Pesticide pollution in and around Thirumeni Lake, Thiruvarur District, Tamil Nadu, India.

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Abstract

Pesticide residue analyses were carried out in and around Thirumeni lake, Thiruvarur District, Tamilnadu, India. At least 240 MT of fertilizers such as urea, DAP, etc., and about 3300 litres of pesticides such as monocrotophos, metacid, endosulfan, ekalux, caroban, and karathae (synthetic pyrethroid) and 1.6 kg of Folidal dust (Methyl parathion) are being applied in the immediate catchments and drainage areas of the lake every year. The water samples had detectable amounts of HCH isomers, metabolites of DDT, alpha and beta-endosulfan, aldrin, dialdrin, heptachlor, heptachlor epoxide, enorin, enorin aldehyde and methoxychlor. Total pesticide residue in the lake water was 1040.565 ng/l. The residues of endosulfan sulphate, DDD, dialdrin and endrin were at below detectable levels. The bore well water collected from near by villages of Thirumeni lake had detectable amounts of alpha-HCH, alpha-endosulfan, and PP-DDE . Total pesticide residues in them ranged from 12.5 to 167.89 parts per trillion . The muscles of fish collected from the lake had detectable amounts of α–BHC, β–BHC, γ- BHC, dieldrin, heptachlor, hept-epox, endrin, endrin aldehyde, DDT, DDE, DDD, endosulfan-I, endosulfan–II and endosulfan sulphate

Key wors: BHC, DDT,HCH isomers, pesticide residues, pollution

INTRODUCTION

Agriculture is one of the important occupations of the people in the catchments and "ayacuts" of Thirumeni lake, Thiruvarur District, Tamilnadu, India. With the advent of green revolution agriculture and the drive towards more crop production, this area along with other areas of the country has seen the use of excessive amounts of fertilizers and pesticides. The organochlorine pesticides commonly occur in waters that have been affected by agricultural discharges. Several of these pesticides are bioaccumulative and relatively stable, as well as toxic or carcinogenic, thus they require close monitoring (APHA, 1995).

Edwards (1973) has stated that once the insecticides get released, they move in the direction of flow of water. The persistence of some pesticides in the environment cþoupled with repeated or multiple uses of the different chemical agents to increase their effectiveness (Macek, 1975) can result in hazardous effects on aquatic species. Increased pesticide concentration can kill eggs and larvae of bivalve molluscs (Davis, 1961) kill or immobilize fishes (Westman and Compton, 1960; Butler *et al.*, 1986), and decrease the productivity of phytoplankton populations (Kumar *et al.*, 1996; Srivastava and Vidyarthi, 2002). The disruption of the ecological balance in the ecosystem due to pesticide pollution results in affecting food chain organisms and affects the productivity of the entire ecosystem in aquatic courses.þ Biologically these pesticides exhibit the phenomenon of Biomagnification and these factors have far reaching consequences in the aquatic system.þ þIn aquatic media, the bioconcentration factor or "BCF" has been defined as the ratio of substance concentration in an organism to concentration in water (Murty, 1986). Bioaccumulation was defined as accumulation in a species from all sources (food, water etc.) and biomagnification was defined as concentration in trophic level representative. These have been used to "back calculate" an acceptable concentrations in varioþus exposure media (Murty, 1986).

The pesticide pollution affects adversely the growth and survival of commercial aquatic resources also (Hold, 1973; Johnson, 1973). Pesticide contamination of aquatic environment reduces the fish production. þEstimates of economic loss of fisheries have been up to $15 million per year (EPA, 1973). Other costs from toxicant pollution include suppressed shoreline property values, recreation loss, and water treatment costs (Srivastava and Vidyarthi, 2002).

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Repeated application of DDD (a pesticide related to DDT) at rates ranging from one part per 17 million parts water to one part DDD per 50 million parts water in the 46,000 acre Clear lake, 100 þmiles north of San Francisco, California to control gnats has eliminated a 1000 pair breeding colony of Western Grebes due to reproductive failure in their body (Rudd, 1964). Heptachlor at 1.5 to 2 pounds granular application per acre in parts of Alabama and Louisiana has resulted in severe to complete destruction of Frog, Turtle, Snake and Lizard populations (Rudd, 1964).

The farmers in the present study area (i.e. living around Thirumeni lake) are þmostly illiterates as far as knowledge regarding the consequences of agrochemicals is concerned aggravating the situation. Along with the harm the agrochemical cause to the farmers and the consumers of produced crops, into also affects the lake near by, adversely. So, analysis of pesticide residues in the lake water in essential to evaluate the impacts of agriculture pollution near by on this lake ecosystem.

STUDY AREA

The Thirumeni Lake

Thirumeni lake is one of the major freshwater habitats and resources of old Thanjavur District, Tamil Nadu, Southern India . After trifurcation of the old Thanjavur District it now comes under the Thiruvarur District. The lake extends from 10° 33′ 28" to 10° 34′ 30.9" N and from 79° 26′ 17.7" to 79° 27′ 54.1" E.

Pesticide Residue Analysis

Pesticide Residue Analysis in Water Sample

Water samples collected randomly from the lake and deep bore wells in the villages nearby were analyzed for the presence of pesticide residues.

Totally 2-3 litres of water samples were collected using glass or plastic containers from lake during December 2001. Water samples extracted with methylene chloride – n – hexane mixture and after cleaning the residues were taken in – n – hexane for analysis through Gas Chromatography. This method was applicable to acid-stable organo-chlorine compounds. The limit of detection for various insecticide residues was 0.001-0.005 mg/l. The insecticide residues in the given tube were extracted with 150ml ethanol under mild pressure exerted by nitrogen gas.

The extract was partitioned thrice with 100, 100 and 50ml portions of dichloromethane: hexane (15% v/v) in a 1000ml separatory funnel in the presence of saturated sodium chloride solution. The organic layer was pooled and dried by passing through anhydrous sodium sulphate, evaporated to near dryness and taken in 5ml of hexane for final determination. Chemito model 3800 Gas chromatograph equipped with Ni63 Electron Capture Detector (ECD) and 2.0m long and 2mm. I.d. coiled glass column packed with 1.5% OV 17+1.95% QF 1 on gas chrom Q was used with the following operating conditions.

Temperature°C – column 180; injection 220; detector base 240′ detector source 246.

Carrier gas flow – nitrogen @ 30 ml / min; chart speed – 25 cm/hr; Aliquot injected – 1 µ1

The amount of residues was measured by comparing the sample response with the response of the standards by suing the formula.

Where,

Hs - Peak height of the sample

$$\text{Residues} \quad \frac{Hs}{Hstd} \times \frac{M}{M1} \times \frac{V}{V1}$$

Hstd - Peak height of the standard

M - Quantity of standard injected in ng.

M1 - Mass of the sample in ‘g’ volume of the water in ml

V - Volume of the final extract in ml

V1 - Quantity of the sample injected in µ1

Pesticide Residue Analysis in Fish

The processing for pesticide residue analysis in fish constituted the following phases.

a. Sample dissection

b. Grinding

c. Extraction

d. Column-clean up and condensing

e. Sample Analysis – GC-ECD.

Sample Dissection

The fish samples collected were placed in fresh polythene covers and stored in deep freezer till the time of dissection. Fish samples were dissected and the muscle was taken for pesticide analysis.

Grinding

About 10g of the homogenate fish muscle sample was ground with anhydrous sodium sulphate and the blend mixture was packed in a thimble (13cm long x 3cm dia. Whatmann chromatography paper) and kept in desiccator overnight before extraction.

Extraction

The desiccated thimble was loaded on the Soxhlet extractor and the sample was extracted with 250ml of pesticide grade Hexane (Merck) for a period of 6 hrs. The extractant was condensed in a rotary flask evaporator to a specific aliquot (3-5ml).

Column Clean-up and Condensation

The condensed aliquot was passed through a column packed with silica gel (60-120 mesh) and eluted with 250ml of 4:1 ratio of hexane and acetone.

The collected eluent was condensed in a rotary flask evaporator and stored in freezer at 20°C till analysis with Gas Chromatography.

Table 1. Data on Agriculture Pollution at Thirumeni lake catchment areas.

S. No.	Pollutant	Annual Use
1	Fertilizers (Urea, DAP, etc.,)	240.2 M T (approx.)
2	Pesticides	
a	Monocrotophos	1154 L (approx.)
b	Metacid	1154 L (approx.)
c	Endosulfan	448 L (approx.)
d	Ekalux	131 L (approx.)
e	Coraban	383 L (approx.)
f	Karathae (Synthetic Pyrethroid)	32 L (approx.)
g	Folidal Dust (Methyl Parathion)	1.6 Kg. (approx.)

Table 2. Residues of chlorinated hydrocarbon insecticides in the water samples of Thirumeni lake.

S. No.	Name of the Insecticide/ metabolite/isomer	Quantity in ng/l
1	α – HCH	0.84
2	γ – HCH	22.9
3	β – HCH	595
4	D – HCH	5.1
5	α - endosulfan	1.935
6	B – endosulfan	1.06
7	R – endosulfan sulphate	BDL
8	DDE	0.575
9	DDD	BDL
10	DDT	326.9
11	Aldrin	2.11
12	Dieldrin	BDL
13	Heptachlor	58.5
14	Heptachlor epoxide	8.55
15	Endrin	BDL
16	Endrin aldehyde	1.445
17	Methoxy chlor	15.65

BDL - Below detectable level

Table 3. Pesticide residues detected in bore well water collected from areas near by Thirumeni lake.

S.No.		Water Source and name of the insecticide/metabolite/isomer	Quality detected PPT (Parts per trillion)
1		**Over head water tank**	
	a	α- HCH	84.86
	b	α – Endosulfan	66.67
2		**Bore well 100m deep**	
	a	PP – DDE	21.8
	b	β - Endosulfan	41.7
3		**Bore well 150m deep**	
	a	PP – DDE	16.36
	b	α - HCH	3

Table 4. Organochlorine pesticide residues (ppm) in fishes of Thirumeni lake.

S. No.	Name of the insecticide/ metabolite/isomer	Amount (ppm)
1.	α-BHC	0.002
2.	β-BHC	0.011
3.	γ-BHC	0.034
4.	δ-BHC	0.007
5.	DIELDRIN	0.001
6.	HEPTACHLOR	0.033
7.	HEPT-EPOX	0.002
8.	ENDRIN	0.005
9.	ENDRIN ALDEHYDE	0.002
10.	DDT	0.001
11.	DDE	0.001
12.	DDD	0.001
13.	ENDOSULFAN I	BDL
14.	ENDOSULFAN II	0.001
15.	ENDOSULFAN SULPHATE	0.028

Sample Analysis

The processed sample was analyzed with a Hewlett-Packard Model 5890 Series II gas chromatography equipped with a linearized Ni^{63} Electron Capture Detector. The operating conditions were as follows.

Column : DB-608, 30ml L x 0.321mm ID with the thickness of 0.50μm

Temperature : Column 180°C/3 Min-4° C/Min-260° C/15Min.

Injector 250°C

Detector 300°C

Carrier gas : Nitrogen gas 1ml/Minute.

Samples (1 μl) were injected into a split less injector port. Initially the instrument was calibrated with a standard mixture of organo chlorine residues.

An array of 21 organo chlorine pesticide residues *viz.*, pp-DDT, pp-DDE, pp-DDE, α-BHC, β-BHC, γ-BHC, δ-BHC, Heptachlor, Heptachlor Epoxide, Aldrin, Endrin, Endrin aldehyde, Diedrin, Endosulfan I, Endosulfan II, Ednosulfan Sulphate and Methoxychlor were analyzed in the sample.

The results were expressed in ppm.

RESULTS

Extent of Agricultural Pollution in the Lake Catchments

Details of annual extent of agricultural pollution, *viz.*, annual use of fertilizers and pesticides, have been given the table 1. At least 240 MT of fertilizers such as urea, DAP, etc., and about 3300 litres of pesticides such as monocrotophos, metacid, endosulfan, ekalux, caroban, and karathae (synthetic pyrethroid) and 1.6 kg of Folidal dust (Methyl parathion) are being applied in the immediate catchments and drainage areas of the lake every year (Source : Tamilnadu Agricultural Department).

Pesticide Residue Analyses

Pesticide Residues in Lake Water

Results of pesticide residue analyses in the surface water samples collected from Thirumeni lake are given table 2. The water samples had detectable amounts of HCH isomers, metabolites of DDT, alpha and beta-endosulfan, aldrin, dialdrin, heptachlor, heptachlor epoxide, enorin, enorin aldehyde and methoxychlor. Total pesticide residue was 1040.565 ng/l. The residues of endosulfan sulphate, DDD, dialdrin and endrin were at below detectable levels (Table 2).

Pesticide Residues in Bore Well Waters

The results of pesticide residue analyses in the ground water samples collected from various sources at Painganadu village near by Thirumeni lake have been shown in table 3. The bore well water collected from near by villages of Thirumeni lake had detectable amount of alpha-HCH, alpha-endosulfan, and PP-DDE (Table 3). Total pesticide residues in them ranged from 12.5 to 167.89 parts per trillion (Table 3).

Pesticide Residues in Fish

Results of pesticide residue analysis in the muscle of two specimens of fish *Orechromis mossambicus* have been given in table 3. The muscles of fish had detectable amounts of á –BHC, â –BHC, ã- BHC, dieldrin, heptachlor, hept-epox, endrin, endrin aldehyde, DDT, DDE, DDD, endosulfan-I, endosulfan–II and endosulfan sulphate (Table 4.).

DISCUSSION

The water samples of Thirumani lake has detectable amounts of HCH isomers, metabolites of DDT, endosulfan, aldrin heptachlor, heptachlor epoxide, endrin aldehyde and methoxychlor (vide Table 2). The residues of endosulfan sulphate, DDD, dieldrin and endrin are at below detectable levels. The borewell waters in the near by village of Thirumeni lake viz., Painganadu are also found to have alarming amounts of pesticide residues (vide Table 3). Since DDT, dieldrin, aldrin, and heptachlor endrin have been banned for agricultural use, the presence of these compounds in water samples collectively (above the permissible limit of 0.001 ppm) warrants attention.

Earlier reports on the water bodies, i.e. rivers, canals, lakes, tanks, ponds and coastal waters, of different regions of India have been found contaminated with high amount of DDT, HCH and other organochlorine pesticides (Gupta, 1992; CPCB, 1996; Kumari *et al.*, 1996; Reedy *et al.*, 1997). In Yamuna water DDT, HCH and other organochlorine pesticides have been reported to be present in the ranges of 8-203, 11-219 and 80-110ppb, respectively (CPCB, 1996). In Cauvery river methyl parathion has been reported to the extent of 1300ppb while other pesticides were present up to 1000ppb (Gupta, 1992). Reedy *et al*. (1997) have reported that Krishna waters in Andhra Pradesh showed the presence of DDT and HCH to the tune of 4-17 and 23-51 ppb, respectively in addition to 19 ppb of other organochlorine insecticides. Contamination of drinking water with DDT and HCH has also been reported from different states like Haryana, Gujarat, Uttar Pradesh and Delhi (Kumari *et al*., 1996). Since the concentration of pesticide residues are collectively higher than the permissible limit of 0.001ppm in Thirumeni lake, the situation warrants immediate attention and action.

During the course of the present investigation, large scale mortality of juvenile gastropods was observed in the lake at few occasions. When the probable reasons for that was probed, it was found that large scale pesticide applications in the agricultural lands in the catchments and surrounding areas of the lake preceded such mortalities. Various agricultural pesticides are reported to be toxic to molluscs (Mane *et al*., 1979; Akarte and Mane,1985; Muley and Mane, 1987; Kulkarni and Keshavan, 1989,1992; Chaudhary and Lomte, 1990; Rajyalakshmi *et al*., 1996).

Further the muscles of fish collected from the lake have also contained high amounts of pesticide residues (vide Table 4). This has dangerous potentials in this area because these pesticides could cause health hazards to humans as the average per capita consumption for an adult of 70 kg body weight is 2 litres of water per day and 6.5 g of fish per day (EPA, 1991), which could result in bio concentration of pesticides if such polluted water and fish are consumed. Slow, and almost invisible pesticide contamination leads to cancer, liver, and kidney damage, disorders of the human nervous system, damage to the immune system and birth defects (Anonymous, 2003). According to APHA (1995), several of these pesticides are bio accumulative and relatively stable, as well as toxic or carcinogenic. DDT is often viewed as the typically dangerous synthetic pesticide because it concentrates in adipose tissues and persists for years. EPA (1988) has used potency and exposure estimates of EPA and has concluded that dietary risks for 23 pesticides for a potential cancer risk are greater than one in a million and therefore were not negligible. About 193 pesticides are reported to have carcinogenic potency (Gold and Zeiger, 1997). There are many research reports stating that pesticide residues in food are having carcinogenic effects on humans (Nigg *et al.,* 1990; Quest *et al.,* 1991, 1993; Irene, 1995; Gold and Zeiger, 1997; Gold *et al.,* 1997a, b, 1999; Takayama *et al.,* 1999; Burnham, 2000). In fact the prevalence of gastrointestinal cancer in the village Painganadu near by Thirumeni lake is very high and based on the foregoing discussion it is inferred that the high level of agricultural pollution in this area might be the major cause for such a prevalence of cancer.

In fact agrochemical usage behavior in the catchments of Thirumani lake is excessive (vide Table 1) and erratic. Most of the farmer's literally have no idea regarding the harmful effects of these toxic chemicals. Precautionary measures taken are inadequate and faulty. The farmers' education programme are non-functional and ineffective. This is matter of grave concern as regards the well being of the farmer himself and also of the lake which is a source of livelihood to most of the people in this region directly or indirectly. The Agricultural Department must maintain a constant vigil on the illegal use of banned agrochemicals in this area and initiate legal actions against non-compliance of environmental safety regulations and laws. Farmers may be encouraged for the use of bio fertilizers and biological control of pests by giving financial benefits and technical know how. The farmers must be educated on the ill effects of pesticides in the environment by extension activities by the Tamilnadu Agricultural Department and Tamilnadu Agricultural University.

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