DYNAMICS OF PESTICIDES IN THE BACKWATERS OF KUTTANAD

A THESIS SUBMITTED TO
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL CHEMISTRY
UNDER THE FACULTY OF MARINE SCIENCES

By
BABU V.

DEPARTMENT OF CHEMICAL OCEANOGRAPHY
SCHOOL OF MARINE SCIENCES
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 016

JUNE 2001

CERTIFICATE

This is to certify that this thesis is an authentic record of the research carried out by Shri. Babu.V, under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the degree of ***Philosophiae Doctor*** of the Cochin University of Science and Technology.

Kochi – 16
June 2001.

Dr. S.Muraleedharan Nair
Supervising Teacher

DECLARATION

I hereby declare that the thesis entitled " DYNAMICS OF PESTICIDES IN THE BACKWATERS OF KUTTANAD" is an authentic record of research work carried out by me under the supervision and guidance of Dr. S. Muraleedharan Nair, Lecturer, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part of it has previously formed the basis for the award of any degree, diploma or associateship, fellowship or other similar title or recognition.

Kochi – 16
June 2001.

BABU.V

ACKNOWLEDGEMENT

I would like to record my deep sense of gratitude and indebtedness to Dr. S. Muraleedharan Nair, Lecturer. Department of Chemical Oceanography. School of Marine Sciences. Cochin University of Science and Technology, my supervising teacher, for suggesting the research topic and for his invaluable and inspiring guidance as well as his ceaseless encouragement during the entire course of this study.

I express my sincere thanks to Dr. N. Chandramohanakumar, Head. Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and technology, for his ceaseless help, cooperation and interest and valuable suggestion and discussions during the course of the research work.

I take this opportunity to thank Dr. Jacob Chacko, Professor. Department of Chemical Oceanography. Cochin University of Science and Technology for his cooperation, support and the keen interest during the course of this study.

I am grateful to Dr. C.H. Sujatha, Lecturer. Department of Chemical Oceanography. Cochin University of Science and Technology, for her ceaseless inspiration and help in the work.

I am grateful to Prof. (Dr) N.R. Menon, Director, School of Marine Sciences and Prof. (Dr) R. Damodaran, Dean, School of Marine Sciences for their keen interest and co-operation in this study.

I place on record, my gratitude to the Cochin University of Science and Technology for providing the necessary facilities.

I am thankful to Hindustan Insecticides Limited, Udyogamandal, for having given permission to do this research work with my job.

I appreciate the encouragement and help given by Mr. P. Unnikrishnan, Mrs. Lizen Mathews, Mr.Daniel Munga and all of the research Scholars in Department of Chemical Oceanography and all of my colleagues in the School of Marine Sciences and thankfully acknowledge their whole hearted cooperation at every stage of this work.

I express my sincere gratitude to the Director, School of Industrial Fisheries for availing the boat facilities to me during the tenure of my work. I take this opportunity to thank Dr. Harikrishnan and Dr. Suresh Kumar, former research scholars of School of Industrial Fisheries, for their help and co-operation during the entire cruises. I am also thankful to Mr.Anilajan and other crew members of the boat for their assistance during the cruises.

Last but not least, I am immensely indebted to my wife, Anitha.V, my children Nanda Lakshmi and Nithin Babu for their inspiring attitude during the busy days of my doctoral programme. I am also thankful to my family members for their inspiring attitude throughout the study.

PREFACE

The tremendous growth in industrial production and the consequent improving in the standards of living have provoked worldwide discussion on environmental quality. The question of abusive use of pesticides for crop protection and vector control programmes is only one aspect of this entire complex. Inspite of this, tendentious publications such as Rachel Carson's *Silent spring* have brought crop protection into the foreground of environmental discussions. The persistence and high stability of organochlorine pesticides are regarded as problematic and the accumulation of pesticides residues and its metabolites in the different compartments of the environment is one of the major concerns. Because of their persistence in the aquatic environment and biomagnifications in food chain, the continuous use of pesticides will have wider implications not only in aquatic environmental quality but also on human health. The residual levels of these persistent chemicals exceed their permissible limits, and get partitioned among the constituent phases of the aquatic systems. Crop protection is only part of the agricultural economy and in agriculture itself has led to the most fundamental changes in the human environment. So, in all areas of life one must weigh the desired advantages against possible disadvantages.

The proposed thesis is based on the investigations on the distributions of organochlorine and organophosphorus pesticides in the waters and sediments of Kuttanad backwaters. Kuttanad, a unique agricultural area, which forms the southern part of the Vembanad lake, is a deltaic formation of four river systems entering the southern part of the Cochin estuary. No systematic study has ever been done to assess the ecotoxicological impact of these diverse chemicals and their metabolites in Kuttanad area. So, a detailed systematic and rigorous investigation on the distributions of these persistent chemicals is carried out.

The thesis is divided into 7 Chapters.

Chapter 1 describes a brief introduction of estuarine environment with special reference to the features of Kuttanad waters, and the status and implications of pesticide usages in India along with the aim and scope of the present study. Chapter 2, deals the description of the study area, sampling protocols for water and sediment samples and the various analytical methods employed in the estimation of organochlorine and organophosphorus pesticides in water and sediment.

Chapter 3 discusses the spatial and seasonal distributional characteristics of the various hydrographical and sedimental parameters such as salinity, dissolved oxygen, pH, temperature, organic carbon, sediment texture etc.,

Chapter 4 presents the spatial and temporal distributions of organochlorine pesticides viz. HCH isomers (α, β, γ and δ isomers), p,p'-DDT and its metabolites (p,p'-DDE and p,p'-DDD), cyclodienes such as endosulfan, heptachlor, heptachlor-epoxide, aldrin, dieldrin, endrin and endrin aldehyde, in the fluvial system of Kuttanad backwaters. The role of seasonality in the fluctuations of dissolved concentrations of the various metabolites of organochlorine pesticides is explained against the background of physico-chemical setting of the Kuttanad ecosystem.

Chapter 5 deals with the distributional characteristics of the organochlorine pesticides [viz. HCH isomers (α, β, γ and δ isomers), p,p'-DDT and its metabolites (p,p'-DDE and p,p'-DDD), cyclodienes such as endosulfan, heptachlor, heptachlor-epoxide, aldrin, dieldrin, endrin and endrin aldehyde] on a temporal and spatial basis, in the sedimentary environment of Kuttanad backwaters. The inter-relationships with other environmental parameters are traced, so as to explain the fate and transport of these pesticides in the aquatic environment of Kuttanad.

Chapter 6 gives the fluctuations in the distributions of organophosphorus pesticides via., malathion, methyl-parathion and chlorpyrifos in the fluvial and sedimental phases of the Kuttanad backwaters during different seasons. The physico-chemical factors, controlling the partitioning of organophosphorus pesticides between the water and the sediment compartments of the aquatic system of Kuttanad, are also explained.

Chapter 7 summarises the dynamic equilibria existing between the environmental compartments of Kuttanad backwater system, on taking into account of the salient features obtained from the temporal and spatial diversity of various organochlorine and organophosphorus pesticides investigated.

A list of references cited in the above Chapters is included at the end.

CONTENTS

CHAPTER 1

INTRODUCTION

Man is probably better able than many other species to survive in a hostile environment. It needs to be pointed out rather forcibly that human life, like other forms, is a complex equilibrium between processes of chemical synthesis and degradation that is supported by the continual intake of gaseous, liquid and solid chemicals of all kinds from the external environment. There is no doubt that some of these chemicals from natural sources have deleterious effects on human life in the long term.

The usage of man-made chemicals, including pesticides, contributes greatly to increased agricultural yield, protection of livestock, and the elimination of vector-transmitted disease. However, the global contamination and ecological risk caused by indiscriminate usage of these chemicals and their large scale production over the past four decades have been of great concern all over the world. These contaminants have been noted to be ubiquitous and persistent in various environmental media and biota (Woodwell et al., 1971, Mohamed and Mohamed, 1985a; Waid, 1986; Tanabe et al., 1990; Kawano et al., 1992; Dua et al., 1998; Atuma, 1999; Shannon, 1999; Samia El-Kabbany et al., 2000). The organochlorines are known to spread all over the globe, even to the remote areas like the North Pole, through long-range atmospheric transport. Global contaminations by environmentally persistent chlorinated hydrocarbon pesticides and industrial chemicals have been well documented (Iwata et al. 1993 & 1994; Tanabe et al. 1994). Many of these compounds are resistant to biological and physical degradation processes. Although oceans appear to be the main sink (Tanabe and Tatsukawa, 1986) and ocean currents play a role especially under ice-covered seas, global distribution is mainly via the atmosphere (Iwata et al. 1993).

Over 70% of the earth's surface consists of oceans, coastal seas and estuarine zones. The importance of marine ecosystem is also illustrated by the fact that the coastal area is inhabited by about 60% of the world's population. Thus, in particular, estuarine and coastal systems, showing considerable chemical and biological activity, are exposed to a high degree of contamination. The load of anthropogenic compounds and persistent organochlorine compounds affects the environmental quality of ecosystems.

ESTUARY

The estuary, where the flow of the river meets the flood of the tide, is a unique and important part of the aquatic environment. It forms the transition zone between the inland world of fresh water and the sea water lying offshore. As such, it retains some characteristics of both fresh water and the marine environment but it also has unique properties of its own. Estuaries constitute a major interface between land and oceans and have been regarded as one of the most important aquatic systems. Distribution of chemical constituents in an estuarine environment is controlled by physical, chemical and biological processes since they govern the fate and fluvial transport of weathered materials from continents to the oceans. Fresh water is an essential component of estuaries. Land runoff, glacial melt and stream and river discharge are all prime examples.

As an ecosystem, the estuary performs several vital functions. Conditions in the estuary are more variable than those in either the fresh-water or the coastal marine environment. The variation is primarily in salinity of the water, which increases horizontally from, virtually zero in the river water to the coastal water salinity of more or less 30 parts per thousand. The salinity of the water may vary vertically by several parts per thousand and similar large variations may occur as the tide ebbs and flows. Seasonal changes in river flow introduce another time scale of salinity variation and annual differences occur between wet and dry years. Estuaries have been classified on the basis of the geomorphology, distribution of salinity and density and the characteristic type of circulation. These systems are interdependent to a large extent since the geomorphology combined with the tidal range and river flow determine to a large degree the type of salinity distribution and this in turn determines the dominant mechanisms influencing the circulation.

Rivers that carry large amounts of suspended sedimentary materials may deposit this material in the shallow coastal waters outside the mouth of the river as the water spreads over wider and wider area and the current flow slows down. These deltas can become very complex with many channels connecting the areas of the original river mouth with the coastal waters offshore. In the main channel of these rivers, a salt wedge is commonly formed with very limited mixing between the sea water below and the fresh water at the surface.

Mixing and dispersion in an estuary result from a combination of advective and diffusive processes and are closely related to patterns of circulation. The intensity and scale of turbulence depend largely on the stability of the density distribution and so affect directly the vertical fluxes of momentum and matter. Indirectly, the state of turbulence also influences the longitudinal and transverse mixing. The mixing concerned in an estuary is that of the river water with the intruding sea water, or of a discharged substance with the ambient water. Mixing is brought about, in general, by the combined action of currents and turbulent distribution. Dispersion and mixing are two aspects of the same process since the dispersion of one water mass within another brings about the mixing of the two. Dispersion is usually produced by the combined effect of advection and diffusion.

KUTTANAD

Kuttanad is a low-lying area near the coast of the State of Kerala in southwest India. The area is a deltaic formation of four river systems entering the southern part of the Cochin lagoon. Originally it was a part of the shallow coastal area of the Arabian Sea. As a result of geological uplift, a shallow bay was formed into which the rivers draining from the mountains to the east discharge. The silt deposits carried by these rivers have formed the coast. The bay has become an extensive brackish water lagoon and backwater system extending from Alleppey in the south, to Cochin in the north, and connected to the sea by the Cochin bar mouth. In 1976, the lagoon was divided into two by the construction of Thanneermukkam barrier. South of the barrier, where water lagoon is comparatively fresh, is known as Vembanad Lake.

Kuttanad is about 1100 km^2 in area (110,000 ha). There are three identifiable topographic features: the dry (or garden) lands, wet lands and water areas. The dry lands vary in elevation from 0.50 to 2.50 m above sea level and are about 31,000 ha in area. Most of the population lives on these lands, which mainly occur in the peripheral areas of the Kuttanad. The wet lands include low lying areas slightly above the mean sea level (11.000 ha) and area below mean sea level reclaimed from the lagoon (55,000 ha). Lakes, rivers and channels make up the remaining 13,000 ha.

The rainfall in the Kuttanad is about 3000 mm/year. Two seasons are apparent; the wet season from May to November and the dry season from December to April. The wet season starts with the southwest monsoon, which lasts until September, and continues, with the northeast monsoon until November. Conditions are generally less severe in the northeast than in the southwest monsoon. Some rain usually falls in the dry season. The amounts are very variable, although significant rainfall can occur in March and April.

Vembanad Lake

The Vembanad Lake, extending to a stretch of 60 km from Cochin barmouth in the north to Alleppy in south, is the largest estuarine system in the southwest coast of India. It is located between 9° 28' and 10° 10'N latitude and 76° 13' and 76° 31' E longitude with an estimated area of 21,050 ha. The lake is connected to Arabian Sea at Cochin through a 425 m wide channel, which is the only source for tidal incursion in the lake. Tides are of semidiurnal type, showing substantial range and time. The hydrographic features of this estuary are controlled mainly by discharge from five rivers such as Pampa, Manimala, Meenachal, Achencoil and Muvattupuzha and also by tidal intrusion of saline waters from Cochin estuarine system. The aquatic system was highly productive and contained high fishery resources.

Salinity barrier

A salinity barrier of 1.4 km length was commissioned at Thanneermukkam in 1976 for preventing salinity intrusion in the dry season and also to retain the fresh water from the rivers flowing into the lake created by the barrier. The barrier was originally envisaged to close for a period of three months from 15th of December to 15th of March every year, while shutters remained open during monsoon months so as to facilitate the evacuation of floodwater. However, alterations in the operation schedule such as prolonged closure period up to April-May has brought in some adverse effects besides causing serious conflicts between fishermen and agriculturists. Furthermore, a shifting of salinity gradient zone towards the north of the lake has also been resulted. There is practically no tidal exchange in the areas south of the barrier through out the year The deterioration of the water quality after the construction of Thanneermukkam bund is suspected to be one of the reasons of the massive spreading of fish diseases and fish mortality during the recent years.

The sole objective of this regulator was to facilitate two term (double cropping) paddy culture per annum. It was expected that the Thottappally spillway would drain away floodwaters during monsoon and the bund would prevent brackish water intrusion during the summer Though the bund obstructed the intrusion of saline waters, it paved the way for devastating ecological and socioeconomic problems.

Agriculture in Kuttanad

Agriculture is the major activity in the area, employing about 40% of the population directly. Paddy is virtually the only crop grown in the padasekharams and the poor drainage conditions makes most of the land in the padasekharams unsuitable for other crops. Coconut is grown on the bunds and on higher areas, but they do not suffer usually from floods, lack of water or salinity intrusion. The main paddy crop in the Kuttanad is still the punja crop grown in early part of the dry season, November to March. With the commissioning of the Thanneermukkam barrier, the period of crops has been substantially advanced. The agro climatic conditions in most parts of Kuttanad are unfavourable for perennial crops and soils are often too wet to raise crops other than rice. The major constraints to agriculture production in padasekharams are greatly depending on flood, soil fertility and the saline water intrusion.

Climate, land forms and soils

The Kuttanad region experiences fairly uniform temperature throughout the year ranging from a minimum of 21°C to a maximum of 36°C. The average rainfall is between 2800 mm in the north and southwest to 3200 mm in the middle of the eastern periphery. Most of the rainfall occurs in the southwest monsoon, about 60 %, with a further 20 % in northeast monsoon. The remainder most falls in the pre-monsoon period of March, April and May (KWBS, 1989).

The Kuttanad area is a recent sedimentary formation (KWBS, 1989). The major part of the Kuttanad consists of flat low-lying plains, formed by the deposition of fluvial sediments in the lake basin and the adjoining areas. The soil characteristics of the wetland in Kuttanad exhibit the effects of accumulation of toxic products from anaerobic decomposition of organic matter, production of ammonia, the reduction of nitrates and sulphates, mobilization of iron and manganese, and variations in soil reaction and conductivity (KWBS, 1989).

Environmental pollution in Kuttanad

About 500 tonnes of pesticides and about 20,000 tonnes of fertilizers are used annually in the Kuttanad and some enters the waterways and lakes when water is pumped out of the paddy fields (KWBS, 1989).

The ecosystem of the backwaters of Kuttanad has been adversely affected by the increasing population, their economic activities and the infrastructure built to increase agricultural production. Most of the waters in Kuttanad are not suitable for the production of drinking water because of salinity. The amount of dissolved oxygen in the water has considerably effected on the quality of aquatic life (KWBS, 1989).

The main pests affecting paddy crops in Kuttanad are stem borer, leaf roller, case worm, brown plant hopper, thrips, Siberian ducks and rats (KWBS, 1989). February to March is the peak period of pest incidence, particularly the brown plant hopper. Another peak period of pest occurs after the main floods. There is no systematic surveillance and farmers arbitrarily apply pesticides at regular intervals. This means treatments can be ineffective and wasteful as well as causing severe ecological damage. The ineffective crop protection and higher use of pesticides in an unscientific way caused environmental pollution. Staggering of crop has increased considerably since the construction of Thanneermukkam bund (KWBS, 1989).

PESTICIDES

Pesticides are chemicals or mixtures of chemicals, which are used for controlling, preventing, destroying, repelling, mitigating or reducing any pests. A great many pesticides are available today for the control of unwanted organisms. Pesticides have made a great impact on human health, production and preservation of foods, fiber and other cash crops by controlling disease vectors and by keeping in check many species of unwanted insects and plants. More than 55 percent of the land used for the agricultural production in developing countries uses about 26 percent of the total pesticides produced in the world (Dollacker,1991). However, the rate of increase in the use of pesticides in developing countries is considerably higher than that of the developed countries. Pesticides are necessary to protect crops from losses that may amount to about 45 percent of total food production world wide (Pimentel and Levitan, 1986).

The annual global consumption of pesticides accounts for more than 3 million metric tones (WHO, 1990). Because of the important role played by chemical pesticides in agriculture and public health, many developing countries are placing high .reliance on them in their battle against poverty, disease and hunger (WHO, 1990). The role of pesticides in agricultural production is likely to expand at least in the developing countries even though the greater severity and complexity of pest problems in the tropics indicate that losses continue to be high (Olembo, 1987). Hence, utmost care should be practiced to use pesticides only when needed and to minimize their adverse effect on non-target organisms and the environment.

The total loss from pests for rice is about 46.4 percent in which insects constitute the main problem and accounts for about 26.7 percent (Wittwer, 1979). Lim and Heong (1984) reported the extent of the rice crop suffers from insect pest damage in Asia, and it may be seen that the yield increases as a result of insecticide use has been from 0.44 to 3.19 MT/ha at experimental stations, and from 0.5 to 2.6 t/ha at farmer's fields. It has been amply demonstrated that the current rice yields can be improved by 50 percent by proper crop management practice even without insect control, but can be increased by 2.5 times if proper pest management practices are also followed (Pathak and Dhaliwal, 1986). The losses of crops caused by pests are quite high both in developed as well as developing countries. In north America, Europe and Japan, losses are estimated to be in the range of 10-30 percent, but in developing countries of the world, the losses are substantially higher (Edwards, 1986). Even greater and often more significant losses occur after the crop is harvested which are caused by pests that attack the stored products, particularly in the tropics (FAO, 1985).

Perspective of pesticide development

The first insect stomach poison was probably arsenic, which was mixed with honey in the mid 1600s on an ant bait. In the late 1810s, Paris green, which consisted of copper salts of arsenic, was found to control Colorado potato beetles and other leaf-eating insects when dusted on plant foliage (Osborn, 1952). One serious drawback in the application of most of these compounds was, of course, their high toxicity to mammals, including humans. Other inorganic compounds containing mercury, tin or copper were also used as stomach poisons during this period. The Chinese were employing moderate amounts of arsenicals as insecticides by the sixteenth century, and not long afterwards nicotine, in the form of tobacco extracts, was used to control the plum curculio (Hassal, 1990; WHO, 1990). Perhaps the first organic insecticide was nicotine that was applied in its natural form as crushed tobacco leaves for control of aphids as early as 1763.

Chemical insect control changed dramatically following a major discovery of a chemical dichlorodiphenyltrichloroethane (later known as DDT) by Paul Muller in 1939. This organochlorine compound revolutionized insect control around the world (Brooks, 1976). DDT was found to be a low cost and a broad-spectrum pesticide, and is a widely used pesticide ever manufactured. In an attempt to find other compounds as successful as DDT, a number of synthetic organochlorine insecticides were introduced in the 1940s and 1960s including methoxychlor, aldrin, dieldrin, endrin, heptachlor, chlordane, toxaphene, HCH and mirex. Like DDT, most of these chemicals were lipid soluble nerve poisons, although most were more toxic to mammals than DDT Because of the environmental problems associated with the wide spread application of DDT, its use in the USA was banned in 1972 by Environmental Protection Agency. This was followed in subsequent years by banning or severely restricting the use of other organochlorine pesticides. However, these compounds are widely used in most of the developing countries.

Almost parallel to the development of DDT during World War II was the discovery of the organophosphorus pesticides (Eto, 1977). The discovery of parathion in 1944 opened the door for the synthesis of thousands of organophosphorus analogues commonly known as second generation insecticides. Carbamates constitute the third major group of synthetic insecticides (Kuhr and Dorough, 1976), discovered in the early 1950s, and the first commercial product was carbaryl. The carbamates are similar to the organophosphorus compounds in many aspects. The next generation of pesticides belongs to synthetic pyrethroids, and these compounds are effective at extremely low rates and are among the least toxic to mammals and humans.

Classification of pesticides

Pesticides are broadly classified into three categories based on their target species, chemical nature and site of action. Based on the target species, pesticides are classified into insecticides, fungicides, herbicides, acaricides, rodenticides etc. The classification of pesticides based on their chemical nature is more complex and in general they are classified into organic and inorganic pesticides. The organic pesticides are further subdivided into classes based on their molecular structure such as organochlorines, organophosphates, carbamates, thiocarbamates, acetanilides, ureas etc. The classification based on site of action of pesticides are based on their entry into the body system of the target pest and are classified into stomach poisons, contact poisons, systemic poisons, fumigants, etc.

Stomach poisons enter the body of pest through the mouth during feeding into the digestive tract from where these are absorbed into the systems and this type of poisons are more effective against chewing insects. Dieldrin, sulphur, lead arsenate are examples of stomach poisons. Contact poisons generally penetrate a pest's body as a result of contact of the pests cuticle with the treated surface or other external portions such as sprayed leaves, stem etc. Contact poisons act on the nervous system on the pest, and examples of contact poisons are BHC, DDT, endrin, methyl parathion, carbamates etc. Systemic poisons are applied on the absorptive surfaces of plants like the foliage, green parts of the stem, near the roots etc. from where these are translocated into the plant body. Examples of systemic poisons are monocrotophos, phosphamidon, dimethoate, carbofuran etc. Fumigants are volatile poisons and enter the body of the pest through the respiratory system and are widely used in controlling stored grain pests. Hydrogen cyanide, ethylene dichloride, carbon tetrachloride etc. are examples of fumigants.

Pesticide formulations

Pesticides were originally manufactured as technical grade (active ingredient or a.i.). The technical grade pesticides are generally waxy or lumpy solids or viscous liquids and also have unsuitable physical characteristics for application. They also have high purity and hence required dose is difficult to disperse. The toxicity of the active ingredient is much higher compared to the formulations. So most of the pesticides are sold as formulations. Formulating a pesticide improves its performance and increases its safety to the consumer. Formulations of pesticides contain the active ingredient in a definite concentration together with other materials like emulsifiers, wetting agents, dispersing agents, thickeners, inert carriers, solvents, anticaking agents encapsulants etc. The major formulation of pesticides are grouped as follows:

- Emulsion concentrates (EC)
- Wettable powders (WP or WDP)
- Dusts (D)
- Granules (GR)
- Ultra low volume concentrates (ULV)
- Suspension concentrate (SC)
- Fumigants etc.

Pesticide toxicity

Pesticide toxicity or LD_{50} is measured by exposing a population of test animals to measured dose of the pesticides delivered by the route of absorption under study. The test animal could be a mouse, rat, dog, bird, fish etc. Routes of exposure could be oral, dermal and or inhalation. The level of dose at which 50% of the test population dies is known as the median lethal dose or LD_{50}. It is expressed in terms of the weight of the substance per unit body weight of the animal. It is generally expressed as mg/kg. LD_{50} of a pesticide is an indication of how toxic it is to the test animal. However, an LD_{50} does not have a direct relationship to its toxic effects on human beings. But, LD_{50} values of different animals are an indication of the degree of toxicity the pesticide may have on human beings. LD_{50} values represent the effect due to a single dose only, and the long term effects are called chronic effects. Inhalation toxicity is measured as the LC_{50} value, and it indicates the amount of pesticide in the air, which is being breathed by the test animal. The toxicity tables of EPA, WHO and Indian standards of pesticides are given in Table 1 1

Usage of pesticides in India and the world

The global agriculture has relied heavily on pesticides to feed the expanding population. It has been estimated that about 4.4 million metric tones of pesticides are used annually in world agriculture. About 70 percent of this quantity is used in developed countries, and the remaining 30 % in developing countries.

On global basis, herbicides constitute major percent of the total consumption, followed by insecticides, fungicides and others. However, in developing countries like India, the predominant groups of pesticides used are insecticides followed by herbicides and fungicides (Table 1.2). The Indian agrochemical usage by chemical class is included in Table 1.3.

The usage of pesticides in Indian market by crop basis is given in Table 1.4. About 45% of market share for pesticides is accounted for cotton and the second rank comes to rice (22%). The consumption of pesticides in developing countries is quite low as compared to the developed countries (Table1.5). Among the developed countries, Japan tops the list of pesticides consumers with 12 kg/ha followed by Europe (3 kg/ha) and USA (2.5 kg/ha). The consumption of pesticides in India is about 0.57 kg/ha.

The production of basic pesticides in India was reported as 1,02,240 tones per annum in 1997-98 period (Pestology Annual, 1999). The growth of pesticide production in India from 1955 to 1998 was given in Table 1.6. The accumulation of pesticides in different components of environments has

Table 1.1 Classifications of pesticides based on toxicity

1. Indian standard

Classification	LD_{50}	LC_{50}	Colour code
Extremely toxic	1 – 50	1 – 200	Bright red
Highly toxic	51 –500	201-2000	Bright yellow
Moderately toxic	501- 5000	2001 – 20000	Bright blue
Slightly toxic	More than 5000	More than 20000	Bright green

The Insecticides Act, 1968, with Rules 1971. Government of India.

2. WHO Toxicity classification

LD_{50} for rat (mg/kg body weight)

	Oral		Dermal	
Class	Solids	Liquids	Solids	Liquids
Ia Extremely hazardous	≤ 5	≤ 20	≤ 10	≤40
Ib Highly hazardous	5 – 50	20 – 200	10 – 100	40 – 400
II Moderately hazardous	50 – 500	200 – 2000	100 – 1000	400 – 4000
III Slightly hazardous	≥ 501	≥ 2001	≥ 1001	≥ 4001

3. EPA Toxicity classification

Acute toxicity to rat

Class	Oral LD_{50}	Dermal LD_{50}	Inhalation LC_{50}
I	≤ 50	≤ 200	≤ 0.2
II	50 – 500	200 - 2000	0.2 – 2.0
III	500 – 5000	2000 – 20000	2.0 – 20
IV	≥ 5000	≥ 20000	≥ 20

The Pesticides Manual, 1995.

Table 1.2 Agrochemicals usage pattern: India and the World

CONSUMPTION	(In percentage)	
	INDIA	WORLD
Insecticides	76.0	43.6
Herbicides	10.0	29.6
Fungicides	13.0	20.6
Others	1.0	6.2

Pesticides Statistics (1998)

Pesticide Database (1997-98)

Table 1.3 Indian agrochemical usage by chemical class

Chemical class	**Use in percentage**	
	India	**World**
Organochlorine	16	6
Organophosphorous	50	37
Carbamates	4	23
Synthetic pyrethroids	19	22
Bio-pesticides	1	12
Others	10	6

Pesticides Statistics (1998)

Pesticide Database (1997-98)

Table 1.4 Usage of Indian pesticides market by crops (1995)

Total Market Size: Rs.2300 crore

Item	**Market Size (in %)**
Cotton	45
Plantation crops	7
Vegetables	9
Rice	**22**
Pulses	4
Wheat	4
Others	9
Total	100

Pesticide Database (1997-98)

Pesticides Statistics (1998)

Table 1.5 Country wise consumption of pesticides

Country	Consumption in gms/hectare
Japan	12000
Europe	3000
USA	2500
Argentina	960
Mexico	750
India	570

Pesticide Database (1997-98)

Table 1.6 Production of basic pesticides in India

Year	Production in tones per annum
1955 – 56	2,836
1960 – 61	8,448
1965 – 66	13,951
1973 – 74	32,951
1978 – 79	52,528
1988 – 89	61,100
1989 – 90	65,800
1990 – 91	74,300
1991 – 92	72,809
1992 – 93	76,933
1993 – 94	83,428
1994 – 95	90,758
1995 – 96	96,500
1996 – 97	1,02,240
1997 – 98	1,02,240

Pestology Annual (1999)

endangered the survival of fish and soil microorganisms. Pesticides have been detected in excessive amounts in almost all the food materials including food grains, vegetables, fruits, meat, fish, eggs, milk and milk products, and even human milk. In addition, they have poisoned and killed many non-target organisms, thus leading to secondary pest outbreaks and pest resurgence. The side effects of pesticides in various environmental compartments are listed in Table 1 7

Pesticides have made a great impact on human health, production and preservation of foods, fiber and other cash crops by controlling disease vectors and by keeping in check many species of unwanted insects and plants. More than 55 percent of the land used for agricultural production in developing countries uses about 26% of total pesticides produced in the world (Dollacker, 1991).

Pesticide residues in the environment

Residues of pesticides and their degradation products have been reported in a wide variety of environmental samples. Pesticides are used to control the population of certain organisms, which, at a particular time and in a particular place, are considered to be inimicable to man's welfare. All pesticides have measurable vapour pressure and solubilities in water

Chemical pesticides hold a unique position among the environmental contaminants since distribution in the environment is the way they are used. Adding to their impact is the fact that pesticides are fashioned and valued for their deadly effect on living organisms. Pesticides have been spread throughout the environment; they have been found in the air we breathe, in the streams and lakes that supply our drinking water, in the clothing we wear, and indeed, on our very bodies. Large numbers of birds, fish, and forest animals have succumbed to these poisons. The lipophilic organochlorine compounds such as DDTs, HCH isomers and PCBs are known to accumulate in adipose tissues of terrestrial and aquatic animals (Tirpenou et al., 1998).

Table 1.7 Side effects of pesticides in the environment

Environmental element	**Potential side effect**
1. Abiotic environment	Presence of residue in soil, water and air
2. Plants	a. Presence of residues b. Damage due to phytotoxicity c. Vegetation changes
3. Animals	a. Presence of residues in domestic animals and wild life b. Physiological effects (e.g. non-viability of bird eggs) c. Mortality in certain wild life species (e.g. mammals, birds, fish) d. Mortality in beneficial insects, predatory and parasitic insects. e. Insect population changes (e.g. the development of secondary pests as a result of d)
4. Man	a. Presence of residues in tissues and organs b. Effects of occupational exposure
5. Food	Presence of residues
6. Target organism	Development of resistance

The danger arises from the basic nature of pesticides. They are poisons, and while much is known about their effect on humans and livestock, there is an inherent danger in the simple presence of such materials in the farmyard. Illiteracy is common in developing countries, and the warning on the pesticide bags is frequently not read and understood.

The development of resistance is undoubtedly one of the undesirable effects of pesticide usage, although it presents a special problem as compared with most other side effects, which are more directly concerned with the persistence and accumulation of residues. The development of resistance is basically a phenomenon caused by a population shift within the same species, ie., from the susceptible to the resistant strain, as a result of the selection pressure of the pesticide. The study of this phenomenon is mainly of a physiological and biological nature.

The side effects of pesticides concerns the interaction between plant and animal life and its abiotic environment as far as this interaction is influenced by the presence of pesticide residues at biologically active levels. Such effects are, among others damage to plants, vegetation changes and changes in micro flora, direct or indirect mortality in wildlife species (mammals, birds, fish) or beneficial insects. Certain elements in the balance of nature are disturbed as a result of pesticide interfering with the ecosystem. Pesticides residues in the abiotic environment can be taken up by plant or animal organisms, which in turn are consumed by larger animal species, in which the concentration of the chemical is increased. These processes may be repeated until the residue reaches a lethal concentration in the animal at the end of the food chain (Kannan et al., 1997).

For nearly three decades, bioaccumulation of pesticides primarily of the persistent organochlorines such as DDT and HCH in birds, fishes, and mammals and in commodities like milk products has been extensively studied in many countries world over In view of the serious concern voiced by environmentalists and possible health hazards, many developed countries have banned the organochlorines such as HCH, DDT, aldrin, dieldrin etc. On the other hand, developing countries have to depend on DDT and HCH for control of agricultural pests and also in malaria eradication programmes. These pesticides continue to enjoy an enviable position in India, in spite of the newer groups of pesticides like organophosphates, carbamates, pyrethroids, etc., due to their very low price and availability in huge quantities because of indigenous manufacture of technical grade of these pesticides.

The possible reason for the bioaccumulation of persistent organochlorine pesticides was correlated with the spray applications of these pesticides in agriculture and malaria eradication programmes. The use of chlordane, heptachlor and aldrin were banned in India in early nineties (Pawar, 2000). The use of BHC was totally banned in 1997 (Pawar, 2000). But the use of lindane (γ-isomer of HCH) was still used for agriculture in India. Due to the ubiquitous nature of these pesticides, the residues and metabolites of these pesticides were still observed in various environmental compartments.

SCOPE OF THE PRESENT STUDY

Like many other nations of Asia, India is predominantly an agricultural country In Kerala. rice is the predominant cereal crop, of which Kuttanad area accounts for more than 20% of rice production. The use of pesticides in rice is more in comparing with other crops. Several persistent pesticides, including DDT were banned for use in agriculture, but are used for the eradication of vector-transmitted diseases. Furthermore, with the recent liberalization of agrochemicals market, there was a tendency towards the application of cheaper pesticides, including more hazardous and persistent compounds.

Environmental contamination of waters by pesticide residues is of great concern. Pesticides are divided into many classes, of which the most important are organochlorine and organophosphorus compounds. Organochlorine pesticides are known to resist biodegradation and therefore they can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain (Miliadis, 1994). Organophosphorus pesticides on the other hand are known to degrade rapidly depending on their formulation, method of application, climate and the growing stage of the plant. Use of pesticides in India is increasing @ 2 to 5% per annum and is about 3% of total pesticides used in the world (Nigam and Murthy, 2000). About 90,000 metric tones of technical grade pesticides are currently produced in India (Pesticide Database, 1999) and more than 67% is used in agriculture sector alone. The potential pesticide load (ppl) is increasing over the years and was estimated to be 0.633 kg/tonne by the end of 2000 AD (Dhaliwal and Arora, 1996), while the projected demand would be 100,00 metric tones. Currently about 153 pesticides have been registered for the use in India and 35 are widely used (Nigam and Murthy, 2000).

The backwaters of Kuttanad receive considerable amounts of agricultural run-off from the "padasekharams" as well as run-off from four major river systems. Since preliminary investigations revealed that the most prominent organic pollutants discharged to these estuarine waters were mainly pesticide residues and their metabolites. The present study was designed to analyse the seasonal and spatial distributions of some of the ubiquitous persistent organochlorine pesticides and also some of the highly toxic organophosphorus pesticides in the different environmental compartments, mainly in water and sediment, of the Kuttanad backwaters.

The proposed thesis is based on the investigations on the distributions of organochlorine and organophosphorus pesticides in the waters and sediments of Kuttanad backwaters. Kuttanad, a unique agricultural area, which forms the southern part of the Vernbanad Lake, is a deltaic formation of four river systems entering the southern part of the Cochin lagoon. No systematic study has ever been done to assess the ecotoxicological impact of diverse chemicals and their metabolites in Kuttanad area. So, a detailed systematic and rigorous investigation on the distributions of these persistent chemicals was to be carried out.

The main objectives of the present study are:

- to study the pollution history due to pesticides in various environmental compartments of Kuttanad backwaters.

to understand the contamination dynamics of different organochlorine pesticides viz. DDT and its metabolites, HCH and its isomers, some cyclodiene pesticides and also organophosphorus pesticides like malathion, methyl parathion and chlorpyrifos

- to describe the seasonal and spatial distributions of major organochlorine pesticides and organophosphorus pesticides in the dissolved and sedimental phases of Kuttanad backwaters.
- to study the diagenetic processes occurring within the sediment and sediment-water interface.
- to understand the transport and dissipation of pesticides from the tropical estuaries.
- to assess the influence of various environmental parameters and processes on pesticide recycling.
- to generate a baseline report for the levels of pesticides and their metabolites in the backwaters of Kuttanad.

CHAPTER 2

MATERIALS AND METHODS

This Chapter describes the location of study area and the analytical methods employed in the estimation of various parameters.

2.1. Description of the study area

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. Before the commissioning of the salinity barrier, tidal effects were extended upto 80 kms south of the Cochin barmouth (KWBS, 1989). 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 viz Manimala, Meenachal, Pamba and Achencoil, 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. Pamba and Manimala Rivers join together before meeting the Achencoil river at Veeyapuram and all of these rivers influx at the southern most part of the lake. River Meenachal opens at the middle of the lake.

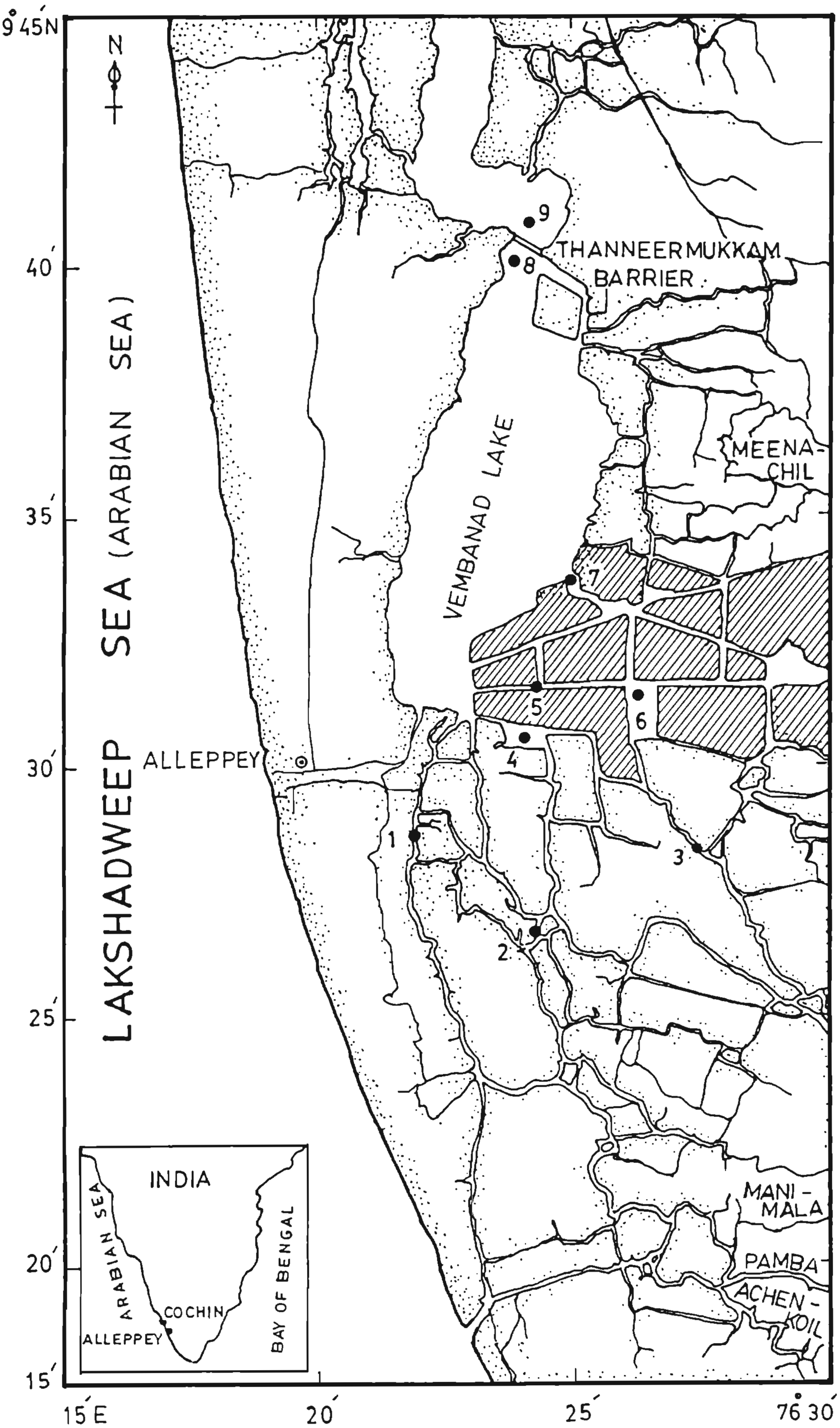
Kuttanad is contributing nearly 20% of the total rice production in the Kerala state. The total area of Kuttanad region is estimated as 1,10,000 ha which comprises of 28% dry lands, 60% wet lands and 12% of other water bodies such as lakes, rivers, channels etc. About 55,000 ha of the wet lands are available 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 aquatic system was highly productive and contained high fishery resources. The amount of pesticides used in this area is about 500 tones per year (KWBS, 1989).

Thanneermukkam bund was commissioned in 1976 for regulating the saline water intrusion into Kuttanad paddy fields during December to March and thereby for protecting the 'Punja crop' The shutters of the barrier remain open during the monsoon period so as to facilitate the evacuation of flood water. However, alterations in the operating schedule such as prolonged closure period brought in some adverse effects in that area. The deterioration of the water quality after the construction of Thanneermukkam bund is one of the major problems facing in Kuttanad.

The area of investigation and stations sampled are given in Figure 2.1. The regions lying between north of salinity barrier and Alappuzha were divided into nine stations. The stations were fixed in such a way that they reflected the complex environmental and geographical variability in a representative manner The nine stations are:

1. **Pallathuruthy**

   This station is situated near Alappuzha town. Agriculture is the main occupation of the people in this area. The water characteristics are mainly controlled by the riverine discharges from Pampa and Achencoil Rivers. Municipal effluents also influence this station.



MAP OF STUDY AREA SHOWING SAMPLING LOCATIONS.
Figure 2.1.

2. **Nedumudi**

Agriculture is the main occupation in this area. This station is mainly influenced by riverine discharges. This station remains as almost as a fresh water region throughout the year.

3. **Kavalam**

This is an agricultural area influenced by riverine discharges. This station also remains almost as a fresh water region throughout the year.

4. **Vattakayal**

Paddy and coconut are the main agricultural crops in this area. The quality of water is influenced by discharges from various rivers and paddy fields.

5. **C-Block**

Paddy is the main cultivation in this area. The station is influenced by the discharge of water from paddy fields and "Padashekarams"

6. **24000**

The station is influenced by the discharge of water from "Padashekarams"

7. **Chithira**

Paddy is the main cultivation in this area and is influenced by the discharge of paddy fields and "Padashekarams" This station is situated in the Vembanad lake.

8. **Thanneermukkam south**

This station is situated near to the salinity barrier and shows slightly estuarine characteristics.

9. **Thanneermukkam north**

This station is located north to the Thanneermukkam bund and is estuarine in character.

Considering the salinity distributions, geographical characters and the nature of various human activities prevailing in this area, the study area was divided into three zones. Stations 1 to 3 constituted zone 1, the zone 2 contains stations 4 to 7 and the stations 8 and 9 forms the zone 3. In all seasons, zone 1 showed riverine character. The runoff from the rivers Pampa, Manimala and Achencoil influenced these stations more prominently. The municipal effluents also have a contribution in polluting this zone. Zone 2 was fresh water dominated zone in monsoon and post-monsoon seasons, but in pre-monsoon, the zone showed estuarine character. Zone 3 is estuarine in nature in pre-monsoon and post-monsoon seasons.

The data were pooled and divided into three seasons for getting reliable trends for explaining the variations in different parameters. The monsoon season comprised of the months June, July, August and September. October, November, December and January were considered as post-monsoon seasons. February, march, April and May were considered to be the pre-monsoon periods. These classifications were based on the rainfall data prevailing in the study area.

2.2 Sampling and storage

Surface water, bottom water and sediment samples were collected from October 1995 to November 1996, at monthly intervals. The entire cruise were carried out by using a fiberglass boat, "King Fisher" of the School of Industrial Fisheries, Cochin University of Science and technology, Cochin.

Surface water samples were collected using clean glass bottles and bottom samples were collected using a pre-cleaned teflon coated Hytech water sampler. Sediments were collected using a stainless steel Van-Veen grab. From each location, three grab full of sediment had been collected. The top 5 cm layer sediment samples were homogenized after removing the decayed leafy particles and shells and were stored in closed glass containers. The samples were stored at –20° C till analyses were performed. The dissolved oxygen of surface and bottom water samples was fixed in situ. All the reagents used were analytical grade and the solvents used were HPLC grade. Milli-Q water was used for the preparation of standards and reagent solutions.

2.3 Analytical Methods

2.3.1 General hydrographical parameters

pH was measured in situ by using a portable pH meter. Temperature was measured at respective collection centers with a sensitive alcohol–in-glass thermometer. Dissolved oxygen was determined by the modified Winkler method (Grasshoff et. al., 1983a). Salinity was determined argentometrically by the modified Mohr's method developed by Knudsen (Grasshoff et al., 1983b).

2.3.2 General sedimentary characteristics

Moisture content

Moisture content of the sediment was estimated by drying approximately 10 g of homogenized wet sediment sample in an oven at 90°C for 48 hours. The difference in weights of the wet and dry samples gave the moisture content.

Organic carbon

Sediment organic carbon was estimated by chromic acid oxidation method (El Wakeel and Riley, 1957; Gaudette et al., 1974).

Texture analysis

Texture analysis was carried out by sieving and pipette analysis. A known weight of wet sediment was dispersed overnight in 0.025 N sodium hexametaphosphate (Calgon) solution. The sand fraction was separated from the dispersed sediments by wet sieving using a 230 mesh (63µm) ASTM sieve

(Carvar, 1971). The filtrate containing silt and clay fractions was subjected to pipette analysis (Krumbein and Pettijohn, 1938; Lewis, 1984).

2.3.3 Analysis of organochlorine pesticides in water

Liquid – liquid extraction gas chromatographic method was used for the extraction and analyses of organochlorine compounds (APHA, 1995; AOAC. 1995). 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 using electron capture detector (ECD).

Each water sample was filtered through GF/C Whatman filter paper under reduced pressure. One litre of filtered water sample was measured accurately and poured into a two litre separating funnel. The sample bottle and measuring cylinder were rinsed with 60 ml of 15% methylene chloride in hexane, poured this solvent into seperatory funnel, and shaked vigorously for 2 minutes. After the phase separation, drained the water phase from seperatory funnel into sample bottle and carefully poured the organic phase through a 2 cm OD column containing 10 cm of sodium sulphate into a Kuderna-Danish apparatus fitted with a 10 ml concentrator tube. The sample was poured back into separating funnel.

The sample bottle was rinsed with 60 ml mixed solvent, and the rinsed solvent was used for the second extraction of sample, and organic phase was passed through sodium sulphate. A third extraction was completed with 60 ml of mixed solvent that was used to rinse sample bottle again, and passed the organic phase through sodium sulphate. The sodium sulphate was washed with several portions of hexane and drained well. Kuderna-Danish apparatus was fitted with a three-ball Snyder column and reduced the volume to about 7 ml in hot water bath (90-95°C). At this point all the methylene chloride present in the initial extracting solvent had been distilled off. The concentrator tube was removed from the Kuderna-Danish apparatus after cooling, rinsed the ground glass joint, and diluted to 10 ml with hexane.

To separate interfering substances from pesticide materials, magnesia-silica gel (florisil) cleanup procedure was used. Florisil column chromatography clean up was used for fractionation of organochlorine pesticides from the water samples by elution with solvents of increasing polarity. The chromatographic columns (50cm x 15mm I.D) were slurry packed with 7g florisil activated at 450°C overnight, made into a 1.5% v/w water/florisil with distilled water and stirred for 3 hours before use. About 0.5 cm anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or solvent.

First elution was made with 200 ml 6% ethyl ether in petroleum ether, and second with 200 ml 15% ethyl ether in petroleum ether. Third elution was made with 200 ml 50% ethyl ether petroleum ether and the fourth with 200 ml 100% ethyl ether. The elutes were concentrated in Kuderna-Danish evaporator in a hot water bath and diluted to 2 ml with hexane. Then GC-ECD analysis was performed.

Determination of extraction efficiency:

Water samples were fortified with organochlorine pesticides at levels of 0.05 and 0.1 μg l^{-1} 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 80% to 105%.

2.3.4 Analysis of organochlorine pesticides in sediment

Organochlorine pesticides in sediments were extracted using hexane – acetone mixture and analysed by gas chromatography (AOAC, 1995). 10 g undried soil was weighed, sieved through 2 mm sieve and mixed thoroughly and put into a 250 ml Erlenmeyer flask 7 ml 0.2 M ammonium chloride solution (10.7 g/l) was added and allowed to stand for 15 minutes. 100 ml hexane – acetone mixture (1 + 1) was added, stoppered tightly and shaked overnight (≥12 hour) on wrist action shaker at 180 rpm.

Supernatant liquid was carefully poured avoiding aqueous clay phase, through a 2 –3 cm column (22 mm id) of flurosil, and collected the elute in a 1 L separator. The flask and soil were rinsed with two 25 ml portions of hexane – acetone mixture and decanted through the column. The column was rinsed with 10 ml hexane – acetone mixture.

200 ml water was added to separator and shaken gently. The aqueous phase was drained into second separator and extracted with 50 ml hexane. The hexane layers were combined in first separator and washed with 100 ml water. Drained and discarded water. The hexane was poured through 2 cm column (22 mm id) sodium sulphate, concentrated to 100 ml and further concentrated to 10 ml in Kuderna-Danish concentrator and analysed the sample in gas chromatograph in ECD detector. For dry basis calculation, 10g of the sample was dried at 105°C for 16 hours.

Determination of extraction efficiency

Sediment samples were fortified with known concentrations of organochlorine pesticides in ethyl acetate solution to 10 g sediment sample and carried out the same procedure as for sediment samples for the determination of extraction efficiency. Mean recoveries of all organochlorine pesticides were between 75% to 110%.

2.3.5 Analysis of organophosphorus pesticides in water

The method adopted for the extraction of organochlorine pesticides was used for organophosphorus pesticides also.

Water samples were fortified with known concentrations of organophosphorus pesticides in ethyl acetate solution to 1litre water and carried out the same procedure as for samples for the determination of extraction efficiency. Mean recoveries of all organophosphorus pesticides were between 65% to 95%.

2.3.6 Analysis of organophosphorus pesticides in sediment

The method adopted for the extraction of organochlorine pesticides in sediments was used for the extraction of organophosphorus pesticides also.

Sediment samples were fortified with known concentrations of organophosphorus pesticides in ethyl acetate solution to 10 g sediment sample and carried out the same procedure as for sediment samples for the determination of extraction efficiency. Mean recoveries of all organophosphorus pesticides were between 65% to 90%.

2.3.7 Gas chromatographic conditions

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. The details of column used and chromatographic conditions are described below.

Column	DB-5 fused silica capillary column by Perkin – Elmer (30m x 0.50mm I.D., 0.25µm film thickness).
Column temperature	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)

The following organochlorine pesticides were quantified and the order of elution was as below. It is chromatographically represented in Figure 2.2.

- α-HCH
- β-HCH
- γ-HCH
- δ-HCH
- Heptachlor
- Aldrin
- Heptachlor epoxide
- α-endosulfan
- p,p'-DDE
- Dieldrin
- Endrin
- p,p'-DDD
- Endrin aldehyde
- p,p'-DDT

The following organophosphorus pesticides were quantified in this study and the order of elution is chromatographically represented in Figure 2.3.

- Methyl parathion
- Malathion
- Chlorpyrifos

Identification and quantification of pesticides were accomplished using reference solutions of analytical grade pesticides, supplied by EPA, USA and Supelco Inc (USA). Minimum detection limit for organochlorine pesticides in water was 0.05 ng l^{-1} and for the sediments was 0.01 ng g^{-1} The minimum

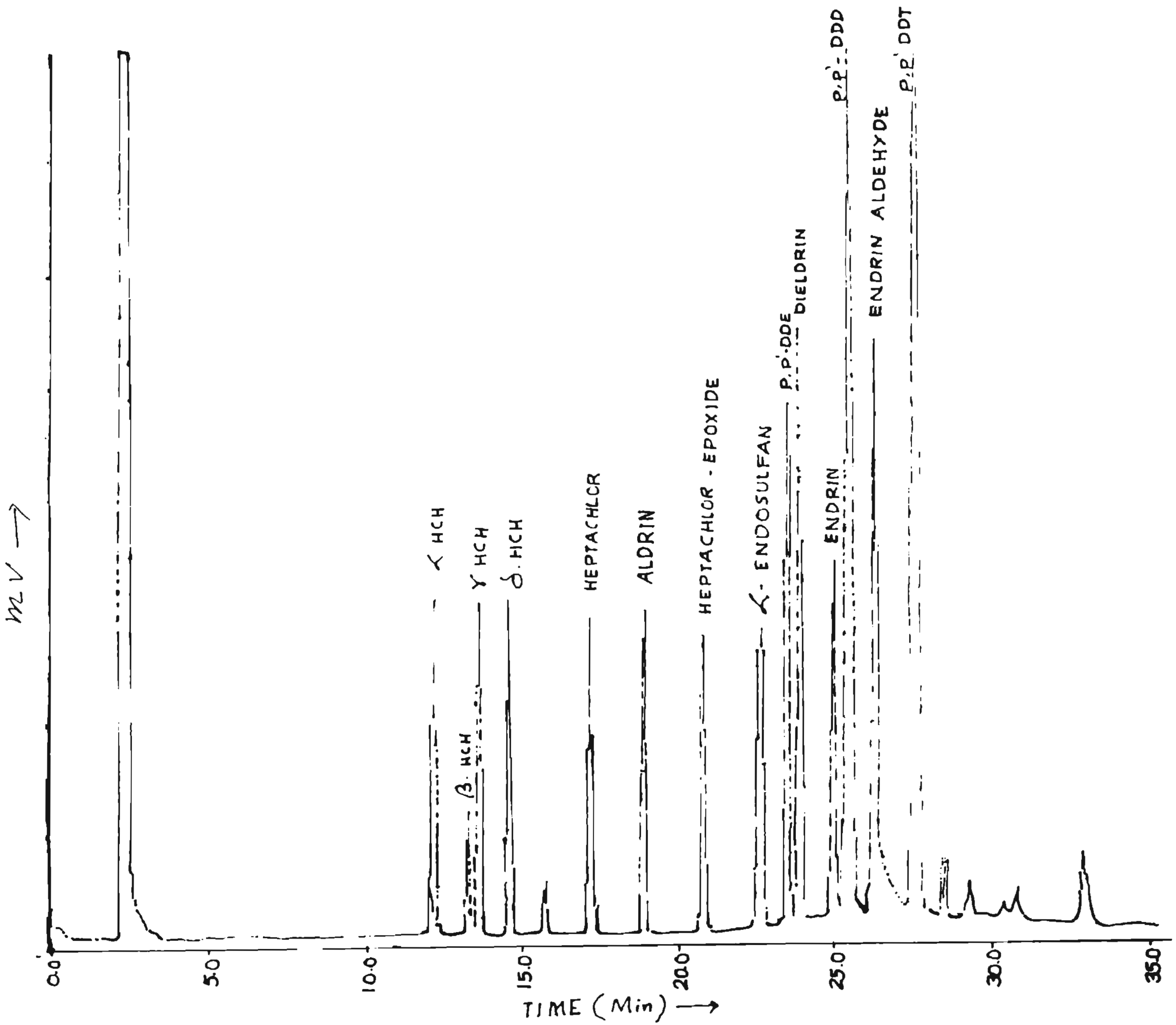


Figure 2.2 Gas chromatogram of standard organochlorine pesticides.

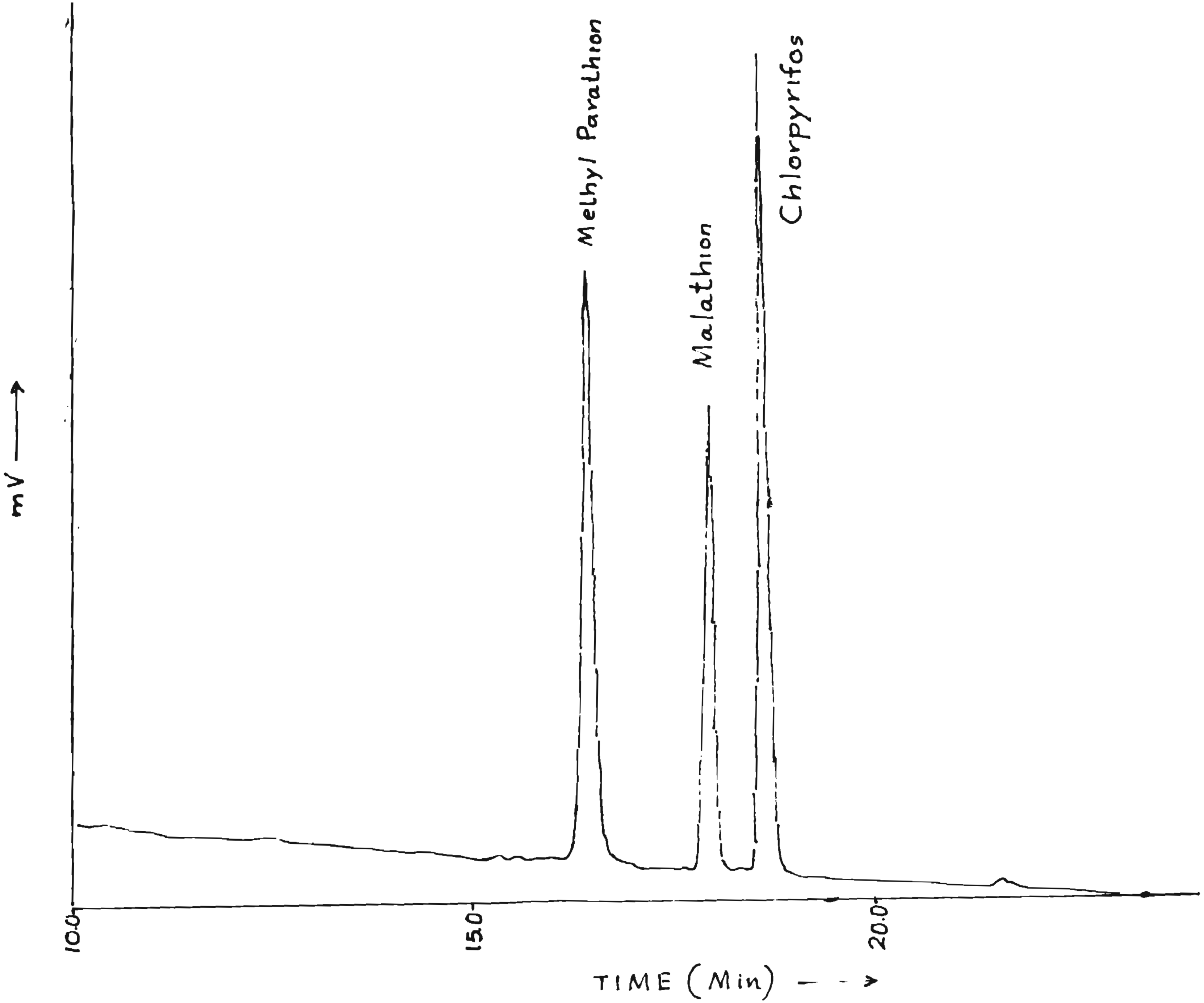


Figure 2.3 Gas chromatogram of standard organophosphorus pesticides.

detection limit for organophosphorus pesticides in water was 0.05 µg l^{-1} and for sediments was 0.4 ng g^{-1} The initial calibration of GC was carried out by injecting, suitable amounts of standard pesticide solutions. Analysis of the solvent blanks confirmed the absence of any of the pesticides under investigation in the solvent. The analytical reproducibility was checked by duplicate measurements. 0.5 µl to 2.0 µl samples were injected in previously conditioned GLC.

2.4 Analyses of data

Statistical analyses of the data were done wherever necessary. Regression analyses were performed between different pesticides with environmental parameters.

CHAPTER 3

GENERAL HYDROGRAPHICAL AND SEDIMENTARY PARAMETERS

3.0 INTRODUCTION

The study of the hydrographical parameters has great importance in characterizing the general features of an estuarine system. With regards to water management and pollution control, these studies are very important. It provides the background information necessary for the understanding of the estuarine processes. Hydrochemical factors can influence the colour, odour, taste, temperature and degree of mineralisation of water derived from surface runoff, underground spring etc. (Clark and Snyder, 1970). They are equally significant for pollution control, harbour design, marine traffic routing etc. The structure of the physical and chemical environment is commonly expressed in terms of water quality parameters. The hydrographical conditions of an estuary generally depend on the intrusions of sea water associated with tides, and the influx of fresh water from rivers. Precipitation, coagulation and evaporation processes also contribute to hydrographical changes. Moreover, the bottom topography and geographical conditions in the estuary exert a profound influence on the hydrographical conditions of the estuary. The hydrographical parameters of an estuary are also affected by the natural and anthropogenic changes occurring in an ecological system.

The variations in hydrographical and sedimentary parameters in estuaries affect the transport mechanisms, degradation nature and also the persistence of pesticides. The water pH, dissolved oxygen, temperature and salinity are greatly influencing the distribution and degradation of pesticides in the fluvial systems. The distributional behaviour of pesticides in sediments are always dependent on sedimentary parameters like organic carbon, sediment moisture and grain size variations. So, the studies of hydrographical and sedimentary parameters are essential for characterising the distributional patterns of pesticides in the different environmental compartments.

The hydrography of Kuttanad and Cochin backwater systems has also been reported earlier by Qasim and Reddy (1967), Qasim et al. (1968), Sankaranarayanan and Qasim (1969), Josanto (1971), Shynarnma and Balakrishnan (1973), Silas and Pillai (1975), Lakshmanan et al. (1982), Anirudhan (1988), KWBS (1989), Babukutty (1991), Nair (1992), Shibu (1992), Harikrishnan (1997), Suresh Kumar (1998) and Lizen (2000).

3.2 MATERIALS AND METHODS

Materials and methods are described in Chapter 2.

3.3 RESULTS AND DISCUSSION

3.3.1 General hydrographical parameters

Temperature

The mixing of inflowing river water and tidally influenced sea water plays an important role in the distribution of temperature in an estuary. Processes like exchange of heat with atmosphere, and any localized phenomenon are also likely to influence the distribution of temperature. The volatilizations of pesticides are also directly related to the increase in temperature. The temperature observed in this estuary showed only moderate variations. The station wise annual mean variations of temperature are depicted in Figure 3.1 and the station wise summary statistics of temperature is given in Table 3.1. The annual mean variations of temperature ranged from 29.6 to 30.2 °C in surface waters and 29.3 to 29.9°C in bottom waters. In all stations, the surface temperatures were slightly higher than that of bottom temperature.

Table 3.1 Station wise summary statistics of temperature on surface and bottom waters

Surface (°C)

Stations	Minimum	Maximum	Mean	SD	CV
1	27.5	32.5	30.1	1 7	5.7
2	27.0	32.5	30.1	1 7	5.7
3	28.0	32.0	29.9	1.5	5.0
4	28.0	32.0	30.1	1.5	4.8
5	27.8	32.0	30.0	1 7	5.8
6	27.2	33.0	30.2	1.8	5.8
7	27.0	32.0	29.6	1.5	5.1
8	27.0	32.0	29.6	1.7	5.6
9	27.0	32.0	29.7	1.6	5.4

Bottom (°C)

Stations	Minimum	Maximum	Mean	SD	CV
1	27.0	32.0	29.3	1.5	5.1
2	27.0	32.0	29.4	1.6	5.4
3	27.5	31.0	29.3	1.5	5.0
4	27.8	32.0	29.7	1.5	4.9
5	27.5	32.0	29.7	1 7	5.8
6	27.0	33.0	29.9	1.8	6.2
7	27.0	32.0	29.3	1.5	5.3
8	27.0	31.5	29.4	1.5	5.2
9	27.0	31.5	29.4	1.4	4.8

SD - Standard deviation; CV - Coeficient of variation

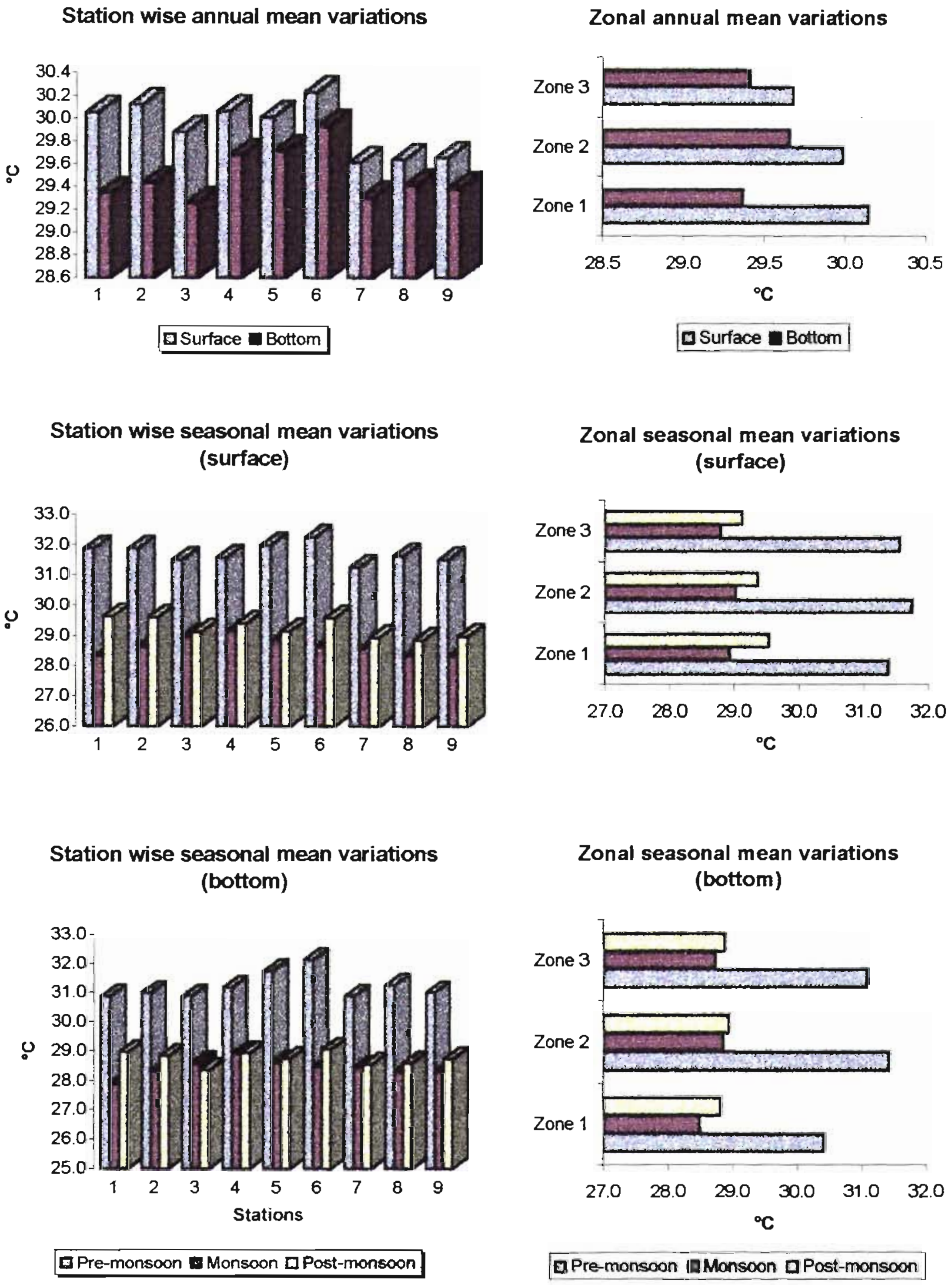


Figure 3.1 Seasonal and spatial variations of temperature in surface and bottom waters

The station wise seasonal mean variations of temperature for surface and bottom waters are also shown in Figure 3.1. The pre-monsoon values varied between 30.5 to 33.0 °C in surface and 30.0 to 33.0 °C in bottom waters. During monsoon, the temperature in all stations varied from 27.0 to 31.0 °C, both in surface and bottom waters. The post-monsoon values of temperature ranged from 28.0 to 31.0 °C in surface waters and 27 1 to 30.2 °C in bottom waters. The values of temperature were slightly high during pre-monsoon period. In monsoon and post-monsoon periods, the mean values of temperature were almost constant and show only a narrow range of variability.

The zonal variations of temperature for surface and bottom waters in zones 2 and 3 were almost constant but zone 1 showed maximum variation in temperature and was primarily associated with the depth of the water column. In pre-monsoon period, all the three zones of surface and bottom waters recorded higher values of temperature than monsoon and post monsoon periods.

The observations of Harikrishnan (1997), Suresh Kumar (1998) and Lizen (2000) about the temperature variations of surface and bottom waters are also comparable with the present study. The combined effect of large influx of river run-off and monsoonal rains accounts for the lowering in surface temperature values during monsoon period.

pH

pH is an important hydrological feature indicating the level of dissolved carbon dioxide in water, which may inturn reflect the activity of phytoplankton and the level of dissolved oxygen in the sea (Skirrow, 1975). Many of the life process are dependent on the hydrogen ion concentration in the surrounding medium. The factors influencing the pH in this estuary are mild, like photosynthesis and the extent of salinity changes during salt-water intrusion. Monitoring of pH values is therefore essential for identifying zones of pollution and other quality conditions of water (Clark et al., 1977). Natural turbulence with concomitant aeration can also influence the pH, though to a limited extent

(Zingde and Desai, 1987). The pH has some influence on the degradation of pesticides in the aquatic environment.

The station wise annual mean variations of the pH at surface and bottom waters are given in Figure 3.2 and the station wise summary statistics of pH is given in Table 3.2. It is noted from the Figure that the annual mean values of surface pH were generally higher than that of bottom pH in all stations except at station 9. Wide ranges of pH values were observed during this study, 4.3 to 8.0 in surface waters and 4.5 to 7.4 in bottom waters. The lowest pH was recorded at station 7 both in surface and bottom waters and the highest at station 1 both in surface and bottom waters. The mean values of pH ranged from 6.3 to 7 1 in surface waters and 6.2 to 6.7 in bottom waters. Generally, low values of pH were observed during pre-monsoon period and higher values of pH were observed during post-monsoon period (Figure 3.2). During monsoon, the pH in all stations varied in a narrow range and was from 6.4 to 7.0 in surface waters and 6.1 to 7 1 in bottom waters.

The zonal annual and seasonal mean variations of pH in surface and bottom waters are also shown in Figure 3.2. The main factors influencing the pH of Kuttanad backwaters are discharge of fresh waters from the four river systems, extent of salinity changes due to the operation of salinity barrier and also due to the photosynthetic activity of phytoplanktons. The biochemical decomposition of organic matter brought to the estuarine waters by monsoonal land runoff may increase the carbon dioxide content and subsequently lower the pH. The values of pH obtained are in full agreement with the earlier observations (Harikrishnan, 1997; Suresh Kumar, 1998; Lizen, 2000). It was reported that the soil acidity of the kuttanad region increases during pre-monsoon season (KWBS, 1989). Thus, the variations in pH observed may also be due to the effect of acidic soils of Kuttanad, run-off associated with monsoon and also due to the significant utilization of dissolved oxygen by organic matter.

Table 3.2 Station wise summary statistics of pH in surface and bottom waters

Surface

Stations	Minimum	Maximum	Mean	SD	CV
1	6.6	8.0	7.1	0.4	6.1
2	6.6	7.7	7.0	0.3	5.0
3	6.4	7.3	6.9	0.3	4.4
4	6.2	7.3	6.7	0.3	4.9
5	6.4	7.1	6.8	0.2	3.6
6	5.7	7.1	6.7	0.4	5.5
7	4.3	7.2	6.3	0.9	14.8
8	6.2	7.2	6.8	0.3	4.6
9	5.9	7.0	6.5	0.5	7.2

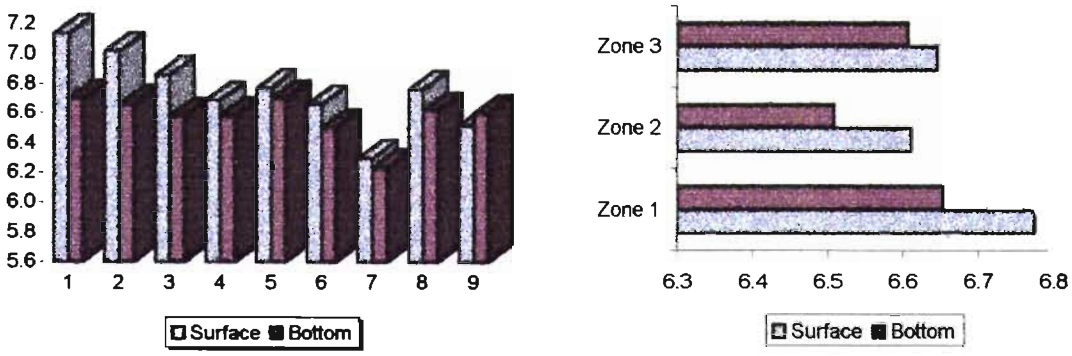
Bottom

Stations	Minimum	Maximum	Mean	SD	CV
1	6.1	7.4	6.7	0.4	6.3
2	6.2	7.1	6.7	0.3	4.6
3	6.2	7.1	6.6	0.3	4.3
4	6.1	7.2	6.6	0.4	5.6
5	6.4	7.1	6.7	0.2	3.6
6	5.7	7.1	6.5	0.4	6.0
7	4.5	7.0	6.2	0.9	13.7
8	6.1	7.0	6.6	0.4	5.4
9	5.9	7.1	6.6	0.4	6.8

SD-Standard deviation; CV-Coefficient of variation

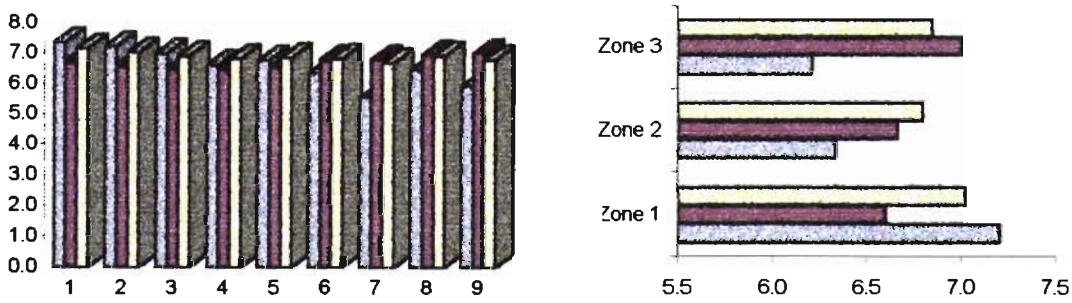
Station wise annual mean variations

Zonal annual mean variations



Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)



Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

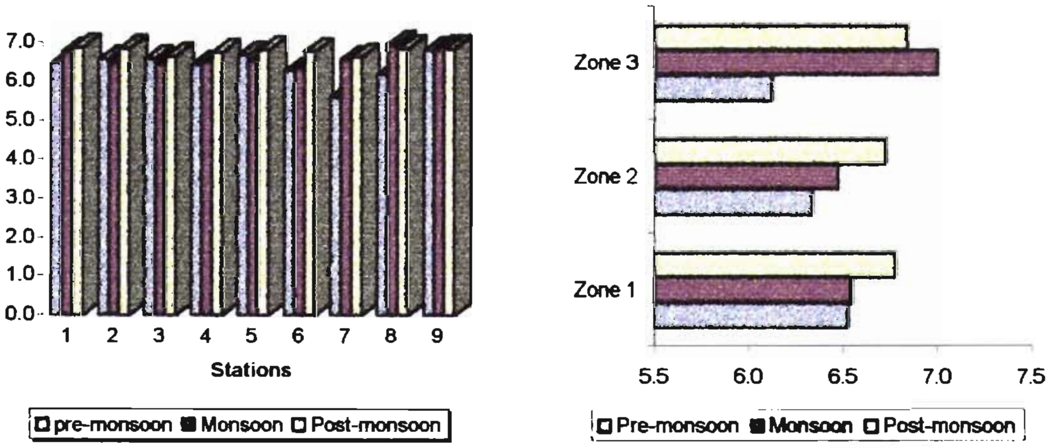


Figure 3.2 Seasonal and spatial variations of pH in surface and bottom waters

Dissolved oxygen

Dissolved oxygen is one of the most valuable water quality parameters in assessing water pollution. It is also important since the existence of aquatic life is intimately linked with the availability of oxygen for their survival. Though atmospheric oxygen is abundant, its solubility in water is low, 9.94 ml l^{-1} at 1°C and 5.28 ml l^{-1} at 30°C in fresh water and 7.97 ml l^{-1} at 1°C and 4.41 ml l^{-1} at 30°C in sea water of salinity 33 x 10^{-3} (Riley and Chester, 1971). The depletion of oxygen content leads to considerable obnoxious odour under extreme anaerobic condition and damage to aquatic life (Doudoroff Shumway and Peter, 1970). The concentration and distribution of oxygen in natural waters depend on various factors such as temperature, partial pressure, turbulence of water, photosynthesis, salinity etc. Studies of salinity dependent oxygen solubility may help to elucidate the various physical, chemical and biological processes taking place in the estuarine system (De Sousa and Sen Gupta, 1986).

The station wise mean variations of surface and bottom dissolved oxygen are plotted in Figure 3.3. The station wise summary statistics of dissolved oxygen is given in Table 3.3. The dissolved oxygen contents of bottom waters in almost all stations were slightly lower than that of surface waters except at station 7 This may be attributed to the partial utilization of dissolved oxygen by organic rich sediments. Oxygen can diffuse in surface waters to support aerobic process. The minimum and maximum values of dissolved oxygen observed at surface waters were 3.33 and 7.55 ml l^{-1} and in bottom waters were 1.88 and 7.69 ml l^{-1} In bottom water, the lowest value of dissolved oxygen (1.88 ml l^{-1}) was recorded at station 2 and the highest value of 7.69 ml l^{-1} at station 4. The mean values of dissolved oxygen ranges from 4.63 to 5.38 ml l^{-1} in surface waters and 4.35 to 5.34 ml l^{-1} in bottom waters.

The seasonal mean variations of dissolved oxygen in both surface and bottom waters are also shown in Figure 3.3. The pre-monsoon values varied between 3.77 to 7.55 ml l^{-1} at surface and 1.88 to 6.67 ml l^{-1} at bottom waters.

Table 3.3 Station wise summary statistics of dissolved oxygen in surface and bottom waters

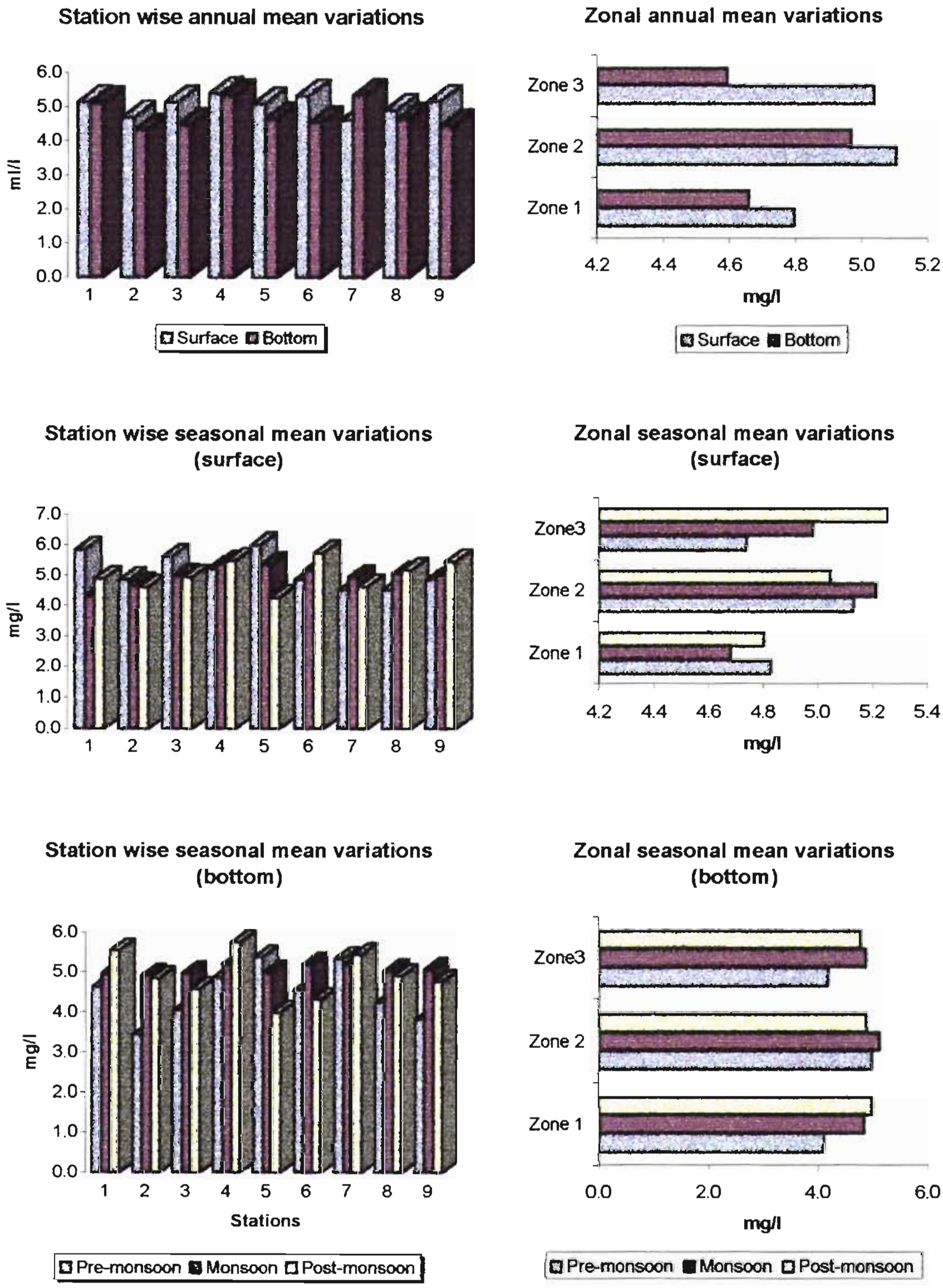
Surface (ml l^{-1})

Stations	Minimum	maximum	Mean	SD	cv
1	4.28	6.93	5.14	0.93	18.05
2	3.64	5.67	4.71	0.71	14.97
3	4.61	6.88	5.15	0.67	12.91
4	4.80	6.09	5.38	0.38	7.12
5	3.74	7.55	5.10	1.26	24.63
6	4.38	7.14	5.33	0.95	17.89
7	3.33	6.20	4.63	0.88	19.04
8	3.78	6.41	4.92	0.81	16.42
9	4.20	7.06	5.17	0.85	16.52

Bottom (ml l^{-1})

Stations	Minimum	maximum	Mean	SD	cv
1	2.81	6.62	5.10	1.06	20.86
2	1.88	5.77	4.35	1.24	28.61
3	3.54	4.98	4.50	0.42	9.32
4	4.38	7.69	5.33	1.09	20.49
5	2.99	6.05	4.67	0.86	18.47
6	3.91	5.20	4.56	0.47	10.34
7	4.35	6.67	5.34	0.69	12.96
8	3.57	5.91	4.67	0.74	15.78
9	3.34	5.73	4.47	0.84	18.78

Standard deviation; CV-Coefficient of variation



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 3.3 Seasonal and spatial variations of dissolved oxygen in surface and bottom waters

During the monsoon period, the dissolved oxygen values ranged from 4.32 to 5.40 ml l^{-1} at surface and 4.73 to 5.40 ml l^{-1} at bottom. The post-monsoon values of dissolved oxygen ranged from 3.33 to 7.06 ml l^{-1} in surface waters and 2.99 to 7.69 ml l^{-1} in bottom waters. Comparatively higher dissolved oxygen content was observed during monsoon at almost all stations and is partially due to the greater solubility of oxygen in fresh water. The annual zonal mean variations and zonal seasonal mean variations of dissolved oxygen for surface and bottom waters are also shown in Figure 3.2. High dissolved oxygen recorded in zones 1 and 2 in surface and bottom waters during monsoon period is again due to the greater solubility of oxygen in fresh water and high turbulence. Pre-monsoonal low values of dissolved oxygen in zone 3 for surface and bottom waters are partially governed by the effect of temperature on solubility, and the high value of salinity in zone 3.

Suresh Kumar (1998) reported prominent fluctuations in the dissolved oxygen content in the range of 2.2 to 9.5 ml l^{-1} in Kuttanad backwaters. The oxidation of organic compounds in zone 1 may further reduce the oxygen content of bottom water. Phytoplankton acts as an important source of oxygen as a photosynthetic product (Chan, 1965), and thus the dissolved oxygen values may provide a general indication of primary productivity (Mountford, 1969). The observed low oxygen content at stations 1 and 2 in bottom waters in pre-monsoon period may be due to the higher utilization of oxygen for the decay of organic matter in the areas. Further, the estuarine sediments contain high concentration of oxygen demanding materials and when they are discharged to water, a high oxygen demand is exerted.

Salinity

The salinity distribution pattern is largely influenced by the mixing and diffusion phenomena occurring in the estuaries. Wide fluctuations in salinity are generally observed in an estuarine system. Variations of salinity in an estuarine system are largely influenced by the influx of fresh water, intrusion of sea water and the tidal influx into the estuary. Salinity is one of the most fluctuating water parameters in this estuary and varies with season. The operation of salinity

Table 3.4 Station wise summary statistics of salinity in surface and bottom waters

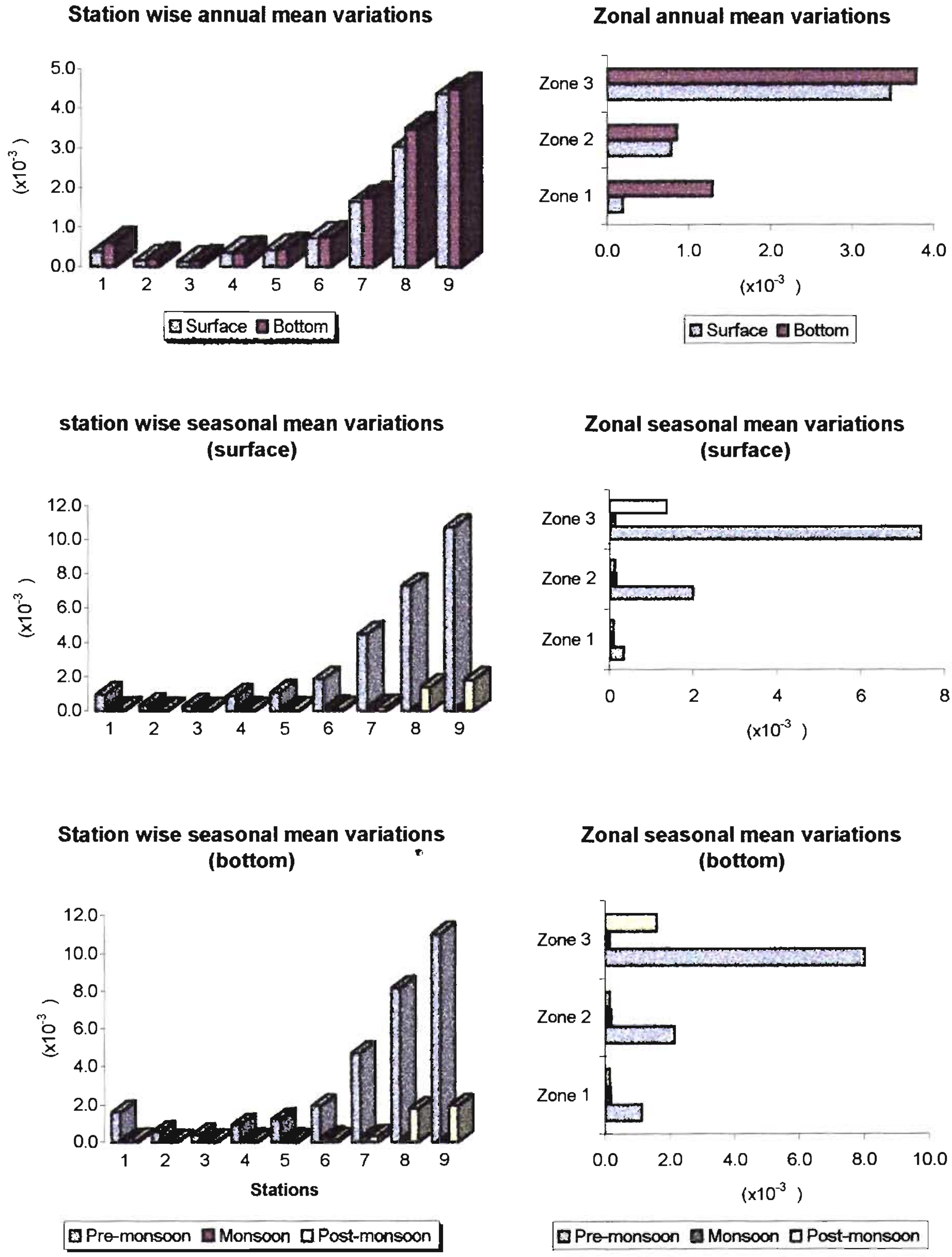
Surface $(x\ 10^{-3})$

Stations	Minimum	Maximum	Mean	SD	CV
1	0.07	2.15	0.38	0.68	179.47
2	0.05	0.59	0.15	0.19	129.27
3	0.05	0.52	0.13	0.15	114.37
4	0.05	1.77	0.36	0.55	152.00
5	0.05	1.63	0.43	0.59	138.71
6	0.07	2.96	0.73	0.99	136.35
7	0.07	7.98	1.67	2.47	148.22
8	0.07	10.36	3.06	3.68	120.35
9	0.08	12.08	4.38	4.96	113.21

Bottom $(x\ 10^{-3})$

Stations	Minimum	Maximum	Mean	SD	CV
1	0.07	4.57	0.61	1.31	213.10
2	0.05	1.35	0.22	0.38	173.52
3	0.05	0.53	0.15	0.17	108.22
4	0.07	1.76	0.37	0.57	151.75
5	0.07	1.91	0.47	0.66	141.48
6	0.07	2.98	0.75	1.02	135.26
7	0.07	8.22	1.77	2.58	145.66
8	0.05	9.89	3.50	3.89	111.17
9	0.06	12.34	4.53	5.13	113.29

SD - Standard deviation; CV - Coeficient of variation



Station wise annual mean variations

Zonal annual mean variations

station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 3.4 Seasonal and spatial variations of salinity in surface and bottom waters

barrier at Thanneermukkam plays a major role in the distribution of salinity in the backwaters of Kuttanad.

Figure 3.4 shows the station wise annual mean variations of salinities in surface and bottom waters and Table 3.4 shows the station wise summary statistical data of surface and bottom salinities. In general, the bottom salinity was found to be slightly higher than that of surface salinity. The minimum value of salinity (0.05×10^{-3}) was recorded at stations 2 to 5 in surface waters and 2 and 3 in bottom waters. The maximum values of salinity for both surface and bottom waters were recorded at station 9, and the values were 12.08×10^{-3} and 12.34×10^{-3} respectively. The mean values of salinity ranged from 0.13×10^{-3} to 4.38×10^{-3} in surface waters and 0.15×10^{-3} to 4.53×10^{-3} in bottom waters. A gradual increase in salinities could be observed from station 1 to station 7 and high increase in salinities at stations 8 and 9. The northern regions of the estuary recorded maximum salinity, which indicates the effect of sea water influx in that region.

The seasonal distributions of surface and bottom salinities are presented in Figure 3.4. It was noticed that the salinity values in all stations were high in pre-monsoon period and low in monsoon period both in surface and bottom waters. During pre-monsoon, the surface salinity values varied from 0.07×10^{-3} at station 3 to 12.08×10^{-3} at station 9. During monsoon season, both surface and bottom values showed almost fresh water condition. During post-monsoon, the minimum and maximum surface salinities recorded were 0.05×10^{-3} at stations 2 and 3, and 4.28×10^{-3} at station 9. In general, stations 1, 2 and 3 showed lowest values of salinity in all three seasons, both in surface and bottom waters, because these stations are influenced by the influx of fresh water from the rivers. A gradual increase in salinity values could be observed as the season progressed to post-monsoon and pre-monsoon.

The zonal annual mean and seasonal variations of salinity in surface and bottom waters are also plotted in Figure 3.4. Zone 1 recorded the lowest values of salinity due to the discharge of fresh water from the rivers. Zone 3 recorded the maximum values of salinity due to the influence of saline water. The annual mean variations clearly indicated that the variations of salinity were observed only in zone 1, and in zones 2 and 3, the surface and bottom salinities were almost equal. This indicates a well-mixed zone in these parts of the estuary. A horizontal salinity gradient was observed during the period of survey with declining values from the salinity barrier (zone 3), to the riverine stations (zone 1). The most obvious water movement is caused by tidal currents and is considered as the prime factor responsible for the supply of energy required for the vertical and horizontal mixing of estuaries.

An increase in salinity during the dry months when the fresh water discharges got reduced, and a corresponding decrease in salinity during monsoon when fresh water pushes salt water down the lake are the usual observations. Josanto (1971) reported a bottom salinity fluctuation between 18 and 22×10^{-3} prior to the commissioning of the salinity barrier. The reduction of salinity values may be due to the diminishment of tidal action as the same is strongly sensitive to physical obstructions (Josanto, 1971). Harikrishnan (1997) and Suresh Kumar (1998) reported that the fluctuations of salinity were in a range of 0 to 8×10^{-3} The recent studies established that a total change in the pattern of salinity distribution in the lake has been taken place since the commissioning of the salinity barrier across the lake in 1976. Thus, the salinity distribution pattern in Kuttanad backwaters is largely determined by the operation schedule of salinity barrier at Thanneermukkam. Table 2.1 gives a detailed record of the operating schedule of Thanneermukkam bund.

Depth

The station wise annual mean variations and seasonal mean variations of depth of the water column are given in Figure 3.5. The station wise summary statistics of depth is given in Table 3.5. A minimum depth of 1 m was noted at station 8 and maximum depth of 10 m was recorded at stations 1, 2 and 3. Monsoon periods recorded maximum depth than in other seasons. The zonal annual mean and seasonal variations of depth are also plotted in Figure 3.5. On approaching from zone 1 to zones 2 and 3, the depth was gradually decreased.

Table 3.5 Station wise summary statistics of depth and sediment organic carbon

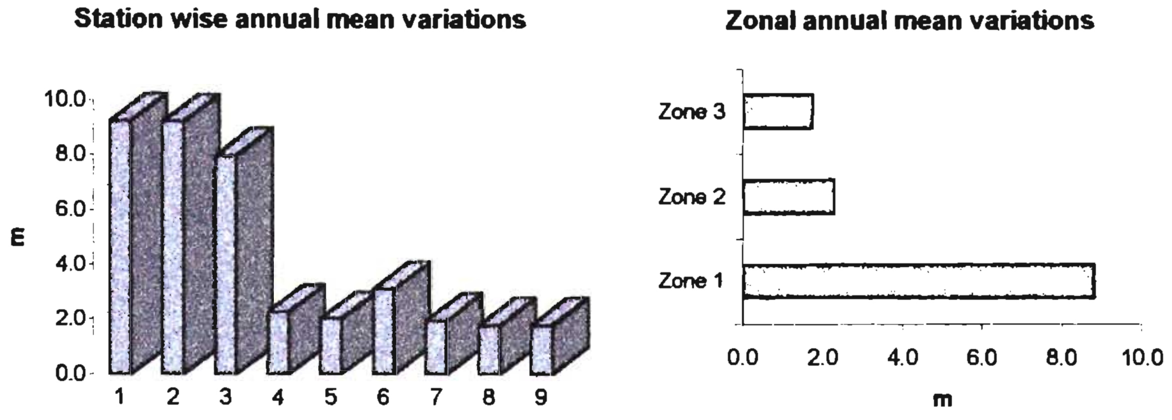
Depth (m)

Stations	Minimum	Maximum	Mean	SD	CV
1	5.0	10.0	9.3	1.4	15.4
2	6.0	10.0	9.2	1 1	12.1
3	4.5	10.0	8.0	1.6	19.6
4	1.5	3.0	2.3	0.5	20.1
5	1.0	3.0	2.0	0.8	38.4
6	1.5	4.5	3.1	0.7	23.8
7	1.5	3.0	1.9	0.5	26.9
8	1.0	2.0	1.8	0.3	19.3
9	1.5	2.0	1.8	0.3	14.9

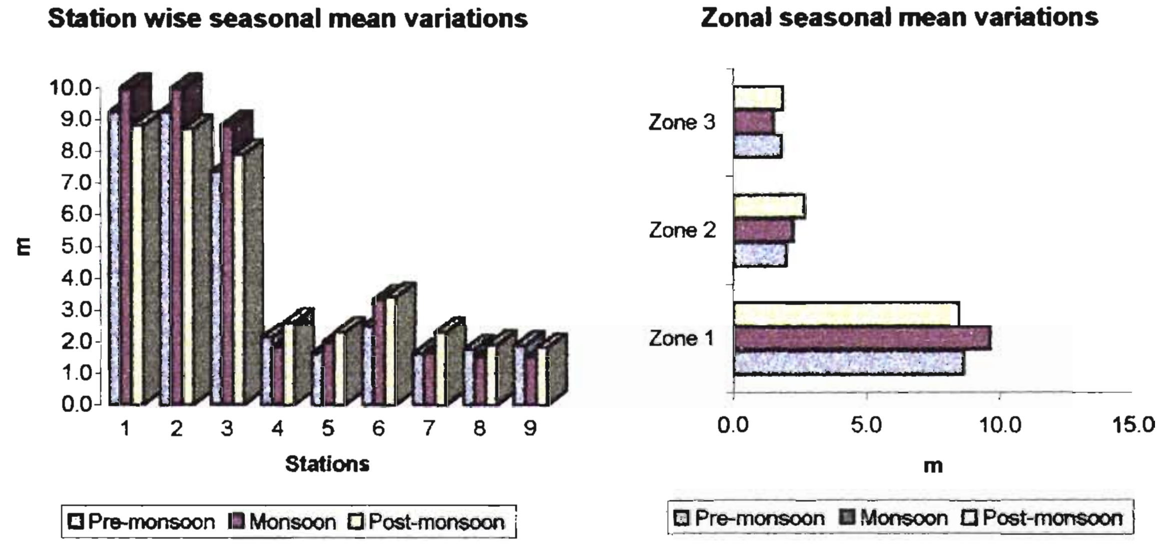
Sediment organic carbon (mg g-1)

Stations	Minimum	Maximum	Mean	SD	CV
1	24.35	42.52	35.22	4.96	14.09
2	11.09	39.39	30.77	9.60	31 19
3	26.00	47.88	37.16	6.07	16.33
4	28.89	36.91	32.53	2.16	6.63
5	9.88	36.81	27.11	7.81	28.81
6	18.74	38.76	28.08	6.49	23.10
7	10.33	39.56	29.78	7.85	26.35
8	3.03	36.56	9.42	9.14	97.03
9	1.04	22.38	7.98	6.08	76.14

SD - Standard deviation; CV - Coefficient of variation


Station wise annual mean variations

Zonal annual mean variations


Station wise seasonal mean variations

Zonal seasonal mean variations

Figure 3.5 Seasonal and spatial variations of depth of the water column

Zone 1 recorded maximum depth, and zones 2 and 3 recorded almost comparable depths. The mean values of depth ranged from 1.75 to 9.25 meters.

3.3.2 General sedimentary parameters

The general sedimentary characteristics like organic carbon, sediment moisture and grain size distribution of the sediments in the Kuttanad backwaters are described below.

Sediment organic carbon (SOC)

Organic carbon plays a major role in controlling the redox potential of the sediment, thereby regulating the behaviour of other chemical species. Organic carbon compounds have an affinity for both trace metals and trace organics like pesticides. Hence, organic carbon has been recommended as a readily measured pollution indicator. Knowledge of the nature, origin and transformation of organic matter in estuarine sediments may provide valuable information on the sedimentary environment of basin sediment.

Organic matter in sediments has to be regarded as the residue of organic life and this became more important and more abundant with the development and diversification of life. The physical and chemical properties of sediments such as water retention capacity, porosity and compressibility are to a great extent controlled by the amount of organic material within the sediments. Organic matter supports microbial metabolism. This, inturn, influences the organic chemical reactions by regulating pH and Eh conditions. In closed seas and in highly productive coastal waters, the mean amount of organic carbon increases three or four times and even more (Menzel and Vaccaro, 1964). The organic matter in the sea water is chemically complex, physically heterogeneous and variable with time and space (Azam and Cho, 1987). In estuarine mixing zones, additional complexity is encountered because of transformation of chemicals and biological species under extreme salinity gradient (Morris et al., 1978; Mantoura, 1987).

The station wise annual mean variations of the organic carbon of sediment are given in Figure 3.6 and the station wise summary statistics of organic carbon is given in Table 3.5. Station 9 showed the lowest value of organic carbon (1.04 mg g^{-1}) and station 3 showed the highest value of organic carbon (47.88 mg g^{-1}). The mean values of organic carbon for stations 8 and 9 were less than that of other stations. The mean values of organic carbon ranged from 7.98 to 37 16 mg g^{-1} In zone 3, the value of organic carbon was found to be lower than that of zones 1 and 2.

The reported values of organic carbon content in sediments of Cochin estuary were 0.18 to 34.98 mg g^{-1} (Nair, 1992); 0.63 to 71.44 mg g^{-1} (Jayasree, 1993); 1.0 to 60.0 mg g^{-1} (Padmalal and Seralathan, 1995). The higher values of organic carbon in zone 1 may be attributed to the run-off from rivers and also due to the domestic sewage. Lower organic content in zone 3 may be due to the sandy nature of sediments in that area.

Sediment moisture content

The annual mean and seasonal mean variations of sediment moisture are given in Figure 3.7 and the station wise summary statistics of moisture is given in Table 3.6. The lowest and highest values of moisture were recorded at station 8. Figure 3.7 shows that the moisture content gradually decreased from station 1 to station 9 both annually and seasonally. The annual mean values of moisture ranged from 24.62 to 48.60 %.

The zonal annual mean and seasonal mean variations of sediment moisture are shown in Figure 3.7 Zone 1 recorded the highest mean value and zone 3 recorded the lowest mean value of moisture for the entire period of study. This is primarily due to the difference in the sediment type from riverine zone to estuarine zone. No such difference in variation was seen in the seasonal variation of moisture in zones 1 and 2. The high value of moisture in zone 1 was due to the presence of loose and non-rigid surficial sediments showing comparatively more moisture content.

Table 3.6 Stationwise summary statistics of moisture

Stations	Minimum	Maximum	Mean	SD	CV
1	36.82	56.53	45.99	5.82	12.65
2	26.94	54.43	45.49	7.48	16.45
3	40.79	54.06	48.60	4.42	9.09
4	40.33	50.52	46.39	3.07	6.61
5	29.32	50.96	42.50	6.50	15.31
6	37.64	49.23	41.04	3.12	7.60
7	29.50	47.95	39.50	5.01	12.69
8	20.05	63.86	28.93	11.95	41.32
9	20.34	33.32	24.62	3.87	15.73

SD - Standard deviation; CV - Coefficient of variation

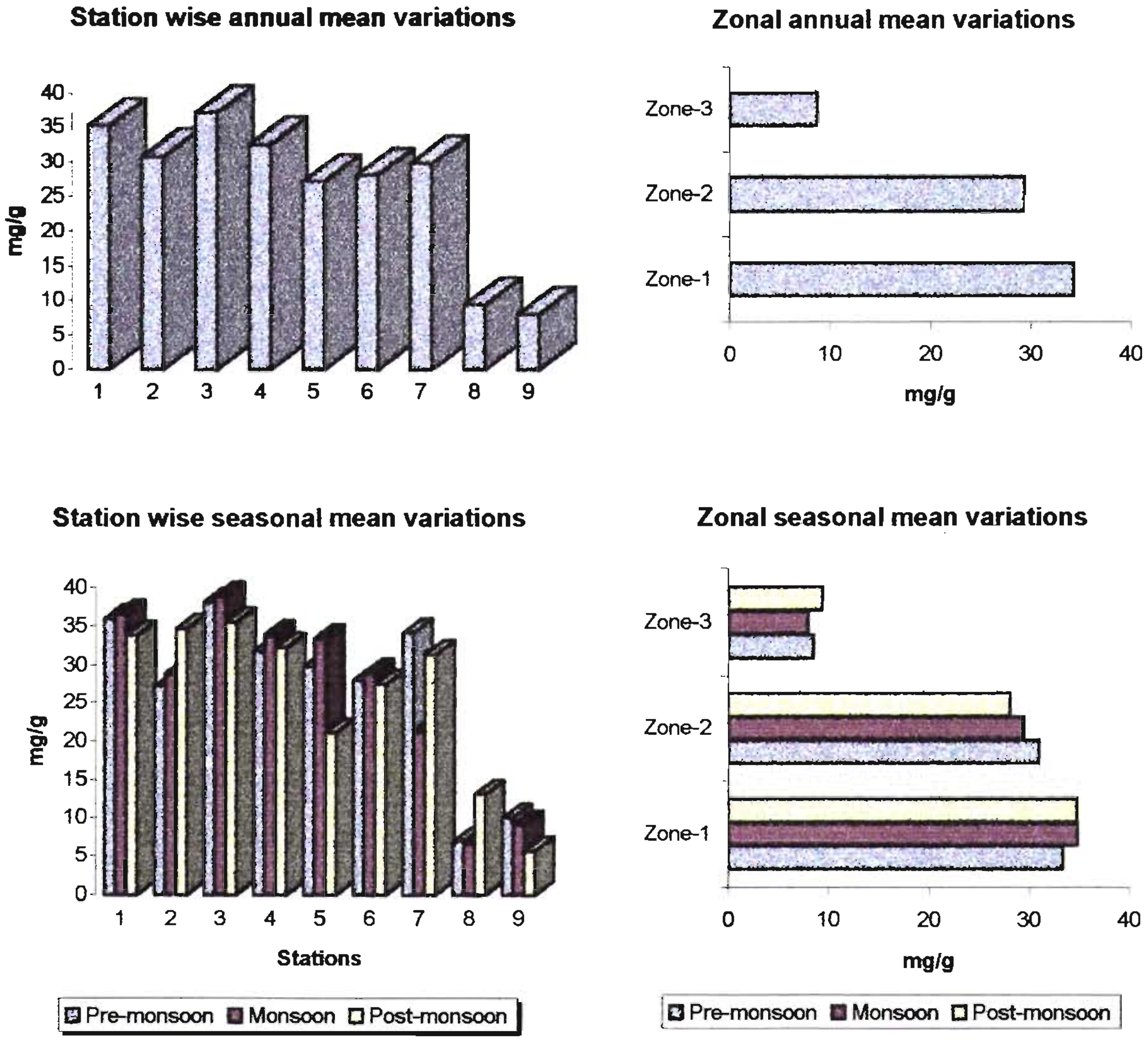
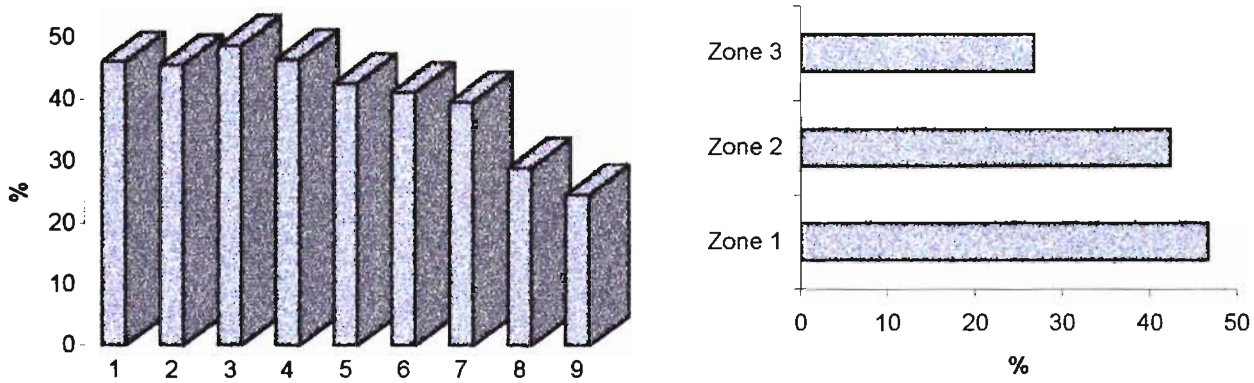
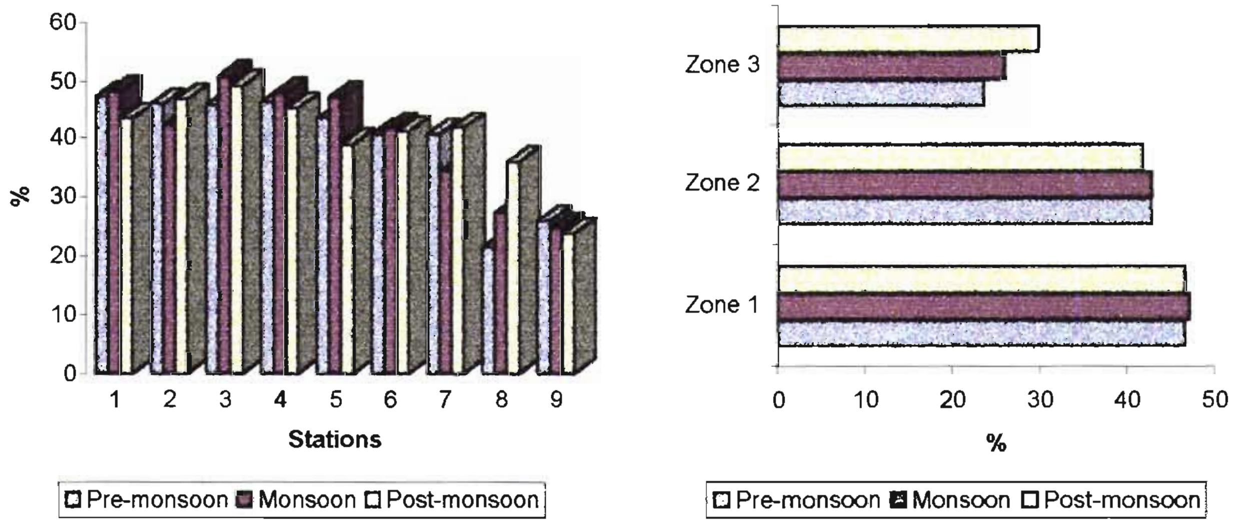


Figure 3.6 Seasonal and spatial variations of organic carbon in sediments



Station wise anuual mean variations

Zonal annual mean variations



Station wise seasonal mean variations

Zonal seasonal mean variations

Figure 3.7 Seasonal and spatial variations of moisture in sediments

Textural characteristics of sediments

The study of grain size distribution reveals the physical effects of the environment on deposition, and the hydrodynamic conditions existing at the time of deposition. Grain size is one of the basic characteristics of sediments and its determinations are necessary to delineate the sedimentary environments. Textural characteristics of sediments play a significant role in the distribution and concentration of carbon, nitrogen, and phosphorous both in sediment and in the overlaying water column. The textural characteristics of sediments have also an influence on the adsorption of pesticides. In Kuttanad backwater system, the three rivers Pampa, Achencoil and Manimala are supplying the bulk of the sedimentary material, mainly on rainy season. The sediments are transported as bed load as well as suspended load (Veerayya and Murthy, 1974).

The station wise seasonal variations of sand, silt and clay fractions are presented in Figure 3.8. Sand represents particles of size greater than 63µ, silt indicates sizes between 63µ and 4µ, and clay includes particles less than 4µ (Krumbein and Pettijohn, 1938). The seasonal averages of sand, silt and clay fractions at each of the stations along with their textural classifications according to Shepard (1954), are summarised in Table 3.7

The sand content gradually increased from zone 1 to zone 3 in all seasons and highest percentage of sand was seen in zone 3 (Figure 3.8). The slight increase of sand in post-monsoon period in zone 1 was due to the run-off from rivers. The silt and clay percentages were maximum in zone 1 in all seasons. Silt was maximum in monsoon both in zones 1 and 2, and comparably less in zone 3. Clay percentages were maximum in pre-monsoon both in zones 1 and 2 and very low in zone 3.

The textural characteristics of the sediments at stations 8 and 9 (zone 3) in all seasons were sandy in nature. In stations 1 to 3 (zone1), sediment was

Table 3.7 Size composition of sediments

Station	Season	Nature of sediment	sand >63µm	silt 4-63µm	clay <4µm
1	Pre-monsoon	sand silt clay	40.51	24.73	34.76
	Monsoon	sand silt clay	25.68	49.36	24.96
	Post-monsoon	sand silt clay	46.19	25.16	28.65
2	Pre-monsoon	clayey silt	7 70	47.53	44.77
	Monsoon	sand silt clay	42.43	26.42	31 15
	Post-monsoon	sand silt clay	38.52	35.33	26.14
3	Pre-monsoon	clayey silt	9.58	48.14	42.28
	Monsoon	clayey silt	13.37	50.89	36.04
	Post-monsoon	silty sand	60.17	30.64	9.19
4	Pre-monsoon	clayey silt	6.09	50 31	43.60
	Monsoon	sand silt clay	30.5	44.88	24.62
	Post-monsoon	clayey silt	10.21	47.39	42.40
5	Pre-monsoon	clayey silt	36.74	27.44	35.82
	Monsoon	sand silt clay	22.71	47.9	29.39
	Post-monsoon	silty sand	73.76	13.41	12.83
6	Pre-monsoon	sandy silt	40.05	52.08	7.87
	Monsoon	sandy silt	41.94	43.95	14.11
	Post-monsoon	sand silt clay	49.12	23.07	27.82
7	Pre-monsoon	silty sand	72.62	23.12	4.26
	Monsoon	silty sand	73.09	15.82	11.09
	Post-monsoon	sand silt clay	32.6	44.23	23.17
8	Pre-monsoon	sand	94.60	4.76	0.64
	Monsoon	sand	83.31	9.31	7.38
	Post-monsoon	sand	89.31	2.67	8.02
9	Pre-monsoon	sand	91.06	7.39	1.55
	Monsoon	sand	82.44	10.05	7.51
	Post-monsoon	sand	83.65	7.08	9.26

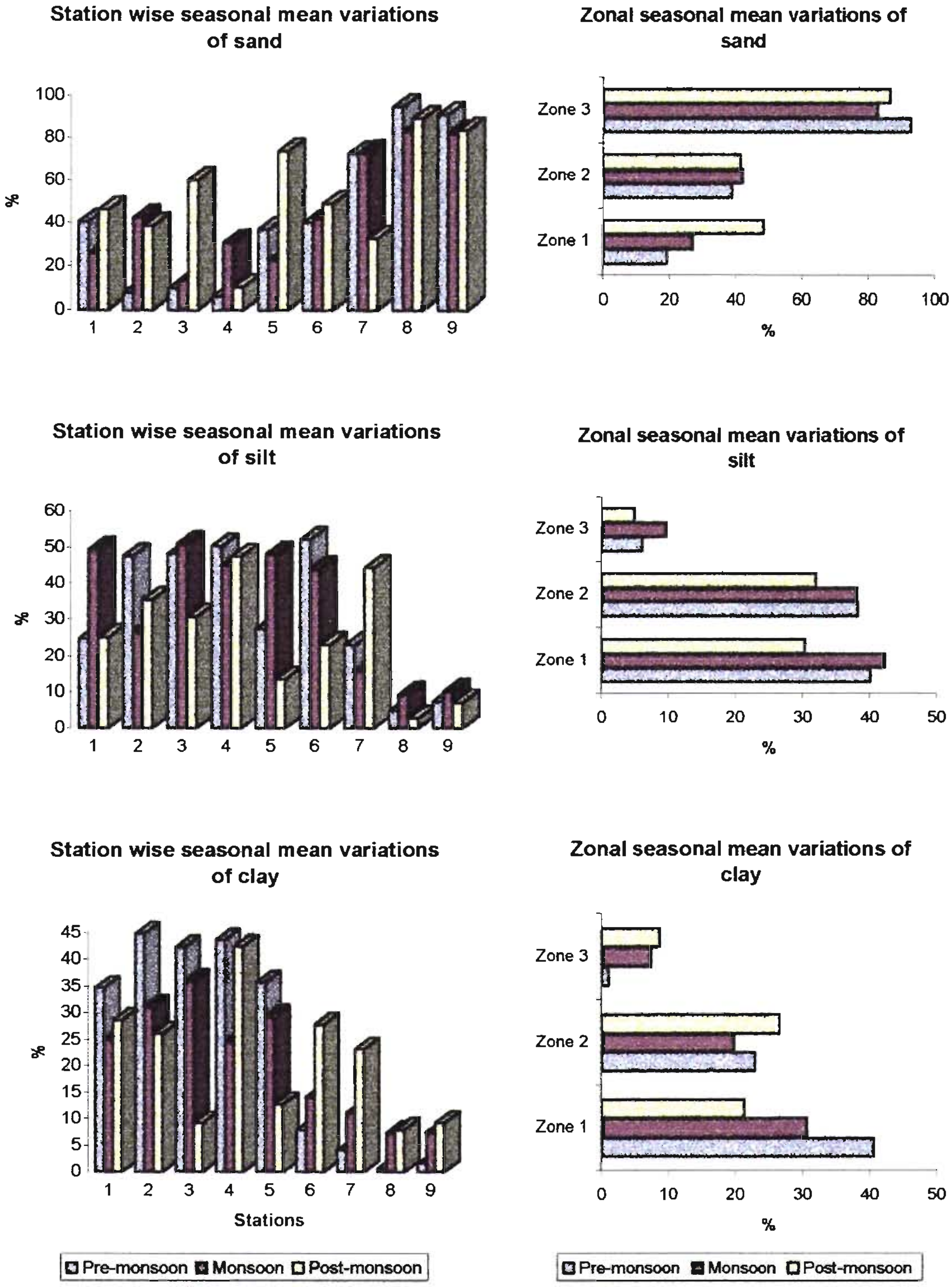


Figure 3.8 Seasonal variations of sand, silt and clay in sediments

more or less sand-silt-clay in nature. In zone 2, the sediment nature was varying and more or less silty or clayey in nature. The studies of textural analysis reveals dominant clay and silt fractions in zones 1 and 2 and higher amounts of sand in zone 3.

CHAPTER 4

DISTRIBUTIONS OF DISSOLVED ORGANOCHLORINE PESTICIDES IN THE BACKWATERS OF KUTTANAD

4.1 INTRODUCTION

Toxic organic chemicals are ubiquitous in the aquatic environment, resulting from transport to and internal cycling within estuarine systems. Natural processes occurring in estuaries work to remove the toxic chemicals from the water column and by possible interaction with biota. Chemical contaminants, including pesticides may enter the lake from river inflows, ground water flow and atmospheric deposition in the form of rain and snow and particle deposition and direct and indirect discharges from industrial and municipal facilities. Losses of chemicals from the estuaries occur as a result of incorporation into particles (biotic and abiotic) and subsequent settling, volatalisation across the air-water interface and chemical and biological transformations. The internal processes of resuspension of bottom sediments and diffusion of pore water may release chemicals into the water column reducing the net loss in the estuaries. The hydrophobic organic contaminants, such as organochlorines and polychlorinated biphenyls are characterized by their ability to partition into biotic pools, as a result of their low aqueous activities and general resistance to chemical and biological degradation. The hydrophobic organic chemicals have low aqueous solubilities and high octanol-water partition coefficients (K_{ow}), and as a result, are particle reactive (Karickhoff, 1984; Eisenreich, 1987; Eadie and Robbins, 1987; Elzerman and Coates, 1987). The combination of low vapour pressure and low Henry's Law constants suggests that hydrophobic organic compounds have a significant atmospheric pathway (Eisenreich et al., 1981; Bidleman, 1988).

The fate of hydrophobic organic pollutants, including organochlorine pesticides, in the aquatic environment is controlled by a variety of physical, chemical and biological processes. Some of the most important are physical transport, chemical and biological transformations, and distributions of these compounds between the various environmental compartments viz water, sediment, biota and atmosphere. The aquatic environment is practically sensitive to pollution because of its fragile ecology. Pollutants in water and aquatic organisms may also pose a direct threat to human health. The prediction of the aquatic fate of pesticides, and their distributions between the different environmental compartments is, therefore, of great importance in environmental chemistry.

Like many other nations in Asia, India is predominantly an agricultural country. In Kerala, rice is the predominant cereal crop in which Kuttanad area accounts for more than 20% of rice production. The use of pesticides in rice is more in comparing with other crops. Several persistent pesticides, including DDT are banned for use in agriculture, but are still used for the eradication of vector-transmitted diseases. Furthermore, with the recent liberalization of agrochemical market, there was a tendency towards the application of cheaper pesticides, including more hazardous and persistent compounds.

4.1.1 Organochlorine compounds

Organochlorine compounds are mainly synthetic organic pesticides and may also be named as "chlorinated hydrocarbons" or "chlorinated pesticides" They comprise a group of pesticides, among them are dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH); both of these were synthesized more than a hundred years ago. It was only around 1940 that their insecticidal properties were recognized. This event gave birth to the era of synthetic organic pesticide manufacture. As the use of pesticides reached massive proportions, a darker side of these toxic chemicals revealed itself. Carried by natural forces such as wind, rain, and the flow of rivers and ocean currents, residues of organochlorine pesticides began to appear everywhere on the globe, from tropical forests to Antarctic snows (Iwata et al., 1993 and 1994; Shannon, 1999). The slowly decomposing organochlorines were taking their toll among many non-target fish and wildlife species. It became clear from the residues found in the bodies of dead and dying birds and fishes that pesticides were responsible for their deaths.

Organochlorines are ubiquitous pollutants of the marine environment. Being highly persistent, these compounds accumulate in organisms. Such accumulation become greater in organisms higher in food chain, leading to biomagnifications in top level predators, such as fish eating birds and most marine mammals (Tanabe et al., 1994 and 1998; Douthwaite, 1995; Peakall, 1996; Wiemeyer, 1996; Borrell et al., 1997; Tu Binh et al., 1999; Barry and Frank, 2001). HCH and DDT, like most organochlorines are lipid soluble and tend to accumulate in adipose tissue, and in lipid rich organs, such as brain, liver and lipid fractions of biological membranes (Salter, 1984; Wolff, 1984; Ferreira et al., 1990; Needham et al., 1995; Waliszewski et al., 1996; Dua et al., 1998; Atuma, 1999). Death of aquatic invertebrates and accumulation of pesticide residues into the tissues of these organisms are the main hazards of pesticides in an aquatic environment.

DDT became famous for its efficacy against flies, mosquitoes, body lice and fleas, which are vectors, transmit human diseases such as malaria, yellow fever, typhus and bubonic plague. DDT was also used on large scale in agriculture and horticulture. Because of its low cost, probably it was the most economical insecticide ever sold. The organochlorine compounds are mainly classified into three groups.

a. Diphenyl aliphatics (eg. DDT, dicofol, methoxychlor etc.)
b. Benzene derivatives (eg. HCH, lindane, pentachlorophenol etc.)
c. Cyclodienes (eg. Endosulfan, heptachlor, aldrin, endrin etc.)

4.1.1.1 Diphenyl aliphatics

(Dichlorodiphenyltrichloroethane (DDT))

Muller in Switzerland first discovered the insecticidal property of DDT in 1939. It was the first synthetic insecticide to supplant the arsenicals for the control of chewing insects. DDT is also highly effective for the control of many insects important for public health. It was widely used during the second world war for the control of typhus and as a larvicide for the control of mosquito vectors of malaria, and still the most widely used pesticide for this purpose.

The insecticide DDT, which has the empirical formula $C_{14}H_9Cl_5$, contains 50 % chlorine. It is synthesized by the Baeyer condensation of chlorobenzene with chloral (or an equivalent amount of chloral hydrate) in the presence of concentrated sulphuric acid. The technical DDT is essentially a mixture of two isomeric compounds comprising 65 to 70 percent of p,p'-DDT and 30 to 35 percent of o,p-DDT The physico-chemical properties of technical DDT are listed in Table 4.1. DDT is highly insoluble in water, a property, which makes the solubility difficult to define, and the amount actually present in solution difficult to determine. Brooks (1976) reported the "true water solubility of DDT" as 2×10^{-4} ppm. Other values recorded range from 1 or 2×10^{-3} ppm upto 0.1 ppm, but the higher values undoubtedly represent colloidal solutions (Kenaga, 1972; Brooks, 1976).

DDT has a long residual life or persistence in the soil and aquatic environments. Also, because it accumulates in the tissues of animals and plants, it is banned for agricultural use. However, its use continues as in health programmes for mosquito control. The photochemistry of DDT is of considerable interest, both in connection with its influence on the efficiency of DDT deposits under conditions of practical use and because it is necessary to determine the nature of the residue left on crops following DDT applications. DDE (dichlorodiphenyl dichloroethylene), and DDD (dichlorodiphenyl dichloroethane) are the major and persistent DDT metabolites. DDE being more persistent and toxic compared to DDT, is not desirable to accumulate in soil (Mitra and Reghu, 1998). One of the most important chemical changes undergone by DDT is the loss of one molecule of hydrogen chloride by various means to give the corresponding ethylenic derivative known as DDE. Since this conversion results in the loss of toxicity, its occurrence under various conditions has been thoroughly explored (Brooks, 1976). The aromatic rings of DDT and DDE are dechlorinated, and extensive molecular disruption occurs to give a variety of

Table 4.1 Physico-chemical properties of technical DDT

Sl.No.	Properties	Properties of technical DDT
1	Molecular formula Molecular weight	$C_{14}H_9Cl_5$ 354.5
2	Composition	Technical product contains about 30% o,p-DDT and about 70% of p,p'-DDT (a)
3	Form	Waxy solid (a & b)
4	M.P °C	Indefinite (a)
5	B.P °C	185-187°C at 0.07 mbar (with decomposition) (b)
6	V.P:mPa 20°C	7×10^{-7} mbar at 20°C (b)
7	Solubility in water	1.2×10^{-3} mg/l at 27°C (b) Practically insoluble in water (a)
8	Solubility in organic solvents	Readily soluble in aromatic and chlorinated solvents. Moderately soluble in polar organic solvents and petroleum oils. (a)
9	Mode of action	Persistent non-systemic insecticide with contact and stomach action.
10	Stability	Loses hydrogen chloride in solutions of alkalis and organic bases (a & b). Generally stable to oxidation (a).
11	Ecotoxicology	Toxic to fish and aquatic life (b). Toxic to fish and to animals of fish diet (a).
12	LD_{50} – Oral mg/kg	Rat: 113-118 Mice: 150-300 (a).
13	Toxicity class	EPA: II WHO: II
14	Environmental fate:	In rats DDT is metabolised in to DDE, DDD and DDA. Accumulates in the fatty tissues of mammals and is excreted in milk (a). In warm-blooded organisms, oxidation of the benzene residue and hydroxylation of the side chain (b).
15	Major Formulations	WP; EC; DP; GR; Aerosol.

(a) The Pesticide Manual (1995)
(b) The Agrochemicals Handbook (1983)

products. When oxygen is present, products arising from its reaction with radical intermediates are 4,4'-dichlorobenzophenone. Some chemical reactions of DDT and its metabolites are shown in Figure 4.1.

The use of the pesticide, DDT, ended in almost all developed countries by 1970s, but the persistence of DDT, and its metabolites DDD and DDE, in the environment continues to make this a chemical of common concern. These chemicals bioaccumulate and are listed as possible human carcinogens (Ware, 1978; IRIS, 1992).

4.1.1.2 Benzene derivatives

Hexachlorocyclohexane (HCH)

The outstanding insecticidal property of hexachlorocyclohexane (HCH), also called benzenehexachloride (BHC), was discovered independently and simultaneously in France and United Kingdom during the second world war Theoretically, there are eight possible isomeric benzenehexachlorides (Brooks, 1976). Benzenehexachloride is an addition product of benzene and chlorine in presence of UV light or sunlight. This reaction leads to the mixture of isomers of hexachlorocyclohexane and some other products that are known as technical HCH.

Technical HCH is off white to brown amorphous powder with a very characteristic penetrating musty odour. It begins to melt at about 65°C and consists of a mixture of the α, β, γ, δ and ε isomers, together with upto 4% heptachlorocyclohexane and upto 1% of octachlorocyclohexane, and the last two compounds being at least partly responsible for the characteristic odour (Brooks, 1976). The ή-isomer has also been isolated from technical HCH. The composition of the technical material is inevitably somewhat variable, depending upon the nature of the manufacturing processes (Brooks, 1976). The physico-chemical properties of technical HCH are shown in Table 4.2.

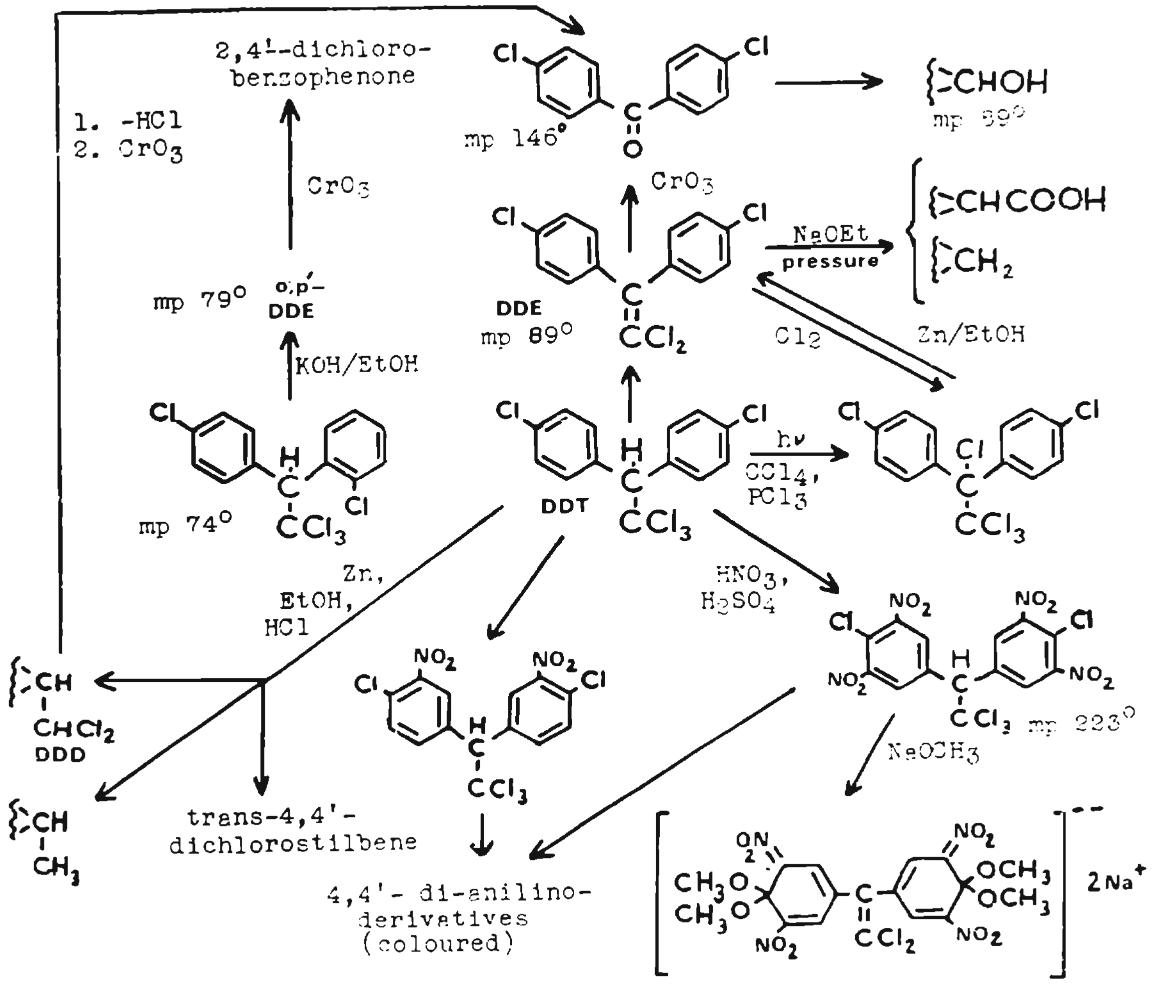


Figure 4.1 Chemical reactions of DDT and its metabolites (Brooks, 1976).

Table 4.2 Physico-chemical properties of HCH isomers

Isomer	α-HCH	β-HCH	γ-HCH	δ-HCH
Molecular formula	$C_6H_6Cl_6$	$C_6H_6Cl_6$	$C_6H_6Cl_6$	$C_6H_6Cl_6$
Molecular weight.	290.8	290.8	290.8	290.8
Crystalline Form	Monoclinic prisms	Cubic (octahedral)	Tablets, plates prisms	Fine plates
M.P °C	159-160 (159.2)	309-310 (311.7)	112-113 (112.9)	138-139 (140.8)
Solubility in Water At 25°C (ppm)	1.63 (a)	0.70 (a)	7.90 (a)	21.3 (a)
V.P: mm Hg at 20°C	2.5×10^{-5}	2.8×10^{-7}	9.4×10^{-6}	1.7×10^{-5}
Dipole moment (D) in benzene	2.16	0	2.84	2.24
Stability	stable	stable	Stable (b)	
Mode of action	No insecticidal action	No insecticidal action	Insecticide with contact, stomach and respiratory action (a)	No insecticidal action
Acute oral LD_{50} rat (mg/kg)			88-270 (b)	
Ecotoxicology	Toxic to fish and bees.	Toxic to fish and bees.	Toxic to fish and bees.	Toxic to fish and bees.
Toxicity class WHO EPA	 II II	 II II	 II II	 II II
Solubility in organic solvents	Soluble	Moderately soluble	Soluble	Soluble
Percentage composition	65 – 70 % (c)	7 – 10 % (c)	14 – 15 % (c)	5 – 7 % (c)

(a) Brooks (1976)
(b) The Pesticide Manual (1995)
(c) WHO (1992)

Technical HCH is synthesized from benzene and chlorine in the presence of ultraviolet light and it averages 65-70 % of α-HCH, 7-10 % of β-HCH, 14-15 % of γ-HCH, 7 % of δ-HCH, 1-2 % of ε-HCH, and approximately 1 to 2 % of other components (WHO, 1992). The α, β, γ and δ-HCH isomers are chemically stable and slowly biodegradable compounds, and have similar n-octanol-water partition coefficients (log K_{ow} ranging from 3.2 to 3.8) (WHO, 1991 and 1992). The isomers however differ regarding their persistence in soil, water and living organisms (Deo et al., 1994). It has been reported, for instance that β-HCH presents the highest bioaccumulation ratio and the slowest elimination rate in *P.reticulata* (Yamato et al., 1983).

The hexachlorocyclohexanes are rather stable chemically, and unlike DDT, do not lose hydrogen chloride when heated with traces of iron and other metals and their salts. They are also stable to light and oxidation; β-isomer is the most stable form (Brooks, 1976). In HCH isomers, insecticidal properties were shown only by γ-isomer. HCH formulations were popular among the farmers in spite of its containing the other inactive isomers of HCH, via α, β and δ isomers, which does not possess insecticidal activity. The use of these unwanted isomers leads to their accumulation, which is responsible for the bioaccumulation in the food chain.

4.1.1.3 Cyclodienes

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. The synthetic reaction used to prepare these compounds is the diene-synthesis or Diels-Alder reaction, which consists of the addition of a compound containing a double bond or triple bond to the 1,4-positions of a conjugated system. The ability of the halogenated cyclopentadienes to participate in the Diels-Alder reaction is clearly the most important aspect of their chemistry and many such addition reactions, especially involving hexachlorocyclopentadiene as the diene (Brooks, 1976).

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. Endosulfan is used extensively throughout Australia for a variety of agricultural activities (Peterson and Batley, 1993).

The use of cyclodienes as pesticides is assumed as their immediate release into the environment. Aldrin is rapidly converted into dieldrin, its epoxide, as is heptachlor to its epoxide, heptachlor epoxide. 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.

Endosulfan

Endosulfan is a non-systemic insecticide with contact and stomach action. Endosulfan exists as two stereoisomers, α and β isomers of endosulfan, and that has quite different physical properties, such as melting point, solubility and vapour pressure. In water, solubility of alpha-endosulfan is 0.32 mg l^{-1} and for beta 0.33 mg l^{-1} at 22°C. Endosulfan is stable to sunlight and slowly hydrolysed in aqueous acids and alkalies with the formation of the diol and sulphur dioxide. Endosulfan, one of the major pesticides used in cotton growing and other crops, is of environmental concern because of its toxicity to fish and its apparent persistence in the environment. It is prepared by the Diels-Alder addition of hexachlorocyclopentadiene with butenediol, and the adduct formed is subsequently treated with thionyl chloride to form a seven membered ring. Endosulfan has wide application, although its persistence in soil is not exactly known. In endosulfan, the two isomeric forms have been shown to arise on account of the pyramidal structure of the sulfite moiety, which can take up two configurations relative to the ring system containing it. The physico-chemical properties of technical endosulfan are shown in Table 4.3. Endosulfan is subjected to slow hydrolysis to the corresponding diol and sulfur dioxide. Mild oxidation of the endosulfan isomers converts them into endosulfan sulphate (M.P.180 to 181°C) in which isomeric forms are no longer possible. The

Table 4.3 Physico-chemical properties of technical endosulfan

Sl.No.	Properties	Properties of technical endosulfan
1	Molecular formula Molecular weight.	$C_9H_6Cl_6O_3S$ 406.9
2	Composition	Endosulfan is a mixture of two stereoisomers, comprising approximately 64-67% of α-endosulfan and 29-32% of β-isomer (a).
3	Form	Cream to brown, mostly beige (a).
4	M.P °C	80°C (a) 70-100°C (b)
5	B.P °C	106°C at 0.9mbar (with partial decomposition) (b)
6	V.P:mPa,20°C	0.83mpa (20°C) for 2:1 mixture α- and β- isomers (a) 1.2 x 10^{-2} mbar at 80°C (b)
7	Solubility in water	α-endosulfan: 0.32 mg/l at 22°C (a) β-endosulfan: 0.33 mg/l at 22°C (a)
8	Solubility in organic solvents	Variable solubility in organic solvents.
9	Mode of action	Non-systemic insecticide and acaricide with contact and stomach action.
10	Stability	Stable to sunlight. Slowly hydrolysed in aqueous acids and alkalis, with the formation of the diol and SO_2.
11	Ecotoxicology	Highly toxic to fish. LC_{50} (96h) for *golden orfe* is 0.002mg/l water. Not toxic to bees. Practical life should be harmless to wildlife (a).
12	LD_{50} – Oral mg/kg	Rat: 70 mg (in aqueous suspension)/kg. 110 mg technical.(in oil)/kg (a)
13	Toxicity class	EPA: I WHO: II
14	Environmental fate:	The plant metabolites (mainly endosulfan sulfate) were also found in animals. The endosulfan (α & β) is degraded in soil with DT_{50} 30 to 70 days. DT_{50} for total endosulfan in the field is 5-8 months. No leaching tendency was observed (a).
15	Major Formulations	EC; DP; GR; WP ETC.

(a) The Pesticide Manual (1995)
(b) The Agrochemicals Handbook (1983)

possible photochemical conversions of endosulfan are of interest from an environmental standpoint, the α-isomer has been reported to lose one or both of the vinylic chloride atoms.

Endosulfan is known to degrade into two major products, both of which degrade further as shown in Figure 4.2. Endosulfan sulphate is the product of biological degradation; it is as toxic as the parent compound to fish. Endosulfan diol is formed by chemical or biological hydrolysis and is non-toxic. The sulphate is more likely to be formed in sediments where bacterial populations are high. Diol may form wherever there is moisture.

Heptachlor and heptachlor epoxide

Heptachlor, a chlorinated cyclodiene, is a non-systemic insecticide with contact, stomach and some respiratory action. It is used as an agricultural and domestic pesticide for the control of termites and soil insects in cultivated and uncultivated soils. Heptachlor is also a major component of technical chlordane, another heavily used pesticide in human history. It is difficult to distinguish the relative importance of technical heptachlor and chlordane sources of heptachlor, and its environmentally important degradation products and metabolites. Its water solubility is 0.056 mg/l at 25 - 29 °C. It is not readily dehydrochlorinated, but is susceptible to epoxidation. The physico-chemical properties of heptachlor are shown in Table 4.4. Animal experiments have indicated that heptachlor is carcinogenic in some mice and rat strains, perhaps acting as a promoter, rather than an initiator, of carcinogenesis (Jiping et al., 1995). The principal metabolites in animals are heptachlor epoxide found in the tissues, faeces and urine. There is a strong tendency for the epoxide to accumulate in the body fat. In plants, heptachlor epoxide is the metabolite. In water and soil, heptachlor undergoes hydrolysis to 1-hydroxy chlordane (The Pesticide Manual, 1995). The half-life period of heptachlor is 9-10 months when used at agricultural rates (The Pesticide Manual, 1995).

The main heptachlor related compound found in the environment is heptachlor epoxide, which is the major heptachlor metabolite formed through

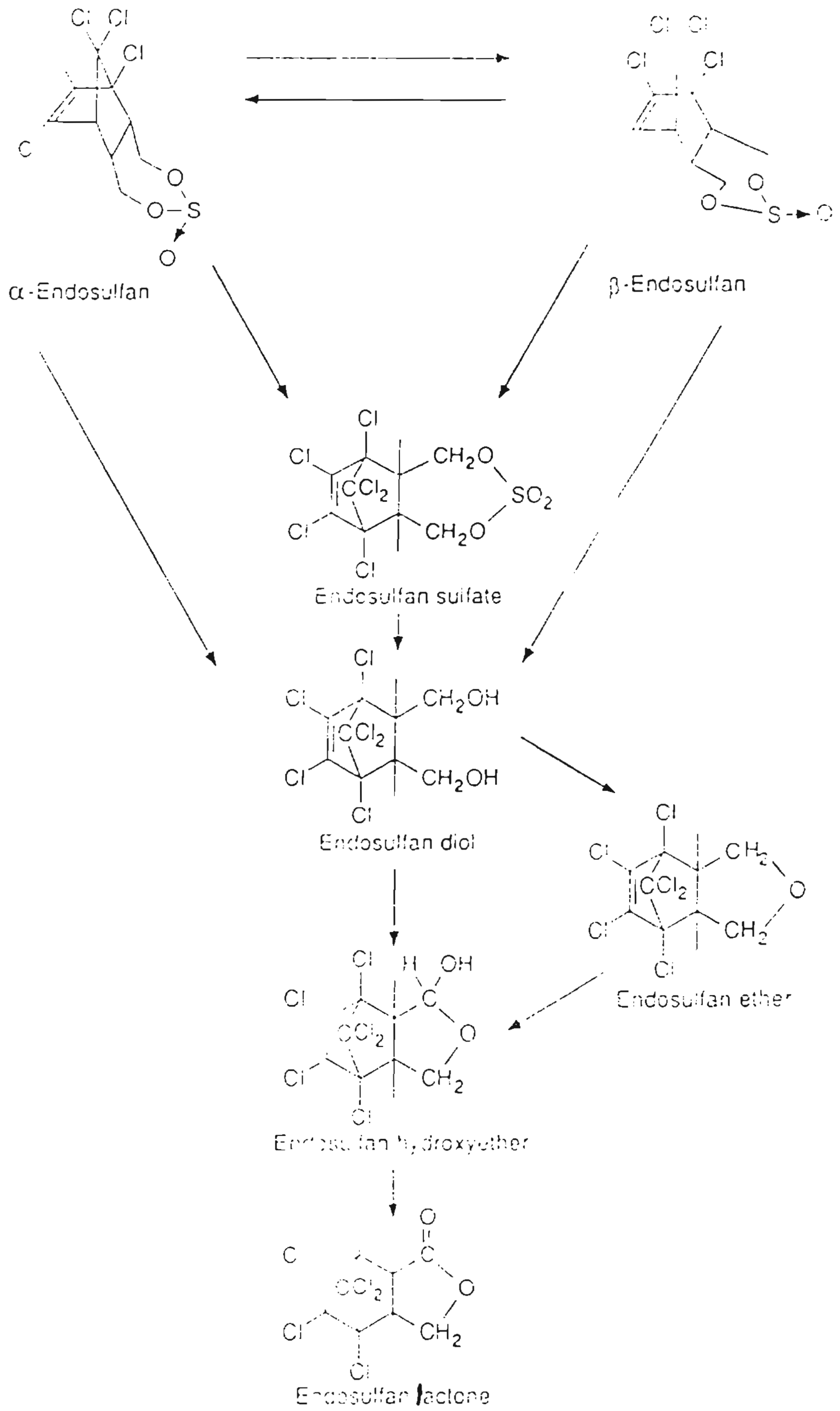


Figure 4.2 Endosulfan and its degradation products.

Table 4.4 Physico-chemical properties of technical heptachlor

Sl. No.	Properties	Properties of heptachlor
1	Molecular formula Molecular weight	$C_{10}H_5Cl_7$ 373.34
2	Composition	Technical grade is 72% heptachlor and 28% related Products (a)
3	Form	Technical waxy solid
4	M.P °C	46-74°C (technical); 95-96°C (pure) (a & b)
5	B.P °C	135-145°C (a)
6	V.P	53 mPa at 25°C (a) 4×10^{-4} mbar at 25°C
7	Solubility in water	0.056 mg/l at 25 -29°C (a) Practically insoluble in water (b)
8	Solubility in organic solvents	Soluble in organic solvents
9	Mode of action	Non-systemic insecticide with contact, stomach and respiratory action.
10	Stability	Wide stability, slow loss of hydrogen chloride with alkalies (b). Susceptible to epoxidation (a)
11	Ecotoxicology	Highly toxic to fish Toxic to bees.
12	LD_{50} – Oral mg/kg	Rat: 147-220 Mice: 68
13	Toxicity class	WHO II EPA II
14	Environmental fate:	The principal metabolite in animals is heptachlor epoxide (a). In water rapidly undergoes hydrolysis to 1-hydroxy chlordane, which then undergoes microbial epoxidation. Similar degradation pathways occur in moist soil. The half-life in soil is 9-10 months.
15	Major Formulations	EC; WP; DP; UL; GR

(a) The Pesticide Manual (1995)
(b) The Agrochemicals Handbook (1983)

epoxidation of the non-chlorinated double bond in the molecule (Jiping et al., 1995). The toxicity, including the carcenogenicity, of both heptachlor and heptachlor epoxide has been studied (Cavender et al., 1987).

Aldrin and dieldrin

Aldrin is produced by the Diels-alder reaction of excess norbornadiene and hexachlorocyclopentadiene in refluxing toluene. Aldrin is used for the control of pests in the soil. Its mode of action is contact, stomach and respiratory. It is stable in neutral, basic and weakly acidic media and reacts with strong acids and phenols in presence of oxidizing agents to give dieldrin. The physico-chemical properties of technical aldrin are shown in Table 4.5.

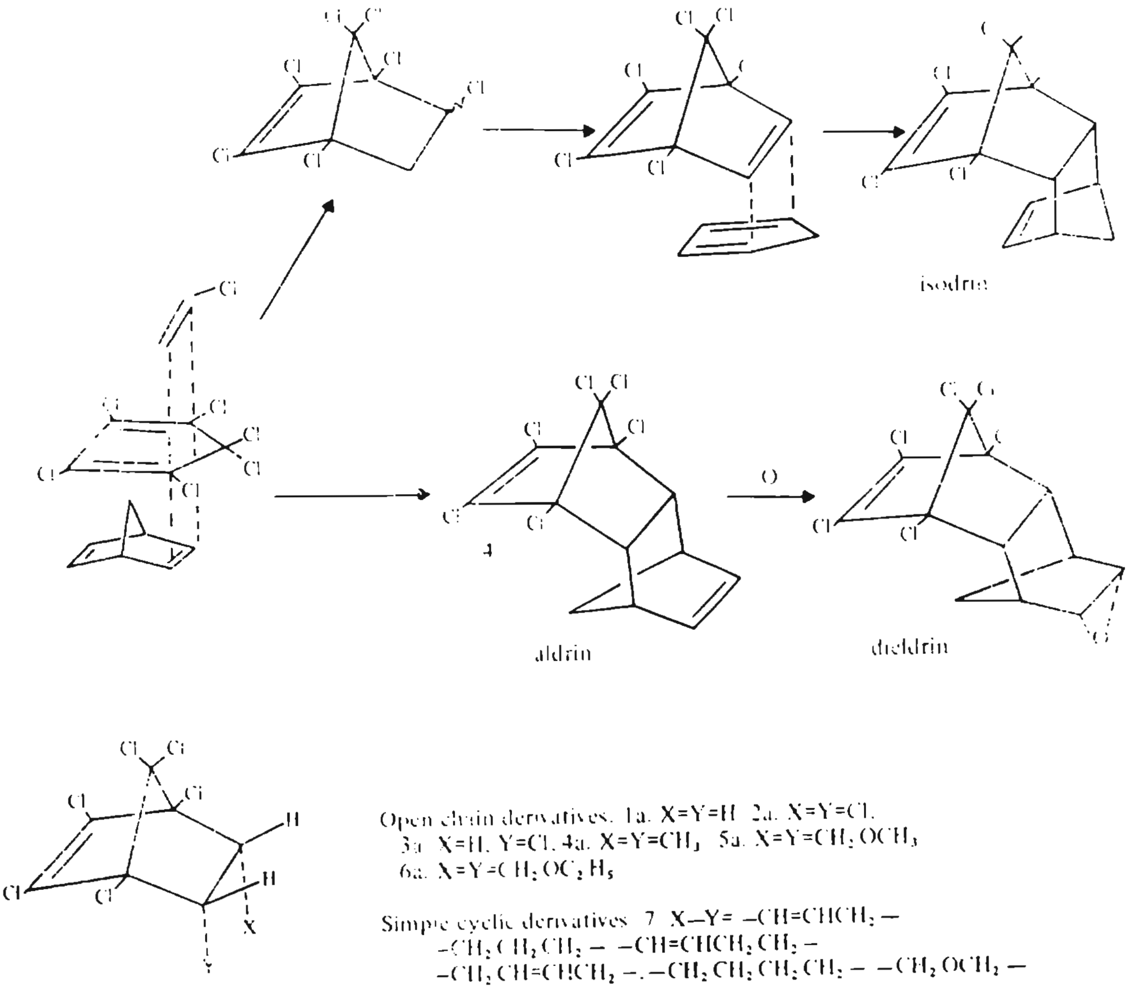
Aldrin is a chlorinated cyclodiene with high acute toxicity. Aldrin may have a potential for contaminating surface water, degrades readily to dieldrin, which is persistent in the environment and the vapour pressure of aldrin is 6.6 x 10^{-6} mm Hg at 25°C (Pesticide Fact Handbook, 1988.). The chlorinated part of the aldrin molecule is chemically almost inert, numerous reactions are possible at the double bond of the unchlorinated ring, and epoxidation of aldrin to dieldrin is such a typical reaction. The activation of aldrin to dieldrin by enzymatic oxidation has been shown in mammals, insects, microorganisms, and on plants. Some derivatives of aldrin and dieldrin are shown in Figure 4.3.

Numerous experiments to reduce the volatility of aldrin by chemical variation and thus improve the duration of activity lead to the epoxidation of aldrin to dieldrin. Dieldrin is a persistent insecticide with contact and stomach action, having a wide spectrum of activity. Because it is a metabolite of aldrin, environmental concentrations of dieldrin most likely represent the cumulative use of both aldrin and dieldrin. It has long-term persistence in the environment and has been identified as a human neurotoxin (ATSDR, 1987) and a probable carcinogen (IRIS, 1992). Because these lipid soluble compounds are not easily metabolized or excreted, they are stored in the fatty tissues and can readily bioaccumulate in biota with high lipid content. Low volatility and chemical stability make dieldrin an insecticide with very good duration of activity.

Table 4.5 Physico-chemical properties of technical aldrin

Sl.No.	Properties	Properties of technical aldrin
1	Molecular formula	$C_{12}H_8Cl_6$
2	Molecular weight	364.93
3	Form	Colourless crystalline solid
4	M.P °C	104-104.5°C (a & b)
5	B.P °C	145°C at 2.7 mbar (b)
6	V.P:mPa,20°C	3.1×10^{-5} mbar at 20°C (b)
7	Solubility in water	27 µg/l at 27°C (a) less than 0.05mg/l at room temperature (b).
8	Solubility in organic solvents	>600g/l in acetone, benzene, and xylene (a).
9	Mode of action	Contact cum ingestion insecticide, effective against a range of soil-dwelling pests (a)
10	Stability	Stable in neutral basic and weakly acidic media. React with acids and phenols in presence of oxidizing agents to give dieldrin (a & b).
11	Ecotoxicology	Toxic to fish and bees.
12	LD_{50} – Oral mg/kg	Rat: 38-60 (a) Rat: 67 (b)
13	Toxicity class	EPA/WHO (1977) reviewed that acceptable daily intake for man is 0-0.0001 mg/kg
14	Environmental fate:	Aldrin is readily epoxidised to dieldrin in living organisms. Aldrin is rapidly epoxised in living tissues, the long term toxicology of dieldrin to laboratory animals cab be regarded as representative of aldrin.
15	Major Formulations	EC; WP; Dust concentrates.

(a) The Pesticide Manual (1995)
(b) The Agrochemicals Handbook (1983)



Open chain derivatives. 1a. X=Y=H 2a. X=Y=Cl.
3a X=H. Y=Cl. 4a. X=Y=CH_3 5a. X=Y=CH_2OCH_3
6a. X=Y=$CH_2OC_2H_5$

Simple cyclic derivatives 7 X—Y= $-CH=CHCH_2-$
$-CH_2CH_2CH_2-$ $-CH=CHCH_2CH_2-$
$-CH_2CH=CHCH_2-$, $-CH_2CH_2CH_2CH_2-$ $-CH_2OCH_2-$

Figure 4.3 Structures of some derivatives (aldrin and dieldrin) of hexachlorobicyclo (2.2.1) hept-2-ene (hexachloronorbornene). (Brooks, 1976)

Endrin and endrin aldehyde

Endrin is a persistent insecticide with contact and stomach action. Epoxidation of the aldrin isomer, isodrin, leads to endrin. Isodrin is formed by the Diels-alder reaction of hexachloronorbornadiene and cyclopentadiene. It is practically insoluble in water and slightly soluble in alcohols. It is stable to dilute acids and unstable to strong acids. It is toxic to fish and to the animals of fish diet. In warm-blooded animals and insects, endrin is converted to hydrophilic metabolites (The Agrochemicals Handbook, 1983). The physico-chemical properties of endrin are shown in Table 4.6.

Endrin is a sterio-isomer of dieldrin, with similar physico-chemical properties and comparable stability towards alkali and dilute acid. As a foliar insecticide, endrin is more active than dieldrin. Endrin is also used as a rodenticide. The endo-endo structure of endrin has a possibility of a thermal or photochemical rearrangement into the 'half-cage ketone' and the pentacyclic aldehyde, both products are insecticidally inactive.

4.1.2 Contaminant sources, transport and fate

It has been reported that about 25 % of the pesticides used for agriculture and vector control purposes are expected to reach the coastal environment (Gupta, 1986). Because of their persistence in the aquatic environment and biomagnifications in food chain, their continuous use will have wider implications not only in aquatic environmental quality but also on human health. The residual levels of these persistent chemicals exceed their permissible limits, and get partitioned among the constituent phases of the aquatic systems, viz water, sediment and biota.

Water and the sediment at the bottom of the rivers, stream, lakes, ponds or the seabed are the major reservoirs for persistent pesticide residues. There are many ways in which pesticides can reach water. Kilgore and Li (1976), Edwards (1977), Kalara and Chawla (1981), Miliadis (1994) and Dua et al.

Table 4.6 Physico-chemical properties of technical endrin

Sl.No.	Properties	Properties of technical endrin
1	Molecular formula	$C_{12}H_8Cl_6O$
2	Molecular weight	380.93
3	Form	Colourless crystals
4	M.P °C	226-230°C (decomposes) (a) greater than 200°C (decomposes) (b)
5	V.P	20 mPa at 20°C (a) 2.6×10^{-7} mbar at 25°C (b)
6	Solubility in water	Negligible in water (a) Practically insoluble in water (b)
7	Solubility in organic solvents	Slightly soluble in alcohols and mineral oils Moderately soluble in acetone, benzene.
8	Mode of action	Persistent insecticide with contact and stomach action.
9	Stability	Stable to alkalies, unstable to acids.
10	Ecotoxicology	Toxic to fish and to animals of fish diet. Toxic to bees
11	LD_{50} – Oral mg/kg	Rat: 7.5 – 17.5 Rat: 15
12	Toxicity class	EPA: 1
13	Environmental fate	Rapidly metabolised in animals to hydrophilic metabolites. In soil and plants, rapid degradation to phosphoric acid, ethylene and chloride ions.
14	Major Formulations	EC; WP; and granules.

(a) The Pesticide Manual (1995)
(b) The Agrochemicals Handbook (1983)

(1998) have indicated the various routes by which pesticides can reach the aquatic environment such as rivers, lakes, ponds, and oceans. These can be (i) pesticides may be directly applied as aerial sprays or granules to control water-inhabitating pests (ii) they may fall on to the surface of water when forests or agricultural land are sprayed from the air (iii) spray drift from normal agricultural operations may reach the water (iv) residues may reach water as surface run-off from treated soil (v) pesticides may be discharged into rivers with factory or sewage effluents (vi) insecticidal containers may be split or washed into rivers and (vii) there may be uptake from the atmosphere or residues may be carried down with rain or dust. Among these routes, run-off from agricultural land is the main source of gradual pesticidal pollution of aquatic environments. Direct application of pesticides to water and soil may be responsible for localized contamination problems. The persistent organochlorine pesticides and its metabolites are most commonly associated with pollution of aquatic system.

Even the more persistent pesticides do not remain long in water unless they are carried in suspension by adsorbed onto particulate matter. Within hours or days of contamination, the amounts in water fall to low background levels. There are several factors that influence the persistence of pesticides in water. The main factors are (1) solubility (2) mud bottom (3) organic matter (4) temperature and (5) pH.

The organochlorine pesticides are all relatively insoluble, but they differ considerably in their water solubilities, which rare very much temperature dependent. For instance, over a temperature range 60-95°F, the solubility of lindane increased as much as five times, three to five times for aldrin, dieldrin and endrin and two times for p,p'-DDT (Edwards,1973). Even the more soluble pesticides disappear from water after quite rapidly and the pesticides are gradually taken up by the bottom mud and organic matter. When a persistent pesticide reaches water, a large proportion disappears rapidly, with little remaining longer than one week (Edwards, 1973).

It is established that pesticides show affinity for both living and dead organic matter, particularly the lipid portions of such material. Ferreira et al.

(1990), Kelly (1995), Borrell et al. (1997) were confirmed this conclusion. If the organic matter is floating, the pesticide tends to remain in suspension in the water, whereas if it is in the bottom mud, it tends to remove the pesticide from the water above it. The evidence that the temperature and pH influence the persistence of pesticides in natural waters is purely inferential. It is well established that temperature affects both solubility and volatility of pesticides, and there is good evidence that they are much more stable at some hydrogen ion concentration than at others.

The unscientific and widespread usages of pesticides in agricultural applications and vector controlling practices have resulted in an easy entry of the pesticides into the aquatic systems. During application, a considerable quantity of the sprayed pesticide fails to hit the target area and is thus lost to the atmosphere as spray drift. The persistence of pesticides in the aquatic system and their long range of transport in the atmosphere are the main factors that contribute the accumulation of pesticides in the aquatic environment. Agricultural practices like tilling also contribute significantly to the erosion of soils and hence to the transportation of pesticides to the aquatic environment. Significant quantities of pesticides are thus transported by sediment, which constitutes an important source of contamination.

The important factors involved in the transportation of pesticide residues towards natural water bodies are aerial dispersion by wind, volatilisation, and conveyance by rain and irrigation waters (Ferrando et al., 1992; Watanabe, 1998; Shannon, 1999; Asterios and Euphemia, 2001). The toxic action of pesticide residues in water systems depends on the concentration of these and the length of persistence prior to degradation by the environment. Fox and Matthiessen (1982) reported that the concentration of endosulfan in water detected after spraying the delta, Botswana ranged from 0.5 to 4.2 µg l^{-1}, which is equal to, or more than the 96h LC_{50} values for many species of fish. The transport and fate of chemicals in the aquatic system provide information on the extent of partitioning of these compounds in various phases of aquatic system and on the residence time of these chemicals in the environmental compartments and also gives a picture on the bioaccumulation in biota. A scientific evaluation of this information would help to assess the potential impact of these chemicals in the environment. Chiefly, processes such as solubilisation, precipitation, volatilization, leaching, surface erosion and adsorption, complexation etc., regulate transport of pesticides from the non-point or point source to the aquatic environment. Concentrations of the pesticides at 150~800 m in height on a paddy field were below the detection limit of 5~50 ng/cu m (Watanabe, 1996). The distribution patterns of lipophilic organochlorine contaminants in the southern hemisphere were reviewed by Connell et al. (1999), and suggests that the long-term transport of these chemicals occurred probably by global distillation.

It is more difficult to determine the sources of the pesticides in drinking water wells. The physical properties of the pesticides would seem to indicate that they should not migrate to a deep underground aquifer, though the presence of pesticides residues in shallow well as reported by others does show some potential for transport (Kolpin et al., 1988; Grady and Mullaney, 1998; Wade et al., 1998). In European Union countries, the directive concerning the quality of water intended for human consumption set a maximum permissible level of 0.1 µg/L in tap water and 1 3 µg l^{-1} in surface water for each compound (E.C.Council Directive, 1980).

The long-term use of pesticides has allowed the pesticides to leach into the groundwater source, despite their unfavorable physical characteristics. The aquatic environment acts as the ultimate sink for the persistent and non-degradable pesticides that were/are widely used in all the countries.

4.2 MATERIALS AND METHODS

The materials and methods are discussed in Chapter 2.

4.3 RESULTS AND DISCUSSION

The occurrence of pesticides and their metabolites in aquatic systems is of major concern worldwide. Therefore, monitoring of aquatic environment, in order to verify whether inadmissible levels of pesticides are present, is highly important. Monitoring of aquatic environment for pesticide residues in India, especially in Kerala, has not received adequate attention. Vishweswariah et al. (1976) reported HCH residues in drinking water samples from ponds in coffee plantations in Karnataka. Pillai and Agarwall (1979) while analysing samples of water from Jammu reported that all samples contained DDT residues ranging from 0.062 to 0.963 ppb. Trace amounts of organochlorine pesticides were detected in various water sources around Nagpur by Thakur and Mathal (1980). Karla and Chawla (1981) noticed DDT and HCH at 0.89 and 0.90 ppb respectively in a stream near Ludhiana.

Kaphalia et al. (1986) have stated that when the pesticide residues get into the hydrosphere, they are partially lost to the atmosphere because of volatilisation, partly degraded, partly incorporated in the biota, and partly move into the sediment. According to Matsumura (1985), the rate of bioaccumulation in aquatic environments generally appears to be higher than that in terrestrial environments, which might be due to the lipophilic nature of the persistent pesticides. In aquatic environments, compounds with low water solubility and high liposolubiility are forced to seek organic–lipid containing material. Further, water provides an excellent medium for transport of these pesticides and thus phytoplankton and aquatic plants tend to concentrate persistent pesticides from water than the terrestrial plants. Fish continuously exposed to trace contamination by persistent organochlorine pesticides may bioconcentrate and store these compounds in fat tissues in thousand to million fold amounts (Metcalf, 1982). Because of their lipophilic nature, chlorinated pesticides are bound to the adipose tissues of aquatic animals. Thus, the residue levels of majority of pesticides in fishes indicate their feeding habits. Higher levels of pesticide residues were noted in carnivorous fishes (Kulshrestha et al., 1989). The monitoring of PCBs and DDT, including two major metabolites DDD and

DDE, in various environmental matrixes has been extensive (de Vooget et.al., 1990). Ramasamy and Annamalai (1996) quantified the residue levels of organochlorines in River Kaveri, Tamilnadu and observed that HCH showed higher levels in River Kaveri, and the level of DDT is below the EEC's maximum acceptable concentration. Kan-Atireklap et al. (1997) determined the organochlorine residues in green mussel, collected along the coastal waters of India and suggested that DDTs and HCHs are not controlled in India, their contamination in the aquatic environment may increase unless regulatory measures are imposed. Xinru Zhu et al. (1998) studied the distribution of organochlorine pesticides in water, sediment and fish in Lake Baiyangdian, China, and found that among the pesticides, DDT was widely distributed and high levels occurred in fish, despite a ban of its production and use in 1983. Karunagaran and Subramanian (1999) determined the organochlorine contaminants (HCHs, DDTs and PCBs) in the muscle tissues of 12 bird species from Vellar river watershed area (South India), and found that HCH residues were generally found in higher concentrations than DDTs reflecting increasing use of HCH pesticides since banning of DDT for agriculture. The occurrence and spatial distribution of pesticide residues in ground water of major corn-growing areas of Greece was well documented by Asterios and Euphemia (2001). Barry and Frank (2001) investigated the reasons for the bioaccumulation of persistent organic pollutants in Lichen-Caribou-Wolf food chains of Canada's central and western artic.

Subramanian et al. (1998) measured the concentrations of HCH and DDT residues in blubber, muscle and oil samples from three specimens of river dolphins from River Ganges and found that HCH concentrations ranged from 94 to 289 ng g^{-1} and DDT concentrations were in the range of 1324 to 9388 ng g^{-1} The cumulative effect of pesticides on the costal environment can be expected to be considerable as is evident from their accumulation in marine organisms (Kannan and Sen Gupta, 1987). Sujatha (1992) quantified the pesticide levels in Cochin estuary and summarized that the most prominent organochlorine pesticides present in Cochin estuary were the DDT and HCH compounds. Sujatha et al. (1999) elucidated the distribution pattern of an organochlorine pesticide, endosulfan in Cochin estuary.

The backwaters of Kuttanad situated on the southwest of India, is one of the typical estuaries like many other major estuarine systems. The Kuttanad backwater is also subjected to increasing human activities and receives huge amounts of pollutants from agricultural run-off, domestic sewage works, storm water channels, coconut husk retting yards, fishery industries etc. No systematic study has ever been done to quantify the residual levels of pesticides, and their metabolites in Kuttanad backwaters. The present study was aimed at elucidating the distribution pattern of organochlorine pesticides, and their metabolites in this water system. The organochlorine pesticides quantified in water in the study area were broadly classified into three main structural groups:

- DDT and its metabolites include
  p,p'-DDT, p,p'-DDE and p,p'-DDD

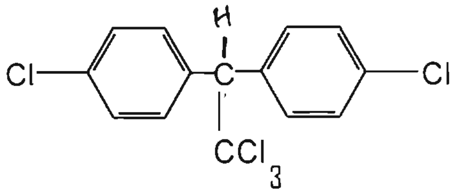
- HCH isomers include
  α-HCH, β-HCH, γ-HCH and δ-HCH.

- Cyclodiene compounds include
  α-Endosulfan
  Heptachlors (Heptachlor and Heptachlor epoxide)
  Aldrins (Aldrin and Dieldrin)
  Endrins (Endrin and Endrin aldehyde)

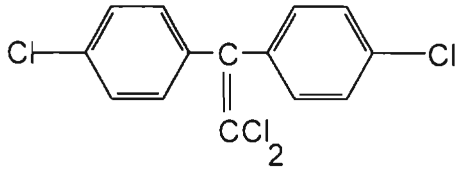
The structural formulae of these pesticides are included in Figure 4.4.

4.3.1 Distributions of total organochlorine pesticides

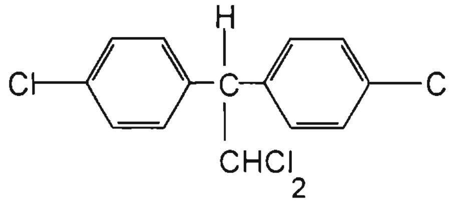
The total organochlorine pesticides quantified in this study include the sum of ΣDDT, ΣHCH, α-endosulfan, Σaldrins, Σendrins and Σheptachlors. The percentage compositions of total organochlorines in surface waters are presented in Figure 4.5, and the bottom percentage compositions are depicted in Figure 4.6. A well defined seasonal and spatial dependence of pesticide



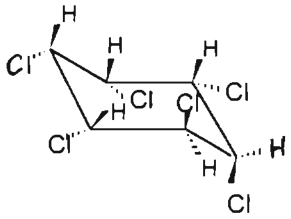
p,p'- DDT [1, 1, 1-trichloro-2, 2-bis (p-chlorophenyl) ethylene].



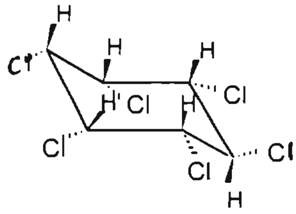
p,p'- DDE [1, 1-dichloro-2, 2-bis (p-chlorophenyl) ethylene].



p,p'- DDD [1, 1-dichloro-2, 2-bis (p-chlorophenyl) ethane].

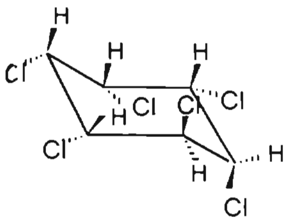


α-HCH [α- 1, 2, 3, 4, 5, 6- hexachlorocyclohexane].

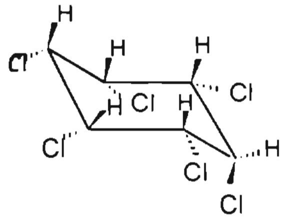


β-HCH [β- 1, 2, 3, 4, 5, 6- hexachlorocyclohexane].

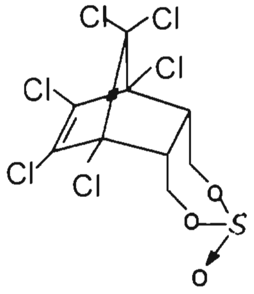
Figure 4.4 Structural formulae of organochlorine pesticides



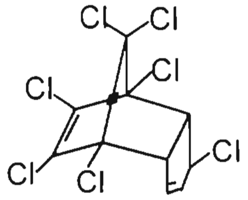
γ-HCH [γ- 1, 2, 3, 4, 5, 6- hexachlorocyclohexane].



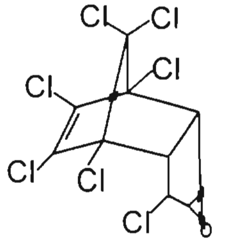
δ-HCH [δ- 1, 2, 3, 4, 5, 6- hexachlorocyclohexane].



α- endosulfan [α- (1, 4, 5, 6, 7, 7- hexachloro-8, 9, 10- trinorborn-5-en-2, 3- ylene-bis-methylene) sulphate].

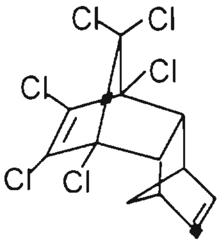


Heptachlor [1-exo- 4, 5, 6, 7, 8, 8- heptachloro-3a, 4, 7, 7a- tetrahydro-4,7-methanoindene].

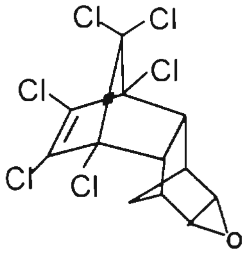


Heptachlor epoxide [1-exo-4, 5, 6, 7, 8, 8- heptachloro-3a, 4, 7, 7a- tetrahydro -2,3- exo-epoxy-4,7-methanoindene].

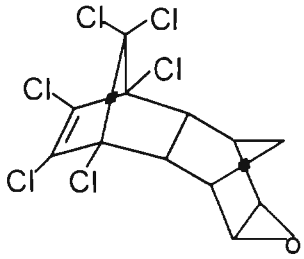
Figure 4.4 (contd...) Structural formulae of organochlorine pesticides



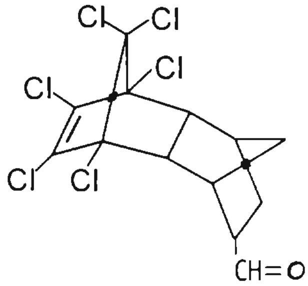
Aldrin [(1R, 4S, 5S, 8R)- 1, 2, 3, 4, 10, 10- hexachloro- 1, 4, 4a, 5, 8, 8a- hexahydro- 1, 4, 5, 8- dimethanonaphthalene].



Dieldrin [(1R, 4S, 5S, 8R)- 1, 2, 3, 4, 10, 10- hexachloro- 1, 4, 4a, 5, 6, 7, 8, 8a-octahydro- 6, 7- epoxy-1, 4, 5, 8-dimethanonaphthalene].

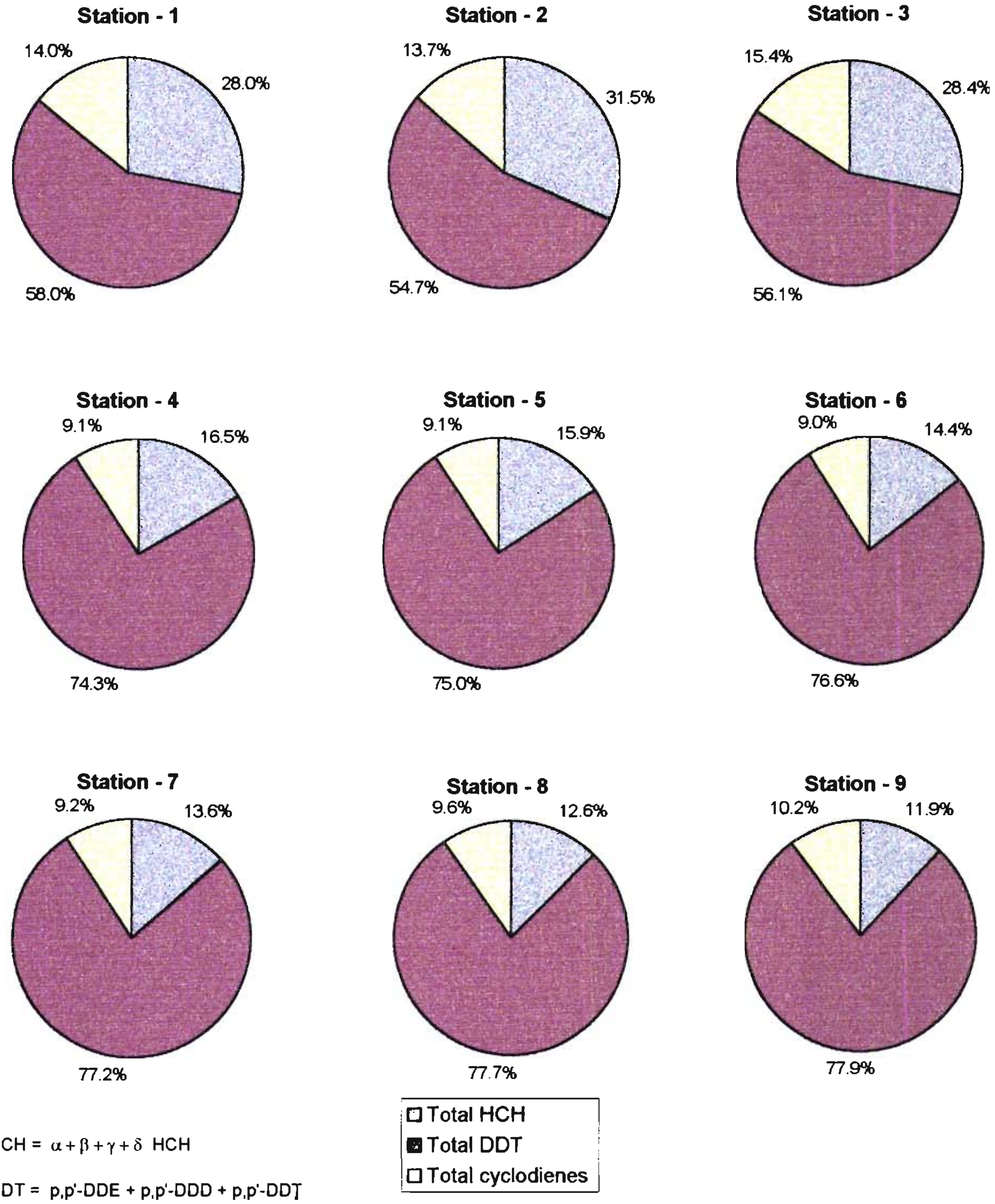


Endrin [1, 2, 3, 4, 10, 10- hexachloro-1, 4, 4a, 5, 8, 8a- octahydro-6, 7- epoxy-1, 4, 5, 8-dimethanonaphthalene].



Endrinaldehyde [1, 2, 3, 4, 10, 10- hexachloro-1, 4, 4a, 5, 8, 8a- octahydro-6- aldo-1, 4, 5, 8- dimethanonaphthalene].

Figure 4.4 (contd...) Structural formulae of organochlorine pesticides

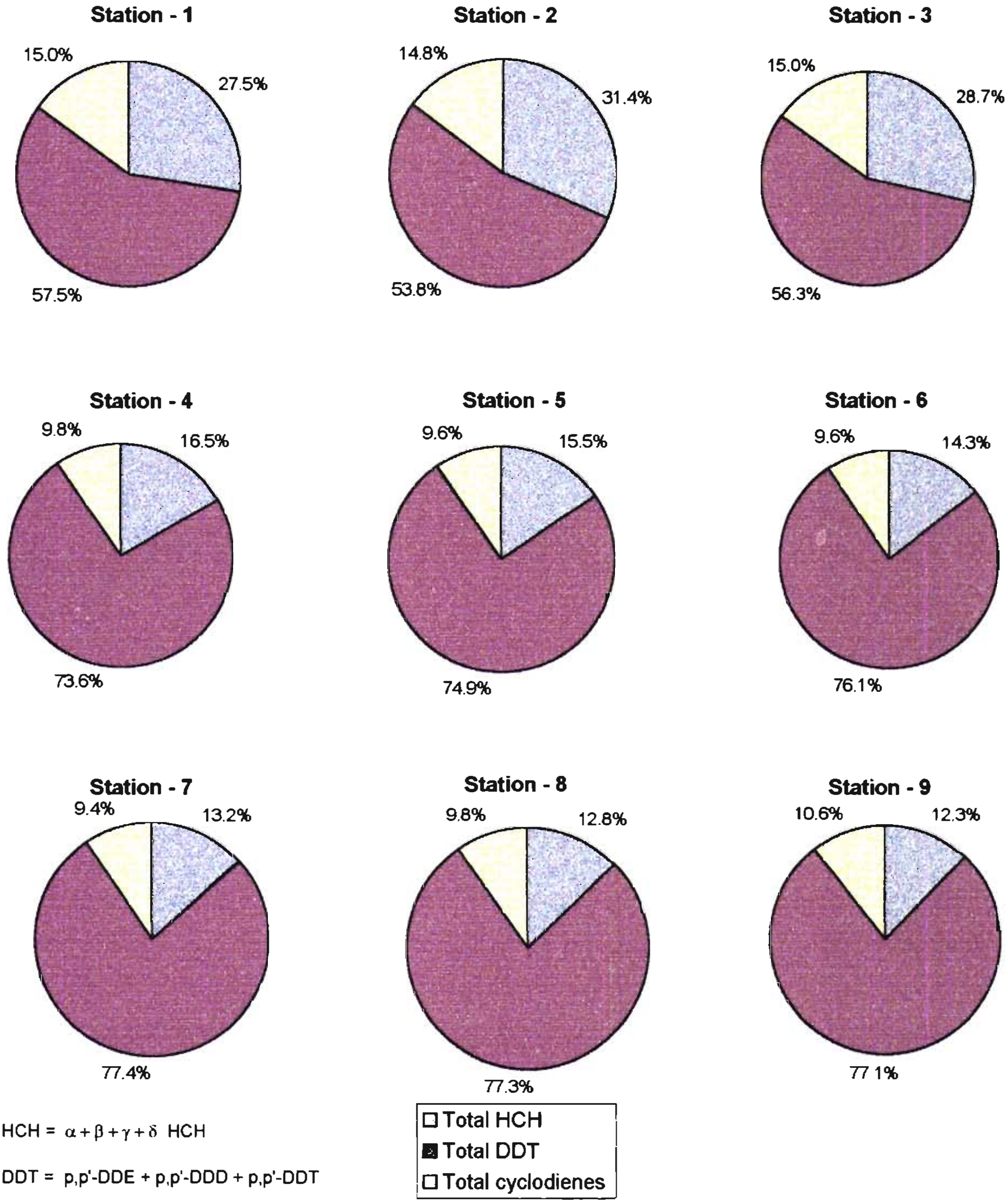


Total HCH = $\alpha + \beta + \gamma + \delta$ HCH

Total DDT = p,p'-DDE + p,p'-DDD + p,p'-DDT

Total cyclodienes = α - endosulfan + Σaldrins + Σendrins + Σheptachlors

Figure 4.5 Station wise percentage composition of total organochlorine pesticides in surface waters



Total HCH = $\alpha + \beta + \gamma + \delta$ HCH

Total DDT = p,p'-DDE + p,p'-DDD + p,p'-DDT

Total cyclodienes = α - endosulfan + Σaldrins + Σendrins + Σheptachlors

Figure 4.6 Station wise percentage composition of total organochlorine pesticides in bottom waters

concentrations were observed in all stations and the concentration factors compared well with those reported for other water systems elsewhere (Philips, 1989; Montanes et al., 1990; Sujatha, 1992; Nayak et al., 1995; Dua et al., 1996; Dua et al., 1998). More than 50% of the organochlorine pesticides found in Kuttanad backwaters were DDT and its metabolites. The second highest concentration comes to HCH and its isomers. Comparatively, the cyclodienes were found lesser amount than DDTs and HCHs. The mean values of total organochlorines ranged from 563.8 to 2186.3 ng l^{-1} in surface waters and 591.1 to 2184.5 ng l^{-1} in bottom waters (Table 4.7). In total organochlorine pesticides, the percentage composition of ΣDDT ranged from 54.7 to 77.9% in surface waters and 53.8 to 77.4 % in bottom waters (Figures 4.5 and 4.6). The percentage composition of ΣHCHs ranged from 11.9 to 31.5% in surface waters and 12.3 to 31.4% in bottom waters. The percentage composition of Σcyclodienes ranged from 9.0 to 15.4% in surface and 9.4 to 15.0% in bottom waters (Figures 4.5 and 4.6). Generally, at stations 1, 2 and 3 (zone 1) the values of ΣDDT were found to be lower than in other stations (Figures 4.5 and 4.6). The ΣHCH and Σcyclodienes concentrations were higher in zone 1 than in other zones. The distributions of residue levels of total organochlorines in Kuttanad backwaters were found in the order of Σ DDTs > Σ HCHs > ΣCyclodienes. The overall summary statistics of different organochlorine pesticides analysed in water (surface and bottom mean) are given in Table 4.8.

The presence of organochlorine pesticides in Kuttanad backwaters can be accounted due to the unscientific and misuse of these chemicals in agriculture, the huge amount of DDT formulations used in vector control programmes and also due to the run-off of these pesticides through the major rivers. Multiple residues of organochlorines were monitored in Ganges River water in the district of Farrukhabad in North India, and reported the dominance of α-HCH, p,p'-DDT and α-endosulfan in the aquatic environment (Agnihothri et al., 1996). The levels of priority organochlorine pesticides were detected in fish, algae, sediment and water samples from the Gulf of Aqaba and the results showed that all the investigated samples were unequally contaminated with organochlorine pesticides. Organochlorine residues determined in green mussel collected along

Table 4.7 Station wise overall mean concentrations of organochlorine pesticides

Surface water (ng l^{-1})

Stations	Total organochlorines	Σ DDT	Σ HCH	Σ Cyclodienes
1	563.8	326.8	157.8	79.2
2	638 5	349.4	201.4	87 7
3	735.4	412.8	209.1	113.5
4	1275.0	947.8	211.0	116.2
5	1660.3	1245.1	264.0	151.3
6	1963.6	1503.8	283.3	176.6
7	2105.7	1625.8	285.8	194.1
8	2186 3	1699.1	276.2	211.0
9	1635.7	1274 5	195.0	166.2

Bottom water (ng l^{-1})

Stations	Total organochlorines	Σ DDT	Σ HCH	Σ Cyclodienes
1	591 1	339.9	162.8	88.4
2	669.2	360.3	210.0	99.0
3	846.2	425.1	216.6	113.5
4	1267.2	933.2	209.7	124.3
5	1717.0	1286.8	265.7	164.6
6	1971.5	1500.4	282.6	188.5
7	2127.5	1645.8	280.9	200 8
8	2184.5	1689.2	280 4	214.9
9	1709.5	1317.4	210.1	182.0

Table 4.8 Overall summary statistics of organochlorine pesticides in water (ng l^{-1})

Pesticides/isomers/metabolites	Minimum	Maximum	Mean	SD	CV
p,p'-DDE	31.5	2100.5	614.5	90.5	61.1
p,p'-DDD	12.0	941.0	219.8	9.6	61.3
p,p'-DDT	ND	698.4	220.7	35.3	67.1
α - **BHC**	ND	360.0	148.0	13.1	72.1
β - **BHC**	ND	33.5	15.6	613.3	99.8
γ - **BHC**	ND	181.5	52.6	179.9	81.9
δ - **BHC**	ND	50.8	18.1	173.4	78.5
Endosulfan	ND	262.0	75.7	62.8	82.9
Heptachlor	ND	26.5	9.4	6.1	64.4
Heptachlor-epoxide	ND	42.0	17.3	11.6	67.1
Aldrin	ND	31.3	10.5	8.4	79.3
Dieldrin	ND	44.5	14.3	10.1	70.6
Endrin	ND	30.5	10.2	8.4	82.0
Endrin aldehyde	ND	34.3	11.3	8.5	74.7

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

the costal waters of India elucidate the distribution pattern of organochlorine pesticides and were in the order DDTs > HCHs > PCBs (Kan-Atireklap et al., ~~1997)~~. The same trend was observed in the present study also. Xinru Zhu et al. (1998) studied the distribution of organochlorine pesticides in water, sediment and fish in Lake Baiyangdian, China, and found that among the pesticides, DDT was widely distributed and high levels occurred in fish, despite a ban of its production and use in 1983. Jimenez et al. (1998) studied the effect of pesticide treatments on small lakes in the vicinity of cultivated lands and suggested that these pesticides were mobile enough to reach the water in the small lakes. This must be considered because this water is used in some cases to irrigate the neighbouring crops. Samia El-Kabbany et al. (2000) reported the occurrence of sixteen organochlorine pesticides in most of the water samples in some water supplies and agricultural lands in El-Haram, Giza (A.R.E) and the percentage of positive samples followed the order, aldrins > total HCH > total DDT > total endosulfan > heptachlor epoxide>heptachlor. In the present study area, there are so many "padasekharams" (paddy fields) for rice cultivation, and small streams connect the "padasekharams" to one another. The run-off water from the paddy fields has a great contribution of pesticide pollution in the study area. Further, the closure of bund at Thannermukkam for about more than six months in every year also accounts for the accumulation of pesticides in the backwaters of Kuttanad.

4.3.2 Distributions of ΣDDT

ΣDDT, described here, is the sum of p,p'-DDE, p,p'-DDD and p,p'-DDT Station wise distribution of ΣDDT in surface waters is shown in Figure 4.7 The mean values of ΣDDT ranged from 326.8 ng l^{-1} to 1699.1 ng l^{-1} in surface waters (Table 4.7). The minimum value of ΣDDT was observed at station 1 and the maximum value was seen at station 8, both in surface and bottom waters. From the Figure 4.7, it is clearly noted that the percentage composition of p,p'-DDE was higher than that of p,p'-DDD and p,p'-DDT In surface water, p,p'-DDE was the major isomer distributed in all stations, and the percentage ranged from 40.5

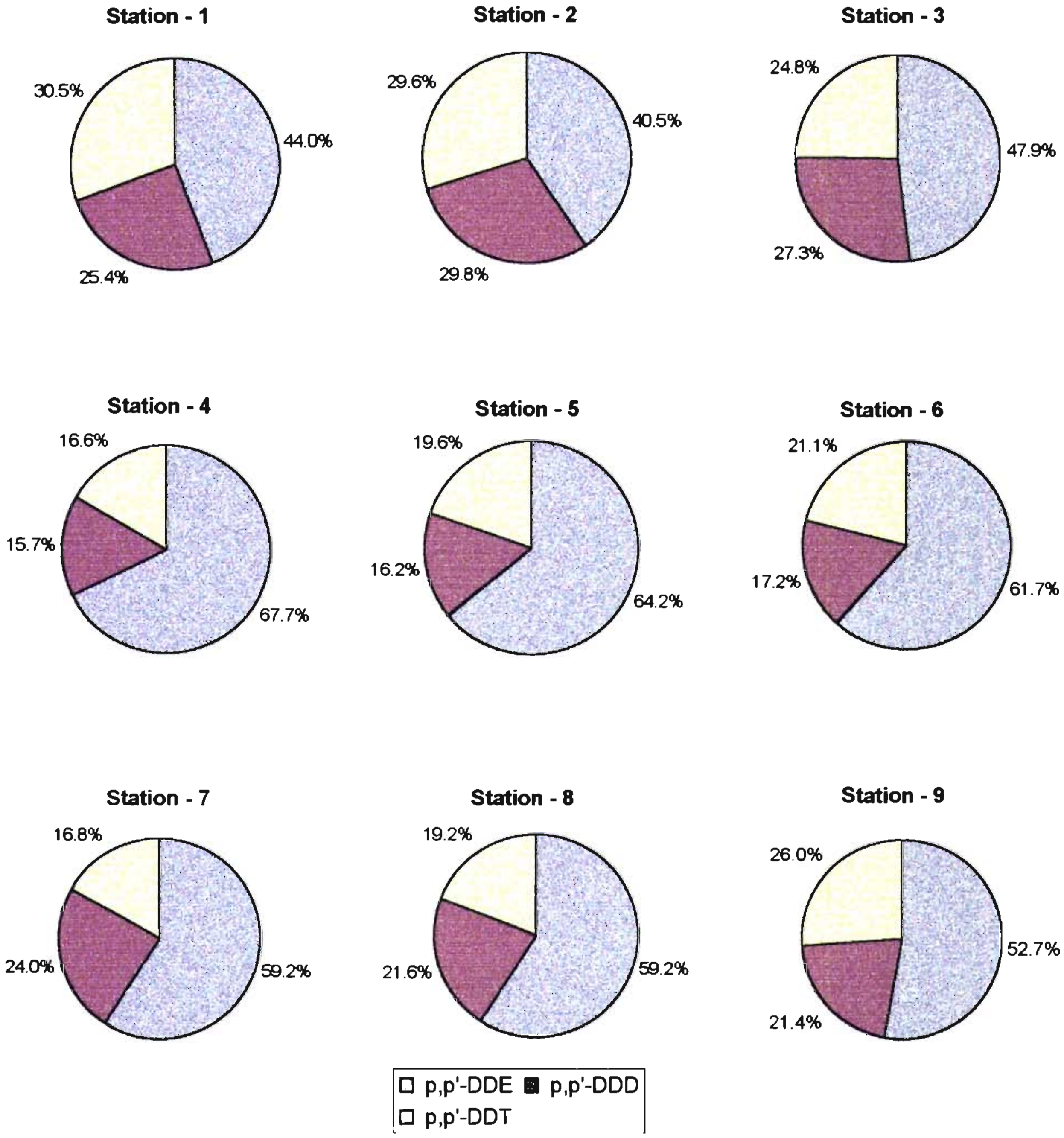


Figure 4.7 Station wise percentage composition of ΣDDT in surface waters

to 67.7 The percentage of p,p'-DDD in surface waters ranged from 15.7 to 29.8 and the percentage of p,p'-DDT ranged from 16.6 to 30.5 (Figure 4.7).

Figure 4.8 illustrates the percentage composition of ΣDDT in bottom waters. Like that of surface waters, p,p'-DDE contributes the major amount to the percentage composition of the DDT metabolites. The ΣDDT mean values in bottom waters ranged from 339.9 ng l^{-1} to 1689.2 ng l^{-1} (Table 4.7). The percentage of p,p'-DDE ranged from 41.5 to 66.0 of total DDT metabolites. The percentage of p,p'-DDD ranged from 15.9 to 28.9, and the percentage of p,p'-DDT ranged from 17.2 to 29.6 of total DDTs (Figure 4.8).

In zone 1, (stations 1, 2 and 3) in surface waters, the percentage of p,p'-DDE (40.5 to 47.9) was less compared to that of zones 2 and 3 (up to 67.7 %) (Figure 4.7). In zones 1 and 2, the percentage of p,p'-DDT dominated over p,p'-DDD in almost all of the stations in surface and bottom waters. Higher percentage of p,p'-DDE was observed in zone 2.

The degradation products of DDT are mainly the dechlorination products DDE and DDD. The pathway from DDT to DDD can be DDT→ DDE→ DDD, and these routes have not been completely established, even after 40 years of studies (Wayland et al, 1991; Corona-Cruz, 1999). Larsson et al. (1995) describes the fate of DDT in tropical and temperate regions and found that degradation of p,p'-DDT seemed to be higher in Zimbabwe compared to temperate regions. The same authors also suggested that volatilization dominates the distribution pattern of ΣDDT in tropical regions and once the DDT spread near the equator may well be driven by global distributions to the polar region, where it will accumulate in biota.

ΣDDT has been reported to be the most prominent among the pesticides commonly observed in coastal and riverine waters (Nimno, 1985; Sarkar and Sen Gupta, 1987; Muthanna et al., 1989; Dikshith, 1990; Tan and Vijayaletchumy,1994; Tsipi and Hiskia., 1996; Dua et al., 1998). Tan and Vijayaletchumy (1994) reported high levels of DDT (maximum concentration upto 190 ng/l) in the rivers from the rice growing region than those from non-rice

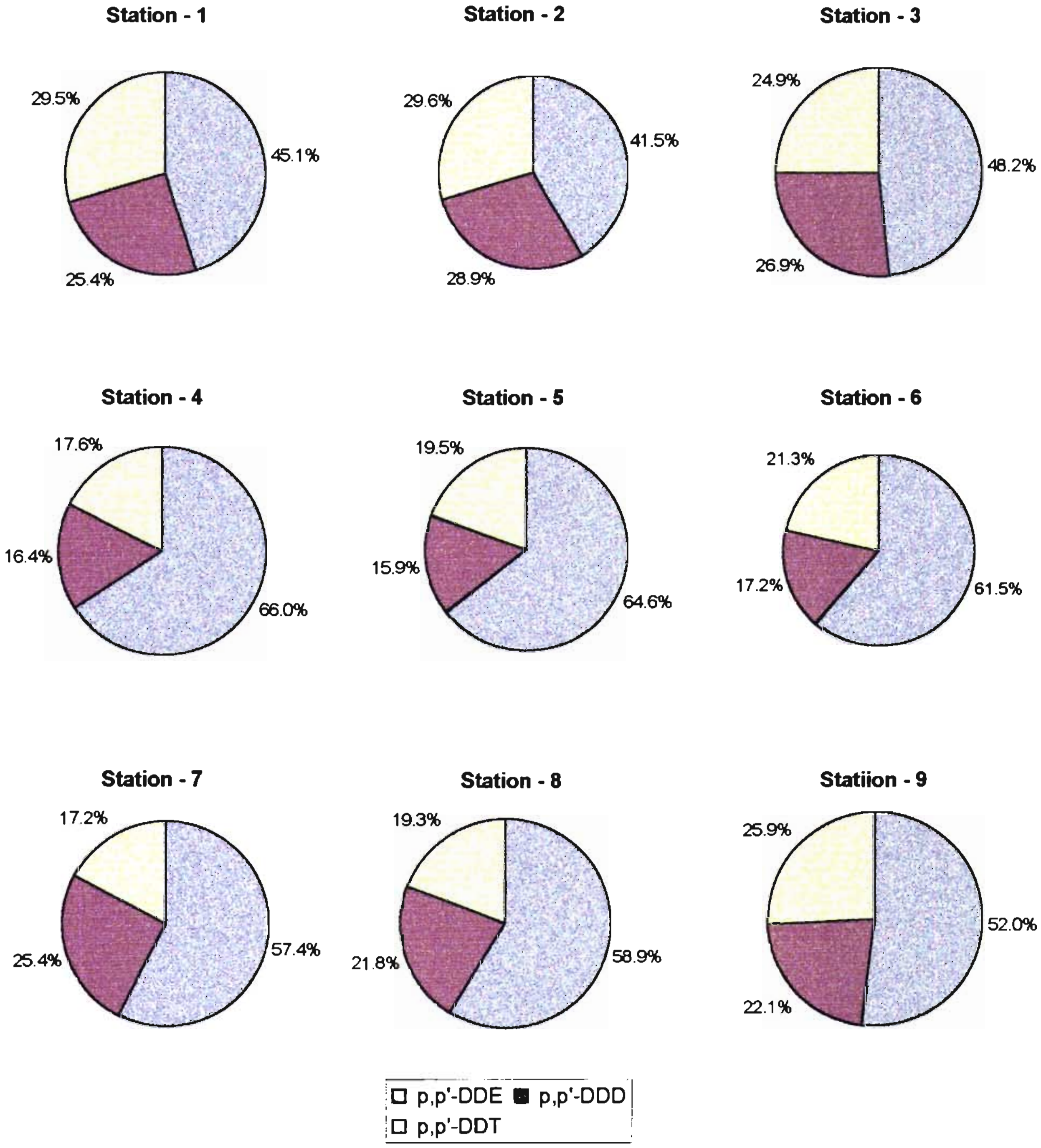


Figure 4.8 Station wise percentage composition of ΣDDT in bottom waters

growing regions. This observation is significant in Kuttanad area too, because Kuttanad is known as the 'rice bowl of Kerala', and as a result significant amounts of organochlorine pesticides were used in this area for the control of pests of paddy, before the banning of this pesticide for agriculture. Among the DDT compounds quantified in water samples collected from River Kaveri, p,p'-DDE and p,p'-DDT showed higher percentages of the ΣDDT (Ramasamy and Annamalai,1996). The presence of DDT and its metabolites in the Kuttanad backwaters again confirms the accumulation of DDT and its metabolites from the DDT formulations, which were widely used in these regions for the malaria eradication programme, and also the fact that these compounds are highly stable with low degradability.

Some scanty values of pesticides were reported in Kuttanad area by Kuttanad Water Balance Study (KWBS, 1989). The KWBS report stated that at some stations in Kuttanad area, the DDT concentrations had gone up to 4000 ng l^{-1} and at some other stations around the area, the values were found upto 12000 to 22000 ng l^{-1} Lower values of DDTs were observed in the present study which suggested the limited use of DDT at present compare with the massive use of DDT in earlier times.

A minimum value of not detectable levels (ND) to a maximum of 55.42 µg l^{-1} of $\sum$DDT was reported by Sujatha (1992) from Cochin estuary and as reported, the high concentration was due to the industrial effluents in that area and also the massive use of this pesticide for mosquito control programme. But in Kuttanad backwaters, the source of DDT was from vector controlling outlets in that area and also from run-off from rivers, and there were no entry of industrial effluents in that area. This may be a reason for the lower level of DDT in the study area than in Cochin estuarine system. Iwata et al. (1993; 1994) observed that southeast Asia and India are probably the most significant global sources of DDT (and therefore DDE), but most of the atmospheric burden is deposited to oceans close to the sources, resulting in a very steep decrease in concentration between tropical and arctic waters in the Pacific. Norstrom et al. (1998) suggested that the least volatile compounds such as DDT and highly chlorinated

PCBs, will tend to have higher particulate/gaseous phase distribution ratio, and therefore will be more readily scavengered by precipitation and dry deposition close to the source of emission than more volatile compounds.

4.3.2.1 Distributions of p,p'-DDE

p,p'-DDE (dichlorodiphenyldichloroethylene) is the major and most persistent DDT derivative, and it may better resume historic contamination, while total DDT and DDT alone would be more representative of contamination from recent users of the pesticide (IARC, 1991).

The station wise annual mean variations of p,p'-DDE in surface and bottom waters in the study area are depicted in Figure 4.9. The surface and bottom values were almost equal and no uniform distribution pattern was observed. Low values of p,p'-DDE were noted in the first three stations and an increasing tendency was seen upto station 8, and at station 9, the values were slightly low. The station wise summary statistics of p,p'-DDE in surface and bottom waters are listed in Table 4.9. Minimum value of 32.0 ng l^{-1} was recorded at station 4 in surface waters and 31.0 ng l^{-1} was recorded at the same station in bottom waters. A maximum value of 2215.0 ng l^{-1} was recorded at station 7 in surface waters and 2350.0 ng l^{-1} was recorded at station 5 in bottom waters. The station wise mean values of p,p'-DDE ranged from 141.6 ng l^{-1} to 1005.0 ng l^{-1} and 149.6 ng l^{-1} to 994.8 ng l^{-1} in surface and bottom waters respectively.

The seasonal mean variations of p,p'-DDE, both in surface and bottom waters are plotted in Figure 4.9. Higher concentrations of p,p'-DDE were observed in pre-monsoon period at stations 4 to 9 and lower values were recorded at stations 1 to 3, than in other seasons, both in surface and bottom waters. Station 8 recorded the highest value of p,p-'DDE. In monsoon, from stations 4 to 9, the p,p'-DDE concentrations were very low than in other seasons. In post-monsoon, the values were almost same at stations 1 to 3 in surface waters, but station 3 in bottom water recorded slightly higher values than in other

Table 4.9 Station wise summary statistics of p,p'-DDE in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	41.0	456.0	143.9	115.7	80.4
2	38.0	429.0	141.6	99.0	69.9
3	34.0	563.0	197.8	169.9	85.9
4	32.0	1874.0	641.8	601.6	93.7
5	45.0	1805.0	798.8	617.7	77.3
6	65.0	1984.0	927.5	688.8	74.3
7	55.0	2215.0	962.1	742.9	77.2
8	51.0	2067.0	1005.0	763.8	76.0
9	61.0	1453.0	671.1	378.3	56.4

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	45.0	463.0	153.4	116.7	76.1
2	45.0	443.0	149.6	103.0	68.9
3	41.0	550.0	205.0	173.5	84.6
4	31.0	1755.0	615.5	572.3	93.0
5	47.0	2350.0	830.7	698.8	84.1
6	71.0	2001.0	923.1	686.8	74.4
7	61.0	1986.0	944.7	713.7	75.5
8	54.0	1954.0	994.8	742.9	74.7
9	69.0	1488.0	685.1	381.8	55.7

SD - Standard deviation; CV - Coefficient of variation

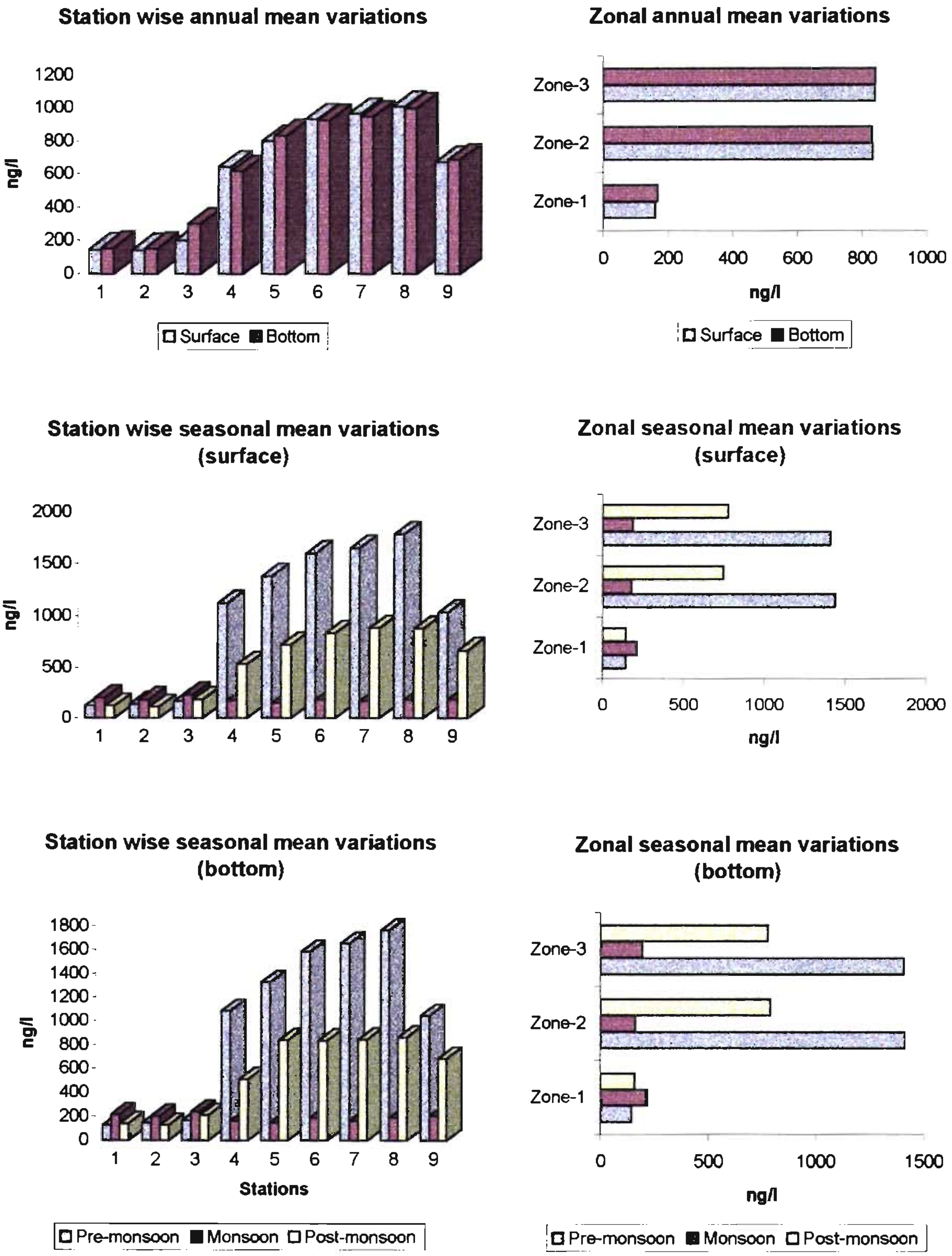


Figure 4.9 Seasonal and spatial distributions of p,p'-DDE in surface and bottom waters

seasons. In general, a marked seasonal variation in the distribution of p,p'-DDE was observed in almost all stations.

The annual zone wise mean variations and zonal seasonal variations of p,p'-DDE are also illustrated in Figure 4.9. From zones 1 to 2, the annual mean values of p,p'-DDE increased sharply and in zones 2 and 3, the values were almost same. From the zonal seasonal variation, it was noticed that, in pre-monsoon, the values of p,p'-DDE in zones 2 and 3 were higher than in other seasons, and the values in zone 1 was the lowest compared to other seasons, both in surface and bottom waters. Monsoon recorded the lowest values of p,p'-DDE in zones 2 and 3.

p,p'-DDE was found to be present in all stations with higher concentrations than the other metabolites of DDT (Figure 4.7 and 4.8). This could most probably be due to the fact that the most persistent metabolite of technical DDT is dichlorodiphenyl dichloro ethylene (DDE) (Brooks, 1976). Generally, high values have been reported for p,p'-DDE residues in other aquatic systems as well (O' Shea et al., 1980; Mwanthi, 1988; Sujatha, 1992; Tsipi and Hiskia., 1996; Dua et al., 1998). DDE was found to be more persistent and toxic than technical DDT DDT degraded faster in warm and moist tropical countries compared with temperate countries, and the main metabolites formed are DDE and DDD. The rate of degradation of DDT to DDE was found to be directly proportional to the increase in temperature, moisture and microbial activities in soil (Mitra and Reghu, 1998). The physico-chemical properties of technical DDT and the environmental conditions prevailing in the study area enhanced the decomposition of DDT to DDE. In technical DDT, the percentage of p,p'-DDT is about 70 % and the decomposition of p,p'-DDT to p,p'-DDE was more predominant. Moreover, DDT was widely used in these regions for the malarial eradication programme. DDE is the highly stable metabolite of technical DDT with very low degradability, and this may be another reason for the highest distribution of p,p'-DDE in the study area. DDT is transformed to DDE through a dehydrochlorination process (Walker, 1975) and it is the most abundant among the DDT metabolites dispersed in the aquatic environment and accumulated in the biota.

The seasonal variations of p,p'-DDE in the present study was almost same as those reported by Sujatha (1992) in Cochin estuary, and the maximum concentration of p,p'-DDE was observed in pre-monsoon season in both studies. The slightly higher levels of p,p'-DDE at zone 1 in monsoon periods may be mainly due to the run-off from rivers. The high concentrations of p,p'-DDE in zones 2 and 3 were explained by the residual DDE deposited on the sediments for the last so many years , when DDT was used in agriculture, and also the run-off from rivers. This is significant, because of the fact that, under aerobic conditions, a high rate of formation of p,p'-DDE from p,p'-DDT take place (Richard, 1976; Pereira et al., 1996). In the study area, because of the aerobic conditions of the soils, the active oxidative transformation of p,p'-DDT to p,p'-DDE was facilitated. The observed higher proportion of p,p'-DDE in technical DDT may be a reflection of the greater persistence of p,p'-DDE (EPA, 1980).

From this study, it is apparent that the ability for aquatic life such as fish to propagate in this water system may be adversely affected by the presence of higher levels of DDE, because the levels of DDE in Kuttanad waters were exceeded the critical levels. This is significant that in pre-monsoon and post-monsoon, fish mortality is common in the study areas.

4.3.2.2 Distributions of p,p'-DDD

The station wise annual mean variations of p,p'-DDD in surface and bottom waters are shown in Figure 4.10. The bottom distribution of p,p'-DDD at all stations were slightly greater or equal to that of surface, and at station 7, bottom values were distinctly higher than surface values. Station wise summary statistics of p,p'-DDD is listed in Table 4.10. The minimum and maximum values recorded in surface waters were 11.0 ng l^{-1} (at stations 3 & 6) and 987.0 ng l^{-1} (at station 7) respectively. The minimum and maximum values observed in bottom waters were 12.0 ng l^{-1} (at station 5) and 895.0 ng l^{-1} (at station 7) respectively. The station wise mean values of p,p'-DDD ranged from 83.1 ng l^{-1} to 390.5 ng l^{-1} in surface waters and 86.3 ng l^{-1} to 417.9 ng l^{-1} in bottom waters. The highest

Table 4.10 Station wise summary statistics of p,p'-DDD in surface and bottom waters

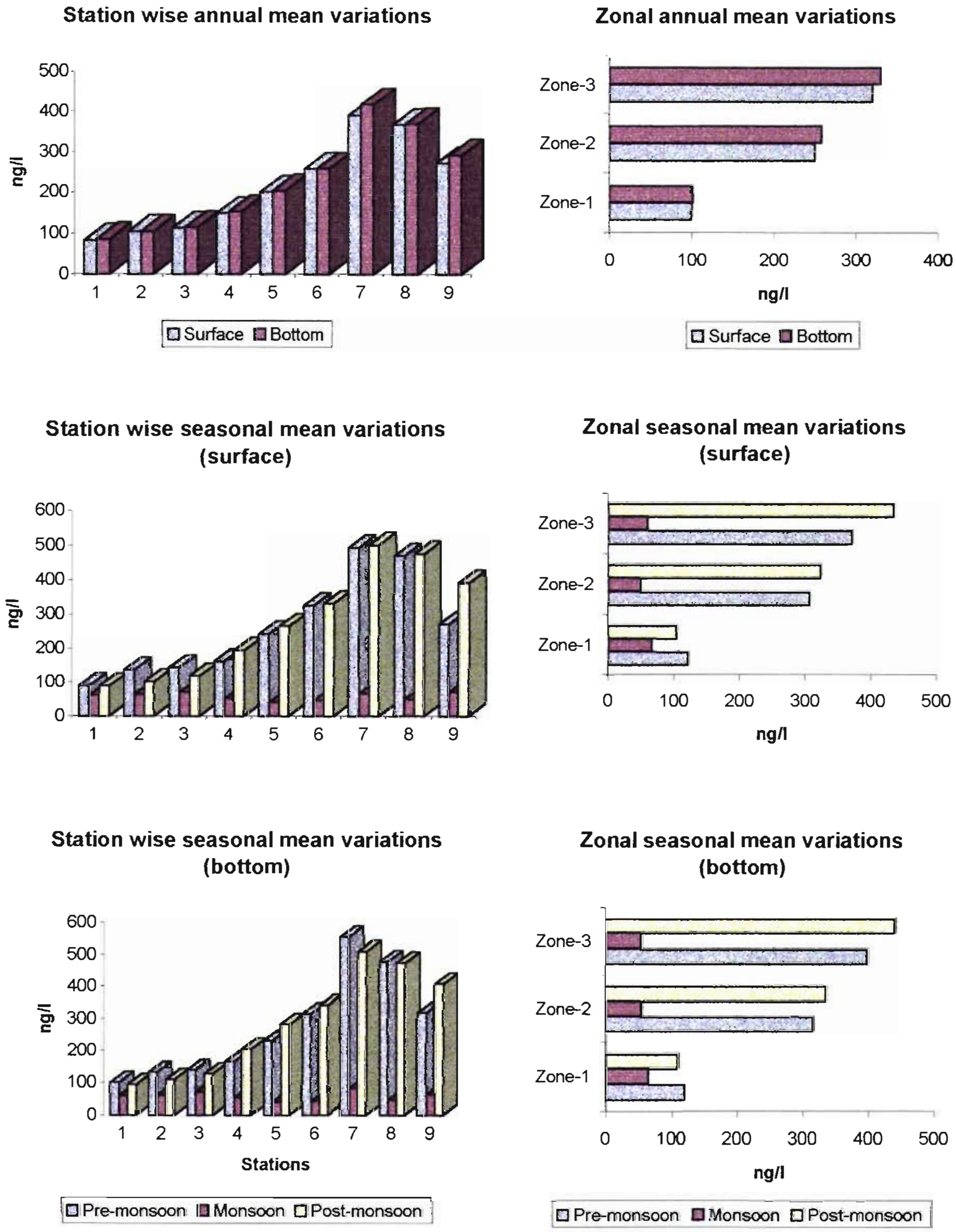
Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	12.0	178.0	83.1	44.5	53.5
2	14.0	154.0	104.3	45.6	43.8
3	11.0	180.5	112.7	53.3	47.3
4	17.0	432.8	148.9	103.8	69.7
5	12.0	421.0	201.7	115.2	57.1
6	11.0	474.8	258.4	139.4	53.9
7	21.0	987.0	390.5	260.1	66.6
8	16.0	876.0	367.5	237.6	64.6
9	25.0	456.0	272.3	144.8	53.2

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	14.0	155.0	86.3	37.2	43.1
2	19.0	155.0	104.2	42.8	41.1
3	15.0	165.0	114.2	48.2	42.2
4	15.0	435.0	153.2	104.5	68.2
5	12.0	442.0	204.9	118.1	57.6
6	15.0	454.0	258.0	140.1	54.3
7	27.0	895.0	417.9	258.7	61.9
8	18.0	869.0	368.7	241.8	65.6
9	29.0	465.0	291.5	154.5	53.0

SD - Standard deviation; CV - Coefficient of variation



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 4.10 Seasonal and spatial distributions of p,p'-DDD in surface and bottom waters

values of p,p'-DDD were observed at station 7, both in surface and bottom waters.

Figure 4.10 illustrates the seasonal mean distributions of p,p'-DDD in surface and bottom waters. In pre-monsoon period, stations 1 to 3 showed higher values of p,p'-DDD in surface waters, and stations 1 to 3 and 7 showed higher values of p,p'-DDD in bottom waters. At other stations, values of p,p'-DDD were higher in post-monsoon periods than in other seasons. In pre-monsoon and post-monsoon periods, stations 8 and 9 showed lower values of p,p'-DDD compared to station 7 Monsoon period showed the lowest values of p,p'-DDD at all stations in surface and bottom waters.

The annual zone wise mean variations and zonal seasonal variations of p,p'-DDD are also plotted in Figure 4.10. The distributions of p,p'-DDD were almost uniform in surface and bottom waters, and a narrow range of surface and bottom variations were seen. The values of p,p'-DDD were increasing linearly from zones 1 to 3. Monsoon recorded the lowest values of p,p'-DDD in all zones, both in surface and bottom waters. In zones 2 and 3, the post-monsoonal values of p,p'-DDD in surface and bottom waters were high in comparing with monsoon and pre-monsoon periods. In pre-monsoon, zone 1, recorded slightly higher values of p,p'-DDD than in post-monsoon and monsoon periods.

In India, restricted use of DDT was recommended for certain crops. For public health, mainly for the control of vector-transmitted diseases, the major pesticide used in India is DDT In Indian conditions, DDT may degrade faster and the formation of DDD is enhanced, and the faster disappearance is due to the more volatilisation and biodegradation process (Samuel and Pillai, 1988; Zhengsheng and Haibo, 1994). DDT was reductively dechlorinated under anoxic conditions to DDD and several minor degradation products, DDMU, DDMS and DDNU (Pereira et al., 1996). The distribution of p,p'-DDD in zone 3 of the study area was found to be more than in other zones. This may be due to the anaerobic conditions of the soil characteristics in this zone, where the pH was varying frequently. Further, the long use of DDT for agriculture, in early years also contributed to the formation of DDT metabolites mainly DDD and DDE. The continuous use of DDT for the Malaria Eradication Programme in the study area, also contributed to the formation of this isomer. Richard (1976), established that the conversion of p,p'-DDT to p,p'-DDD takes place more rapidly under anaerobic conditions. This is especially significant in zones 2 and 3 where higher values of p,p'-DDD were observed in post-monsoon season, and was due to the constant rains during the wet season coupled with the anaerobic conditions of the soils.

Climate appears to be an important factor in the transformation of DDT to its metabolites (Richard, 1976). Among the various factors that regulate the proportionate concentrations of DDT metabolites, microbial degradation has an important place. In one such study, Johnson (1976) inferred that anaerobic metabolisation of p,p'-DDT in the biota leads to the formation of p,p'-DDD. The anaerobic biotransfermation of DDT enhances the formation of DDD (You et al., 1996). The persistence and non-degradation property of p,p'-DDD made this isomer to be present for many years in various water systems. The overall mean concentration of p,p,-DDD was found to be 219.8 ng l^{-1} in Kuttanad backwaters. The other reported values are 2.3 to 28.7 ng l^{-1} from River Nile, Egypt (Mohamed and Mohamed, 1985b); 0.001 to 0.17 µg l^{-1} in community water supplies, Kenya (Mwanthi, 1988); ND to 0.002 µg l^{-1} in drinking water of Athens (Tsipi and Hiskia., 1996); ND to 0.041 ppm in the drinking water from South Spain (Garcfa-Repetto and Repetto, 1997).

4.3.2.3 Distributions of p,p'-DDT

No significant difference in the concentrations of p,p'-DDT was observed in surface and bottom distributions except at stations 7 and 9 (Figure 4.11). At stations 7 and 9, the surface values were slightly lower than the bottom values. The station wise summary statistics of p,p'-DDT in surface and bottom waters were listed in Table 4.11. The surface and bottom waters at stations 1, 2, 3, 5 and 6 recorded non-detectable levels of p,p'-DDT, both in surface and bottom waters. The maximum values observed were 675.8 ng l^{-1} and 721.0 ng l^{-1} in surface and bottom waters respectively at station 9. The station wise mean

Table 4.11 Station wise summary statistics of p,p'-DDT in surface and bottom waters

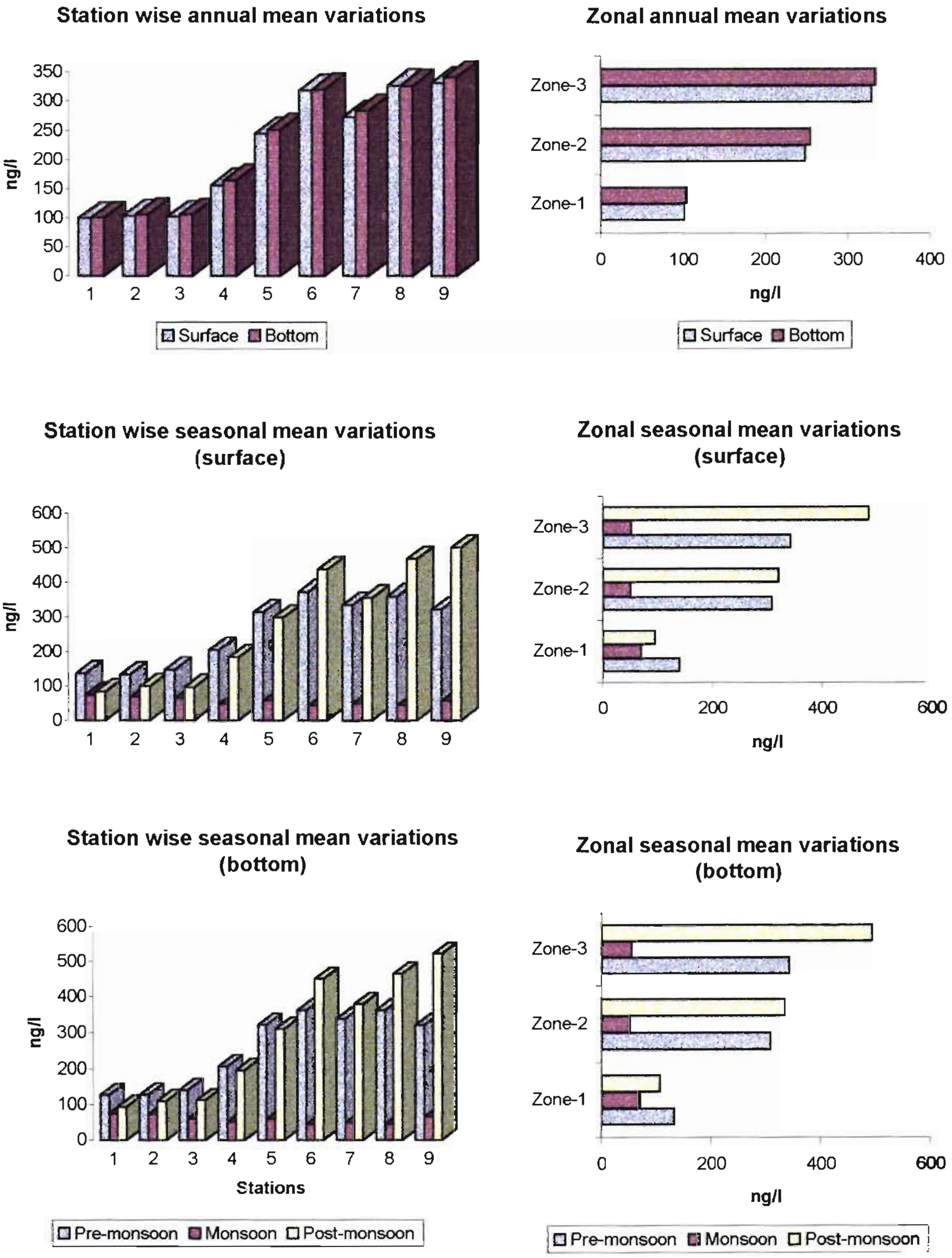
Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	198.0	99.8	59.1	59.2
2	ND	176.0	103.6	54.3	52.5
3	ND	167.0	102.3	53.9	52.7
4	12.0	234.0	157.0	73.7	46.9
5	ND	423.0	244.6	151.8	62.1
6	ND	557.4	317.8	210.9	66.4
7	11.0	476.0	273.3	166.4	60.9
8	14 0	567.9	326.6	200.6	61.4
9	28.0	675.8	331.0	214.7	64.9

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	200.0	100.2	58.6	58.5
2	ND	188.0	106.5	56.8	53.3
3	ND	156.0	105.9	54.7	51.6
4	17.0	231.0	164.5	74.8	45.5
5	ND	431.5	251.2	156.6	62.3
6	ND	570.0	319.4	213.3	66.8
7	16.0	465.0	283.2	175.5	62.0
8	18.0	559.0	325.7	200.6	61.6
9	30.0	721.0	340.8	223.2	65.5

SD - Standard deviation CV - Coefficient of variation; ND - Not detected


Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 4.11 Seasonal and spatial distributions of p,p'-DDT in surface and bottom waters

values of p,p'-DDT ranged from 99.8 ng l^{-1} to 331.0 ng l^{-1} in surface waters and 100.2 ng l^{-1} to 340.8 ng l^{-1} in bottom waters.

The surface and bottom seasonal mean variations of p,p'-DDT are also shown in Figure 4.11. In pre-monsoon, stations 1 to 5 recorded almost higher values of p,p'-DDT, both in surface and bottom waters. From stations 6 to 9, the pre-monsoon values were lower than post-monsoon values. Monsoon recorded lower values of p,p'-DDT in surface and bottom waters at all stations than in other seasons. In post-monsoon period, a steady increase of p,p'-DDT was observed from stations 1 to 9 except at station 7

The annual zone wise mean variations and zonal seasonal variations of p,p'-DDT are also plotted in Figure 4.11. p,p'-DDT was distributed almost uniformly in surface and bottom waters. The values of p,p'-DDT were found increasing almost linearly from zones 1 to 3. In pre-monsoon, the values of p,p'-DDT in zone 1 was higher and in zones 2 and 3, the values were lower than post-monsoon season, both in surface and bottom waters. Monsoon recorded the lowest values of p,p'-DDT in all zones, both in surface and bottom waters.

Appreciable concentrations of p,p'-DDT were found in the study area, which probably suggested that technical DDT was deposited into the waters due to the application of this pesticide for the control of malaria eradication programme occasionally. Apart from the climatic conditions, the mode of application and the time elapsing after application may influence the distributions of p,p'-DDT in the study area. The p,p'-DDT used for vector control purposed also reach the estuary through run-off from the major rivers.

The p,p-DDT levels detected were found to be rather low and exhibited a uniform distribution pattern in the study area, compared to the high values (0.027 to 79.818 µg l^{-1}) reported in North India in the middle stream of Ganga River (Nayak et al., 1995) suggesting a smaller quantity of insecticide usage and low aerial deposition from point-source application sites for vector control in places such as urban and suburban areas. It has been pointed out that approximately 98% of DDT applied to the cowpea crop in Nigeria was volatilised during a period of four years (Perfect, 1980). These trends should also be taken into account in relation to the observed low residue levels and uniform concentration pattern of pesticides observed in the present study.

The other reported values of p,p'-DDT were 0.2 to 56 µg l^{-1} in Meditaranian sea (Mohamad and Mohamed, 1985a); 0.1 to 24.2 ng l^{-1} in River Nile water, Egypt (Mohamed and Mohamed, 1985b); 0.001 to 0.24 µg l^{-1} in Community water supplies, Kenya (Mwanthi, 1988); not detectable levels in drinking water of Athens (Tsipi and Hiskia., 1996).

4.3.3 Distributions of ΣHCH

ΣHCH, described here, is the sum of α-HCH, β-HCH, γ-HCH and δ-HCH. The percentage compositions of ΣHCH in surface waters are shown in Figure 4.12. The overall mean concentrations of ΣHCH in the study area ranged between 157.8 ng l^{-1} to 285.8 ng l^{-1} in surface waters (Table 4.7). The minimum value of ΣHCH in surface water was seen at station 1 and the maximum value was seen at station 7 In surface waters, the percentage of α-HCH was the major isomer distributed in the study area, and was ranged from 60.6 to 67.5% of the total isomers of HCH. The percentage of β-HCH in surface waters ranged from 5.4 to 7.8 % and that of γ-HCH from 19.3 to 25.2% of total HCH. The percentage of δ-HCH also ranged from 6.3 to 8.7% in surface waters.

Figure 4.13 illustrates the percentage compositions of various isomers of HCH in bottom waters of the study area. Like that of surface distribution, here also α-HCH contributes the major share of the total isomers of HCH. The ΣHCH values in bottom water ranged from 162.8 ng l^{-1} to 282.6 ng l^{-1} (Table 4.7). The percentage of α-HCH ranged from 59.8 to 66.0% of total HCH. The percentage of β-HCH ranged from 5.6 to 8.0% of total HCH. The percentages of γ-HCH ranged from 20.3 to 25.2% and δ-HCH ranged from 5.9 to 8.3% of total HCH (Figure 4.13).

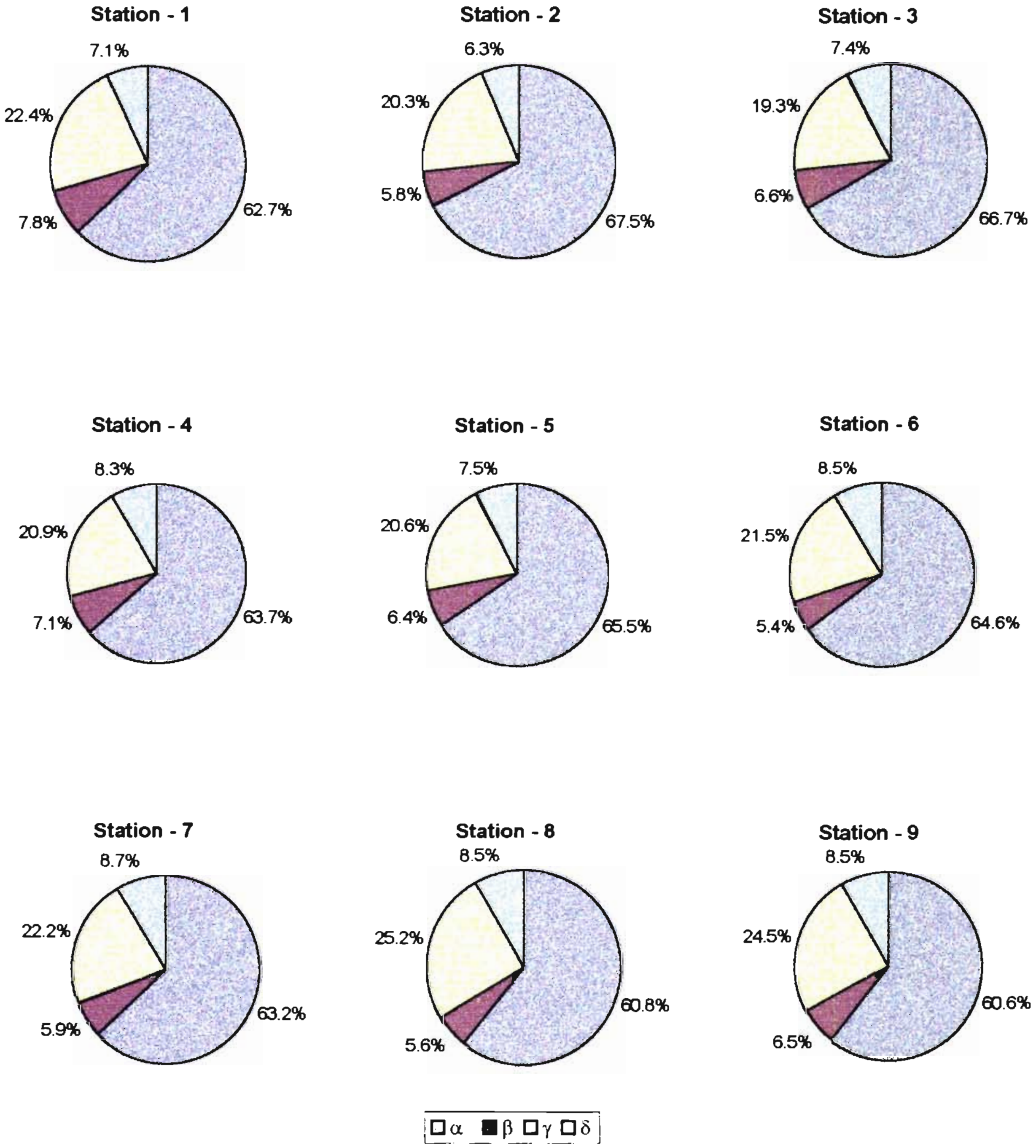


Figure 4.12 Station wise percentage composition of HCH isomers in surface waters

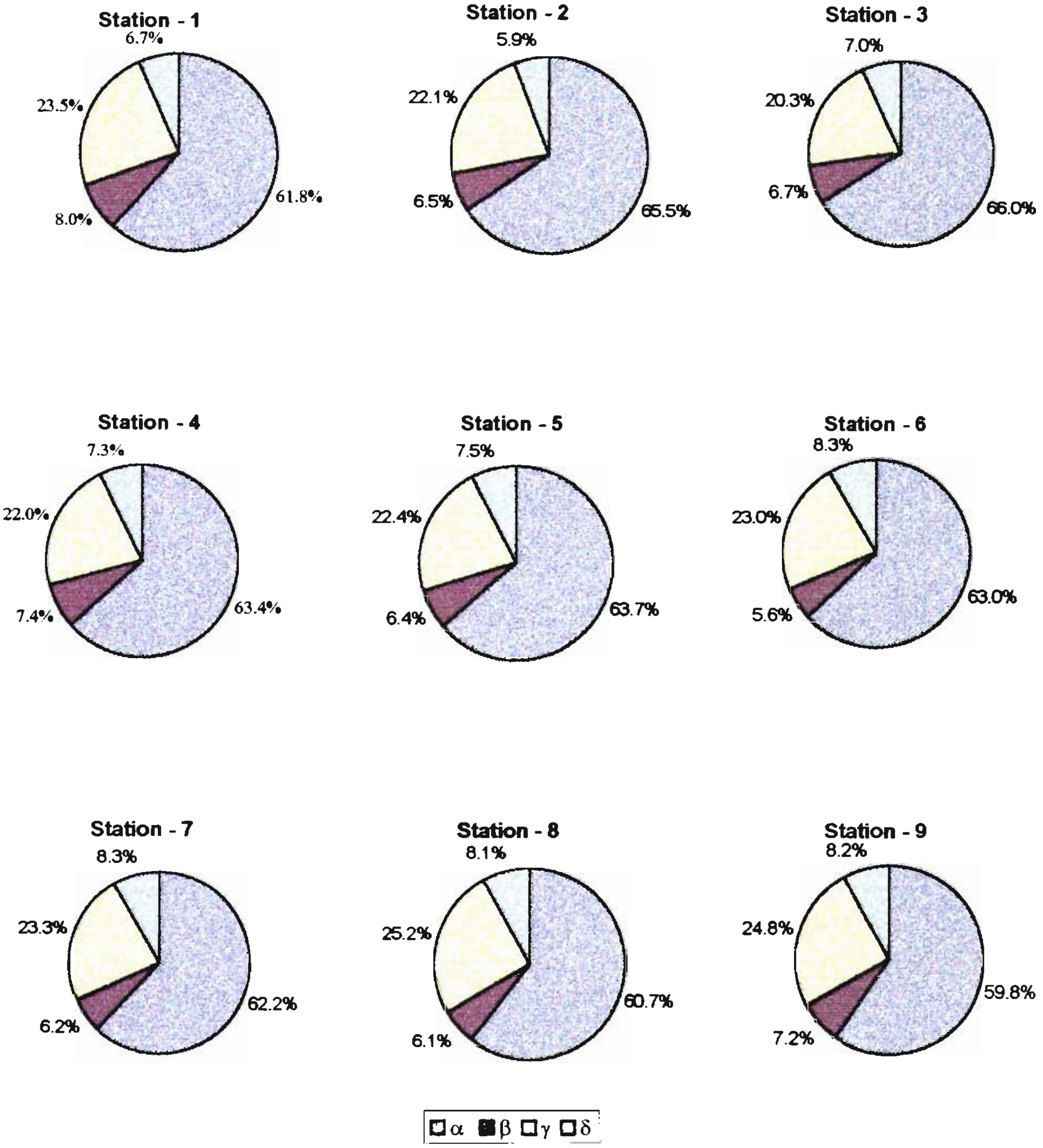


Figure 4.13 Station wise percentage composition of HCH isomers in bottom waters

In the distribution pattern of total HCH isomers in surface and bottom waters of zone 3, the percentage of α-HCH was slightly lower, whereas the percentage of γ-HCH was slightly greater than in other zones. In zone 1, stations 2 and 3 recorded more amount of α-HCH than in other stations (Figures 4.12 & 4.13). In zone 1, all the stations (1, 2 & 3) recorded minimum percentage of γ-HCH than in other stations. In the total distribution patterns of HCH isomers in the entire study area, β-HCH isomer accounts the lowest distribution percentage in surface and bottom waters.

HCH isomers detected in different regions of Indian ocean were observed to be mainly composed of α, β and γ isomers of HCH, of which α and γ isomers contribute 45 to 48%, whereas the β isomer only 5-10% (Sarkar and Sen Gupta, 1987; 1988a; 1988b). Sujatha (1992) quantified the ΣHCH in Cochin estuary, and the concentrations of ΣHCH ranged between 0.013 and 1.125 µg l^{-1} The order of abundance in the distribution of ΣHCH in the Kuttanad backwaters was α-HCH > γ-HCH > δ-HCH > β-HCH. These results were comparable with results obtained in the above studies.

The KWBS (1989) reported some of the pesticides in Kuttanad area and the values of α-HCH and γ-HCH concentrations in the water samples of Kuttanad area vary between 0 to 400 ng l^{-1} These values were almost comparable with the present study also as the use of HCH were predominant during the sampling period.

Reports of HCH isomer studies carried out on the Indian coastal waters (Sarkar and Sen Gupta, 1989) reported overall concentrations ranged between 0.06 to 9.40 ng l^{-1} in Arabian sea. Dua et al. (1998) reported higher levels of ΣHCH in waters from different lakes of Ninital, India and the values were 2.40 to 5.34 µg l^{-1} (Khurpatal Lake); 2.308 to 5.176 µg l^{-1} (Sattal lake); 2.529 to 8.834 µg l^{-1} (Bhimtal Lake); 1.337 to 3.229 µg l^{-1} (Naukuchiatal lake) and 2.530 to 5.408 µg l^{-1} (Ninital lake). The above authors stated that the higher contamination of pesticides in these lakes may be due to the location of lakes at a height of 1036 to 1936 m above sea level and the run off from agriculture fields near the particular lake command areas. In Peninsular Malasian Rivers, the $\sum$HCH ranged between ND levels to 320 ng l^{-1} (Tan and Vijayaletchumy, 1994). Ramasamy and Annamalai (1996) quantified the residue levels of organochlorines in River Kaveri, Tamilnadu and observed that HCH levels were high in pre-monsoon and monsoon periods, and the same was attributed to the usage of this pesticide for paddy crops. In the present study also, the higher levels of HCH-isomers were found in pre-monsoon period. In the case of spatial distribution, a uniform pattern of distribution was not observed. The high contamination of HCH in the study areas, especially in zones 2 and 3 (Table 4.7) may be due to the higher use of HCH for the control of pests of rice in that area. During the period of sampling, HCH was quite common in agricultural farming and the uncontrolled use of HCH thereby resulting high contamination in the Kuttanad backwaters. The annual mean variations mainly depend on the opening and closing of bund and also the run-off from the major river systems in Kuttanad area.

4.3.3.1 Distributions of α-HCH

α-HCH is the major isomer of technical HCH and is about 65-70% of total HCH (WHO, 1992). The station wise annual mean variations of α-HCH in surface and bottom waters are plotted in Figure 4.14. The station wise summary statistics of α-HCH in surface and bottom waters are shown in Table 4.12. From the Figure 4.14, it was observed that at stations 1, 2, 3, 8 and 9, the bottom values of α-HCH values were higher than that of surface waters. The minimum and maximum values of α-HCH observed at surface and bottom waters were non-detectable levels to 365.0 ng l^{-1} The non-detectable levels of α-HCH were mostly noticed at stations 1, 2 & 3, both in surface and bottom waters. The highest value of 365.0 ng l^{-1} was recorded at station 8 in surface waters and at station 7 in bottom waters. The station wise annual mean values of α-HCH ranged from 99.0 ng l^{-1} to 183.0 ng l^{-1} for surface waters and 100.6 ng l^{-1} to 178.0 ng l^{-1} for bottom waters.

Table 4.12 Station wise summary statistics of α - HCH in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	235.5	99.0	57.4	58.0
2	ND	235.0	136.0	70.3	51 7
3	ND	289.0	139.4	81.0	58.1
4	24.0	232.0	134.5	67.0	49.8
5	15.0	312.0	173.0	106.3	61.5
6	12.0	345.0	183.0	115.6	63.2
7	21.0	354.0	180.5	113.7	63.0
8	20.0	365.0	167.9	115.8	69.0
9	24 0	205.5	118.1	57.1	48.3

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	225.0	100.6	55.7	55.4
2	ND	225.5	137.5	68.5	49.8
3	ND	274.8	143.0	79.2	55.4
4	22.0	213.0	132.9	62.8	47.2
5	26.0	312.0	169.4	105.3	62.2
6	11.0	355.0	178.0	117.6	66.0
7	9.0	365.0	174.8	115.7	66.2
8	22.0	355.0	170.2	113.2	66.5
9	31.0	211.0	125.6	58.1	46.3

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

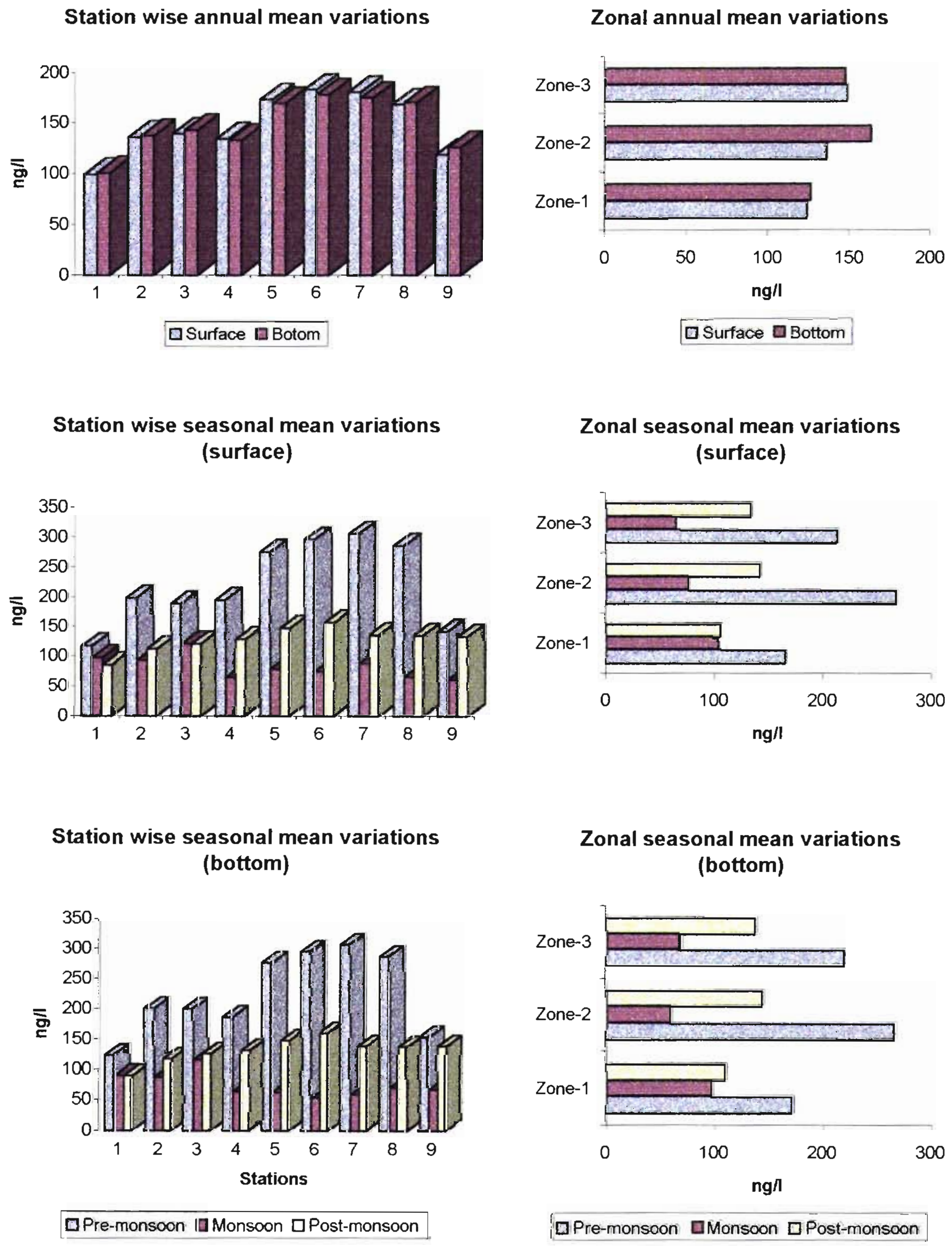


Figure 4.14 Seasonal and spatial distributions of α -HCH in surface and bottom waters

The seasonal mean variations of α-HCH of both surface and bottom waters are also shown in Figure 4.14. Higher values of α-HCH were seen in all stations in pre-monsoon period. In pre-monsoon period, the values of α-HCH generally increased from station 1 to 8, and at station 9 the values were diminished. In monsoon period, higher values of α-HCH were observed at stations 1 to 3, and other stations recorded lower values of α-HCH. At stations 1 to 3, the values of α-HCH in monsoon period were nearly equal to that of post-monsoonal values in both surface and bottom waters. The post-monsoon values of α-HCH in both surface and bottom waters were increasing linearly from stations 1 to 6, and from stations 7 to 9, it gradually decreased. In general, the variation of α-HCH was clearly distinct in all the three seasons.

The annual zone wise mean variations, and zonal seasonal variations of α-HCH are also plotted in Figure 4.14. High mean values of α-HCH were seen in zone 2 in bottom water, whereas in zones 1 and 2 the values were almost comparable. In zonal seasonal variation of α-HCH, both in surface and bottom waters, pre-monsoon values were high in all three zones, and zone 2 recorded the maximum distribution of α-HCH. In monsoon, all the three zones recorded minimum values of α-HCH, but in zone 1, the values were higher or equal to that of post-monsoon period, both in surface and bottom waters. In pre-monsoon, the α-HCH values were less in zone 1, and gradually increased to zone 2 and again declined slightly in zone 3. In general, zones 2 and 3 showed high values of α-HCH in pre-monsoon and post-monsoon periods.

α-HCH was found to be present in almost all stations with higher concentrations throughout the study area. The α-HCH isomer was found to be distributed as the major isomer in the study area than other isomers of HCH, and its distributional properties were influenced by both station wise and seasonal variations. It may be due to the fact that technical HCH consists of about 65 to 70 % of α-HCH isomer, which is the major portion in technical HCH (WHO, 1992). Granby and Kinze (1991) reported a similar trend, the α-isomer of HCH being about ten times higher than γ-isomer. The high percentage of α-isomer in technical BHC accounts for the higher distribution of this isomer in the study area, even though the solubility of α-isomer in water is 1.63 ppm (Brooks, 1976). The high concentrations of α-HCH observed in waters, especially in zones 2 and 3 of Kuttanad backwaters, were mainly due to the agricultural run-off from the "Padasekharams" Technical HCH formulations were widely used in agriculture for almost all corps. The run-off from rivers and the non-degradable property of α-isomer also influence the high concentration of this isomer in the study area.

Sujatha (1992) reported the concentration of α-HCH in Cochin backwaters, and the concentrations ranged from ND to 1.002 μg l^{-1} The same author also observed that the α-isomer concentrations were invariably the highest in pre-monsoon, and lowest in monsoon in all most all stations. The same trend was observed in the present study also, because the study area is an extension of Cochin backwaters. The concentration of α-isomer (overall mean concentration 148 ng l^{-1}) observed in the study area was found to be less than in Cochin estuary. During monsoon, the possibility of greater accumulation of pesticides in the particular matter increased, by the absorption onto the humic acids. This is significant because in zone 1, during monsoon, the values were found to be slightly more than that of other zones.

The α-isomers reported from other areas were: 0.002 to 0.045 μg l^{-1} in rain water, Hardwar, India (Dua et al., 1994); ND to 31.02 μg l^{-1} in middle streams of Ganga (Nayak et al., 1995); ND to 0.35 μg l^{-1} in rural ponds of India (Dua et al., 1996); ND to 0.001 μg l^{-1} in drinking waters of Athens (Tispi and Hiskia, 1996); <0.1 to 2.7 ng l^{-1} in Scottish coastal sites (Walter et al., 1999).

The hexachlorocyclohexanes are rather stable chemically and α-isomer is also a stable isomer of technical HCH. It is also stable to light and oxidation (Brooks, 1976). These properties also influence the distributional characteristics of this isomer in Kuttanad backwaters. Thanneermukkam bund also plays an important role in the accumulation of these pesticides in pre-monsoon and post-monsoon periods. The study reveals that the distribution of α-isomer was influenced by seasonal and spatial variations. The pre-monsoon loadings were always higher than post-monsoon periods. Even in monsoon, the low levels of α-isomer were detected from most of the stations. The higher percentage of α-HCH may also be related to the rapid photo and bacterial degradation of γ-isomer to the more stable α-isomer (Benezet and Matsumura, 1973).

4.3.3.2 Distributions of β-HCH

The station wise annual mean variations of β-HCH in surface and bottom waters are plotted in Figure 4.15. The station wise summary statistics of β-HCH in surface and bottom waters are shown in Table 4.13. From the Figure 4.15, it was clear that the bottom β-HCH concentrations were higher than that of surface waters. The minimum and maximum values of β-HCH observed at surface waters were not detectable levels to 36.0 ng l^{-1} and not detectable levels to 32.0 ng l^{-1} in bottom waters. Highest value of 36.0 ng l^{-1} was recorded at station 8 in surface waters and 32.0 ng l^{-1} at stations 4,5,7 and 8 in bottom waters. The station wise annual mean values of β-HCH ranged from 11.8 ng l^{-1} to 16.8 ng l^{-1} in surface waters and 13.0 ng l^{-1} to 17.5 ng l^{-1} in bottom waters.

Figure 4.15 clearly illustrates the seasonal variation of β-HCH in all the three seasons. Higher values of β-HCH were seen in all stations in pre-monsoon period. No uniform station wise variations were observed in the distributions of β-HCH, in both surface and bottom waters. In monsoon, higher values of β-HCH were observed in station 1, and in other stations, values of β-HCH were very low. The post-monsoon values of β-HCH of both surface and bottom waters were slightly increasing from stations 1 to 7 and were gradually decreasing from stations 8 to 9.

The annual zone wise mean variations and zonal seasonal variations of β-HCH are also plotted in Figure 4.15. The bottom values of β-HCH in all zones were greater than that of surface values. Low mean values of β-HCH were seen in zone 1, both in surface and bottom waters. In surface waters, zones 2 and 3 recorded almost same values of β-HCH, but zone 3 in bottom water recorded

Table 4.13 Station wise summary statistics of β - HCH in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	26.0	12.3	8.2	66.9
2	ND	22.0	11.8	7.2	61.5
3	ND	26.0	13.8	9.6	69.5
4	ND	32.0	15.0	11.9	79.2
5	ND	35.0	16.8	11.3	67.4
6	ND	31.0	15.2	11.0	72.4
7	ND	34.0	16.8	12.8	76.4
8	ND	36.0	15.4	11 3	73.1
9	ND	21.0	12.7	7.5	58.7

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	29.5	13 0	8.4	64.5
2	ND	25.0	13.7	7.7	56.3
3	ND	28.0	14.6	9.6	66.0
4	ND	32.0	15.4	11.5	74.3
5	ND	32.0	17.0	11.3	66.7
6	ND	30.0	15.9	11.0	69.5
7	ND	32.0	17.5	12.4	71 1
8	ND	32.0	17.0	11.4	67.0
9	ND	28.5	15.2	8.7	57.2

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

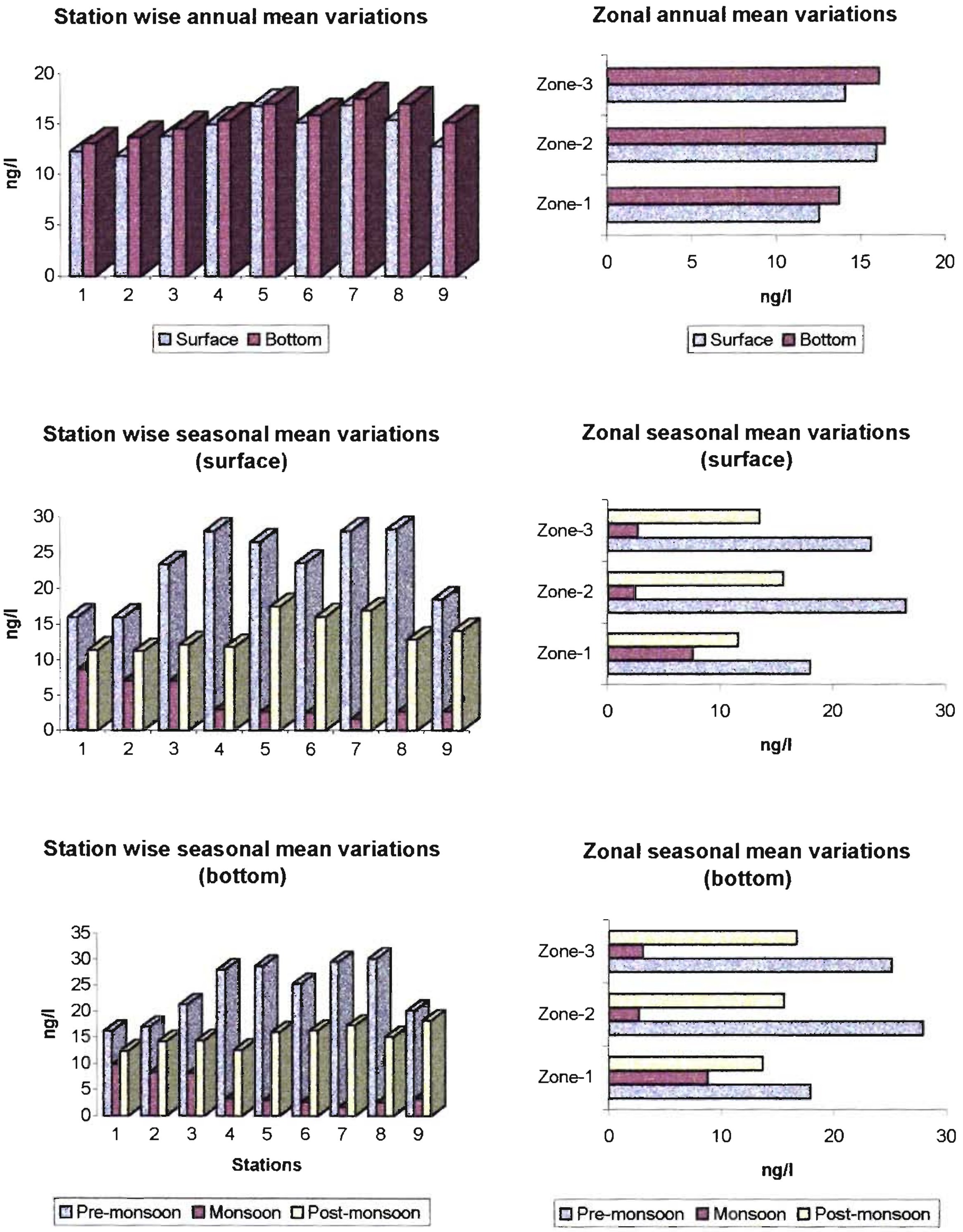


Figure 4.15 Seasonal and spatial distributions of β-HCH in surface and bottom waters

lower values than zone 2. In zonal seasonal variation of β-HCH, both in surface and bottom waters, pre-monsoon values were high in all three zones, and zone 2 recorded the maximum distribution of β-HCH. In monsoon, all the three zones recorded minimum values of β-HCH. In pre-monsoon, the β-HCH values were less in zone 1, and gradually increased to zone 2 and again slightly decreased in zone 3. In general, all the three zones showed seasonal variations in the distribution of β-HCH.

The proportion of β-HCH in technical grade HCH is less than that of α and γ isomers (Ramesh et al., 1989). The physico-chemical properties of β-HCH (Table 4.2) could also augment the distribution pattern of this isomer in the study area. The distribution of β-HCH was observed in all seasons, but in monsoon period, the values were very less or not detected in some stations. Among the isomers of technical HCH, β-HCH has the lowest water solubility and vapour pressure, but is the most stable and is relatively resistant to microbial degradation (Bachmann et al., 1988). β-HCH was found to be extremely persistent in the environment under aerobic conditions (Middeldrop et al., 1996). The low values of β-HCH distribution in the study area were mainly due to the low solubility of β-isomer in water. Due to the low solubility, and the low vapour pressure of this isomer, it has a tendency to settle down to the bottom part of the water column. This may be a reason for the low levels of β-HCH in the study area. The high values of β-isomer in pre-monsoon suggest the discharge of low levels of water from paddy fields, during that season which inturn avoid the possibility of dilution to an appreciable extent. In monsoon, the run-off of large volume of water from rivers and the opening of the bund enhances lower levels of this isomer. At zones 2 and 3, the concentration of β-isomer was found to be higher than that of zone 1 and is due to the run-off of pesticides from paddy fields. As observed in the present study (overall mean concentration of 15.6 ng l^{-1}), reported values also suggested the low values of β-isomer in different water systems, as the values of β-isomer ranged from ND - 0.003 μg l^{-1} in the drinking water of Athens (Tsipi and Hiskia, 1996) and 0.005 to 0.01 ng l^{-1} in natural waters of Greece (Miliadis, 1998). High values of β-HCH (ND to 36.35 μg l^{-1}) were reported from some stations in the middle stream of Ganga river, India

(Nayak et al., 1995) and also from the rural ponds (0.01 to 93 μg l^{-1} of β-HCH) of India (Dua et al., 1996).

4.3.3.3 Distributions of γ-HCH

The station wise annual mean variations of γ-HCH in surface and bottom waters are plotted in Figure 4.16. The station wise summary statistics of γ-HCH in surface and bottom waters are shown in Table 4.14. The bottom water values of γ-HCH in all stations were higher than that of surface water values. Figure 4.16 illustrates a gradual increasing trend of γ-HCH from stations 1 to 8 and then declined at station 9, both in surface and bottom waters. The minimum and maximum values of γ-HCH observed in surface waters were ND to 187.0 ng l^{-1} and in bottom waters were ND to 176.0 ng l^{-1} Non-detectable (ND) values of γ-HCH were noticed at stations 1 to 4 both in surface and bottom waters. The highest value of 187.0 ng l^{-1} was recorded at station 8 in surface waters and 176.0 ng l^{-1} at station 8 in bottom waters. The station wise mean values of γ-HCH ranged from 35.4 ng l^{-1} at station 1 to 69.6 ng l^{-1} at station 8 for surface waters and 38.2 ng l^{-1} at station 1 to 70.6 ng l^{-1} at station 8 in bottom waters.

Figure 4.16 shows the seasonal mean variations of γ-HCH both in surface and bottom waters. Pre-monsoon season recorded the highest values of γ-HCH in all stations both in surface and bottom waters. In pre-monsoon, the γ-HCH values linearly increased from stations 1 to 8 and at station 9, the value decreased. The maximum concentrations of γ-HCH were recorded in pre-monsoon period and were at station 8, both in surface and bottom waters. Monsoon period recorded the lowest values of γ-HCH at stations 4 to 9, but at stations 1 to 3, the values were higher or equal to that of post-monsoon periods. In post-monsoon season, the distributions of γ-HCH were almost constant and no significant variations were observed. In general, there were distinct seasonal variations in the distribution of γ-HCH in the study area.

Table 4.14 Station wise summary statistics of γ - HCH in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	104.0	35.4	25.9	73.2
2	ND	93.0	41.0	23.4	57.1
3	ND	92.7	40.4	26.6	65.8
4	ND	80.0	44.1	25.7	58.4
5	6.0	111.0	54.5	35.3	64.8
6	8.0	129.0	61.0	40.4	66.3
7	7.0	155.0	63.5	43.0	67.7
8	12.0	187.0	69.6	50.6	72.8
9	18.0	112.5	47.7	27.7	58.0

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	108.0	38.2	26.5	69.5
2	ND	101.0	46.5	26.4	56.8
3	ND	102.7	43.9	27.7	63.1
4	ND	78.0	46.1	26.3	57.0
5	7.0	109.0	59.4	36.0	60.7
6	9.0	123.0	65.1	41.5	63.8
7	11.0	153.0	65.4	44.3	67.8
8	12.0	176.0	70.6	50.7	71.8
9	20.5	115.5	52.2	30.3	58.1

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

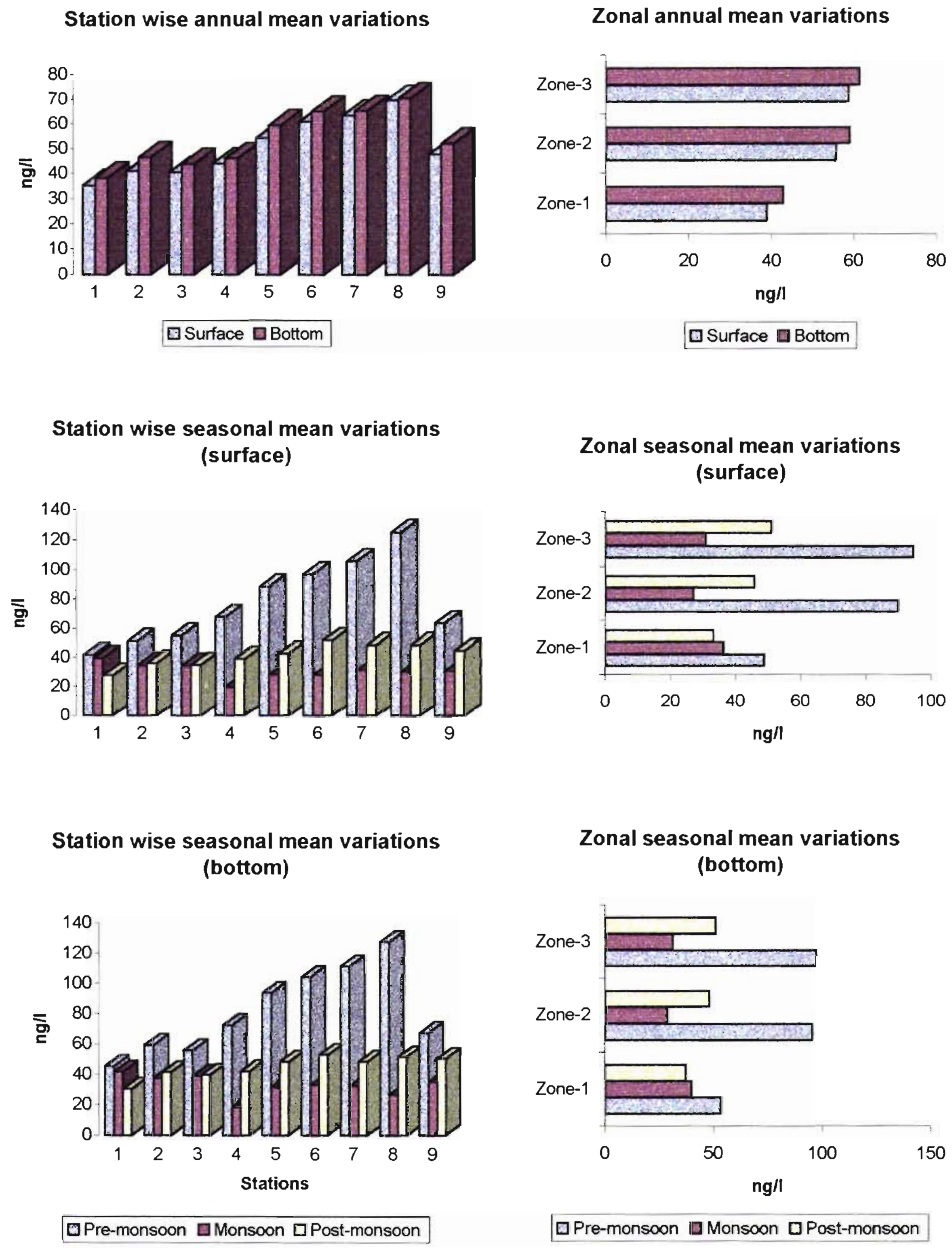


Figure 4.16 Seasonal and spatial distributions of γ- HCH in surface and bottom waters

The annual zone wise mean variations and zonal seasonal variations of γ-HCH are also shown in Figure 4.16. From zones 1 to 2, the values of γ-HCH were increasing steadily and from zones 2 to 3, the values were slightly increasing. In the zonal seasonal variations (Figure 4.16), in pre-monsoon, the values of γ-HCH were higher than in other seasons, and the values were slightly increasing from stations 1 to 2 and almost constantly distributed in zones 2 and 3, for both surface and bottom waters. Monsoon season recorded the lowest values of γ-HCH in zones 2 and 3, both in surface and bottom waters. In zone 1, the monsoonal values of γ-HCH were high in comparing with post-monsoon period. A slight gradation was seen in the values of γ-HCH from zones 1 to 3 in post-monsoon period particularly in surface waters.

Lindane, a persistent and lipophilic pesticide, is still used in large quantities and this chemical can be fond with appreciable concentrations in biota, atmosphere and in other environmental compartments in the adsorbed form (Bintein and Devillers, 1996). Lindane (γ-HCH) was detected throughout the entire period of study at an overall mean concentration of 52.6 ng l^{-1} (Table 4.8). Sujatha (1992) reported the lindane concentration in Cochin backwaters between the range ND to 0.118 µg l^{-1} and an average value of 0.031 µg l^{-1} A slightly high value of lindane was observed in the present study area, indicating the wide spread usage of HCH formulations and Lindane formulation in the Kuttanad area, and also the run-off from the major river systems.

Lindane (γ-HCH) is degraded slowly in the environment (Kilikidis et al., 1992). Its half-life is usually well above 100 days (Wauchope et al., 1992), depending on many factors e.g. the specific site, the type of the soil and the climate. Lindane migrates slowly in soil, however it has been found in ground, natural and drinking waters at very low concentrations (U.S.E.P.A., 1988). The introduction of lindane EC (emulsion concentrate) in agriculture and its slow degradation properties also promotes higher concentrations of γ-HCH in Kuttanad backwaters. Miliadis (1994) reported a range of 3 to 15 ng l^{-1} of lindane in the water of the Iliki Lake, Greece, and indicated the agricultural origin of the lake's pollution. He also observed that lindane decreases gradually during summer, but the decrease in residues was slower in winter months. The high concentration of lindane in pre-monsoon season in the study area may possibly be attributed to the environmental factors that influence the pesticide concentration in water, as the very low precipitation in that season, which resulted in the drop of water volume of the lake and, therefore in increased concentration of the residues. A higher percentage of γ-HCH observed in zone 2 was probably owing to the use of lindane formulations for agriculture and vector control in that area.

As a result of the high vapour pressure (Table 4.2), lindane is released in the atmosphere during application or afterwards by volatilization from sprayed plants and soils. It is reported that within 24 hours, 28 – 95% of lindane is lost via this route (Voldner and Li, 1995). The concentration of lindane in the rainwater in Hannover, Germany was found to be 41 ng l^{-1} (Maria et al, 1998). This result established the loss of lindane through atmosphere, which is more relevant in tropical countries also.

4.3.3.4 Distributions of δ-HCH

Figure 4.17 represents the station wise annual mean variations of δ-HCH in surface and bottom waters in the study area. The station wise summary statistics of δ-HCH in surface and bottom waters are listed in Table 4.15. In station wise distribution, δ-HCH was not uniformly distributed in surface and bottom waters as in the case of other isomers of HCH. The surface mean values of δ-HCH dominate in almost all stations than the bottom values. In station wise variation, the minimum values of non-detectable levels of δ-HCH were seen at all stations in surface and bottom waters. Maximum value of 52.0 ng l^{-1} was recorded at station 3 in surface water and 52.0 ng l^{-1} was recorded at station 7 in bottom water. The station wise mean values of δ-HCH ranged from 11.2 ng l^{-1} to 25.0 ng l^{-1} in surface waters and 11.0 ng l^{-1} to 23.6 ng l^{-1} in bottom waters.

The seasonal mean variations of δ-HCH of both surface and bottom waters are also depicted in Figure 4.17 A clear seasonal variation of δ-HCH

Table 4.15 Station wise summary statistics of δ - HCH in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	40.0	11.2	10.3	92.5
2	ND	46.6	12.7	12.1	95.6
3	ND	52.0	15.5	14.9	96.2
4	ND	32.0	17.4	10.6	60.8
5	ND	38.0	19.7	12.8	65.3
6	ND	48.0	24.1	14.3	59.3
7	ND	49.6	25.0	16.3	65.2
8	ND	42.0	23.3	13.2	56.6
9	ND	32.0	16.5	9.4	56.9

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	36.0	11.0	9.3	85.3
2	ND	41.6	12.3	10.5	85.4
3	ND	45.5	15.1	13.1	86.2
4	ND	38.0	15.3	12.3	80.4
5	ND	41.0	19.9	13.5	68.0
6	ND	50.6	23.6	17.3	73.5
7	ND	52.0	23.2	18.1	77.8
8	ND	41.0	22.6	13.8	60.9
9	ND	34.0	17.2	9.8	57.0

SD - Standard deviation   CV - Coefficient of variation; ND - Not detected

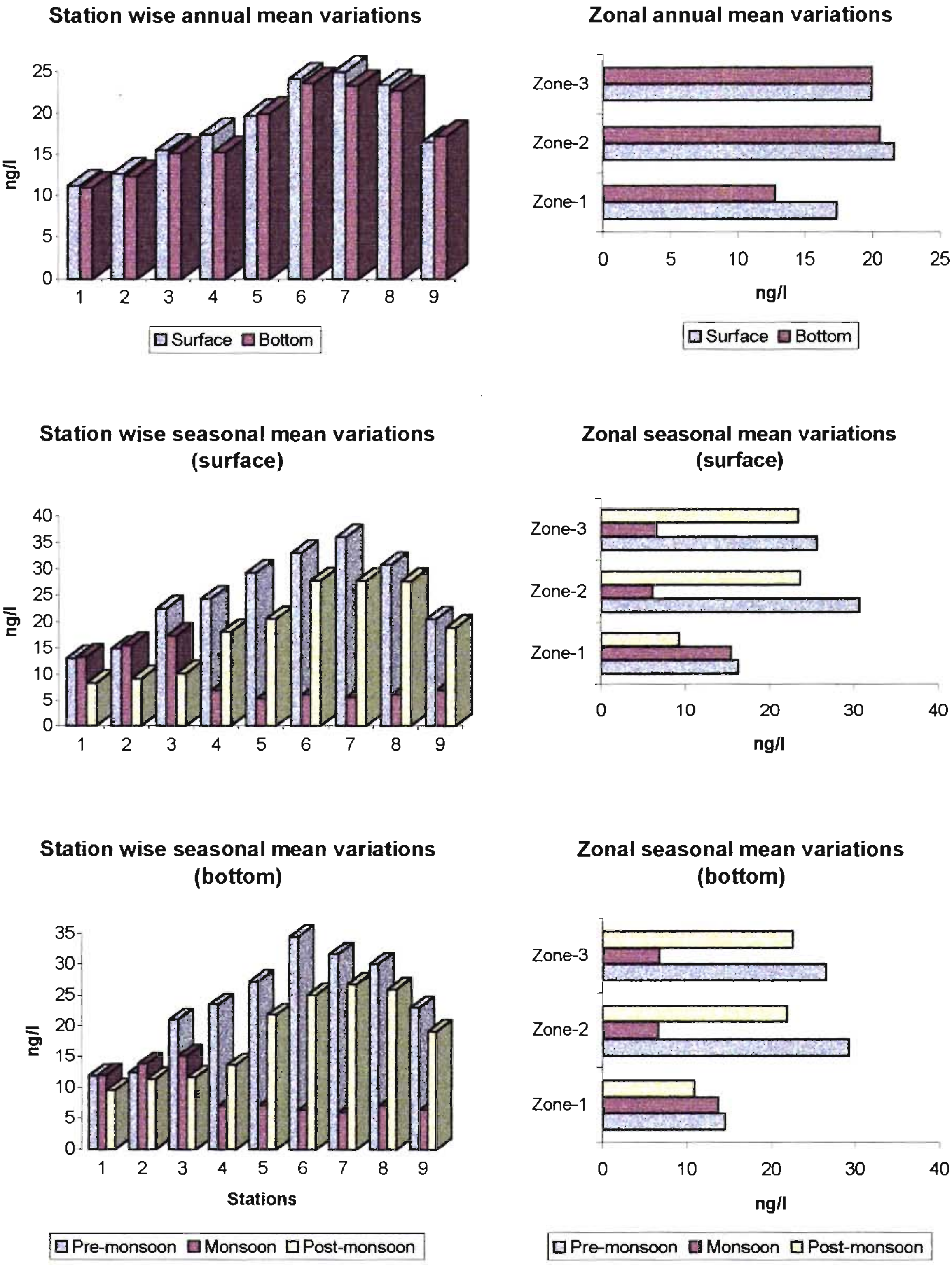


Figure 4.17 Seasonal and spatial distributions of δ-HCH in surface and bottom waters

from stations 4 to 9 is seen in the Figure. From stations 1 to 3, the variations were not uniform as compared to other stations. Pre-monsoon period recorded the maximum values of δ-HCH in almost all stations, except at stations 1 and 2. In pre-monsoon, the values of δ-HCH in surface water increased linearly from stations 1 to 7 and declined to stations 8 and 9. In bottom water, the same trend was seen, but from station 7 onwards the values were declining. Monsoon period recorded the highest values of δ-HCH at stations 1 and 2 than in other seasons, both in surface and bottom waters. In post-monsoon, the values of δ-HCH slightly increased from stations 1 to 6 and at stations 6 to 8, it was almost constant and slightly declined at station 9. In post-monsoon, the lowest values of δ-HCH were recorded at stations 1 to 3, both in surface and bottom waters. In general, distinct seasonal variations of δ-HCH were seen only from stations 4 to 9.

The annual zone wise mean variations and zonal seasonal mean variations of δ-HCH are also plotted in Figure 4.17 From the Figure, it is clear that the concentrations of surface δ-HCH at zones 1 and 2 were slightly higher than that of bottom water and in zone 3, the concentrations were almost same. In zonal seasonal variations of δ-HCH, both in surface and bottom waters, pre-monsoon values were higher in all zones. In monsoon, the zone 1 values were almost equal to that of pre-monsoon values, and were higher than post-monsoon values, both in surface and bottom waters. Zones 2 and 3 in monsoon recorded lowest values of δ-HCH. In post-monsoon, zone 1 recorded the lowest values of δ-HCH, and in zones 2 and 3, the values were almost same in both surface and bottom waters.

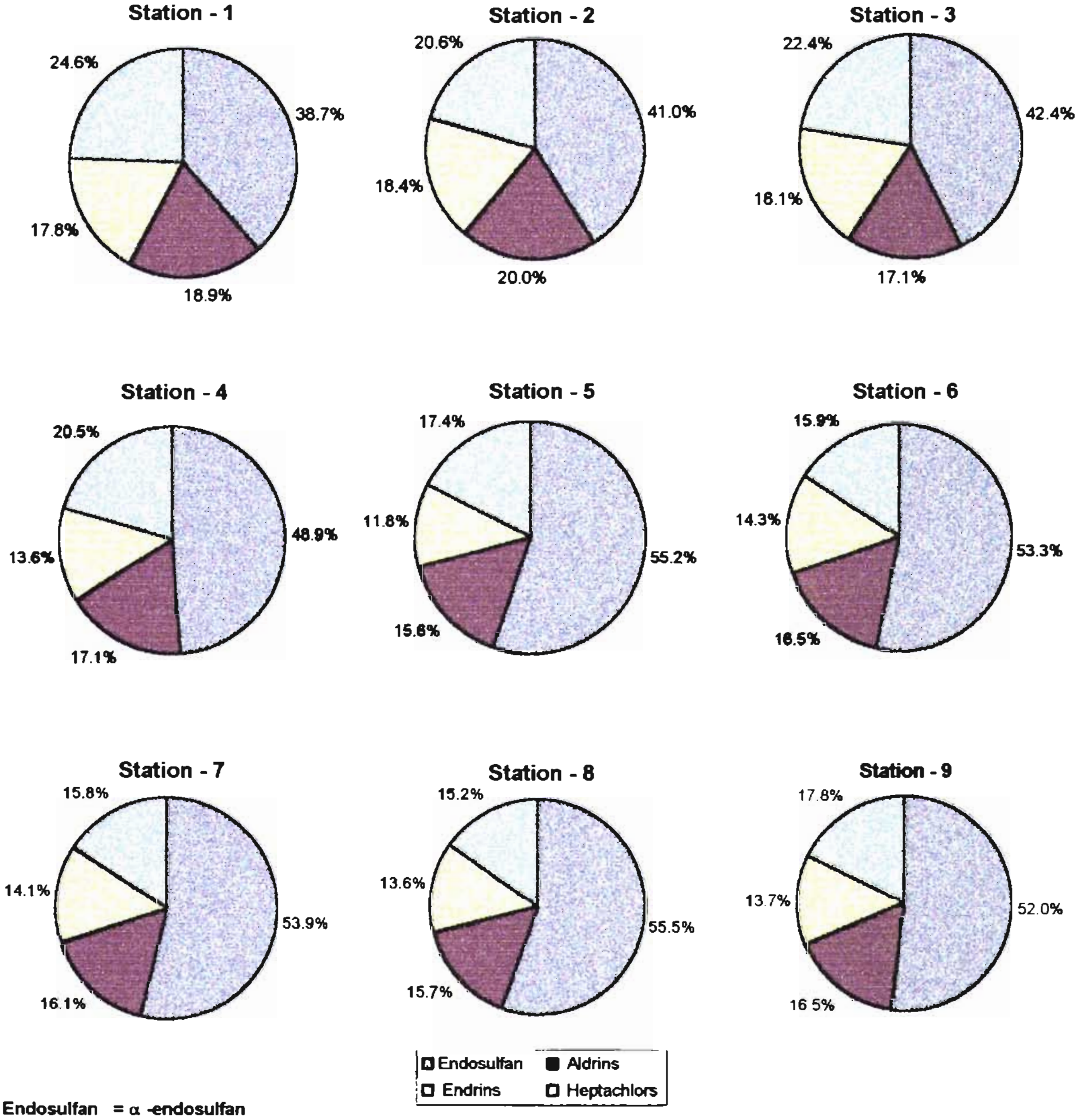
Technical HCH contains lesser percentage of δ- isomer (about 4-6 %), and the water solubility of this isomer is 21.3 ppm at 25°C (Brooks, 1976). In spite of the small percentage of this isomer in technical HCH, an overall mean concentration of 18.1 ng l^{-1} δ-isomer was observed in the waters of the study area. It may be due to the high solubility of δ-isomer in water. The same reason accounts for the high concentration of this isomer observed in pre-monsoon and post-monsoon periods. In monsoon, run-off water from rivers diluted the concentration to a large extent and gives non-detectable levels of this isomer.

Sujatha (1992) reported concentration of δ-isomer in Cochin backwaters between the ranges ND to 0.080 μg l^{-1} and at one station the value was 0.214 μg l^{-1} The same author also observed that pre-monsoon values were higher than that of post-monsoon periods and in monsoon the values were lowest. These observations were comparable with the results obtained in the present study. The distribution pattern of δ-HCH also followed the trends observed in the distribution of other isomers of HCH. Some values reported on the distribution of δ-isomer were: ND to 0.047 μg l^{-1} for rain water from Hardwar, India (Dua et al., 1994) and ND to 0.001 μg l^{-1} for drinking water of Athens (Tsipi and Hiskia, 1996). Values ranging from ND to 36.35 μg l^{-1} were reported from Middle stream of Ganga, India (Nayak et al., 1995) and ND to 0.68 μg l^{-1} was reported from rural ponds of India (Dua et al., 1996).

4.3.4 Distributions of Σcyclodienes

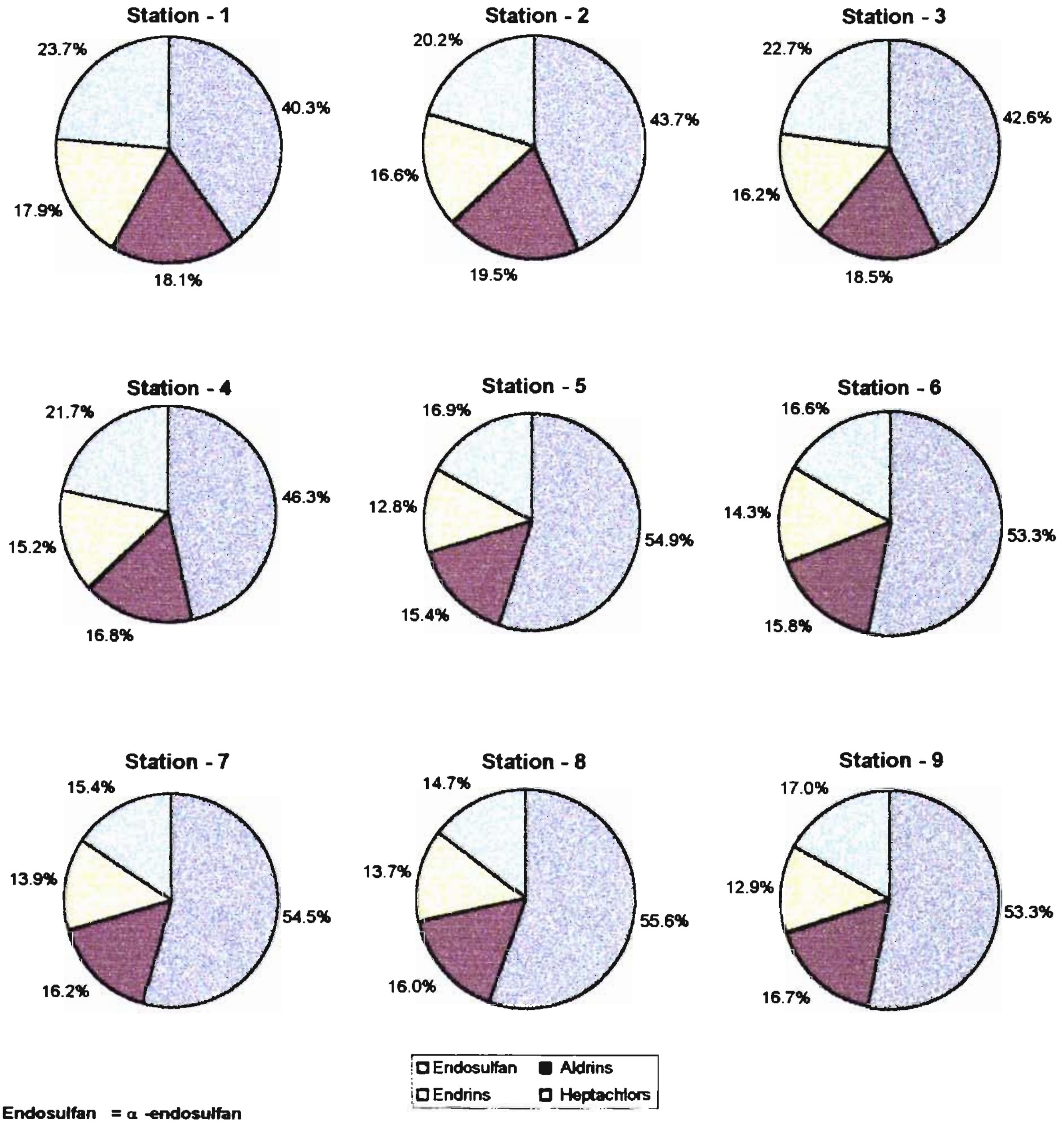
ΣCyclodienes described here, is the sum of α-endosulfan, aldrins (aldrin+dieldrin), heptachlors (heptachlor+heptachlor epoxide) and endrins (endrin+ endrin aldehyde). The percentage compositions of Σcyclodienes in surface waters are shown in Figure 4.18. The total cyclodienes values in surface waters ranged between 79.2 ng l^{-1} to 211.0 ng l^{-1} (Table 4.7). From the Figure 4.18, it is clearly noted that the percentage composition of endosulfan exceeds than that of other cyclodienes. In surface waters, the percentage of endosulfan ranged from 38.7 to 55.5, and total aldrins ranged from 15.6 to 20% (Figure 4.18). The percentage of total heptachlors ranged from 15.2 to 24.6 and the total endrins ranged from 11.8 to 18.4% (Figure 4.18). Endosulfan percentage was lower in zone 1 (Stations 1, 2 & 3) than that of other zones (Figure 4.18) while the percentages of other cyclodienes were higher in zone 1 than in other zones.

Figure 4.19 illustrates the percentage composition of total cyclodienes in the bottom waters. The total cyclodienes values in bottom water ranged



Endosulfan = α -endosulfan
Aldrins = Aldrin + Dieldrin
Endrins = Endrin + Endrin aldehyde
Heptachlors = Heptachlor + Heptachlor epoxide

Figure 4.18 Station wise percentage composition of Σcyclodienes in surface waters.



Endosulfan = α -endosulfan
Aldrins = Aldrin + Dieldrin
Endrins = Endrin + Endrin aldehyde
Heptachlors = Heptachlor + Heptachlor epoxide

Figure 4.19 Station wise percentage composition of Σcyclodienes in bottom waters.

between 88.4 ng l^{-1} to 214.9 ng l^{-1} (Table 4.7). Like that of surface water, the minimum mean values of total cyclodienes were observed at station 1 and maximum mean values were observed at station 8. Percentage composition of endosulfan also contributes more in bottom water than other cyclodienes. In bottom waters, the percentage of endosulfan ranged from 40.3 to 55.8, and total aldrins ranged from 15.8 to 19.5% (Figure 4.19). The percentage of total heptachlors ranged from 14.7 to 23.7 and the total endrins ranged from 12.8 to 17.9% (Figure 4.19). Like that of surface waters, endosulfan percentage was lower in zone 1 (Stations 1, 2 & 3) than that of other zones (Figure 4.18), while the percentages of other cyclodienes were higher in zone 1 than in other zones.

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 (emulsion concentrate) and is the major formulation used in India. This pesticide is also 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 ~~aldrins~~, endrins 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 except endosulfan all other cyclodiene pesticides were higher than in zones 2 and 3. Endosulfan is still used for the pest control in agricultural fields, and the release of this pesticide from agricultural fields may be attributed to the higher concentration of endosulfan in zones 2 and 3. In zone 3, comparatively lower levels of all cyclodienes were found at station 9 than that of station 8. It may be due to the operation schedule of the salinity barrier at Thannermukkam bund. The closure of the bund for about more than 6 months may lead to the accumulation of pesticides at station 8 than that of station 9.

4.3.4.1 Distributions of α-endosulfan

The station wise mean variations of α-endosulfan in surface and bottom waters are depicted in Figure 4.20. The station wise summary statistics of α-endosulfan in surface and bottom waters are given in Table 4.16. The bottom concentrations of α-endosulfan were higher than surface concentrations at all stations (Figure 4.20). Both surface and bottom values of endosulfan were gradually increasing from stations 1 to 8, except at station 4, and at station 9, the values decreased. Minimum of non-detectable values were noticed at stations 1 to 4 both in surface and bottom waters. The highest value of 248 ng l^{-1} was recorded at station 8 in surface waters and 276 ng l^{-1} at the same station in bottom waters. The station wise mean values of α-endosulfan ranged from 30.7 to 117 ng l^{-1} in surface waters and 35.6 to 119.5 ng l^{-1} in bottom waters.

Figure 4.20 also illustrates the seasonal mean variations of α-endosulfan both in surface and bottom waters. Distinct seasonal variations were noticed from stations 4 to 9, but from stations 1 to 3, the seasonal variations were not distinct. Pre-monsoon values were higher at stations 3 to 9. The highest concentration of endosulfan was recorded at station 8, both in surface and bottom waters. In pre-monsoon, the endosulfan values were increasing gradually from stations 1 to 8 and a sudden decline was observed at station 9. Monsoon season recorded the lowest values from stations 4 to 9. In surface waters, at stations 1 and 2 and in bottom waters at station 1, the endosulfan values in monsoon season were slightly higher than that in other seasons. At stations 1 to 3, the post-monsoon values were lower both in surface and bottom waters than in other seasons.

Figure 4.20 also illustrates the annual zone wise mean variations and zonal seasonal variations of α-endosulfan in surface and bottom waters. In all the zones, the bottom endosulfan concentrations were higher than the surface concentrations. The surface and bottom variations were almost uniform in all the three zones. In pre-monsoon, the endosulfan concentrations were high in surface waters and bottom waters of zones 2 and 3. The maximum surface and

Table 4.16 Station wise summary statistics of α - endosulfan in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	124.0	30.7	32.2	104.9
2	ND	132.5	36.0	36.3	101.0
3	ND	122.6	48.1	40.5	84.2
4	ND	120.0	56.8	39.7	69.9
5	12.0	198.0	83.6	58.1	69.5
6	13.0	187.0	94.1	60.6	64.5
7	11.5	225.0	104.7	74.7	71.4
8	9 0	248.0	117.0	84 3	72.1
9	10.5	234.0	86.5	64.0	74.0

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	138.0	35.6	35.7	100.2
2	ND	143.5	43.3	39.2	90.6
3	ND	131.0	48.3	40.5	83.7
4	ND	115.0	57.5	39.4	68.5
5	14.0	175.0	90.3	58.5	64.8
6	15.0	199.0	100.5	65.1	64.8
7	11 0	213.0	109.4	78.6	71.9
8	11.0	276.0	119.5	89.7	75.1
9	12.0	221.5	97.0	65.8	67.8

SD - Standard deviation   CV - Coefficient of variation; ND - Not detected

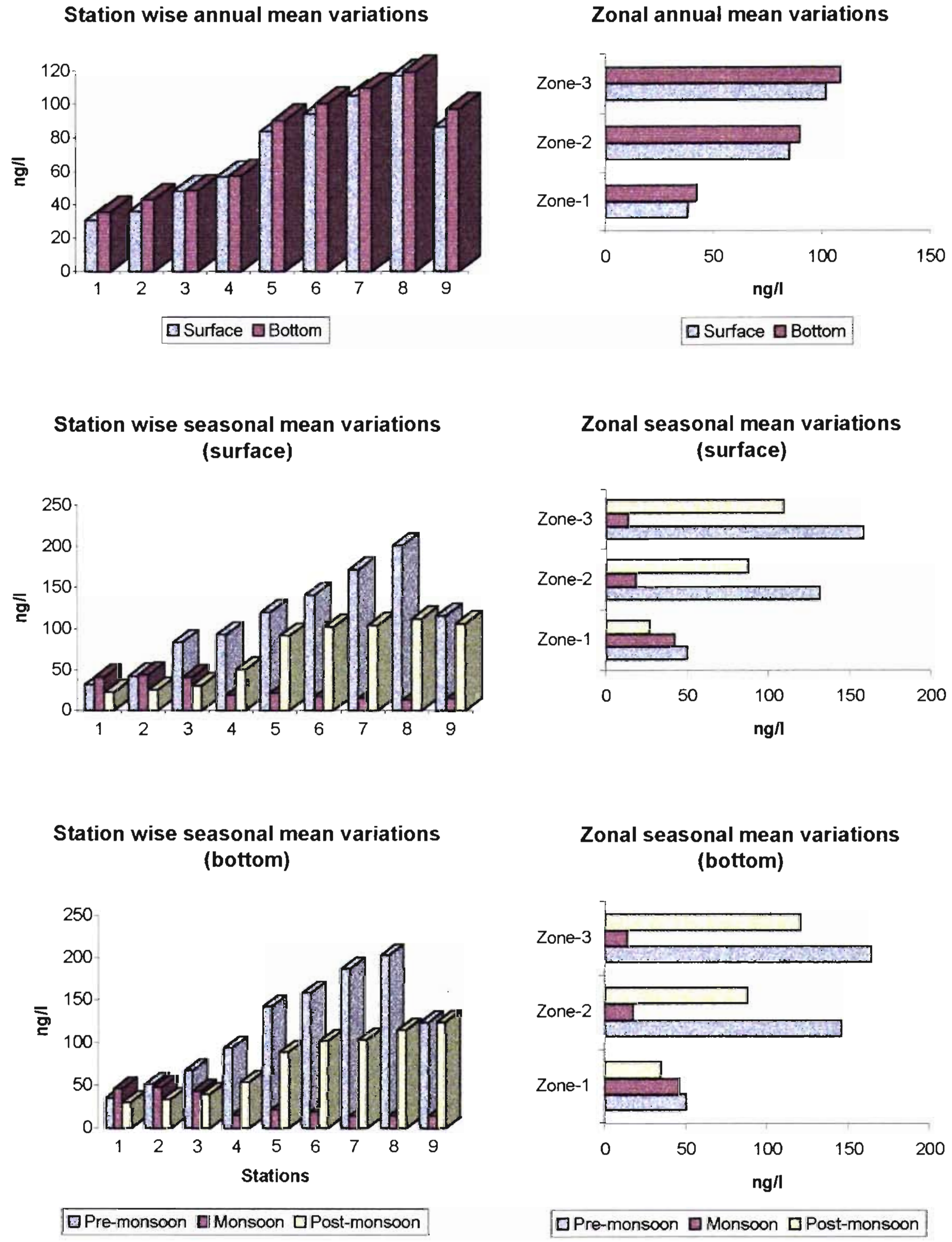


Figure 4.20 Seasonal and spatial distributions of α-endosulfan in surface and bottom waters

bottom concentration of endosulfan was observed at zone 3 in pre-monsoon season. Monsoon recorded the lowest concentrations of endosulfan in zones 2 and 3. In zone 1, monsoon values of endosulfan were higher than post-monsoon values.

Endosulfan, one of the major pesticides currently used for agriculture, including the pest control of paddy fields, is of environmental concern because of its toxicity to fish. The monitoring studies carried out for finding the residue levels of endosulfan were found to be more in rice growing regions (Tan, 1992). The overall mean concentration of endosulfan in the study area was 75.7 ng l^{-1} In Rhine and Mars rivers the endosulfan concentrations were 0.81 and .09 µg l^{-1} respectively (Wegman and Greve,1978). In the Peninsular Malaysian rivers, the endosulfan values ranged from ND to 310 ng l^{-1} (Tan and Vijayaletchumy, 1994). Tan and Vijayaletchumy (1994) have also observed that the concentrations of endosulfan in water samples from rivers in the rice growing areas were all much higher than those from non-rice growing regions. The same observations were seen in the Kuttanad backwaters also. The endosulfan values reported from the coastal Lagoon, Gulf of California were <0.20 to 73.20 ng l^{-1} (Walter et al., 1999). The slightly higher values of endosulfan in zone 1 in monsoon season than in other zones were due to the run-offs from the major river systems in the study area. Higher values in pre-monsoon season were due to the run-off from the nearby agricultural lands, mainly from the "Padashekarams"

The earlier reported values of endosulfan in Kuttanad area were up to 266 ng l^{-1} in the lakeside and Thannermukkam areas and these values were comparable with the present study also.

Higher concentrations of α-endosulfan were reported from middle stream of Ganga river, India, and were ranged from ND to 48.8 µg l^{-1} (Nayak et al., 1995). Tsipi and Hiskia. (1996) reported a concentration range of 0.001 – 0.006 ng l^{-1} of α-endosulfan from the drinking waters of Athens. Endosulfan from ground water samples from south Spain (Almeria) was found to be in the range of 0.5 – 540 ng l^{-1} (Gustavo and Damia, 1998). The present study reveals that the continuous use of endosulfan in agriculture has been a contributing factor to the high levels of this pesticide in the backwaters of Kuttanad.

4.3.4.2 Distributions of heptachlor

Figure 4.21 represents the station wise annual mean variations of heptachlor in surface and bottom waters. The station wise summary statistics of heptachlor in surface and bottom waters are listed in Table 4.17 The bottom mean concentrations of heptachlor in all stations except at station 8 were more or less greater than the surface values and at station 8 the value was lower than the surface values. From stations 4 to 7, the surface and bottom heptachlor concentrations showed more variations than in first three stations. Station 1 showed higher values than stations 2 and 3. The bottom heptachlor values were gradually increasing from stations 3 to 6 and then gradually declined upto station 9. Minimum of non-detectable levels of heptachlor was found in all stations both in surface and bottom waters (Table 4.17). The highest mean value of 23.5 ng l^{-1} was recorded at station 8 in surface water and 31.0 ng l^{-1} at station 7 in bottom water The station wise mean values of heptachlor ranged from 6.6 ng l^{-1} to 11.5 ng l^{-1} at surface waters and 7.0 ng l^{-1} to 11.4 ng l^{-1} at bottom waters.

The seasonal mean variations of heptachlor in surface and bottom waters are also plotted in Figure 4.21. The station wise seasonal variations of heptachlor in pre-monsoon and post-monsoon periods were not uniform in all stations. High values of heptachlor were recorded in surface waters from stations 1 to 5 and 8 in pre-monsoon. Almost the same trend was observed in bottom waters also. At station 2 in bottom water, all seasons recorded same values of heptachlor, but in surface water, pre-monsoon values were higher than post-monsoon and monsoon values. In post-monsoon, stations 6, 7 and 9 recorded higher values than in other seasons. Monsoon season recorded lowest values of heptachlor in all stations of surface and bottom waters. In monsoon, minimum values of non-detectable levels were observed in almost all stations of surface and bottom waters.

Table 4.17 Station wise summary statistics of heptachlor in surface and bottom waters

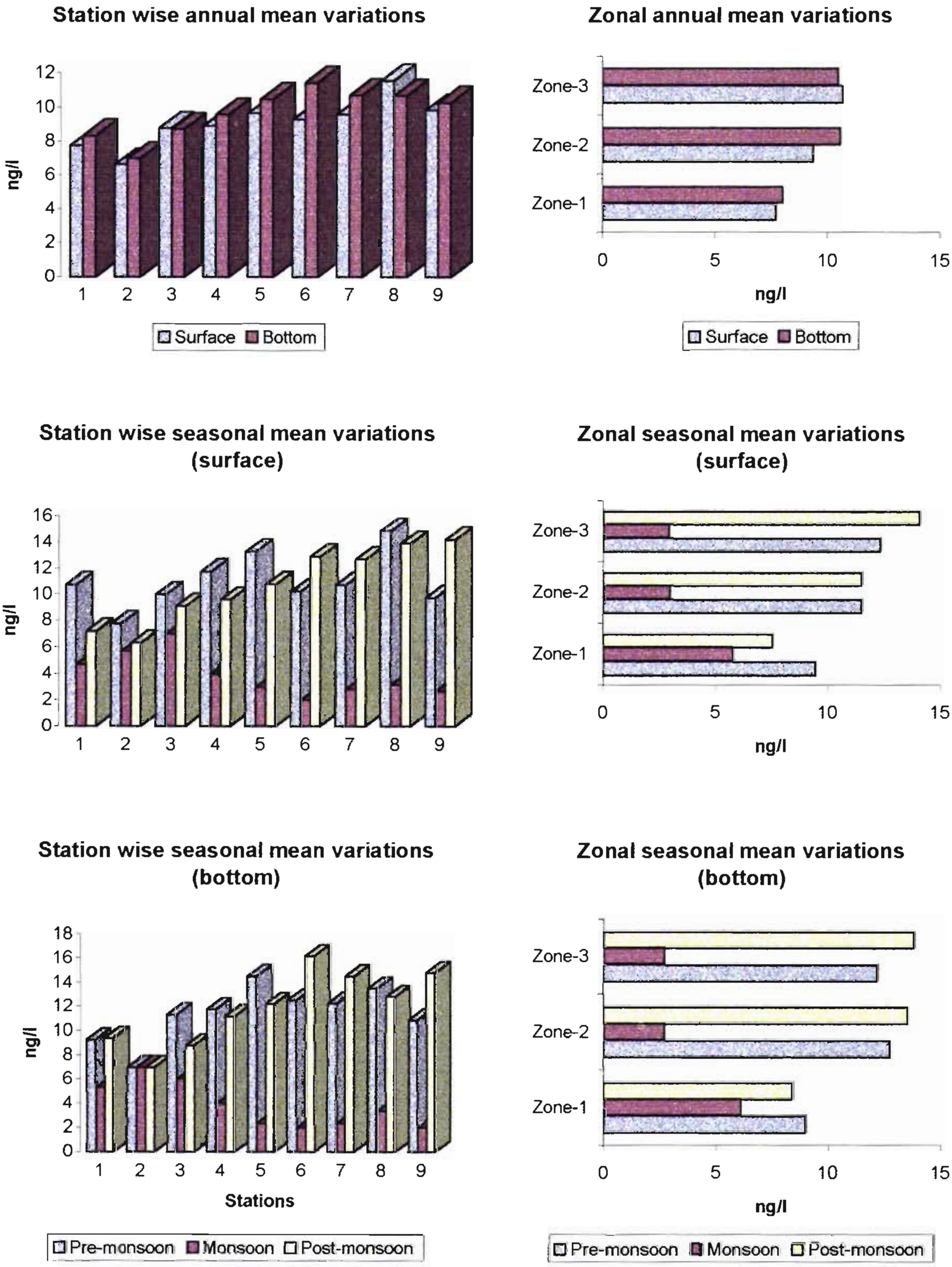
Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	16.0	7.8	6.1	78.2
2	ND	17.0	6.6	5.3	79.2
3	ND	21.0	8.8	6.7	76.2
4	ND	16.0	8.9	5.0	56.5
5	ND	18.0	9.7	5.6	58.4
6	ND	18.0	9.3	5.6	60.6
7	ND	22.0	9.6	6.4	66.3
8	ND	23.5	11.5	6.9	59.4
9	ND	20.0	9.8	6.1	61.8

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	20.0	8.3	6.7	80.6
2	ND	21.0	7.0	6.1	86.6
3	ND	18.0	8.7	5.9	67.4
4	ND	18.0	9.6	5.1	53.7
5	ND	20.0	10.5	6.2	59.5
6	ND	29.0	11.4	7.9	69.6
7	ND	31.0	10.7	8.1	75.8
8	ND	22.0	10.7	6.4	59.9
9	ND	19.0	10.3	6.1	59.6

SD - Standard deviation; CV - Coefficient of variation; Not detected



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 4.21 Seasonal and spatial distributions of heptachlor in surface and bottom waters

The annual zone wise mean variations and zonal seasonal variations in surface and bottom waters are also plotted in Figure 4.21. The bottom mean concentrations of heptachlor in zones 1 and 2 were higher than surface mean concentrations. In zone 3, a slightly higher value of heptachlor was recorded in surface water than in bottom water. Zone 2 of pre-monsoon and post-monsoon seasons in surface and bottom waters recorded almost comparable values. In monsoon, all zones recorded lower values of heptachlor than in other seasons.

Before the banning of heptachlor, this pesticide was used as an agricultural and domestic pesticide in India. The use of chlordane and heptachlor was banned in India in 1992 (David et al., 1993). The lower levels of heptachlor detected in the study area may be attributed to the persistence of this chemical and also due to the significant portion of the past production still cycling in the environment. The run-off from rivers contributed to the major portion of this compound. The earlier use of chlordane also enhances the contribution of this compound in the study area. The physico-chemical properties of heptachlor (Table 4.4), mainly solubility and vapour pressure, also influence the low degradation of this pesticide.

The values of heptachlor ranged between ND to 120 ng l^{-1} in Peninsular Malaysian rivers (Tan and Vijayaletchumy, 1994). Non-detectable levels of heptachlors were reported from the drinking waters of Athens (Tsipi and Hiskia, 1996). The reported values of heptachlors (heptachlor + heptachlor epoxide) were 0.096 to 1.456 µg l^{-1} in Diyala river, Iraq (Muthanna et al., 1989) and 0.05 to 0.1 ng l^{-1} in natural waters of Greece (Miliadis, 1998).

4.3.4.3 Distributions of heptachlor epoxide

The station wise annual mean variations of heptachlor epoxide in surface and bottom waters are illustrated in Figure 4.22. The station wise summary statistics of heptachlor epoxide in surface and bottom waters are presented in Table 4.18. The bottom mean concentrations of heptachlor epoxide were higher at all stations except at station 7 At stations 8 and 9, the values were almost the

Table 4.18 Station wise summary statistics of Heptachlor epoxide in surface and bottom waters

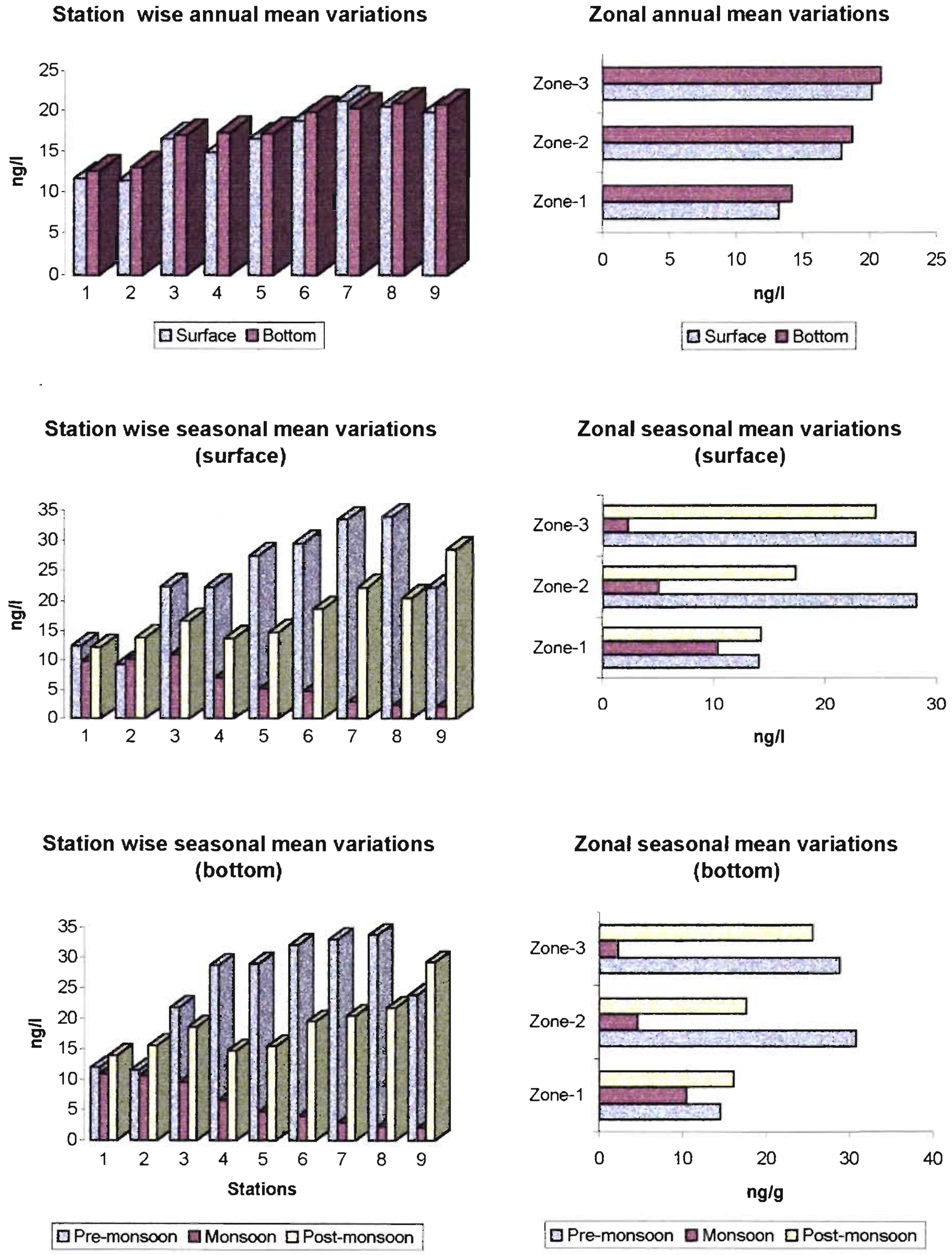
Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	29.5	11.7	8.5	72.4
2	ND	30.6	11.4	9.2	80.6
3	ND	33.0	16.7	10.9	65.5
4	ND	28.0	14.9	9.6	64.6
5	ND	34.0	16.6	11.5	69.5
6	ND	36.0	18.8	11.9	63.3
7	ND	39.0	21.2	13.7	64.5
8	ND	42.0	20.5	14.4	70.2
9	ND	38.5	19.8	12.9	65.3

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	33.0	12.6	9.1	72.3
2	ND	32.0	13.0	9.9	76.0
3	ND	32.0	17.1	10.4	61.3
4	ND	34.0	17.4	11.4	65.5
5	ND	34.0	17.3	11.2	64.7
6	ND	38.0	19.8	12.6	63.5
7	ND	41.0	20.3	13.5	66.3
8	ND	42.0	20.9	13.7	65.5
9	ND	36.6	20.7	13.1	63.3

SD - Standard deviation CV - Coefficient of variation; ND - Not detected



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 4.22 Seasonal and spatial distributions of heptachlor epoxide in surface and bottom waters same. In general, the surface and bottom values were slightly increasing from stations 1 to 9. Minimum values of non-detectable levels were observed at surface and bottom waters in all stations (Table 4.18). Maximum value of 42 ng l^{-1} was observed at station 8 in both surface and bottom waters. The station wise mean values of heptachlor epoxide ranged from 11.4 to 21.2 ng l^{-1} in surface waters and 12.6 to 20.9 ng l^{-1} in bottom waters.

Seasonal variations were observed at almost all stations except first two stations (Figure 4.22). From stations 3 to 8, pre-monsoon values of heptachlor epoxide were higher. Surface water at station 2 recorded lowest value in pre-monsoon than in other seasons. In post-monsoon, surface and bottom waters at station 9 showed higher values than pre-monsoon values. At stations 1 and 2 of bottom waters and at station 2 of surface water, post-monsoon values were higher than in other seasons. Monsoon season recorded lowest values in all most all stations. From the Figure 4.22, it is observed that the bottom values in all the three zones were higher than those of the surface values. Expect in zone 1, pre-monsoon values were higher in zones 2 and 3. In zone 1, post-monsoon value was high. In monsoon, all zones recorded lowest values.

The main heptachlor related compound found in the environment is the heptachlor epoxide, which is the major heptachlor metabolite, formed through epoxidation of the non-chlorinated double bond in the molecule (Figure 4.3) (Jiping et al., 1995). This may be a reason for the comparatively higher amount of heptachlor epoxide seen in the study area than heptachlor. Walter et al. (1999) reported 0.23 ng l^{-1} of heptachlor epoxide from the coastal lagoon in Gulf of California. Non-detectable concentrations of heptachlor epoxide were reported from the drinking waters from Athens (Tsipi and Hiskia., 1996).

4.3.4.4 Distributions of aldrin

The station wise annual mean variations of aldrin in surface and bottom waters are plotted in Figure 4.23. It was noted that the bottom aldrin values were almost equal or slightly higher than surface values. From stations 1 to 6,

Table 4.19 Station wise summary statistics of aldrin in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	14.0	4.7	4.2	89.7
2	ND	15.0	5.1	4.6	90.9
3	ND	21.0	6.9	6.3	91.2
4	ND	12.0	7.8	4.3	55.7
5	ND	19.0	10.4	5.9	56.3
6	ND	30.0	14.9	9.7	64.7
7	ND	29.5	14.8	10.0	67.8
8	ND	29.5	15.6	9.7	62.2
9	ND	30.6	11.6	9.3	80.4

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	15.0	4.7	4.4	94.7
2	ND	17.6	5.5	5.2	95.4
3	ND	23.0	8.0	7.0	87.2
4	ND	15.0	8.4	4.8	57.4
5	ND	20.0	11.5	6.4	55.9
6	ND	27.0	14.6	9.2	62.8
7	ND	27.0	15.2	9.7	63.9
8	ND	29.0	16.5	10.6	64.2
9	ND	32.0	13.2	10.0	75.9

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

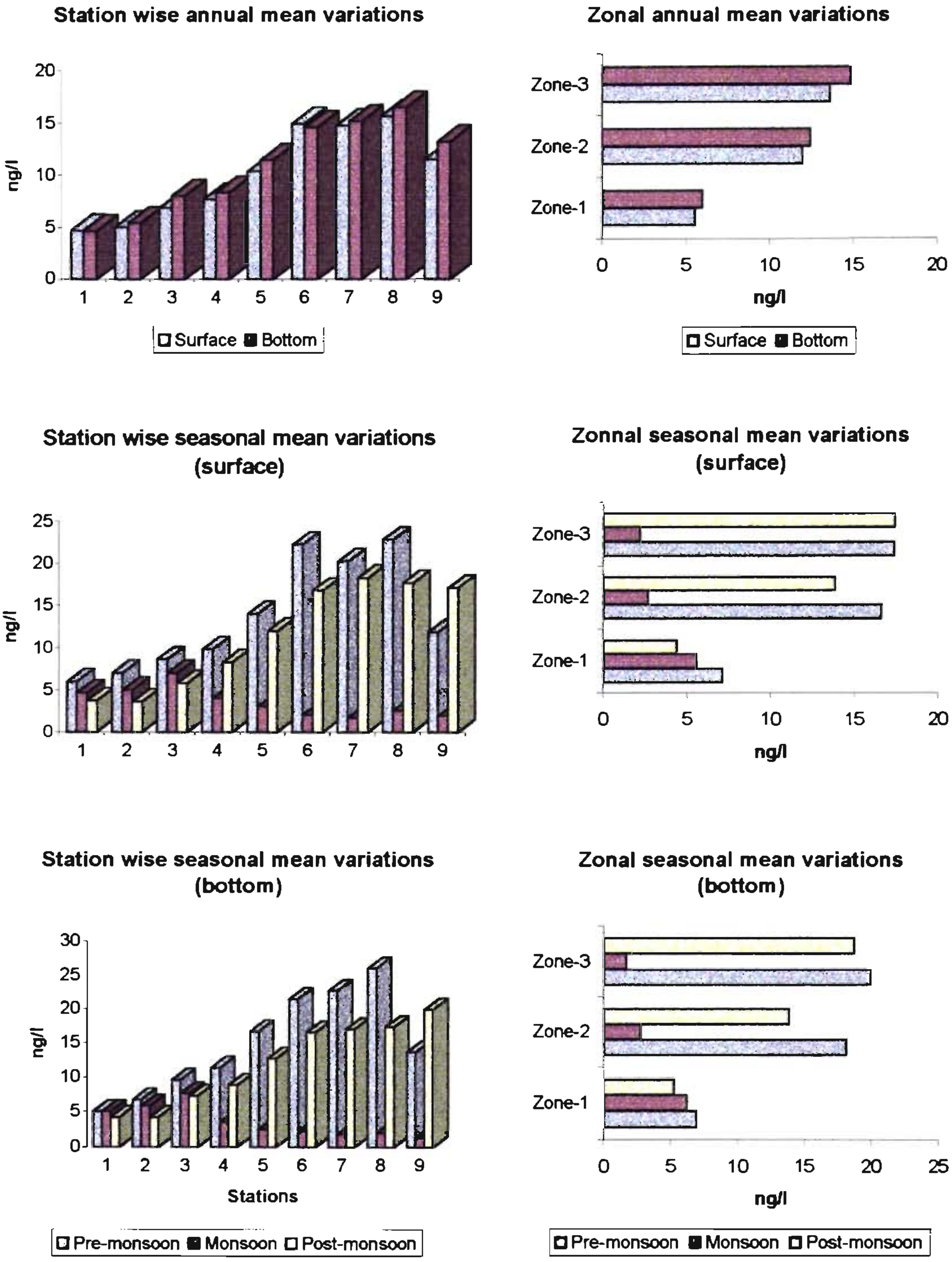


Figure 4.23 Seasonal and spatial distributions of aldrin in surface and bottom waters

the values gradually increased and were almost constant upto station 8 and at station 9, the values declined. The station wise summary statistics of aldrin are shown in Table 4.19. Minimum of non-detectable levels of aldrin were seen in all stations of surface and bottom waters. The maximum value of 30.6 ng l^{-1} was observed at station 9 in surface water and 32.0 ng l^{-1} in bottom water. The station wise mean values of aldrin ranged from 4.7 to 15.6 ng l^{-1} in surface waters and 4.7 to 16.5 in bottom waters.

The seasonal mean variations of aldrin in surface and bottom waters are also plotted in Figure 4.23. Pre-monsoon values in surface and bottom waters were higher at stations 1 to 8, and at station 9, the value was lower than in post-monsoon. In pre-monsoon, the aldrin values gradually increased from stations 1 to 8 and a sudden decline was observed at station 9. In monsoon, stations 4 to 9 recorded the lowest values than in other seasons and in post-monsoon, values at stations 1 to 3 were lower than in other seasons.

The annual zone wise mean variations and zonal seasonal mean variations of aldrin are also plotted in Figure 4.23. The bottom values of aldrin were slightly higher in zone 1 and more in other zones. Zone 3 recorded highest values of aldrin both in surface and bottom waters. Zones 1 and 2 of surface water in pre-monsoon period showed higher values than in other seasons. In zone 3, the pre-monsoon and post-monsoon values were almost equal. In zones 2 and 3, monsoon values were lower than in other seasons.

Organochlorine residues were monitored in Ganga river water in Farrukhabad in 1991-92 periods and found that the concentration of aldrin was more than that of dieldrin, and often exceeded the WHO guideline value for drinking water (Agnihotri et al., 1994). The low values of aldrin observed in water in the present study may be due to the non-use of this pesticide currently in agriculture. Aldrin was banned in early nineties (David et al., 1993). The presence of aldrin in the study area may be due to the run-off from rivers, because it is highly persistent and accumulate in the soil and from the soil through run-off, it enters in the water systems. A mean concentration of 0.001 µg l^{-1} aldrin in drinking water of Athens was reported (Tsipi and Hiskia., 1996).

Muthanna et al. (1989) reported high values ranged from 0.152 to 1.566 µg l^{-1} of aldrins (aldrin + dieldrin) from the Diyala River in Iraq. The aldrin concentrations from Shallow ground waters in Punjab, Pakistan were very high and ranged from 2.0 to 31.5 ppb (Jabbar et al., 1993).

4.3.4.5 Distributions of dieldrin

From the station wise annual mean variations of dieldrin (Figure 4.24), it was clear that the bottom concentrations of dieldrin in all stations were slightly higher than surface concentrations. From stations 1 to 8, the values were increasing uniformly, but at station 2, a slightly higher value was observed and at station 9 slightly lower value was observed. The station wise summary statistics of dieldrin are given in Table 4.20. Minimum of non-detectable levels was observed at all stations of surface and bottom waters. The maximum values of dieldrin observed in surface and bottom waters were 48 ng l^{-1} and 41 ng l^{-1} respectively. The station wise mean values of dieldrin ranged from 10.3 to 17.6 ng l^{-1} and 11.3 to 18.0 ng l^{-1} in surface and bottom waters respectively.

The seasonal mean variations of dieldrin in surface and bottom waters are shown in Figure 4.24. Higher values of dieldrin were found either in pre-monsoon or in post-monsoon periods. Stations 3 to 5 recorded higher values in pre-monsoon periods. Other stations recorded higher values of dieldrin in post-monsoon period. Maximum values were observed at stations 8 and 9 in post-monsoon periods. Monsoon season recorded lower values from stations 3 to 9. From the annual zonal variation (Figure 4.24), it was noticed that in all zones bottom values of dieldrin were higher than surface values. In surface water, post-monsoon recorded higher values in all the zones. In post-monsoon, zones 1 and 3 of bottom water had higher values, but in zone 2, the pre-monsoon and post monsoon values were almost the same. Zones 2 and 3 in monsoon period recorded lowest values of dieldrin, but in zone 1, the values were all most equal to pre-monsoon and post-monsoon values.

Table 4.20 Station wise summary statistics of dieldrin in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	32.0	10.3	8.8	85.9
2	ND	34.5	12.5	10.9	87 7
3	ND	33.7	12.5	9.5	76.2
4	ND	22.0	12.1	7.0	58.1
5	ND	29 0	13.2	8.8	66.8
6	ND	32.0	14.2	8.8	62.2
7	ND	38.0	16.5	10.8	65.4
8	ND	48.0	17.6	13.8	78.4
9	ND	40.0	15.8	11.9	75.2

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	34.0	11.3	9.3	81.9
2	ND	40.0	13.8	11.3	81.8
3	ND	38.0	12.9	10.2	79.3
4	ND	25.0	12.5	7.6	60.5
5	ND	29.0	13.9	9.3	67.0
6	ND	34.0	15.1	9.4	62.2
7	ND	35.0	17.3	11.0	63.9
8	ND	41.0	18.0	12.4	68.7
9	ND	40.0	17.2	12.0	70.0

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

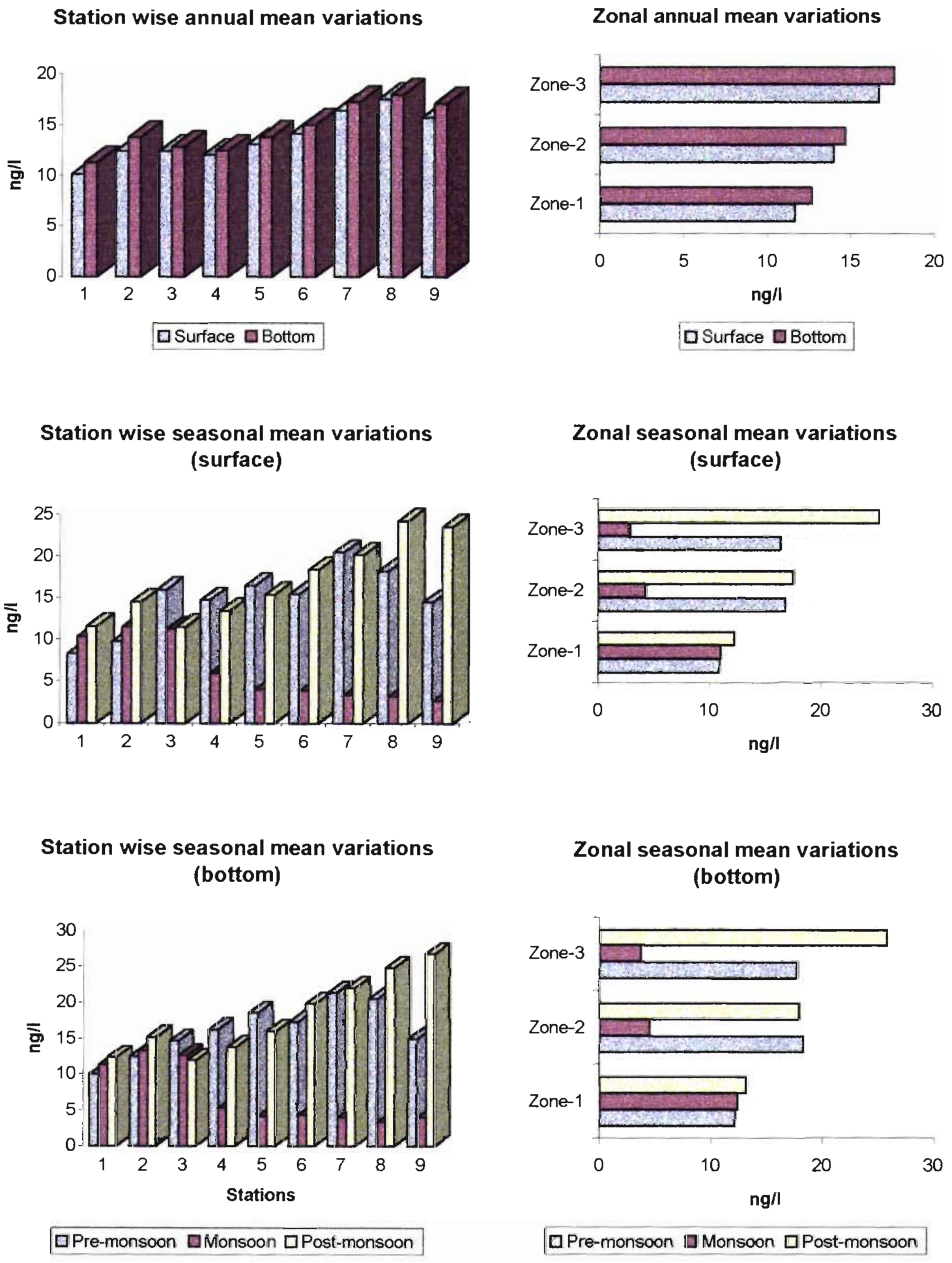


Figure 4.24 Seasonal and spatial distributions of dieldrin in surface and bottom waters

The lower vapour pressure of dieldrin, a chemical property, which when combined with considerable chemical stability (Brooks, 1976) has contributed to its greater persistence. This may be a reason that the residues of this compound still existing in the environment. In India, this pesticide was banned and is not used now in agriculture and the residual effect of this pesticide may be due to the transportation from surrounding land and also from run-off from the rivers. Aldrin and dieldrin were used for agriculture before banning of this pesticide. Moreover, under favourable conditions, dieldrin was formed from aldrin, because dieldrin is a metabolite of aldrin. This may be due to the epoxidation reaction of aldrin to dieldrin.

The other values reported earlier for dieldrin in different waters were: 7 1 to 110 ng l^{-1} in water areas (Ontario), Canada (Miles and Harris, 1978). Tan and Vijayaletchumy (1994) reported dieldrin concentrations, ranging between the ND to 47 ng l^{-1} from the Peninsular Malaysian rivers. An average concentration of 19 ng l^{-1} was repored from Coastal lagoon, Gulf of California (Walter et al., 1999). Balls and Cambell (1999) reported an average value < 0.2 ng l^{-1} from the Scottish coastal sites. These values were reported after the banning of this pesticide long before, and the values reported from the present study area were almost comparable with the above values.

4.3.4.6 Distributions of endrin

The station wise annual mean variations of endrin in surface and bottom waters are plotted in Figure 4.25. Bottom concentrations of endrin were higher than surface concentrations at all stations except at station 3. From stations 6 to 8, higher values of endrin were observed. The station wise statistics summaries of endrin in surface and bottom waters are shown in Table 4.21. Minimum of non-detectable levels of endrin was seen at almost all stations in surface and bottom waters. The maximum value of 29.5 ng l^{-1} was observed at station 3 in surface waters and 33 ng l^{-1} was observed at station 8 in bottom waters. The station wise mean values of endrin ranged from 6.5 to 13.3 ng l^{-1} in surface and 7.3 to 14.5 ng l^{-1} in bottom waters (Table 4.21).

Table 4.21 Station wise summary statistics of endrin in surface and bottom waters

Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	19.0	6.5	6.1	93.8
2	ND	27.5	7.3	7.8	107.1
3	ND	29.5	10.0	10.0	99.6
4	ND	22.0	7.0	6.9	98.0
5	ND	19.0	7.3	6.4	87.1
6	ND	26.0	12.1	8.7	71.6
7	ND	28.0	13.3	8.9	67.3
8	ND	28.0	12.8	8.7	67.9
9	ND	25.0	11.0	8.1	73.3

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	21.0	7.3	6.7	92.3
2	ND	24.5	7.7	7.4	96.1
3	ND	28.5	9.5	9.5	100.4
4	ND	25.5	8.2	7.7	94.5
5	ND	22.0	8.6	6.9	80.0
6	ND	28.0	13.5	9.4	69.7
7	ND	32.0	14.5	9.7	66.6
8	ND	33.0	14.5	10.1	69.9
9	ND	27.5	12.5	8.9	71.1

SD - Standard deviation CV - Coefficient of variation; ND - Not detected

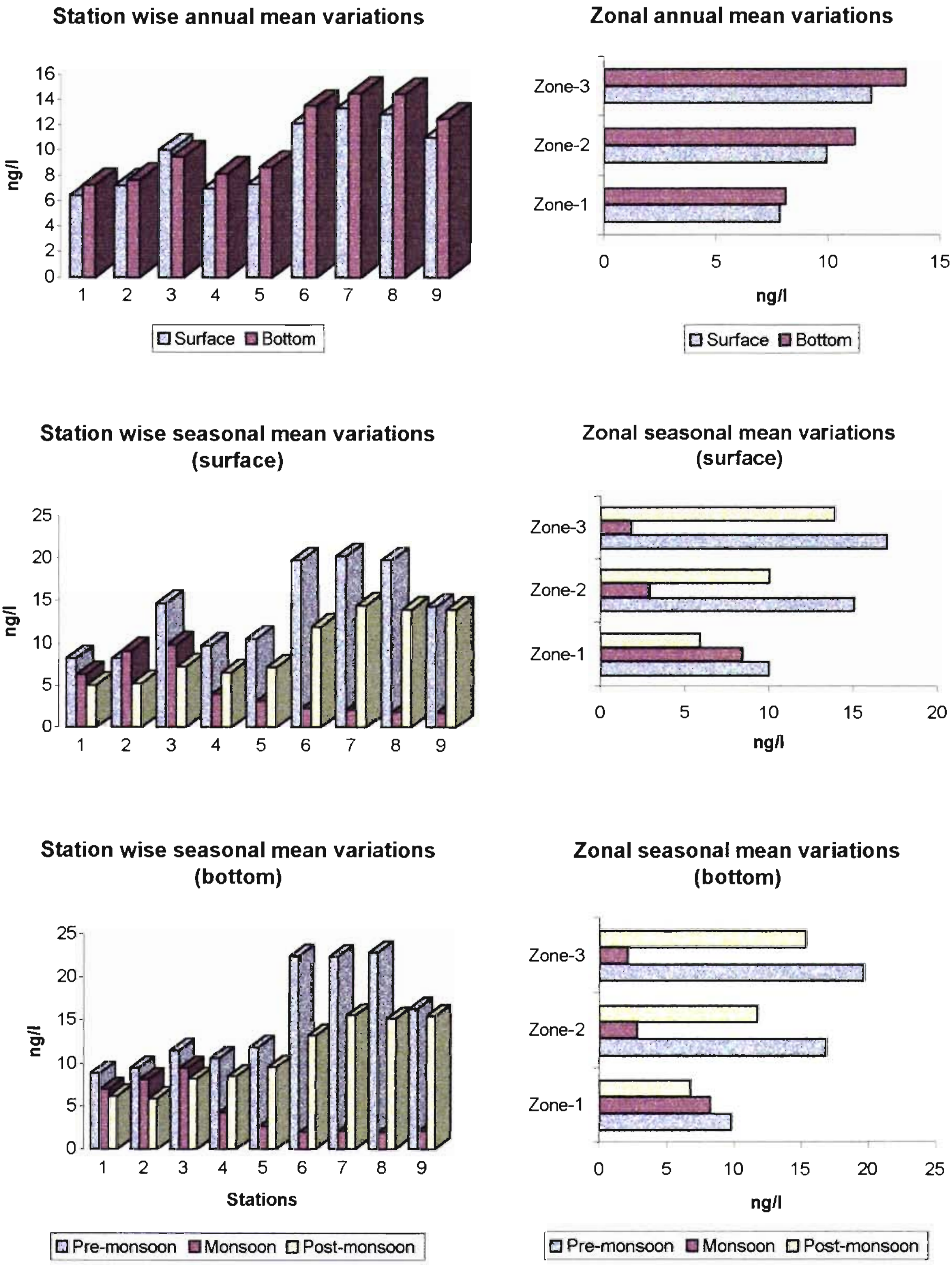


Figure 4.25 Seasonal and spatial distributions of endrin in surface and bottom waters

High fluctuations in pre-monsoonal values were observed in surface and bottom waters (Figure 4.25). Higher values were observed from stations 6 to 8 in pre-monsoon period, both in surface and bottom waters. At station 9, both pre-monsoon and post-monsoon values were found to be almost same. In monsoon season, from stations 4 to 9, the values were lower than other seasons. From stations 4 to 9, endrin values in surface and bottom waters in post-monsoon lie in between pre-monsoon and monsoon values. The annual zone wise mean variations and zonal seasonal mean variations of endrin are also plotted in Figure 4.25. In zone 1, both surface and bottom values were almost equal, but in zones 2 and 3 the bottom values were higher than surface values. Pre-monsoon values in all zones were higher in surface and bottom waters. In zone 1, post-monsoon values were lower than in other seasons. In zones 2 and 3, monsoon season recorded the lowest values.

Relatively lower levels of endrin were seen in the study area. This compound was banned in India and the earlier use of this compound for paddy fields may be the reason for the low concentration. Concentrations ranging from 2 to 133 ng l^{-1} of endrin were reported from surface waters of USA (Lichtenberg et al., 1970). Mohamed and Mohamed (1985b) reported the endrin values in River Nile, Egypt and the values ranged from 3.8 to 18.9 ng l^{-1} Higher values (0.0001 – 0.0002 ppm) of endrin were reported from the shallow ground waters of Punjab, Pakistan (Jabbar et al., 1993). Non-detectable to 0.001 µg l^{-1} of endrin was reported from the drinking waters of Athens (Tsipi and Hiskia, 1996).

4.3.4.7 Distributions of endrin aldehyde

In most of the stations, the surface values of endrin aldehyde were slightly higher than bottom values (Figure 4.26). Station 8, in surface and bottom waters, recorded maximum annual mean values of endrin aldehyde. The station wise summary statistics of endrin aldehyde in surface and bottom waters are included in Table 4.22. Minimum of non-detectable levels of endrin aldehyde was observed at almost all stations in surface and bottom waters. The

Table 4.22 Station wise summary statistics of endrin aldehyde in surface and bottom waters

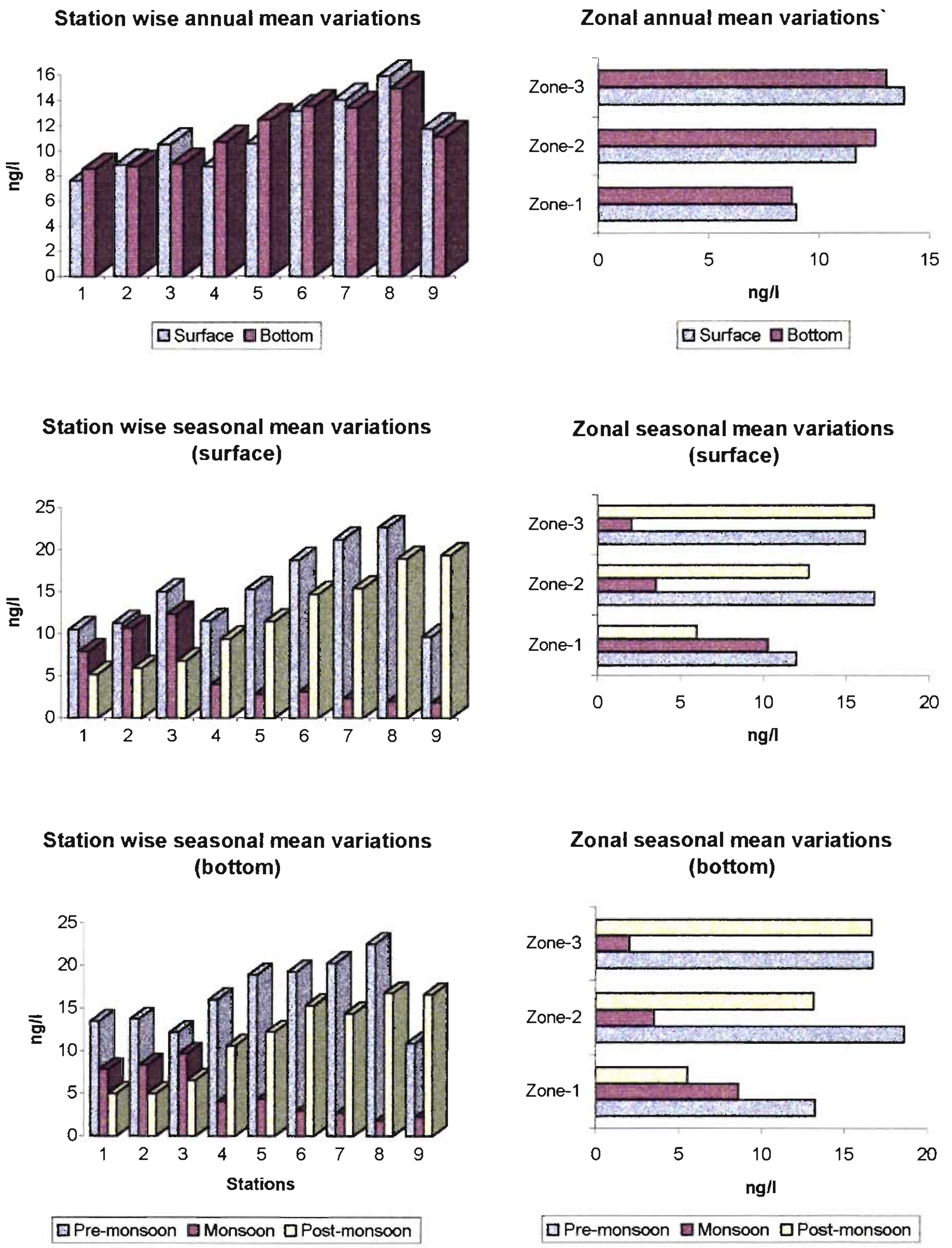
Surface water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	23.5	7.6	7.5	98.0
2	ND	32.0	8.9	9.3	105.0
3	ND	37.0	10.5	11.5	109.5
4	ND	16.0	8.8	5.2	59.1
5	ND	19.5	10.6	6.1	57.3
6	ND	24.0	13.2	8.0	60.9
7	ND	32.8	14.1	10.0	71.2
8	ND	39.5	15.9	11.5	72.4
9	ND	32.7	11.7	9.9	84.8

Bottom water (ng l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	23.5	8.5	7.9	92.3
2	ND	25.0	8.8	8.6	98.1
3	ND	29.0	9.0	9.0	100.5
4	ND	17.0	10.8	6.4	59.2
5	ND	23.0	12.5	7.3	58.9
6	ND	24.0	13.5	8.1	60.1
7	ND	25.0	13.4	8.5	63.0
8	ND	29.0	14.9	10.1	67.5
9	ND	26.9	11.1	7.6	68.3

SD - Standard deviation CV - Coefficient of variation; ND - Not detected


Station wise annual mean variations

Zonal annual mean variations`

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Figure 4.26 Seasonal and spatial distributions of endrin aldehyde in surface and bottom waters maximum value of 39.5 ng l^{-1} was recorded at station 8 in surface waters and 29.0 ng l^{-1} recorded at stations 3 and 8 in bottom waters. The station wise annual mean values of endrin aldehyde ranged from 7.6 to 15.9 ng l^{-1} in surface and 8.5 to 14.9 in bottom waters.

Pre-monsoon season recorded higher values of endrin aldehyde at all stations in surface and bottom waters except at station 9 (Figure 4.26). In monsoon, low values were found at stations 4 to 9. From stations 1 to 3, post-monsoon season recorded lower values than in other seasons. At station 9, post-monsoon season recorded higher values than in other seasons. Figure 4.26 also illustrates the zone wise mean variations and zonal seasonal variations of endrin aldehyde in surface and bottom waters. In zones 1 and 3, the surface values dominated over bottom values. In pre-monsoon, zones 1 and 2 recorded higher values than in other seasons. In zone 3, post-monsoon season recorded higher value than in other seasons. In monsoon, zones 2 and 3 recorded the lowest values than in other seasons.

Endrin aldehyde is a metabolite of endrin and the concentration of this compound in the study area was very low compared with other cyclodiene pesticides. This may be due to the ban of endrin in India. The reported values of endrin aldehyde were less, and the drinking water of Athens had a concentration of ND to 0.002 µg l^{-1} of endrin aldehyde (Tsipi and Hiskia., 1996).

4.4 CORRELATION OF PESTICIDES WITH THE HYDROGRAPHICAL PARAMETERS

The correlations of DDTs with various hydrographical parameters are summarized in Table 4.23. The p,p,-DDE, p,p'-DDD and the ΣDDT concentrations were found to be significantly influenced by the mean salinity ($p < 0.001$, n=108). The Pearson coefficient 'r' showing the correlation of p,p'-DDE, p,p'-DDD and p,p'-DDT with salinity were 0.509, 0.433 and 0.276 respectively. The correlation of ΣDDT with salinity showed an 'r' value 0.506. But the dissolved oxygen concentrations do not show any significant correlation with the

Table 4.23 Correlations of DDTs with environmental parameters

	p,p'-DDE	p,p'-DDD	p,p'-DDT	Σ DDT
Salinity	-0.509	0.433	0.276	0.506
Dissolved oxygen	0.036	0.022	-0.050	0.021
ph	-0.342	-0.250	-0.149	-0.324
Temperature	0.433	0.232	0.244	0.388
Depth	-0.474	-0.446	-0.452	-0.525
Σ DDT	0.964	0.899	0.651	
p,p'-DDT	0.452	0.631		
p,p'-DDD	0.798			

DDT levels. p,p'-DDE, p,p'-DDD and ΣDDT concentrations were found to be significantly correlated (though negatively), by the hydrogen ion concentration (pH). p,p'-DDE displayed a significant correlation with pH with an 'r' value of – 0.342. As in the case of pH, p,p'-DDE also showed significant correlation with temperature ('r' = 0.433, n = 107).

All the isomers of HCH concentrations have significant correlation with salinity, and the 'r' values for α-HCH, β-HCH, γ-HCH and δ-HCH were 0.362, 0.407, 0.487 and 0.321 respectively (Table 4.24). α-HCH and γ-HCH were displayed significant negative correlation with pH and the 'r' values were – 0.304 and – 0.410 respectively. All the HCH isomers showed no significant correlation with dissolved oxygen as in the case of DDTs.

The correlations of cyclodiene pesticides with hydrographical parameters are given in Table 4.25 Significant correlations were observed for almost all cyclodienes except heptachlor and dieldrin with salinity. No significant correlation was observed for cyclodiene pesticides with dissolved oxygen. Considering the correlation with pH only aldrin and endosulfan showed significant correlations and the 'r' values were – 0.302 and – 0.360 respectively. All the cyclodiene pesticides showed a significant positive correlation with temperature.

The organochlorine pesticides are all relatively insoluble, but they differ considerably in their water solubilities, which are very much temperature dependent. The solubility of lindane increased as much as five times, and that of aldrin, dieldrin and endrin increases three to five times, whereas the solubility increased two times for p,p'-DDT with the increase of temperature (Edwards, 1973). These results were relevant, because significant positive correlations were observed among temperature and almost all organochlorine pesticides. When temperature increases, the solubility also increases and it may be one of the reasons for the higher levels of pesticides in water. It is also established that temperature affects the volatility of pesticides also.

Table 4.24 Correlations of HCH isomers with environmental parameters

Parameter	α –HCH	β–HCH	γ–HCH	δ–HCH	Σ HCH	pH	Salinity	DO
Temperature	0.613	0.607	0.627	0.514	0.607	-0.271	0.395	-0.114
Dissolved oxygen	0.023	-0.012	0.067	0.105	0.040	0.039	-0.214	
Salinity	0.362	0.407	0.487	0.321	0.408	-0.516		
pH	-0.304	-0.251	-0.410	-0.237	-0.333			
Σ HCH	0.987	0.918	0.954	0.799				
δ–HCH	0.724	0.749	0.792					
γ–HCH	0.904	0.863						
β–HCH	0.892							

Table 4.25 Correlation of cyclodienes pesticides with environmental parameters

	Heptachlor epoxide	Heptachlor	Endrin aldehyde	Endrin	Dieldrin	Aldrin	Endosulfan
Salinity	0.456	0.230	0.309	0.423	0.198	0.414	0.554
DO	-0.005	0.074	0.047	0.012	0.093	-0.021	-0.013
pH	-0.081	-0.040	-0.144	-0.228	0.047	-0.302	-0.360
Temperature	0.552	0.440	0.493	0.491	0.300	0.445	0.473
Endosulfan	0.865	0.728	0.784	0.877	0.672	0.833	
Aldrin	0.851	0.812	0.846	0.832	0.766		
Dieldrin	0.748	0.857	0.858	0.789			
Endrin	0.887	0.812	0.871				
Endrin aldehyde	0.808	0.854					
Heptachlor	0.792						

4.5 SUMMARY

The levels of organochlorine pesticides reported in this study constitute the first attempt to ascertain the baseline data of ∑HCH, ∑DDT, ∑cyclodienes in the backwaters of Kuttanad. The study revealed the following observations.

- The main sources of pesticide which controlled or regulated the fluvial loadings of pesticides in the Kuttanad backwaters are the agricultural land run-off from 'Padashekarams" and the discharge of water from the major river systems, viz Pampa, Manimala, Achencoil and Meenachal.

- The major chlorinated pesticides found in the study area were still DDT and its metabolites viz DDE and DDD. In Kuttanad waters, DDE was the major individual metabolite seen throughout the study area. The high concentrations of these compounds may be attributed to the use of DDT formulations for National Malaria Eradication Programme.

- The results of the study show that the continued usage of certain pesticides such as DDT, HCH and endosulfan in agriculture and vector controlling programmes has been a contributing factor to the high levels of these pesticides in the Kuttanad water system.

- The levels of organochlorine pesticides in zone 1 were still tolerable in terms of quality for domestic use, whereas some of those rice-growing areas, in zone 2 and zone 3, have exceeded the levels to maintain aquatic life.

- The higher levels of some of the organochlorine pesticides reported in this study may be attributed to the continuous use of these pesticides due to their cheap cost, broad-spectrum activities, economic constraints and ignorance about their deleterious effects.

- Monitoring of pesticides and their residues in the various compartments of water 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 eco-friendly pesticides.

- The higher residual levels of some organochlorine pesticides in the Kuttanad backwaters may affect the aquatic life and or lead to their accumulation in the food chain. The fish diseases reported from the Kuttanad backwaters might have been influenced by the higher residual levels of pesticides and their metabolites. The lipophilic nature and low chemical and biological degradation rates of organochlorine pesticides lead to the accumulation of these compounds in biological tissues.

CHAPTER 5

DISTRIBUTIONS OF ORGANOCHLORINE PESTICIDES IN THE SEDIMENTS OF KUTTANAD BACKWATERS

5.1 INTRODUCTION

The sediments of a water body record information about natural events and anthropogenic activity that have occurred in surrounding ecosystems. One of the most important records that sediments store is the rate of supply of pollutants. Such information can be used to describe past and present pollution inputs and to assist the estimation of the impact of pollutants on the water body. Identification of sediment sources through the use of chemical tracers such as pesticides or metals may provide a clearer picture of the contribution of specific anthropogenic activities to sediment and contaminant loads. A great variety of organic and inorganic materials are deposited in lake sediments in sizes ranging over several orders of magnitude. Sediments are deposited materials that consist of organic matter in various stages of decomposition, particulate mineral matter and inorganic materials of biogenic origin (David et al., 1993). Lake sediments are quite variable, coarser sediments, sands and silts are usually confined to littoral and shallow regions. In lakes, the organic fraction of the sediment is continually being broken down by bottom living animals, fungi, bacteria and perhaps also by free enzymes. At the same time, fresh organic material is continuously added at the sediment surface. Qualitative changes occur, analogous to but not identical with those in soils, with the result that the more readily decomposable organic fractions disappear first, leaving humic residues resistant to further breakdown. Sediments can play a critical role in determining the tropic status of lakes.

Estuarine sediments generally have a high organic content, due to high rates of sedimentation, which lowers the oxygen status. Sediments are the major sinks for chemical components of water bodies and sediment chemical analyses afford methods for measurements of the quality of overlying water and the levels of potential pollutants. Since the sediment is a substrate for biological and chemical reaction, it plays a pivotal role in chemical and biological processes. Estuarine sediments act as a short or long term reservoir for many hydrophobic organic compounds (Prahl and Carpenter, 1984). Diffusion, advection and mixing and resuspension of the sediment will also affect the distributions of hydrophobic organic compounds in the sediment and pore water A comprehensive idea of the bottom sediments is thus a pre-requisite to water quality management procedures.

Organochlorine pesticides are worldwide distributed organic pollutants; such compounds are characterized by their stability for long periods and may lead to marked changes in the aquatic ecosystem (Addison, 1976). The physico-chemical properties of organochlorine pesticides make them very resistant to biological degradation and, thus, highly persistent (Fowler, 1990; Wesen et al., 1992; Martijn et al., 1993; Iwate et al., 1994; Jiping et al., 1995; Corona-Cruz et al., 1999; John et al., 2001). Uptake and accumulation of such chlorinated hydrocarbons by sediments, microorganisms and fish lead to the build up of such compounds in the food chain (Everaarts et al., 1998). The bulk of the pesticides applied are adsorbed and retained on the soil during irrigation (Chen and Chen, 1979; Watanabe et al., 1984). Studies have shown much shorter half-lives of organochlorine pesticides in tropical soils (Sleicher and Hopcraft, 1984; Samuel et al., 1988; Vu Duc et al., 1993; Dang et al., 1998). A clear understanding of the fate and behaviour of soil-applied pesticides following repeated additions is, therefore, absolutely essential in devising environmentally acceptable pest control strategies. These studies assume considerable significance, because in India, HCH and DDT together account for more than two-thirds of the total pesticide consumption (Pillai, 1986; Pestology Annual 1995).

A pesticide residue in soil or sediment may be considered as any substance or mixture of substances in or on soil resulting from the use of a pesticide. This includes any derivatives, such as conversion and degradation products, reaction products, metabolites and impurities. The organochlorine compounds have high affinity to the soil and are also retained in the sediment. Large amounts of pesticides reach the soil, either as direct applications, as fall-out from aerial spraying, in rain or dust or from plant or animal remains, which become incorporated with the soil. Organochlorines entering the estuaries and coastal waters with river or surface run-off as well as with atmospheric fallout eventually accumulate in sediments. Thus, the soil is an environmental reservoir for these residues from which they are taken up by plants, move into the body of invertebrates, get transported into water or air and are broken down to innocuous substances. The organochlorine pesticides are extremely liposoluble hydrophobic substances readily absorbed in the organic portion of suspended particles in waste water and urban run-off, and eventually end up in coastal sediments close to sewage outfalls, bays and harbours. Sediments are sources for these toxics to enter chains, and thus endanger public health and coastal ecosystems (NRC, 1994; Shannon, 1999).

Direct application of pesticides may result in an accumulation of their residues in soil. A large proportion of foliar sprays that do not reach their target may also contribute greatly to soil residues. Pesticides may also reach the soil when leaves that have been sprayed fall to the ground or crops that contain small amounts of pesticides are ploughed in or when bodies of animals with residues in their tissues are buried. Another source of pesticide residue in soil is the residue of these chemicals in the atmosphere, either in dust or rain water, which can be washed out by precipitation and fall onto the soil.

5.1.1. Factors affecting the persistence of pesticides in soil/sediments

The main factors, which affect the persistence of pesticides in soil, are (1) chemical nature of the pesticide (2) type of the sediment/soil (3) organic matter content (4) clay content (5) soil acidity (6) temperature (7) sediment moisture and (8) mineral ion content.

The chemical nature of pesticides, which affect the persistence in soil/sediment, includes the chemical stability of the pesticide, its volatility, solubility, concentration and formulation type. Most of the organochlorine pesticides are non-volatile but there is some correlation between the vapour pressure and persistence of these pesticides in soils. Haris and Lichtenstein (1961) found that the volatalisation of pesticides from soil increased with the concentration of pesticide, the relative humidity of the air over the soil, temperature, and movement of air over the soil surface, and the amount of moisture in the soil. Solubility of an environmental pollutant plays an important role in determining the aquatic fate. Solubility of the pesticide is also an important factor influencing its persistence. Most of the organochlorine pesticides are relatively insoluble in water but although the more soluble pesticides are generally leached much more readily from soils, leachability and solubility are not always associated. Polar compounds will dissolve in water, whereas hydrophobic compounds will be incorporated into organic rich particulate matter and preferentially accumulate in sediments (Rudolf, 1991). The accumulation into sediments was found to be a partitioning rather than an adsorptive process for hydrophobic pollutants (Chiou et al., 1979 and 1985; Kyle et al., 1981). The water solubility of a pesticide is often inversely related to its degree of absorption onto soil fractions (Bailey and White, 1964), but this may not be true for some pesticides. When the water solubilities of pesticides are compared with their persistence in soil, they seem strongly correlated (Edwards, 1966). The pesticide formulations may greatly affect the persistence of pesticides in soil or sediments. For instance, the water soluble formulations leach faster from soil than the oil-soluble water miscible formulations. The size of the particles of pesticides in a formulation is also important.

The pesticides are retained in heavier soils and those with much organic matter. The soil type influences not only the persistence and activity of pesticides in soils, but also the rate at which they are converted into other chemicals. Soil organic matter seems to be the most important single factor influencing the persistence of pesticides. The hydrogen ion concentration may influence the breakdown of pesticides in soil. HCH and DDT broke down more rapidly in alkaline soil (pH 9.5) than in normal soil (The Agrochemical Handbook, 1983). Edwards (1973) claimed that soils with a low pH have a high anion exchange capacity, and would tend to adsorb more DDT than soils of higher pH.

Pesticides are lost from soil mainly by chemical degradation, bacterial decomposition and volatilization, and all these processes are influenced by temperature, so that at low temperature these processes slow down and little pesticide is lost. Haris and Lichtenstein (1961) found that increased temperatures increased the rate of volatilization of aldrin from soil. Temperature also influences the adsorption of pesticides in soils because sorption tends to be exothermic, so that increased temperature decreases adsorption and release pesticide. It is also clear that the solubilities of pesticides usually depend on temperature, so that more pesticide becomes dissolved in the soil moisture as temperature increase, and the amounts of pesticides that are leached from soils may increase. The influence of temperature on the persistence of pesticides in soils is not simple because increased temperatures increase the rate of conversion to other metabolites, and dry soils hold pesticides much more firmly than wet soils.

The main influence of soil moisture on the persistence of pesticides in soil is by its effect on the adsorption of pesticides onto the various soil fractions. Water can compete for adsorption sites with pesticide because it is a very polar molecule, strongly adsorbed by the soil colloids, and in drier soils, there are fewer water molecules to compete with the pesticide molecules for adsorption sites. Soil humidity, which is directly related to soil moisture, can influence the adsorption of pesticides. Secondly, it can affect the rate at which it diffuses into soil, and finally it can affect the availability of the adsorbed toxicant (Edwards, 1973).

5.1.2. Disappearance of pesticide residues from soil

The disappearance of organochlorine pesticides from soils may be mainly attributed to rapid volatilisation of the parent compound and the degradation of more volatile products and their subsequent volatilisation. Although volatilisation of DDT and HCH is reported to be very slow under temperate climates, it has been identified as the principle mechanism of dissipation from tropical soils (Sleicher and Hopcraft, 1984; Samuel et al., 1988; Samuel and Pillai, 1989 and 1990; Tanabe et al., 1994). Organochlorine pesticides are all very stable chemicals that are relatively non-volatile and poorly soluble. Samuel et al. (1988) observed that organochlorine pesticides have shorter half-lives in tropical soils and found that half life of HCH in an Indian sandy loam soil to be only 4-5 months and that of DDT to be 8-10 months. Likewise, a half-life of only 4 months was reported for DDT in Kenyan soils (Sleicher and Hopcraft, 1984). In contrast, the half-lives of DDT and HCH, under temperate conditions have been estimated to be 2.8 and 1.2 years, respectively (Edwards, 1966). Nevertheless, most of these reports are based on a single application of the pesticide to soil, but it is a common practice in both agriculture and public health operations to repeatedly use the pesticide at regular intervals, so that the insect-pest populations are subjected to sustained pressure. The relatively faster dissipation of DDT and HCH following repeat treatments is the manifestation of increased volatile loses (Samuel and Pillai, 1991). It has been assumed that the low volatilities of organochlorine pesticides mean that only a small proportion of them are lost through volatilisation from the soil surface.

Potential volatility of a chemical is related to its vapour pressure, but actual vapourisation rate will depend on environmental conditions and all factors that modify or attenuate the effective vapour pressure of a chemical. Volatilisation could proceed at a rate almost proportional to the vapour pressure of the compound, immediately after the application period (Spencer and Cliath, 1973). The pesticides adsorbed to the soil organic matter subsequently act as a rate limiting factor (Spencer and Cliath, 1973). In soil, the vapour pressure of a pesticide is not constant, but changes with its concentration, because the pesticide is dissolved in the soil water and adsorbed onto the soil fractions (Grahm-Bryce, 1972). Hence, the amount of volatilisation occurring may depend upon the concentration of the pesticide.

Vapourization of a pesticide from soil is controlled by many variables, including temperature, soil properties, soil and water content, and nature of the pesticide; particularly its solubility and its degree of adsorption (Hamaker and Thompson, 1972). There is also much less volatilisation from very dry soils than from wet ones, because unless they are displaced by water molecules, the pesticide remains tightly bound to adsorptive surfaces in the soil. Even DDT can volatilise from soil in quite considerable amounts, and Lloyd-Jones (1971) calculated half the amount of DDT applied to soil may volatilise, but Spencer and Cliath (1973) showed that o,p-DDT and p,p'-DDE volatilised much more than p,p'-DDT, so some degradation is necessary before much volatilisation occurs. Moreover, vapour pressure is not constant but varies with temperature, so more volatilises from warm soils than from cold soils. Microorganisms chiefly mediate pesticides degradation in soil, and their involvement is generally established by an initial lag in degradation due to the adaptation of microbes. Prior exposure to, or successive additions of, a pesticide would cause the initial lag period to become shorter, due to the enrichment of pesticide degrading microorganisms (Sethunathan et al., 1982). The degradation of pesticides may begin much earlier in pre-treated soils than in previously untreated soils, due to the conditioning of the microbial population following pre-treatment (Samuel and Pillai, 1991).

5.2. MATERIALS AND METHODS

The materials and methods are discussed in Chapter 2.

5.3. RESULTS AND DISCUSSION

Very few data are available for the levels of chlorinated pesticides in the Indian estuaries. As India is predominantly an agricultural country, large quantities of pesticides have been in use in agriculture for many years. A clear understanding of the fate and behaviour of the pesticides is absolutely essential in devising environmentally acceptable chemical pest strategies. For quantifying the residual levels of pesticides and their metabolites in the sediments of Kuttanad backwaters, a systematic study was conducted. The following organochlorine pesticides and their isomers/metabolites were quantified in the sediments of the study area.

- ΣDDT, which includes
    p,p'-DDE
    p,p'-DDD
    p,p'-DDT

- ΣHCH, which includes
    α-HCH
    β-HCH
    γ-HCH
    δ-HCH

- $\sum$Cyclodienes, which includes
  α-endosulfan
  Heptachlors (heptachlor and heptachlor epoxide)
  Aldrins (aldrin and dieldrin)
  Endrins (endrin and endrin aldehyde)

The structural formulae and physico-chemical properties of these pesticides are included in Chapter 4 (Figure 4.4; Tables 4.1 to 4.6).

5.3.1. Distributions of total organochlorine pesticides in sediments

Total organochlorine pesticides in the sediments of the study area comprises of $\sum$DDT, $\sum$HCH and $\sum$cyclodienes. The percentage compositions of the total organochlorine pesticides in the sediments are plotted in Figure 5.1. As in the case of water, DDT and its metabolites were ranking as first, and accounts more than 60% of the total organochlorine pesticides found in the sediments of Kuttanad backwaters (Figure 5.1). The $\sum$HCH accounts more than 28% and $\sum$cyclodienes were below 1.2 % of the total organochlorine pesticides in the study area (Figure 5.1). Station wise overall minimum mean concentration of 92.5 ng g^{-1} organochlorines was observed at station 9 and overall maximum mean concentration of 430.9 ng g^{-1} was observed at station 7 of the study area (Table 5.1). The station wise overall mean concentrations varied from 60.7 to 303.5 ng g^{-1} for $\sum$DDT, 30.5 to 122.4 ng g^{-1} for $\sum$HCH and 0.83 to 5.0 ng g^{-1} for $\sum$cyclodienes (Table 5.1). Comparatively higher concentrations of total organochlorines were distributed in zone 2 and lesser amounts in zone 1 of the study area. The overall distribution of organochlorine pesticides and their residue levels in the sediments of Kuttanad backwaters were also found in the same order as that of water ($\sum$DDT > $\sum$HCH > $\sum$cyclodienes).

Relatively high levels of $\sum$DDT and $\sum$HCH, and low levels of $\sum$cyclodienes were recorded in the sediment samples of the study area, indicating almost uniform distributional pattern of these compounds in the three zones. Eventhough higher amounts of HCH formulations were used in the study area, HCHs showed lower residual levels than those of DDTs in the sediment samples. This could be due to the difference of physico-chemical properties of the two compounds (Tanabe and

Table 5.1 Station wise overall mean concentrations of organochlorines in sediments (ng g^{-1} dry wt.)

Stations	Total organochlorines	Σ DDTs	Σ HCHs	Σ Cyclodienes
1	107.8	67.9	39.1	0.83
2	106.4	63.9	41.6	0.93
3	109.2	70.4	37.9	0.88
4	208.6	129.7	77.2	1.68
5	272.5	173.0	96.7	2.76
6	329.1	220.0	105.3	3.86
7	430.9	303.5	122.4	5.02
8	100.8	65.8	33.4	1.6
9	92.5	60.7	30.5	1.3

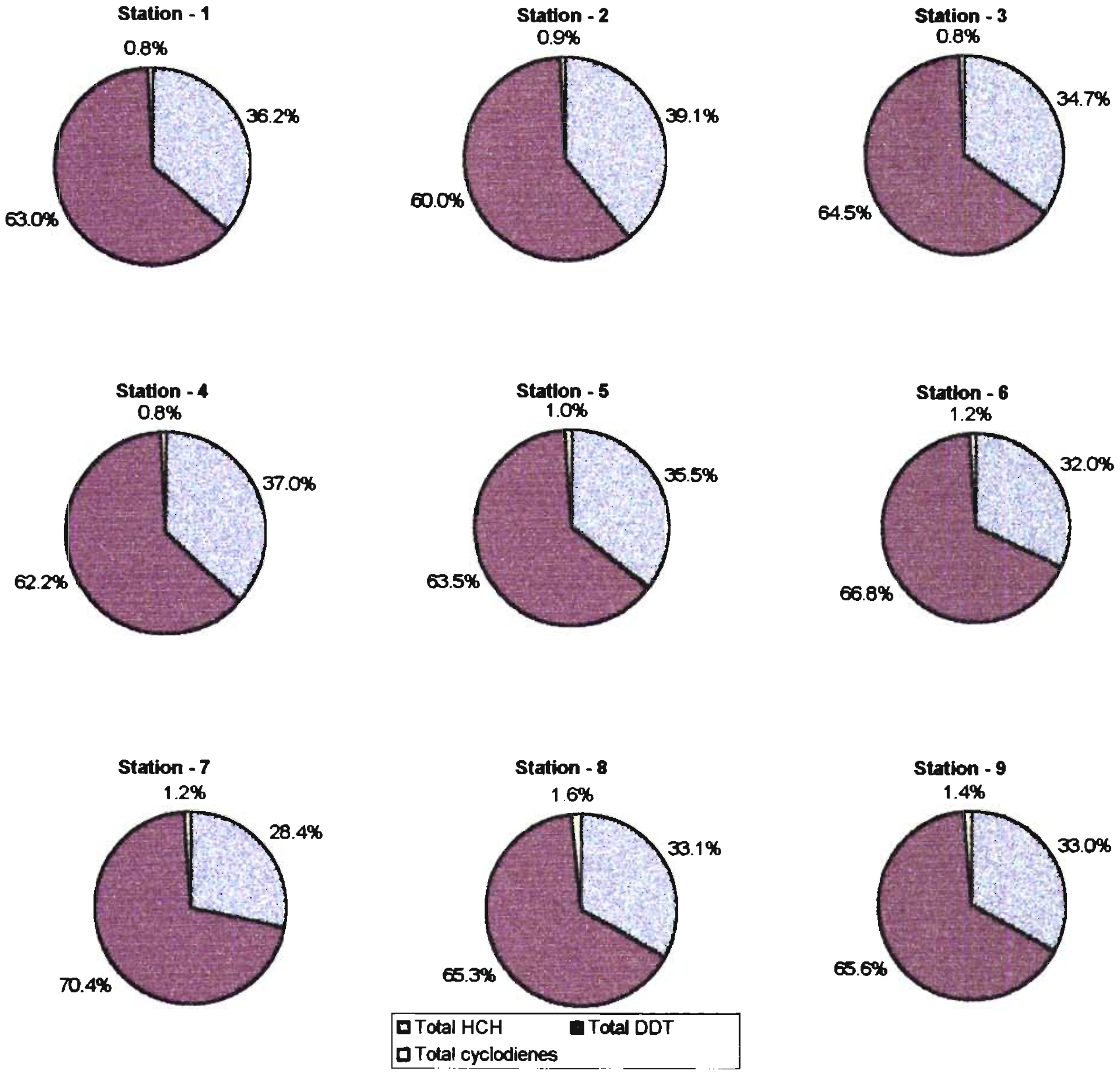


Figure 5.1 Station wise percentage composition of total organochlorines in sediments

Tatsukawa, 1981). The dissipation rates of HCHs are higher than those of DDTs because HCHs have higher vapour pressure and water solubility compared to that of DDTs. The soils with low pH have a high anion capacity and would tend to adsorb more DDT than soils of higher pH. With regards to residue distribution in different sediment types, DDT, HCH and endosulfan concentrations in paddy-field sediments were higher (zone 2) than those in riverine or estuarine sediments. Variability in the concentrations of the residues of organochlorine pesticides in the riverine zone (zone 1) may be attributed to the presence of the major river systems flowing towards the Vembanad Lake, and in zones 2 and 3, may be attributed to the cumulative effect of the run-off from the rivers and the discharge of effluents from the paddy fields. The annual mean variations of all pesticides and their metabolites depend to an extent on the opening and closing of Thanneermukkam bund.

Mohamed and Mohamed (1985a) observed the presence of p,p'-DDT and its degradation products at relatively high concentrations in surface sediments of Mediterranean Sea at Port-Said and the concentrations of the organochlorine compounds were in the order p,p'-DDE > p,p'-DDD > endrin > p,p'-DDT > lindane > chlordane. Sarkar and Sen Gupta (1991) observed the residue levels of different organochlorine pesticides in the sediments from the Arabian sea along the west coast of India as follows: dieldrin < aldrin < HCH < DDT The same trend was observed in the case of DDT and HCH in Kuttanad sediments. A mean concentration of 4.33 ng g^{-1} of total pesticides was reported from the sediments in Rio palizada, Mexico (Gold-Bouchot et al., 1993). Vu Duc et al. (1993) studied the persistent organochlorine residues in soils from tropical and sub-tropical Asian countries and found that the order was mainly $\sum$DDT > PCBs >$\sum$HCH in soils from Vietnam and Thailand, whereas that in Taiwanese soils was: PCBs > $\sum$DDT > $\sum$HCH. India being a tropical country, these observations were relevant in the Kuttanad sediments also, and in both studies, the levels of DDT and HCH were in the same order.

In aquatic environment, both particle-feeders and bottom feeders play an important role in accumulating pesticides. This is significant as bulks of lipophilic pesticides are expected to be bound to the particles and to the bottom sediment. Various shellfish, crabs, etc. are known to accumulate pesticides (Matsumura, 1985).

The information on pesticide residues in sediments, their persistence and degradation, in India are limited. It has been shown that both DDT and HCH have significantly shorter half-lives in tropical environments than in temperate zones (Sleicher and Hopcraft, 1984; Samuel et al., 1988; Nair et al., 1992).

The studies conducted by Singh and Chawla (1978) revealed that 91 (86%) of the 106 soil samples collected from agricultural lands of the Punjab were contaminated with pesticide residues. Like that of Punjab, agriculture is common in Kuttanad and due to that, most of the soil samples were contaminated with pesticides. The studies conducted by Karla and Chawla (1983) revealed the presence of both DDT and HCH residues in the soil of Punjab. Yadev et al. (1981) reported that the soil samples collected from different areas covering Delhi contained DDT residues, ranging from 0.01 to 2.61 mg kg^{-1} Albanis et al. (1994) studied the transportation of pesticides in the estuaries of the Axios, Loudias and Aliakmon rivers, Greece and found that the three major organochlorine compounds, αHCH, lindane and p,p'-DDE were found in significant amounts in the estuarine sediments. But in kuttanad along with the above compounds, β-HCH was also found as a major isomer in sediments of the study area. Tan and Vijayaletchumy (1994) while studying the organochlorine residues levels in sediment samples from rivers flowing through rice growing areas found high levels of organochlorine pesticides in sediments. Gold-Bouchot et al. (1995) reported an average concentration of 1.77 ng g^{-1} of total pesticides from the sediments in Rio palizada, Mexico. Williams et al. (1997) reported 0.1 mg kg^{-1} (100 ng g^{-1}) of total organochlorines from the surficial sediments from inshore estuary, Mombassa. Efrain et al. (1998) reported the $\sum$pesticides from marine sediments of the Baja California, and the values ranged from 0.2 to 4.5 ng g^{-1} with an average of 3.23 ng g^{-1} The same authors observed that the most abundant pesticides in that area were p,p'-DDE, β-HCH and γ-HCH and these observations were significant in Kuttanad sediments also as p,p-DDE and β-HCH were the major compounds found in the study area. Norena-Barroso et al. (1998) reported the total pesticides in the sediments from Bay of Chetumal, Mexico and the values ranged from 8.12 to 13.54 ng g^{-1} Venkatesan et al. (1999) observed that the total DDT constitutes a major fraction (>84%) of the total pesticides in the top 70 cm of the Richardson Bay sediments in San Francisco. These results were also in agreement with the present study, as the major portions of pesticides reported from Kuttanad sediments were DDT and its metabolites as well as HCH and its isomers.

5.3.2. Distributions of ∑DDT in sediments

∑DDT includes p,p'-DDE, p,p'-DDD and p,p'-DDT The station wise percentage compositions of ∑DDT in sediments are depicted in Figure 5.2. The overall mean concentrations of ∑DDT ranged from 60.7 ng g^{-1} to 303.5 ng g^{-1} (on dry weight basis) (Table 5.1). In ∑DDT, as in the case of water, the major portion distributed in all stations were mainly p,p'-DDE (Figure 5.2). The percentage of p,p'-DDE ranged from 56.3 to 75.8% of ∑DDT, whereas the percentage of p,p'-DDD ranged from 13.5 to 21.4% and that of p,p'-DDT ranged from 8.7 to 22.3% of ∑DDT Higher percentage of both p,p'-DDD and p,p'-DDT were observed in zone 1 (stations 1, 2 & 3) than in other zones (Figure 5.2 and Table 5.2).

Considering the overall mean value of DDT and its metabolites, the residue levels of DDTs were found to be in the order of p,p'-DDE > p,p'-DDD > p,p'-DDT Similar observations were reported from the paddy field soils from Vietnam, and the residue levels of DDTs were found to be in the order of p,p'-DDE > p,p'-DDD > p,p'-DDT >o,p-DDT (Vu Duc et al., 1993). Mohamed and Mohamed (1985a) observed the presence of p,p'-DDT and its degradation products in Mediterranean Sea at Port-Said and the concentrations of the organochlorine compounds were in the same order as observed in the present study. The same authors also observed that the levels of p,p'-DDT and metabolites (260.7 to 826.0 µg kg^{-1}) were at relatively higher concentrations in surface sediments, and is an indication of its recent application and that active microbial degradation was taking place.

The higher levels of DDT and its metabolites found in the sediments of Kuttanad backwaters, despite the ban of this pesticide in agriculture, could be due to the continuous use of this pesticide for National Malaria Eradication Programme and their earlier use in agriculture. The residual levels of DDTs in paddy field soils in Malaysia were reported from a minimum of 4.7 ng g^{-1} to a maximum of 5.8 ng g^{-1} and a mean value of 5.3 ng g^{-1} (Meier et al., 1983). Kuwatsuka et al. (1986) observed the residue levels of DDTs in paddy field soils of Indonesia and found a maximum value of 20 ng g^{-1} and a mean value of 1.2 ng g^{-1} Sarkar and Sen Gupta (1987)

Table 5.2 Overall summary statistics of organochlorine pesticides in sediments

(ng g^{1} dry wt.)

Organochlorines	Minimum	Maximum	Mean	SD	CV
p,p'-DDE	2.45	376.52	92.52	90.96	98.32
p,p'-DDD	0.13	90.67	20.60	19.10	92.71
p,p,-DDT	0.11	41.56	15.74	11 70	74.34
α - BHC	0.23	43.23	12.22	10.61	86.81
β - BHC	3.45	140.43	48.92	36.34	74.27
γ - BHC	0.08	24.56	3.86	5.01	129.84
δ - BHC	ND	0.95	0.14	0.18	132.50
α - endosulfan	ND	5.45	1 17	1.26	107.67
Heptachlor	ND	0.78	0.09	0.10	114.37
Heptachlorepoxide	ND	2.65	0.25	0.43	168.14
Aldrin	ND	0.14	0.06	0.05	81.94
Dieldrin	ND	3.26	0.43	0.73	169.86
Endrin	ND	0.14	0.05	0.04	82.97
Endrin aldehyde	ND	0.14	0.04	0.04	100.66

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected

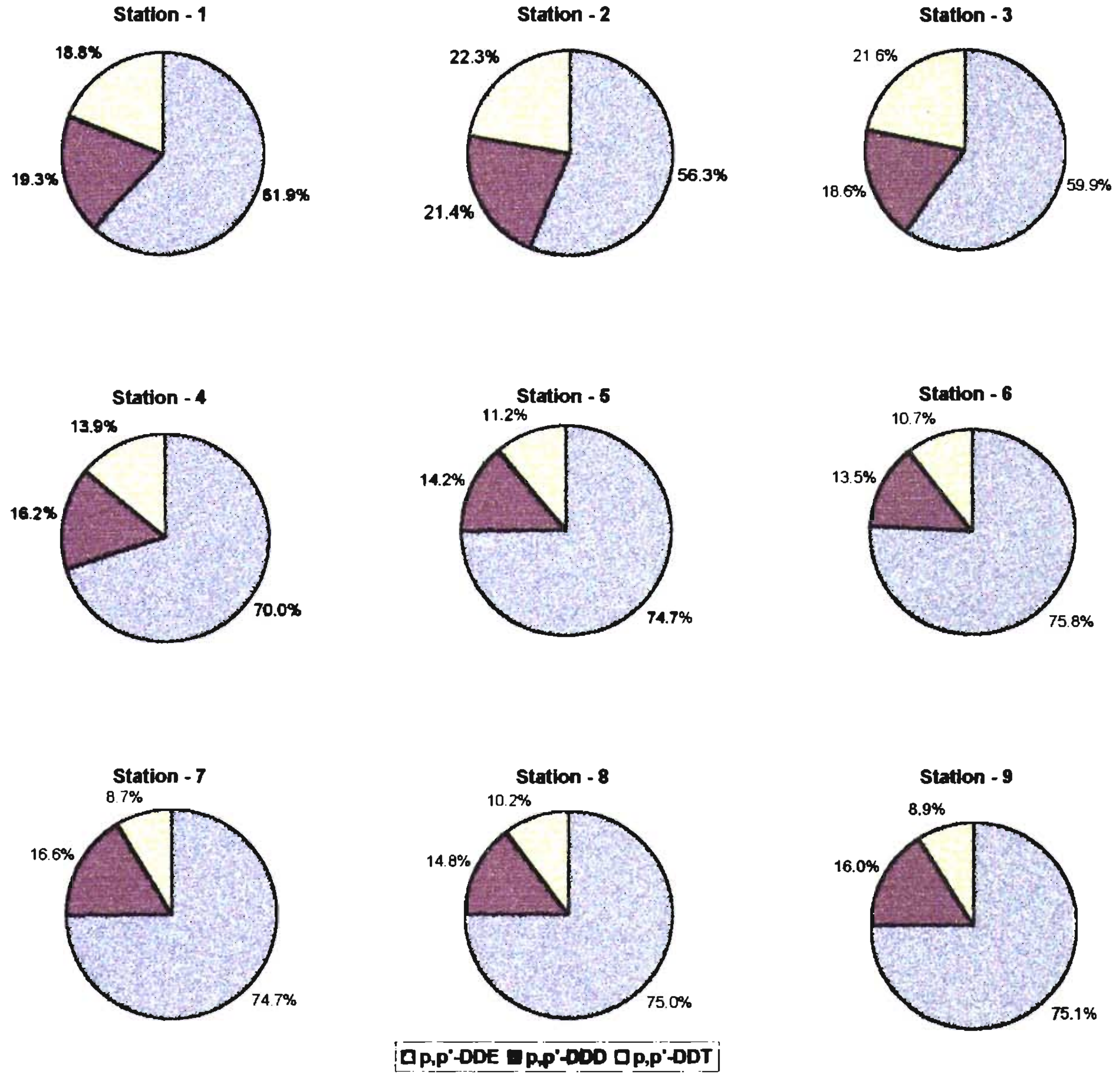


Figure 5.2 Station wise percentage composition of ΣDDT in sediments

reported the $\sum$DDT in sediments from the Arabian Sea along the central west coast of India and the value ranged between ND levels to 179.10 ng g^{-1} wet weight. Sarkar and Sen Gupta (1988a) also reported the $\sum$DDT in sediments collected along the east coast of India and the values ranged between 0.02 to 0.78 µg g^{-1} wet weight. Kawano et al. (1992) studied the $\sum$DDT concentrations in the paddy field soils of India, and reported a minimum value of 0.85 ng g^{-1}, a maximum value of 2200 ng g^{-1} and a mean value of 99 ng g^{-1} This observation is relevant in the present study, as the mean values of both studies were comparable. Vu Duc et al. (1993) studied the organochlorine residues in soils from tropical and sub-tropical Asian countries, and found that $\sum$DDT in Vietnamese paddy field and upland soil samples ranged from 5.5 ng g^{-1} to 1300 ng g^{-1} and 73 ng g^{-1} to 280 ng g^{-1} respectively. The concentrations of $\sum$DDT in Taiwanese soil samples ranged from 2.4 ng g^{-1} to 78 ng g^{-1} and were highest in paddy field samples and lowest in upland samples (Vu Duc et al., 1993). The same authors found that the pesticide concentrations in paddy field soils were higher than those in upland and urban soils and the results were comparable with Kuttanad sediments also. Venkatesan et al. (1999) reported the total DDTs in the sediment cores from San Francisco Bay, which ranged from 4 to 21 ng g^{-1} The same author also observed that the total DDT constitutes a major fraction (>84%) of the total organochlorine pesticides in the top 70 cm of the sediments.

Very limited studies were performed for the organic contaminants in Kuttanad backwaters. One such study is the Kuttanad Water Balance Study (KWBS, 1989) and some incomplete results of pesticide residues were published by them. As per the above study, the DDT concentrations in sediment samples of river in the kayal areas were gone up to 100,000 ng l^{-1} and in some stations, the values gone upto 1 – 45 x 10^6 ng l^{-1}

Some of the recent studies reporting the $\sum$DDT from other locations were: 308 to 963 µg kg^{-1} (ppb) in marine sediments, Moss landing harbour, California (David et al., 1993); 13 to 31 ppb in marine sediments, Elkhorn slough, California (David et al., 1993); 6 to 10 ppb in marine sediments, near shore Monterey Bay, California (David et al., 1993); 2.5 to 12.0 ng g^{-1} in sediments of Osaka Bay (Iwata et al., 1994); 1.38 ng g^{-1} to 25.4 ng g^{-1} in the sediments of Victoria Harbour, Hong Kong (Hong et al., 1995); 0.8 to 30.6 ng g^{-1} in Coastal bottom sediments of Japan sea (Tkalin, 1996); 3.04 to 14.30 ng g^{-1} in sediments of Red River delta, North Vietnam (Dang et al., 1998); 7 to 180 ng g^{-1} in sediments from the coastal zone and continental slope of Kenya (Everaarts et al., 1998); 0.70 to 5.83 ng g^{-1} in the sediments from Bay of Chetumal, Mexico (Norena-Barroso et al., 1998); 1.1 ng g^{-1} in sediments of Arcachon Bay (Thompson et al., 1999); 1.36 ng g^{-1} to 8.99 ng g^{-1} in surface sediments of Pearl River estuary (Huasheng Hong et al., 1999).

Anton et al. (1986) suggested that a combination of the mixing of DDT into the soil column and soil erosion rates would result in continued release of DDT well into the 21st century in the Central Valley, California. This observation is significant in the study area, because before the ban of DDT, this pesticide was widely used in agriculture through out the study area and in the surrounding areas, and the presence of major metabolites of DDT may be from the earlier contamination. The variations in the distribution of these compounds are mainly dependent on the physico-chemical properties of the compounds, the opening and closing of Thanneermukkam bund, the nature of the sediments of Kuttanad backwaters and the frequency of the use of pesticides in agriculture and vector control.

5.3.2.1. Distributions of p,p'-DDE in sediments

The seasonal and spatial distributions of p,p'-DDE in sediments are illustrated in Figure 5.3. The p,p'-DDE values at stations 1 to 3 were found to be almost constant. From stations 4 to 7, the p,p'-DDE values were increasing slightly and at station 7, the highest value was observed. Again at stations 8 and 9, the values were found to be decreasing to a lower range. The station wise summary statistics of p,p'-DDE in sediments are listed in Table 5.3. The minimum value of 2.45 ng g^{-1} was recorded at station 2 and the highest value of 376.52 ng g^{-1} was recorded at station 7 in sediments. The station wise mean values of p,p'-DDE ranged from 35.96 ng g^{-1} to 226.61 ng g^{-1} in sediments.

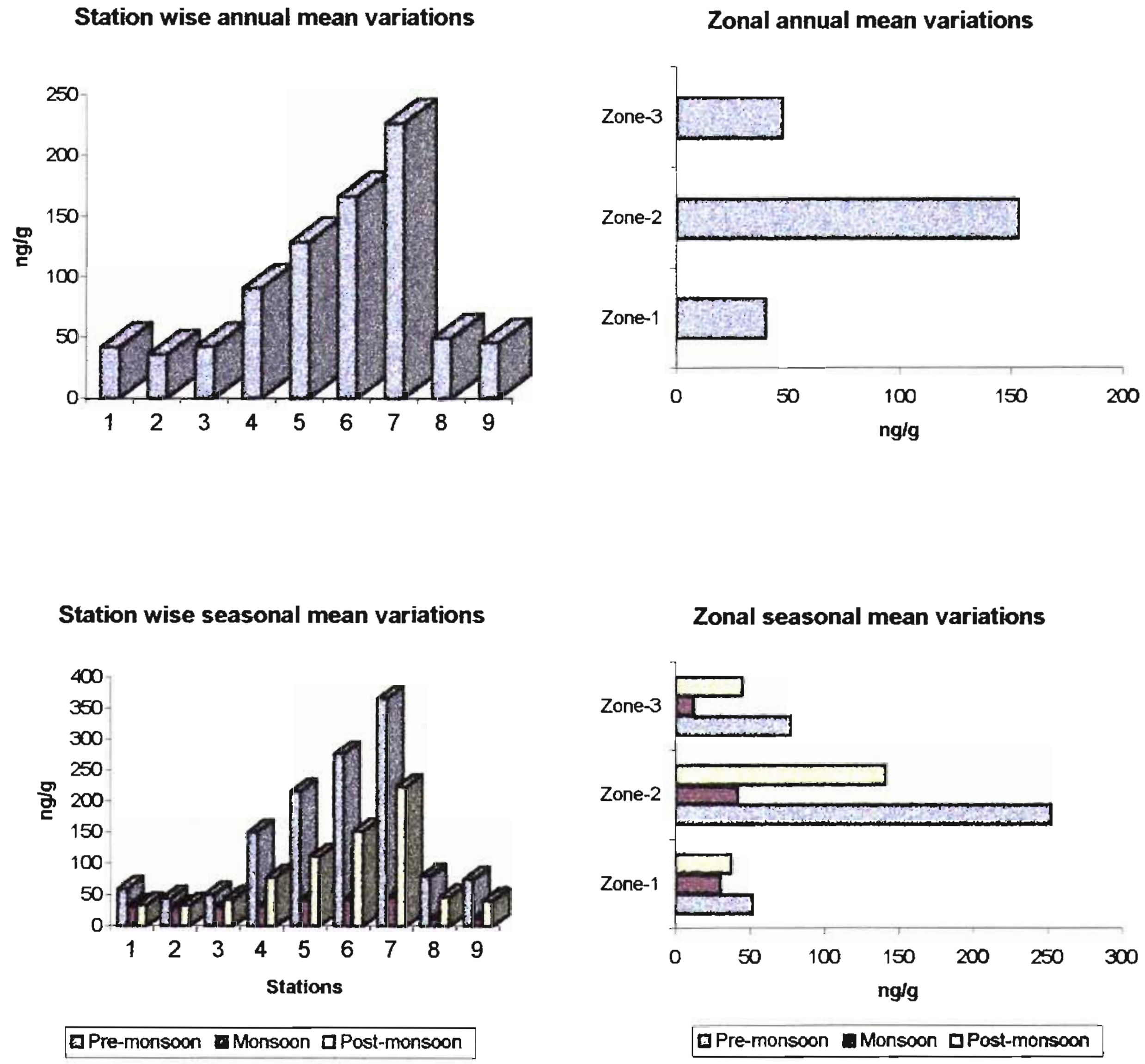
The seasonal mean variations of p,p'-DDE in sediments of the study area are also plotted in Figure 5.3. Higher concentrations of p,p'-DDE were observed at all stations in pre-monsoon season. Comparatively, high values of p,p'-DDE were observed at stations 4 to 7 in pre-monsoon period. The values of p,p'-DDE observed

Table 5.3 Station wise summary statistics of p,p'-DDE in sediments

(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	4.24	76.56	42.00	22.73	54.13
2	2.45	69.65	35.96	17.26	48.00
3	3.45	70.25	42.16	18.67	44.29
4	7.45	165.54	90.78	52.19	57.49
5	6.45	231.56	129.19	76.71	59.38
6	8.56	298.25	166.79	98.36	58.97
7	10.11	376.52	226.61	135.80	59.93
8	4.66	88.76	49.37	28.42	57.56
9	6.88	80.56	45.59	26.73	58.63

SD - Standard deviation; CV - Coefficient of variation


Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Figure 5.3 Seasonal and spatial distributions of p,p'-DDE in sediments (ng g^{-1} dry wt.)

in monsoon season were less compared to that of other seasons. In general, well defined seasonal variations were observed in the distribution pattern of p,p'-DDE in the entire study area.

In the annual zonal distribution pattern, the p,p'-DDE values in zone 2 were higher than that of other zones (Figure 5.3). Zone 1 showed slightly lower values of p,p'-DDE than zone 3. In zonal seasonal variation graph, pre-monsoon season recorded higher values of p,p'-DDE than in other seasons. Monsoon recorded lower values of p,p'-DDE than in other seasons.

One of the major degradation products of DDT is DDE and it is still commonly found in the environment, especially in the soil, due to the strong adsorption to soil particles, which results in a great persistency (EPA, 1980). Considerable amounts of DDT are degraded to DDE in the marine and estuarine environment. Addision (1976) found that the phytoplankton organisms convert p,p'-DDT to p,p'-DDE. Richard (1976) also observed that under aerobic conditions, a high rate of formation of p,p'-DEE from p,p'-DDT take place. DDTs are metabolized to DDEs by the dehydrochlorination under aerobic conditions (Aguliar, 1984; Corona-Cruz et al., 1999). These observations were significant because the major portion of the metabolite of DDT observed in the study areas was p,p'-DDE. This is also significant during dry season, because of the aerobic conditions of the soils, the active oxidative transformation of p,p'-DDT to p,p'-DDE was facilitated. The significant levels of p,p'-DDE in the coastal and estuarine sediments may be attributed to the various kinds of degradation of DDT to DDE in the estuarine environment. The physico-chemical characteristics of the estuarine sediments are considered to be of great importance towards the degradation of DDT to DDE. The rate of degradation of DDT to DDE was found to be directly proportional to the increase in temperature, moisture and microbial activities in soil (Mitra and Reghu, 1998). The presence of different kinds of marine organism (e.g. benthic) is expected to be highly responsible for the biodegradation of DDT to DDE (Sarkar and Sen Gupta, 1987). The chemical characteristics of estuarine sediments such as pH, salinity, clay mineral concentrations, organic matter (humic substances) and major elemental concentrations are likely to play important role towards the degradation of DDT to DDE. Vu Duc et al. (1993) also made the same observations, that the p,p'-DDE was the major metabolite of ∑DDT in paddy field soils of Vietnam. Dang et al. (1998), while studying the organochlorine pesticides in sediments of Red River delta, North Vietnam, found that the majority of DDT present was p,p'-DDE. These results highlight the known stability and persistence of DDE in the environment. High concentrations of p,p'-DDE compared to p,p'-DDT in sediments (Figure 5.2) are also likely to reflect the enhanced transport of DDE from the terrestrial to the aquatic environment by surface runoff, due to the higher water solubility of p,p'-DDE (1.3×10^{-4} mol m^{-3}) in comparison with that of p,p'-DDT (8.5×10^{-6} mol m^{-3}) (Calamari et al., 1991). The high levels of p,p'-DDE observed in zone 2 is primarily due to the residual deposition of DDE to the sediments for the last so many years. Relatively lower levels of DDE concentration in zone 3 may be explained by the nature of sediment (Table 3.7) and the lower amount of organic carbon (Figure 3. 5) present in that zone.

Mohamed and Mohamed (1985a) observed the presence of p,p'-DDE in sediments from Mediterranean Sea at Port-Said and the concentrations ranged from 95.5 to 600 µg kg^{-1} and found that p,p'-DDE was the major metabolite of DDT present in that area. Sarkar and Sen Gupta (1987) reported that the major portion of the contamination in sediments from the Arabian Sea along the central west coast of India was p,p-DDE and the values ranged between ND levels to 47.6 ng g^{-1} wet weight. Tkalin (1996) observed p,p'-DDE in coastal bottom sediments of Japan sea and the values ranged from <0.1 to 5.9 ng g^{-1} Williams et al. (1997) observed a concentration of <0.1 mg kg^{-1} of p,p'-DDE in the inshore sediments of Mombassa, Kenya. Dang et al. (1998) reported values ranging from 1.52 to 10.17 ng g^{-1} of p,p'-DDE in the sediments of Red River delta, North Vietnam. Cavanagh et al. (1999) reported p,p'-DDE concentrations in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from <0.005 to 6.217 ng g^{-1} in Herbert region and <0.005 to 19.9 ng g^{-1} in Burdekin region. In almost all the above studies, p,p'-DDE was found to be the major metabolite among the total DDTs, and almost comparable observations were made in the sediments of Kuttanad backwaters also. Huasheng Hong et al. (1999) observed slightly lower levels of p,p'-DDE, compared with other metabolites of DDT, in the surface sediments of Pearl River estuary and the values ranged from 0.21 to 1.44 ng g^{-1}

5.3.2.2. Distributions of p,p'-DDD in sediments

The sediment samples collected from all stations in the study area were found to contain detectable levels of p,p'-DDD. Next to p,p'-DDE, 10 to 21 percentage of p,p'-DDD was observed in all most all stations of the study area (Figure 5.2). The station wise annual mean variations of p,p'-DDD in sediments are shown in Figure 5.4. At stations 1 to 3, the p,p'-DDD values were almost same and the highest value of p,p'-DDD was recorded at station 7 Stations 8 and 9 recorded lower values of p,p'-DDD than that of other stations. The minimum value of 0.13 ng g^{-1} of p,p'-DDD was observed at station 1, and the highest value of 90.67 ng g^{-1} was recorded at station 7 in sediments of the study area (Table 5.4). The station wise mean values of p,p'-DDD in sediments ranged from 9.71 ng g^{-1} to 50.38 ng g^{-1} (Table 5.4).

The station wise seasonal mean variations of p,p'-DDD in sediments are plotted in Figure 5.4. A distinct seasonal variation was observed in the distributions of p,p'-DDD in all stations. Like that of water, the values of p,p'-DDD in sediments in pre-monsoon season, were higher than that of other seasons. The p,p'-DDD values of monsoon season were lower than that of other seasons. At station 7, pre-monsoon recorded highest value of p,p'-DDD than that of other seasons.

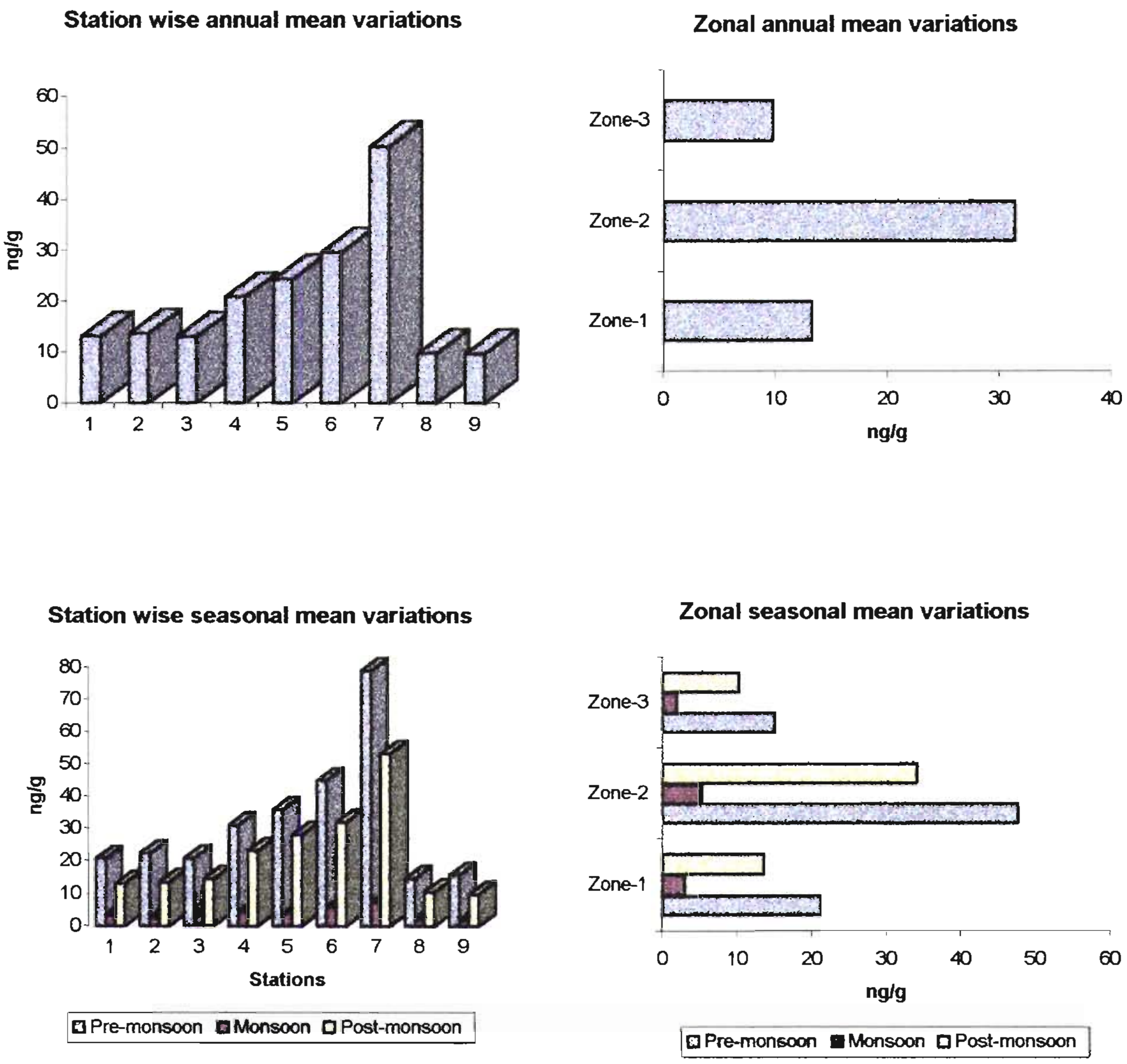
The annual zonal mean variations and zonal seasonal variations are also illustrated in Figure 5.4. Higher values of p,p'-DDD were observed in zone 2 and lower values in zone 3. In zone 3, the p,p'-DDD values were lower than that of zone 1. From the zonal seasonal variations graph (Figure 5.4), it is clear that zone 2 recorded maximum values of p,p'-DDD than in other seasons. Here also the monsoon values were lower than that of other seasons.

Richard (1976) observed that the conversion of p,p'-DDT into p,p'-DDD take place rapidly under anaerobic conditions. Corona-Cruz et al. (1999) also observed the anaerobic dechlorination of DDT to DDD. Johnson (1976) also observed that the anaerobic metabolism of p,p'-DDT in the biota leads to the formation of p,p'-DDD. Higher values of p,p'-DDD was observed in zone 2 of the study area because of the

Table 5.4 Station wise summary statistics of p,p'-DDD in sediments
(ng g^{1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	0.13	24.65	13.08	8.92	68.20
2	0.16	24.90	13.64	8.91	65.32
3	0.17	24.65	13.06	8.17	62.51
4	0.26	32.98	20.96	12.09	57 70
5	0.35	38.90	24.49	13.96	56.98
6	0.46	45.76	29.73	17.39	58.50
7	0.99	90.67	50.38	32.64	64.79
8	0.25	18.65	9.74	6.17	63.29
9	0.23	19.56	9.71	6.68	68.78

SD - Standard deviation; CV - Coefficient of variation



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Figure 5.4 Seasonal and spatial distributions of p,p'-DDD in sediments (ng g^{-1} dry wt.)

constant rains during the wet season coupled with the anaerobic conditions of the soils in that area. Apart from the anaerobic condition of the soil, the degradation of p,p'-DDT to p,p'-DDD is controlled by various factors such as the climatic conditions, soil properties and the soil pH. According to Patil et al. (1972), 35 of 100 microbials isolated from miscellany of sources, including open ocean water, surface films and sediments, could degrade p,p'-DDT to p,p'-DDD which was the main metabolite. The reductive dechlorination of DDT to DDD was favoured under anaerobic conditions (Wedemeyer, 1967; Baxtor, 1990). The higher value of p,p'-DDD observed at station 7 may be due to the higher anaerobic conditions prevailing in that area. Vu Duc et al. (1993) while studying the residue levels of organochlorines in tropical and sub tropical countries, found that the p,p'-DDD levels in paddy field samples of Vietnam had a concentration below p,p'-DDE and above p,p'-DDT

Mohamed and Mohamed (1985a) reported the presence of p,p'-DDD in sediments of Mediterranean Sea at Port-Said and the concentrations of p,p'-DDD ranged from 110 to 400 µg kg^{-1} Sarkar and Sen Gupta (1987) reported the levels of p,p'-DDD below the detection limit in sediments of Arabian Sea, along the central west coast of India and they suggested that the conversion of p,p'-DDT to p,p'-DDD is very insignificant in marine sediments. Jabbar et al. (1993) quantified the levels of p,p'-DDD in soils in Punjab, Pakistan and the values ranged from traces to 0.002 ppm. Tkalin (1996) reported p,p'-DDD values in the range <0.1 to 12.0 ng g^{-1} in coastal bottom sediments of Japan Sea. Dang et al. (1998) while quantifying the levels of organochlorines in sediments of Red River delta, North Vietnam, reported values between 0.40 and 3.23 ng g^{-1} of p,p'-DDD. Cavanagh et al. (1999) reported p,p'-DDD concentrations in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from <0.005 to 0.031 ng g^{-1} in Herbert region and <0.005 to 0.313 ng g^{-1} in Burdekin region. Huasheng Hong et al. (1999) reported p,p'-DDD in the surface sediments of Pearl River estuary and the values ranged from 0.41 to 3.52 ng g^{-1}

5.3.2.3. Distributions of p,p'-DDT in sediments

More or less a slight increasing trend was observed for p,p'-DDT from stations 1 to 7, and then decreased to station 9 (Figure 5.5). The station wise summary statistics of p,p'-DDT in sediments are included in Table 5.5. A minimum

Table 5.5 Station wise summary statistics of p,p'-DDT in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	0.65	22.53	12.79	7.44	58.16
2	0.56	25.36	14.27	7 76	54.41
3	0.46	25.35	15.20	8.21	54.02
4	0.24	31.54	17.97	10.98	61 13
5	0.14	36.54	19.37	12.60	65.06
6	0.19	41.56	23.45	14.14	60.32
7	0.25	36.56	26.47	14.56	55.01
8	0.11	12.65	6.72	3.81	56.72
9	0.11	8.98	5.42	3.10	57.15

SD - Standard deviation; CV - Coefficient of variation

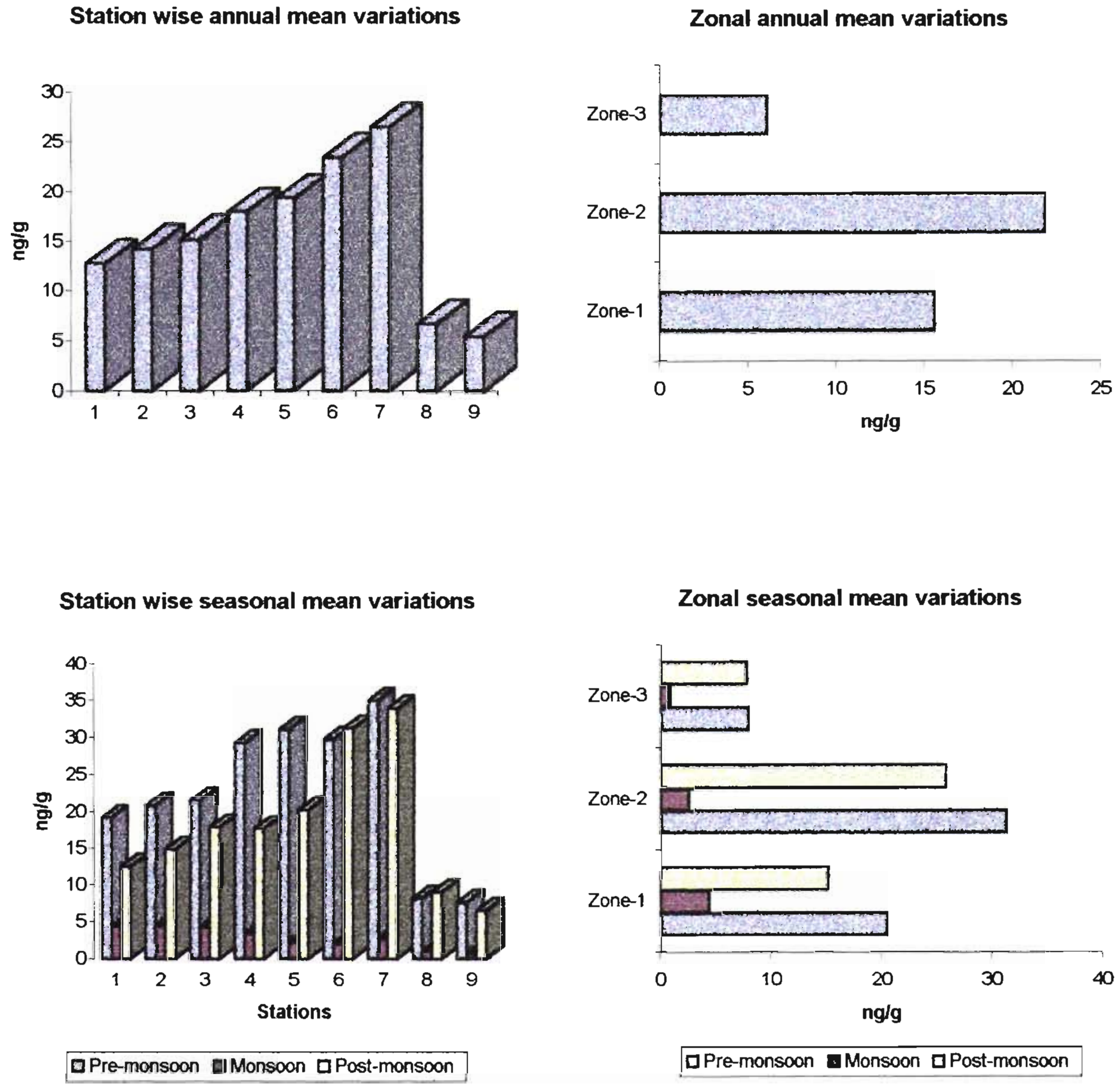


Figure 5.5 Seasonal and spatial distributions of p,p'-DDT in sediments (ng g^{-1} dry wt.)

value of 0.11 ng g^{-1} of p,p'-DDT was observed at stations 8 and 9 in sediments. A maximum value of 41.56 ng g^{-1} was observed at station 6 in sediments. The station wise mean value of p,p'-DDT in sediments ranged from 5.42 ng g^{-1} to 26.47 ng g^{-1}

The seasonal mean variations of p,p'-DDT in sediments are also plotted in Figure 5.5. From stations 1 to 5, pre-monsoon values were higher than post-monsoon season. But from stations 6 to 8, post-monsoon values were higher than pre-monsoon values. In all stations, monsoon period recorded lower values than in other seasons. In monsoon, slightly higher values were observed at stations 1 to 3 than in other stations.

The annual zonal mean variations and zonal seasonal mean variations are also included in Figure 5.5. The distribution pattern of p,p'-DDT in three zones showed notable variations and zone 2 recorded slightly higher levels of p,p'-DDT, while zone 3 showed lower values of p,p'-DDT than in other zones. In the zonal seasonal variation, it was observed that in zones 1 and 2, the pre-monsoon values were slightly higher than post-monsoon period, and in zone 3, the post-monsoon values and pre-monsoon values were almost same. In all zones the monsoon values were lower than in other seasons. In monsoon period, slightly higher values were observed in zone 1 than in other zones.

Percentage of p,p'-DDT in $\sum$DDT is slightly greater in zone 1 (stations 1,2,3) than in other zones (Figure 5.2). This slightly higher concentration of p,p'-DDT in these stations suggest the continuous usage of technical DDT formulations for vector-controlling programmes and had a greater influence on sediment contamination in these regions. Lower levels of p,p'-DDT found in the sediments of zone 3 than zone 2 were associated with the sandy nature of sediments and its low organic carbon content. The lower levels of p,p'-DDT may also be attributed to its conversion to p,p'-DDE and p,p'-DDD.

The p,p'-DDT observed in the sediments of Kuttanad backwaters may be from the DDT formulations used for the vector control programmes in Kuttanad and the near by areas. The DDT formulations are widely used in Kerala for the malaria eradication programme and the p,p'-DDT may enter the Kuttanad water system, and thereby to the sediments, through run-off from major river systems. Mohamed and thereby to the sediments, through run-off from major river systems. Mohamed and Mohamed (1985a) observed the presence of p,p'-DDT in sediments of Mediterranean Sea at Port-Said and the concentrations of p,p'-DDT were in the range of 0.2 to 53 µg kg^{-1} Sarkar and Sen Gupta (1987) observed low levels of p,p'-DDT (ND to 4.63 ng g^{-1} wet wt.) in sediments from the Arabian Sea along the central west coast of India. The p,p'-DDT concentrations in coastal bottom sediments of Japan Sea were ranged from <0.1 to 18.1 ng g^{-1} (Tkalin, 1996). The inshore sediments of Mombasa, Kenya had a p,p'-DDT concentration of <0.1 mg kg^{-1} (Williams et al., 1997). Dang et al. (1998) reported values in the range 0.47 to 2.43 ng g^{-1} in sediments of Red River delta, North Vietnam. Cavanagh et al. (1999) reported p,p'-DDT concentrations in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from <0.005 to 0.411 ng g^{-1} in Herbert region and <0.005 to 0.972 ng g^{-1} in Burdekin region. Huasheng Hong et al. (1999) observed slightly higher levels of p,p'-DDT in the surface sediments of Pearl River estuary and the values ranged from 0.48 to 4.03 ng g^{-1}

5.3.3. Distributions of $\sum$HCH in sediments

The percentage compositions of the major isomers of $\sum$HCH viz, α-HCH, β-HCH, γ-HCH and δ-HCH in different stations were depicted in Figure 5.6. Station wise overall mean concentrations of $\sum$HCH in sediments ranged from 30.5 ng g^{-1} to 122.4 ng g^{-1} (Table 5.1). The minimum mean concentration was observed at station 9 and maximum mean concentration was observed at station 7 (Table 5.1). The major HCH isomer observed was β-HCH and more than 64 percentage of this isomer was distributed in the study area. The percentage of α-HCH isomer ranged from 14 to 30 %. The γ-isomer percentage ranged from 4 to 7 % and that of δ-isomer from 0.1 to 0.3 % of $\sum$HCH. At stations 1 to 3, the percentage of α-isomer was found to be slightly greater than that of other stations, and at the same time the percentage of β-isomer was slightly lower in these stations. The overall mean concentrations of the HCH isomers recorded in this study were 12.22 ng g^{-1} of α-isomer, 48.92 ng g^{-1} of β-isomer, 3.86 ng g^{-1} of γ-isomer and 0.14 ng g^{-1} of δ-isomer (Table 5.2).

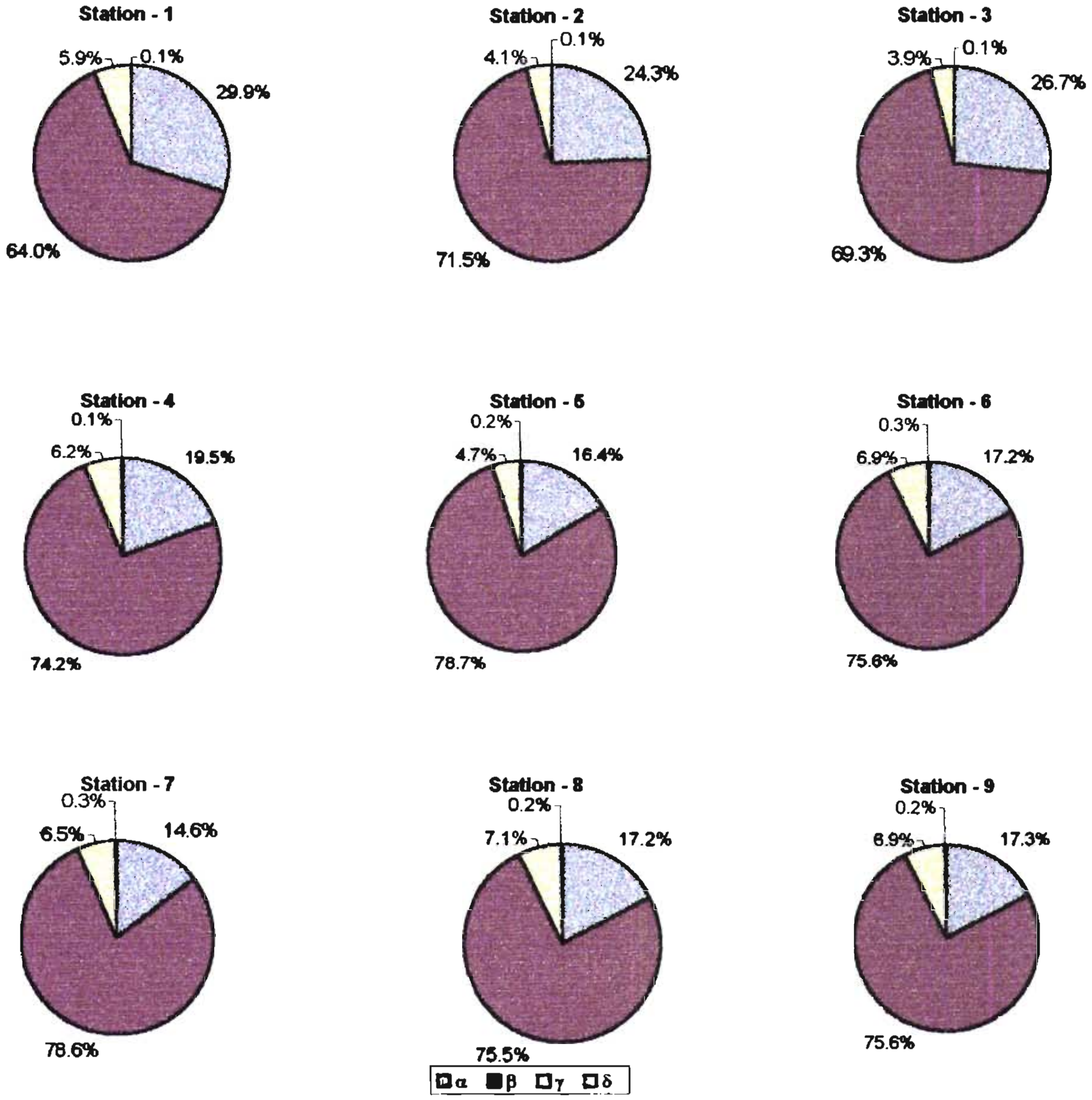


Figure 5.6 Station wise percentage composition of ΣHCH in sediments

The residue levels of isomers of HCH were found to be in the order of β-HCH > α-HCH > γ-HCH > δ-HCH in the backwaters of Kuttanad (Figure 5.6). Vu Duc et al. (1993) had also observed higher levels of β-HCH in the paddy field soil samples from tropical and sub-tropical Asian countries, and the order of abundance of HCH isomers were same as that observed in the present study. The observed levels of HCH isomers in the sediments of the study area may be attributed to the higher application of HCH formulations in agriculture and vector control programmes. It could, therefore, be said that the use of HCHs would cause contamination of soils, despite the fact that HCHs dissipate easily through volatilisation (Takeoka et al., 1991). The recommended dosage of HCH 50 WP (wetable powder) for rice pest control is 2.5 kg per hectare (KAU, 1996). In Kerala, especially in Kuttanad area, higher amounts of HCH formulations were used for rice pest control. Compared to the amounts of HCH applied in Kuttanad area, the residual values of HCH observed in that area was found to be less. Tanabe et al. (1992) reported that 90 percent of the HCH applied to the paddy fields in India dissipated within two weeks through atmospheric transport. This finding tends to support the observed results and these trends should also be taken in account for the observed low levels of HCHs than DDTs. Kawano et al. (1992) observed the ΣHCH residue levels from paddy field of India, and the values ranged from 0.42 ng g^{-1} to 280 ng g^{-1} These results are found to be comparable with the present study because both studies are based on the sediments of paddy field. While studying the organochlorine residues in tropical and sub-tropical countries, Vu Duc et al. (1993) reported ΣHCH concentrations from Vietnamese paddy field and upland soil samples ranged from 0.15 ng g^{-1} to 55 ng g^{-1} and from 0.09 ng g^{-1} to 2.5 ng g^{-1} respectively. The same author also reported that the concentrations of ΣHCH in Taiwanese soil samples ranged from 0.33 ng g^{-1} to 4.8 ng g^{-1}

Some scanty data on α-HCH and γ-HCH levels on Kuttanad sediments were reported by KWBS (1989). As per their report, in sediments, the concentration vary between 0 and 20000 ng l^{-1} and also reported that the concentration of α-isomer is about 4 to 5 times greater than that of γ-isomer.

Kuwatsuka et al. (1986) reported the HCHs levels in soil samples of Indonesia and the values ranged from 4.9 ng g^{-1} to 18 ng g^{-1} Among the organochlorine pesticides detected in the sediments from the Arabian Sea along the central west coast of India, HCH was found to be detected in almost all sediment samples and its concentration ranged between 0.44 and 17.9 ng g^{-1} (Sarkar and Sen Gupta, 1987). A mean value of 5 ng g^{-1} ΣHCH was reported from the coastal bottom sediments, Seto Inland Sea, Japan (Tanabe et al., 1989). Iwata et al. (1994) reported values in the range 4.5 to 6.2 ng g^{-1} of ΣHCH from sediments of Osaka Bay. Hong et al. (1995) reported values ranging from ND levels to 2.3 ng g^{-1} of HCHs from the sediments of Victoria Harbour, Hong Kong. HCHs values in the range 0.14 ng g^{-1} to 1.12 ng g^{-1} were reported from the sediments of Xiamen Western Bay, PRC (Hong et al., 1995). Norena-Barroso et al. (1998) reported values ranging from 0.76 to 6.77 ng g^{-1} in the sediments from Bay of Chetumal, Mexico. Huasheng Hong et al. (1999) observed HCHs in the surface sediments of Pearl River estuary and the values of ΣHCH ranged from 0.28 to 1.23 ng g^{-1}

5.3.3.1. Distributions of α-HCH in sediments

Unlike that of water, the concentrations of α-HCH were comparatively lower in the sediments of Kuttanad backwaters. The station wise annual mean variations of α-HCH in sediments are illustrated in Figure 5.7 From the annual mean variations plot (Figure 5.7), it was observed that in the first three stations, the distributions of α-isomer were more or less the same. A slight increase in the concentrations of α-isomer from stations 4 to 7 and a decrease in the concentrations of this isomer from stations 8 to 9 was observed. The station wise summary statistics of α-HCH in sediments is given in Table 5.6. A lowest value of 0.23 ng g^{-1} was observed at stations 2 and 3 and a maximum value of 43.23 ng g^{-1} was observed at station 6 (Table 5.6). The station wise mean values of α-isomer ranged from 5.27 ng g^{-1} to 18.08 ng g^{-1} (Table 5.6). The overall mean value of 12.22 ng g^{-1} of α-isomer was recorded in the study area (Table 5.2).

Comparatively higher values of α-isomer were observed in pre-monsoon period than in other seasons (Figure 5.7). Lower values of α-isomer were observed in monsoon period. The highest values of α-isomer were observed at stations 6 and 7 of pre-monsoon period. The zonal annual mean variations and zonal seasonal mean variations are also plotted in Figure 5.7 From the annual mean variations

Table 5.6 Station wise summary statistics of α - HCH in sediments

(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	0.35	23.4	11.69	9.27	79.31
2	0.23	21.45	10.12	8.20	81.05
3	0.23	23.45	10.09	8.63	85.45
4	0.44	33.56	15.07	10.74	71.26
5	0.37	35.65	15.82	11.85	74.91
6	0.47	43.23	18.08	14.59	80.69
7	0.55	41.45	17.90	12.68	70.84
8	0.26	12.54	5.74	3.87	67.38
9	0.36	11.89	5.27	3.88	73.70

SD - Standard deviation; CV - Coefficient of variation

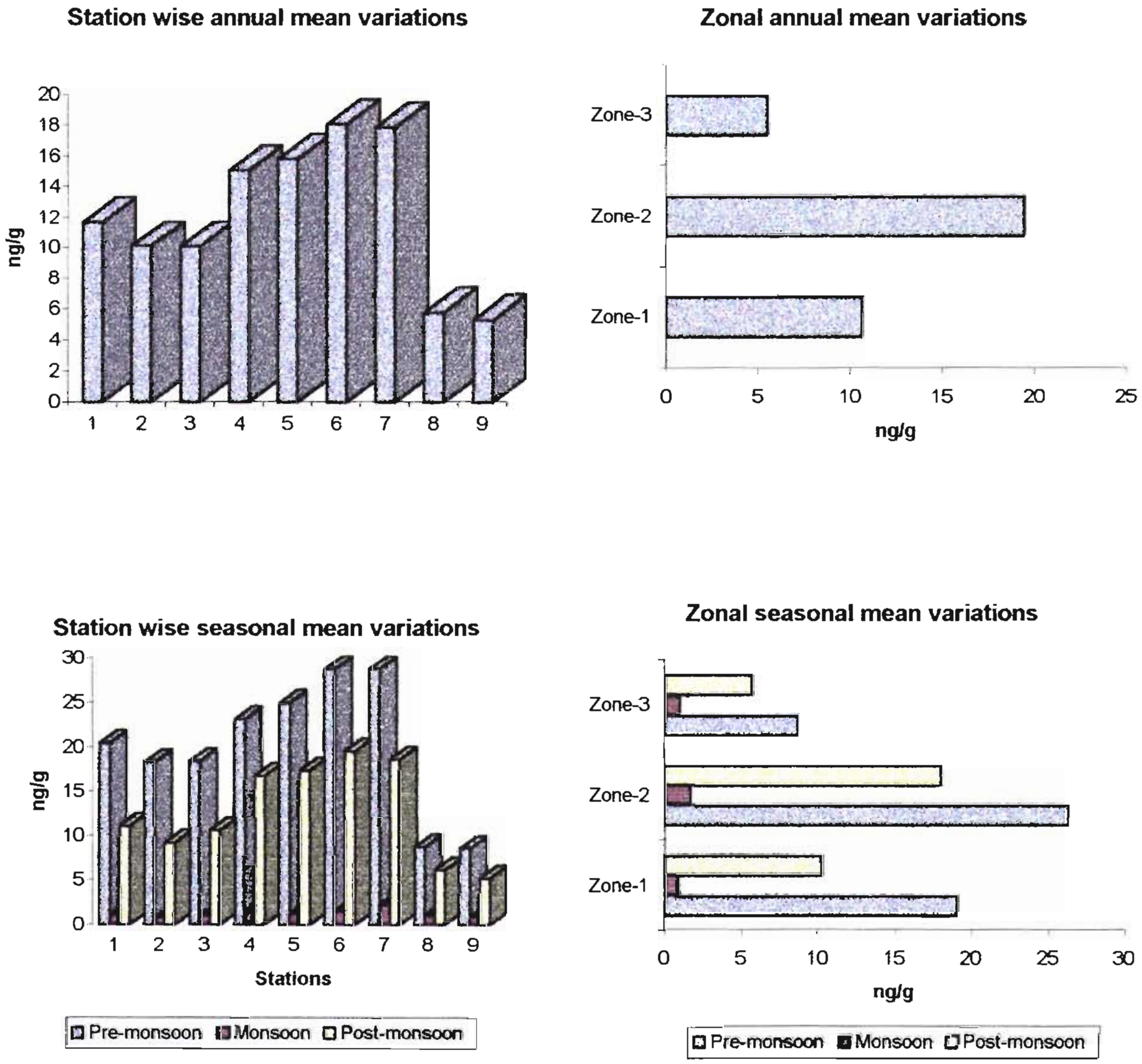


Figure 5.7 Seasonal and spatial distributions of α-HCH in sediments (ng g^{-1} dry wt.)

(Figure 5.7), it was observed that zone 2 recorded higher values of α-isomer than in other zones. Zone 3 recorded lower values of α-HCH than in other zones. In zonal seasonal variations, it was observed that in all zones, the maximum values of α-isomer recorded were in pre-monsoon season. In all zones, monsoon periods recorded lower values of α-isomer than in other seasons. The post-monsoon values of α-isomer in all zones were lower than pre-monsoon values.

Hydrocarbons that enter the aquatic environment rapidly become associated with sediments and suspended particulates (Means et al., 1980 (a)(b); Nau-Ritter and Wurster, 1983). Many researchers have demonstrated that the sorption of hydrocarbons is directly related to the organic content of the sediments (Boehm and Farrington, 1984; Karickhoff, 1984; Galassi and Migliavacca, 1986). The sorption of pesticides to sediment is also related to the organic content and the size composition of the sediments. The bulk of the pesticides applied are adsorbed and retained on the soil during irrigation (Watanabe et al., 1984). The variations in the distributions of pesticides found in different stations may have some influence on the above factors. The α-isomer has higher water solubility and vapour pressure than β-isomer (Table 4.2), and due to these reasons this isomer has a tendency to volatilise more than β-isomer. The volatilisation of pesticides from soil increased with the concentration of the pesticide (Haris and Lichtenstein, 1961). These observations were significant because in technical HCH, the major portion is α-HCH, and it may have a tendency to volatilise more than that of other isomers of HCH. This may be a reason for the lower level of α-isomer in sediments than β-isomer.

Tkalin (1996) reported the α-HCH concentration from the coastal bottom sediments of Japan sea and the values ranged from <0.1 to 10.2 ng g^{-1} Dua et al. (1996) observed 6.2% to 18.5% of α-HCH in total HCH from the sediments of rural ponds of India. Williams et al. (1997) observed <0.1 mg kg^{-1} of α-HCH in inshore sediments of Monbasa, Kenya. Everaarts et al. (1998) reported α-isomer concentrations in sediments from the coastal zone and continental zone of Kenya and the values ranged from 0.4 to 17.9 ng g^{-1} Cavanagh et al. (1999) reported α-HCH concentrations in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from 0.006 to 6.23 ng g^{-1} in Herbert region and

<0.005 to 0.204 ng g^{-1} in Burdekin region. Huasheng Hong et al. (1999) reported the presence of α-HCH in the surface sediments of Pearl River estuary and the values ranged from 0.03 to 0.38 ng g^{-1}

5.3.3.2. Distributions of β-HCH in sediments

β-HCH is the most persistent isomer of technical HCH and degrade slowly from the environment. Among the isomers of HCH, β-HCH is the major isomer distributed in the sediments of Kuttanad backwaters, and the overall mean concentration was 57 12 ng g^{-1} (Figure 5.6 and Table 5.2). The β-isomer values at stations 1 to 3 were almost constant and from stations 4 to station 7, the values were increasing, and at station 7 maximum values were observed (Figure 5.8). At stations 8 and 9, the values were decreasing in nature. The lowest value of 3.45 ng g^{-1} was observed at station 1 and the maximum value of 140.43 ng g^{-1} was observed at station 7 (Table 5.7). The station wise mean values of β-isomer ranged from 25.0 ng g^{-1} to 96.24 ng g^{-1}

From the station wise seasonal mean variations (Figure 5.8), it was observed that at all stations, the pre-monsoon values were higher than in other seasons. Compared to other seasons, monsoon season recorded lower values of β-HCH. Post-monsoon recorded slightly lower values of β-HCH than in pre-monsoon period. In station wise seasonal variations (Figure 5.8), a clear seasonal dependence on the distributions of β-HCH was observed.

The annual zonal mean variations and zonal seasonal mean variations are also plotted in Figure 5.8. Higher values of β-HCH were observed in zone 2 and almost comparable values were observed in zones 1 and 3. Higher values of β-isomer were observed in pre-monsoon period in all zones. High values of β-isomer were recorded in zone 2 for both pre-monsoon and post- monsoon periods.

The organochlorine compounds have a high affinity to the soil and are retained in the sediment (Corona-Cruz et al., 1999). Enhanced percentage of β-HCH concentrations suggests the accumulation of this isomer in the aquatic environment and it eventually trapped in sediments. Vu Duc et al. (1993) had also got higher

Table 5.7 Station wise summary statistics of β - HCH in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	3.45	32.65	25.00	9.08	36.31
2	7.49	42.45	29.74	12.02	40.43
3	6.73	43.41	26.25	12.37	47 12
4	7.34	82.45	57.23	26.83	46.89
5	12.45	112.80	76.12	33.34	43.80
6	14.63	112.50	79.57	35.66	44.81
7	18.53	140.43	96.24	42.11	43.75
8	4.78	39.67	25.21	11.54	45.78
9	4.67	42.87	23.06	10.72	46.51

SD - Standard deviation; CV - Coefficient of variation

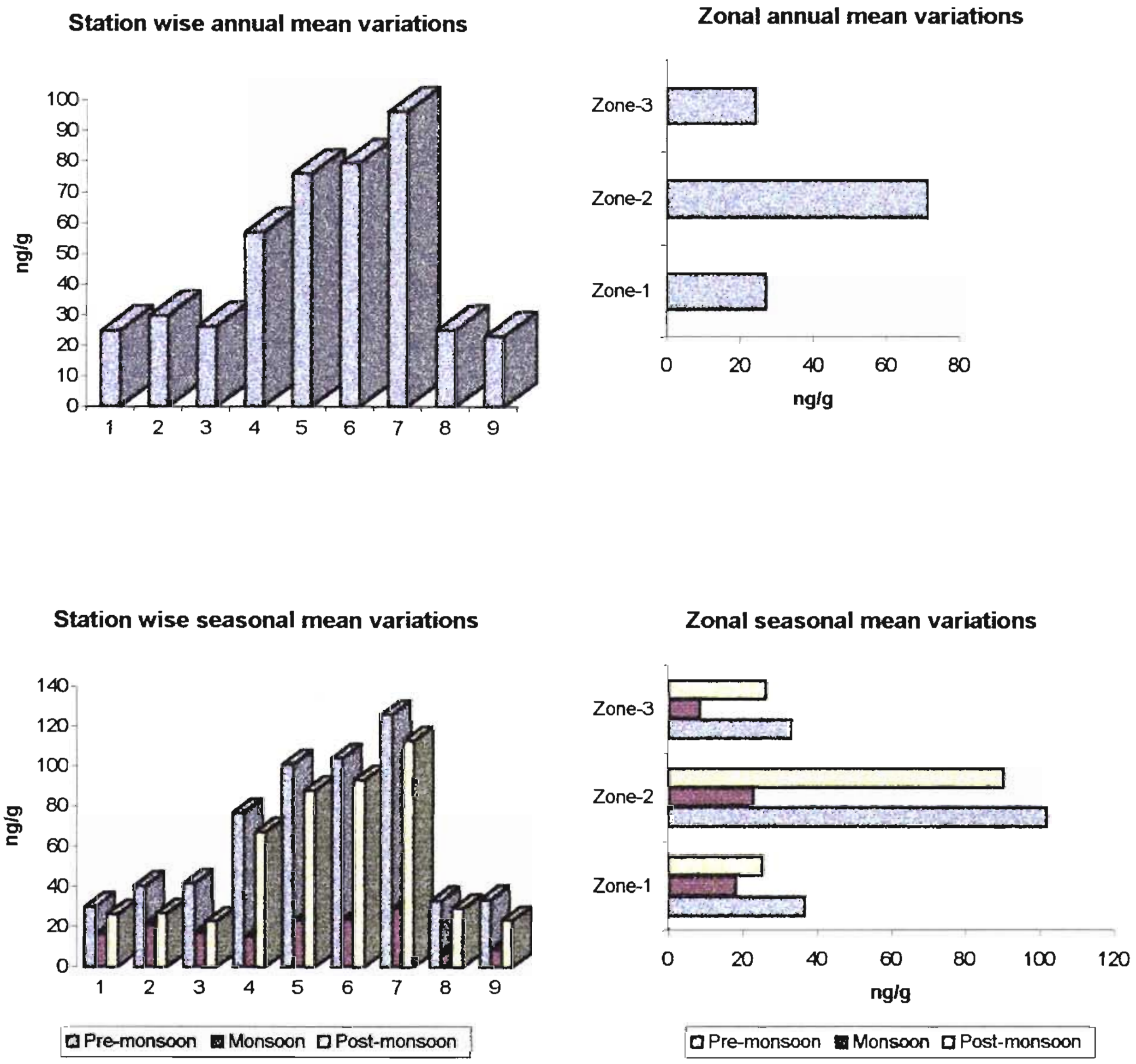


Figure 5.8 Seasonal and spatial distributions of β-HCH in sediments (ng g^{-1} dry wt.)

levels of β-HCH in the paddy field soil samples from tropical and sub-tropical Asian countries, and the order of distribution of HCH isomers was same as observed in the present study. Dua et al. (1996) also observed higher levels of β-isomer in the sediments of rural ponds of India, and the percentage of β-isomer ranged between 49.03 to 71.7 %. In technical HCH, the proportion of β-HCH is less than that of α and γ isomers (Brooks, 1976; Remesh et al., 1989). Even though the proportion of β-isomer is less, sediment samples contained higher levels of β-HCH and this could be explained mainly by the physico-chemical properties of β-HCH. Among the isomers of HCH, the β-isomer has the lowest water solubility and vapour pressure but is most stable and is relatively resistant to microbial degradation (Bachmann et al., 1988). This may be attributed to the higher values of β-isomer observed in the sediments of Kuttanad backwaters. Williams et al. (1997) observed <0.1 mg kg $^{-1}$ of β-HCH in the inshore sediments of Mombasa, Kenya. Cavanagh et al. (1999) reported higher concentrations of β-HCH in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from 0.020 to 45.6 ng g^{-1} in Herbert region and <0.005 to 2.12 ng g^{-1} in Burdekin region, and also, β-isomer concentrations were found to be higher than other isomers of HCH. But, Huasheng Hong et al. (1999) observed slightly lower levels of β-HCH, compared with other isomers of HCH, in the surface sediments of Pearl River estuary and the values ranged from ND levels to 0.33 ng g^{-1}

5.3.3.3. Distributions of γ-HCH in sediments

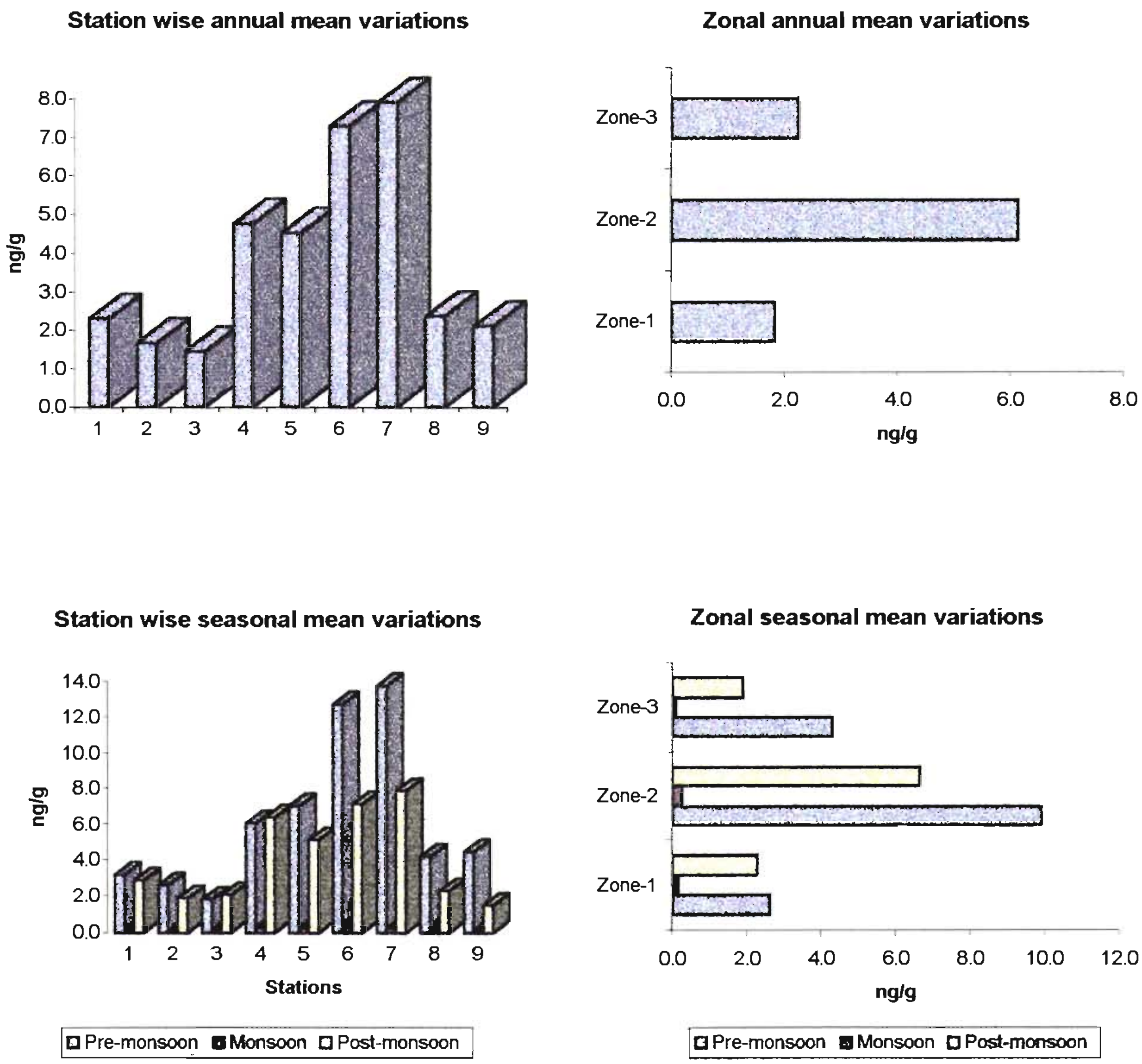
In technical HCH, only the γ-isomer has shown insecticidal property. An overall mean concentration of 3.86 ng g^{-1} of γ-HCH was observed in the study area (Table 5.2). The station wise annual mean variations of γ-HCH in sediments are plotted in Figure 5.9. From stations 1 to 3, the γ-isomer distributions were decreasing slightly, and from stations 4 to 7, the values increased and at stations 6 and 7, higher values were observed (Figure 5.9). The minimum value of 0.08 ng g^{-1} and a maximum value of 24.56 ng g^{-1} were observed (Table 5.8). The station wise mean values of γ-HCH ranged from 1.47 ng g^{-1} to 7.93 ng g^{-1} (Table 5.8).

Table 5.8 Station wise summary statistics of γ - HCH in sediments

(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	0.10	4.56	2.32	1.45	62.73
2	0.09	3.54	1.69	1 11	66.03
3	0.10	2.56	1.47	0.94	63.97
4	0.09	9.11	4.77	2.99	62.69
5	0.10	13.11	4.54	4.41	96.97
6	0.09	22.34	7.30	8.12	111 12
7	0.10	24.56	7.93	8.87	111.89
8	0.09	6.87	2.37	2.42	102.06
9	0.08	7.96	2.11	2.65	125.25

SD - Standard deviation; CV - Coefficient of variation



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Figure 5.9 Seasonal and spatial distributions of γ -HCH in sediments (ng g^{-1} dry wt.)

The seasonal mean variations of γ-HCH are also illustrated in Figure 5.9. Clear seasonal variations were observed for the distributions of γ-isomer in the entire study area. In pre-monsoon, all stations observed higher values of lindane than in other seasons. Monsoon recorded lower values of lindane than in other seasons. In pre-monsoon season, stations 6 and 7 recorded higher values of lindane than in other stations. From the zonal annual mean variations (Figure 5.9), it was observed that higher values of lindane were distributed in zone 2 and lower values in zones 1 and 3. The zonal seasonal mean variations are also included in Figure 5.9. Higher values of lindane were observed in pre-monsoon season in all zones. In all zones, the monsoon values were lower than in other seasons.

Cherif and Wortham (1997), while studying the volatilisation of pesticides from soils, found that 11% of the lindane initially adsorbed on the soil was volatilised after 26 days from the wet soils against 0.8% from the dry soils during the same period and they suggested that this difference is probably due to a soil-water extraction of the lindane adsorbed on the soil or to a competition between water and pesticide molecules for the adsorption sites on soil surfaces. This may be one of the reasons for the lower distribution of γ-isomer in sediments, eventhough the application rate of lindane is higher in the study area. The sediment type may be one reason that in zone 3 (stations 8 and 9), the values of γ-isomer was lower than in zone 2. The accumulation of pesticides in zone 2 is also attributed to the operations of Thanneermukkam bund and the stagnancy of water in pre-monsoon seasons.

Sarkar and Sen Gupta (1988a) reported the γ-HCH in sediments collected along the east coast of India and the values ranged between 0.01 to 0.21 $\mu g\ g^{-1}$ wet weight. The percentage of γ-HCH in the sediments of rural ponds of India ranged from 15.68% to 24.1% (Dua et al., 1996). But in the present study, the percentage of γ-isomer was found to be less and it may be due to the difference in the location of the area, climatic conditions and the difference in usage of the pesticide. The lindane concentrations ranged from 0.025 to 0.62 $ng\ g^{-1}$ from the sediments of Red River delta, Vietnam (Dang et al., 1998). Cavanagh et al. (1999) reported the levels of γ-HCH in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from <0.005 to 3.99 $ng\ g^{-1}$ in Herbert region and

<0.005 to 0.849 ng g^{-1} in Burdekin region. Huasheng Hong et al. (1999) reported γ-HCH concentrations in the surface sediments from Pearl River estuary, and the values ranged from 0.04 to 0.38 ng g^{-1}

5.3.3.4. Distributions of δ-HCH in sediments

δ-HCH distributions in the study area were comparatively lower than that of other isomers of HCH. The station wise annual mean variations of δ-isomer are illustrated in Figure 5.10. The station wise summary statistics of δ-isomers are included in Table 5.9. Lower values of δ-isomer were observed at stations 1 to 3. From stations 4 to 7, the values were increasing gradually and at station 7 maximum value was observed. Minimum values of non-detectable levels of δ-isomer were observed in all stations. The maximum value of 0.95 ng g^{-1} of δ-isomer was observed at station 7 The station wise mean values of δ-isomer ranged from 0.04 to 0.35 ng g^{-1} (Table 5.9).

The station wise seasonal mean variations are also plotted in Figure 5.10. Relatively higher values of δ-isomer were observed in pre-monsoon season. In monsoon, non-detectable levels of δ-isomer were observed in all stations. In post-monsoon, the first three stations recorded lower levels of δ-isomer and in other stations, except at station 9, the post-monsoon values were lower than pre-monsoon values.

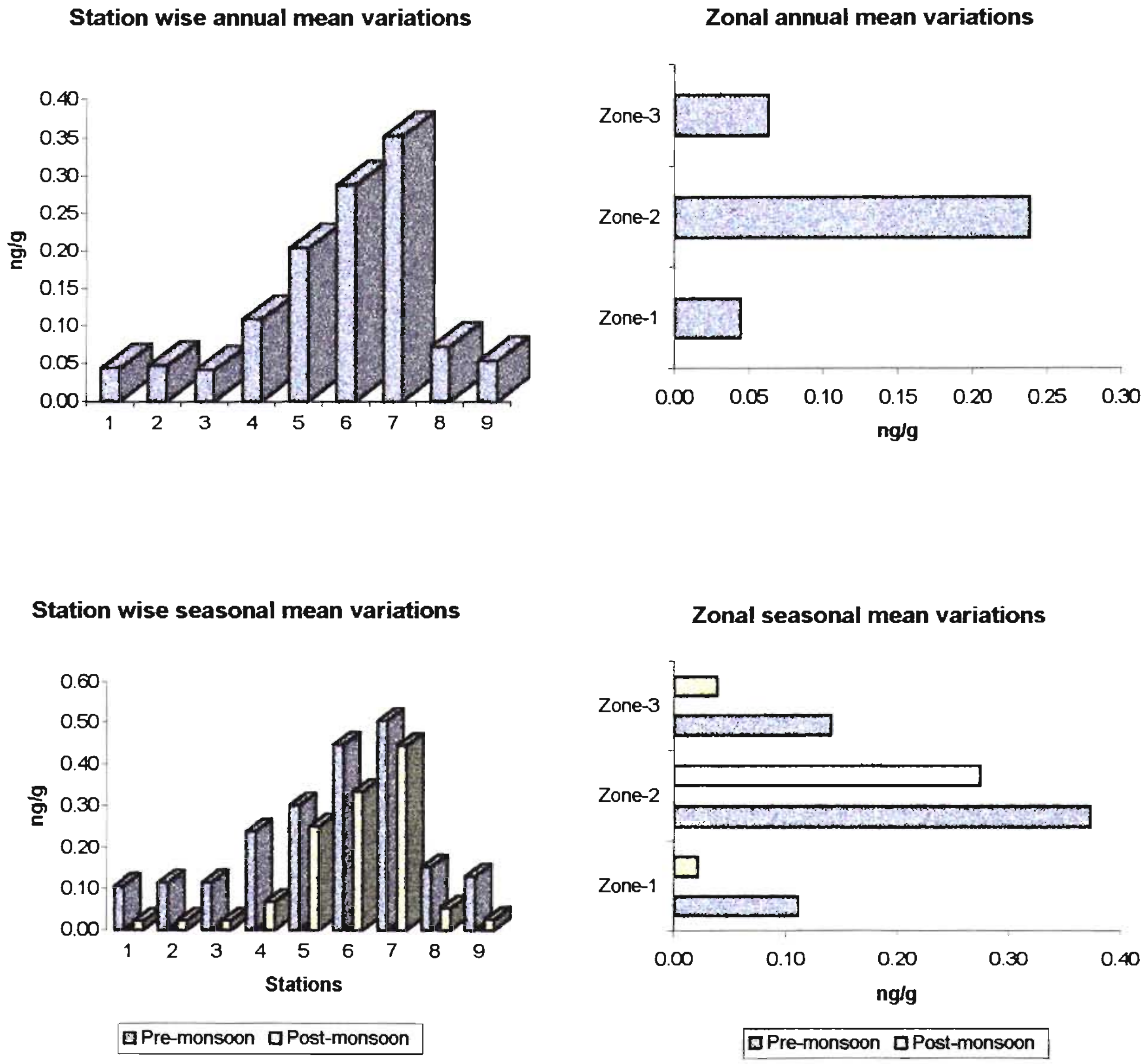
From the zonal annual mean variations (Figure 5.10), relatively higher levels of δ-isomer were noticed in zone 2 than in other zones. Zone 1 recorded the lower levels of δ-isomer. In the zonal seasonal mean variation, it was noted that both in pre-monsoon and post-monsoon periods, higher levels of δ-isomer were observed in zone 2, and the pre-monsoon values were higher than post-monsoon. All zones were free from δ-isomer in monsoon period.

The sediment type greatly influences not only the persistence and activity of pesticides in soils but also the rate at which they are converted into other chemicals. Solubility also affects the persistence of pesticides in the sediments. The soluble

Table 5.9 Station wise summary statistics of δ - HCH in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.11	0.04	0.05	123.71
2	ND	0.12	0.05	0.06	123.75
3	ND	0.13	0.04	0.06	139.12
4	ND	0.45	0.11	0.13	123.90
5	ND	0.41	0.20	0.15	74.09
6	ND	0.65	0.29	0.21	72.92
7	ND	0.95	0.35	0.29	82.14
8	ND	0.20	0.07	0.08	111.05
9	ND	0.18	0.05	0.07	127.70

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Monsoon - Non detectable

Figure 5.10 Seasonal and spatial distributions of δ -HCH in sediments (ng g^{-1} dry wt.)

pesticides are generally leached out much more readily from soils. δ-isomer has a greater solubility in water than that of the other isomers of technical HCH, and leached much more readily and as a result, its concentration in sediments is less than that of other isomers of HCH.

Cavanagh et al. (1999) reported δ-HCH concentrations in soils and sediments of Herbert and Burdekin River regions, North Queensland, and the values ranged from 0.005 to 2.77 ng g^{-1} in Herbert region and <0.005 to 0.038 ng g^{-1} in Burdekin region. Huasheng Hong et al. (1999) observed the presence of δ-HCH in the surface sediments from Pearl River estuary, and the values ranged from ND levels to 0.49 ng g^{-1} In the above studies, the value of δ-isomer was found to be lower than the other isomers of HCH and these observations are in full agreement with the findings of present study.

5.3.4. Distributions of ∑cyclodienes in sediments

∑cyclodienes, in this study, include α-endosulfan, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin and endrin aldehyde. The percentage compositions of ∑cyclodienes are shown in Figure 5.11. The station wise overall mean concentrations of ∑cyclodiene values, in the study area, ranged from 0.83 ng g^{-1} to 5.02 ng g^{-1} (Table 5.1). Higher values of cyclodienes were found from stations 5 to 7 and the highest value was recorded at station 7 The overall summary statistics of the cyclodienes are included in Table 5.2. The major cyclodiene compound distributed in the study area was endosulfan and the percentage of this compound ranged between 51.2 to 62.1% (Figure 5.11). The percentages of heptachlor and heptachlor epoxide ranged between 1.8 to 7.0% and 7.5 to 16.6% respectively (Figure 5.11). The percentages of aldrin and dieldrin ranged between 1.7 to 4.4 and 12.0 to 26.6%, respectively (Figure 5.11). Lower levels of endrin and endrin aldehyde were also noticed in the study area (ranged between 1.6 to 4.3 and 1.1 to 3.9%) (Figure 5.11).

∑cyclodienes were broadly found to be in the order of α-endosulfan > ∑aldrins (aldrin + dieldrin) > ∑heptachlors (heptachlor + heptachlor epoxide) > ∑endrin (endrin + endrin aldehyde). The individual metabolites of these pesticides in the study area

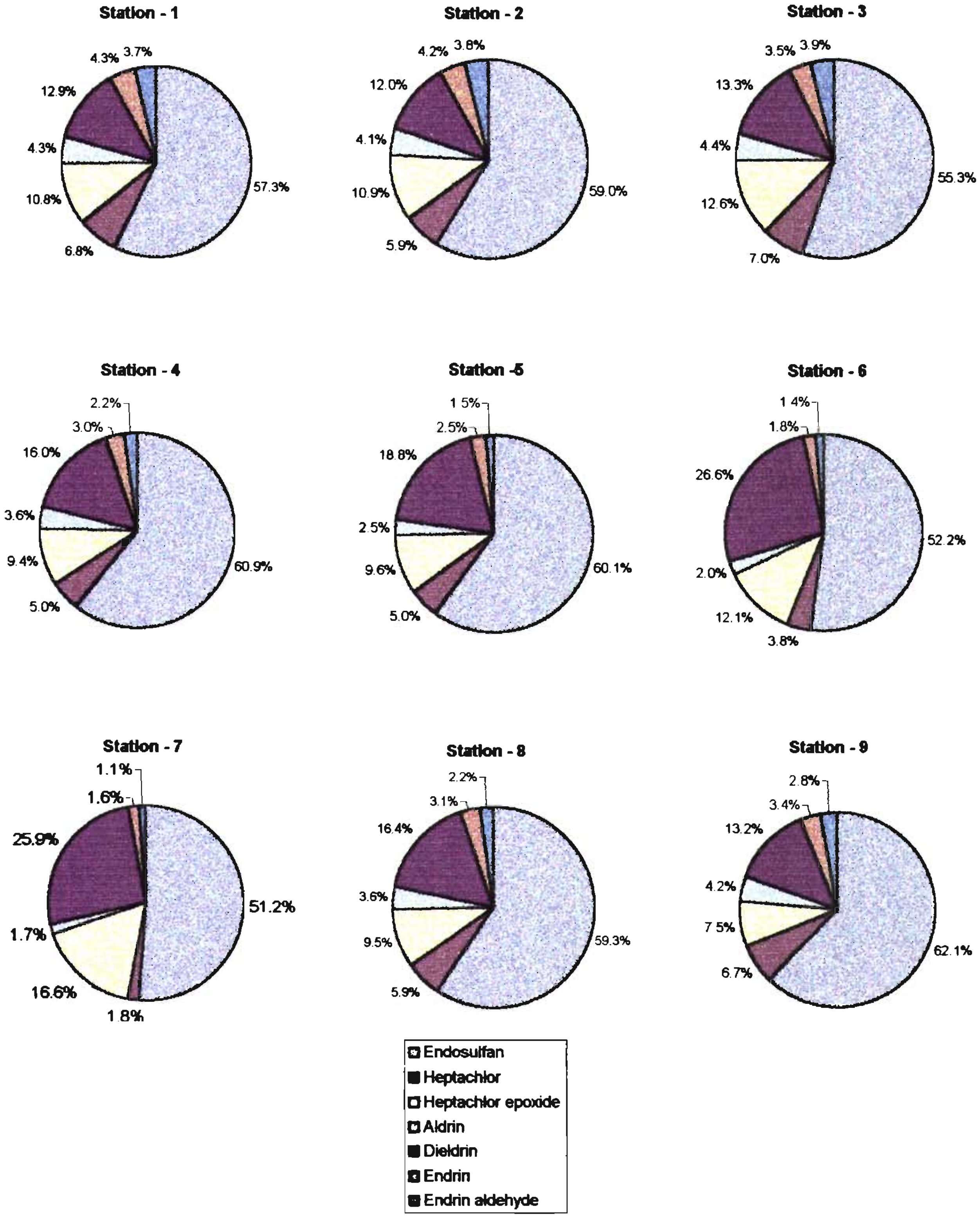


Figure 5.11 Station wise percentage compositions of Σcyclodienes in sediments

were found to be in the order of α-endosulfan > dieldrin > heptachlor epoxide > heptachlor > aldrin > endrin > endrin aldehyde.

Long-lived organochlorine pesticides were prohibited for agricultural use in early 1970's in the advanced nations. But these pesticides are detected even now in field soils (Martijn et al., 1993) and foodstuffs (Yoshida et al., 1992; Mc Dougall et al., 1995). But in developing countries, like India, some of these pesticides are still used, and the use of some others was banned or their use was restricted. The cyclodiene pesticides are still found in the different compartments of the environment, even after the ban of some of these pesticides, and it may be due to the higher persistence of these compounds in the soil environment. The process of epoxidation of cyclodiene pesticides in sterile and non-sterile soils was suggested by Lichtenstein and Schulz (1965). They also suggested the metabolic activity of soils involving the oxidation process leading to the formation of an epoxy ring from the unsaturated CH = CH bond of the less chlorinated ring.

Soil organic matter plays an important role in affecting the fate of pesticides in the soil environment. Thus, the organic carbon content of the sediments affects the partitioning of pesticides in sediments. The lower levels of cyclodiene pesticides in zone 3 compared to zone 2 may be due to the low organic carbon content in that region. The grain size of the sediments also affects the lower levels of cyclodiene pesticides in zone 3 compared to zone 2, because in zone 3 the sandy nature of sediments was prevailing. When the pesticide residues get into the hydrosphere they are partially lost to the atmosphere because of volatilization, partly degraded, partly incorporated into biota, and partly move into the sediment. The same authors highlighted the importance of accumulation of pollutants including pesticides in the sediments, which serve as a habitat for various organisms forming aquatic food chain leading to fish.

Dang et al. (1998) observed that the cyclodiene pesticides including aldrin, dieldrin and endrin were practically absent (below detection limits) in the aquatic environment of the Red river watershed and coastal area, North Vietnam, and they stated that the cyclodienes were never used in significant amounts in North Vietnam.

Norena-Barroso et al. (1998) reported the concentrations of drins (aldrin + dieldrin + endrin) in the sediments from Bay of Chetumal, Mexico in the range of 0.01 ng g^{-1} to 0.59 ng g^{-1} Venkatesan et al. (1999), while studying the chlorinated hydrocarbon pesticides in the sediment cores from San Francisco Bay, observed that the cyclodiene compounds vary from 8 to 21% of the total pesticides in Richardson Bay. The low values of cyclodienes reported in the sediments of the study area may be attributed to the fact that the use of these pesticides were banned or restricted for agriculture except endosulfan.

5.3.4.1. Distributions of α-endosulfan in sediments

Among the cyclodiene compounds observed in Kuttanad backwaters, the major portion of the cyclodiene compound found was α-endosulfan. An overall mean value of 1.17 ng g^{-1} of α-endosulfan was found in the study area (Table 5.2). The station wise annual mean variations of α-endosulfan in the sediments are illustrated in Figure 5.12. Lower values of endosulfan were observed in the first three stations. From stations 4 to 7, the values of endosulfan were increasing gradually, and at stations 8 and 9, again lower values were recorded. The station wise summary statistics of α-endosulfan is included in Table 5.10. Minimum of ND levels to a maximum of 5.45 ng g^{-1} of endosulfan was observed in the study area. The highest value of 5.45 ng g^{-1} of endosulfan was observed at station 7 The station wise annual mean values of endosulfan in sediments ranged from 0.48 ng g^{-1} to 2.57 ng g^{-1}

The seasonal mean variations of endosulfan are also shown in Figure 5.12. At stations 1 and 2, the post-monsoon values were higher than pre-monsoon values. In monsoon the endosulfan values were lower than that in other seasons. In monsoon, season, no endosulfan was detected in the months, July and September. The annual zonal mean variations and zonal seasonal mean variations of endosulfan are plotted in Figure 5.12. Higher values of endosulfan were observed in zone 2 and lower values in zone 1. Pre-monsoon values in zones 2 and 3 were higher than that of other seasons, but in zone 1, the pre-monsoon and post-monsoon values were almost same. In all zones, monsoon period recorded the lowest values of endosulfan.

Table 5.10 Station wise summary statistics of α - endosulfan in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.99	0.48	0.28	59.72
2	ND	0.90	0.55	0.30	55.36
3	ND	0.89	0.49	0.28	56.74
4	ND	2.13	1.02	0.72	69.96
5	ND	3.54	1.66	1.30	78.43
6	ND	4.56	2.01	1 71	84.69
7	ND	5.45	2.57	2.14	83.35
8	ND	1.88	0.93	0.60	64.87
9	ND	1.32	0.79	0.48	60.89

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected

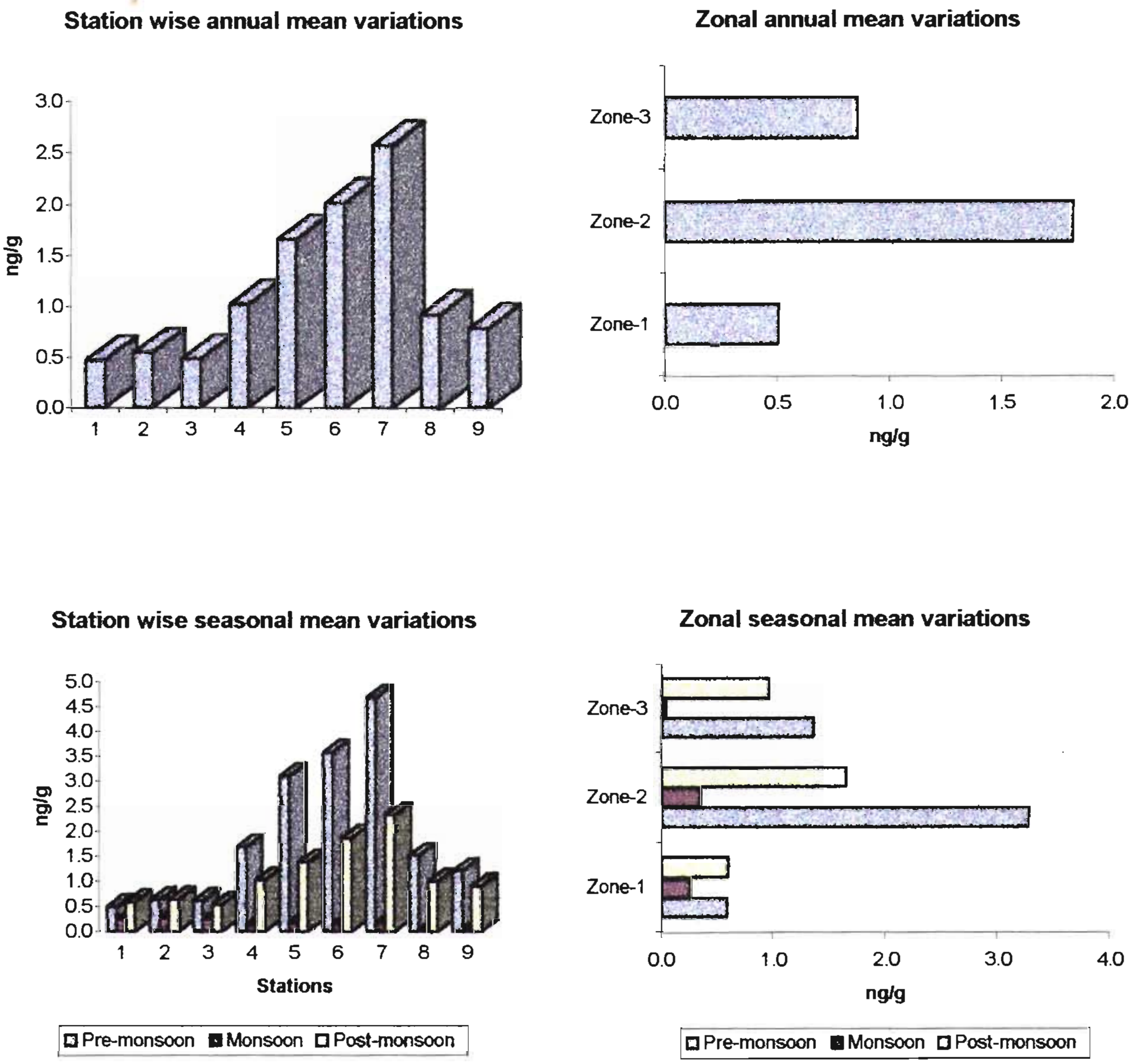


Figure 5.12 Seasonal and spatial distributions of α -endosulfan in sediments (ng g^{-1} dry wt.)

Endosulfan is relatively less persistent (Gopal and Mukherjee, 1993) among the existing organochlorine pesticides, and is used in the control of pests of many crops. The α-endosulfan is known to be undergoing inter-conversion in plants to β-endosulfan (Mukherjee and Gopal, 1994). Williams et al. (1997) reported <0.1 mg kg^{-1} of α-endosulfan from the inshore sediments of Mombasa, Kenya. Norena-Barroso et al. (1998) reported the concentrations of β-endosulfan in the sediments from Bay of Chetumal, Mexico and were in the range of not detectable levels to 0.66 ng g^{-1} Cavanagh et al. (1999) observed low levels of α-endosulfan (<0.005 ng g^{-1}) in soils and sediments of Herbert and Burdekin River regions, North Queensland. Galindo-Reyes et al. (1999) reported very high values of α-endosulfan and the values ranged from 2.6 to 155.02 ng g^{-1} in sediments from Ohuira Bay, Gulf of California.

The station wise variations of endosulfan may also depend on the organic carbon of the sediment and difference in sediment grain size. This may be a reason that stations 8 and 9 (zone 3) were found to contain less levels of endosulfan than stations 6 and 7 (zone 2), because the organic carbon content of zone 3 was found to be less than that of zone 2 and this may also be due to the sandy nature of sediment prevailing in zone 3 (Tables 3. 5 & 3.7).

5.3.4.2. Distributions of heptachlor in sediments

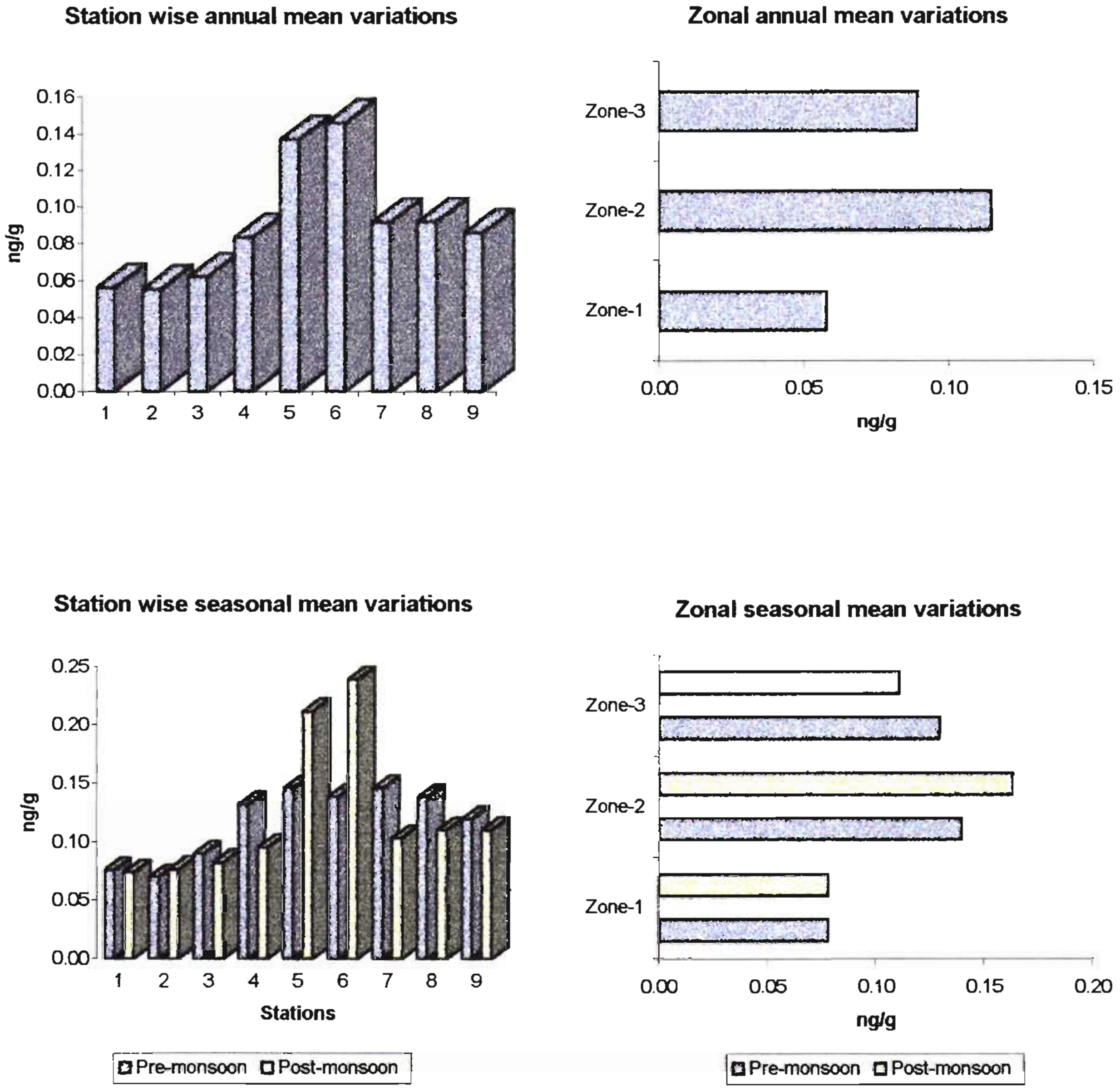
Comparatively lower levels of heptachlor were found in the study area. The station wise annual mean variations of heptachlor in the sediments are plotted in Figure 5.13. Higher values of heptachlor were observed at stations 5 and 6 than in other stations. A minimum of not detectable levels to a maximum of 0.78 ng g^{-1} of heptachlor was observed in the study area (Table 5.11). The station wise annual mean values of heptachlor in sediments ranged from 0.06 ng g^{-1} to 0.15 ng g^{-1}

The station wise seasonal mean variations are also plotted in Figure 5.13. Relatively higher values of heptachlor were observed in pre-monsoon season except at stations 5 and 6. At stations 5 and 6, the post-monsoon values were higher than pre-monsoon levels. In the entire monsoon season, non-detectable levels of heptachlor were observed at all stations.

Table 5.11 Station wise summary statistics of heptachlor in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.11	0.06	0.05	86.15
2	ND	0.11	0.06	0.05	86.09
3	ND	0.14	0.06	0.06	95.59
4	ND	0.15	0.08	0.05	63.95
5	ND	0.65	0.14	0.17	125.32
6	ND	0.78	0.15	0.21	142.18
7	ND	0.20	0.09	0.06	68.50
8	ND	0.17	0.09	0.06	63.43
9	ND	0.13	0.09	0.05	62.14

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 5.13 Seasonal and spatial distributions of heptachlor in sediments (ng g^{-1} dry wt.)

The annual zonal mean variations and zonal seasonal mean variations of heptachlor are plotted in Figure 5.13. Higher values of heptachlor were observed in zone 2 and slightly lower values were found in zone 3. Zone 1 exhibited the lowest values compared to the other two zones. Pre-monsoon values were higher in zone 3, but lower in zone 2 than post-monsoon values. In zone 1, both the pre-monsoon and post-monsoon values were almost equal. In all zones, non-detectable levels of heptachlor were observed during monsoon period.

The use of chlordane and heptachlor was banned in India in 1992 (David et al., 1993; Pesticides Information, 2000). Low values reported from the study area are attributed to the earlier use of heptachlor in paddy fields. The past residues of heptachlor in the sediments also contribute to the presence of this pesticide in the study area. The lesser amounts of heptachlor in the study area also can be attributed to the epoxidation of heptachlor to heptachlor epoxide (Jiping et al., 1995). The use of chlordane also accounts for the presence of heptachlor in the sediments and soils because it is difficult to distinguish the relative importance of technical heptachlor and chlordane as sources of heptachlor and its environmentally important degradation products and metabolites (Jiping et al., 1995).

The heptachlor values in river sediments and soils were found to be in the range of <0.005 to 0.06 ng g^{-1} in Herbert region and <0.005 to 0.288 ng g^{-1} in Burdekin region (Cavanagh et al., 1999). High values of heptachlor were reported from the sediments of Ohuira Bay, Gulf of California and the values ranged from 11.0 to 60.01 ng g^{-1} (Galindo-Reyes et al., 1999).

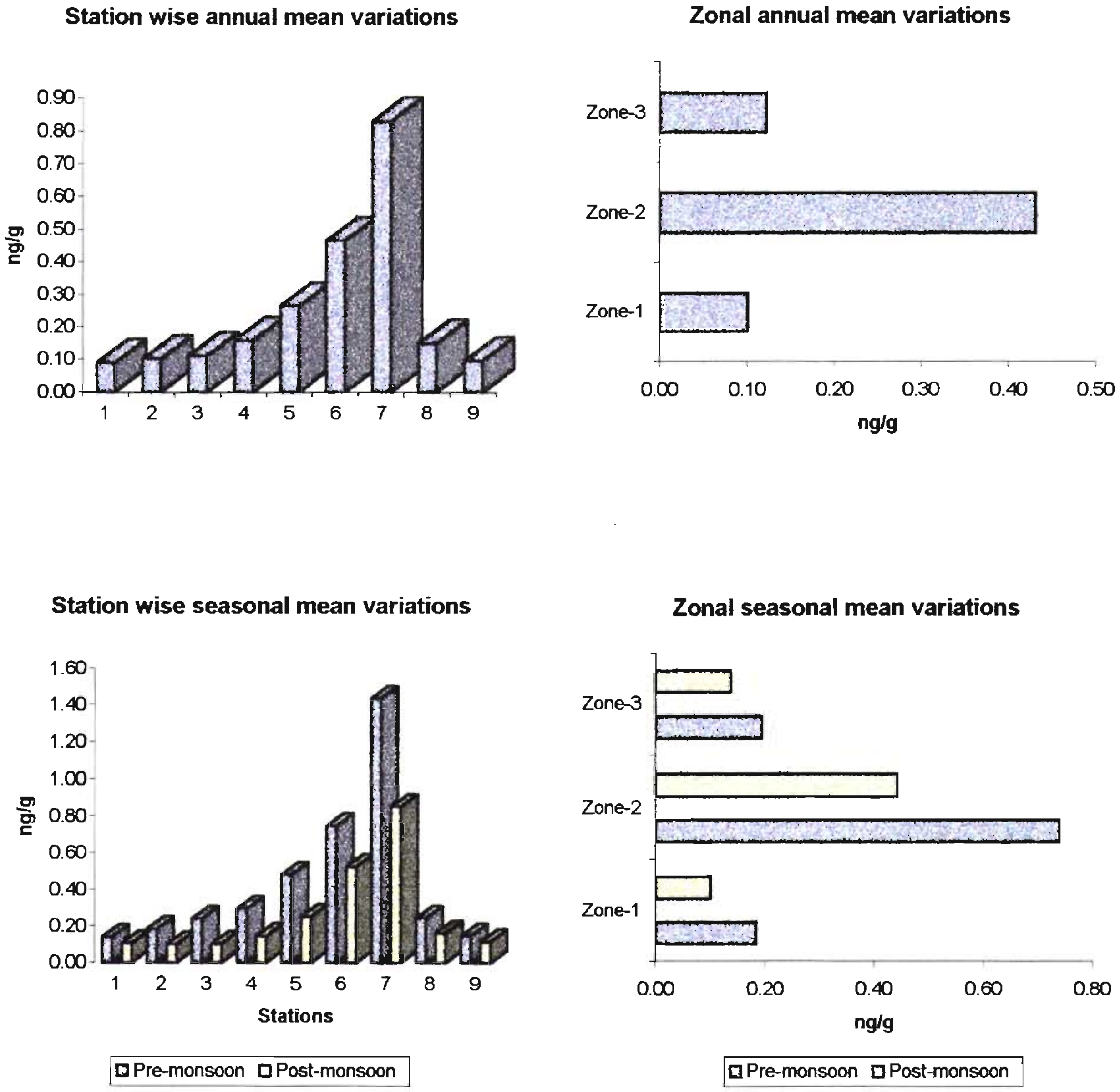
5.3.4.3. Distributions of heptachlor epoxide in sediments

The station wise annual mean variations of heptachlor epoxide in the sediments are plotted in Figure 5.14. The heptachlor epoxide values were increasing slightly from stations 1 to 7 and relatively higher values of heptachlor epoxide were observed at stations 5, 6 and 7 A minimum of non-detectable levels to a maximum of 2.65 ng g^{-1} of heptachlor epoxide was observed in the study area (Table 5.12). The station wise annual mean values of heptachlor epoxide in sediments ranged from 0.09 ng g^{-1} to 0.83 ng g^{-1} (Table 5.12).

Table 5.12 Station wise summary statistics of heptachlor epoxide in sediments
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.21	0.09	0.06	69.81
2	ND	0.26	0.10	0.08	82.68
3	ND	0.27	0.11	0.10	86.03
4	ND	0.45	0.16	0.13	84.16
5	ND	0.66	0.27	0.24	89.85
6	ND	1.25	0.47	0.49	104.58
7	ND	2.65	0.83	0.93	111 73
8	ND	0.30	0.15	0.10	69.83
9	ND	0.23	0.10	0.07	70.71

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 5.14 Seasonal and spatial distributions of heptachlor epoxide in sediments (ng g^{-1} dry wt.)

The station wise seasonal mean variations of heptachlor epoxide are also illustrated in Figure 5.14. Relatively higher values of heptachlor epoxide were observed in pre-monsoon than in post-monsoon at all stations. In entire monsoon season, non-detectable levels of heptachlor epoxide were observed at all stations. The annual zonal mean variations and zonal seasonal mean variations of heptachlor epoxide are also plotted in Figure 5.14. Higher values of heptachlor epoxide were observed in zone 2 and lower values were found in zones 3 and 1. Pre-monsoon values were higher in all zones than that of post-monsoon. In all zones, non-detectable levels of heptachlor were observed in monsoon period.

Huasheng Hong et al. (1999) stated that considerable quantities of organochlorines were deposited into bed sediments at low salinity during early stages of estuarine mixing. Kuttanad backwaters are receiving fresh water inputs resulting from run-off. Compared to other estuaries, the salinity in this estuary was found to be less and due to run-off, the pesticides entering to the backwaters may get deposited in the sediments. This may be a reason for the seasonal variations of this pesticide in the study area.

Heptachlor is oxidized to heptachlor epoxide in soils (Lichtenstein and Schulz, 1965. Heptachlor epoxide is the principal metabolite of the insecticide heptachlor. Jiping et al. (1995) also observed that the main heptachlor related compound found in the environment is heptachlor epoxide, which is the major heptachlor metabolite formed through epoxidation of the non-chlorinated double bond in the molecule (Figure 4.3). This is relevant here because the levels of heptachlor epoxide were found more than that of heptachlor in the study area and it may be due to the epoxidation of heptachlor to heptachlor epoxide.

The values reported for heptachlor epoxide in the sediments and soils of Hebert and Burdekin River regions, which ranged from <0.005 to 3.964 ng g^{-1} and 0.005 to 15.9 ng g^{-1} (Cavanagh et al., 1999). Galindo-Reyes et al. (1999) reported a value of 43.03 ng g^{-1} of heptachlor epoxide in sediments from Ohuira Bay, Gulf of California.

5.3.4.3. Distributions of aldrin in sediments

Low levels of aldrin were observed in the sediments of the study area. An overall mean value of 0.06 ng g^{-1} of aldrin was observed (Table 5.2). From the station wise annual mean variations (Figure 5.15), it was observed that the levels of aldrin were almost uniformly distributed at stations 1 to 3, and slightly increasing linearly from stations 4 to 7, and from stations 8 to 9 a decreasing trend was observed. A minimum of non-detectable levels to a maximum of 0.14 ng g^{-1} of aldrin was observed (Table 5.13). The station wise mean values of aldrin ranged from 0.04 ng g^{-1} to 0.09 ng g^{-1} in sediments.

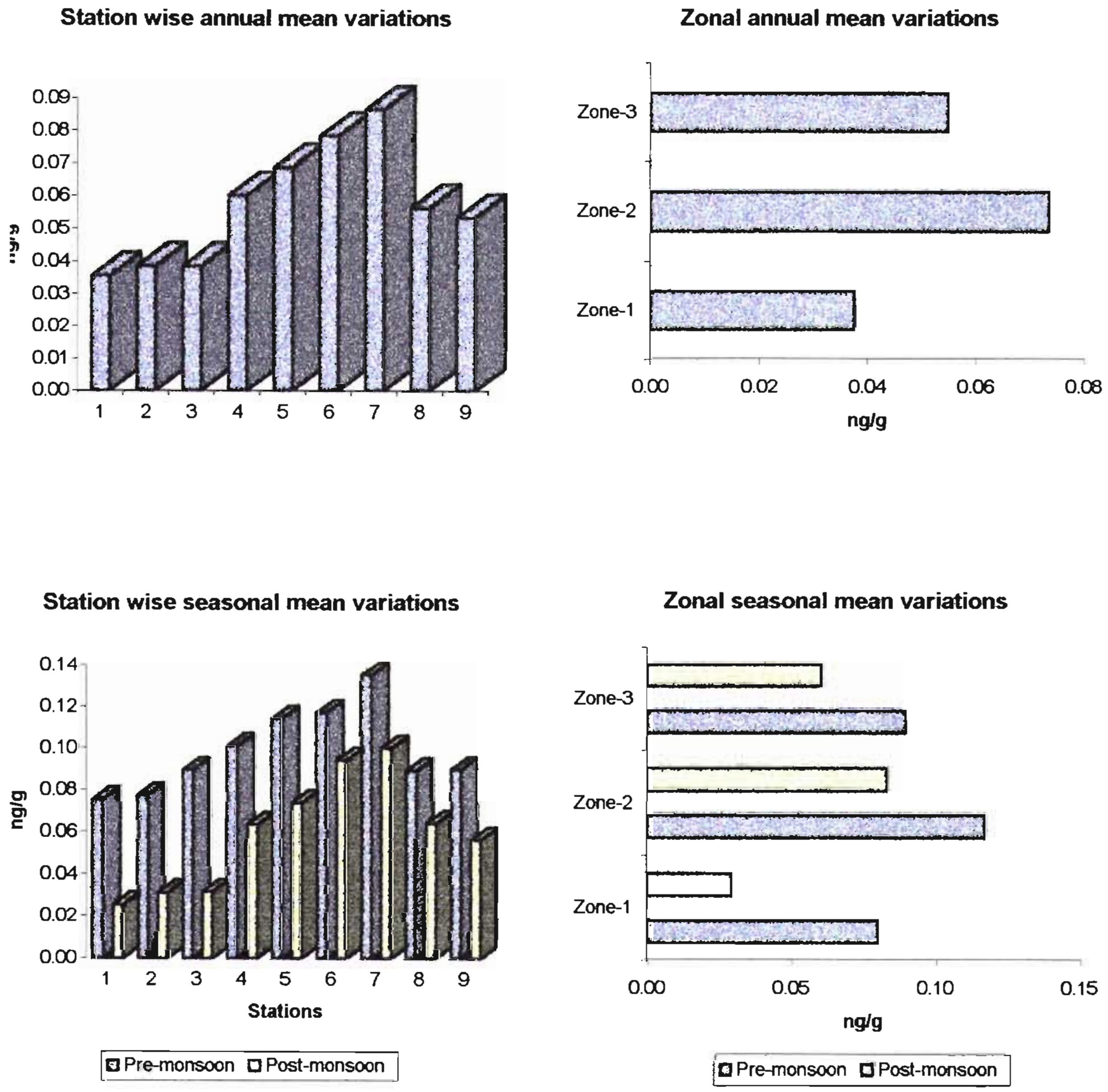
Higher levels of aldrin were observed in all stations in pre-monsoon season than in other seasons. In pre-monsoon, the levels of aldrin increased slightly from stations 1 to 7 and from stations 8 to 9, the values were decreasing (Figure 5.15). The post-monsoon values were lower than pre-monsoon values in all stations. In monsoon, non-detectable levels of aldrin were observed in all stations. Zone 2 recorded slightly higher levels of aldrin than in zones 3 and 1 (Figure 5.15). In the zonal seasonal mean variation graph (Figure 5.15), the pre-monsoon values of aldrin dominated slightly than post-monsoon values. Non-detectable levels of aldrin were observed in all zones in monsoon period.

Aldrin levels in the study area were found to be less than dieldrin. It may be due to the oxidation of aldrin to dieldrin in soils mediated by soil microorganisms as reported by Lichtenstein and Schulz (1965). Sarkar and Sen Gupta (1987) reported that aldrin concentration in the sediments from the Arabian Sea along the central west coast of India ranged from 0.95 to 35.7 ng g^{-1} wet weight and also noticed that among the cyclodiene compounds, aldrin was found to be much more prevalent than dieldrin. Sarkar and Sen Gupta (1988a) also reported that the concentrations of aldrin in marine sediments collected from the east coast of India ranged from 0.02 to 0.53 ng g^{-1} wet weight. Jabbar et al. (1993) observed the presence of aldrin in soils from agricultural areas in Punjab, Pakistan and the values ranged from 0.0013 to 0.0018 ppm. Cavanagh et al. (1999) reported the levels of aldrin in soils and sediments of Herbert river regions and Burdekin River regions, North Queensland and the values ranged from <0.005 to 0.132 ng g^{-1} and <0.005 to 0.096 ng g^{-1}

Table 5.13 Station wise summary statistics of aldrin in sediments
($ng\ g^{-1}$ dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.09	0.04	0.04	106.25
2	ND	0.10	0.04	0.04	106.68
3	ND	0.10	0.04	0.05	117.84
4	ND	0.11	0.06	0.05	76.36
5	ND	0.13	0.07	0.05	68.68
6	ND	0.13	0.08	0.05	63.31
7	ND	0.14	0.09	0.06	65.40
8	ND	0.10	0.06	0.04	76.98
9	ND	0.10	0.05	0.04	77.40

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 5.15 Seasonal and spatial distributions of aldrin in sediments (ng g^{-1} dry wt.)

respectively. The aldrin values reported in the sediments from Ohuira Bay, Gulf of California ranged from 0.95 to 1.96 ng g^{-1} (Galindo-Reyes et al. 1999).

5.3.4.4. Distributions of dieldrin in sediments

Next to endosulfan, dieldrin was the most abundant cyclodiene compound in the sediments of Kuttanad backwaters. An overall mean value of 0.43 ng g^{-1} of dieldrin was found in the sediments of the study area (Table 5.2). From the station wise annual mean variation plot (Figure 5.16), it was observed that the dieldrin values were almost uniform at stations 1 to 3, and from stations 4 to 7, the values were increasing and from stations 8 to 9 the values were decreasing. A minimum of non-detectable levels and a maximum of 3.26 ng g^{-1} of dieldrin were observed in the study area (Table 5.14). The station wise mean values of dieldrin in sediments ranged from 0.11 ng g^{-1} to 1.30 ng g^{-1}

The pre-monsoon values of dieldrin were higher than that of post-monsoon period (Figure 5.16). Stations 6 and 7 showed comparatively higher values of dieldrin in pre-monsoon than in other stations. All stations in monsoon period observed non-detectable values of dieldrin (Figure 5.16). The annual zone wise mean variation and zonal seasonal mean variations of dieldrin are also shown in Figure 5.16. As in the case of aldrin, dieldrin also had higher values in zone 2 than in zones 1 and 3. Zonal seasonal mean variations also showed higher levels of dieldrin in zone 2 in pre-monsoon period than that of post-monsoon period. In monsoon, all zones showed non-detectable levels of dieldrin.

Edwards (1966) reviewed 13 reports and generalized that half-life period of dieldrin in soil was about 2 years. Freeman et al. (1975), summarised that 95% disappearance time of dieldrin in field soil in Ohio, USA was 13 years. Hermason et al. (1971) estimated that the half-life of dieldrin in field soils in California, USA was 13 years. These reports can be summarised that half life of dieldrin in field soils was found to be many years and it may be attributed to the levels of dieldrin found in the study area, even though aldrin and dieldrin were banned in India.

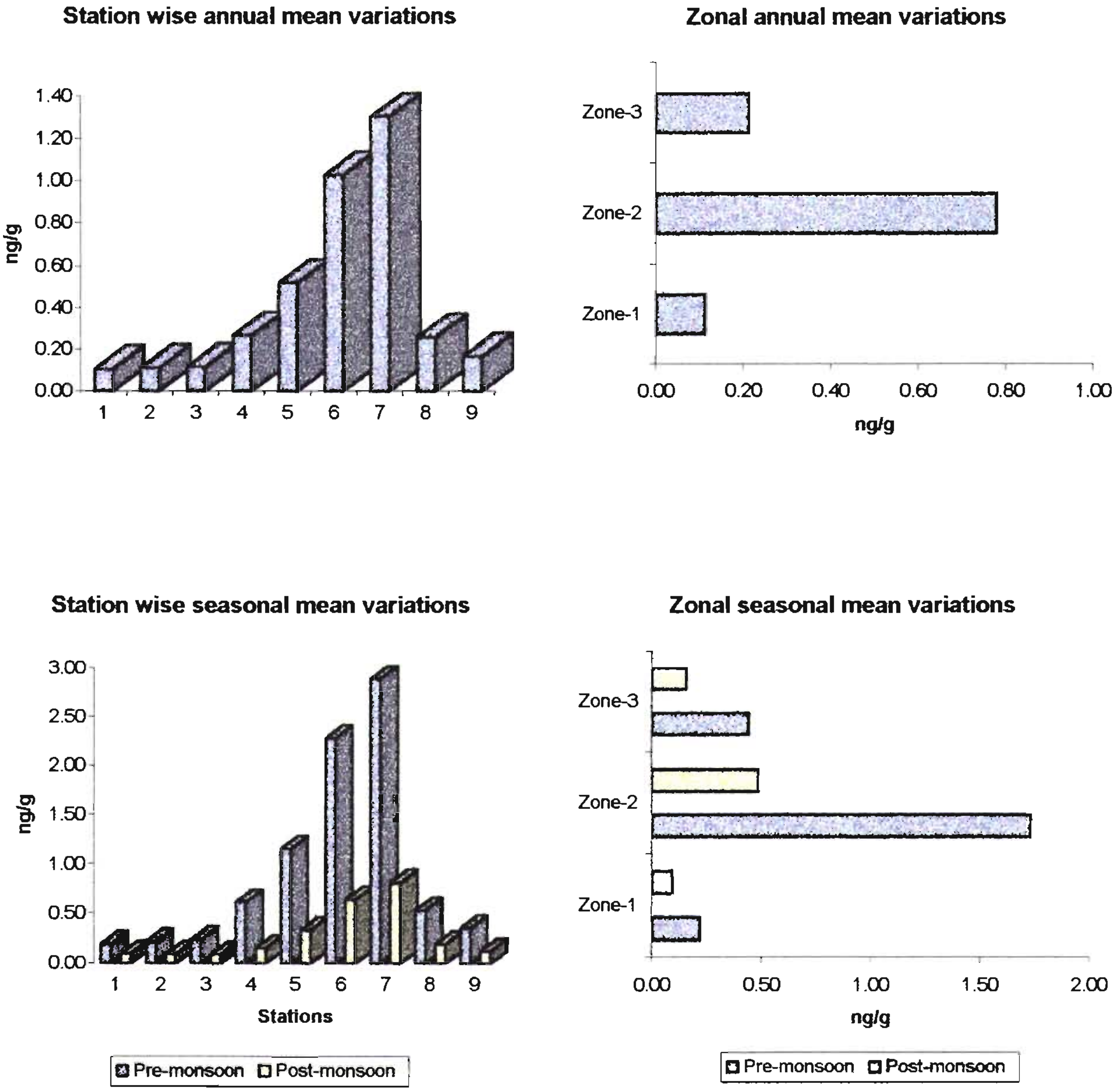
Nakamura (1990) investigated in Saitama, Japan during 1971-86, and described that the average of dieldrin residue amounts in 50 field soils was 0.288

Table 5.14 Station wise summary statistics of dieldrin in sediments

(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.25	0.11	0.08	78.46
2	ND	0.27	0.11	0.09	83.67
3	ND	0.37	0.12	0.11	91.64
4	ND	0.99	0.27	0.30	112.39
5	ND	1.56	0.52	0.55	106.24
6	ND	2.65	1.03	1 10	106.97
7	ND	3.26	1.30	1.34	102.94
8	ND	0.65	0.26	0.26	100.33
9	ND	0.54	0 17	0.18	107.29

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Monsoon - Non detectable

Figure 5.16 Seasonal and spatial distributions of dieldrin in sediments (ng g^{-1} dry wt.)

ppm in 1971 and decreased to 0.088 ppm in 1972, but did not decrease in following 15 years at the level of 0.1 ppm. Martijn et al. (1993) examined in Wageningen, Netherlands, and reported that half-life of dieldrin in soil was estimated about 15 to 20 years and dieldrin seemed to be more persistent. High values of dieldrin residues (an amount of 0.05 µg g^{-1}) were reported from soils of agricultural fields in Japan (Nagami, 1997), and this residue is guessed as the result of the agricultural use of aldrin or dieldrin products before 1975. These studies suggest that dieldrin residue in soil is seriously persistent in the temperate region.

Sarkar and Sen Gupta (1987) observed the presence of dieldrin only in one sediment sample (0.88 ng g^{-1} wet weight) from the Arabian Sea along the central west coast of India. Fox et al. (1988) reported that dieldrin had a uniform distribution and the values ranged from 0.3 to 0.5 ng g^{-1} in the superficial sediments of Manukau Harbour, New Zealand. Sarkar and Sen Gupta (1988a) observed the presence of dieldrin in marine sediments collected from the east coast of India and the values ranged from 0.05 to 0.51 ng g^{-1} wet weight. Everaarts et al. (1998) reported values ranging from 0.1 to 5.4 ng g^{-1} of dieldrin in the sediments from the coastal zone and continental slope of Kenya. The dieldrin values in soils and sediments of Herbert and Burdekin River regions, North Queensland ranged from 0.028 to 22.2 ng g^{-1} and <0.005 to 3.297 ng g^{-1} (Cavanagh et al., 1999). Galindo-Reyes et al. (1999) reported values in the range of 2.06 to 51.04 ng g^{-1} of dieldrin in sediments from Ohuira Bay, Gulf of California.

5.3.4.5. Distributions of endrin

Low levels of endrin were observed in the study area, and the station wise annual mean variations of endrin are plotted in Figure 5.17 Variations were observed in the station wise distribution pattern of endrin in sediments. Stations 5 to 7 recorded higher values of endrin than in other stations. The station wise summary statistics of endrin is shown in Table 5.15. A minimum of non-detectable levels to a maximum of 0.14 ng g^{-1} of endrin was observed. The mean values of endrin in sediments ranged from 0.03 ng g^{-1} to 0.08 ng g^{-1}

In all stations, the pre-monsoon values of endrin were higher than that of post-monsoon values (Figure 5.17). Non-detectable levels of endrin were observed at all

Table 5.15 Station wise summary statistics of endrin in sediments

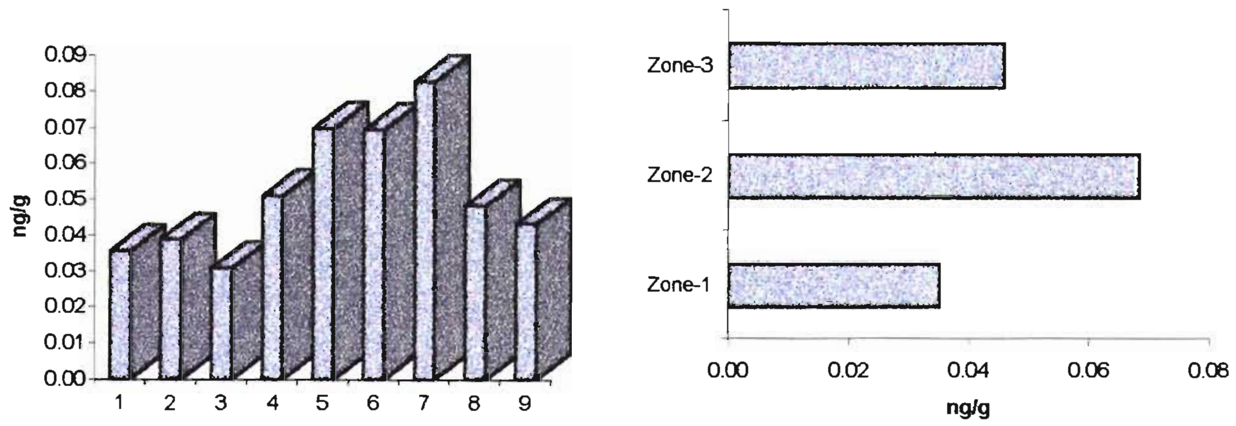
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.07	0.04	0.03	90.09
2	ND	0.10	0.04	0.04	93.48
3	ND	0.07	0.03	0.03	90.85
4	ND	0.12	0.05	0.04	86.51
5	ND	0.13	0.07	0.05	66.96
6	ND	0.14	0.07	0.05	78.80
7	ND	0.14	0.08	0.06	66.91
8	ND	0.10	0.05	0.04	76.95
9	ND	0.08	0.04	0.03	64.65

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected

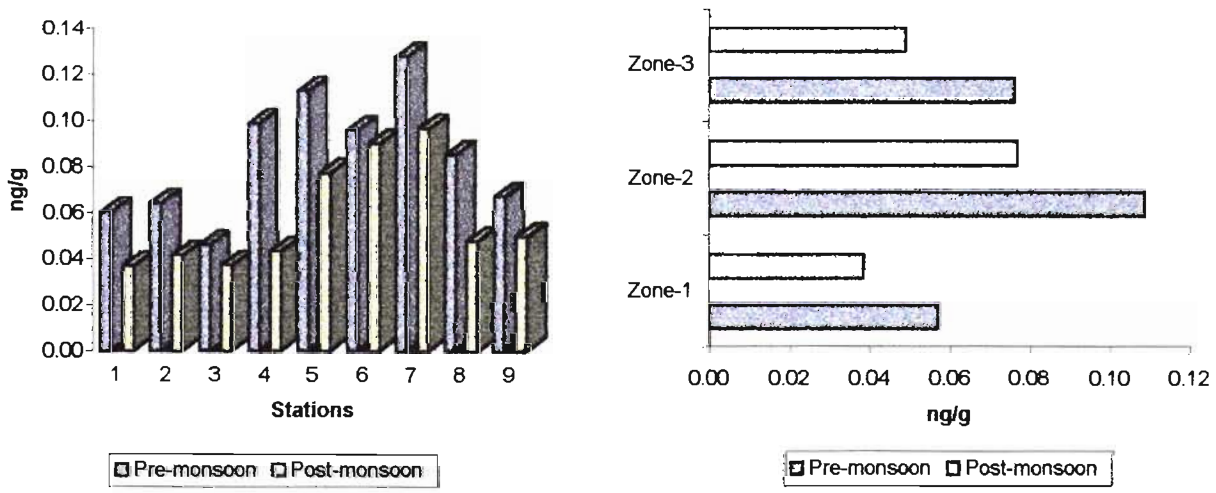
Station wise annual mean variations

Zonal annual mean variations



Station wise seasonal mean variations

Zonal seasonal mean variations



Monsoon - Non detectable

Figure 5.17 Seasonal and spatial distributions of endrin in sediments (ng g^{-1} dry wt.)

stations during monsoon period. The zonal annual mean variations and zonal seasonal mean variations of endrin are also included in Figure 5.17 Zone 2 observed higher levels of endrin than in other zones. Pre-monsoon period showing higher values than post-monsoon season in all the zones.

Jabbar et al. (1993) observed the presence of endrin in soils from agricultural areas in Punjab, Pakistan and the values ranged from 2 to 6 ng^{-1} Williams et al. (1997) reported <0.1 mg kg^{-1} of endrin in the inshore sediments of Mombasa, Kenya. Cavanagh et al. (1999) observed low levels of endrin (<0.005 ng g^{-1}) in soils and sediments of Herbert and Burdekin River regions, North Queensland. The presence of detectable amounts of endrin in the sediments of the study area, despite an effective ban on the use of this pesticide for the last many years, suggests that it is likely that some pesticides would move from the land to the near shore estuarine environment during the period of maximal usage of this pesticide in early years, and the process is still continuing. Mohamed and Mohamed (1985a) reported higher values of endrin from the sediments of Mediterranean Sea and the values ranged from 0.1 to 100.0 μg kg^{-1}

5.3.4.6. Distributions of endrin aldehyde

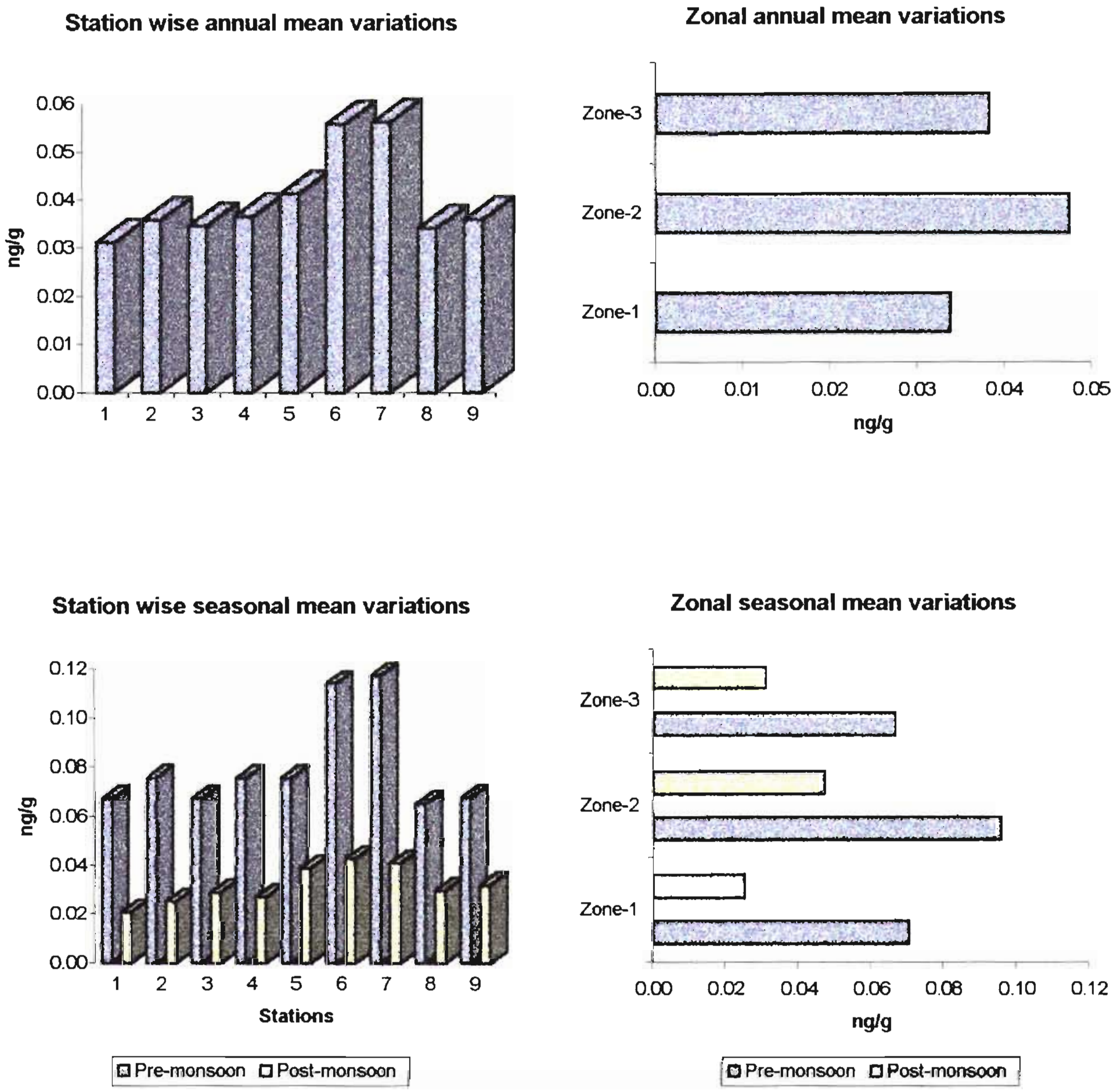
Endrin aldehyde is the least observed compound among the cyclodiene compounds in the study area. As in the case of endrin, the station wise distribution pattern of endrin was not uniform (Figure 5.18). Slightly higher values of endrin were found at stations 6 and 7 than in other stations. A minimum of non-detectable levels and a maximum of 0.14 ng g^{-1} endrin were observed in the study area (Table 5.16). The mean values of endrin ranged between 0.03 ng g^{-1} to 0.06 ng g^{-1}in the sediments (Table 5.16).

Higher values of endrin aldehyde were observed in pre-monsoon season than in post-monsoon season (Figure 5.18). In monsoon, non-detectable levels of endrin aldehyde were observed at all stations (Figure 5.18). As in the case of endrin, higher levels of endrin aldehyde were observed in zone 2. Pre-monsoon values were higher in all zones.

Table 5.16 Station wise summary statistics of endrin aldehyde in sediments (ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.09	0.03	0.03	109.53
2	ND	0.10	0.04	0.04	108.40
3	ND	0.10	0.03	0.04	110.09
4	ND	0.09	0.04	0.04	107.91
5	ND	0.10	0.04	0.04	94.26
6	ND	0.13	0.06	0.05	94.21
7	ND	0.14	0.06	0.05	97.02
8	ND	0.09	0.03	0.03	93.65
9	ND	0.08	0.04	0.03	96.18

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 5.18 Seasonal and spatial distributions of endrin aldehyde in sediments (ng g^{-1} dry wt.)

Low levels of endrin aldehyde (<0.005 ng g^{-1}) were observed in soils and sediments of Herbert and Burdekin River regions, North Queensland (Cavanagh et al., 1999). The main factors, which are responsible for the low levels of endrin aldehyde in the study area, were the land management practices, sediment dilution and the chemical and biological degradation of the pesticide in sediment environment. Galindo-Reyes et al. (1999) reported a value of 1.05 ng g^{-1} of endrin aldehyde in sediments from Ohuira Bay, Gulf of California.

5.4. CORRELATION OF ORGANOCHLORINE PESTICIDES WITH SEDIMENTARY PARAMETERS

The correlation of DDT and its metabolites with the sedimentary characteristics are given in Table 5.17 DDT and its metabolites with sedimentary parameters displayed no significant correlations. A negative correlation was observed for sand and a positive correlation with silt fraction of the sediment with DDT metabolites. Table 5.18 gives the correlation of HCH isomers with the sedimentary parameters. As in the case of DDT, HCH isomers also showed no appreciable correlation with sedimentary parameters. Negative correlations were found with sand and positive correlations with silt were observed for all isomers of HCH. As in the above cases the correlations of cyclodienes with sedimentary parameters were negligible (Table 5.19).

The absence of significant correlations of organochlorine pesticides with sedimentary parameters indicated that a large part of the variability associated with organochlorine concentrations in the sediment samples and can be explained by the relationships with the different fractions of sediment and organic carbon percentage and with the absorption ability of the sediment. Major organochlorine pesticides are applied as wetable powders (WP) and it has a tendency to settle down to the surface sediments of the water column. This may be a reason for the non-significant correlations among the texture nature of sediments with organochlorine pesticides. Moreover, the correlations of texture nature with pesticides were taken in seasonal basis and the seasonal fluctuations also influence the concentrations of pesticides in sediments.

Table 5.17 Correlation of DDT and its metabolites with environmental parameters

	p,p'-DDE	p,p'-DDD	p,p'-DDT	ΣDDT
Organic carbon (n =107)	0.154	0.207	0.313	0.178
Sediment moisture (n=107)	0.035	0.066	0.236	0.060
Sand (n=27)	-0.014	-0.064	-0.276	-0.038
Silt (n=27)	0.123	0.125	0.247	0.129
Clay (n=27)	-0.119	-0.022	0.259	-0.080

Table 5.18 Correlation of HCH isomers with environmental parameters

Parameter	α –HCH	β–HCH	γ–HCH	δ–HCH	Σ HCH
Organic carbon (n=107)	0.217	0.196	0.084	0.108	0.196
Sediment moisture (n=107)	0.134	0.107	-0.032	-0.026	0.103
Sand (n=27)	-0.230	-0.123	0.000	-0.012	-0.120
Silt (n=27)	0.198	0.157	0.084	0.086	0.149
Clay (n=27)	0.226	0.059	-0.100	-0.078	0.063

Table 5.19 Correlation of cyclodiene pesticides with environmental parameters

	Endosulfan	heptachlors	Aldrins	Endrins	Σ cyclodiens
Organic carbon	0.036	0.075	0.068	0.032	0.053
Sediment moisture	-0.081	-0.057	-0.066	-0.093	-0.076
Sand	0.079	0.082	0.061	0.022	0.081
Silt	0.009	-0.004	0.062	-0.025	0.019
Clay	-0.169	-0.160	-0.198	-0.014	-0.185

5.5 SUMMARY

- The major portions of the organochlorine pesticides found in the Kuttanad backwaters are DDT and its metabolites and HCH and its isomers. Compared to DDTs and HCHs, the residues of cyclodienes were found to be less.

- The highest concentrations found in the sediments of Kuttanad backwaters were the p,p'-DDE in ΣDDT, β-HCH in ΣHCH and α-endosulfan in Σcyclodienes.

- Expansion of agricultural activities becomes more critical to understand the factors influencing the transport of sediment and sediment bound pesticides on both a fine-scale (e.g. soil erosion within paddocks) and a large scale (e.g. influences of water currents and climatic factors).

- Concentrations of organochlorines, mainly DDT and its metabolites and HCH isomers observed in the sediments of the study area may be attributed to the wide application of HCH formulations in agriculture and the use of DDT formulations in vector control programmes.

- Through the understanding of the transport mechanisms, a useful assessment of the current and future potential impact of changing land-use on the sediment and contaminant loads in the sediments of Kuttanad backwaters can be made.

- The low levels of some of the cyclodiene pesticides in the sediments of Kuttanad backwaters may be attributed to the sediment transport process from the near-shore or catchment areas and also the movement of soil/sediment particles from these areas to the estuary.

- The distribution patterns of organochlorine pesticides in the sediments of Kuttanad backwaters were dependent on the distributions of organic carbon of the sediments and also the nature of the sediments. The organic carbon distribution and nature of the sediments pattern in the surface sediments were mainly related to the tributary runoff and the anthropogenic inputs.

- The organochlorine pesticides detected in most of the sediment samples were ubiquitous throughout the Kuttanad backwaters and these compounds in the estuary were transported within both the water body and sediments and mixed between them. Organochlorine pesticides were, however, inclined to partition into surface sediments because of their particle reactivity.
- Considerable quantities of organochlorines were deposited into bed sediments due to low salinity during the early stage of estuarine mixing. Hydrodynamic flows then diluted and mixed sediments and transported them to the sea.
- Data obtained from the present study are useful for an understanding of the contamination dynamics of the different organochlorine pesticides present in the sediments of Kuttanad backwaters. Variations of flow have been shown to have an effect on concentration fluctuations of pesticides with different effects on the major river systems flowing towards the estuary and also the flow from the paddy fields.
- Strict regulations for the use of pesticides in agriculture, wastewater discharge from agriculture, and municipal sewage system are absolutely essential to keep the estuarine/marine environment clean and sustainable.

CHAPTER 6

DISTRIBUTIONS OF SOME ORGANOPHOSPHORUS PESTICIDES IN THE BACKWATERS OF KUTTANAD

6.0 INTRODUCTION

Organic compounds of phosphorus are the essential constituents of protoplasm and play important role for the maintenance of life. It is surprise to know that such great varieties of chemical, physical and biological properties are governed by the selection of groups attached on the phosphorus atom. Lannge and Krueger first observed physiologically abnormal effects of organophosphorus compounds in dialkyl phosphorofluoridates in 1932, when they intended to find new types of organic pesticides. The great advancement in agricultural practice and scientific knowledge on the structure-activity relationship of organophosphorus insecticides were achieved by the discovery of a compound, No.605, named parathion, diethyl p-nitrophenyl phosphorothionate, by Schrader in 1944. Although parathion itself is extremely toxic to mammals as well as to insects, many less toxic insecticides have been developed by slight structural modifications. Another important compound with low mammalian toxicity, malathion, discovered by American Cynamide Company in 1950, has the carboxy ester group. There are about 140 phosphorus compounds used as practical pesticides in the world.

Organophosphorus group of pesticides are known to be the best insecticides and acaricides, and also they are equally effective as fungicides, nematicides, herbicides, plant growth regulators, insect chemosterilants and rodenticides. All organophosphorus pesticides are derived from phosphoric acid. Pesticides containing phosphorus include phosphates, phosphoronates, phosphoroamides, pyrophosphates and their sulphur analogues. Phosphates are esters of orthophosphoric acid and are named like normal esters with the alcoholic group name appearing first.

Organophosphorus compounds are the most widely used group of pesticides in the world. Out of the 900 pesticides in use globally, more than 250 belongs to this group (Gayartri and Singh, 2000). Organophosphorus pesticides constitute the second generation of pesticides and are also recognised as the potential substitutes for the organochlorine pesticides. Organophosphorus pesticides offer a broad range of toxicity to insect-pests, and are generally among the most toxic of all pesticides to vertebrate animals. Organochlorine pesticides are, in general, of lower toxicity than organophosphorus pesticides, but are causing environmental problems due to their higher persistence and higher toxicity (Eto, 1977). The organophosphorus pesticides are easily degradable and consequently less persistent and are often preferred to organochlorines in conventional agricultural applications. Organophosphorus compounds are highly effective and rapid in its action on aphides, spider mites, small caterpillars and many other insects. It is highly toxic to man and other animals. In water solution, it gets easily decomposed by hydrolysis into non-toxic water-soluble products.

6.1 Organophosphorus pesticides

One of the most important classes of present day pesticides is the organophosphorus compounds, of which more than 100 compounds are used in agriculture. Substances with a great variety of pesticidal properties are found among the organophosphorus compounds, including insecticides, acaricides, nematicides, herbicides, defoliants and fungicides. Organophosphorus compounds are widely used as agents to combat plant pests and ectoparasites of domestic animals. The most important advantages of organophosphorus compounds as pesticides are (1) high insecticidal and acaricidal activity (2) wide spectrum of action on plant pests (3) low persistence and breakdown to form products, non-toxic to man and animals (4) systemic action of a number of compounds (5) low dosage of compound per unit area treated and (6) relatively rapid metabolism in vertebrate organisms and absence of accumulation in their bodies, and also comparatively low chronic toxicity.

With the very few exceptions, all organophosphorus pesticides are neutral phosphoryl or thiophosphoryl compounds. A great majority of them are ester derivatives. The polarized phosphoryl group creates a positive charge on the phosphorus atom, which consequently becomes highly electrophilic and reactive with nucleophiles. This is the basic principle of the various reactions of organophosphoryl compounds (Eto, 1977). Trivalent phosphorus compounds having an unshared electron pair on the phosphorus atom are quite different in chemical properties from phosphoryl compounds; they are highly nucleophilic agents except for the halides, which have some electrophilic character. Trivalent phosphorus compounds are rarely utilized as pesticides but are very useful as starting materials for the preparation of organophosphorus pesticides (Eto, 1977).

The hydrolysis rates of organophosphorus pesticides are dependent on the chemical structure and reaction conditions such as pH, temperature, the kind of solvent, and existence of catalytic reagents. In aqueous solutions, many organophosphorus pesticides are stable at pH 1 to 5. For example, the half-lives of malathion and mehyl parathion at pH 6 and at 70°C are in the orders of 7.8 and 8.4 hours respectively (Ruzicka et al., 1967). The organophosphates are much more unstable under alkaline conditions. The hydrolysis rate increases steeply at pH higher than 7 to 8 (O'Brien, 1967).

A disadvantage of many organophosphorus compounds is their relatively higher toxicity to vertebrates, requiring suitable protective measures when using them. However, a large number of organophosphorus compounds that have moderate or low toxicity for mammals have been synthesized; the use of such compounds in agriculture is safe.

The global use of organophosphorus pesticides in agriculture for the last so many years showed an increasing trend, the residual levels in environmental compartments and food commodities were found to be lower than that of organochlorine pesticides. Leoni et al. (1995) studied the estimated daily intake of organophosphorus pesticides and compared the data with the acceptable daily intake (FAO/WHO) to assess the risk connected with the organophosphorus pesticide residues in dietary intake. The above authors reported the estimated intake of malathion, mehyl parathion and chlorpyrifos as 6.46, 0.15 and 0.12 µg/man/day against the acceptable intake of the above pesticides in the order as 1200, 1200 and 600 µg/man/day.

The organophosphorus pesticides have got wider acceptance due to their shorter persistence in the environmental compartments as well as their adsorption tendency in soils (Sharom et al., 1980). Smith and Willis (1987) observed the presence of organophosphorus pesticides only less than 3 to 6 weeks in the environment. Studies revealed that organophosphorus pesticides are known to cause acute toxic effects to aquatic life (Agarwal and Nair, 1989). Kang et al. (1995) well documented the toxic effects and symptoms of organophosphorus pesticides in humans.

Investigations of the mechanism of action of organophosphorus compounds on mammals and insects have shown that in animals, the phosphorylate, a vitally important esterases, inhibits the normal functions in mammals. The action of these compounds is directed mainly towards inhibition of cholinesterase, the physiological functions of which are very important in the animal organisms. Pluth et al. (1996) established the association between malathion exposure and specific mutations in human T-lymphocytes.

To a great extent, the physical and chemical properties of a compound determine its behaviour in the environment. Although environmental variables are important in modulating transformation and transport processes, the basic pattern of persistence and partitioning is fundamentally derived from their chemical characters of the compound, and therefore the physical and chemical properties play in the modelling and prediction of environmental fate. So, brief descriptions of the three organophosphorus pesticides viz malathion, methyl parathion and chlorpyrifos were described here under.

Malathion

Malathion was introduced in 1950 by American Cyanamide Company and has been acknowledged as the first organophosphorus pesticide with high selective toxicity. Malathion is a non-systemic insecticide and acaricide with contact, stomach, and respiratory action (The Pesticide Manual, 1995). Malathion is a widely used pesticide with high potential for human exposure (Pluth et al., 1996). It is a cholinesterase inhibitor and is used for the control of insects and pests of wide range of crops including rice, vegetables, fruits etc. Malathion is also used extensively for the control of major arthropod disease vectors (Culicidae) in public health programme, ectoparasites (Diptera, Acari, Mallophaga) of cattle, poultry, dogs and cats, human head and body lice, house hold insects and the protection of stored grains (The Pesticide Manual, 1995). The physico-chemical properties of malathion are given in Table 6.1.

Malathion is synthesized by the addition of dimethyl hydrogen phosphorodithioate to diethyl maleate (Eto, 1977). Malathion is rapidly hydrolysed in aqueous solutions above pH 7 and below pH 5 and the presence of heavy metals, particularly iron, catalyses the decomposition (Eto, 1977). The high selective toxicity of malathion is attributed to the presence of the carboxy ester group which is readily hydrolysed by mammalian carboxyesterase. The esterase activity is low in susceptible insects. Some impurities in technical malathion, increase the mammalian toxicity of malathion.

Methyl parathion

Methyl parathion is O,O-dimethyl O-4-nitrophenyl phosphorothioate and is a white crystalline substance. Its vapour pressure at 20°C is 0.97×10^{-5} mm of Hg and its solubility in water at 25°C is about 55 mg l^{-1} (Eto, 1977). The rate of hydrolysis of methyl parathion is considerably higher than that of parathion; at pH 1-5, 50% is hydrolysed in 175 days at 20°C, and in 11 hours at 70°C, the rate of hydrolysis in alkaline medium is still greater (Eto, 1977). The physico-chemical properties of methyl parathion are included in Table 6.2.

Table 6.1 Physico-chemical properties of technical malathion

Sl.No.	Properties	Properties of technical malathion
1	Molecular formula Molecular weight	$C_{10}H_{19}O_6PS_2$ 330.3
2	Composition	Technical grade is 95% pure.
3	Form	Technical grade is a clear amber liquid.
4	M.P	2.85°C (a) 2.8 – 3.7°C (b)
5	B.P	156 – 157°C / 0.7 mm Hg. (a) 156 - 157°C at 1 mbar (b)
6	V.P	5.3 mPa at 30°C (a) 1.6 x 10^{-4}mbar at 20°C (b)
7	Solubility in water	145 mg/l at 25°C (a & b)
8	Solubility in organic solvents	Miscible with most organic solvents. Slightly soluble in petroleum ether and some mineral oils.
9	Mode of action	Non-systemic insecticide and acaricide with contact and stomach and respiratory action. Cholinesterase inhibitor.
10	Stability	Relatively stable in neutral aqueous media. Decomposed by acid and alkalis.
11	Ecotoxicology	Toxic to fish and bees
12	LD_{50} – Oral mg/kg	Rat 1375 – 2800 Mice: 775 - 3320
13	Toxicity class	WHO III EPA : III
14	Environmental fate	In insects, oxidation to the thiophosphates, malaoxon and hydrolysis to derivatives of succinic acid and other carboxylic acids.
15	Major Formulations	EC; WP; DP; UL

(a) The Pesticide Manual (1995)
(b) The Agrochemical Handbook (1983)

Table 6.2 Physico-chemical properties of technical methyl parathion

SI.No.	**Properties**	**Properties of technical methyl parathion**
1	Molecular formula	$C_8H_{10}NO_5PS$
2	Molecular weight	263.2
3	Form	Technical is light to dark tan coloured liquid
4	M.P	29°C for technical and 35-36°C for pure compound. (a)
5	B.P	154°C/136Pa (a) 119°C at 0.13 mbar (b)
6	V.P	0.2 mPa at 20°C (a) 1.3×10^{-4}mbar at 20°C (b)
7	Solubility in water	55 mg/l at 20°C (a) 55-60 mg/l at 25°C (b)
8	Solubility in organic solvents	Readily soluble in common organic solvents. Sparingly soluble in petroleum ether and some mineral oils.
9	Mode of action	Non-systemic insecticide and acaricide with contact, stomach and respiratory action. Cholinesterase inhibitor.
10	Stability	Hydrolysed in alkaline and acidic media. Photo-degrades in water. Isomerise on heating.
11	Ecotoxicology	Toxic to fish and animals of fish diet.. Toxic to bees.
12	LD_{50} – Oral mg/kg	Rat: 6 Mice: 30
13	Toxicity class	WHO 1 EPA I
14	Environmental fate	Major metabolites in man are 4-nitrophenol and dimethyl phosphate. It is a compound of low-medium mobility. In biologically active soils, it is rapidly degraded.
15	Major Formulations	EC; WP; DP; UL; CS

(a) The Pesticide Manual (1995)
(b) The Agrochemical Handbook (1983)

Methyl parathion is relatively unstable thermally and when it is heated to 140 – 160°C, it is almost completely converted to corresponding thiol isomer Among the products of the thermal decomposition of methyl parathion are found trimethyl sulfonium salts that are formed as a result of methylation of dimethyl sulphide. Methyl parathion is a powerful alkylating agent and can methylate sulphides, amines, thiourea and many other compounds. It is possible that the high methylating ability of methyl parathion is the cause of its lower toxicity for mammals, because part of the compound is decomposed as a result of the demethylation reaction before it reaches the reactive centers of the cholinesterase.

The other chemical properties of methyl parathion are similar to those of parathion. The toxicity of methyl parathion for mammals is considerably lower; it also penetrates the skin with greater difficulty than parathion and this facilitates working with it.

Methyl parathion is marketed in the form of emulsions, wettable powders and dusts. Methyl parathion is used for the control of a wide variety of plant pests.

Chlorpyrifos

Chlorpyrifos is a member of the organophosphorus class of pesticides and is a broad-spectrum pesticide, displaying insecticidal activity against a wide range of insects and arthropod pests. Chlorpyrifos possesses ingestion or stomach toxicity towards insect representatives of the Orthoptera, Diptera, and Lepidoptera. The only major roots of chlorpyrifos exposure that are not effective for insect control involve plant systemic activity; insecticidally sufficient levels of chlorpyrifos are not taken up via the roots or translocated with in plant tissues (Kenaga et al., 1965). The physico-chemical properties of chlorpyrifos are listed in Table 6.3.

The final synthetic step of chlorpyrifos involves the reaction of 3,5,6-trichloro-2-pyridinol with O,O-diethyl phosphorochloridothioate under basic

Table 6.3 Physico-chemical properties of technical chlorpyrifos

SI.No.	**Properties**	**Properties of technical chlorpyrifos**
1	Molecular. formula	$C_9H_{11}Cl_3NO_3PS$
2	Molecular weight	350.6
3	Form	Colourless crystals with mild mercaptan odour.
4	M.P	42-43.5°C
5	V.P	2.7 mPa at 25°C (a) 2.4 x 10^{-5}mbar at 25°C (b)
6	Solubility in Water	1.4 mg/l at 25°C (a) 2 mg/l at 35°C (b)
7	Solubility in organic solvents	In benzene 7900, acetone 6500, xylene 5000, methanol 450 (all in g/kg at 25°C)
8	Mode of action	Non-systemic insecticide with contact, stomach and vapour action. Cholinesterase inhibitor.
9	Stability	Rate of hydrolysis increases with pH, and in presence of copper or other metals that can form chelates.
10	Ecotoxicology	Toxic to fish Toxic to bees.
11	LD_{50} – Oral mg/kg	Rat: 135-163
12	Toxicity class	WHO II EPA II
13	Environmental fate:	Residues taken up by plants tissues are metabolised to 3,5,6-trichloro 2-pyridinol which is conjugated and sequestered. In soil chlorpyrifos is slowly degraded with a half-life of c.60-120 days.
14	Major Formulations	EC; WP; DP; UL; GR.

(a) The Pesticide Manual (1995)
(b) The Agrochemical Handbook (1983)

conditions in dimethyl formamide. Chlorpyrifos is formulated as a number of different commercial products. The most commonly available formulations include emulsifiable concentrates (EC), granules (GR), and wettable powders (WP). The various available formulations are often tailored for a specific use pattern, as in the case of granular formulations which are commonly employed for soil insect control due to their extended release of chlorpyrifos, which in turn results in increased persistence (Getzin, 1985).

6.2 MATERIALS AND METHODS

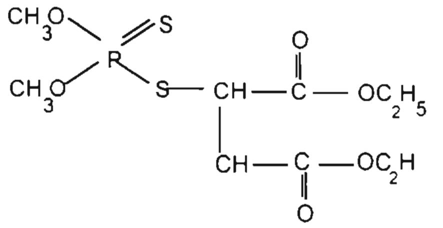
The materials and methods are discussed in Chapter 2.

6.3 RESULTS AND DISCUSSION

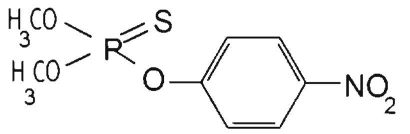
The reports on organophosphorus pesticides in the aquatic environment are fewer than that of organochlorine pesticides. The organophosphorus pesticides do not tend to persist in the environment as that of organochlorine compounds. It may be due to the easier degradability of these groups of pesticides than organochlorine pesticides. However, the organophosphorus pesticides figure in many official causes for concern priority lists because of their toxicity, especially to the aquatic environment. This chapter describes the distribution profiles of some of the common organophosphorus pesticides found in the aquatic and sedimental phases of Kuttanad backwaters. The following organophosphorus pesticides were identified in the aquatic and sedimental phases of the study area.

- Malathion
- Methyl parathion
- Chlorpyrifos

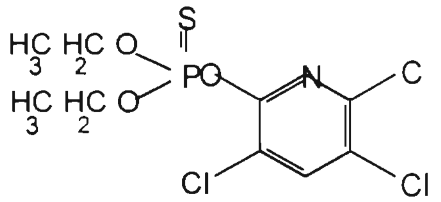
The structural formulae of the three organophosphorus pesticides are included in Figure 6. 1.



Malathion [S- (1,2- dicarbethyoxyethyl) O,O- dimethyl dithiophosphate].



Methyl Parathion [O,O- dimethyl O, p-nitrophenyl phosphorothioate].



Chlorpyrifos [O,O -diethyl O-3, 5, 6- trichloro-2- pyridyl phosphorothioate].

Figure 6.1 Structural formulae of organophosphorus pesticides.

6.3.1 Distributions of organophosphorus pesticides in water

6.3.1.1 Distributions of total organophosphorus pesticides in water

The total organophosphorus pesticides included in this study are malathion, methyl parathion and chlorpyrifos. The overall summary statistics of organophosphorus is included in Table 6.4. The station wise overall mean concentrations of organophosphorus pesticides in surface and bottom waters are given in Table 6.5. The station wise total organophosphorus pesticides ranged from 0.27 to 2.72 $\mu g\ l^{-1}$ in surface waters and 0.28 to 2.81 $\mu g\ l^{-1}$ in bottom waters respectively.

The station wise percentage composition of organophosphorus pesticides in the surface waters is depicted in Figure 6.2. The individual pesticide mainly distributed in the surface waters of the study area was methyl parathion and ranged from 46.9 to 64.4% of total organophosphorus pesticides. The percentage of malathion ranged from 23.9 to 35.5 and chlorpyrifos ranged from 10.0 to 18.7% that of total organophosphorus pesticides (Figure 6.2).

Figure 6.3 illustrates the station wise percentage composition of organophosphorus pesticides in bottom waters. The distributions of organophosphorus pesticides in bottom waters were almost identical to that in surface waters. The station wise percentage compositions of methyl parathion ranged from 46.4 to 63.1, malathion ranged from 24.1 to 34.4% and that of chlorpyrifos ranged from 10.6 to 20.1% in bottom waters (Figure 6.3).

The organophosphorus pesticides are easily biodegradable and they do not persist long in the aquatic environment. Therefore, comparatively lesser studies were reported on the levels of organophosphorus pesticides in the aquatic environment. The physico-chemical properties of organophosphorus pesticides also have an effect on the distribution of this pesticide in the aquatic environment (Tables 6.1, 6.2 and 6.3). The higher water solubility of a compound shows higher mobility. The organophosphorus pesticides have

Table 6.4 Overall summary statistics of organophosphorus pesticides in water
(µg/l)

	Malathion	Methyl-parathion	Chlorpyrifos
Minimum	ND	ND	ND
Maximum	2.13	3.07	0.68
Mean	0.44	0.82	0.19
SD	0.54	0.87	0.20
CV	122.9	106.7	107.6

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected

Table 6.5 Station wise overall mean concentrations of organophosphorus pesticides

Surface water (µg l^{-1})

Stations	Total organophosphrus	Malathion	Methyl parathion	Chlorpyrifos
1	0.28	0.08	0.15	0.05
2	0.27	0.09	0.13	0.05
3	0.29	0.10	0.14	0.05
4	1.17	0.28	0.75	0.14
5	1.75	0.48	1.09	0.18
6	1.98	0.57	1.14	0.27
7	2.35	0.72	1.33	0.30
8	2.72	0.88	1.52	0.32
9	1.94	0.66	1.04	0.24

Bottom water (µg l^{-1})

Stations	Total organophosphrus	Malathion	Methyl parathion	Chlorpyrifos
1	0.29	0.08	0.15	0.06
2	0.28	0.09	0.14	0.06
3	0.30	0.10	0.14	0.06
4	1.23	0.30	0.78	0.16
5	1.84	0.51	1.13	0.20
6	2.09	0.61	1.17	0.31
7	2.47	0.76	1.37	0.34
8	2.81	0.93	1.52	0.36
9	2.03	0.68	1.07	0.28

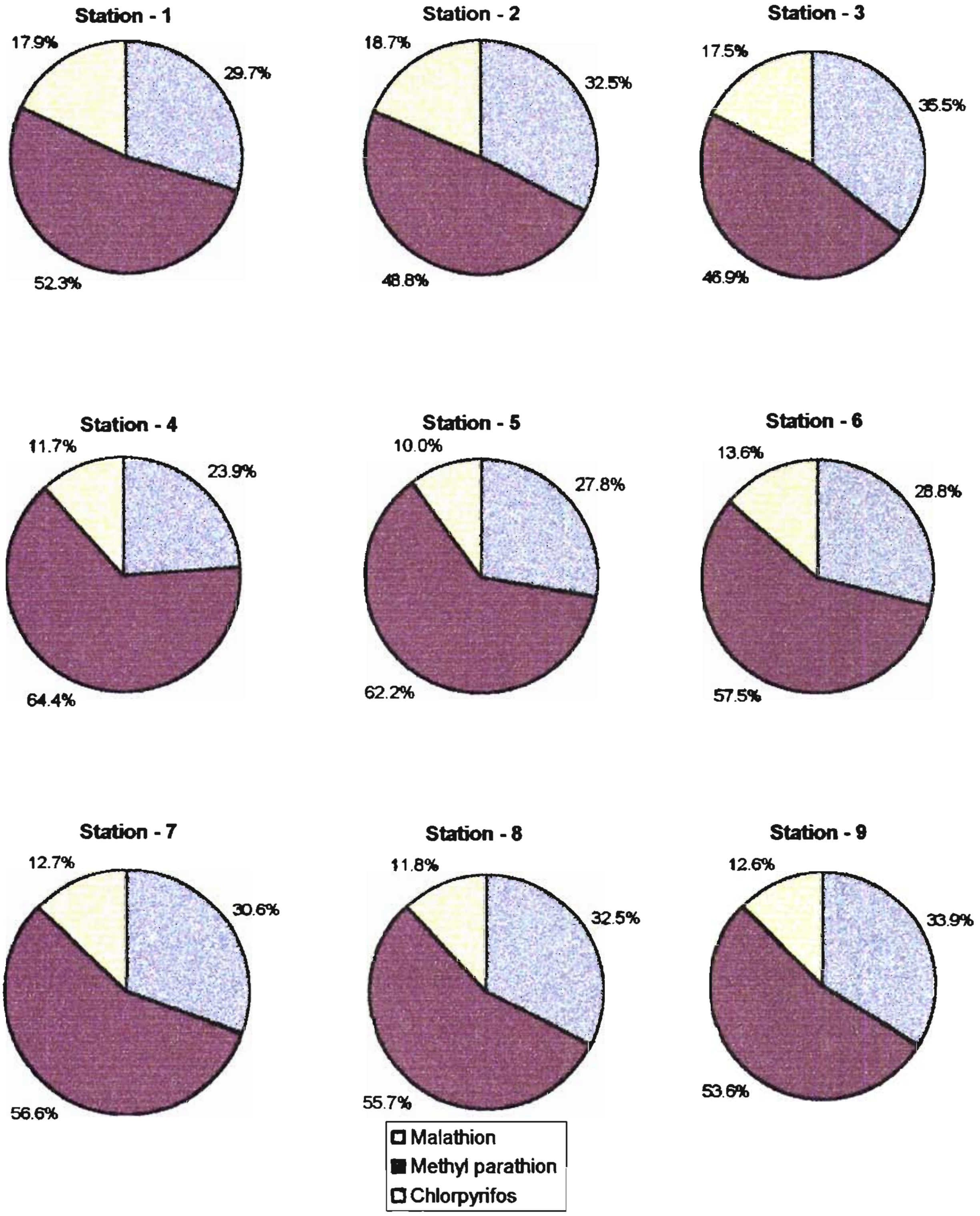


Figure 6.2 Station wise percentage composition of total organophosphorus pesticides in surface waters

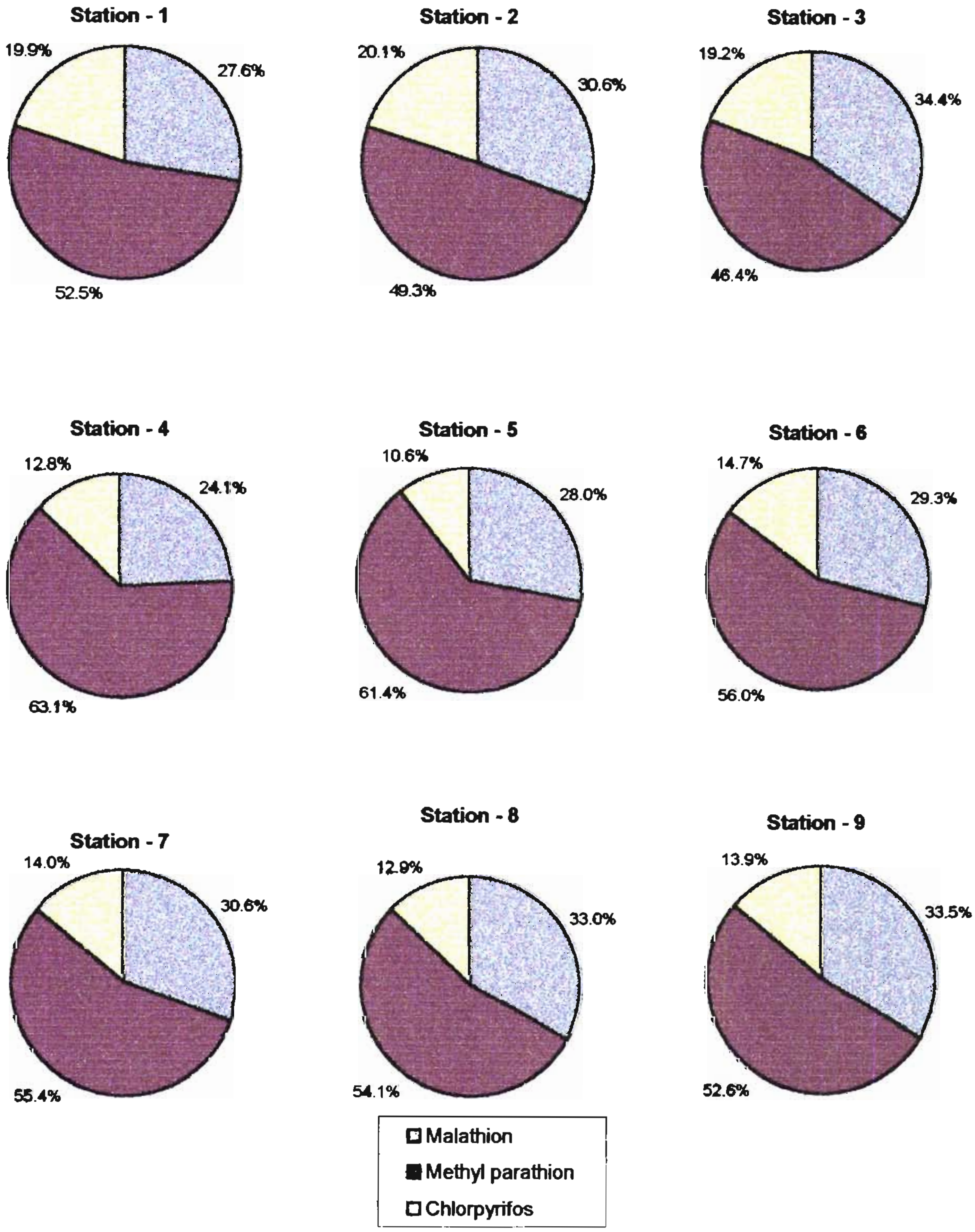


Figure 6.3 Station wise percentage composition of organophosphorus pesticides in bottom waters

higher water solubility and are more mobile than organochlorine pesticides. Organophosphorus compounds are widely used in agriculture for crop protection, especially in the control of rice pests, because of its high levels of efficiency. Foster and Lippa (1996) studied the fluvial loadings on organophosphorus and organonitrogen pesticides in Chesapeake Bay and found that the annual loads of these pesticides were directly correlated with field application rates and stream discharge. The massive application of organophosphorus pesticides in Kuttanad paddy fields may be attributed to the higher levels of organophosphorus compounds observed in the aquatic environment of Kuttanad.

Solvent solubility is also an important property that depends on the inherent polarity of a pesticide. The more non-polar a compound, the more soluble it will be in organic solvents and the less water soluble it will be. The polarity of organophosphorus compounds is also reflected in its water solubility. The water solubilities of malathion, methyl parathion and chlorpyrifos are shown in Tables 6.1, 6.2 and 6.3. Malathion has slightly higher solubility than methyl parathion, but in the present study the concentration of methyl parathion in water was found to be higher than that of malathion. This may be due to the higher use of methyl parathion than malathion for the control of rice pests in the study area.

6.3.1.2 Distributions of malathion in water

Appreciable concentrations of malathion were observed in the backwaters of Kuttanad. The station wise annual mean variations of malathion are illustrated in Figure 6.4. Lower values of malathion were observed at stations 1 to 3. From stations 4 to 8, the values were increasing linearly and at station 9, the value was found to be lower than at station 8. The station wise summary statistics of malathion is included in Table 6.6. The minimum values of non-detectable levels were observed at all stations both in surface and bottom waters. The maximum values recorded in surface and bottom waters were at station 8 and the values were 2.05 µg l^{-1} and 2.21 µg l^{-1} respectively. The station wise mean value of

Table 6.6 Station wise summary statistics of malathion in surface and bottom waters

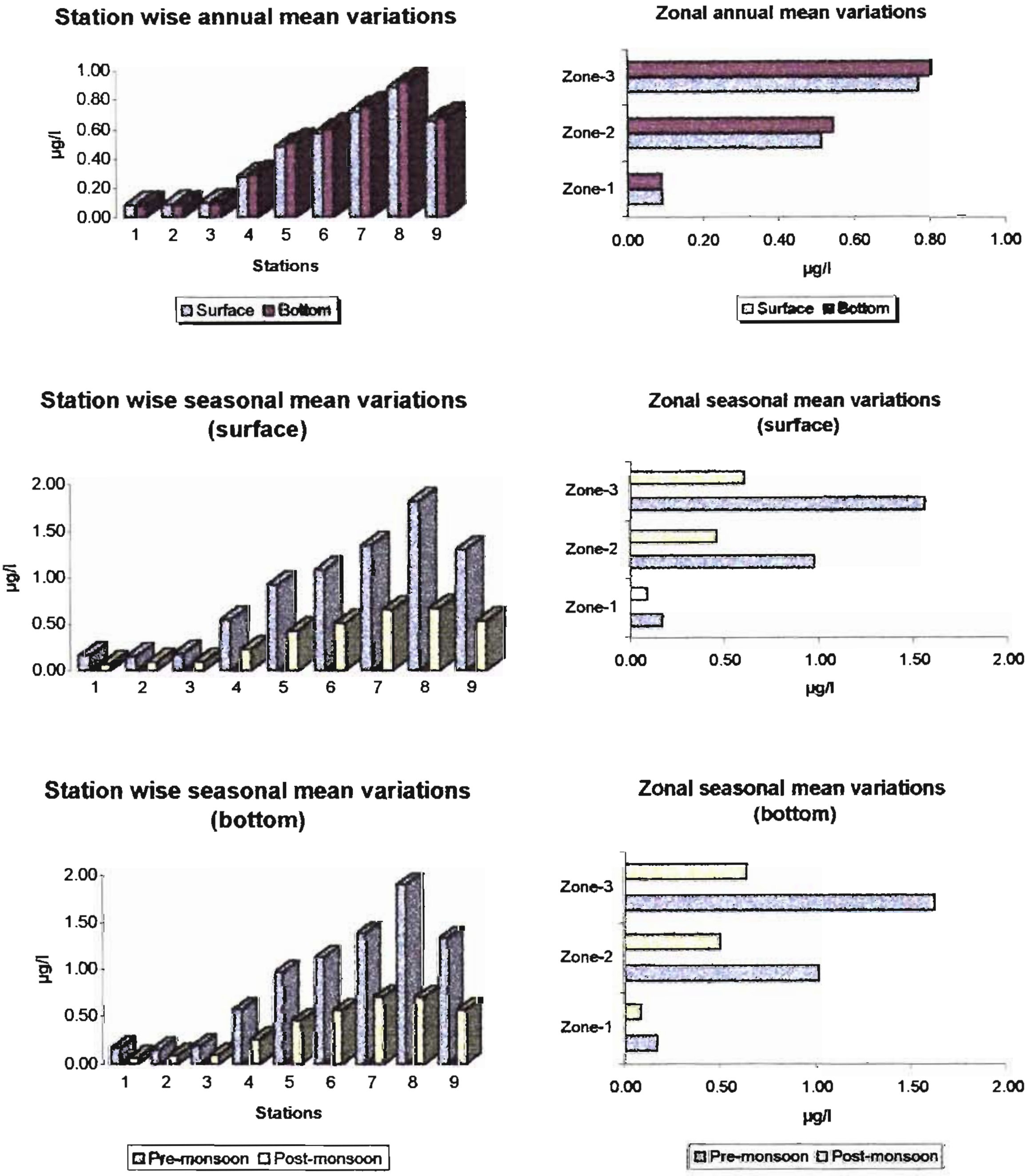
Surface water (µg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.212	0.083	0.079	94.14
2	ND	0.198	0.089	0.083	92.99
3	ND	0.288	0.103	0.102	99.35
4	ND	0.687	0.279	0.255	91.54
5	ND	1.212	0.484	0.454	93.75
6	ND	1 154	0.571	0.483	84.56
7	ND	1.985	0.719	0.632	87.81
8	ND	2.052	0.884	0.804	90.92
9	ND	1.841	0.656	0.593	90.47

Bottom water (µg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.212	0.081	0.078	95.93
2	ND	0.201	0.086	0.080	92.78
3	ND	0.290	0.102	0.101	98.99
4	ND	0.712	0.297	0.269	90.38
5	ND	1.258	0.514	0.476	92.62
6	ND	1.201	0.611	0.502	82.21
7	ND	2.012	0.755	0.650	86.00
8	ND	2.210	0.928	0.844	90.98
9	ND	1.910	0.681	0.613	89.99

SD - Standard deviation; CV - Coefficient of variation; ND-Not detected



Monsoon - Non detectable

Figure 6.4 Seasonal and spatial distributions of malathion in surface and botom waters

malathion ranged between 0.083 μg l^{-1} to 0.884 μg l^{-1} in surface waters and 0.081 μg l^{-1} to 0.928 μg l^{-1} in bottom waters.

In pre-monsoon, both surface and bottom waters recorded higher values of malathion concentrations than that of post-monsoon periods and is plotted in Figure 6.4. In monsoon, non-detectable levels of malathion were observed at all stations. In the station wise zonal variation (Figure 6.4), it was observed that slightly higher values of malathion were observed in zone 3 than that of zone 2.

Agricultural consumption of technical malathion in India was estimated as 1500 metric tonnes in 1995-96 and 1200 metric tonnes in 1996-97 (Pestology Annual, 1999) and this pesticide was profoundly used for the control of rice pests. The higher consumption of malathion may also be a reason for the higher concentration of malathion in the Kuttanad area. Sujatha et al. (1999) reported malathion concentrations in the range 1.373 μg l^{-1} to 13.013 μg l^{-1} from Cochin estuary. The same author has observed higher values in pre-monsoon and non-detectable levels of malathion in most of the stations during monsoon period. These studies were relevant here because the Kuttanad backwaters and Cochin estuarine system are nearby estuaries and almost similar observations were found in both the studies. Moreover, malathion was used for the control of pests of rice and as a result appreciable levels of malathion were present in the study area.

Zhou et al. (1996) reported lower concentrations of malathion (1 to 9 ng l^{-1}) in the Humber estuary. Miliadis and Malatou (1997) reported the malathion concentrations in Pinious River, Greece and the mean concentration was 0.1 μg l^{-1} Kashiwada et al. (1995) studied the degradation abilities of organophosphorus pesticides in zooplankton in environmental water and found that malathion degrading activity of zooplankton was high.

6.3.1.3 Distributions of methyl parathion in water

The most frequently distributed organophosphorus pesticide in the waters of the study area is methyl parathion. The station wise annual mean variations of methyl parathion are illustrated in Figure 6.5. The first three stations of the study area recorded lower values of methyl parathion than in other stations. Stations 7 and 8 recorded higher values than in other stations. The bottom values of methyl parathion in almost all stations were slightly higher than that of surface waters. The station wise summary statistics of both surface and bottom waters of methyl parathion are given in Table 6.7 Minimum values of non-detectable levels of methyl parathion were observed in all stations, both in surface and bottom waters. Maximum values of methyl parathion observed in surface and bottom waters were 3.13 µg l^{-1} and 3.05 µg l^{-1} respectively (Table 6.7).

Higher values of methyl parathion were observed at all stations in pre-monsoon period. In this season, higher values were observed at stations 7 and 8 (Figure 6.5). The post-monsoon values in all stations were lower than that of pre-monsoon values. As in the case of malathion, methyl parathion was also not detected at any of the stations in monsoon period. In the zonal mean variation (Figure 6.5), it was observed that zone 3 recorded higher values and zone 1 recorded lower values of methyl parathion than in zone 2. The same trend was observed for both surface and bottom waters.

Agricultural consumption of technical methyl parathion in India was estimated as 2400 metric tones in 1995-96 and 2000 metric tones in 1997-98 (Pestology Annual, 1999). The usage of methyl parathion was higher than that of malathion (1500 MT) in 1995-96 periods. Methyl parathion is widely used for the control of insect pests of rice viz. rice bug, leaf roller etc. So a huge amount of this pesticide was applied in Kuttanad areas and as a result the waters of the estuary were contaminated with methyl parathion. So higher levels of this pesticide were observed in zones 2 and 3 of the study area.

Miliadis (1995) reported a mean concentration of 0.2 µg l^{-1} of methyl parathion from the waters of Pinious River, Greece. Triantafyllos and Dimitra (1998) reported the levels of methyl parathion in Louros River and the values ranged from non-detectable levels to 5 ng l^{-1} Galindo-Reyes et al. (1999) quantified the methyl parathion levels in the waters from the coastal lagoon, Gulf

Table 6.7Station wise summary statistics of methyl parathion in surface and bottom waters

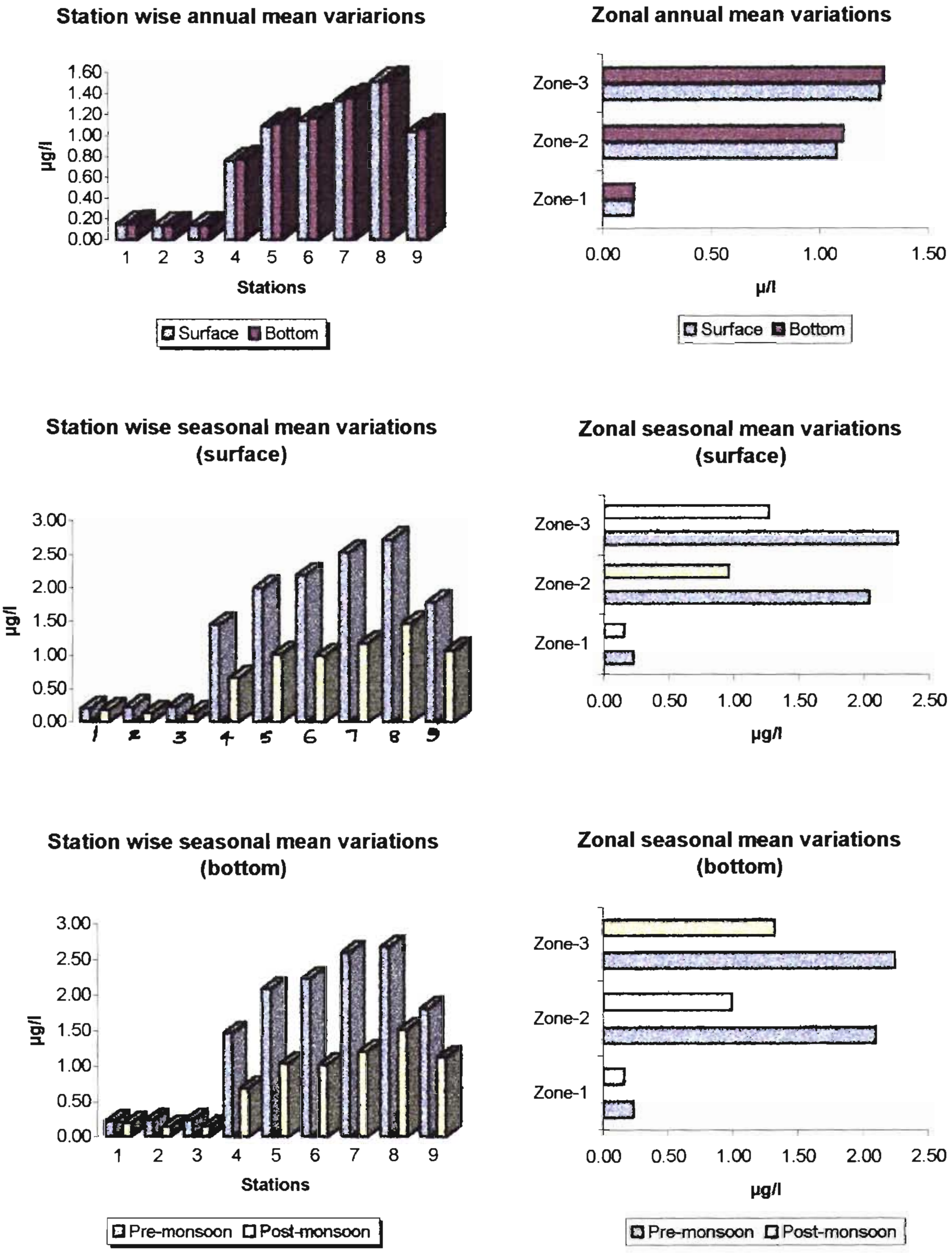
Surface water (µg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.250	0.147	0.094	64.36
2	ND	0.251	0.133	0.105	78.96
3	ND	0.284	0.136	0.107	79.22
4	ND	1.654	0.754	0.596	79.05
5	ND	2.040	1.086	0.823	75.83
6	ND	2.455	1.140	0.891	78.19
7	ND	2.980	1.330	1.041	78.27
8	ND	3.125	1.516	1 130	74.55
9	ND	2.010	1.038	0.729	70.22

Bottom water (µg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.264	0.155	0.101	65.07
2	ND	0.264	0.138	0.108	78.38
3	ND	0.298	0.138	0.109	79.29
4	ND	1.650	0.776	0.604	77.84
5	ND	2.154	1.126	0.861	76.49
6	ND	2.550	1.169	0.910	77.81
7	ND	3.010	1.367	1.065	77.95
8	ND	3.045	1.520	1.103	72.61
9	ND	2.055	1.070	0.740	69.10

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected


Station wise annual mean variarions

Zonal annual mean variations

Station wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Monsoon - Non detectable

Figure 6.5 Seasonal and spatial distributions of methyl parathion in surface and bottom waters

of California and the values ranged from 1.13 to11.05 ng l^{-1} Methyl parathion was also detected in rainfall water samples collected in the agricultural area in Imathia , N. Greece (Albanis et al., 1998).

6.3.1.4 Distributions of chlorpyrifos in water

Among the organophosphorus pesticides quantified, chlorpyrifos was found to be the lesser distributed compound in Kuttanad backwaters. Slightly higher values of chlorpyrifos were found in bottom waters than in surface waters (Figure 6.6). Higher values of chlorpyrifos were observed at stations 6 to 8, both in surface and bottom waters. Station wise summary statistics of chlorpyrifos in surface and bottom waters is shown in Table 6.8. Minimum non-detectable values of chlorpyrifos were observed both in surface and bottom waters. Maximum values of chlorpyrifos observed in surface and bottom waters were 0.645 µg l^{-1} and 0.705 µg l^{-1}, respectively. The station wise mean value ranged from 0.050 to 0.323 µg l^{-1} and 0.056 to 0.363 µg l^{-1} in surface and bottom waters, respectively.

The station wise seasonal mean variations of chlorpyrifos in surface and bottom waters are also plotted in Figure 6.6. In pre-monsoon, higher values of chlorpyrifos were observed both in surface and bottom waters than in post-monsoon season. In monsoon, as observed in other organophosphorus pesticides, non-detectable levels of chlorpyrifos were observed in Kuttanad backwaters. Higher values of chlorpyrifos were observed in zone 3 than in other zones (Figure 6.6) during pre-monsoon and post-monsoon seasons, both in surface and bottom waters.

The non-polar nature of chlorpyrifos is also reflected in its water solubility (Table 6.3). Other reported values of water solubilities (23-25°C) varying from 0.94 to 2 ppm. The water solubilities of chlorpyrifos are about 40 times lesser than that of methyl parathion and also about 100 times lesser than that of malathion. The rate of consumption of chlorpyrifos was comparably less than that of malathion and methyl parathion. These may be attributed to the lower levels of chlorpyrifos in water than that of malathion and methyl parathion.

Table 6.8 Station wise summary statistics of chlorpyrifos in surface and bottom waters

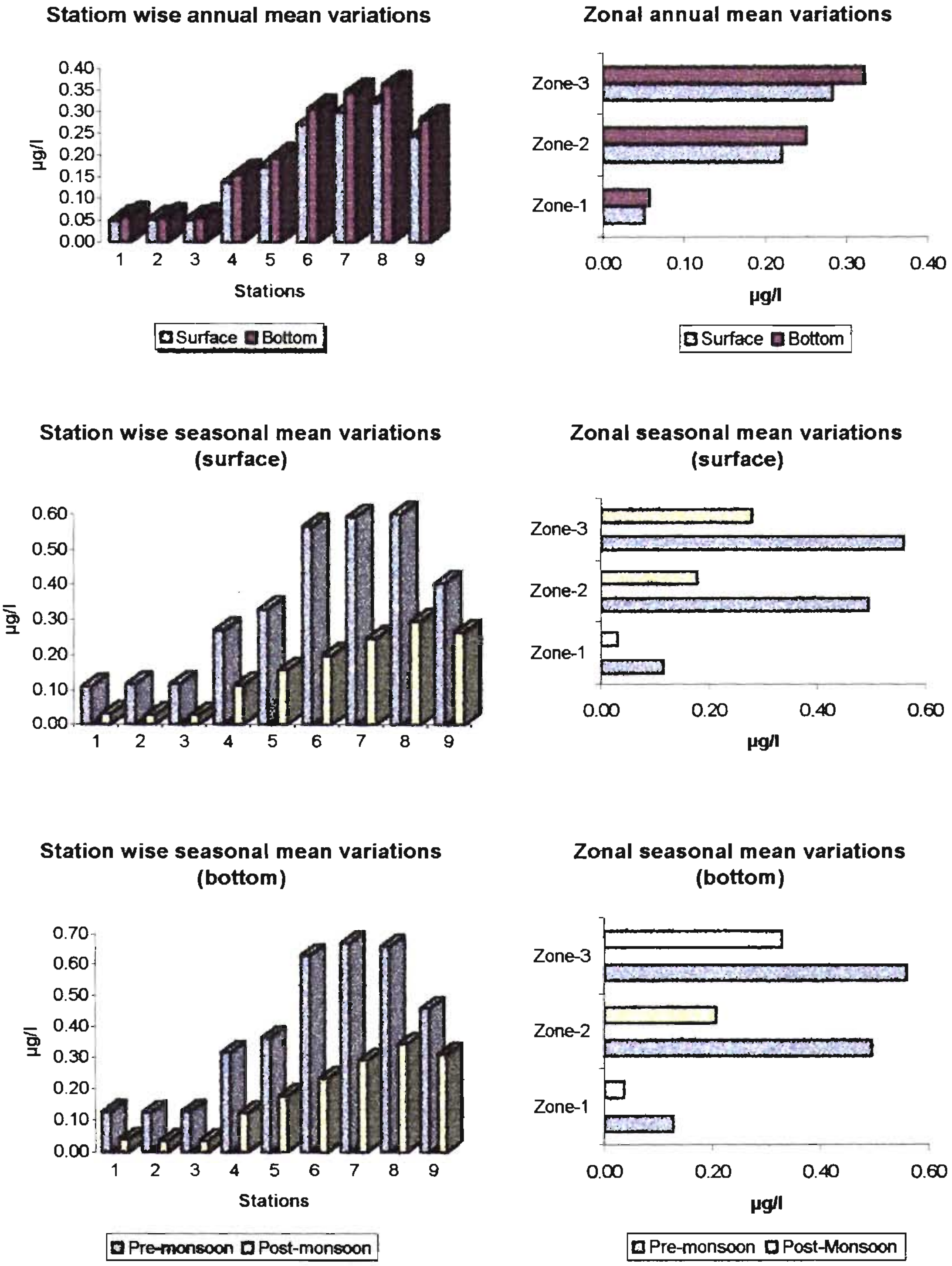
Surface water (μg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.114	0.050	0.054	107.50
2	ND	0.154	0.051	0.057	112.55
3	ND	0.125	0.051	0.056	109.95
4	ND	0.325	0.137	0.118	86.59
5	ND	0.356	0.175	0.140	79.93
6	ND	0.625	0.270	0.241	89.24
7	ND	0.625	0.299	0.248	82.96
8	ND	0.645	0.323	0.251	77.78
9	ND	0.495	0.243	0.166	68.31

Bottom water (μg l^{-1})

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	0.154	0.059	0.063	107.50
2	ND	0.169	0.056	0.063	111.39
3	ND	0.139	0.057	0.062	108.18
4	ND	0.401	0.157	0.140	89.04
5	ND	0.405	0.195	0.153	78.48
6	ND	0.705	0.307	0.268	87.17
7	ND	0.702	0.344	0.279	80.95
8	ND	0.705	0.363	0.275	75.67
9	ND	0.525	0.283	0.191	67.43

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 6.6 Seasonal and spatial distributions of chlorpyrifos in surface and bottom waters

Eitzer and Chevalier (1999) observed the presence of chlorpyrifos from the residential drinking water wells in Connecticut and a mean value of 0.06 µg l^{-1} was reported.

6.3.1 Distributions of organophosphorus pesticides in sediments

6.3.2.1 Distributions of total organophosphorus pesticides in sediments

The total organophosphorus pesticides studied in sediments of Kuttanad backwaters also include malathion, methyl parathion and chlorpyrifos. The station wise percentage compositions of total organophosphorus pesticides in sediments are depicted in Figure 6.7 The major portions of pesticides found at all stations were chlorpyrifos (45.0 to 55.0). The percentage compositions of malathion ranged from 28.6 to 35.5 and that of methyl parathion ranged from 13.2 to 20.2 of total organophosphorus pesticides in sediments (Figure 6.7).

The overall summary statistics of organophosphorus compounds is given in Table 6.9 and the station wise overall mean concentrations of organophosphorus pesticides in sediments are given in Table 6.10. The station wise overall mean concentration of total organophosphorus pesticides varied from 2.23 to 9.07 ng g^{-1}

Comparatively lesser values of organophosphorus pesticides were observed in the sediments of the study area. Chiefly, processes such as solubilisation, precipitation, sorption, complexation etc regulate transport of pesticides from non-point or point sources to the aquatic environment. Pesticide adsorption to the soil or sediment is inversely related to the water solubility of that compound (Sujatha et al., 1999). Thus, the pesticides may be transported through the aquatic system by diffusive or sorptive process. There is also a continuous interchange of pesticides between sediments and water that is influenced by water movement, turbulence, dilution, temperature, pH, ionic strength etc. Organophosphorus pesticides are generally short lived in the environment and biological systems; they are commonly degraded through

Table 6.9 Overall summary statistics of organophosphorus pesticides in sediments
(ng g^{-1} dry wt.)

	Malathion	Methyl parathion	Chlorpyrifos
Minimum	ND	ND	ND
Maximum	8.35	3.55	9.66
Mean	1.40	0.69	2.25
SD	1.95	0.92	2.42
CV	139.40	132.28	107.40

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected

Table 6.10 Station wise overall mean concentrations of organophosphorus pesticides in sediments (ng $^{-1}$)

Stations	Total Organophosphorus	Malathion	Methyl parathion	Chlorpyrifos
1	2.23	0.64	0.41	1 18
2	2.27	0.71	0.39	1 16
3	2.39	0.76	0.45	1 18
4	4.91	1.46	0.75	2.70
5	7.61	2.42	1 17	4.02
6	9.07	2.98	1.37	4.72
7	5.96	2.06	0.79	3.11
8	2.40	0.85	0.47	1.08
9	2.26	0.72	0.46	1.09

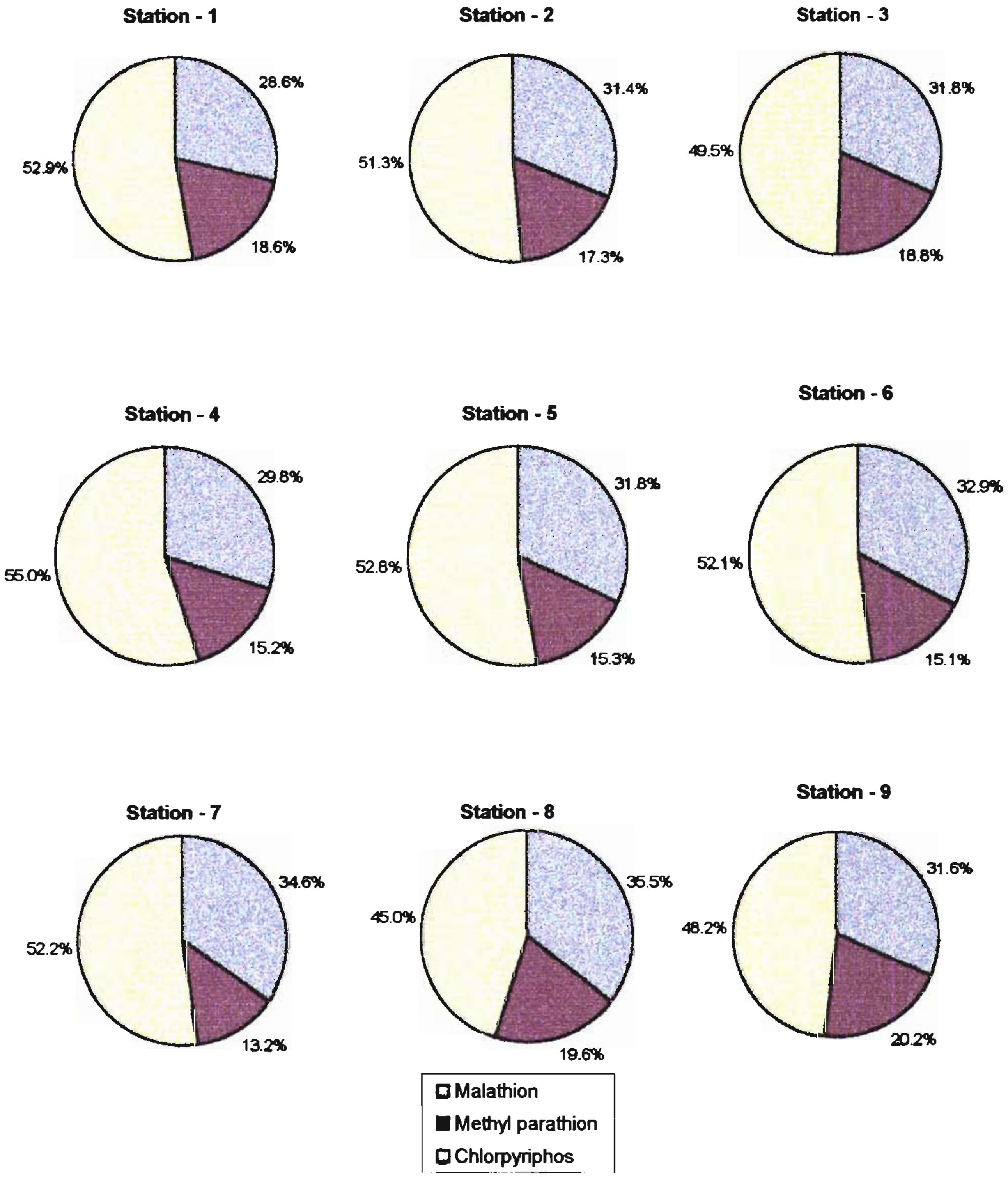


Figure 6.7 Station wise percentage composition of total organophosphorus pesticides in sediments

hydrolysis and other reactions into non-toxic and water soluble compounds (Eto, 1977). These may be the reasons for the lower levels of organophosphorus pesticides in sediments than in water.

6.3.2.2 Distributions of malathion in sediments

Low values of malathion were observed in the sediments of the study area. In the first three stations and the last two stations, the distributions of malathion were almost comparable and at stations 5 and 6, higher values of malathion were observed (Figure 6.8). The station wise summary statistics of malathion in sediments is given in Table 6.11 Minimum of non-detectable levels of malathion was observed in sediments at all stations. A maximum value of 8.35 ng g^{-1} of malathion in sediments was observed at station 6. The station wise mean values of malathion in sediments ranged from 0.64 ng g^{-1} to 2.98 ng g^{-1} (Table 6.11).

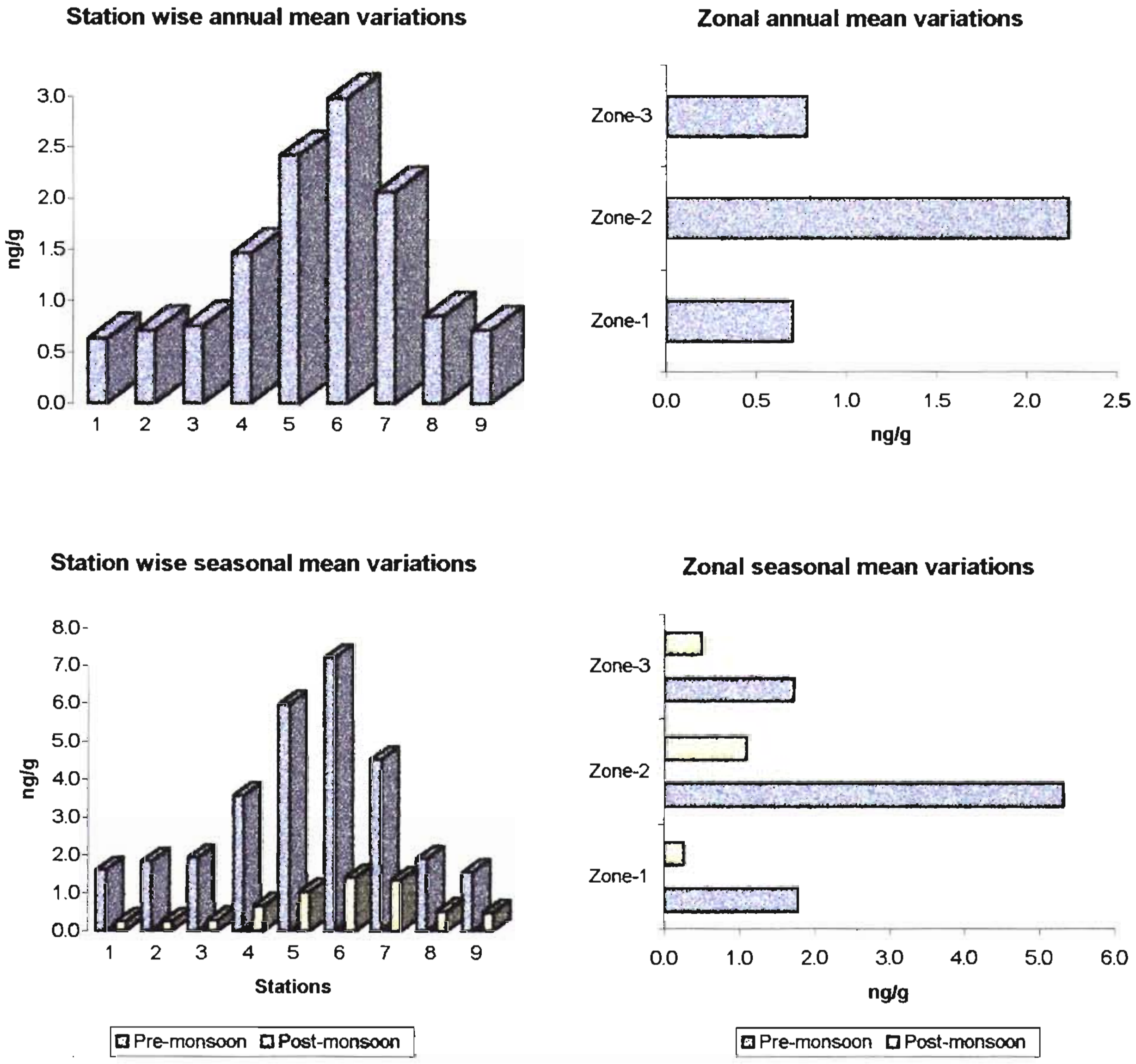
The station wise seasonal mean variations (Figure 6.8) showed that the pre-monsoon values of malathion were higher in sediments than in post-monsoon period. In monsoon, non-detectable levels of malathion were observed in sediments. The zonal annual mean variations (Figure 6.8) showed higher levels of malathion in the sediments of zone 2. Higher values of malathion were also found in zone 2 in pre-monsoon period. In all zones, post-monsoon values of malathion in sediments were lower than that of pre-monsoon periods. In monsoon, non-detectable levels of malathion were found in all zones.

Lower levels of malathion were present in the sediments of the study area. The higher solubility of malathion in water and its higher degradation property were the major reasons for the lower levels of malathion in sediments. The lower percentage of organic carbon in zone 3 also influenced the lesser amounts of malathion in that zone. Giovanni Melluso et al. (1994) reported a mean concentration of 240 ng g^{-1} of malathion in river sediments in Campania, Italy.

Table 6.11 Station wise summary statistics of malathion in sediment
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	2.15	0.64	0.83	130.1
2	ND	2.99	0.71	1.00	140.8
3	ND	2.16	0.76	0.96	126.2
4	ND	4.66	1.46	1.73	118.2
5	ND	6.55	2.42	2.78	114.9
6	ND	8.35	2.98	3.34	111.8
7	ND	5.35	2.06	2.11	102.1
8	ND	2.15	0.85	0.90	105.1
9	ND	1.99	0.72	0.76	106.7

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 6.8 Seasonal and spatial distributions of malathion in sediments

The rate of chemical and biochemical transformation of organophosphorus pesticides may depend on a number of factors involving the nature of the compound, application method and the climate (Eto, 1977). Metallic ions in soil interact with organophosphorus pesticides (Eto, 1977). Malathion is quickly incorporated into the inter layer region of some metallic montmorillonite and adsorbed through hydrogen bonding interaction between the carbonyl oxygen and a water molecule in the primary hydrogen shell of the metallic ion (Bowman et al., 1970). In the dehydrated state, the carbonyl group interacts directly with the metallic ion, and the intensity of the ion dipole interaction increases with the cationic valence of the metal (Bowman et al., 1970). Though malathion is highly degradable, traces of this pesticide can be found in Kuttanad backwaters, and this may also be due to the above reason.

6.3.2.3 Distributions of methyl parathion in sediments

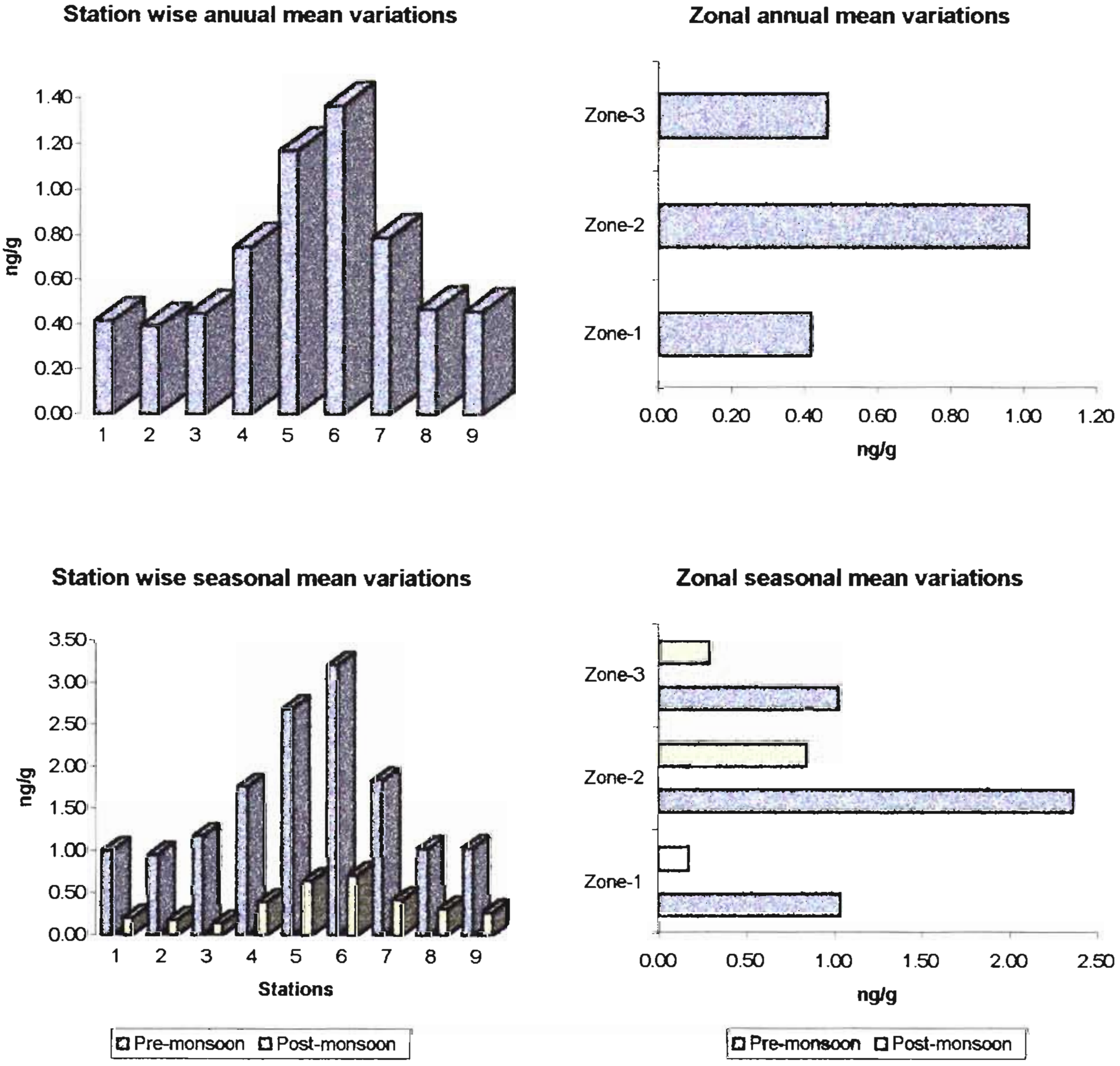
As in the case of malathion, low values of methyl parathion were also observed in the study area. Almost uniform distributions of methyl parathion were observed at first three stations and from stations 4 to 6 the values were increasing and from stations 7 to 9, the values were decreasing (Figure 6.9). The station wise summary statistics of methyl parathion is given in Table 6.12. Like that of malathion, minimum of non-detectable values of methyl parathion were observed in sediments at all stations. A maximum value of 3.55 ng g^{-1} of methyl parathion was observed at station 6. The station wise mean values of methyl parathion ranged from 0.39 ng g^{-1} to 1.37 ng g^{-1} in sediments.

The station wise seasonal mean variations of methyl parathion in sediments are plotted in Figure 6.9. Higher values of methyl parathion in sediments were observed in pre-monsoon period. Lower values were observed in post-monsoon period and non-detectable levels of methyl parathion were observed in monsoon period. Higher levels of methyl parathion were observed in zone 2 than in other zones (Figure 6.9). The zonal seasonal mean variations (Figure 6.9) also showed higher values of methyl parathion in pre-monsoon period than in other seasons.

Table 6.12 Station wise summary statistics of methyl parathion in sediment
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	1.03	0.41	0.51	123.7
2	ND	1.25	0.39	0.50	127.6
3	ND	1.62	0.45	0.60	133.4
4	ND	2.15	0.75	0.85	114.5
5	ND	3.21	1.17	1.31	112.0
6	ND	3.55	1.37	1.57	114.7
7	ND	2.13	0.79	0.90	114.7
8	ND	1.05	0.47	0.51	107.7
9	ND	1.15	0.46	0.50	110.2

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Monsoon - Non detectable

Figure 6.9 Seasonal and spatial distributions of methyl parathion in sediments

Giovanni Melluso et al. (1994) reported a mean concentration of 90 ng g^{-1} of methyl parathion in river sediments in Campania, Italy. Methyl parathion was also observed from the coastal lagoon off the Gulf of California, and the values ranged from 6.05 to 98.68 ng g^{-1} (Galindo-Reyes, 1999). Somara and Siddavattom (1995) observed the microbial degradation of methyl parathion in agricultural soils to paranitrophenol. The lower levels of methyl parathion observed in the sediments of the study area may be attributed to the higher degradation of methyl parathion and also the high volatilisation of this compound due to tropical nature of the study area. Pignatello and Day (1996) studied the mineralisation of chlorpyrifos in a fine sandy loam soil containing organic carbon and found that temperature had a marked effect on the reaction.

6.3.2.4 Distributions of chlorpyrifos in sediments

The station wise annual mean variations of chlorpyrifos in sediments are illustrated in Figure 6.10. At the first three stations, the chlorpyrifos values were almost same, and from stations 4 to 6, slightly increasing trend of chlorpyrifos was observed. The chlorpyrifos values at stations 8 and 9 were lower than that of stations 4 to 7 Minimum of non-detectable levels of chlorpyrifos was observed at all stations and a maximum of 9.66 ng g^{-1} of chlorpyrifos was observed at the sediments of station 5 (Table 6.13). The mean values of chlorpyrifos in sediments ranged from 1.08 ng g^{-1} to 4.72 ng g^{-1}

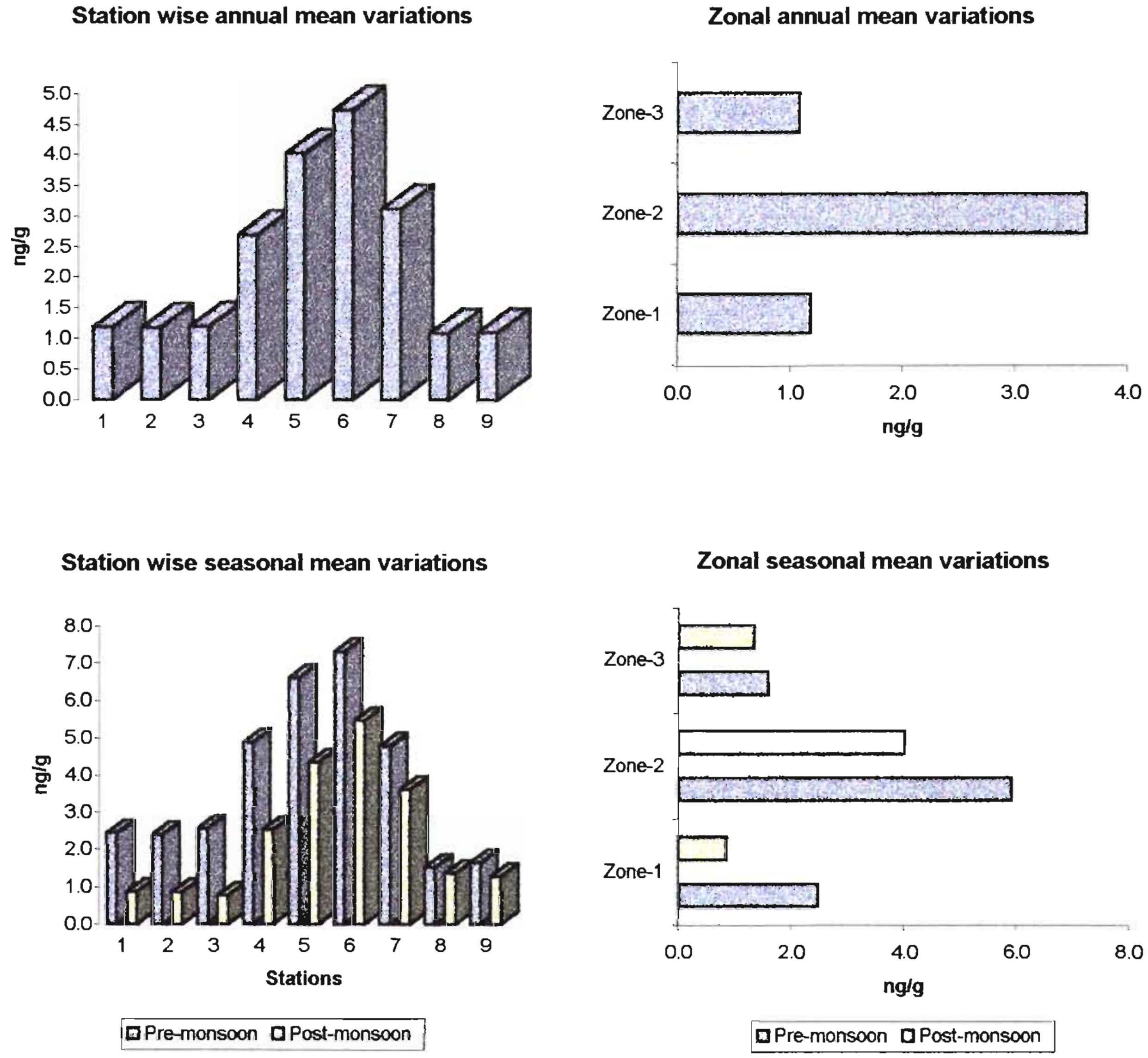
From the station wise seasonal mean variations (Figure 6.10), it was observed that the pre-monsoon values of chlorpyrifos at all stations were higher than that of post-monsoon values. In monsoon, non-detectable levels of chlorpyrifos were observed at all stations. Higher values of chlorpyrifos were observed in zone 2 and lower values in zones 1 and 3 (Figure 6.10). The zonal seasonal mean variations (Figure 6.10) also showed higher levels of chlorpyrifos in pre-monsoon than in post-monsoon periods.

Octonoal/water partition coefficients (P) expresses the relative affinity a compound has for organic vs. aqueous solution, and are key parameters in the

Table 6.13 Station wise summary statistics of chlorpyrifos in sediment
(ng g^{-1} dry wt.)

Stations	Minimum	Maximum	Mean	SD	CV
1	ND	3.55	1.18	1.39	118.0
2	ND	2.99	1.16	1.26	107.7
3	ND	3.15	1 18	1.32	111.1
4	ND	6.59	2.70	2.54	94.1
5	ND	9.66	4.02	3.39	84.4
6	ND	8.95	4.72	3.16	66.9
7	ND	5.25	3.11	2.10	67.6
8	ND	2.75	1.08	0.86	79.4
9	ND	2.01	1.09	0.78	72.0

SD - Standard deviation; CV - Coefficient of variation; ND - Not detected



Station wise annual mean variations

Zonal annual mean variations

Station wise seasonal mean variations

Zonal seasonal mean variations

Monsoon - Non detectable

Figure 6.10 Seasonal and spatial distributions of chlorpyrifos in sediments

estimation of environmental partitioning (eg., sediment/water). The moderately high partition coefficients that have been determined for chlorpyrifos results from its non polar nature and indicated to a great degree its tendency to associate strongly with organic phases of the environment. (Experimentally determined P values for chlorpyrifos have ranged from 4.7 to 5.3 (de Bruijn et al. 1989). This may be attributed to the higher levels of chlorpyrifos in sediments than that of malathion and methyl parathion.

Cavanagh et al. (1999) observed the residues of chlorpyrifos in the soils and sediments of the Herbert and Burdekin river regions, North Queensland and the values ranged from <0.005 to 0.936 ng g^{-1} in Herbert region and <0.005 to 0.987 ng g^{-1} in Burdekin region. Racke et al. (1996) examined the abiotic hydrolysis of chlorpyrifos and found that although both microbial and hydrolytical mechanisms contributed to chlorpyrifos degradation in all soils, there were soils in which hydrolysis constitutes the major route of degradation. Also observed that chlorpyrifos degradation was greatly accelerated under low moisture conditions, both in acid and alkaline conditions. In the sediments of the study area the moisture content was found to be high, and it may also be a reason for the higher levels of chlorpyrifos than malathion and methyl parathion.

6.4 CORRELATION OF ORGANOPHOSPHORUS PESTICIDES WITH ENVIRONMENTAL PARAMETERS

The correlations of organophosphorus pesticides with various hydrographical and sedimentary parameters are summarized in Tables 6.14 The malathion, methyl parathion and chlorpyrifos concentrations in water were found to be significantly influenced by the mean salinity ($p < 0.001$, $n=108$). The Pearson coefficient 'r' showing the correlation of malathion, methyl parathion and chlorpyrifos with salinity were 0.724, 0.624 and 0.654 respectively. But the dissolved oxygen concentrations in water have no correlation with the organophosphorus pesticides. The malathion, methyl parathion and chlorpyrifos concentrations were found to be significantly correlated (though negatively), by the hydrogen ion concentration (pH).

Table 6. 14 Correlation of organophosphorus pesticides with environmental parameters

(Water)

	Malathion	Methyl parathion	Chlorpyrifos
Salinity	0.724	0.624	0.654
Dissolved oxygen	-0.106	-0.026	-0.082
pH	-0.488	-0.469	-0.434
Temperature	0.416	0.481	0.513

(Sediment)

	Malathion	Methyl parathion	Chlorpyrifos
Organic carbon	0.073	0.022	0.088
Sediment moisture	-0.006	-0.026	0.018
Sand	-0.105	-0.104	-0.137
Silt	0.161	0.135	0.126
Clay	0.017	0.047	0.125

The correlations of organophosphorus pesticides with the sedimentary characteristics are also given in Table 6.14. The organophosphorus pesticides with sedimentary parameters displayed no significant correlations. A negative correlation was observed for sand and positive correlations with silt and clay fraction of the sediment with malathion, methyl parathion and chlorpyrifos metabolites.

6.5 SUMMARY

- The presence of organophosphorus pesticides in the water and sedimental compartments of Kuttanad backwaters was found to be seasonal and higher concentrations were found in pre-monsoon season and non-detectable levels were observed in monsoon season.

- The residual levels of different organophosphorus pesticides in the waters of the backwaters of Kuttanad are as in the order chlorpyrifos < malathion < methyl parathion.

- The organophosphorus residues in the sediments of the study area are in the order methyl parathion < malathion < chlorpyrifos.

- Organophosphorus pesticides are degradable compounds, and both abiotic and biotic transformation processes effect its degradation within the environmental compartments and due to that the distribution profiles of these compounds are lower in sediments.

- A baseline data for the persistence of pesticides are essential for understanding the environmental fate of pesticides in the aquatic systems. The baseline data of organophosphorus pesticide residues in water and sedimental compartments depend on the concentration of these compounds, and the length of persistence prior to the degradation by the environment.

Data obtained from the present study are useful for understanding the contamination dynamics of the different organophosphorus pesticides present in the aquatic and sedimental compartments of Kuttanad backwaters.

CHAPTER 7

SUMMARY

The growing demand and supply of new chemicals, including pesticides, in the industrialized society in this century places increasingly higher stress on the environment. Large amounts of these diverse chemicals enter the different compartments of the environments by various means. Pesticide cycle in the environment is well represented diagrammatically and is shown in Figure 7 1. The hydrophobic and persistent nature of pesticides has concern about their ability to accumulate in the environment. The aquatic environment is particularly sensitive to pollution because of its fragile ecology. The prediction of aquatic fate of pesticides, and their distribution in different compartments of the environment can be useful in the assessment of the effect of pollution episodes on human health and ecological systems. A schematic diagram showing the biological transfer of pesticides to man is illustrated in Figure 7.2.

The fate of hydrophobic organic pollutants in the aquatic environment is controlled by a variety of physical, chemical and biological processes. Some of the principal biogeochemical processes, which govern the distribution and fate of hydrophobic organic pollutants in the aquatic environment is shown in Figure 7.3.

The main sources of pesticide which controls or regulate the fluvial loadings of pesticides in the Kuttanad backwaters were the agricultural land run-off from 'Padashekarams" and the discharge of water from the major river systems, viz Pampa, Manimala, Achencoil and Meenachal. The Thannermukkam bund also plays a crucial role in accumulating the pesticides in Kuttanad backwaters, especially in pre-monsoon period.

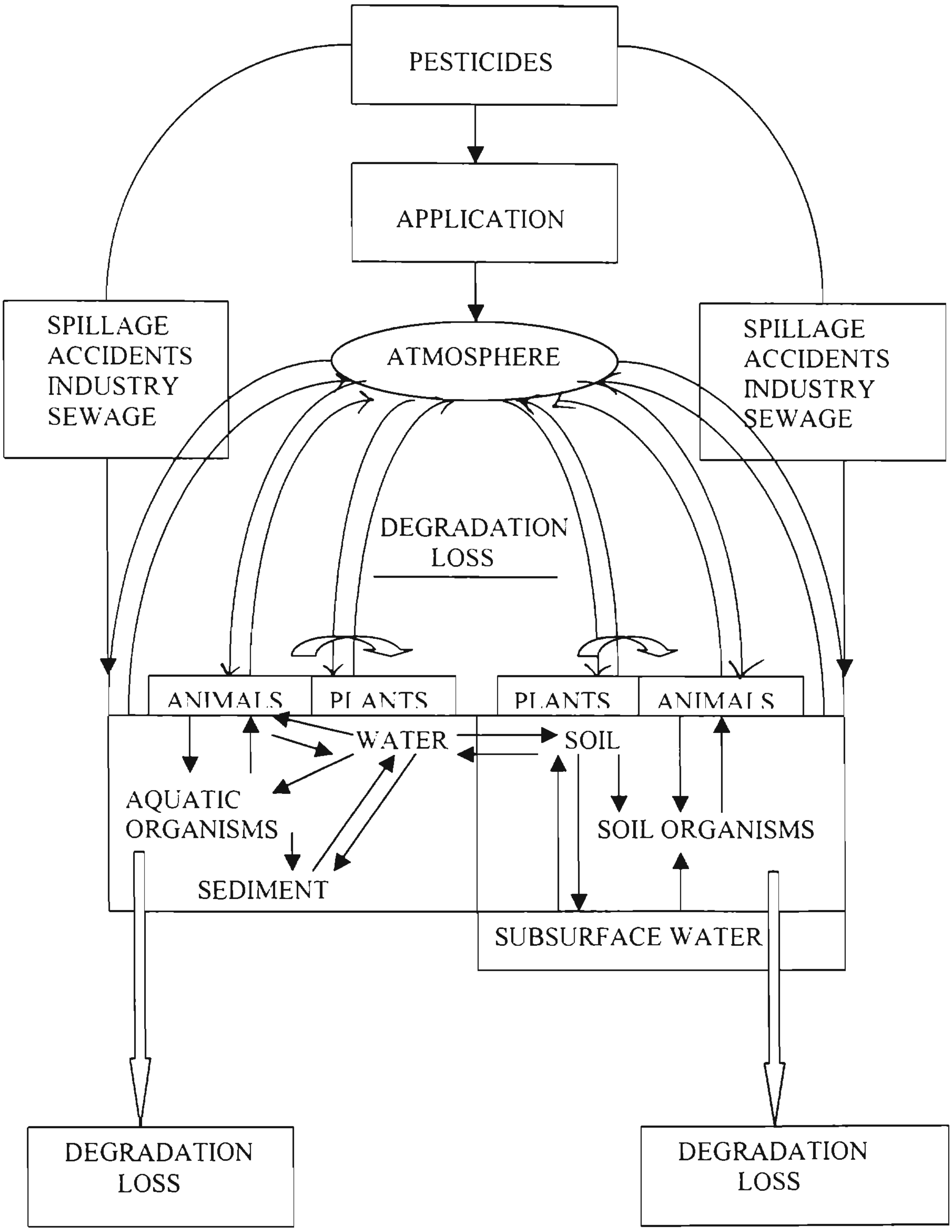


Figure 7.1 Pesticide cycle in the environment (Karla and Chawla, 1981)

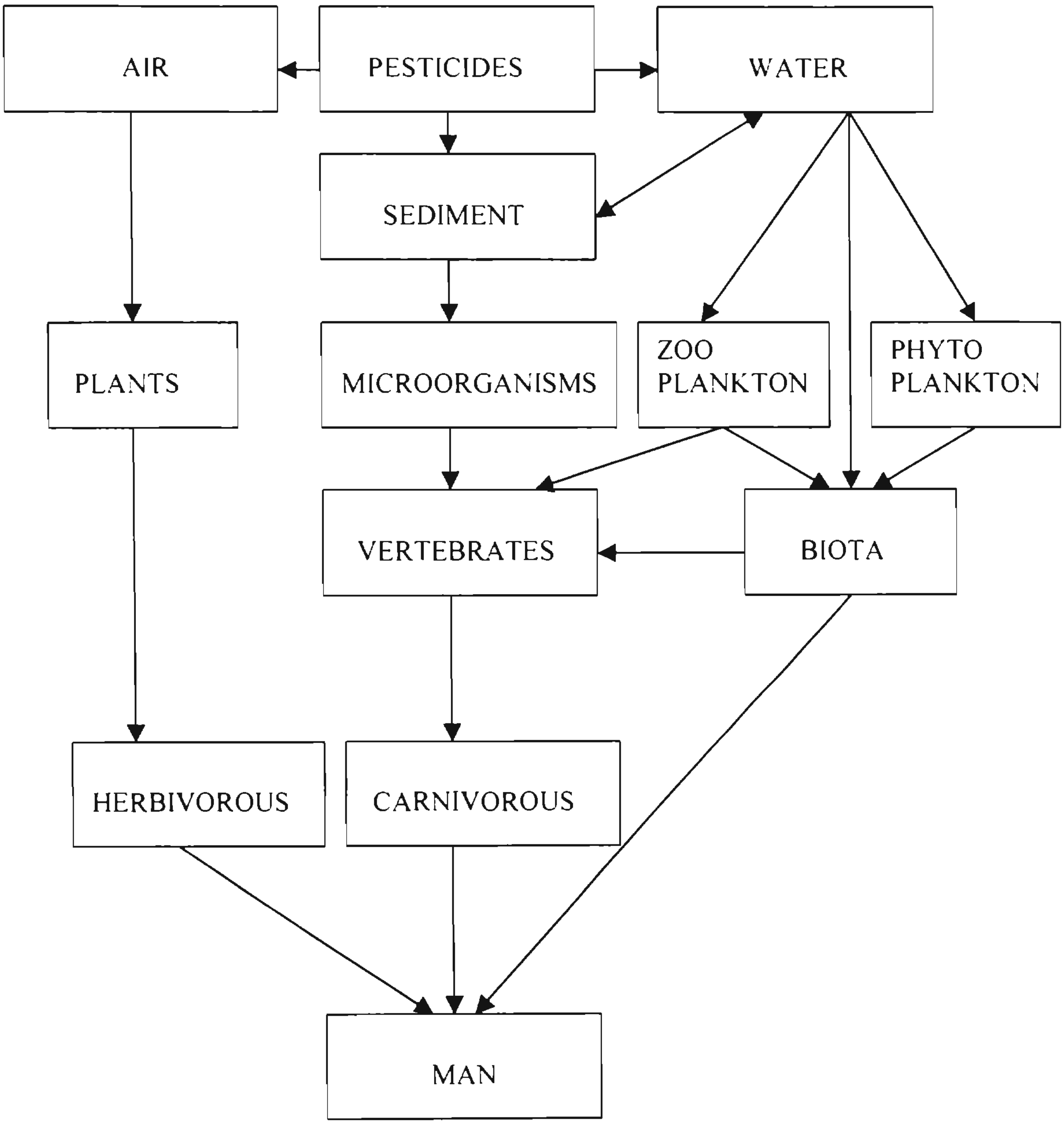


Figure 7. 2 Schematic representation of biological pesticide transfer to man

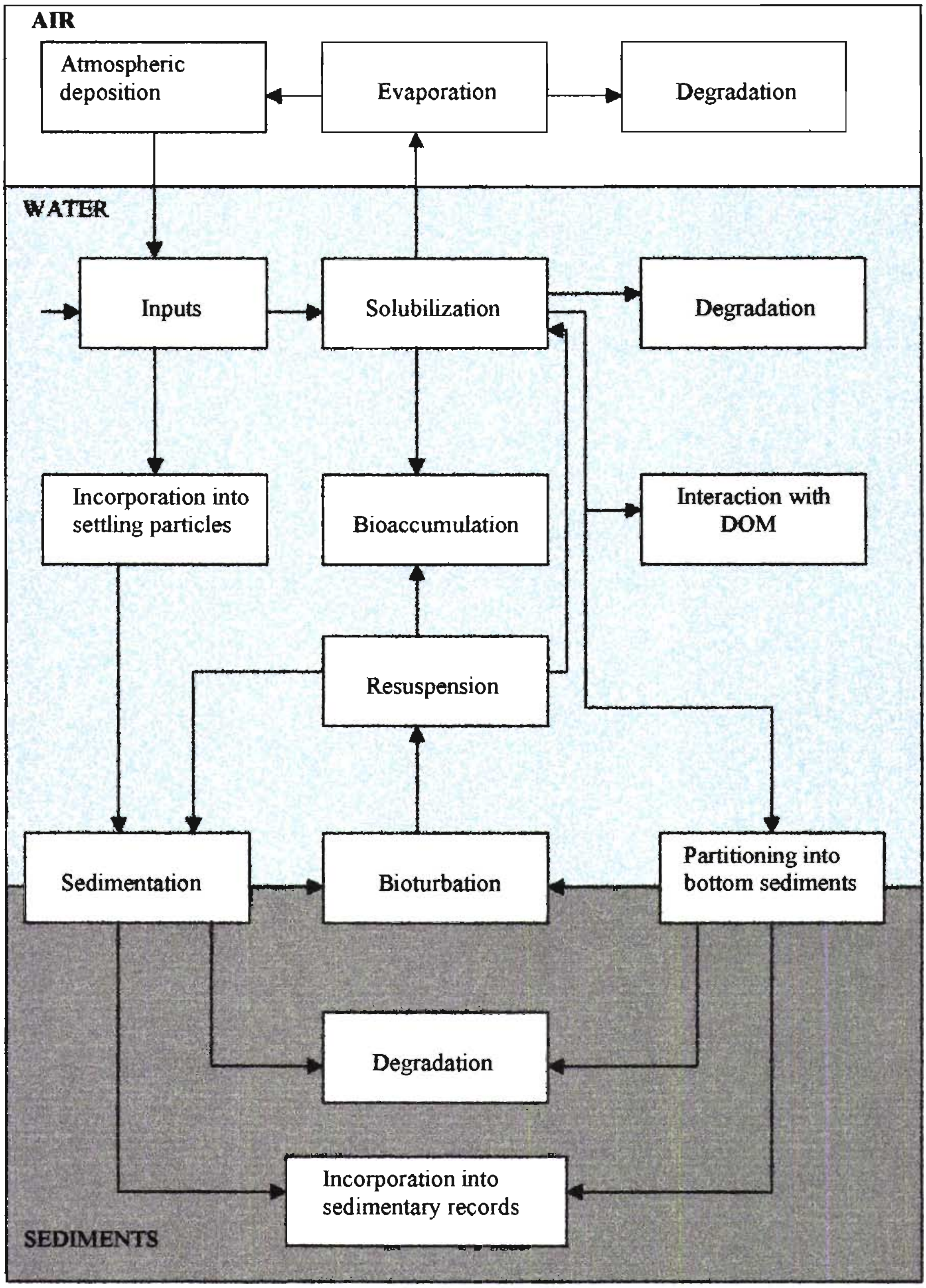


Figure 7.3 Schematic diagram of the biogeochemical processes of hydrophobic pollutants in the aquatic environment (Rudolf, 1991).

The continued usage of certain pesticides such as DDT, HCH and endosulfan in agriculture and vector control programmes has been a contributing factor to the high levels of these pesticides in the Kuttanad water system. The major chlorinated pesticides found in the study area were still DDT and its metabolites viz DDE and DDD. In Kuttanad waters, DDE was the major individual metabolite seen throughout the study area. The levels of organochlorine pesticides in zone 1 were still tolerable in terms of quality for domestic use, whereas some of those rice-growing areas, in zone 2 and zone 3, have exceeded the levels to maintain aquatic life. The higher residue levels of some organochlorine pesticides in the Kuttanad backwaters may affect the aquatic life and or lead to their accumulation into the food chain.

The major portions of the organochlorine pesticides found in the sediments of Kuttanad backwaters are DDT and its metabolites and HCH and its isomers. Compared to DDTs and HCHs, the residues of cyclodienes were found to be less. The highest concentrations found in the sediments of Kuttanad backwaters were the p,p'-DDE in $\sum$DDT, β-HCH in $\sum$HCH and α-endosulfan in $\sum$cyclodienes. Concentrations of organochlorine pesticides, mainly DDT and its metabolites and HCH isomers observed in the sediments of the study area may be attributed to the wide application of HCH formulations in agriculture and the use of DDT formulations in vector control programmes. The low levels of some of the cyclodiene pesticides in the sediments of Kuttanad backwaters may be attributed to the sediment transport process from the near-shore or catchment areas and also the movement of soil/sediment particles from these areas to the estuary. The distribution patterns of organochlorine pesticides in the sediments of Kuttanad backwaters were dependent on the distributions of organic carbon of the sediments and also the nature of the sediments. The organic carbon distribution and nature of surface sediments were mainly related to the tributary runoff and the anthropogenic inputs. The organochlorine pesticides detected in most of the sediment samples were ubiquitous throughout the

Kuttanad backwaters and these compounds in the estuary were transported within both the water body and sediments and mixed between them.

The presence of organophosphorus pesticides in the water and sedimental compartments of Kuttanad backwaters were found to be seasonal and higher concentrations were found in pre-monsoon season and non-detectable levels in monsoon season. The residual levels of different organophosphorus pesticides in the waters of the backwaters of Kuttanad are as in the order chlorpyrifos < malathion < methyl-parathion. The organophosphorus residues in the sediments of the study area are in the order methyl parathion < malathion < chlorpyrifos. Organophosphorus pesticides are degradable compounds, and both abiotic and biotic transformation processes effect its degradation within the environmental compartments and due to that the distribution profiles of these compounds are lower in sediments. The baseline data of organophosphorus pesticide residues in water and sedimental compartments depend on the concentration of these compounds, and the length of persistence prior to the degradation by the environment.

The solubility of a pollutant plays an important role in determining its fate in the aquatic environment. Because of the ubiquity, persistence, and possible toxicity of pesticides, their mobility in soil-water environment is of great concern. Polar compounds will dissolve in water, whereas hydrophobic compounds like pesticides will be incorporated into organic rich particulate matter, and preferentially accumulate in the sediments. Sorption onto soils, sediments, and suspended particles, volatilization into atmosphere, degradation, and bioaccumulation are attenuation process that affect the levels and mobility of pesticides in different environmental compartments.

The partitioning process will strongly affect the fate of chemicals. The particulate associated contaminants will have shorter residence times in the water column than dissolved phase contaminants, due to the rapid removal of particles by sedimentation, relative to hydraulic flushing times (Swackhamer and Eisenreich, 1991). The accumulation into sediments was found to be a partitioning rather than an adsorptive process for hydrophobic pollutants (Chiou et al., 1979, 1985; Kyle et al., 1981). The ratio of the concentration of a compound in solid phase versus its concentration in water phase is the partition coefficient, K_p. The partition coefficient is a useful parameter for estimation of the fate of pollutants in the aquatic environment (Rudolf, 1991). Its value depends upon the characteristics of a particular sediment. Partition coefficient depends on both particle properties as well as compound properties (Swackhamer and Eisenreich, 1991). The particle properties include chemical composition, size/shape, and type. Particles are classified by source, as biotic or abiotic, as organic or inorganic. The most important particle property that affects partitioning of hydrophobic compounds is the fraction of organic carbon (f_{oc}) of sediment. Non-ionic organic chemicals will associate strongly with the organic carbon portion of the particulate phase (Lambert and Omega, 1978; Karickchoff et al., 1979).

The K_p and K_{oc} values of the organochlorine pesticides are shown in Tables 7 1 and 7.2. Very high values of K_p were observed for β-HCH and higher values also observed for DDTs and α-HCH. Partition coefficients are frequently normalized to the organic carbon content of the soil, the soil organic carbon is the dominant sorbent for hydrophobic organic compounds and the K_ps show an increase with increasing organic carbon content of the sediment (Karickchoff et al., 1979). This is significant in Kuttanad backwaters as the K_p values were higher in organic rich sediments. The low organic carbon values were reported from sediments of stations 8 and 9 of the study area and the K_p values were lower in these stations. By dividing K_p by the fractional mass of organic carbon in the sediment, the partition coefficient into the organic carbon fraction (K_{oc}) is obtained (Karickchoff et al., 1979; Rudolf, 1991). The values of K_{oc} increased with decreased temperature (Weber et al. 1983). This observation was not so relevant in the Kuttanad area because the fluctuations in temperature were in a narrow range of linearity. Chiou and

Table 7.1 k_p Values of organochlorine pesticides

Stations	p,p'-DDE	p,p'-DDD	p,p'-DDT	α -HCH	β -HCH	γ -HCH	δ -HCH	α –endosulfan	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin aldehyde
1	282.5	154.4	127.9	117.2	1852.2	63.0	4.0	14.4	7.0	7.4	7.6	9.9	0.6	3.9
2	247.1	130.9	135.8	74.0	2202.6	38.6	3.8	13.9	8.1	8.3	7.3	8.5	0.6	4.1
3	170.8	115.1	146.1	71.5	1749.5	34.8	2.7	10.1	7.1	6.6	5.2	9.2	0.6	3.5
4	144.4	138.7	111.8	112.7	3682.1	105.8	6.6	17.9	9.1	9.8	7.5	21.8	0.6	3.7
5	158.6	120.5	78.1	92.4	4401.0	79.8	10.3	19.1	13.6	15.7	6.3	38.5	0.6	3.6
6	180.3	115.1	73.6	100.2	4999.4	115.9	12.1	20.7	14.1	24.2	5.3	70.1	0.6	4.2
7	237.7	124.6	95.1	100.7	5358.0	123.1	14.7	24.0	9.1	40.1	5.8	77.0	0.6	4.1
8	49.4	26.5	20.6	34.0	1501.6	33.9	3.2	7.9	8.3	7.2	3.5	14.5	0.6	2.2
9	67.2	34.4	16.1	43.3	1529.0	42.3	3.2	8.6	8.6	4.7	4.3	10.2	0.6	3.1

Table 7.2 K_{oc} Values for organochlorine pesticides

Stations	p,p'-DDE	p,p'-DDD	p,p'-DDT	α -HCH	β -HCH	γ -HCH	δ -HCH	α -endosulfan	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin aldehyde
1	8.02	4.38	3.63	3.33	52.59	1.79	0.11	0.41	0.20	0.21	0.22	0.28	0.02	0.11
2	8.03	4.25	4.41	2.41	71.58	1.25	0.12	0.45	0.26	0.27	0.24	0.28	0.02	0.13
3	4.67	3.15	3.99	1.95	47.83	0.95	0.07	0.28	0.19	0.18	0.14	0.25	0.02	0.10
4	4.44	4.26	3.44	3.47	113.19	3.25	0.20	0.55	0.28	0.30	0.23	0.67	0.02	0.12
5	5.85	4.44	2.88	3.41	162.34	2.94	0.38	0.71	0.50	0.58	0.23	1.42	0.02	0.13
6	6.42	4.10	2.62	3.57	178.04	4.13	0.43	0.74	0.50	0.86	0.19	2.50	0.02	0.15
7	7.98	4.19	3.20	3.38	179.92	4.13	0.49	0.81	0.30	1.35	0.19	2.59	0.02	0.14
8	5.24	2.81	2.19	3.61	159.40	3.60	0.34	0.83	0.88	0.76	0.37	1.54	0.07	0.24
9	8.43	4.32	2.02	5.42	191.61	5.30	0.40	1.08	1.07	0.59	0.54	1.28	0.08	0.39

Shoup (1985) found that interaction of organic pollutant with soils has shown that their uptake by soils is not only dependent on f_{oc}, but also is strongly influenced by ambient humidity as well as the type of organic matter in the soil, based on carbon and oxygen content (Garbarini and Lion, 1986). K_{oc} should be relatively independent of particle type for a given particle size (Mackay, 1982).

The concentrations of organochlorine and organophosphorus pesticides reported in this study constitute the first attempt to ascertain the baseline data of the above pesticides in the backwaters of Kuttanad. The lipophilic nature and low chemical and biological degradation rates of organochlorine pesticides may lead to the accumulation of these compounds in biological tissues. The higher residual levels of pesticides and their metabolites may have some influence on the fish diseases reported from the Kuttanad backwaters. Monitoring of pesticides and their residues in the various compartments of water system would help to show any trend in the levels of contamination of the environment and generate data for future legislations. Data obtained from the present study are also useful for an understanding of the contamination dynamics of the different organochlorine and organophosphorus pesticides present in the different environmental compartments of Kuttanad backwaters. It also helps to divert for the use of more eco-friendly pesticides.

Expansion of agricultural activities becomes more critical to understand the factors influencing the transport of sediment and sediment bound pesticides on both a fine-scale (e.g. soil erosion within paddocks) and a large scale (e.g. influences of water currents and climatic factors). Through the understanding of the transport mechanisms, a useful assessment of the current and future potential impact of changing land-use on the sediment and contaminant loads in the sediments of Kuttanad backwaters can be made. Organochlorine pesticides were, however, inclined to partition into surface sediments because of their particle reactivity. Considerable quantities of organochlorine pesticides were deposited into bed sediments due to low salinity during the early stages of estuarine mixing. Hydrodynamic flows then diluted and mixed sediments and transported them to the sea. Variations of flow have been shown to have an effect on concentration fluctuations of pesticides with different effects on the major river systems flowing towards the estuary and also the flow from the paddy fields.

Pesticide use in developing countries like India is indispensable for crop protection and the control of epidemic disease. Therefore, proper emphasis is given to the judicious and safe use of chemical pesticides. In view of the adverse effects, resulting from the indiscriminate use of pesticides in the different compartments of the environment, a system for the monitoring of pesticide usage is essential. At present the effectiveness of pesticides is determined only by product yield, and there is no monitoring of the effect on users and the non-target flora and fauna. Strict regulations for the use of pesticides in agriculture, wastewater discharge from agriculture, and municipal sewage system are absolutely essential to keep the marine environment clean and sustainable. New strategies should be developed for the better management for the use of pesticides and this can be achieved by (1) increasing biological control through integrated pest management and thereby reducing the chemical pesticides (2) adopting plant species resistant to insect and disease and (3) better training and information of new application methods and an overall reduction of pesticides to the bare minimum using different techniques.

REFERENCES

Addison, R.F 1976. Organochlorine compounds in aquatic organisms: Their distribution, transport and physiological significance. In: *Effects of pollutants on aquatic organisms* (Lookwood, A.P.M., Ed.). Cambridge Univ. Press, Cambridge.

Agarwal, S. and Nair, N.B. 1989. Physiological effect of malathion on the brain of *Sarotherodon mossambicus*. *Curr. Sci.*, **58**: 1046-1047

Agnihothri, N.P Kulshrestha, G., Gajbhiye, V T Mohapatra, S. P and Singh, S.B. 1996. Organochlorine insecticide residues in agricultural soils of the Indo-Gangetic plain. *Environ. Monit. Assess.*, **40**: 279-288.

Aguliar, A. 1984. Relationship of DDE/DDT in marine mammals to the chronology of DDT input into the ecosystem. *Canadian J. Fish Aquatic Sci.*, **41**: 840-844.

Albanis, T.A., Hela, D.G., Sakellarides, T.M. and Konstantinou, I.K. 1994. Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by means of solid-phase extraction disks and gas chromatography. *J. Chromatography* A., **823**: 59-71

Anirudhan, T.S. 1988. Studies on the nutrient chemistry of a tropical estuary. Ph.D. Thesis. Cochin University of Science and Technology, Kochi, India.

Anton, E.C., Lininger, M., Youngerman, J.M. and Agee, B.A. 1986. DDT in the Salinas Valley. A special report on the probable source of technical grade DDT found in the Blanco Drain near Salinas, California. Special Water Quality Monitoring Report No. 86-2 WQ. 49.

AOAC. 1995. Association of Official Analytical Chemists. Official Methods of Analysis, 16th edition. INC, Arlington, Virgina.

APHA (American public health association) 1995. Standard methods for the examination of water and wastewater, 18th Ed. APHA, Washington, USA, 5540C.

Asterios, P and Euphemia, P.M. 2001. Occurrence and spatial and temporal distribution of pesticide residues in groundwater of major corn-growing areas of Greece (1996-1997). *Environ. Sci. Technol.*, **35**: 63-69.

ATSDR (Agency for Toxic Substances and Disease Registry), 1987 Draft toxicological profile for aldrin/dieldrin. US Public Health Service, Washington, DC.

Atuma, S.S. 1999. Method for the determination of PCB congeners and chlorinated pesticides in human blood serum. *Bull. Environ. Contam. Toxicol.*, **62**: 8-15.

Azam, F and Cho, B.C. 1987 Bacterial utilization of organic matter in the sea. In: *Ecology of microbial communities* (Fletcher, M., Gray, T.R.G. and Jones, J.G., Eds.). Cambridge University Press, Cambridge, 261-281.

Babukutty, Y 1991. Studies on the inter-compartmental exchange of trace metals in an estuarine system. Ph.D. Thesis, Cochin University of Science and Technology, Kochi, India.

Bachmann, A., Walet, P Wijnen, P de Bruin, W., Huntjens, J.L.M., Roelofsen, W. and Zehnder, A.J.B. 1988. Biodegradation of alpha and beta hexachlorocyclohexane in a soil slurry under different redox conditions. *Appl. Environ. Microbiol.*, **54**: 143-149.

Bailey, G.W. and White, J.L. 1964. Review of adsorption and decomposition of pesticides by soil colloids with implications concerning pesticide bioactivity. *J. Agric. Food Chem.*, **24:** 324-332.

Balls, P.W. and Cambell, D.C. 1999. Organochlorines in sea water and suspended particulates from Scottish Coastal sites. *Mar. Pollut. Bull.*, **38**:142-145.

Banerjee, S., Yalkowsky, S.H. and Valvani, S.C. 1980. Water solubility and octanol-water partition coefficient of organics. Limitations of the solubility-partition coefficient correlations. *Environ. Sci. Technol.*, **14**: 1227-1229.

Barry, C.K. and Frank, A.P.C.G. 2001. Bioaccumulation of persistent organic pollutants in Lichen-Caribou-Wolf food chains of Canada's central and western arctic. *Environ. Sci. Technol.*, **35**: 325-334.

Baxtor, R.M. 1990. Reductive dechlorination of certain chlorinated organic compounds by reduced haematin compared with their behaviour in the environment. *Chemosphere*, **21**: 451-458.

Benezet, H.J. and Matsumura, F 1973. Isomerisation of gamma-BHC to alpha – BHC in the environment. *Nature*, **243**: 480-481

Bidleman, T.F 1988. Atmospheric process. *Environ. Sci. Technol.*, **22**: 361-367

Bintein, S. and Devillers, J. 1996. Evaluating the environmental fate of lindane in France. *Chemosphere*, **32**: 2427-2440.

Boehm, P.D. and Farrington, J.W. 1984. Aspects of the polycyclic aromatic hydrocarbon geochemistry of recent sediments in the Georges Bank region. *Environ. Sci. Technol.*, **18**: 840-845.

Borrell, A., Aguilar, A. and Pastor, T 1997 Organochlorine pollutant levels in Mediterranean monk seals from the western Mediterranean and the Sahara coast. *Mar. Pollut. Bull.*, **34**: 505-510.

Bowman, B. T Adams, R. S. (Jr.), and Fenton, S. S. 1970. Effect of water on malathion adsorption on five montmorillonite systems. J. Agric. Food Chem., **18**:723.

Brooks, G.T (Ed.) 1976. Chlorinated insecticides. In: *Technology and application.* CRC Press, INC, Cleveland, Ohio. **Vol.1**

Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M. and Vighi, M. 1991 Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. *Environ. Sci. Technol.*, **25**: 1489-1495.

Calderoni, P 1992. Pesticide industry outlook promising. *Pestic. Inf.*, **17**· 23-25.

Carvar, R.E. (Ed.) 1971. In: *Procedures in sedimentary petrology* Wiley-Interscience, New York, 427-478.

Cavanagh, J.E., Burns, K.A., Brunskill, G.J. and Coventry, R.J. 1999. Organochlorine pesticide residues in soils and sediments of the Herbert and Burdekin river regions, North Queensland – Implications for contamination of the Great Barrier Reef. *Mar Pollut. Bull.*, **39**: 367-375.

Cavender, F.L., Cook, B.T and Norbet, P.P 1987 Office of Health and Environmental Assessment, US Environmental Protection agency, Washington, DC. EPA/600/S6-87/004.

Chan, K.T (Ed.) 1965. In: *The chemistry of seawater analysis.* Scientific Publications, Peking, China.

Chen, Y.L. and Chen, J.S. 1979 Degradation and dissipation of herbicide butachlor in paddy fields. *J. Pestic. Sci.*, **4**: 431-438.

** Cherif, S. and Wortham, H. 1997 A new laboratory protocol to monitor the volatilisation of pesticides from soils. *Int. J. Eniron. Anal. Chem.*

Chiou, C.T Peters, L.J. and Freed, V.H. 1979. A physical concept of soil-water equilibria for non-ionic organic compounds. *Science*, **206**: 831-832.

Chiou, C.T and Shoup, T.D. 1985. Soil sorption of organic vapours and effects of humidity on sorptive mechanism and capacity. *Environ. Sci. Technol.*, **19**: 1196-1200.

Chiou, C.T Shoup, T.D. and Porter, P.E. 1985. Mechanistic roles of humans and minerals in the sorption of non-ionic organic compounds from aqueous and organic solutions. *Org. Geochem.*, **8**: 9-14.

Clark, J.W., Viessman, W. and Hammer, M.J. (Eds.) 1977 In: *Water supply and pollution control.* Dum-Donnelley publishers, New York, 242-257

Clark, S.M. and Snyder, G.R. 1970. Limnological study of Lower Columbia River, 1967-68. U.S. Fish and Wildlife Service, Special Scientific Report – Fisheries No.610, 14. 1968.

Connell, W.D., Gregory J.M., Munro, R. M., Glen, R.S. and Shelly, M.A. 1999. Persistent lipophilic contaminants and other chemicals residues in the southern hemispheres. *Crit. Rev Environ. Sci. Technol.,* **29**: 47-82.

Corona-Cruz, A., Gold-Bouchot, G., Gutierrez-Rojas, M., Monroy-Hermosillo, O. and Favela, E. 1999. Anaerobic-aerobic biodegradation of DDT (Dichlorodiphenyl Trichloroethane) in soils. *Bull. Environ. Contam. Toxicol.*, **63**: 219-225.

Dang, D.N., Nguyen, M.A., Nguyen, C.H., Luu, V.D., Carvalhos, F.P Villeneuves, J.P and Cattini, C. 1998. Organochlorine pesticide and

PCBs in the Red River delta, North Vietnam. *Mar Pollut. Bull.*, **36**: 742-749.

David, W.R., Craig, P.S., Robert, B.S. and Marilyn, L.K. 1993. Seasonal and annual distributions of organic contaminants in marine sediments from Elkhorn slough, moss landing harbor and near shore Monterey bay, California. *Environ. Pollut.*, **82**: 79-91.

de Bruijn, J., Busser, F Swinen, W. Hermeans, J. 1989. Determination of octanol-water partition coefficients of hydrophobic organic chemicals with the slow stirring method. *Environ. Toxicol. Chem.*, **8**: 499-512.

Deo, P.G., Karanth, N.G., Karanath, N.G.K. 1994. Biodegradation of hexachlorocyclohexane isomers in soil and food environment. *Crit. Rev. Microbiol.,* **20**: 57-78.

De Sousa, S.N. and Sen Gupta, R. 1986. Variations of dissolved oxygen in Mandovi and Zuari estuaries. *Indian J. Mar. Sci.,* **15**: 67-71

de Vooget, P Wells, D.E., Reutergardh, L. and Th. Brinkman, U.A. 1990. Biological activity, determination and occurrence of planar, mono- and di-ortho PCB. *Int. J. Anal. Chem.*, **40**: 1-46.

Dhaliwal G.S. and Arora, R. 1996. Principles of Insect Pest Management national Agricultural Technology Information center. Ludhiana, 374.

Dikshith, S.S.T, Raizada, B.R., Kumar, S.N., Srivastava, M.K., Kulsherestha, S.K. and Adholia U.N. 1990. Residues of DDT and HCH in major sources of drinking water in Bhopal, India. *Bull. Environ. Contam. Toxicol.,* **45**: 389-393.

Dollacker, A. 1991 Pesticides in third world. *Pflanz. Nachr. Bayer.* **44**: 89-99.

Doudoroff Shumway, D,L. and Peter 1970. Dissolved oxygen requirements of fresh water fishes. FAO (UN) Fish. Tech. Paper., **86**, 291-298.

Douthwaite, R.J. 1995. Occurrence and consequences of DDT residues in woodland birds following testse fly spraying operations in NW Zimbabwe. *J. Appl. Ecol.*, **32**: 727-738.

Dua, V.K., Kumari, R. and Sharma, V.P 1996 HCH and DDT contamination of rural ponds of India. *Bull. Environ. Contam. Toxicol.*, **57** 568-574.

Dua, V.K., Kumari, R., Johri, R.K., Ojha, V.P Shukla, R.P and Sharma, V.P 1998. Organochlorine insecticides residues in water from five lakes of Ninital (U.P.), India. *Bull. Environ. Contam. Toxicol.,* **60**: 209-215.

Dua, V.K., Pant, C.S. and Sharma, V.P 1994. HCH residues in rain water from Hardwar, India. *Bull. Environ. Contam. Toxicol.*, **52**: 797-801.

E.C. Council Directive (1980) relating to the quality of water intended for human consumption (1980/778/EEC), *Off. J. Eur. Commun.*, No L 229/11-29.

Eadie, B.J. and Robbins, J.A. 1987 The role of particulate matter in the movement of contaminants in the Great Lakes. In: *Sources and Fate of Aquatic Pollutants* (Hites, R.A and Eisenreich, S.J., Eds.). *Advances in Chemistry series,* American Chemical Society, Washinton,DC., **216**: 319-364.

Edwards, C.A. 1966. Insecicide residues in soils. *Residue Reviews*, **13**: 83-132.

Edwards, C.A. 1973. Pesticide residues in soil and water. In: *Environmental pollution by pesticides* (Edwards, C.A., Ed.). Plenum Press, London.

Edwards, C.A. 1977 Nature and origins of pollution of aquatic systems by pesticides. In: *Pesticides in aquatic environment.* (Khan, M.A.Q., Ed.) Academic Press, New York, 11-28.

Edwards, C.A. 1986. Agrochemicals as environmental pollutants. In: *Control of pesticides and residues in food: A guide and Directory* (Von Hofsten, B. and Elaspern, G., Eds.). Swedish Science Press, Uppsala, Sweden, 1-19.

Efrain, A.G.G., Lorena, M.R.M., Gilberto, F.M. and Julio, A.V.C. 1998. Chlorinated hydrocarbons in marine sediments of the Baja California (Mexico)-California (USA) border zone. *Mar. Pollut. Bull.*, **36**: 27-31

Eisenreich, S.J. 1987 Chemical limnology of non-polar organic contaminants in large lakes: PCBs in the lake Superior. In: *Sources and fates of aquatic pollutants* (Hites, R.A. and Eisenreich, S.J., Eds.). Advances in Chemistry series, American Chemical Society, Washington, DC., **216**: 394-469.

Eisenreich, S.J., Looney, B.B. and Thornton, J.D. 1981. Air borne organic contaminants in the Great Lake ecosystem. *Environ. Sci. Technol.*, **5**: 30-38.

Eitzer, B.D. and Chevalier, A. 1999. Landscape care pesticide residues in residential drinking water wells. *Bull. Environ. Contam. Toxicol.*, **62**: 420-427

El-Dib, M.A. and Badawy, M I. 1985. Organochlorine insecticides and PCBs in water, sediment, and fish from the Mediterranean Sea. *Bull. Environ. Contam. Toxicol.*, **34**: 216-227

* El Wakeel S.K. and Riley, J.P 1957 The determination of organic carbon in marine muds. *J. Con. Int. Pour. Expior. Mer.*, **22**: 180-183.

Elzerman, A.W. and Coates, J. T 1987 Hydrophobic organic compounds on sediments equilibria and kinetics of sorption. In: *Sources and fate of* *aquatic pollutants* (Hites, R.A and Eisenreich, S.J., Eds.). Advances in Chemistry Series No.216, American Chemical Society, Washinton, DC, 263-317

EPA (Environmental Protection Agency. 1980. Ambient water quality criteria for DDT EPA 440/5-80-038.

Eto, M. (Ed.) 1977 Organophosphorus pesticides: Organic and biological chemistry. CRC press, Inc, Cleveland Ohio, USA. 1- 215.

Everaarts, J.M., Van Weerlee, E.M., Fischerm, C.V. and Hillebrand, T.J. 1998. Polychlorinated biphenyls and cyclic pesticides in sediments and macro-invertibrates from the coastal zone and continental slope of Kenya. *Mar. Pollut. Bull.*, **36**: 492-500.

FAO (Food and Agricultural Organisation). 1985. Prevention of post-harvest Food losses. Rome.

Ferrando, W.D., Alarcon, V Fernandez-Casalderry, A., Gamon, M. and Andreu-Moliner, E. 1992. Persistence of some pesticides in aquatic environment. *Bull. Environ. Contam. Toxicol.,* **48**: 747-755.

Ferreira, A.M., Cortesao, C., Castro, O.G. and Vale, C. 1990. Accumulation of metals and organochlorines in tissues of the oyster *Crassostrea angulata* from the Sado Estuary, Portugal. *Sci. Total. Environ., **97/98**: 627-639.*

Foster, G.D., Lippa, K.A. 1996. Fluvial loadings of selected organonitrogen and organophosphorus pesticides to Chesapeake Bay. *J. Agric. Food Chem.*, **44**: 2447-2454.

Fowler, S.W. 1990. Critical review of selected heavy metal and chlorinated hydrocarbon concentrations in the marine environment. *Mar. Environ. Res.*, **29**: 1-64.

Fox, M.E., Roper, D.S. and Thrush, S.F 1988. Organochlorine contaminants in the surficial sediments of Manukau Harbour, New Zealand. *Mar. Pollut. Bull.*, **19**: 333-336.

Fox, P.J. and Matthiessen, P 1982. Acute toxicity to fish of low-dose aerosol application of endosulfan to control testse fly in Okavango delta, Botswana. *Environ. Pollut.*, **27A**: 129.

Freeman, H.P Taylor, A.W. and Edwards, W.M. 1975. Heptachlor and dieldrin disappearance from a field soils measured by annual residue determinations. *J. Agric. Food Chem.*, **23**: 1101-1105.

Galassi, S. and Migliavacca, M. 1986. Organochlorine residues in River Po sediment: testing the equilibrium condition with fish. *Ecotoxicol. Environ. Safety.*, **12**: 120-126.

Galindo-Reyes, J.G., Fossato, V.U., Villagrana-Lizarraga, C. and Dolci, F 1999. Pesticides in water, sediments and shrimp from a coastal lagoon off the Gulf of California. *Mar. Pollut. Bull.*, **38**: 837-841

Garbarini, D.R. and Lion, L.W 1986. Influence of the nature of soil organics on the sorption of toluene and trichloroethylene. *Environ. Sci. Technol.*, **20**: 1263-1269.

Garcfa-Repetto, R. and Repetto, M. 1997 HCH and DDT residues in drinking water from the south of Spain, 1991-1994. *Bull. Environ. Contam. Toxicol.,* **59**: 875-881.

Gaudette, H.E., Flight, W.R., Toner, L. and Folger, D.W. 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sed. Petrol.*, **44**: 249-253.

Gayartri, V and Singh, K.K. 2000. Organophosphate pesticides and their environmental impact. *Pestic. Inf..*, **XXVI**: 6 - 10

Giovanni Melluso, A.E., Marco Guida, F.M., Norman, M.T and Giovanni, P 1994. Distributions of inorganic and organic pollutants in river sediments in Campania, Italy. *Bull. Environ. Contam. Toxicol.*, **52**: 13-18.

Gold-Bouchot, G., Silva-Herrera, T and Zapata-perez, O. 1993. Chlorinated pesticides in the Rio Palizada, Campeche, Mexico. *Mar. Pollut. Bull.*, **26**: 648-650.

Gold-Bouchot, G., Silva-Herrera, T and Zapata-perez, O. 1995. Organochlorine residue concentrations in biota and sediments from Rio Palizada, Mexico. *Bull. Environ. Contam. Toxicol.*, **54**: 554-561.

Gopal, M. and Mukherjee, I. 1993. Determination of residues of endosulfan and endosulfan sulphate on egg plant, mustard and chickpea. *Pestic. Sci.*, **37**: 67-72.

Grady, S.J. and Mullaney, J.R. 1998. Natural and human factors affecting water quality in surficial aquifers in the Connecticut, Housatonic and Tames River basins. USGS water-resources investigations report 98-4042, Malborough, MA.

Grahm-Bryce, I, J. 1972. Proc. 1st Int. Congr. Pollut. Engnr Sci. Sol., Tel Aviv. Plenum Press, London.

Granby, K. and Kinze, C.C. 1991. Organochlorines in Danish and west Greenland harbour porpoise. *Mar. Pollut. Bull.*, **22**: 458-462.

Grasshoff, K., Ehrhardt, M. and Kremling, K. (Eds.) 1983a. Determination of oxygen. In: *Methods of sea water analysis*. Verlag Chemie, Weinheim, 61-72.

Grasshoff, K., Ehrhardt, M. and Kremling, K. (Eds.) 1983b. Determination of salinity. In: *Methods of sea water analysis.* Verlag Chemie, Weinheim, 31-58.

Gupta, P.K. 1986. In: *Pesticides in the Indian environment.* Interprint Publishers, New Delhi. 91.

Gustavo, A.P and Damia, B. 1998. Application of C_{18} disks followed by gas chromatography techniques to degradation kinetics, stability and monitoring of endosulfan in water *Journal of Chromatography A.*, **795**: 93-104.

Hamaker, J.W. and Thompson, J.M. 1972. Adsorption. In: *Organic chemicals in the soil environment, Vol.I* (Goring, C.A.I., Hamaker, J.W., Eds.). Marcel Dekker Inc., New York.

Harikrishnan, M. 1997 Population characteristics, fishery and post larval distribution of *Machrobachium rosenbergi and M.idella* in Vembanad lake. Ph.D. Thesis. Cochin University of Science and technology, Kochi, India.

Harris, C.R. and Lichtenstein, E.P 1961. Factors affecting the volatilization of insecticidal residues from soils. *J. Econ. Entomol.*, **54**: 1038.

Hassal, K.A. (Ed.) 1990. In *The Biochemistry and uses of pesticides.* VCH, Weinheim.

Hermason, H.P Gunther, F.A., Anderson, L.D. and Garber, M.J. 1971 Installment application effects upon insecticide residue content of a California soil. *J. Agric. Food Chem.*, **19**: 722-726.

Hong, H., Xu, L., Chen, J.C., Wong, Y.S. and Wan, T.S.M. 1995. Environmental fate and chemistry of organic pollutants in the sediments of Xiamen and Victoria harbours. *Mar. Pollut. Bull.*, **31**: 229-236.

Huasheng Hong, Weiqi, C., Li Xu., Xinhong, W and Luoping, Z. 1999. Distributions and fate of organochlorine pollutants in the Pearl River estuary. *Mar. Pollut. Bull.*, **39**: 376-382.

IARC (International Agency for Research on Cancer). 1991 IARC Monographs on the evaluation of carcinogenic risks to humans. Occupational exposures in insecticide application, and some pesticide Lyon (France). **Vol. 53**, IARC.

IRIS (Integrated Risk Information System),1992. US Environmental Protection Agency, Duluth, MN.

Iwata, H., Tanabe, S., Sakai, N., Nishimurs, A. and Tatsukawa, R. 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. *Environ. Pollut.,* **85**: 15-33.

Iwata, H., Tanabe, S., Sakai, N. and Tatsukawa, R. 1993. Distribution of persistent organochlorines in the oceanic air and surface sea water and the role of ocean on their global transport and fate. *Environ. Sci. Technol.*, **27** 1080-1098.

Jabbar, A., Zafar M. S., Zahida, P and Mubaric, A. 1993. Pesticide residues in cropland soils and shallow ground water in Punab, Pakistan. *Bull. Environ. Contam. Toxicol.*, **51**: 268-273.

Jayasree, G. 1993. Influence of humic acid on metal sorption by estuarine sediments. Ph.D. Thesis, Cochin University of Science and Technology, Kochi, India.

Jimenez, J.J., Bernal, J.L., Rivera, J.M., Martin, M.T Fernandez, M. and Fernandez, C. 1998. Seasonal changes in the contents of widely used pesticides in water and sediments from small lakes in the Province of Leon (Spain). *Toxicol. Environ. Chem.*

Jiping, Z., Ross, J.N., Derek, C.G.M., Liliane, A.F Jean-philippe, W. and Eric, D. 1995. Persistent chlorinated cyclodiene compounds in Ringed Seal Blubber, polar bear fat, and human plasma from northern Quebec, Canada: Identification and concentrations of photoheptachlor. *Environ. Sci. Technol.*, **28**: 267-271

John, F.Q., James, M.T Mahendra, K.J. and Sherry, A.M. 2001. Factors controlling the rate of DDE dechlorination to DDMU in Palos Verdes margin sediments under anaerobic conditions. *Environ. Sci. Technol.*, **35**: 286-291.

Johnson, R.E. 1976. DDT metabolism in microbial systems. *Residu Reviews.*, **61**: 1-28.

Josanto, V 1971. Bottom salinity characteristics and the factors that influence the salt water penetration in the Vembanad Lake. *Bull. Dept. Mar. Biol. Oceanogr* **5:** 1-6.

Kalara, R.L. and Chawla, R.P 1981 Occurrence of DDT and BHC residues in human milk in India. *Experientia.*, **37**: 404-405.

** Kan-Atireklap, S., Yen, N.T.H., Tanabe, S. and Subramanian, A.N. 1997 Butyltin compounds and organochlorine residues in green mussel (*Perna viridis L.*) from India. *Toxicol. Environ. Chem.* ? Volume ? page ?

Kang, J., Zettel, V.H. and Ward, N.I. 1995. The organophosphate pesticides. *J. Nutr. Environ.Med.*, **5**: 325-339.

Kannan, S.T and Sen Gupta, R. 1987 Organochlorine residues in zooplankton of Saurahtra coast, India. *Mar. Pollut. Bull.*, **18**: 92-94.

Kannan, K., Tanabe, S., Giesy, J.P and Tatsukawa, R. 1997 Organochlorine pesticides and polychlorinated biphenyls in food stuffs from Asian and Oceanic countries. *Reviews of Environ. Contam. Tocicol.*, **152**: 1-55

Kaphalia, B.S., Nigam, U., Mehrotra, S. and Seth,T.D. 1986. Fresh water fish: An indicator of pesticide contamination in the aquatic environment. *J. Environ. Biol.*, **7**: 1-9.

Karickchoff, S.W. 1984. Organic pollutant sorption in aqueous systems. *J. Hydraulic Eng.*, **110:** 707-735.

Karickchoff, S.W., Brown, D.S. and Scott, T.A. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, **13**: 241-248.

Karla, R.L. and Chawla, R.P 1981. Monitoring of pesticides residues in the Indian environment. In: *Indian Pesticide Industry: Facts and figures* (David, B.V Ed.). Vishvas Publications, Madras, India. 251-285.

Karla, R.L. and Chawla, R.P 1983. Studies on pesticide residues and monitoring of pesticidal pollution. Final Technical Report, PL-480 Project, Department of Entamology, Punjab Agricultural University, Ludhiana.

** Karunagaran, V.M. and Subramanian, A.N. 1999. Organochlorine residues in coastal birds from the Vellar River watershed areas, Parangipettai, South India. *Chemistry and Ecology*

* Kashiwada, S., Mochida, K., Ozoe, Y and Nakamura, T 1995. Contribution of zooplanktonto disappearence of organophosphorus insecticides in environmental water. *Nippon Noyaku Gakkaishi.*, **20**: 503-512.

Kawano, M., Ramesh, A., Thao, V.D., Subramanian, A.N. and Tatsukawa, R. 1992. Persistent organochlorine insecticides residues in some paddy, upland and urban soils of India. *Intern. J. Environ. Anal. Chem.*, **48**: 163-174.

Kelly, A.G. 1995. Accumulation and persistence of chlorobiphenyls, organochlorine pesticides and facal sterols at the Garroch head sewage sludge disposal site, firth of Clyde. *Environ. Pollut.*, **88**: 207-217

Kenaga, E.E. 1972. Factors related to bioconcentration of pesticides. In: *Environmental Toxicology of pesticides* (Matsumura, G.M., Bousch. and Misto, T Eds.). Academic Press, New York, 199-228.

Kenaga, E.E., Whitney, W.K., Hrdy, J.L. and Doty, A.E. 1965. Laboratory tests with Dursban insecticide. *J. Econ. Entamol.*, **58**: 1043-1050.

KAU (Kerla Agricultural University) 1996. Package of practices recommendations 'crops' Kerala Agricultural University, Kerala.

Kilgore, W.W. and Li, M.Y 1976. Environmental toxicology. In: *Insecticide biochemistry and physiology* (Wilkinson, C.F Ed.). Academic Press, New York. 669-713.

Kilikidis, S.D., Kamarianos, A.P and Karamanlis, X.N. 1992. Seasonal fluctuations of organochlorine compounds in water of the Strimon River (N.Greece). *Bull. Environ. Contam. Toxicol.*, **49** 375-380.

Kolpin, D.W., Barbash, J.E. and Gilliom, R.J. 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the national water quality assessment programme. *Environ. Sci. Technol.,* **32**: 558-566.

Krumbein, W.C. and Pettijohn, F.J. (Eds.) 1938. In: *Manual of sedimentary petrography.* Appleton Centuary Crafts Inc., New York, 1- 549.

Kuhr, R.J. and Dorough, H.W. (Eds.) 1976. In: *Carbamate insecticides: chemistry, bio-chemistry and toxicology.* CRC Press, Cleveland, Ohio.

Kulshrestha, S.K. 1991. Pesticides residues in Indian aquatic environment. In: *Environmental pollution and resources of land and water* (Sastry, K.V Mane, U.H., Sahai, S., Awasthi, S.K., Deshmukh, K.V and Gupta, A.K., Eds.). The Academy of Environmental Biology, Muzaffarnagar 43-53.

Kulshrestha, S. K., Adholia, U.N., Bhatnagar, A., Khan, A.A. and Baghail, M.P 1989. Monitoring and surveillance of residues of organochlorine pesticides and heavy metals in fishes from selected environmental components of M.P and Rajasthan. Final technical report, Ministry of Environment and Forests, New Delhi.

Kuwatsuka, S., Moon, Y.H., Ohsawa, K., Yamamoto, I., Hartadi, S., Sastrohamidjoyo, H., Untung, K., Arya, N. and Sumiartha, K. 1986. Comparative studies on pesticide residues in soil, water and vegetables in Indonesia and Japan. In: *Preceedings of the International seminar on comparative agricultural studies in Southeast Asia, Denpasa*, 121-133.

KWBS (Kuttanad Water Balance Study) 1989. Draft Final Report. Volume I and II (Main Report). Published jointly by Kingdom of the Netherlands, Ministry of Foreign affairs, India and State of Kerala.

Kyle, B.G., Chiou, C.T Peters, L.J. 1981. Soil-water equilibria for non-ionic organic compounds. *Science.*, **213**: 683-684.

Lakshmanan, P T Shynamma C.S., Balchand, A.N., Kurup, P.G. and Nambisan, P.N.K. 1982. Distribution and seasonal variations of temperature and salinity in Cochin backwaters. *Indian. J. Mar. Sci.*, **11**. 170-172.

Lambert, S.M. and Omega. 1978. A useful index of soil sorption equilibria. *J. Agric. Food Chem.*, **16**: 340-343.

Larsson, P Berglund, O., Backe, C., Bremle, G., Ekloev, A., Jaernmark, C. and Persson, A. 1995. DDT- fate in tropical and temperate regions. *Naturwissenschaften.*, **82**: 559-561

Lee, H.K., Lee, Y.D. and Shin, Y.H. 1984. A survey on pesticide residue on paddy soils. *Nongsa Sihom Yongu Pogo.*, **26**: 99-104.

Leoni, V Caricchia, A.M., Comi, R., Martini, F Rodolico, S. and Vitali, M. 1995. Risk assessment of organophosphorus pesticides dietary intake for the population of the city of Rome (Italy). *Bull. Environ. Contam. Toxicol.*, **54**: 870-877

Lewis, D.W. (Ed.) 1984. In: *Practical sedimentology* Hutchinson Ross, Stroudsburg, Pennsylvania, 1-229.

Lichtenstein, E.P and Schulz, K.R. 1965. Residues of aldrin and heptachlor in soils and their transformation into various crops. *J. Agric. Food Chem.*, 13: 57

Lim, G.S. and Heong, K.L. 1984. The role of insecticides in rice integrated pest management. In: *Judicious and efficient use of insecticides on rice.* International Rice Research Institute, Los Banos, Philippines, pp.19-30.

Lizen, M. 2000. Studies on the role of sediments on the nutrient dynamics and fertility of Kuttanad backwaters.Ph.D. Thesis, Cochin University of Science and Technology, Kochi, India.

Lloyd-Jones, C. P 1971. Evaporation of DDT *Nature* (London)., **229**: 65

Lopez-Avila, V and Hites, R.A. 1980. Organic compounds in an industrial wastewater. Their transport into sediments. *Environ. Sci. Technol.*, **14**: 1382-1390.

Mackay, D. 1982. Correlation of bioconcentration factors. *Environ. Sci. Technol.*, **16**: 274-278.

Mantoura, R.F.C. 1987 Organic films at the halocline. *Nature.*, **328**: 579-580.

Maria, E.J., Christine, B. and karsten, L. 1998. Analysis of pesticides and their degradation products in rain water· A probe into their atmospheric degradation. *Intern. J. Environ. Anal. Chem.*, **70**: 149-162.

Martijn, A., Bakker, H. and Schreuder, R.H. 1993. Soil persistence of DDT, dieldrin and lindane over a long period. *Bull. Environ. Contam. Toxicol.*, **51**: 178-184.

Matsumura, F (Ed.) 1985. In: *Toxicology of Insecticides.* Plenum Press, New York.

Mc Dougall, K.W., Harris, C.R., Fenton, I.G. and Dowman, A. 1995. Persistence and effect of management practices on organochlorine residues in soils of sub-tropical New South Wales. *Bull. Environ. Contam. Toxicol.*, **54**: 177-184.

Means, J.C., Hassett, J.J., Wood, S.G., Banwart, W.L., Ali, S. and Khan, A. 1980a. Sorption properties of polynuclear aromatic hydrocarbons and sediments: heterocyclic and substituted compounds. In: *Polynuclear aromatic hydrocarbons: Chemistry and biological effects* (Norseth, A. and Dennis, A.J., Eds.). Battelle Press, Columbus, Ohio, 395-404.

Means, J.C., Wood, S.B., Hassett, J.J. and Banwart, W.L. 1980b. Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environ. Sci. Technol.*, **14**: 1524.

Meier, P.G., Fook, D.C. and Lagler,K.F 1983. Organochlorine insecticide in rice paddies in Malaysia. *Bull. Environ. Contam. Toxicol.*, **30**: 351-357

Menzel, D.W. and Vaccaro, R.F 1964. The measurement of dissolved organic and particulate carbon in sea water *Limnol. Oceanogr* **9**: 138-142.

Metcalf, R.L. 1982. Insecticides in pest management. In: *Introduction to insect pest management* (Metcalf, W.H. and Luckmann, W.H., Eds.). John Wiley and Sons, New York, 217-277

Middeldrop, P.J.M., Jaspers, M., Zehnder, A.J.B. and Scnraa, G. 1996. Biotransformation of α-, β-, γ-, and δ- hexachlorocyclohexane under methanogenic conditions. *Environ.Sci. Technol.*, **30**: 2345-2349.

Miles, J.R. and Harris, C.R. 1978. Insecticide residues in water, sediments, and fish of the Holland Marsh, Ontario, Canada, 1972-1981. *J. Econ. Entamol.*, **71**: 125-131

Miliadis, G.E. 1994. Lindane residues in the water of the Iliki lake, Greece. *Bull. Environ. Contam. Toxicol.*, **53**: 598-602.

Miliadis, G.E. 1995. Organochlorine and organophosphorus pesticide residues in the water of the Pinious River, Greece. *Bull. Environ. Contam. Toxicol.*, **54**: 837-840.

Miliadis, G.E. 1998. Analysis of pesticide residues in water samples by gas capillary chromatography. *Bull. Environ. Contam. Toxicol.*, **61**: 255-260.

Miliadis, G.E. and Malatou, P 1997 Monitoring of the pesticide levels in natural waters of Greece. *Bull. Environ. Contam. Toxicol.*, **59**: 917-923.

Mitra, J. and Reghu, K. 1978. Persistence of DDT in soils. In: *Proc Symp. on Nuclear Techniques in Studies of metabolism - effect and degradation of pesticides*. Tirupathi, 134-142.

Mitra, J. and Reghu, K. 1998. Long term DDT pollution in tropical soils: Effect of DDT and degradation products on soil microbial activities leading to soil fertility. *Bull. Environ. Contam. Toxicol.*, **60**: 585-591.

Mohamed, A.E. and Mohamed, I.B. 1985a. Organochlorine insecticides and PCBs in water, sediment and fish from the Mediterranean Sea. *Bull. Environ. Contam. Toxicol.*, **34**: 216-227

Mohamed, A.E. and Mohamed, I.B. 1985b. Organochlorine insecticides and PCBs in River Nile water, Egypt. *Bull. Environ. Contam. Toxicol.*, **34**: 126-133.

Montanes, J.F.C., Risebrough, R.W., Lappe De, B.W., Marino, M.G. and Albaiges, J. 1990. Estimated inputs of organochlorines from the river Ebro into the northwestern Mediterranean. *Mar. Pollut. Bull.*, **21**: 518-523.

Morris, A.W., Mantoura, R.F.C., Bale, A.J. and Howland, R.J.M. 1978. Very low salinity regions of estuaries: Important sites for chemical and biological reactions. *Nature;* **274**: 678-680.

Mountford, K. 1969. Measuring dissolved oxygen as an indicator of primary productivity. Chesapeake Science., 10: 327-350.

Mukherjee, I. and Gopal, M. 1994. Interconversion of stereo isomers of endosulfan on chickpea crop under field conditions. *Pestic. Sci.*, **40**: 103-106.

Muthanna, A.A., Nehla, H.A. and Dhia, A.S. 1989. Effect of a sewage plant in the distribution of organochlorine residue in the Diyala river, Iraq. *Water, Air and Soil pollut.*, **44**: 1-7

Mwanthi, M.A. 1988. Occurrence of three pesticides in community water supplies Kenya. *Bull. Environ. Contam. Toxicol* **60**: 601-608.

Nagami, H. 1997 Dieldrin and chlordane residue in agriculture fields. *Bull. Environ. Contam. Toxicol.*, **59**: 383-388.

Nair, C.K. 1992. Chemical partitioning of trace metals in sediments of a tropical estuary. Ph.D. Thesis. Cochin University of Science and Technology. Kochi, India.

Nakamura, K. 1990 Behaviour of pesticides in soil and other environment. *J. Pestic. Sci.*, **15**: 271-281

Nau-Ritter, G.M. and Wurster, C.F 1983. Sorption of polychlorinated biphenyls (PCB) to clay particulates and effects of desorption on phytoplankton. *Water Res.*, **17**· 383.

Nayak, A.K., Raha, R. and Das, A.K. 1995. Organochlorine pesticide residues in middle stream of the Ganga River, India. *Bull. Environ. Contam. Toxicol.*, **54**: 68-75

Needham, L.L., Ashley, D.L., Hill, R.H., Pirkle, J.L. and Sampson, E.J. 1995. *Organohalogen Compd.*, **26**: 35-38.

Nigam, G.L. and Murthy, K.S. 2000. An optimization of pesticides in integrated pest management technology *Pesticides Information.*, **XXV**· 6-9.

Nimno, D.R. 1985. Pesticides. In: *Fundamentals of aquatic toxicology – Methods and application* (Rands, G.M. and Petrocelli, S.R., Eds.). Hemisphere Publishing Corporation, Washington. 335-373.

Norena-Barroso, E., Zapata-Perez, O., Ceja-Moreno, V. and Gold-Bouchot, G. 1998 Hydrocarbon and organochlorine residue concentrations in sediments from bay of Chetumal, Mexico. *Bull. Environ. Contam. Toxicol.*, **61**: 80-87

Norstrom, R.J., Simon, M., Muir, D.C.G. and Schweinsburg, R.E. 1998. Organochlorine containments in Artic marine food chains: Identification, geographical distribution, and temporal trends in polar bears. *Environ. Sci. Techol.*, **22**: 1063-1071

NRC (National Research Council). 1994. *Priorities for coastal ecosystem science.* National Academy Press, Washington, DC.

O'Brien, R.D. (Ed.) 1967 In: *Insecticides action and metabolism.* Academic Press, New York.

Olembo, R. 1987 Environmentally dangerous products. In: *Towards a second green revolution* (Marini-Bettolo, G.B., Eds.). Elsevier, Amsterdam, 47-70.

Osborn, H. (Ed.) 1952. A brief history of entomology. Spahr and Glenn Co., Columbus, Ohio.

O' Shea, J.J., Brownell, R.L., Ciark, D.R., Walker, W.A., Gay, M.L. and Lamout, T.G. 1980. Organochlorine pollutants in cetaceans from the Pacific and south Atlantic oceans, November 1968-June 1976. *Pest. Mon. J.,* **14**: 35-46.

Padmalal, D. and Seralathan, P 1995. Organic carbon and phosphorus loading in recently deposited marine and estuarine sediments – a granulometric approach. *Indian J. Mar. Sci.*, **22**: 21-28.

Pathak, M.D. and Dhaliwal, G.S. 1986. Insect control. In: *Global aspects of food production* (Swaminathan, M.S. and Sinha, S. K., Eds.). Tycooly International, Oxford, England, 357-381.

Patil, K.C., Matsumura, F and Boush, G.M. 1972. Metabolic transformation of DDT, dieldrin, aldrin and endrin by marine micro-organisms. *Environ. Sci. Technol.*, **6**: 629-632.

Pawar, A.D. 2000. Pesticides registration and regulation to meet the challenges of 21st centuary. *Pesticides information.*, **XXVI**: 15-21.

Peakall, D.B. 1996. Dieldrin and other cyclodiene pesticides in wild life. *Environ. Contam. Wildl.*, 73-97

Pereira, W.E., Hostettler, F.D. and Rapp, J.B. 1996. Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco bay, California. *Mar. Environ. Res.*, **41**: 299-234.

Perfect, J. 1980. The environmental impact on DDT in a tropical agroecosystem. *Ambio.*, **9**: 16-22.

Pesticide Database. 1999. Patel, B and Sukkadia, J (Eds.) Komal Publications, Ahmadabad. 7-67

Pesticide Fact Handbook. 1988. U.S. Environmental Protection Agency, Noyes Data Corporation. U.S.A. 1-811

Pestology Annual. 1999. Sarathy, A. P (Ed.) Scientia Publications P.Ltd., Mumbai.

Peterson, S.M. and Batley, G.E. 1993. The fate of endosulfan in aquatic ecosystems. *Environ. Pollut.*, **82**: 143-152.

Philips, D.J. H. 1989. Trace metals and organochlorines in the costal waters of Hong Kong. *Mar. Pollut. Bull.* **,** **20**: 319-327

Pignatello, J.J. and Day, M. 1996. Mineralisation of methyl parathion insecticide in soil by hydrogen peroxide activated with iron (III)-NTA or –HEIDA complexes. *Hazard. Waste Hazard. Mater.*, **13**: 237-244.

Pillai, M.K.K. and Agarwal, H.C. 1979. DDT residues and its degradation in soil water and few aquatic animals of Jamuna in Delhi. Final report, Dept. of Sci. and Tech., New Delhi.

Pillai, M.K.K. 1986. Pesticide pollution of soil, water and air in Delhi area, India. *Sci. Total Environ.*, **55**: 321-327

Pimentel, D. and Levitan, L. 1986. Amounts applied and amounts reaching pests. *Bio Science.*, **36** 86-91

Pluth, J.M., Nicklas, J.A., O'Neil, J.P and Albertini, R.J. 1996. Increased frequency of specific genomic deletions resulting from invitro malathion exposure. *Cancer Res.*, **56**: 2393-2399.

Prahl, F.G. and Carpenter, R. 1984. Hydrocarbons in Washington coastal sediments. *Estuar Coast. Shelf Sci.*, **18**: 703-720.

Qasim, S.Z., Bhattathiri, P.M.A. and Abidi, S.A.H. 1968. Solar radiation and its penetration in a tropical estuary. *J. Exp. Mar. Biol. Ecol.*, **2**: 87-103.

Qasim, S.Z. and Reddy, C.V.G. 1967 The estimation of plant pigments of Cochin backwater during the monsoon months. *Bull. Mar. Sci.*, **17** 95-110.

Racke, K.D., Steele, K.P Yoder, R.N., Dick, W.A. and Avidov, E. 1996. Factors affecting the hydrolytic degradation of chlorpyrifos in soil. *J. Agric. Food Chem.*, **44**: 1582-1592.

** Ramasamy, B.R. and Annamalai, S. 1996. Pesticides residues in water from River Kaveri, South India. Chemistry and Ecology.

Ramesh, A., Tanabe, S., Tatsukawa, R., Subramanian, A.N., Palamichamy, S., Mohan, D. and Venugopalan, V.K. 1989. Seasonal variation of organochlorine insecticides residues in air from Porto Novo, South India. *Environ. Pollut.*, **62**: 213-222.

Richard, E.J. 1976. DDT metabolism in microbial system. *Residue Reviews.*, **61**: 1-28.

Riley, J.P and Chester, R. (Ed.) 1971. In: *Introduction to marine chemistry*, Academic Press, London. 465.

Rudolf, J. 1991. Fate of hydrophobic organic pollutants in the aquatic environment: a review. *Environ. Pollut.*, **69**: 237-257

Ruzicka, J.H., Thomson, J. and Wheals, B.B. 1967 The gas chromatographic determination of organophosphorus pesticides. II.A comparative study of hydrolysis rates. *J. Chromatogr.*, **31**: 37

Salter, T.F 1984. Free radicals mechanisms in tissue injury. *Biochem.*, **222**: 1-15.

Samia El-Kabbany Rasheed, M.M. and Zayed, M,A. 2000. Monitoring of the pesticide levels in some water supplies and agricultural land in El- Haram, Giza (A.R.E). *Journal of hazardous materials.*, **72**: 11-21.

Samuel, T Agarwal, H.C. and Pillai, M.K.K. 1988. Persistence and binding of DDT and gamma-HCH in a sandy loam soil under field conditions in Delhi, India. *Pestic. Sci.*, **21**: 1-15.

Samuel, T and Pillai, M.K.K. 1988. Persistence and fate of ^{14}C-p,p'-DDT in an Indian sandy loam soil under field and laboratory conditions. IAEA-TECDOC-476 p 27-40.

Samuel, T and Pillai, M.K.K. 1989. The effect of temperature and solar radiations on volatilization, mineralisation and degradation of [14C] –DDT in soil. *Environ. Pollut.*, **57**· 63-77

Samuel, T and Pillai, M.K.K. 1990. Effect of temperature and sunlight exposure on the fate of soil applied [14C] – gamma-hexachlorocylohexane. *Arch. Environ. Contam. Toxicol.*, **19**: 214-220.

Samuel, T and Pillai, M.K.K. 1991. Impact of repeated application of the binding and persistence of [^{14}C]-DDT and [^{14}C]-HCH in a tropical soil. *Environ. Pollut.*, **74**: 205-216.

Sankaranarayanan, V.N. and Qasim, S.Z. 1969. The influence of some hydrographical factors on the fisheries of Cochin area. *Bulletin of the National institute of Sciences of India.* Symposium on Indian Ocean. **38**, 846-853.

Sarkar, A. and Sen Gupta, R. 1987 Chlorinated pesticide residues in sediment from the Arabian Sea along the central west coast of India. *Bull. Environ. Contam. Toxicol.*, **39**: 1049-1054.

Sarkar, A. and Sen Gupta, R. 1988a. Chlorinated pesticide residues in marine sediments. *Mar. Pollut. Bull.*, **19**: 35-37

Sarkar, A. and Sen Gupta, R. 1988b. DDT residues in sediments from the Bay of Bengal. *Bull. Environ. Contam. Toxicol.*, **41**: 664-669.

Sarkar, A. and Sen Gupta, R. 1989. Determination of organochlorine pesticides in Indian coastal water using a moored in-situ sampler. *Water Res.*, **23**: 975-978.

Sarkar, A. and Sen Gupta, R. 1991. Pesticide residues in sediments from the west coast of India. *Mar. Pollut. Bull.*, **22**: 42-45.

Sarkar, A. and Sen Gupta, R. 1993. On chlorinated hydrocarbons in the Indian Ocean. In: *Oceanography of the Indian Ocean* (Desai, B.N., Ed.). A.A. Balkema, Rotterdam, The Netherlands, 385-395.

Sethunathan, N., Adhya, T.K. and Raghu, K. 1982. Microbial degradation of pesticides in tropical soils. In: *Biodegradation of pesticides* (Matsumura, F and Krishnamurthy, C.R., Eds.). Plenum Press, New York, pp. 91-115.

Shannon, M.B. 1999. Global transport of anthropogenic contaminants and the consequences for the artic marine ecosystem. *Mar Pollut. Bull.*, **38**: 356-379.

Shepard, F.P 1954. Nomenclature based on sand-silt-clay ratio. *J. Sed. Petrol.*, **24**: 151-158.

Shibu, M.P 1992. Trace metal speciation in the Cochin estuary. Ph.D. Thesis. Cochin University of Science and Technology, Kochi, India.

Shynamma, C.S. and Balakrishanan, K.P 1973. Diurnal variation of some physico-chemical factors in Cochin backwaters during south-west monsoon. *J. Mar Biol. Ecol.*, **2**: 174-189.

Silas, E.G. and Pillai, P.P 1975. Dynamics of zooplankton in a tropical estuary (Cochin backwaters) with a review on the plankton fauna of the environments. *Bull. Dept. Mar. Sci.* Univ. Cochin. **7**: 329-355.

Singh, P.P and Chawla, R.P 1978. Contamination of the Punjab soils with commonly used insectiocides. In: *Pesticide residues in the environment of India* (Edwards, C.A., Veeresh, G.K. and Krueger, H.R., Eds.). University of Agricultural Science, Bangalore, pp. 357-369.

Skirrow, G. 1975. The dissolved gases – carbon dioxide. In *Chemical Oceanography* (Riley, J.P and Skirrow, G., eds.). Academic Press, London, **2**: 1-192.

Sleicher, C.A. and Hopcraft, J. 1984. Persistence of pesticides in surface soil and relation to sublimation. *Environ. Sci. Technol.*, **18**; 514-518.

Somara, S. and Siddavattam, D. 1995. Plasmid mediated organophosphate pesticide degradation by *Flavobacterium balustinum*. *Biochem. Mol. Biol. Int.*, **36:** 627-631.

Spencer, W.F and Cliath, M.M. 1973. Pesticide volatilization as related to water loss from soil. *J. Environ. Qual.*, **2:** 284-289.

Spencer, W.F and Cliath, M.M. 1975. Vapourisation of chemicals. In: *Environmental dynamics of pesticides* (Haque, R. and Freed, V.H., Eds.). Plenum Press, New York, 61-78.

** Subramanian, A.N., Lal Mohan, R.S., Karunagaran, V.M. and Babu Rajendran, R. 1998. Concentrations of HCHs and DDTs in the tissues of river dolphins, *Plaianista gangetica*, from River Ganges, India. Chemistry and Ecology.

Sujatha, C.H. 1992. Dynamics of some environmentally significant pesticides in a tropical waterway A toxicological approach. Ph.D. Thesis, Cochin University of Science and technology, Kochi, India.

Sujatha, C.H., Nair, S.M. and Chacko, J. 1999. Determination and distribution of endosulfan and malathion in an Indian estuary. *Wat. Res.*, **33**: 109-114.

Suresh Kumar, S. 1998. Systematics, bionomics and seed production of *Machrobachium spp* of Vembanad Lake. Ph.D. Thesis, Cochin University of Science and Technology, Kochi, India.

Takeoka, H., Ramesh, A., Iwata, H., Tanabe, S., Subramanian, A.N., Mohan, D., Magendran, A. and Tatsukawa, R. 1991. Fate of the insecticide HCH in the tropical coastal area of South India. *Mar. Pollut. Bull.*, **22**: 290-297

Tan, G.H. 1992. Comparison of solvent extraction and solid phase extraction for the determination of organochlorine pesticide residues in water. *Analyst* **117**· 1129-1132.

Tan, G.H. and Vijayaletchumy, K. 1994. Organochlorine pesticides residue levels in peninsular Malaysian rivers. *Bull. Environ. Contam. Toxicol.* **53**: 351-357

Tanabe, S., Gondaira, F Subramanian, A.N., Ramesh, A., Mohan, D., Kumaran, P Venugopalan, V.K. and Tatsukawa, R. 1990. Specific pattern of persistent organochlorine residues in human breast milk from south India. *J. Agric. Food Chem.*, **38**: 899-903.

Tanabe, S., Iwata, H. and Tatsukawa, R. 1994. Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Total Environ.*, **154**: 163-177

Tanabe,S., Kannan, N., Fukushima, M., Okamoto, T Wakimoto, T and Tatsukawa, R. 1989. Persistent organochlorines in Japanese coastal waters: An introspective summary from a far east developed nation. *Mar. Pollut. Bull.*, **20**: 344-352.

Tanabe, S., Ramesh, A., Sakashita, D., iwata, H., Mohan, D., Subramanian, A.N. and Tatsukawa, R. 1992. Fate of HCH in tropical paddy field: application test in South India. *Int. J. Environ. Anal. Chem,.*, **45**: 45-53.

Tanabe, S., Senthilkumar, K., Kannan, K. and Subramanian, A.N. 1998. Accumulation features of polychlorinated biphenyls and organochlorine pesticides in resident and migratory birds from south India. *Arch. Environ. Contam. Technol.*, **34**: 387-397

Tanabe, S. and Tatsukawa, R. 1981. The behaviour of manmade chemicals in estuarine and coastal areas. *Engan Kaiyo Kenkyu Note.*, **19**: 9-19.

Tanabe, S. and Tatsukawa, R. 1986. Distribution, behaviour and load of PCBs in the oceans. In: *PCBs and environment* (Waid, J.S., Ed.). Vol.1 CRC Press, Boca Raton, 143-162.

Thakur N. and Mathal, P.L. 1980. Symp. Environmental options for developing countries. Inst. of Sci., Bombay. Abstr.No. 88.

* The Agro chemicals Handbook 1983. Hartely, D. and Kidd, H. (Eds.). The Royal Society of Chemistry, England.

The Insecticide Act, 1968, and the Insecticide Rules, 1971. Government of India.

The Pesticide Manual. 1995. (10th edition) Tomlin, C. (Ed.) Crop Protection Publications, The Royal Society of Chemistry, U.K. 1-1183.

Thompson, H., Budzinski, P Garrigues, p. and Narbonne, J.F 1999. Comparison of PCB and DDT distribution between water column and sediment dwelling bivalves in Arcachon Bay, France. *Mar Pollut. Bull.*, **38**: 655-662.

Tirpenou, A.E., Tsigouri, A.D. and Gouta, E.H. 1998. Residues of organohalogen compounds in various dolphin tissues. *Bull. Environ. Contam. Toxicol.*, **60**: 216-224.

Tsipi, D. and Hiskia, A. 1996. Organochlorine pesticides and triazines in the drinking water of Athens. *Bull. Environ. Contam. Toxicol.*, **57**; 250-257

Tkalin, A.V. 1996. Chlorinated hydrocarbons in coastal bottom sediments of the Japan Sea. *Environ. Pollut.*, **91**; 183-185.

Triantafyllos, A.A. and Dimitra, G.H. 1998. Pesticide concentrations in Louros River and their fluxes into the marine environment. *Intern. J. Environ. Anal. Chem.*, **70**: 105-120.

Tu Binh, M., Mafumi, W., Haruhiko, N., Shinsuke, T and Thomas, A.J. 1999. Contamination by persistent organochlorines in small Cetaceans from Hong Kong coastal waters. *Mar. Pollut. Bull.*, **39**: 383-392.

U.S. E.P.A. (Unites States Environmental Protection Agency) 1988. Office of drinking water health advisories. Lindane. *Rev. Environ Contam Toxicol.*, **104**: 147-160.

Veerayya, M. and Murthy, P.S.N. 1974. Studies on the sediments of the Vembanad Lake, Kerala state. (part III) - distribution and interpretation of bottom sediments. *Indian J. Mar. Sci.*, **3**: 16-27

Venkatesan, M.I., de Leon, R.P van Geen, A. and Luoma, S.N. 1999. Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay. *Mar. Chem.*, **64**: 85-97

Vishweswariah, K., Jayaram, M. and Venkataramiah, G.H. 1976. Investigations of BHC residues in drinking waters from coffee plantations and coffee beans. J. *Coffee. Res.*, **3**: 96-101.

Voldner, E.C. and Li, Y F 1995. Global usage of selected persistent organochlorines. *Sci.Total Environ.* **160/161** 201-210.

Vu Duc, T Kawano, M. and Tatsukawa, R. 1993. Persistent organochlorine residues in soils from tropical and sub-tropical Asian Countries. *Environ. Pollut.*, **81**: 61-71.

Wade, H.F York, A.C., Morey, E., Padmore, J.M. and Rudo K.M. 1998. The impact of pesticide use on ground water in North California. J. *Environ Qual.*, **27**· 1018-1026.

Waid, J.S (Ed.). 1986. In: *PCBs and the environment*, **Vol. 1-3**. CRC Press, Boca Raton, FL, USA.

Waliszewski, S.M., Pardio, V T.S., Chantiri, J.N.P Infanzon, R.M.R. and Rivera, J. 1996. Organochlorine pesticide residue in adipose tissue of Mexicans. *Sci. Total Environ.*, **181**: 125-131.

Walker, C.H. 1975. Variations in the intake and elimination of pollutants. In: *Organochlorine insecticides: persistent organic pollutant* (Moriarty, F Ed.). Academic Press, New York, 73-130.

Walter, V Marion, W., Elke, S., Bernd, L. and Herbert, O. 1999. Levels of organochlorines (DDT, PCBs, toxaphene, chlordane, dieldrin and HCHs) in Blubber of South African Fur Seals (*Arctocephalus pusillus pusillus*) from Cape Cross/ Namibia. *Mar. Pollut. Bull.*, **38**: 830-836.

Ware, G.W. 1978. The pesticide book. W.H. Freeman and Company, San Francisco, CA.

Watanabe, T 1996. Survey of pesticides in the atmosphere at high altitude. *Bull. Agri. Chem. Inspect. Stn.* **36**: 25-32.

Watanabe, T 1998. Determination of the concentration of pesticides in atmosphere at high altitudes after aerial application. *Bull. Environ. Contam. Toxicol.*, **60**: 669-676.

Watanabe, S., Wantabe, S. and Itoh, K. 1984. Effluence of herbicides (CNP, molinate, simetryne) to watercourse and their fates in soil at a model paddy field. *J. Pestic. Sci.*, **9**: 33-38.

Wauchope, R.D., Butter, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., Burt, J.P 1992. The SCS/ARS/CES pesticides properties database for environmental decision-making. *Rev. Environ. Contam. Toxicol.*, **123**: 1-155.

Wayland, J., Hayes, Jr Edward, R., Laws, Jr (Eds.) 1991 DDT and its analoges. In: *Handbook of pesticide toxicology*, **Vol 2**. Classes of pesticides. 743-780.

Weber, W.J. Jr Voice, T.C., Pirbazari, M., Hunt, G. E. and Ulanoff, D.M. 1983. Sorption of hydrophobic compounds by sediments, soils, and suspended solids. II. Sorbent evolution studies. *Water Res.*, **17**· 1443-1452.

Wedemeyer, G.1967 Dechorination of 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane by *Aerobacter aerogenes*. *Applied Microbiol.*, **15**: 569-574.

Wegman, R.C.C. and Greve, P.A. 1978. Organochlorines, cholinesterase inhibitors, and aromatic amines in Dutch water samples, September 1969 – December 1975. *Pest. Monit. J.*, **12**: 149-162.

Wesen, C., Carberg, G.E. and Martinsen, K. 1992 Chlorinated organic substances in aqueous organisms and sediments. *Ambio.*, **19**: 36-38.

WHO (World Health Organisation) 1990. Public health impact of pesticide use in Agriculture, Geneva.

WHO (World Health Organisation) 1991 Lindane. Environ. health criteria 124, Geneva.

WHO (World Health Organisation) 1992. Alpha and beta-hexachlorocyclohexanes. Environ health criteria 123, Geneva.

Wiemeyer, S.N. 1996. Other organochlorine pesticides in birds. *Environ. Contam. Wildl.*, 99-115.

Williams, T.M., Rees, J.G., Ferguson, A., Herd, R.A., Kairu, K.K. and Yobe, A.C. 1997 Metals, petroleum hydrocarbons and organochlorines in inshore sediments and waters of Mombasa, Kenya. *Mar. Pollut. Bull.*, **34**; 570-577

Winters, S.L. and Lee, D.R. 1987 *In situ* retardation of trace organics in groundwater discharge to a sandy streambed. *Environ. Sci. Technol.*, **21**: 1182-1186.

Wittwer, S.H. 1979. An assessment of future technological advances in agriculture and their impact on regulatory environment. In: *Critical food issues of the eighties* (Chou, M. and Harmon, D., Eds.). Pergamon Press, New York.

Wolff, M.S. 1984. Analysis of skin lipids for halogenated hydrocarbons. *Anal. Chem.*, **56**: 1492-1496.

Woodwell, G. M., Craig, P.P and Johnson, H.A. 1971. DDT in the biosphere: Where does it go? *Science.*,**174**: 1101-1107

** Xinru Zhu., Jiang Liu. and Anders Sodergren. 1998. Occurrence and distribution of organochlorine residues and metals in sediment, water and fish in the catchment area of lake Baiyangdian, China. *Toxicol. Environ. Chem.*

Yadev, D.V Mittal, P.K., Aggarwal, H.C. and Pillai, M.K.K. 1981 Organochlorine insecticide residues in soil and earthworms in the Delhi area, India. *Pest. Monit. J.*, **15**: 80-85.

Yamato, Y Kiyonaga, M. and Watanabe, T 1983. Comparative bioaccumulation and elimination of HCH isomers in short-necked clam (*Venerupis japonica*) and guppy (*Poecilia reticulata*). *Bull. Environ. Conntam. Toxicol.*, **31**: 352-359.

Yoshida, S., Murata, H. and Imaida, M. 1992. Distributions of pesticide residues in vegetables and fruits. *Nippon Nohgeikagaku Kaishi.*, **66**: 1007-1011

You, G., Sayles, G.D., Kupferle, M.J., Kim, I.S. and Bishop, P.L. 1996. Anaerobic DDT biotransformation: enhancement by application of surfactants and low oxidation reduction potential. *Chemosphere.*, **32**: 2269-2284.

Zhengsheng, L. and Haibo, L. 1994. Residues and fate of DDT in subtropical soils. In: *Residues and degradations of DDT in subtropical dry fields and flooded fields* (Xuebao, Z.D., Kexueban, Z., Eds.). **33**: 96-102.

Zhou, J.L., Fileman, T.W., Evans, S., Donkin, P manotoura, R.F.C. and Rowland, S.J. 1996. Seasonal distributions of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber estuary and Humber