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Occurrence and Risk Assessment of Organochlorine Pesticides (OCPs) in Surface Water of Veeranam Lake, Tamil Nadu

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Abstract: ***The study aimed at assessing the levels of organochlorine pesticide (OCPs) residues in the surface water of Veeranam Lake, Tamil Nadu, South India and its effects on human beings and aquatic organisms. Pesticide residues were quantified using Gas Chromatograph Mass Spectrometer (GCMS) in Quadrupole analyzer on Electron Ionization (EI) mode. The measured environmental concentration (MEC) of OCPs in the water samples was taken for calculating the carcinogenic risk and ecological risk quotient (ErQ). The most commonly encountered organochlorine pesticides (OCPs) in surface water of Veeranam Lake were isomers of DDT (p, p'-DDD & o, p'-DDT) and HCH (α & β) compounds, aldrin, dieldrin and mirex. The mean concentrations of endrin exceed the permissible limit of Canadian guidelines for fresh water (CGFW). The results of the present investigation showed that the carcinogenic risk among local population through intake of water from Veeranam Lake is more likely due to presence of significant levels of aldrin and mirex. The result also demonstrated acute risk to aquatic animals as a result of high concentrations of aldrin and endrin. Even though the incidence percentage of DDT (p, p'-DDD & o, p'-DDT), HCH (α & β), aldrin, dieldrin and mirex were high, their mean concentrations are well below the international permissible limit (CGFW) except endrin. However, these minimal levels of aldrin and mirex were supposed to cause carcinogenic risk and ecological risk to humans and aquatic organisms respectively.***

Keywords: OCPs, Veeranam Lake, carcinogenic risk, ecological risk quotient

1. Introduction

Organochlorine pesticides are of great concern due to their occurrence in high concentrations despite their ban on production and usage[1]. Ever increasing number of organic compounds being detected in surface waters has raised concern about the contamination of precious water resources. It is impossible to monitor every substance that may be present in the surface water, but it is necessary to define major targets of interest for water resources protection by focusing on substances that might be able to enter the drinking water supply[2]. Several pesticides are being used in India both in agriculture and public health sectors[3]. Since water from the rivers and canals are much used for drinking purposes in India, hence becomes imperative to study the extent and magnitude of pesticides in the water bodies[4].

In India, the residues of chlorinated pesticides have been detected in almost all the segments of environment due to their extensive use in the past, which have shown potential to biomagnify/accumulate in animal tissue, human blood, adipose tissue and breast milk [5, 6, 7]. Many of these compounds are considered to act as environmental hormones, which disrupt reproductive cycles of wildlife and humans[8]. Since pesticides are lipophilic in nature, their cumulative accumulation at low concentrations in the fat tissues of mammal might pose potential hazards in the long run[9].

The aim of the investigation is to analyze OCPs in surface water of Veeranam Lake which is one of the largest lakes located in Cuddalore district of Tamil Nadu state, India. The lake has the water of 1, 100 mcft and covering an agricultural land area of 3885 hectares. It is the major source of irrigation water for agriculture and also main drinking water sources for Chennai the capital city of Tamil N adu state. Nearly 180 MLD of water is supplied from Veeranam to Chennai city. Few studies have assessed occurrence of pesticide in the Indian lakes[10, 11]. Hence, this study assesses the risk of pesticide exposure to human and aquatic organisms through water from Veeranam Lake.

2. Materials and Methods

Chemicals and Solvents: Solvents (hexane, acetone) were purchased from Qualigens Fine Chemicals Pvt Ltd, India and were of HPLC grade. Anhydrous Sodium Sulphate was purchased from Himedia Laboratory Pvt. Ltd., India. Florisil SPE cartridge (Strata FL-PR Florisil 170µm, 80A, 1000 mg/6ml) was imported from Phenomenex, USA.organochlorine pesticides standards were procured from Accu Standard, USA.

Sample Collection: Samples were collected at 10 different locations in Veeranam Lake. High density polyethylene plastic containers (1L capacity) were washed with tap water, distilled water, ultrapure water and air dried before collection of water samples. All the samples were

transported to the laboratory using ice boxes. The water samples were stored at 4^0C.

Extraction of pesticides from surface water: One litre of the well mixed samples was taken in a 2 L separating funnel.30g of NaCl was added to it to facilitate the separation. The samples were extracted twice with 50ml of hexane and the hexane layer was collected. The extract was passed through sodium sulfate to remove the moisture content and condensed using rotary evaporator to 1ml and then purified using a column packed with florisil. The packed column was pre rinsed with 5ml of acetone and 15ml of n-Hexane. The elution was subsequently carried out using 7 ml of 2% acetone in n-Hexane. The eluent was condensed to 1ml for GCMS analysis.

Instrumentation & QA/QC: The samples were analyzed in GCMS (QP 2010 Shimadzu Corp, Japan) equipped with capillary column DB-1 (30m long, ID 0.32mm) and 5% methyl phenyl silicone. From stock solution of organochlorine pesticides standard containing cocktail of 17 pesticides, 200 ppb (200 ng/ml) of working standard was prepared. For the standard calibration, eight different concentrations from 5ng/ml to 200ng/ml were prepared. All standards showed a linear range from 5 ppb to 200 ppb. The coefficient (R2) values ranged from 0.9746 to 0.9985 for 8 concentrations levels. The limit of detection (LOD) as 3S varied from 0.69 to18.23 ng/ml (3S) for OCPs.

Carcinogenic risk Assessment: The carcinogenic risk of pesticides through water from Veeranam Lake was assessed. The measured concentration of OCPs was taken for calculating the risk. Slope Factor (SF) for the risk-dose model was used to estimate the probability of a cancer under a particular exposure scenario.

$$\text{Carcinogenic Risk} = \frac{\text{OSF} \times C_w \times IR_w \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}}$$

Where, C_w is concentration in water; EF is exposure frequency (365 days/year); ED is the exposure duration (70 years), equivalent to average life time; IR_w is daily water ingestion rate (Adult: 95th percentile – 2 L/day: 50th percentile-1.4 L/day; Child: 95 percentile – 1.08 L/day: 50th percentile – 0.38 L/day); BW is body weight (adult-70 kg; child – 30 kg); AT is the average exposure time (Cancer risk-70 years x 365 days/year: noncancer risk-30 years x 365 days/year); OSF is the oral carcinogenic slope factor (mg/kg/day);

Ecological Risk Assessment: The measured environmental concentrations (MEC) of pesticides were used for assessing ecological risk quotient (ErQ). Effective concentration (EC50) or Lethal concentration (LC50) values were used for the calculation of the PNEC [PNEC = (LC50 or EC50) / assessment factor].

Ecological Risk Quotient (ErQ) = MEC/ PNEC

3. Results and Discussion

The mean, range and incidence percentage of OCPs in water samples from Veeranam Lake are represented in Table 1. The water samples collected from Veeranam lake were analyzed for 17 different OCPS Viz., Hexachlorocyclohexane (α, β & γ-HCH), Cyclodiene (aldrin, dieldrin and endrin), heptachlor, hexachloro-benzene (HCB), trans-Chlordane, cis-Chlordane, mirex and metabolites of DDT (p, p'-DDE, o, p'-DDE, o, p'-DDD, p, p'-DDD, o, p'-DDT, p, p'-DDT). Except cis-Chlordane, p, p'-DDE, o, p'-DDE, p, p'-DDD and p, p'-DDT all other compounds were detected. The incidence percentage of p, p'-DDD, o, p'-DDT, α-HCH, β-HCH, heptachlor, aldrin, dieldrin and mirex were high in water samples collected from ten different locations of Veeranam lake. The total OCPs (Σ-OCPs) concentration in water samples were in the range 2.75 – 501.8 ng/L.

The mean concentration of α, β & γ-HCH in Veeranam Lake were 3.34, 1.7 & 9.2 ng/L respectively. According to Canadian Guidelines (CGFW) for freshwater the permissible limit for γ-HCH is 10 ng/L. Only one location (V8: 90 ng/L) in the Veeranam Lake has shown about nine fold higher concentration than the Canadian guidelines. Amaraneni (2006) reported the maximum concentration of γ –HCH (118 ng/L) in the Kolleru lake, India. In Veeranam lake, the mean concentration of both α–HCH (29 ng/L) and γ –HCH (90 ng/L) were lower than levels reported by Amaraneni (2006). In the present investigation only p, p'-DDD & o, p'-DDT were detected and their mean concentrations were 0.8 ng/L & 0.25 ng/L respectively. The presence of DDD & DDT shows fresh input OCP residues to the lake. The permissible limit of total DDT in freshwater was 1 ng/L (CGFW). The concentrations detected in water samples of Veeranam lake were much lower than the international guidelines except for one location (V3) which showed 7.2 ng/L. There is also evidence that o, p'-DDT disrupts the development of the female reproductive tract, thereby impairing the quality of the eggshells produced by the bird once it matures[12].

The average concentrations of HCB in Veeranam Lake was 0.04 ng/L. Xue *et al.* (2005) observed a mean concentration of 12.4 ng/L of HCB in the Guanting reservoir, China. Average concentration of HCB detected by Yang *et al.* (2007) in the rivers and lakes of Yunnan Plateau, China were 1700 ng/L and 110 ng/L, respectively. The mean concentration of heptachlor (4.4 ng/L) in the present investigation is lower than some of the earlier reports which were 181 ng/L in the Kucuk Menderes River in Turkey[15] and 104 ng/L in the Tonghui River, Beijing[16]. The V8 location exhibited elevated concentration (44 ng/L) than the CGFW permissible limit of 10 ng/L.

The detection frequencies of chlorinated cyclodienes such as aldrin and dieldrin were higher in water samples from Veeranam lake whereas the endrin was rarely detected. Aldrin and Dieldrin are closely related organochlorine pesticides. When aldrin is applied in the field, it is rapidly broken down to dieldrin[17]. The mean concentration of aldrin, dieldrin and endrin were 2.8, 1.7 and 50 ng/L

respectively. Amaraneni (2006) reported 11.2 ng/L of dieldrin in the Kolleru Lake, India The average levels of cyclodiene compounds aldrin, dieldrin and endrin were detected in the water samples from Lake Burullus, Egyptian Mediterranean Sea were 56, 29.4 and 37 ng/L[11]. The concentrations of aldrin and dieldrin in the present study were low compared to the earlier studies except endrin. The permissible limit in freshwater proposed by CGFW for aldrin, dieldrin and endrin are 4, 4 and 2.3 ng/L respectively.

The chlordanes (cis and trans isomers) detected in the surface water have been very low, while those found in suspended solids and sediments were always higher[18]. In accordance to this, only trans-Chlordane was detected yet very rarely. The mean concentration was 0.19 ng/L which is negligible compared to permissible limit (6 ng/L) of CGFW and trans-Chlordane in the water samples of Guanting Reservoir, Beijing (7.2 ng/L) [13]. This is the first report of mirex in the surface water of Indian rivers. The average concentration was 7.95 ng/L with highest concentration in V4 location (43 ng/L). The incidence percentage was also high. The higher concentration of mirex may be due to deposition from non-point sources. Mirex was sold under the name Dechlorane, is also used as a fire retardant in plastics, rubber, paint, paper, and electrical goods.

Carcinogenic Risk: Lifetime risks of 10^{-6} are considered acceptable for carcinogens in drinking water[19]. Aldrin and mirex exceeded the acceptable risk level in surface water from Veeranam Lake (Table 2) and may pose carcinogenic risk to the people. The calculation of carcinogenic risk also revealed that risk was higher for child than adult. Drinking water intake per kg of body weight is highest for child and decreases with increasing age, resulting in higher doses of drinking water contaminants among children[20]. The average (50^{th} percentile) and the maximum (95^{th} percentile) water consumption showed higher variation in carcinogenic risk.

Ecological Risk Quotient: The ecological risk for pesticides in Veeranam Lake was assessed (Table 3). According to USEPA, the level of concern for aquatic animals, the acute risk is 0.5 and chronic risk is 1.0. The acute risk for aquatic plant is 1.0. Endrin exceeded 1.0 indicating that the possibility of chronic risk to aquatic animals. The ErQ of Mirex (0.35) was closer to 0.5 that may pose acute risk to fish. The results of the present study revealed that pesticides cause higher risk to zooplankton and fish as reported by Hela *et al.* (2005) and Vryzas *et al.* (2009).

The overall results showed that the detected levels of aldrin and mirex in the surface water of Veeranam Lake pose threat to both humans and aquatic organisms. The study also showed the incidence of almost all OCP residues in V8 location where the human activities such as bathing, washing and fishing are more common. Since, Veeranam Lake is the reservoir of drinking water supply the quality of water must be regularly monitored to prevent the risk to the non-target population.

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Table 1: Range, Mean and incidence percentage of OCPs (ng/L) in the surface water of Veeranam Lake

OCPs	Range (ng/L)	Mean (ng/L)	Incidence Percentage (%)
α-HCH	ND-29	3.34	40
β-HCH	ND-8.4	1.7	40
γ-HCH	ND-90	9.2	20
HCB	ND-0.4	0.04	10
Heptachlor	ND-44	4.4	10
Aldrin	ND-14.2	2.8	50
Dieldrin	ND-4.8	1.7	60
Endrin	ND-501	50.1	10
trans-Chlor	ND-1.99	0.19	10
p, p'-DDD	ND-5.9	0.8	40
o, p'-DDT	ND-1.3	0.25	40
Mirex	ND-43	7.95	60

Table 2: Carcinogenic Risk (CR) of OCPs through drinking water from Veeranam Lake

OCPs			Child		Adult	
	Mean Concentration (ng/L)	OSF/ mg/Kg/day	50^{th} percentile	95^{th} percentile	50^{th} percentile	95^{th} percentile
α-HCH	3.34	6.3	2.7×10^{-7}	7.6×10^{-7}	4.9×10^{-7}	7×10^{-7}
β-HCH	1.7	1.8	3.9×10^{-8}	1.1×10^{-7}	7.1×10^{-8}	1×10^{-7}
γ-HCH	9.2	1.1	1.3×10^{-7}	3.6×10^{-7}	2.4×10^{-7}	3.4×10^{-7}
HCB	0.04	1.6	8.1×10^{-10}	2.3×10^{-9}	1.5×10^{-9}	2.1×10^{-9}
Heptachlor	4.4	4.5	2.5×10^{-7}	7.1×10^{-7}	4.6×10^{-7}	6.6×10^{-7}
Aldrin	2.8	17	6×10^{-7}	1.7×10^{-6}	1.1×10^{-6}	1.6×10^{-6}
Dieldrin	1.7	16	3.4×10^{-7}	9.8×10^{-7}	6.3×10^{-7}	9.1×10^{-7}
Chlordane	0.2	0.35	8.9×10^{-10}	2.5×10^{-9}	1.6×10^{-9}	2.3×10^{-9}
p, p'-DDD	5.9	0.24	1.8×10^{-8}	5.1×10^{-8}	3.3×10^{-8}	4.7×10^{-8}
Mirex	7.95	18	1.8×10^{-6}	5.2×10^{-6}	3.3×10^{-6}	4.8×10^{-6}

Table 3: Ecological Risk Assessment of OCPs through water from Veeranam Lake

OCPs	Toxicity Levels			Assessment Factor (AF)	PNEC (µg/L)			MEC (µg/L)	ErQ		
	Phyto plankon	Zoo plankton	Fish		Phyto plankon	Zoo plankton	Fish		Phytoplankon	Zooplankton	Fish
γ-HCH	0.8*	0.8*	21*	10	0.08	0.08	2.1	0.009	0.113	0.113	0.004
HCB	2**	0.02**	30**	10	0.2	0.002	3	0.00004	0.0002	0.02	0
Heptachlor	26.7**	52**	7**	100	0.27	0.52	0.07	0.0044	0.016	0.008	0.063
Chlordane	338**	28.4**	2.9**	1000	0.34	0.028	0.003	0.0002	0.0006	0.007	0.067
Aldrin	66**	30**	2.6**	1000	0.07	0.03	0.003	0.003	0.043	0.1	1
Dieldrin	100**	79.5**	1.2**	50	2	1.6	0.024	0.002	0.001	0.0013	0.083
Endrin	NA	0.57**	0.06**	100	-	0.006	0.0006	0.05	-	8.33	83.33
Mirex	NA	1000**	23**	1000	-	1	0.023	0.008	-	0.008	0.35
o, p'-DDT	30*	8*	0.23*	50	0.6	0.16	0.005	0.0013	0.002	0.008	0.26