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Pollution Study of Pallickal River water Based on Pesticidal Compounds

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Abstract: ***Pallickal River is one of the smallest river of Kerala, it originate from the cliffs of 'Nellimukal' in Pathanamthitta. People are making use of this river water for their domestic use and agriculture. This river system is less studied by the scientific community. Influx of water into this river is mainly from nearby agricultural paddy fields, where intensive chemical fertilizers and pesticides are in use. The purity of water for portable and other domestic use is to be scientifically assessed. For this assessment pesticide analysis can be used to determine the purity status of the river water. The pesticide residue analysis of Pallickal River water revealed that, these chemicals pose a huge threat to this River. Among organophosphorous pesticides Malathione (4.08 mg / l) and Methidathione (2.644mg/l) reported highest concentration. Pyrithroid Cypermethrin (4.05 mg/l) Cyfluthrin- B (2.33 mg/l) Deltamethrin (2.38 mg/l) showed a slight increase in concentration. Carbamate pesticides, Oxamyl (0.918 mg/l) and Thiodicarb (1.97 mg / l) showed a high concentration among fungicides, Indofil (1.419 mg/l) and Hexaconazole (1.296 mg/l) showed highest concentration. Herbicide such as 2,4-D(2.39 mg/l) Oxyfluorfen (2.638mg/l) and Pendimethalin (2.186mg/l) showed highest concentration. The study revealed that the water from the river Pallickal is of moderate quality***

Keywords: Pallickal River, Pesticides, Herbicides, Purity assessment, Fungicides

1. Introduction

Pallickal River is one of the smallest river of Kerala it is originating from the cliffs of Nellimukal in Pathanamthitta district a small stream from the wetlands of 'Tengamam' joints the main river at 'Anayadi 'and flows through 'Panmana' and'Karunagappally'Panchayath and part of 'Anwarssery' People are making use of this river water for their domestic use and agriculture. This river system is less studied by the scientific community. Influx of water into this river is mainly from nearby agricultural paddy fields, where intensive chemical fertilizers and pesticides are in use. The purity of water for portable and other domestic use is to be scientifically assessed. For this assessment the pesticide analysis can be used as an indicator to determine the purity status of the river water.

The Pallickal River is a wet land origin river and the upstream segment of the river is passing through the settlement area. There is all the possibilities of anthropogenic pollution, which leads the habitat loss. As far as considering Kerala's agriculture sector, farmers are using a large amount of pesticide combinations to improve the yield and quality of the crop products.

Malathione is the common compound of Organophosphorus that widely used in Kerala farms, and the Carbofuran is the most common carbamate pesticides. Malathione, Parathione along with Endosulfan combination are common in vegetable gardens of Kerala. In Kerala, the river bank cultivation is a practice with heavy use of chemical fertilizers and pesticides during the summer season, and it lasts till the onset of Monsoon. The Monsoon rain brings all these compounds to river water and finally to river bed as sediments. Dilution may occur in sediments (Eger, 1974). This will cause a drastic effect on the food web of riverine ecosystem. The agro farming near the riparian ecosystem and the small scale industrial units near the Pallickal River are the major source of such pesticidal contaminations. Hence an attempt has been made to assess the pesticidal contamination of Pallickal River.

2. Methodology

2.1 Sampling

The samples were collected from the three segments of the Pallickal River. Monthly samples were collected from each segment sampling method outlined by Radtke (2005). The water samples were collected from 2013 June to 2014 May. Samples were collected in a 500 ml sterile glass bottle and chilled immediately using ice bags and brought to the laboratory and kept below 0^0C.

2.2 Analysis

Five samples were taken for analyzing pesticides and heavy metals. The organophosphorus pesticides were determined by Liquid- Liquid extraction and Gas Chromatography with flame photometric detector (Krsteska *et al.*, 2008). The carbamate pesticides were determined by High performance Liquid Chromatographic method (APHA, 2012). Herbicides were estimated by micro Liquid-Liquid extraction gas chromatographic method (APHA, 2012). The fungicides were estimated by SPME and Gas Chromatography with Electron Capture and Mass Spectrometric Detection method (Lambropoulou *et al.*, 2000).

2.3 Statistical Analysis

The statistical analysis and test of significance of differences were determined by Analysis of Variance (ANOVA)(SPSS.22). Descriptive statistics were done using Microsoft Excel.

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3. Results

3.1 Pesticides

3.1.1 Organophosphorous Compounds

Six Organo Phosphorous compounds were detected from the upstream, midstream, and downstream segments of Pallickal River. They were, Qunalphos, Dimethoate, Methyl Chlorphiriphos, Methidathione, Malathione, and Monocrotophos. Out of these six compounds Malathione was detected in trace amount from upstream and downstream samples. From upstream the Malathione detected with an average value of 4.086 mg/l with a standard deviation of 0.7764 (Table 3.1 A) and a mean value of 0.0488 mg/l with a standard deviation of 0.0296 (Table 3.1 A) from downstream segment.

From the both segment the leasts detected compound was Qunalphos with a mean value of 1.55 mg/l and Methylchlorphiriphos with a mean value of 0.0027 mg/l. (Table 3.1 A)

From midstream segment Methidathione showed the highest concentration with an average amount of 2.644 mg/l. The least detected compound from the midstream was Malathione with a mean concentration of 1.99mg/l

The trace of other pesticide like Dimethoate with a mean concentration of 3.266 mg/l in upstream, 2.42 mg/l from midstream and 0.03 mg/l from the downstream water was also detected. Methylchlorphiriphos had a detected sconcentration of 2.994mg/l from upstream and 2.55 mg/l from mid stream water. Monocrotophos pesticide was detected with a mean concentration of 3.564 mg/l from upstream, 2.464 mg/l from midstream and 0.015 mg/l from the downstream water. The one way ANOVA of Organophosphorus pesticides showed significant variation between sites (F= 60.60357; P<0.05) (Table 3.1 B)

Table 3.1: (A) Mean Concentration of Organohosphorus compounds from three segments of Pallickal River (Mean±SD)

Compound	Sites		
	Up stream	Mid stream	Down Stream
Qunalphos	1.55 ± 0.324423	2.348±0.169322	0.0178±0.021562
Dimethoate	3.266 ±0.428521	2.42±0.719062	0.03±0.043313
Methyl Chlorphiriphos	2.994 ±0.81356	2.55±1.248219	0.0027±0.001155
Methidathione	3.314 ±0.538776	2.644±0.541138	0.0053±0.001708
Malathione	4.086 ±0.776421	1.99±0.434799	0.0488±0.023618
Monocrotophos	3.564 ±0.747717	2.464±0.436039	0.015±0.013

Table 3.1 (B) ANOVA table of Organophoshorus compounds

Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Between sites	31.74255	2	15.87127	60.60357	6.52E-08	3.68232
Within Groups	3.928302	15	0.261887			
Total	35.67085	17				

3.1.2. Pyrithroids

Pyrithroids are highly toxic and quite expensive insecticides. They are widely using in Kerala farms. From the analysis of Pallickal River water five types of Pyrithroid compounds were detected. They were Cyfluthrin-B, Cyhalothrin, Cypermethrin, Deltamethrin and Fenvalerate.

From the upstream segment the Pyrithroid,Cypermethrin compound showed a higher concentration with average value of 4.05mg/l with a standard deviation of 0.7947.

Deltamethrin is the least detected compound with a mean value of 0.52 mg/l. Cyfluthrin- B detected from the midstream showed a higher average value of 2.998 mg/l with standard deviation of 0.6705.Cypermethrin were the least detected from the midstream with a mean value of 1.084mg/l. The downstream segment showed a higher concentration of Deltamethrin with an average value of 2.3856 mg/l and a standard deviation of 1.1962. The least detected was the Cypermethrin compound with an average value of 0.534 mg/l .(Table 3.2 A) The one way ANOVA of Pyrithroids showing no such significant variation between sites (F=0.55924; P>0.05) (Table 3.2 B)

Table 3.2: (A) Mean Concentration of Pyrithroids compounds from three segments of Pallickal River(Mean±SD)

Compound	Sites		
	Up stream	Mid stream	Down Stream
Cyfluthrin-B	2.53±0.656163	2.998±0.675033	1.48±0.497845
Cyhalothrin	2.99±0.512884	2.386±0.14758	0.5802±0.398368
Cypermethrin	4.054±0.79472	1.084±0.707163	0.534±0.434891
Deltamethrin	0.052±0.023875	1.878±0.468476	2.3856±1.09623
Fenvalerate	0.806±0.158051	1.574±0.46822	1.932±0.68889

Table 3.2: (B) ANOVA table of Pyrithroid compounds

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Site	1.446881	2	0.723441	0.55924	0.58585	3.885294
Within Groups	15.52337	12	1.293614			
Total	16.97025	14				

3.1.3. Carbamates

Trace amounts of Carbamate were only detected from the Upstream and midstream segments, there were five different compounds of carbamates detected. They were Aldicrab, Sevin, Carbofuran, Thiodicrab and Oxamyl.

From the upstream segment Oxamyl compound were detected with high concentration with an average value of 0.918 mg/l. From the midstream Thiodicrab showed a higher concentration, with a mean value of 1.97 mg/l and a standard deviation of 1.000. The least detected Carbamate from the upstream segment was the Aldicrab with a mean value of 0.006 mg/l and a standard deviation of 0.001. Sevin detected from the mid stream water with a least mean value of 0.4548 mg/l and a standard deviation of 0.5343. The one way ANOVA of carbamate concentration showed no such significant variation between sites
(F=4.763061; P>0.05) (Table3.3A and Table 3.3 B)

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Table 3.3: (A) Mean Concentration of Carbamate compounds from two segments of Pallickal River (Mean±SD)

Compound	Sites	
	Up stream	Mid stream
Aldicarb	0.0062±0.001924	1.298±0.443588
Sevin	0.058±0.021679	0.4548±0.534351
Carbofuran	0.488±0.296176	0.7074±0.443084
Thiodicarb	0.832±0.1499	1.97±1.000075
Oxamyl	0.918±0.095846	1.492±0.366497

Table 3.3: (B) ANOVA table of Carbamate compounds

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Site	1.31044	1	1.31044	4.763061	0.060631	5.317655
Within Groups	2.201005	8	0.275126			
Total	3.511445	9				

3.2. Fungicides and Herbicides

The water samples from the three different segments of Pallickal River water analysis revealed that the Fungicidal and Herbicidal compounds were only detected from the upstream and midstream segments of the River. Four different Fungicides and Six Herbicides were detected from these segments.

3.2.1. Fungicides

Coper sulphate , Trycyclozole, Hexalonazole and Indofil were the four different fungicidal compounds detected. Out of these Indofil had a maximum concentration with a mean value of 1.49 mg/l. From the upstream segment, Trycyclozole showed least mean concentration value of 0.060 mg/l and a standard deviation of 0.010512 from the upstream segment. Copper Sulphate with a mean concentration of 0.273 mg/l and Hexconazole with a mean value of 1.296 mg/l were also detected from the upstream water sample.

In midstream segment, Fungicidal concentration were high. Trycyclozole was detected with an average value of 0.258 mg/l, Hexaconazole the least detected with a mean value of 0.296 mg/l and a standard deviation of 0.02583. (Table 3.4 A) The one way ANOVA of Fungicide showing no such significant variation between sites (F=2.919963; P>0.05) (Table 3.4 B)

Table 3.4: (A) Mean Concentration of Fungicide compounds from two segments of Pallickal River (Mean±SD)

Compound	Sites	
	Up stream	Mid stream
Copper Sulphate	0.273±0.397223	0.135±0.104197
Trycyclozole	0.066±0.010512	0.258±0.057184
Hexaconazole	1.296±0.608547	0.0296±0.025832
Indofil	1.419±0.523492	0.2364±0.254253

Table 3.4: (B) ANOVA table Fungicide compounds

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Site	0.717003	1	0.717003	2.919963	0.13835	5.987378
Within Groups	1.473313	6	0.245552			
Total	2.190316	7				

3.2.2. Herbicides

Pendamethalin, Oxyfluorfen, Atrazine, Oxadiargyl, Glyphosphate, and 2-4-D were the major herbicidal compounds detected from the both segments of Pallickal River. From the upstream segment 2-4-D was the most traced compound with a mean value of 2.39mg/l and a standard deviation of 0.6814. Oxadiargyl was the least detected herbicidal compound with an average value of 1.53 mg/l and a standard deviation of 0.426. From the midstream segment Oxyflurofen showed high concentration with a mean value of 2.638 mg/l and the least detected was Atrazine with an average value of 1.07mg/l. (Table,3.5 A) The one way ANOVA of Fungicide showed no such significant variation between sites (F=0.858984; P>0.05)(Table 3.5 B).

Table 3.5: (A) Mean Concentration of Herbicide compounds from two segments of Pallickal River (Mean±SD)

Compound	Sites	
	Up stream	Mid stream
Pendimethalin	2.086±0.613254	2.186±0.704081
Oxyfluorfen	1.858±0.591244	2.638±0.927669
Atrazine	1.724±0.763433	1.073±0.136543
Oxadiargyl	1.534±0.426181	1.4138±0.463619
Glyphosate	2.322±1.141784	1.738±0.50047
2,4-D	2.39±0.681432	1.324±0.334933

Table 3.5: (B) ANOVA of Herbicide compounds

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Site	0.197941	1	0.197941	0.858984	0.37585	4.964603
Within Groups	2.304366	10	0.230437			
Total	2.502308	11				

4. Discussion

The water pollution is major threat to the survival of man on our planet. There are far reaching effects and consequences on living as well as non living environment. The pollution of natural is dangerous to organisms inhabiting in the streams, lakes and oceans. The organic wastes under the influence of bacterial action, depletes dissolved oxygen by consuming it for their biological oxidation reaction. The availability of good quality water is an inevitable feature for preventing water born diseases and improving quality of life

The Pallickal River is a wet land origin river and the upstream segment of the river is passing through the settlement area. There is all the possibilities of anthropogenic pollution, which leads the habitat loss. From this analysis agrochemical components are detected from all the segments. Pesticide residue analysis of Pallickal River water revealed that, these chemicals pose a huge threat to Pallickal River water.

The major sources of the agrochemicals are from the river side vegetable cultivations during the summer seasons. The

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monsoon rain brings fungicides and pesticides from the Rubber plantations of Nellimukal, Thengamam and Anayadi to Pallickal River. The main reason for the high concentration of copper in water is the use of Bordeaux mixture in rubber plantations nearby.

5. Summary and Conclusion

The water analysis of Pallickal River revealed that it is polluted with agro- chemicals like, Herbicides and Organo-phosphorus Peaticides .The presence of Pesticides like Malathione, Dimethoate, Methylchlorophirins etc are detected with heavy concentration. Carbamates like Aldicrab, Thiodicrab, Oxamyl were also detected along with Herbicides like 2-4-D and some Fungicides. Thus from the study it is concluded that the river is degrading with agrochemicals and it is high time to take remedial measures to protect the river and makes the water portable.

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