## DISTRIBUTIONAL CHARACTERISTICS OF CYCLODIENE PESTICIDES IN A TROPICAL BACKWATER ENVIRONMENT

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#### Introduction

The diene-organochlorine or "cyclodiene" chlorinated insecticides constitute a remarkable series of compounds that arise or can be considered to arise from the elaboration of hexachlorocyclopentadiene (hex) or closely related dienes. Generally, cyclodienes are persistent soil insecticides, mainly used against coleopterous insects and termites; they also are generally photostable. Uses of cyclodienes are progressively being cancelled or banned (aldrin, dieldrin and endrin) for reasons of resistance in insects, fish toxicity and serious environmental hazard<sup>1</sup>. Persistence of these compounds in soil is measured in decades and major losses from soil appear to be due to volatilization, leaching, or erosion rather than to degradation.

#### Materials and Methods

The study area, backwaters of Kuttanad, is a part of Cochin estuarine system and forms the southern part of the Vembanad Lake. Cochin estuarine system, situated in Kerala, India, between 9° 28' - 10° 10' N and 76° 13' - 76° 31' E is one of the largest estuarine systems in the south-west coast of India. Lying between Azhikode in the north and Alappuzha in the south, this estuary extends over an estimated length of 60 kms and an area of 21,050 hectares. The lake is connected to the sea at Cochin through a 425 m wide channel, which is the only source of tidal intrusion into the lake. Tides are semidiurnal type, showing substantial range and time. The average tidal range near the mouth of the estuary is 0.9 m. The northern part of Cochin backwater system includes the Cochin estuary and the barmouth. The southern and upstream parts of the backwater system include the Vembanad Lake and the adjoining backwaters of Kuttanad. Kuttanad is the deltaic formation of four river systems, which drain westwards from Western Ghats into the southern part of Cochin backwaters. The hydrographic features of Kuttanad backwaters are mainly controlled by the discharges from the above four river systems, and also by the tidal intrusions of saline waters from Cochin estuarine system The total area of Kuttanad region is estimated as 1,10,000 ha which comprises of 28% dry lands, 60% wet lands and 12% of other water bodies such as lakes, rivers, channels etc. About 55,000 ha of the wet lands are available for paddy cultivation in Kuttanad. Commissioning of Thanneermukkam barrier in 1976 paved the way for two crop cultivation in most of the low lying lands in Kuttanad. The deterioration of the water quality after the construction of Thanneermukkam bund is one of the major problems facing in Kuttanad<sup>2</sup>.

The area of investigation and stations sampled are given in Figure 1. The stations were fixed in such a way that they reflected the complex environmental and geographical variability in a representative manner. Surface water samples were collected using a pre-cleaned teflon coated Hytech water sampler. Liquid – liquid extraction gas chromatographic method was used for the extraction and analyses of organochlorine compounds<sup>3-4</sup>. In this procedure, the pesticides were extracted with a mixed solvent, methylene chloride/hexane. The extract was concentrated by evaporation and was cleaned up by adsorption-chromatography. The individual pesticides were then determined by gas chromatography (Perkin-Elmer XL Gas Chromatograph) using electron capture detector (ECD). Water samples were fortified with organochlorine pesticides at levels of 0.05 and 0.1- $\mu$ g l<sup>-1</sup> in ethyl acetate solution to 1L water sample and carried out the same procedure as for samples for the determination of extraction efficiency. Mean recoveries of all organochlorine pesticides at the above levels of fortification were between 85% to 103%.

The separation and quantification of the pesticides were performed with the Perkin-Elmer XL Gas Chromatograph fitted with electron capture detector (ECD), and coupled with a 1022- PE-Nelson Integrator using DB-5 fused silica capillary column by Perkin – Elmer (30m x 0.50mm I.D., 0.25µm film thickness). The conditions were Column : 180°C for 4 min, 180° to 260°C at 4°C per min, and 260°C for 30 min.; Injector temperature : 250°C; Detector (ECD) temperature: 375°C ; Carrier, Helium (flow rate): 5.0 ml/min; Make-up gas (flow rate) : 30 ml/min (5% methane in

argon). Identification and quantification of pesticides were accomplished using reference solutions of analytical grade pesticides, supplied by EPA, USA and Supelco Inc (USA). The analytical reproducibility was checked by triplicate.



Figure 1. Study area and sampling sites.

#### **Results and Discussions**

Cyclodiene pesticides determined in the backwater include a-endosulfan, aldrin, dieldrin, heptachlor, heptachlor epoxide, endrin and endrin aldehyde. The station-wise summary statistics of cyclodiene pesticide (maximum, minimum, mean, SD and CV) values observed for a period of one year (collection on monthly-basis) are given in Table 1. Except a-endosulfan, at few stations, all other cyclodiene pesticides showed minimum values in non-detectable levels, but invariably all of them indicated mean and maximum values in ng l<sup>-1</sup> level at all stations.

Table 1. Station wise summary statistics of cyclodiene pesticides (Cocn. ng /l; n =12; SD – standard deviation; CV – Coefficient of variation; ND – not detected)

Pesticide	St.	Surfac	e		Bottom						
	No.	Min.	Max.	Mean	SD	CV	Min.	Max.	Mean	SD	CV
a-Endo- sulfan	1	ND	124	30	32	104	ND	138	35	35	100
	2	ND	133	36	36	101	ND	143	43	39	90
	3	ND	122	48	40	84	ND	131	48	40	83
	4	ND	120	56	39	69	ND	115	57	39	68
	5	12	198	83	58	69	14	175	90	58	64

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	6	13	187	94	60	64	15	199	100	65	64
	7	11	225	104	74	71	11	213	109	78	71
	8	9	248	117	84	72	11	276	119	89	75
	9	10	234	86	64	74	12	221	97	65	67
Hepta-	1	ND	16	7.8	6.1	78	ND	20	8.3	6.7	80
chlor	2	ND	17	6.6	5.3	79	ND	21	7.0	6.1	86
	3	ND	21	8.8	6.7	76	ND	18	8.7	5.9	67
	4	ND	16	8.9	5.0	56	ND	18	9.6	5.1	53
	5	ND	18	9.7	5.6	58	ND	20	10.5	6.2	59
	6	ND	18	9.3	5.6	60	ND	29	11.4	7.9	69
	7	ND	22	9.6	6.4	66	ND	31	10.7	8.1	75
	8	ND	23	11.5	6.9	59	ND	22	10.7	6.4	59
	9	ND	20	9.8	6.1	61	ND	19	10.3	6.1	59
Hepta-	1	ND	29	11.7	8.5	72	ND	33	12.6	9.1	72
Cnior	2	ND	30	11.4	9.2	80	ND	32	13.0	9.9	76
Epoxide	3	ND	33	16.7	10.9	65	ND	32	17.1	10.4	61
	4	ND	28	14.9	9.6	64	ND	34	17.4	11.4	65
	5	ND	34	16.6	11.5	69	ND	34	17.3	11.2	64
	6	ND	36	18.8	11.9	63	ND	38	19.8	12.6	63
	7	ND	39	21.2	13.7	64	ND	41	20.3	13.5	66
	8	ND	42	20.5	14.4	70	ND	42	20.9	13.7	65
	9	ND	38	19.8	12.9	65	ND	36	20.7	13.1	63
Aldrin	1	ND	14	4.7	4.2	89	ND	15	4.7	4.4	94
	2	ND	15	5.1	4.6	90	ND	17	5.5	5.2	95
	3	ND	21	6.9	6.3	91	ND	23	8.0	7.0	87
	4	ND	12	7.8	4.3	55	ND	15	8.4	4.8	57
	5	ND	19	10.4	5.9	56	ND	20	11.5	6.4	55
	6	ND	30	14.9	9.7	64	ND	27	14.6	9.2	62
	7	ND	29	14.8	10.0	67	ND	27	15.2	9.7	63
	8	ND	29	15.6	9.7	62	ND	29	16.5	10.6	64

	9		30	11.6	93	80	ND	32	13.2	10.0	75
Dieldrin	1	ND	32	10.3	8.8	85	ND	34	11.3	9.3	81
	2	ND	34	12.5	10.9	87	ND	40	13.8	11.3	81
	3	ND	33	12.5	9.5	76	ND	38	12.9	10.2	79
	4	ND	22	12.1	7.0	58	ND	25	12.5	7.6	60
	5	ND	29	13.2	8.8	66	ND	29	13.9	9.3	67
	6	ND	32	14.2	8.8	62	ND	34	15.1	9.4	62
	7	ND	38	16.5	10.8	65	ND	35	17.3	11.0	63
	8	ND	48	17.6	13.8	78	ND	41	18.0	12.4	68
	9	ND	40	15.8	11.9	75	ND	40	17.2	12.0	70
Endrin	1	ND	19	6.5	6.1	93	ND	21	7.3	6.7	92
	2	ND	27	7.3	7.8	107	ND	24	7.7	7.4	96
	3	ND	29	10.0	10.06.9	99	ND	28	9.5	9.5	100
	4	ND	22	7.0	6.4	98	ND	25	8.2	7.7	94
	5	ND	19	7.3	8.7	87	ND	22	8.6	6.9	80
	6	ND	26	12.1	8.9	71	ND	28	13.5	9.4	69
	7	ND	28	13.3	8.7	67	ND	32	14.5	9.7	66
	8	ND	28	12.8	8.1	67	ND	33	14.5	10.1	69
	9	ND	25	11.0		73	ND	27	12.5	8.9	71
Endrin	1	ND	23	7.6	7.5	98	ND	23	8.5	7.9	92
aldehyde	2	ND	32	8.9	9.3	105	ND	25	8.8	8.6	98
	3	ND	37	10.5	11.5	109	ND	29	9.0	9.0	100
	4	ND	16	8.8	5.2	59	ND	17	10.8	6.4	59
	5	ND	19	10.6	6.1	57	ND	23	12.5	7.3	58
	6	ND	24	13.2	8.0	60	ND	24	13.5	8.1	60
	7	ND	32	14.1	10.0	71	ND	25	13.4	8.5	63
	8	ND	39	15.9	11.5	72	ND	29	14.9	10.1	67
	9	ND	32	11.7	9.9	84	ND	26	11.1	7.6	68

Endosulfan is a broad spectrum insecticide and is widely used in agriculture and forestry throughout the world. The major formulation of endosulfan is endosulfan 35 EC and is the major formulation used in India. Endosulfan is also

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used for controlling pests in rice in the study area, and this may be a reason for the higher percentage of endosulfan in the study area than other cyclodiene pesticides. The low percentage of other cyclodiene pesticides reported in the study area suggested that the aldrin, endrin and heptachlors were banned or their use may be restricted in India. The highly persistent nature of these compounds causes their accumulation in the study area. The run-off from rivers also influences the occurrence of these pesticides in the Kuttanad backwaters. This was well evident from the above results that in zone1 (1 to 3) except endosulfan all other cyclodiene pesticides were higher than in zones 2 (4 to 6) and 3 (7 to 9). The main sources of pesticide in the Kuttanad backwaters were the agricultural land run-off from paddy field and the discharge of water from the major river systems. The salinity barrier also plays a crucial role in accumulating the pesticides in Kuttanad backwaters, especially in pre-monsoon period, consequently, lower levels of all cyclodienes were found at station 9 than of station 8 in accordance with the operation schedule of the barrier. The closure of the bund for about more than 6 months may lead to the accumulation of cyclodienes at station 8 than that of station 9. Distinct seasonal variations were also noticed in the distribution of cyclodienes. Thus, the monitoring of these pesticides and their residues in the backwater system would help to show any trend in the levels of contamination of the environment and generate data for future legislations. It also helps for the usage of more ecofriendly pesticides.

#### Reference

1. Luo X., Mai B., Yang Q., Fu J., Sheng G. and Wang Z. (2004) Mar. Pollut. Bull. 48: 1102-1115.

2. Unnikrishnan P. and Nair S.M. (2004). Intern. J. Environ. Studies. 61: 659-676.

3. AOAC (1995). Association of Official Analytical Chemists. Official Methods of Analysis. 18<sup>th</sup> Ed. INC. Arlington, Virgina.

4. APHA (1995). Standard methods for the examination of water and waste water. 18<sup>th</sup> Ed. APHA, Washington, USA, 5540C.