compound by selected ion monitoring mode along with retention time (Table-2). For quantification purpose, calibration curves of six concentrations were drawn for each standard pesticide mix (1, 5, 10, 50, 100, and 250ppb).

Table-2: OPP compounds, Retention time (RT), Target/ qualifier ions *(m/z)* and Standard chromatogram with RT.

OPPs	RT	*m/z*
O,o,o-triethyphosphorothioate	6.74	93.0
Thionazin	13.81	107.0
Sulfotep	13.81	97.0
Phorate	15.07	121.0
Dimethoate	15.52	125.0
Disulfoton	16.82	142.0
Methyl parathion	17.70	109.0
Parathion	18.93	109.0

Crude fat analysis: Crude fat was analyzed determined by AOAC, 920.39 method[22]. Socplus apparatus (Pelican Equipments Pvt. Ltd., Chennai, Tamil Nadu, India) was used to extract the fat content from fish muscle. Dried fish sample (0.250±0.20) was placed in a thimble fixed in thimble holder and kept in a pre-weighed extraction flask. The extraction flask was placed in over the hotplates and below the thimble. Petroleum ether (boiling point: 40-60°C) was filled with 2/3 volume in the extraction flask. Extraction was done at 200°C for 2h. After the extraction, thimble was taken out of the solvent, the excess ether was carefully collected. The extraction, flask was dried at 102±2°C in a hot air oven for 30 min to evaporate the residual ether. The extraction flask was then allowed to cool in a desiccator at room temperature and the final weight was taken. The difference in the weights of flask in before and after gave the crude fat percentage.

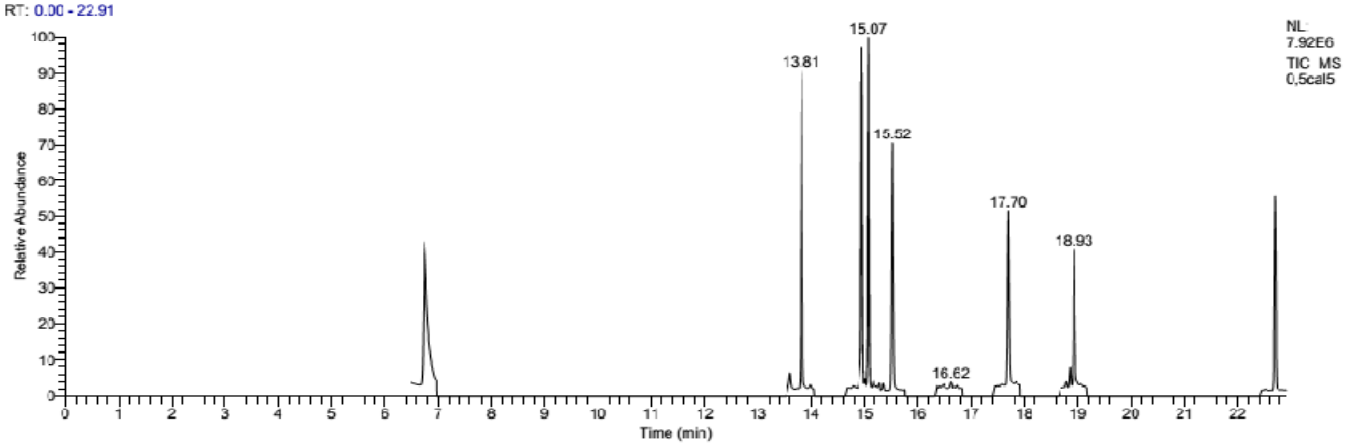

Figure-1:

Statistical analysis: All analysis was performed in triplicate. The average mean ± standard deviation was calculates using SPSS 16.0 for windows 10 (SPSS, Chicago, USA).

Results and discussion

Presence OPP residues in surface water samples: Out of nine OPPs analyzed, 8 OPPs were present in surface water samples. The total OPPs in water samples ranged from 1.01–13.74µg l^{-1}, with a mean concentration of 7.25µg l^{-1} (Table-3). Disulfoton, methyl parathion, parathion, and sulfotep were the most predominant OPPs found in water samples. Methyl parathion level was below the MRLs of 9µg l^{-1} set by World Health Organization, 2003 at all the sites[23]. The highest concentration of methyl parathion was recorded in site 4 (2.82µg l^{-1}), which is in the downstream region of the river. Disulfoton and parathion were also detected at concentrations of 2.41µg l^{-1} and 2.68µg l^{-1}, and these values were below the MRLs of 3µg l^{-1} and 10µg l^{-1}, respectively, set by National Health and Medical Research Council, Australia[24] (NHMRC, 2003) and WHO[23].

Parathion and methyl parathion residues were reported as the major OPPs in surface water of the river Wuchuan, South East China[25]; and river Llage of Nigeria[26]. However, Leena et al. have not detected methyl parathion in the surface shallow waters of river Ganga, India[1]. Solomon et al. have recorded the levels of parathion and methyl parathion as 470µg l^{-1} and 500 µg l^{-1}, respectively in river Llage, Nigeria[26]; which were several folds (165times) higher than the levels found in river Thamirabarani. In river Kali of India, the level of parathion in the surface water was in the range of 0.13 to 3.17ng l^{-1}; which was comparatively lower than the concentration of 0.12 to 2.68 µg l^{-1} recorded in river Thamirabarani[2].

The concentrations of phorate and dimethoate were slightly higher at site 4, with the concentrations of 1.69µg l^{-1} and 1.32 µg l^{-1}, respectively and these values were below the MRLs of 2 µg l^{-1} and 20µg l^{-1}, respectively set by Canadian Environment Health Directorate (CEHD, 2003)[27]. The presence of dimethoate at 3.86ng l^{-1} and disulfoton at 22.86ng l^{-1} in river Wuchaun of SE China was reported by Zhang et al. which was quit less than the concentrations detected in Thamirabarani. Solomon et al. had not detected in dimethoate in the water samples both in summer and rainy seasons. Other OPPs like o,o,o-triethyl phosphorothioate and famphur were not detected in the water samples[26]. Zhang et al. have also reported the absence of o,o,o-triethyl phosphorothioate and famphur in the surface shallow water collected from different stations of river Wuchuan, China[25].

There are several factors that affect the contamination of OPPs in natural resource water. Minerals, salts, photosensitizers, temperature, pH, radiation, metal cations, and micro-organisms have been reported as some important factors[13,28]. The presence of OPPs in the downstream region of the river at sites 3 and 4 are mainly due to farmland runoff and due to the discharge of untreated drainage waste water into the river. The extensive cultivation of paddy, banana, ground nut, green gram, sorghum, ragi, pulses, cotton, and ginger indownstream region of Thamirabarani river basin is identified as the source of these pesticides.

The site 3, Srivaikuntam is a nearby residential area situated in the middle of paddy field, coconut grove, ginger and green gram crops, which receives large amounts of agriculture run-offs from the fields[29]. The site 3, is judicially using the river water and discharging untreated waste water into the river. Similarly, the site 4, Authoor is called as green town, which is surrounded by Thamirabarani river, and also surrounded with paddy and banana fields.

Table-3: Presence of OPP residues (µg l^{-1}) in water.

OPPs	Site 1	Site 2	Site 3	Site 4	Site 5	Range	Mean	SD
O,o,o-triethyl phosphorothioate	NF	NF	0	0.12	NF	NF- 0.12	0.02	0.0848
Thionazin	0.01	0.18	0.22	0.94	0.6	0.01-0.43	0.39	0.3754
Phorate	0.05	0.3	0.36	1.69	0.78	0.05-1.69	0.63	0.645
Sulfotep	0.14	0.48	1.32	1.73	0.96	0.14-1.73	0.92	0.6363
Dimethoate	0.11	0.89	1.15	1.32	1.22	0.11-1.32	0.93	0.4894
Disulfoton	0.26	1.42	2.02	2.41	1.72	0.26-2.41	1.56	0.8168
Methyl parathion	0.32	0.61	1.41	2.82	2.58	0.32-2.82	1.54	1.128
Parathion	0.12	0.32	2.12	2.68	0.94	0.12-2.68	1.23	1.1223
Famphur	NF	NF	0.12	0.15	NF	NF-0.15	0.05	0.0212

NF- Not Found.

As these sites 3 and 4 are high potential agriculture areas, the usage of high level of fertilizers and agrochemicals to increase the production of agri-foods, can ultimately affect the aquatic food chain by way of bioaccumulation. Untreated drain of towns like Ambasamudram, Tirunelveli and Srivaikuntam, also affects the water quality of downstream region. Many industries have come up in the bank of the river surrounding.

Although none of the OPPs were recorded in excess than the guideline values, presence of fairly higher concentrations of phorate and disulfoton, close to the MRLs is a concern of safety. Hence, all these above facts have to taken into consideration, as the levels of some of the OPPs *viz*. disulfoton, methyl parathion and phorate are of safety concern in site 4, Authoor region of the river Thamirabarani.

Presence of OPP residues in sediments: The total OPPs present in sediments of Thamirabarani river basin ranged from 0.81–19.05µg kg^{-1}, with the mean concentration of 9.93µg kg^{-1} (Table-2). The level of OPPs was high in site 4 (19.05µg kg^{-1}) and low in site 1 (0.81µg kg^{-1}). Methylparathion was high at site 4, Authoor, coinciding with their high concentration detected in water. Therefore, this zone is the utmost polluted site in Thamirabarani river basin. High levels of different OPPs (> 3 µg kg^{-1}) were also recorded in sites 3 and 4, as the region are close to paddy fields and banana groves. The presence of OPPs in sediments indicates the extensive application of pesticides in these regions. The highest concentrations of methyl parathion and disulfoton were found in site 4 with values 3.96 µg $kg^{-1}$and 4.31 µg kg^{-1}, respectively, while, the concentration of parathion was slightly higher in 3.12µg kg^{-1} at site 4. In river Ganga of India, high concentration of methyl parathion was reported in sediments (82.93-458.02ng g^{-1}) by Leena et al. which was higher than the values obtained in this study. These parathion, methyl parathion and disulfoton were found to be the major insecticides applied in the paddy fields, banana groves, ground nut fields, ragi and pulses fields of this river basin.

The concentration of o,o,o-triethyl phosphorothioate, famphur and thionazin were found insignificant in the sediments. Earlier studies also indicated that these OPPs were at insignificant level in the sediments samples of river Wuchuan of China[25].OPP residues were more in the sediments of sites 3 and 4, which are potential agriculture areas, as discussed earlier. Besides, the agricultural run-offs, the presence of organic detritus matter can also accumulate OPPs in the sediments.

Besides, the presence of detritus organic matter in the sediments can also to accumulate OPPs residues depending on due to the complex process involving the partition co-efficient of OPPs and chemical properties of sediment (matrix) and pesticides[6,30]. The reason behind the accumulation of OPPs in sediments is that they contain high organic matter than the surface waters. The small differences noticed in the spread out of these OPPs at different sites could be due to the course of the river, which add the partial degradation of pesticides by microbial activities and environmental degradation in the sediments and also varying usage pattern of these pesticides in different regions of the catchment area[6].

At site 5, Punnakayal, the OPP levels were low, although the organic load was maximum. The high range of salinity and pH might have broken down the pesticides through hydrolysis process (Centre for Agriculture, Food and the Environment, Amherst, USA). However, no specific MRLs are available for the presence of OPP residues in the sediments prescribed by any regulatory agencies to examine the extent of contamination.

OPP residues in fish tissues: In general, OPPs present in fish muscle tissues were very low ranging from ND to 1.89µg kg^{-1} (Table-5), thanthose found in water and sediment. Methyl parathion, parathion and disulfoton were the major OPPs in the freshwater fishes *viz.* catla, rohu, and tilapia examined and their levels ranged between 0.01–1.89µg kg^{-1}, 0.05–1.65µg kg^{-1} and 0.02–1.21µg kg^{-1}, respectively. Most of the earlier studies have shown that methyl parathion and parathion were the most frequently identified OPPs in fish tissues. Also, the presence of o,o,o-triethyl phosphorothioate, thiazinon, famphur, disulfoton and dimethoate at very low levels similar to that earlier reported in fish tissues[11,13,28]. The presence of dimethoate, disulfoton, famphur, methyl parathion, o,o,o- triethyl phosphorothioate, parathion and phorate in fish samples aredue to the potential agriculture farmed activity in the cotton, maize, banana and potatoes planted areas and organic chemical used to control the agricultural production affected microbes and insects[28]. Maximum bioaccumulation of OPPs in fish tissues occurred in site 4, Authoor similar to the water and sediment samples.

Selective distribution of OPPs among the different fish tissues was also observed. The bioaccumulation of methyl parathion was higher in rohu (0.019-1.890µg kg^{-1}) than in catla (0.017-1.65µg kg^{-1}) and tilapia (0.018-1.01µg kg^{-1}). Particularly, the bioaccumulation was high at site 4 in rohu and catla tissues. The level of methyl parathion, however, never exceeded the MRL of 50 µg kg^{-}1set by Joint Committee of Food and Agriculture Organization and World Health Organization[31]. The presence of disulfoton ranged from 0.05-1.65µg kg^{-1}, with more bioaccumulation in rohu, followed by catla tissues. In none of the samples, disulfoton residues exceeded the MRL of 20 µgkg^{-1}set by CAC[32] and FAO-WHO.

Parathion was found at an appreciable level in the fish tissues (0.02 -1.21µg kg^{-1}); however, its level never exceeded the MRL of 100µg kg^{-1} set by FAO-WHO. In an earlier study carried out by Yahia and Elsharkawy, parathion and methyl parathion concentrations in the tilapia collected from Assuit city, Egypt were 0.6.38±0.96µg kg^{-1} and 18.50±0.62µg kg^{-1}, respectively, which were far greater than the levels found in Thamirabarani river. The other OPPs such as o,o,o-triethyl phosphorothioate, thiazinon and famphur were not found in significant amounts in fish tissues and their concentration were also lower than the MRL of 50µg kg^{-1} set by FAO-WHO[31] for above the mentioned

OPPs. However, Enbaia et al. have reported high concentration of o,o,o-triethyl phosphorothioate (1.85±0.2 µg kg^{-1}) and famphur (3.43±0.06µg kg^{-1})in yellow fin tuna and mackeral collected from Tripoli Fish market, Libya[28]. In this study, the maximum bioaccumulation of dimethoate recorded was 1.11 µg kg^{-1} in rohu tissues at site 4, Authoor and this level was far below the MRL of 50 µg $kg^{-}1$ set by CAC (2016)and FAO-WHO. According to Mahboob et al. dimethoate was the most predominant OPP in fish muscle samples collected from river Chenab of Pakistan[11]. But, in thefishes of river Thamirabarani, the dominant OPP is methyl parathion because of their large-scale application in the catchment area. The presence of lower levels other OPPs was mainly because of their less usage or rapid degradation potential. Marine fishes analyzed from site 5, did not accumulate significant levels of OPPs. Only in sardine, disulfoton was detected in slightly higher level (0.187µg kg^{-1}) than other marine fishes.

Table-4: Presence of OPP residues (µg kg^{-1}) in sediments.

OPPs	Site 1	Site 2	Site 3	Site 4	Site 5	Range	Mean	SD
O, o,o,o-triethyl phosphorothioate	NF	NF	0.009	0.014	NF	NF-0.014	0.01	0.0035
Thionazin	ND	0.19	0.22	0.62	0.38	NF-0.62	0.4	0.1968
Phorate	0.11	0.9	0.46	1.82	1.11	0.11-1.82	1.13	0.6531
Sulfotep	0.2	1.26	1.96	2.51	0.91	0.2-2.51	1.79	0.9
Dimethoate	0.09	1.21	2.87	3.32	1.56	0.09-3.32	2.58	1.3023
Disulfoton	0.17	2.16	3.22	3.96	1.45	0.17-3.96	2.87	1.4851
Methyl parathion	0.14	1.32	3.79	4.31	1.15	0.14-4.31	3.08	1.8085
Parathion	0.1	1.13	2.05	3.12	1.44	0.1- 3.12	2.2	1.1185
Famphur	NF	NF	0.004	0.01	NF	NF-0.1	0.007	0.0042

NF- Not Found

Table-5a: Occurrence of OPPs in fish muscle (µg kg^{-1}).

OPPs	Site 1			Site 2			Site 3		
	Catla	Rohu	Tilapia	Catla	Rohu	Tilapia	Catla	Rohu	Tilapia
O,o,o-triethylphosphorothioate	NF	NF	NF	0.009	NF	NF	0.009	0.01	NF
Thionazin	0.01	0.014	0.014	0.01	0.02	0.012	0.013	0.021	0.01
Phorate	0.011	0.02	0.05	0.059	0.125	0.048	0.55	0.52	0.36
Sulfotep	0.089	0.1555	0.0505	0.08	0.155	0.032	0.65	0.74	0.21
Dimethoate	0.013	0.0145	0.013	0.013	0.24	0.013	0.55	0.81	0.93
Disulfoton	0.051	0.074	0.095	0.174	0.164	0.187	1.18	1.31	1.06
Methyl parathion	0.0195	0.0195	0.019	0.017	0.019	0.018	1.14	1.57	0.86
Parathion	0.03	0.026	0.0245	0.10	0.31	0.21	0.89	1.15	0.64
Famphur	NF	NF	NF	NF	0.01	NF	0.01	0.02	0.01

NF- Not Found.

Table-5a: Occurrence of OPPs in fish muscle ($\mu g\ kg^{-1}$).

OPPs	Site 4			Site 5			
	Catla	Rohu	Tilapia	Mackerel	Emperor	Sardine	Barracuda
O,o,o-triethylphosphorothioate	0.0045	0.009	NF	NF	0.009	0.01	NF
Thionazin	0.04	0.07	0.012	0.010	0.018	0.012	0.014
Phorate	0.51	0.34	0.27	0.026	0.02	0.01	0.019
Sulfotep	0.70	0.85	0.44	0.042	0.035	0.024	0.034
Dimethoate	0.89	1.11	0.36	0.013	0.023	0.32	0.013
Disulfoton	1.21	1.65	0.92	0.077	0.083	0.178	0.095
Methyl parathion	1.65	1.89	1.01	0.021	0.019	0.17	0.018
Parathion	0.99	1.21	0.71	0.025	0.024	0.21	0.023
Famphur	0.02	0.034	0.019	0.01	NF	0.019	NF

NF- Not Found.

Bioaccumulation of OPP residues in fish tissues is relative to the enrichment of organic and inorganic compounds present in the water[13]. It also depends on the presence of persistent organic pollutants (POPs) in the surrounding environments, species, food web, feeding behavior, habitat, fat content, age, water solubility, degree of ionization, stability, and molecular structure and affinity of the compound in the tissues of organisms[6,33,34]. Bioaccumulation in fish can occur in two ways: aqueous uptake of hydrophilic compounds through the gill, and dietary uptake fromgastrictissue[34,35]. Biological and ecological characteristics, physiochemical properties of certain OPPs such as K_{ow} (water- octanol coefficient)[36,37] and K_d (sediment-water partition coefficient)[38]had contributed for the bioaccumulation of OPPs in fish tissues.

As the bioaccumulation of pesticides is largely dependent on fish species, the pattern observed in this study is: rohu > catla>tilapia. This pattern has got some relation with the fat content of the fish tissues (Table-6). Zhao et al. have reported that the presence of fat content is a key factor to determine bioaccumulation potential[6]. The presence of more fat depots in rohu tissue (16.67%) is therefore responsible for their higher bioaccumulation potential than in catla and tilapia tissues.

Table-6: Level of crude fat content (%) in fish muscles.

Name of the fish	Fat content*
Catla *(Catla catla)*	13.14
Rohu*(Labeorohita)*	16.67
Tilapia *(Oreochromis mossambicus)*	14.86

Note: * Dry weight basis

Conclusion

Based on the study undertaken to examine the extent of contamination of OPPs in water, sediment and fish samples of river Thamirabarani of India, it was found that Srivaikuntam and Authoor regions found in downstream regions was more polluted with the presence of most of OPPs in relatively high proportion. Sediments accumulated more OPPs than surface water and fish tissues, but no MRLs have been prescribed by regulatory agencies to estimate the extent of contamination. In the surface water, the amounts are of disulfoton and phorate are major safety concern; as their concentration are approaching towards the MRLs. Selective distribution of OPPs in different fish tissues was noticed exhibited a pattern:rohu> catla> tilapia, which was depend on the muscle fat content.

The fish inhabiting the Thamirabarani river basin are therefore safe for human consumption in terms of OPP concentration. However, strict vigilance measures have to be implements by the concerned authorities to curtail the presence of phorate and disulfoton in surface waters of downstream region of the river.

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