Residue Analysis of Organochlorine Pesticides in Water and Sediments in the Retting zones of Kadinamkulam Estuary, South India

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Abstract
In India, almost all organochlorine pesticides (OCPs) have been banned but some farmers and industries are still using it for agricultural purpose. The present study has been performed for determination of the range of different types of organochlorine pesticides in the water and sediments samples of Kadinamkulam estuary, South India. For the analysis, water and sediment samples were collected from the six selected stations including five coir retting zones and non-coir retting area of the estuary.

Water samples were extracted and analyzed for the determination of pesticide residues (α, γ and δ BHC, Aldrin, DDT, DDE, Hepatochlor, Endosulphan) using Gas chromatograph with an ECD detector. The study reveals that the concentrations of all pesticides studied in sediment samples and in water samples are above the guideline values for drinking water quality[10].

Keywords: ASE, GC-ECD, Kadinamkulam lake, Organochlorine pesticides.

Introduction

Pesticides are chemicals used to kill or control pests. They are classified according to their chemical class or intended use. OCP residues enter aquatic environments through effluent release, discharges of domestic sewage and industrial wastewater, atmospheric deposition, runoff from agricultural fields, leaching, equipment washing and disposal of empty containers and direct dumping of wastes into the water systems[13]. Organochlorine pesticides have environmental impacts that are usually on non-target organisms. Organochlorine pesticides when applied on a certain area such as farm settlements usually reach a destination other than their target. This is especially from runoffs into aquatic systems. Wind is also a factor that carries such pesticides into pastures, communities, towns and villages affecting unsuspected species[4,6].

Various activities such as farming, fishing, forestry, construction, mining, urban development and land pollution occurring in or near the watershed of a reservoir could bring about water quality problems and disruption in fish[2]. Chlorinated organic pesticides will disappear from the water with secondary mechanisms such as absorption on sediment, biological breakdown by microflora and fauna and absorption by fish through gills, skin and feeding. They are poorly hydrolyzed and slowly biodegrade in environment. Therefore, these compounds are persistent in food chains and are readily accumulated in animal tissues. Fish absorb these compounds directly by water or by ingesting contaminated food.

In particular, organochlorine insecticides are highly stable under different environmental conditions and persistent nature and chronic adverse effects on wildlife and humans[1]. The presence of pesticides in water (particularly organics that is aromatic chlorinated hydrocarbons) impacts objectionable and offensive taste, odours and colors to fish and aquatic plants even when they are present in low concentrations[3]. The toxicity of pesticides could be acute and chronic. There is growing evidence on cancer, neurological damage, endocrine disruption and birth defects arising from exposure[11]. The determination of OC residues in sediments and water may give indication of the extent of aquatic contamination and accumulation characteristics of these compounds in the tropical aquatic biota that will help in understanding the behaviour and fate of these persistent chemicals[5]. The present study was carried out for monitoring the presence of residues of organochlorine pesticides in water and sediment of Kadinamkulam estuary.

Material and Methods

The Kadinamkularn estuary lying in the southern part of Kerala, South India (Lat $8^0$35' - $8^0$40'N; Long 76°44' - 76°51'E) is the largest of its kind in Thiruvananthapuram district connected with the Anchuthengu Kayal in the north and the Veli Kayal in the south. This temporary estuary has no direct connection with the Arabian Sea, but seasonally it becomes connected through the opening of the sand bar at Perumathura. Kadinamkulam lake is the major coir retting area in South Kerala. Retting of coconut husk is basically a biological process involving the release of a variety of biochemical compounds and also produces organic wastes and hydrogen sulphide. This retting activity may also the cause of contamination of the Kadinamkulam estuary. Water samples were collected from six selected stations including five coir retting zones S1 (Chilambil), S2 (Perunguzhi), S3 (Kadinamkulam), S4 (Kotarakiri), S5(Madanvila) and non coir retting area Perumathura (S6) in Kadinamkulam lake (Fig. 1) in clean one liter screw caped glass bottles. The samples were carried to the laboratory on the same day after sampling and were acidified to pH 2.5 with concentrated HCl to inhibit biological activity. Then the water samples were filtered to remove sand and debris and stored in the refrigerator at temperature between 0 to 4°C prior to extraction.

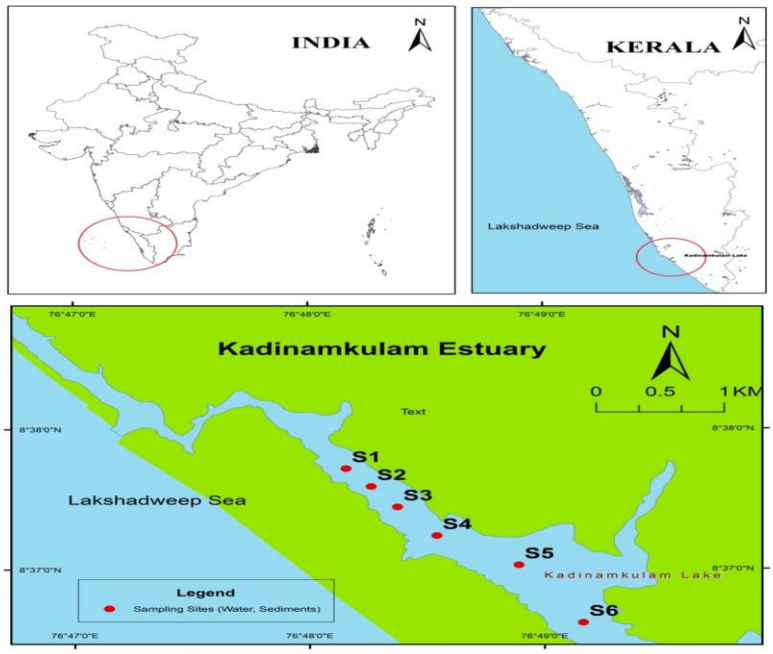

Fig. 1: Location map of the Study area

Sediment samples were collected from the six selected stations in Kadinamkulam estuary by scooping the top 1 to 5 cm using Van Veen grab sampler. After collection, the samples were stored in an ice packed cooler and kept in the refrigerator at 4^{o}C. Pebbles, shells and other substances were manually removed. For the analysis, the organochlorine pesticides in water were extracted using liquid - liquid extraction (LLE). Filter 500 ml water sample and pour into 2 liter separating funnel. For the first LLE, the mixture of 100ml n-hexane and dichloromethane (1:1 v/v) was added and shaken vigorously for 2 min before 2 phase separation.

The water phase was drained from the separating funnel into 1000 ml beaker. The organic phase was carefully poured into glass funnel containing 20 g of anhydrous sodium sulphate followed by the second and third LLE, the water phase was poured back into the separating funnel to re-extract with 50 ml of the same solvent mixture. The extract obtained from the water samples was relatively clean, no emulsions were obtained during the extraction and no further purification was necessary. The extract was concentrated under a rotary evaporator and then analyzed with gas chromatograph equipped with electron capture detector (GC-ECD, Thermo-Trace GC 800).

For the extraction of organochlorine pesticides from the sediment samples, 10 g homogenized sample was weighed and extracted in the Accelerated Solvent Extraction System (ASE- Thermo 150) using hexane- acetone mixture (9:1 v/v). This extract is poured into glass funnel containing 20 g of anhydrous sodium sulphate and then it was made up to 50 ml using the same solvent. 1µL of purified extract was injected to the gas chromatograph with a ECD detector. Quantitative analysis was conducted with a gas chromatography (Thermo- Trace GC 800) with ECD detector and nitrogen as the carrier gas. The column used for separation of OCP was packed column with 30m length. The nitrogen carrier gas was with constant flow and pressure, inlet splitless, injection temperature at 250^{o}C and detector temperature at 300^{o}C. For the analysis, standard mixture organochlorine pesticide was purchased from Sigma Aldrich (CRM47426).

Results and Discussion

Kadinamkulam lake is surrounded by farm lands. A large amount of insecticides and pesticides are used by farmers in agriculture fields which can enter the lake through running water and canals. Also, garbage and waste water are poured in the lake by inhabitants. Also Kadinamkulam lake is the major coir retting area in South India. All of these factors may lead to the contamination of Kadinamkulam lake. Table 1 shows the results obtained from the analysis of the water samples indicating the levels of contamination of the water body by organochlorine pesticides (OCPs) while table 2 shows the concentration of organochlorine pesticides residues in sediment samples.

The results of the study showed that eight organochlorine pesticides α, γ and δ BHC, aldrin, DDT, DDE, Heptachlor and Endosulphan were identified in the selected stations from the study area. This means that the pollution of OCPs in Kadinamkulam estuary is ubiquitous. The total OCPs in sediment samples were varied from 0.29 ppm (Endosulphan) in Perumathura (S6) to 1.16 ppm (Heptachlor) in Madanvila (S5). The highest concentration of heptachlor (1.16 ppm) was identified in station 5 Madanvila, the coir retting area. In the study area, six organochlorine pesticide residues (α-BHS, Aldrin, DDT, DDE, Heptachlor and Endosulphan) are identified in water samples from the estuary. The concentration varied from 0.011 ppm (Endosulphan) in

Perumathura (S6) to 0.035 ppm (Heptachlor) in Madanvila (S5). The guideline value and toxicity of the organochlorine pesticides according to WHO[10] are given in the table 3.

The organic carbon content in the sediment samples collected from the Kadinamkulam estuary varied from 1.81 to 3.42 % (Fig. 2). Retting or coconut husk is one of the principle sources of organic pollution in the Kadinamkulam estuary due to coir retting activity producing organic substances. The accumulation of such organic compounds during the retting process contributed for the high percentage of organic carbon in the retting zones. The high content of organochlorine pesticide residues in the estuary sediments may be due to the accumulation of it over years. The characteristic of the organochlorine pesticides to be adsorbed on the organic matter enables their persistence and detection in the aquatic ecosystem[7].

Organocholrine pesticides have strong affinity for suspended particulate matter and one of their main sink is thought to be lake sediments. Therefore, the determination of organochlorine pesticides in sediment samples can provide valuable records of aquatic contamination[14]. In general, the concentration of organochlorine pesticides in the water was lower sediments because these pesticides are lipophilic and are not soluble in water. This fact can ease the accumulation of organochlorine pesticides in micro-organisms.

Table 1
Organochlorine pesticide content in estuary sediments

OC pesticide (ppm)	Stations					
	S1	S2	S3	S4	S5	S6
α –BHC	0.60	BDL	BDL	BDL	0.74	BDL
γ –BHC	BDL	0.77	BDL	BDL	BDL	0.83
δ -BHC	BDL	BDL	BDL	0.40	BDL	BDL
Aldrin	0.62	BDL	BDL	BDL	0.34	BDL
DDT	BDL	BDL	0.87	BDL	BDL	1
DDE	BDL	BDL	BDL	0.62	BDL	BDL
Heptachlor	BDL	BDL	BDL	1.06	1.16	BDL
Endosulphan	BDL	BDL	BDL	BDL	BDL	0.29

BDL- Below Detectable Limit

Table 2
Organochlorine pesticide content in estuary water

OC Pesticide (ppm)	Stations					
	S1	S2	S3	S4	S5	S6
α –BHC	0.0179	BDL	BDL	BDL	BDL	BDL
Aldrin	BDL	BDL	0.0214	BDL	BDL	BDL
DDT	0.0192	BDL	0.0178	BDL	BDL	BDL
DDE	BDL	BDL	BDL	BDL	0.0156	BDL
Endosulphan	BDL	BDL	BDL	BDL	BDL	0.0111
Heptachlor	BDL	BDL	BDL	0.0292	0.0356	BDL

BDL- Below Detectable Limit

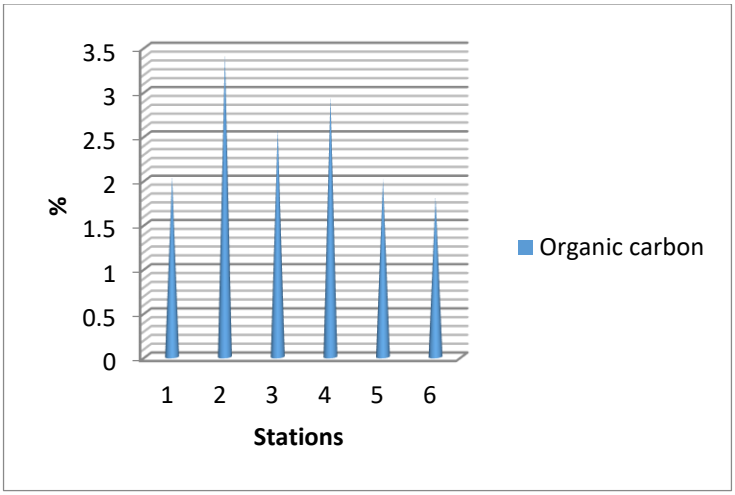

Fig. 2: Organic carbon content in the sediment samples

Table 3
Guideline values for different Organochlorine Pesticides in Drinking water

OC Pesticides	Nature	WHO Guide line value for drinking water quality	Toxicity
Aldrin	Persistent	0.00003 ppm	Central nervous system, liver, cancer
BHC	Persistent	0.002 ppm	Carcinogenic
DDT	Persistent	0.001 ppm	Carcinogenic and liver disease
Endosufan	Persistent	0.0001 ppm	Kidney, Central nervous system
Heptachlor	Persistent	0.00003 ppm	Central nervous system and the liver

Source: WHO, 2011 Guidelines for drinking water quality[10].

The lower levels of pesticide residues were detected in the stations of the water body than in the sediments and might be attributed to the fact that the input of pesticides in water is a function of suspended particulate concentrations, where the residues were absorbed and transported. It also varies from season to season, depending on the rainfall events that control the activities of soil erosion and the amounts of suspended particulates during runoff[9]. Higher levels of pesticides in the sediments exist than in water because sediments are important sinks for various pollutants like pesticides which also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediments[6,8]. Sediments act as secondary contamination source after water in the ecosystem. Sediments are the principal reservoirs of environmental pesticides, representing a source from which residues can be released to the atmosphere, groundwater and living organisms[12].

Conclusion

This study detects the organochlorine pesticide residues in the Kadinamkulam estuary. The results of the study show that there exist different types of organochlorine pesticide residue in the water and sediments of Kadiamkulam estuary. The study reveals that all pesticides residues detected in sediment samples and water samples are above the guideline values for drinking water quality[10]. Monitoring of pesticides should be performed over a period of time and with a frequency that allows all seasonal events to be taken in to consideration. The contamination of lake water by pesticide residues from runoff can have greater impact on the aquatic ecosystem which may lead to deleterious effects on the aquatic organisms, especially fishes and in human's dependent on the water supply from the lake.

Kadinamkulam estuary is the major coir retting area, which is the main cause of the contamination of this lake. The study recommends that continued monitoring and by adopting the combination of policies such as restrictions in the usage and alterations in some of the agricultural management practices will bring a solution towards pesticide loading into aquatic system.

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