ORGANOCHLORINE PESTICIDE RESIDUES IN THE MARINE FISHES OF COIMBATORE MARKET - SUITABILITY FOR HUMAN CONSUMPTION

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P. JAYANTHI

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SACON

Division of Ecotoxicology

Sálim Ali Centre for Ornithology and Natural History (SACON)

(Centre aided by the Ministry of Environment & Forests, Govt. of India)

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CERTIFICATE

This is to certify that the thesis, entitled **"ORGANOCHLORINE PESTICIDE RESIDUES IN THE MARINE FISHES OF COIMBATORE MARKET - SUITABILITY FOR HUMAN CONSUMPTION"** submitted to the Bharathiar University, in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy in **ENVIRONMENTAL SCIENCES** is a record of original research work done by **Ms P. JAYANTHI** during the period **AUGUST 2005 to JANUARY 2012** in the Department of **ECOTOXICOLOGY** at **SÁLIM ALI CENTRE FOR ORNITHOLOGY AND NATURAL HISTORY, ANAIKATTY, COIMBATORE - 641 108** under my supervision and guidance and the thesis has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or any other similar title of any candidate of any University.

Countersigned

Head of the Department/ Director

Salim Ali Centre for Ornithology and Natural History
आनैकट्टी / Anaikatty (Post)
कोयम्बटूर / Coimbatore 641 108

Signature of the Guide

डॉ. एस मनिवन्नन / Dr S Manivannan
प्रधान वैज्ञानिक / Principal Scientist
सालिम अली पक्षि - विज्ञान एवं प्रकृति
Salim Ali Centre for Ornithology and Natural History
आनैकट्टि / Anaikatty (Post)
कोयम्बतूर / Coimbatore-641 108

DECLARATION

I, P. JAYANTHI hereby declare that the thesis, entitled "**ORGANOCHLORINE PESTICIDE RESIDUES IN THE MARINE FISHES OF COIMBATORE MARKET - SUITABILITY FOR HUMAN CONSUMPTION**" submitted to the Bharathiar University, in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy in **ENVIRONMENTAL SCIENCES** is a record of original research work done by me during **AUGUST 2005** to **JANUARY 2012** under the supervision and guidance of **Dr. S. MURALIDHARAN, PRINCIPAL SCIENTIST,** Division of **ECOTOXICOLOGY** at **SÁLIM ALI CENTRE FOR ORNITHOLOGY AND NATURAL HISTORY, ANAIKATTY, COIMBATORE - 641 108** and it has not formed the basis for the award of any Degree / Diploma / Associateship / Fellowship or any other similar title of any candidate of any University.

Signature of the Guide

डॉ. एस. मुरलिधरन / Dr. S. Muralidharan
मुख्य वैज्ञानिक Principal Scientist पर्यावरण विषविज्ञान / Ecotoxicology
सालिम अली पक्षी - विज्ञान एवं प्रकृति - विज्ञान केन्द्र
Sálim Ali Centre for Ornithology and Natural History
अनैकट्टि Anaikatty (Post)
कोयंबत्तूर / Coimbatore-641 108

Signature of the Candidate

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INTRODUCTION

1. INTRODUCTION

Pesticides are ubiquitous chemicals and can persist in the environmental components for decades (Hussen *et al.,* 2007 and Shegunova *et al.,* 2007). Their characteristics, including hydrophobicity and resistance to degradation, enable them to accumulate in soils, sediments, biota (Covaci *et al.,* 2005; Pandelova *et al.,* 2008; Hao *et al.,* 2009 and Shelepchikov *et al.,* 2009), and in human body through dietary intake, inhalation and other indirect exposure (Nandita *et al.,* 2009).

Organochlorine pesticides (OCPs) can get transported to regions such as the Arctic far from their place of original application (Iwata *et al.,* 1994 and Halsall *et al.,* 1998). These organochlorine compounds can cause in human beings, a wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorders, immune suppression, birth defects and they are also suspected to be endocrine disruptors (Van Den Berg *et al.,* 2006 and Wang *et al.,* 2008). Extensive use of organochlorine pesticides in various industrial and agriculture activities have resulted in serious environmental risks to the organisms at higher trophic levels in the food chain, due to high persistence and liposolubility of these compounds (Leyva - Cardosa *et al.,* 2003).

Due to many established ill effects of organochlorines, several of them have been banned in many North American and European countries. However, some developing countries are still using a few of these compounds because of their low cost and versatility in agriculture and sanitation purpose (Tanabe *et al.,* 1994; Rekha *et al.,* 2006 and Abhilash and Singh, 2009). Consequently, environmental problems associated with toxic contaminants in many of these countries are of great concern. It is recorded that approximately three million people are poisoned and 200,000 die each year around the world from pesticide poisoning, and a majority of them belong to developing countries (FAO, 2000). It is also reported that in developing countries, incidence of pesticide poisoning may even be greater than reported due to under-reporting, lack of data and misdiagnosis (Forget, 1991).

In India, organochlorine pesticides (OCPs), especially DDT and HCH were used extensively till recently both for agricultural and sanitary purposes (Pandit *et al.*, 2001 and Kumar *et al.*, 2006). At present, India is the largest producer of pesticides in Asia and it ranks twelfth in the world for the use of pesticides with a present annual (2008 - '09) consumption of 43,860 metric tons (MT) (Source: www.indiastat.com accessed on January 27 2011). Although substantial portions of applied pesticides are dissipated at the site of application through chemical and biological degradation processes, still a reasonable fraction of the OCP residues reach the oceans through agricultural run-off, atmospheric transport and sewerage discharge (GESAMP, 1989). Because OCPs are known for their persistence, toxicity and bioaccumulation characteristics, there is a great concern about their impact on the marine environment. The transport, dispersion and finally the ultimate effects of pesticides in marine systems depend upon the persistence of chemicals under tropical conditions and their bioaccumulation and biodegradation.

India (Lat. 8°4′ N and 37°69′ N and Long. 68°7′ E and 97°25′ E), a tropical south Asian country, has a stretch of ~7500 km coastline, excluding its island territories with 2 million km^2 exclusive economic zone (EEZ). There are 14 major, 44 medium and 162 small rivers in India, with a mean annual run-off of 1645 km^3, although not all these rivers discharge into the sea. The Arabian Sea and the Bay of Bengal are subject to large semi-diurnal tides with amplitudes of 1- 8 m and are also influenced by the biannual reversal of the monsoon winds. These two factors result in the flushing of Indian coastal areas which further help in dispersing pollutants (Glassby and Roonwal, 1995). Catastrophic effects of tsunami and supercyclones also play a major role in changing the coastal morphology and sediment dispersal patterns (Bhattacharya, 2003).

Despite the fact that the pesticide consumption per unit area is low in India compared to developed countries, the indiscriminate use of these pesticides has resulted in wide spread occurrence of their residues in biota and other abiotic compartments. In order to understand the role of tropical developing countries such as India, as possible emission source of Persistent Organic Pollutants (POPs), it is necessary to elucidate the distribution, behavior and fate of these compounds in various environmental

compartments. Among the various environmental components in the marine system, fishes are found to be the most suitable indicators.

Fishes have been selected for monitoring because they concentrate pollutants in their tissues directly from water, and also through their diet, thus enabling easy assessment and transfer of pollutants through the tropic web (Bruggeman, 1982); they generally exhibit a low metabolism for organochlorines and consequently reflect the level of contamination in the aquatic environment (Muir *et al.*, 1990); they occupy different habitats in the same ecosystem and have different feeding behaviors, thus offering the potential to study the influence of environmental and biological factors on the bioaccumulation of pollutants (Porte and Albaiges, 1993) and data on chlorinated compounds in edible fishes are also important from human health point of view (Pastor *et al.*, 1996 and Muralidharan *et al.*, 2009).

Thus an attempt has been made to assess the organochlorine pesticide residues in the marine fishes and the current study is expected to reflect the status of contamination with reference to organochlorine pesticides in Cochin on the west coast and Rameshwaram on the east coast of India.

1.1 Organochlorine pesticides

Rapid industrial development and growing demand for food as a result of increasing human population has led to a substantial increase in the production of agrochemicals such as pesticides and fertilizers, resulting in continued contamination of our aquatic environment (Jacinto, 1997). The accelerated urbanization and industrialization of a region with increase in human settlement, discharge of non-treated urban waters and agriculture wastes have been raising severe pollution problems (Botello, 2000).

The major forms of pollutants to the aquatic environment are industrial waste waters and agricultural chemicals (Klumpp *et al.*, 2002) which are commonly termed as pesticides. The term pesticide covers a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematocides, plant growth regulators and others. Among these, organochlorine (OC) insecticides, used effectively in controlling a number of

diseases, such as malaria and typhus, were banned or restricted after 1960s in most of the technologically advanced countries (Li, 1999).

Pesticides are synthetic chemicals developed to control insect and plant pests. The use of pesticides for agriculture, forestry and health purposes is now so extensive that it has affected almost all forms of living organisms. In many places the soil, plants, animals and waters are found to contain pesticide residues (Allen *et al.*, 1976). However, many of the potential effects of pesticides on humans and aquatic ecosystems remain undocumented.

Among the different type of pesticides, such as organochlorines, organophosphates, carbamates and pyrethroids, the organochlorines have got very slow decomposition rate and long half-life. Some are very persistent and become widely distributed by air, water and other organisms (White and Stickel, 1975). Although in recent years, many new broad spectrum pesticides have been developed OCPs continue to be the potential group of chemicals used in control of agricultural pests and vectors of diseases like malaria still in many countries (David *et al.*, 2003).

A special feature of the organochlorine pesticides in tropical marine environment is their volatile nature, because of which they get released into the air and travel long distances as an aerial source. There are reports on the active transfer of these dissolved organochlorine pesticides into the atmosphere due to volatilization (Pandit and Sahu, 2001).

Use of pesticides in India began in 1948 when Dichloro Diphenyl Trichloro ethane (DDT) was imported for malaria control and Benzene Hexachloride (BHC) for locust control. India started pesticide production with manufacturing plant for DDT and BHC, now known as Hexachloro Cyclo Hexane (HCH), in 1952. In 1958, India was producing over 5000 metric tonnes of pesticides. Currently, there are approximately 145 pesticides registered for use. Pesticide use in India has jumped several hundred folds from 154 metric tons in 1954 to 88,000 metric tons in 2001 (Gupta, 2004). Despite the fact that the consumption of pesticides in India (per unit area) is still very low, which is about 0.5 kg/ha of pesticides against 6.60 and 12.0 kg/ha in Korea and Japan respectively (Gupta, 2004).

Exposure to pesticides both occupationally and environmentally causes a range of human health problems. It is estimated that nearly 10,000 deaths occur annually due to use of chemical pesticides worldwide, with about three-fourths of these deaths occurring in developing countries (Horrigan *et al.,* 2002). The first report of poisoning due to pesticides in India came from Kerala in 1958 where, over 100 people died after consuming wheat flour contaminated with parathion. Subsequently several cases of pesticide-poisoning including the Bhopal disaster have been reported. Vast majority of the population in India (56.7 %) is engaged in agriculture and are therefore exposed to the pesticides used in farms (GOI: Planning Commission report, 2001 and Gupta, 2004).

Pesticides being used in agricultural tracts are released into the environment and come into human contact directly or indirectly. Humans are exposed to pesticides found in environmental media (soil, water, air and food) by different routes of exposure such as inhalation, ingestion and dermal contact. Exposure to pesticides results in acute and chronic health problems. These range from temporary acute effects like irritation of eyes, excessive salivation to chronic diseases like cancer, reproductive and developmental disorders (Yassi *et al.,* 2001). However, information available on these issues is far from desired.

There has been a widespread contamination of food commodities with pesticide residues, basically due to non-judicious use of pesticides. In India, 51% of food commodities are contaminated with pesticide residues and out of these, 20% have pesticides residues above the maximum residue level values. It has been observed that their long-term, low-dose exposures are increasingly linked to human health effects such as immune-suppression, hormone disruption, diminished intelligence, reproductive abnormalities and cancer.

Chlorinated pesticides such as HCH and DDT are effective pest control chemicals, used in agriculture and public health activities (malaria eradication, etc.) worldwide for the past several decades and are still in use in many developing countries. Similar to Polychlorinated Biphenyls, these pesticides also cause endocrine disruption and food chain biomagnifications, because of their lipophilicity and environmental persistence. Although complete ban on DDT was imposed in many developed nations, in India it was

banned only for agricultural use, and still being used for malaria control, and HCH is also not completely banned (still used for agriculture as lindane). About 31 banned or restricted pesticides in other countries are still in use in India (http://www.cseindia.org accessed on 10th November 2011). Persistent organochlorine pesticides thus are widespread in all the components of the environment. Hence, a monitoring study like the present one will help in understanding the situation.

1.2 Impact on marine environment

Environmental occurrence of Persistent Organic Pollutants (POPs) are a global rather than regional problem, because chlorinated pesticides used in tropical regions will be carried by long-range atmospheric transport and ultimately end up in polar and environmentally pristine regions. In 2001, the Stockholm Convention on POPs acknowledged POPs as a global problem.

Long-range atmospheric transport, precipitation and 'cold-condensation' of toxicants from human sources lead to a global distribution and contamination of the environment (Wania and Mackay, 1993 and Simonich *et al.*, 1995). Even in pristine ecosystems such as Antarctica surprisingly high concentrations of persistent chemicals have been detected. In addition, the low temperature in polar and mountain regions slows down the biological degradation and excretion of toxicants in ectothermic organisms. Extreme environmental conditions including low temperatures and short cultivation periods combined with accumulated toxicants may lead to an additive stress to organisms inhabiting these environments (Psenner, 1989 and Locke *et al.*, 1995).

Indiscriminate use of pesticides has posed a serious threat to mankind and eliminates useful insects causing ecological imbalance. Pesticides reach marine environment through run-off, wind action, leaching or combination of above causing toxicity to aquatic food chain reaching to man. Acute concentration of pesticides in water causes mortality to fish, while sub acute condition leave residue in them and make them unsuitable for human consumption.

Residues of OC insecticides, especially DDT and HCH have been detected in man and his environment the world over (Jensen, 1981 and Hayes and Laws, 1991). However, by comparison very high levels of these have been reported in human blood, fat and milk samples in India.

Roughly about 25 % of all the pesticides used in the land once can be expected to ultimately end up in the sea every year. Some of these substances are biodegradable while others are persistent. Their cumulative effect over a long period could be quite harmful to the coastal marine environment. These effects are, as yet, not very perceptible over the entire Indian coast. But near a few big cities and industrial conglomerates the effects are, indeed, becoming near disastrous (Sarkar *et al.*, 2008).

In India, although information on the residue levels of pesticides in water, soil, sediment, fishes and birds are available, information on the daily dietary intake of pesticide through consumption of fishes is scarce, except a few (Kumari *et al.,* 2001). A study conducted by Vijayan *et al.,* (2004) on the levels of organochlorines in fish is first of its kind in India. The study documented many persistent contaminants in about 66 species of fresh water fishes from 173 wetlands spread across 14 states in India. The study also looked at the dietary input to human beings in contrast to the WHO guidelines.

Chlorinated pesticides were reported in harbours, near shore sediments and Bays all over the globe (Iwata *et al.*, 1994; Hong *et al.*, 1995; Strandberg *et al.*, 1998; De Mora *et al.*, 2001; Zhou *et al.*, 2001; Barakat *et al.*, 2002; Fillmann *et al.,* 2002 and Hong *et al.*, 2003). Earlier studies in Indian marine environment showed that organochlorine pesticide residues are comparable with other developing countries, but suggested an increase in future due to continuing usage of organochlorine pesticides in agriculture and vector control measures.

Distribution of organochlorine pesticides in Indian marine environment was documented by several authors (Sarkar *et al.*, 1997; Babu Rajendran *et al.*, 1999 and Tanabe, 2000). Moreover, Tanabe *et al.,* (2000) concluded studies on organochlorines from both east and west coasts of India, mainly in organisms (mussel, fish, birds and mammals). Findings on chlorinated pesticides were only limited to seashore sediments (Pandit *et al.*, 2001),

except a couple of reports on offshore sediments (Sarkar and Sen Gupta, 1988 and Sarkar *et al.*, 1997).

The ability of the fishes to concentrate and accumulate the contaminants particularly organochlorines from the sediments and water, makes them suitable indicators. They play a major role in human diet; unfortunately they are highly contaminated especially by organochlorine compounds. Needless to say that the most common route of exposure of these contaminants to humans is through consumption of contaminated fishes (Faroon *et al.*, 2001 and Schantz *et al.*, 2001). Distribution and concentration of toxic contaminants (i.e. PCBs, OCPs) in fish tissue reflect surrounding water and sediment concentrations (Brown *et al.*, 1988 and Bright *et al.*, 1995). Consumption of biota from contaminated aquatic body is considered to be an important route of exposure to persistent organochlorine compounds (Johansen *et al.*, 1996). Humans, being a final link in the food chain, are mostly affected, and consequently the general public has become increasingly concerned about the potential risk to health from consumption of such polluted biota.

A preliminary study done by Muralidharan *et al.*, (2009) had documented the status of organochlorine pesticides in a few species of marine fishes of commercial importance and its possible exposure to human being through dietary intake. But long-term monitoring of these residues in the environmental components especially fishes is highly warranted. Moreover, effective monitoring of the OCP residues in fishes is crucial for proper assessment of human exposure to these contaminants through food. The present study was aimed to fill up the lacunae existing on the status of organochlorine pesticide residues in marine fishes of Cochin and Rameshwaram coast.

1.3 Objectives

The current study was carried out with the following objectives;

i) To document organochlorine pesticide residues in select species of marine fishes with commercial importance in Coimbatore.

ii) To document spatio-temporal variation in organochlorine residues among the fishes, and

iii) To assess the suitability of the fishes for human consumption.

REVIEW OF LITERATURE

2. LITERATURE REVIEW

Organochlorine pesticides (OCPs) are a class of widespread contaminants ubiquitous in the environment. Longtime uses of the organochlorine pesticides as well as their physical and chemical persistence in nature have resulted in their becoming ubiquitously occurring environmental contaminants (UNEP, 2002). The main reasons for environmental contamination by OCPs are their large production, uncontrolled use, inadequate discharge and persistence in the natural environment (Ross, 2004).

Environmental exposure of living organisms to these OCPs results in their persistence and accumulation in fatty tissues (Falandysz *et al.*, 2004) and cause health effects in wildlife and humans (Tanabe, 2002). In addition, organochlorine pesticides are lipophilic and thus undergo biomagnifications through successive trophic levels in the food chain (Angulo *et al.*, 1999; Borga *et al.*, 2001 and Solomon and Weiss, 2002).

Although many persistent OCPs are restricted or banned in developed countries, they are still produced and used to a large extent in developing countries. Some developing countries in the lower latitude regions have attracted attention as potentially important regional and global sources of organochlorine pesticides (OCPs), because of past and/or continued use (Iwata *et al.*, 1994), with the environmental conditions in tropical regions potentially enhancing emissions and subsequent atmospheric transport. The Stockholm Convention also requires national monitoring of persistent organic pollutants (POPs) (Fiedler H, 2007).

India is a large and important tropical country where OCPs have been widely used in the past. Technical HCH use was banned by developed nations in 1970s followed by many developing countries in 1980s (Li, 1999). A complete ban on the production and sale of HCH in India came into effect in April 1997 (Tomar and Parmar, 1998). Except for termite control in agriculture and buildings, the import, manufacture and use of lindane (γ HCH) is also restricted since August 2007 (The Gazette of India, 2007). Agriculture and health sector are the major consumers of pesticides in India. About 145 pesticides were

registered in India in the mid nineties (Gupta, 2004). Aldrin, BHC, chlordane, heptachlor, endrin and dieldrin are included in the list as banned pesticides and DDT and lindane are included in the list of pesticides restricted for use in India by the Central Insecticides Board and Registration Committee. At present, India is the largest producer of pesticides in Asia and it ranks twelfth in the world for the use of pesticides with a present annual (2008 - '09) consumption of 43,860 metric tons (MT) (Source: www.indiastat.com accessed on January 27 2012).

Per hectare consumption of pesticide is low in India at 381 grams when compared to the world average of 500 grams (Report by Indian Pesticide Industry September, 2011). Although pesticide consumption is low in India compared to the other developed countries, the indiscriminate use of these pesticides has resulted in sporadic occurrence of the residues in biota and other abiotic compartments. In order to understand the role of tropical developing countries as possible emission sources of POPs, it is necessary to elucidate the distribution, behavior and fate of these compounds in various environmental compartments. It has also been emphasized that open seas play a role as a final sink for persistent toxic contaminants and accumulate on marine organisms (Tanabe, 2000).

Among the existing environmental compartments in the marine system, fishes were found to be the most suitable indicators. Hence, an attempt has been made to elucidate the pattern of distribution, spatial and temporal variations of the OCPs in the commercially important marine fishes and thereby assessing their suitability for human consumption.

2.1 Organochlorine pesticides in the marine environment

The chlorohydrocarbon pesticide residues are present in the world's oceans and are at generally greater concentrations in urbanized coastal water and estuaries. During the last few decades, contamination by organochlorines has spread all over the world as evidenced by their detection in a wide range of environmental media and biota (Tanabe, 2000 and Tanabe *et al.*, 2000).

Presence of organochlorine chemicals has been reported in various biota including fishes. Fishes uptake OCPs rapidly from water, sediment or food to different degrees, depending on the species and habitat (WHO, 1993). It has been stated that the assessment of the seasonal trends of the OC pesticide residues in edible fishes is complicated since different factors, including physiology of marine organisms and their feeding habit, do not allow an accurate interpretation of the temporal fluctuations observed in the concentrations (Porte and Albaiges, 1993).

The occurrence of high concentrations of organochlorine compounds such as HCHs (HCH isomers), DDTs (DDT and its derivatives), chlordanes in the Arctic ecosystem, despite the ban on many of these compounds in most of the industrialized nations of the Northern Hemisphere, has prompted the need to identity possible emission sources (Wania and Mackay, 1993). Investigations conducted by numerous researchers during the last decade have revealed that mid and low-latitude countries, particularly those in the tropical region, are possible sources of contamination in the Arctic in recent years. This concept is supported by the high current consumption of organochlorine pesticides in tropical developing countries for enhancing food production and eradicating vector-borne diseases.

Some of the earlier studies showed widespread occurrence of organochlorines in air, water, sediment, soil and foodstuffs in tropical countries of Asia and Oceania. The determination of organochlorine concentrations in fish may indicate the extent of aquatic contamination and the accumulation characteristics of these compounds in tropical aquatic biota (Kannan *et al.*, 1995).

Although a large number of studies are carried out on coastal ecosystems all over the world (Sericano *et al.*, 1995), only a few studies used open sea organism (Minh *et al.*, 2000). Fish exhibit a low metabolism for organochlorines (Muir *et al.*, 1990) and they concentrate the pollutants in their tissues directly through the diet, as well as from water.

All the isomers of HCH, other than γ HCH exhibit much reduced insecticidal activity, both α and β HCH have been shown to disrupt endocrine processes (Kendall *et al.*, 1998). Of

these two isomers, β HCH bioaccumulates more strongly and is more resistant to metabolism and microbial degradation. These characteristics are consistent with the observation that α HCH predominates in human fat, serum and breast milk (Willett *et al.*, 1998 and van Oostdam *et al.*, 1999). Although residues in marine mammals vary, some seal and whale species show preferential accumulation of β HCH, while others contain predominantly α HCH with lesser amounts of β HCH and γ HCH (Willett *et al.*, 1998). Regarding the alicyclic family, β HCH has been reported as the most persistent isomer (ECO/ OPS/ OMS, 1995), it was the compound with the highest concentration with its consequent accumulation in the fatty tissue of marine organisms and humans (Barkatina *et al.*, 2002).

The residue burden in fish has been observed to decline since the banning of many organochlorine insecticides in western countries (Murty, 1986), but their presence is continued, particularly in fish from different regions of developing countries (Kole and Bagchi, 1995). In the study on geographical distribution and accumulation features of organochlorine residues in fish in tropical Asia and Oceania, it has been reported that the concentration of HCH and its isomers were relatively low in fish from all the countries except India. Alpha (α) HCH was the predominant isomer in fish from India and Thailand, while the β HCH constituted a major portion of total HCH in fish from Vietnam, Papua New Guinea and Australia. The predominance of α HCH reflects the use of technical mixture of HCH containing 55 – 70 % α; 5 - 14% β; 10 - 18 % γ and 6 - 10 % δ isomer. In spite of the use of HCH in south East Asian countries until at least the 1980's and in recent years in India, the residue levels in fish were low, illustrating the rapid volatilization of HCH isomers in tropical latitudes. (Kannan *et al.*, 1995).

The test of basic food stuffs and hospital diets from various regions of Belarus as well as fish and fish products of local industry and imported has showed the presence of small quantities of HCH isomers and DDT metabolites. However the mean daily OC intake was below FAO/WHO standards (Barkatina *et al.*, 1999).

The organochlorine pesticide residues in the marine and fresh water fishes of Cambodia showed the higher contribution of α HCH followed by β HCH and γ HCH towards the total

HCH residues. Low residue levels of HCH's and higher α HCH composition in fish suggests their atmospheric transport to Cambodia from other Asian countries. HCH concentration found in Cambodian sample is likely to be reflected by the atmospheric transport from India through the south west monsoon (Monirith *et al.*, 1999).

Muccio *et al.* (2002) selected twelve marine organisms to monitor the contamination of food of marine origin from Adriatic Sea by persistent organochlorine pesticides. In his study the HCH isomers were higher in pelagic fishes (0.96 ng/g) followed by demersal fishes (90. 44 ng/g). Results for DDT groups such as *p,p'* DDT, *p,p'* DDE, *p,p'* DDD show the compound present at higher level is *p,p'* DDE ranging from less than 0.01 to 19.88 ng/g ww compared with *p,p'* DDD (less than 0.01 to 3.42 ng/g ww) and *p,p'* DDT (less than 0.01 to 4.03 ng/g ww). *p,p'* DDE showed the highest levels in fishes especially in three species which have the highest fat content compared with other species examined. Highest value (24.83 ng/g ww) was seen in Mackerel.

The study done by Minh *et al.* (2002) on the seasonal variations of persistent OCs in migratory birds from Lake Baikal wintering in south eastern Asian region has indicated elevated exposure to HCHs and DDTs in the southern wintering sites suggesting the south Asian region as a potential source of OC insecticide contamination for higher latitude areas. Britto *et al.* (2002) stated that the major organochlorine residues involved in water pollution is lindane, the gamma isomer of BHC. It is one of the most widely used OC insecticides for agricultural purposes worldwide.

The study conducted by Manirakiza *et al.* (2002) in the fishes of Lake Tanganyika, Burundi, Africa showed the predominance of γ-HCH isomer with a concentration range of 10.5 ng/g in *Limnothrissa miodon* to 221.5 ng/g in *Boulengerochromis microlepis.* It was also stated that the bioaccumulation process of the contaminants depend on a large number of parameters including age, sex and position in the trophic level.

DDT is recognized since long time as persistent hazardous environmental contaminant among pesticides and appears in the priority pollutant list of some western countries

(Hedgcott, 1994). DDT has been extensively studied due to its widespread usage and adverse toxic effects on aquatic organisms including human beings.

DDT has high fat solubility and long-term persistence in the environment due to its chemical structure. The compounds are low in polarity which contributes to key properties such as bioconcentration in lipids and fats and toxicity to a broad range of organisms (Connell, 1990).

As a part of Mussel Watch Program in Korea, the contamination levels and accumulation features of OCPs were assessed for 82 bivalve samples collected from 66 sites along the entire coast of Korea. The result showed that among the major groups of organochlorine DDTs were three times higher in 18 sites. The concentration of total DDT was 53.26 ng/g.

Technical DDT products generally contains 75 % *p,p'* DDT, 5 % *p,p'* DDE, 15 % *o,p'* DDT, < 0.5 *o,p'* DDE (WHO, 1979) and DDT isomers degrade to DDE or DDD under aerobic and anaerobic conditions (Richard, 1976). Contribution of DDE, DDD and DDT isomers were 42 %, 28 % and 28 % of the total body burden respectively. DDT isomers in Korean coastal bivalves were two times higher than in the Gulf of Mexico (Sericano *et al.*, 1990).

Studies conducted by Long *et al.* (1995) and Buchman, (1999) in marine environment showed the average concentrations of *p,p'* DDT, *p,p'* DDD, *p,p'* DDE and total DDT to be below the ERL (1, 2, 2.2 & 1.58 ng/g respectively). The levels of *p,p'* DDT in the fish muscle tissue depend on the contamination of the aquatic environment and also on the mode of feeding of the fish as well as on the size weight and length and reproductive status of the individual (WHO, 1993).

Brito *et al.* (2002) stated that the major organochlorine residues involved in water pollution is lindane, the gamma isomer of HCH. It is one of the most widely used OC insecticides in controlling crop pests. Regarding the alicyclic family, beta HCH has been reported as the most persistent isomer (ECO/OPS/OMS, 1995).

Picer and Picer, (1991) reported total DDT in the coastal water of Adriatic Sea with the concentration ranging from 0.1 ppb to 93.9 ppb. Whereas, the total DDT concentration 0.07 ng/g to 21.93 ng/g. lindane varied from 0.03 ng/g to 0.50 ng/g, where heptachlor

epoxide and Dieldrin measured not detectable value to 0.06 ng/g and 0.05 ng/g to 0.41 ng/g respectively (Holland *et al.*, 1993).

The monitoring study conducted in Kenya have shown the presence of *p,p'* DDT, *p,p'* DDE, *p,p'* DDD residues in sea water and fish samples sampled from different sites along the Indian coast of Kenya (Everaarts *et al.*, 1996). The fish samples were obtained from Tana and Sabaki rivers. Immature fish *Tilapia zilli* tend to have higher fat content in their muscle, although the residue concentration in river water was low. The concentration levels of these residues ranged from < 0.001 to 0.0064 mg/g in birds and fish from Lake Nakuru, Kenya.

Phoung *et al.* (1998) reported the mean DDT concentration to be 79.9 ng/g in about 9 sites chosen inside the urban waterway and the Saigon River, Ho Chi Minch city. DDT in Ho Chi Minch city sediments ranged from 1.76 to 253.6 ng/g dry weight. The result shows the possibility of continued presence of DDT in the environment. Harding *et al.* (1997) determined the concentration of DDT in the liver of Bluefin tuna collected from Japanese coastal water in order to elucidate the accumulation profile and to evaluate the suitability of this species as a biomonitor for pollution in the open sea ecosystem. Bluefin tuna was caught at sampling locations St. 1-4. The highest concentrations of DDT were observed from St. 2 compared to those from 1, 3 and 4. Concentration of DDT increased significantly with body length (30- 190 cm). This can be explained by high accumulation potential of these compounds. This has been reported earlier in some fishes from Gulf of St. Lawrence and Lake Burtnieku in Latvia (Olsson *et al.*, 2000).

Tsigouri *et al.* (2000) analyzed a total of 36 products of fish oil and fish liver oil produced in European countries (Norway and UK). The result showed that consumption of fish liver oil in capsules fortifies consumers with 0.008 to 1.1 ppb of total DDT per day. WHO has recommended Provisional Tolerable Daily Intake (PTDI) of DDT to be 0.02 mg/kg/bw (JMPR, 1998), this means an adult person (body weight of approximately 60 kg) ingests 1.2 mg of DDT per day. So, the quantities calculated of 0.008 to 1.1 ppb are below these values.

Brito *et al.* (2002) detected organochlorines in about 29 fishes (*Theragra chalcogramma*) collected from the Berring Sea and Gulf of Alaska at six different locations in 1992 and other ten in the Japan Sea at two locations in 1991. Among the OCs analyzed, the concentration of DDT was 1200 ng/g lipid weight. The predominance of DDT residue in Japan Sea may be due to the larger input of this compound in this country. Among DDT and its metabolites *p,p'* DDE was the most predominant compound in the fish from almost all locations. Iwata *et al.* (1993) reported that highest ratio of *p,p'* DDE to *p,p'* DDT has been found in the atmosphere from the North pacific basin, which is far from contamination source.

The adverse effects of DDT, and other pesticides, were recognized in Australia in the late 1960s, including toxic effects on wildlife and residues in beef. By the end of 1987 usage of DDT had declined from 0.45 to 0.002 ppb/ kg/ day. The most consistent occurrence in fish from the 1960 to present time has been of total DDT at large concentration. DDT and its metabolites are the most common pesticide contaminants in aquatic invertebrates. (Connell *et al.*, 2002).

Mwevura *et al.* (2002) analyzed the sediment and biota samples collected from Msibazi and Kizinga rivers for OCP residues like *p,p'* DDT, *p,p'* DDE and *o,p'* DDT. A total of 24 sediment samples and 32 biota samples were collected for analyses during both dry and wet seasons. The result of levels of metabolites shows that concentration of total DDT was high in dry season than the wet season, because the sites were highly affected by erosion during the rainy season.

In biota samples the *p,p'* DDE residues were the most abundant residues as it was detected in all samples at relatively higher concentration compared to other residues. The average concentration of total DDT in the biota samples was 22.6 µg/ kg fresh weight and the range was between 6.6 and 53 µg/ kg fresh weight. Biota samples showed significant difference in levels of residues depending on mode of feeding and age of analyzed biota. *p,p'* DDT to total DDT ratios indicated recent use of DDT. The levels of residues in sediments suggest possible adverse effects to human consuming biota that are directly

exposed to the sediments. These effects associated with bio-concentration of residues in the tissues of edible aquatic biota (Mwevura *et al.*, 2002).

The ratio of concentration of *p,p'* DDT to that of total DDT in sediments and biota samples from different seasons were calculated to know the recent use of DDT and its use was a source of pollution to Msimbazi river. The study showed that *p,p'* DDT contribute 62 % of the total DDT at the site (Mwevura *et al.*, 1999). The mean value and the range of total DDT residues found in biota was 6.6 - 53 µg/ kg fresh weight were significantly below the FAO/ WHO Maximum Acceptable Limits in fish and sea foods (200 µg/ kg fresh weight FAO/ WHO, 1986) so the biota was found to be safe (Mwevura *et al.*, 2002).

The USFWS's monitoring program reports show the DDT residues in fish and wild-life to be declining. In the environment, DDT breaks down gradually into several different metabolites, of which DDE is the most stable and toxic. A downward trend was clearly evident for DDE indicating that the total DDT burden in North America has declined. In fish, DDE increased from about 70 % of the total DDT in 1976 to about 74 % in 1986. As existing DDT is metabolized, DDE increases proportionally if DDT input is reduced. A similar trend towards increasing percentage of DDE relative to DDT has been noted elsewhere (Aguiller, 1984), indicating that the global DDT burden is also declining (Schmitt and Bunck, 2004).

Das *et al.* (2004) reported the DDT concentration in 25 mature fish collected from the river Shad during the dry and wet season. Levels of pesticide concentrations were found to be higher in the muscles of large fish (36- 37 cm) as they contained more fat than the smaller ones (Stout, 1980 and Gregariades *et al.*, 1991). The mean total of DDT residues ranged from 1792.83 to 2254.12 ng/g ww. Between the two seasons, pesticide residues were found to be higher during the dry season because (a) the water was stagnant and the contaminants settled with organic substances fed on by the fish (Ruiz and Lorente, 1991) (b) before spawning the fish stored fat during the dry season and the contaminants accumulated in the fatty tissues. When the fish spawns, the lipid concentration and pollutant body burden decreases in fish (Vassilopoulo and Gregoriades, 1993).

This work by Das *et al.* (2004) provides evidence that somatic lipid concentration and the percentage of fat transferred into the developing eggs significantly influences the transfer of DDT residues in fishes. In all the samples studied *p,p'* DDT group was present, which demonstrated that the *p,p'* DDT group is still being used in various names, although it is banned (Martin *et al.*, 1993) or might be due to environmental persistence of pesticides.

The review clearly shows that DDT is one of the most prevalent persistent organochlorine pesticides across the globe. While the environmental residue levels of DDT and its ill effects have been well documented in North American and European countries, in India it is far from desired.

Among the organochlorine pesticides, cyclodiene group which comprises endosulfan, heptachlor and dieldrin are very significant due to its acute toxic effects. Aldrin is totally banned in 1994. Dieldrin is permitted only for locust control under special permission. It has been reported that smaller concentration of heptachlor in animal meat and fish might be due to its metabolic conversion into heptachlor epoxide (Tashiro and Matsumura, 1978). Niethanmer *et al.* (1984) and Winger *et al.* (1990) reported that the maximum dieldrin in wild channel cat fish was 0.009, 0.01 and 0.11 ppm, respectively. These levels are comparable to the 0.03 ppm maximum reported here but less than the 5.01 ppm levels (1976 through 1977), reported by Schmitt *et al.* (1990). They found that maximum levels of dieldrin decreased to 1.39 ppm in 1984. This is higher than the 0.019 ppm reported here but comparable to the 0.08 ppm reported by Nettleton *et al.* (1990) for pond raised channel cat fish.

Schmitt (1990) reported that reduction in the use of persistent toxic substances namely aldrin, dieldrin, heptachlor and chlordane that accumulate in biota have resulted in lower concentration in fish.

Aktumsek *et al.* (2002) reported the concentration of dieldrin, endrin and aldrin in Pike perch were 15-30 ng/g, 0.8-17 ng/g and 8-16 ng/g respectively. The concentration of these pesticides residues in the fish are about 1000- 10,000 times higher than in water. Another study by the same author on pesticide residues in fresh water and sea fish reported that both were sensitized to dieldrin, heptachlor and other chlorinated

pesticides. More over the concentration of pesticides residues of sediment in lake were 0.014 ppm where as 3035- 5060 ppm of residues was found in fish.

Santerre *et al.* (2000) reported that the residues of dieldrin were detected in 2.7 % and 3.0 % of trout samples. The average concentration of dieldrin in cat fish and trout was 0.019 ppm and 0.01 ppm respectively. The range for dieldrin residue in cat fish and trout were 0.01 to 0.03 and 0.1 ppm respectively. Residues of heptachlor epoxide were detected in catfish, but there were no detectable residue in trout or catfish. The average heptachlor epoxide in cat fish was 0.012 ppm which is close to the lowest limit of quantification for this compound. This level is 40 % of the FDAs action limit for heptachlor epoxide in fish. The range for heptachlor epoxide residues was 0.01 to 0.02 ppm.

The spatial and vertical distribution of organochlorine pesticides (OCPs) has been investigated in Daya Bay, China. The concentration of total OCPs in surface sediment range from 16.66 to 44.04 ng/g dry weight with a mean concentration of 26.60 ng/g. DDTs and HCHs were the predominant species. The ratios of (DDD + DDE)/ DDT reflected a cocktail input pattern of fresh and weathered DDTs. The predominant α HCH and the α/β HCH ratios indicated that the technical HCH contamination was mainly due to historical usage, although there was fresh input of lindane. The variation profiles of concentrations showed that OCPs were extensively applied between the late 1950s and early 1980s in China. A recent increasing trend in concentrations of DDTs and HCHs was found in the soil. The increasing ratios of (DDE + DDD)/ DDT with corresponding decrease of DDE/DDT ratio implied that most of the DDTs deposited after their production ban were more likely "weathered" DDTs derived from soil residues (Wang *et al.*, 2008).

Although residues of organochlorine compounds have been reported in various components, the spatio temporal trends of these residues are still limited in Indian context. In this regard, the current study was initiated to document the present status of organochlorine concentration in the marine fishes caught from Cochin and Rameshwaram and sold in Coimbatore market.

2.2 Effects on fishes and humans

Extensive use of organochlorine pesticide to protect the crops in agricultural fields has resulted in serious health hazards to the non-target aquatic organisms mainly fish, which is directly affected by the pesticides due to residue accumulation in their body (Hazarika, 2003).

Fish exhibit a low metabolism for OC (Muir *et al.*, 1990) and they concentrate the pollutants in their tissues directly through the diet, as well as from water. Bioconcentration in fish depends either on the concentration of chemical compounds in the environment on the physiological and biochemical effect, which occur in the different marine organisms in relation to the species (Barron *et al.*, 1990). Consequently species occupying different habitats in the same ecosystem and having different feeding behavior may manifest a different pollutant load in their tissues.

Marchand *et al.* (1976) examined the environmental samples for DDT isomers. The concentration of DDTs in soft tissues of mussels in the North West Mediterranean Coast was found to be 10608 ng/g dry weight in 1973-1974. The DDT compound in the samples was generally higher than the DDE and DDD metabolites; this is due to the high exposure from pesticide in the environment. But the production of DDT were reduced or controlled in the 1970s so the environmental concentrations of the pollutant declined in the open Mediterranean Sea (Fowler, 1987 and Villeneuve *et al.*, 1999).

Build up of DDT in fish-eating birds has been shown to cause shell thinning in the eggs of these birds, and consequently lead to reproductive failure in these birds (Temple and Weins, 1989 and Weseloh *et al.*, 1995). DDE, a metabolite of DDT has been significantly linked to egg shell thinning (Wienmeyer *et al.*, 1972). The ban on DDT use in the 1970s in the US caused the reduction in DDT concentrations in the environment (Hesselberg *et al.*, 1990) and the subsequent recovery of certain populations of fish-eating birds was partially attributed to the ban on use of DDT (Temple and Weins, 1989 and Weseloh *et al.*, 1995).

Nakagwa *et al.* (1995) reported that the estimated daily intakes of total DDT in Japan, Canada and US were 1.42, 6.38 and 1.3 μg/day respectively. Organochlorine pesticide

intake and consequent health risk may differ with respect to person's residence and the kind of food consumed.

A number of studies regarding the effects of organic xenobiotics on fish have extensively shown that exposure to the current pollutant levels result in many stress responses and disturbances of the normal physiology (Stein *et al.*, 1993; Burgeot *et al.*, 1996 and Vanderoost *et al.*, 1996).

The accepted daily intake for DDT, lindane, dieldrin and heptachlor epoxide is 1200, 480, 6 and 6 µg/ person/ day respectively (Codex Alimentarius, 1996). It has been found that greater than 80 % of the total intake of pesticides residue in human beings is accumulated through food chain (Doong *et al.*, 1999).

Manirakiza *et al.* (2002) reported the presence of endosulfan sulphate, heptachlor epoxide and endrin in the pooled serum samples from Sene-Gambian region. The concentration of these pesticides recorded in fish, shrimps, cattle fat and human serum were below 10 ng/ml.

Although a large number of studies are carried out on coastal ecosystem all over the world (Sericano *et al.*, 1995; Monirith *et al.*, 2000 and Tanabe *et al.*, 2000), only a few studies used open sea organisms (Prudente *et al.*, 1997; Yamada *et al.*, 1997 and Minh *et al.*, 2000).

Dickman and Leung, (1998) estimated that a person in Hong Kong consumes fish or shellfish four or more times a week averaging about 164.4 g/ day, which is higher than the fish consumption rate of 142.2 g/ day, set by USEPA (2000).

Age, fish consumption and place if residue may be related to serum/plasma concentration because of higher cumulative exposure among older women with higher exposure among women with high consumption of organochlorine contaminated fish and higher exposure among women living in contaminated areas (Laden *et al.*, 1999). Moreover, there are indication of association between organochlorine and altered thyroid function in women (Hagmer *et al.*, 2001). Published results show the gonadotoxic impact of BHC (1- 10 ppm)

on ovarian histology of experimental fish *Heteropneustes fossilis*, (Hazarika and Das, 1998 and Hazarika, 2003).

Manirakiza *et al.* (2002) reported persistent chlorinated pesticides in fish and cattle fat and their implications on human serum concentrations in the Sene-Gambian region. Nair *et al.* (1996) studied the DDT and HCH load in mothers and their infants in Delhi, India. Of all the levels of HCH isomers in breast milk, β BHC is the most persistent isomer and is eliminated more slowly than the gamma isomer from the body. Thus, the ratio between different HCH isomers changes from the start of the food chain till excretion in human milk, resulting in more persistent β HCH being the predominant isomer in human milk. The results also demonstrated that considerable amounts of DDT and HCH are transferred from the mother through breast-feeding rather than the placental circulation.

While the Council of the European Communities (1980) suggested the limit for HCH in natural water (3 μg/ l), WHO (1984) reported the maximum permissible limit for γ HCH (4 μg/ l) and DDT in drinking water (1 μg/ l). Singh, (2007) reported 383 ppm of total DDT in ground water of Agra, India. The average concentrations of endosulfan, aldrin, dieldrin and heptachlor in water were 12.27 ppb, 254.47 ppb, 53.13 ppb and 29.40 ppb and in soil showed the values were 0.03 ppb, 0.84 ppb, 0.35 ppb and 0.23 ppb respectively. The concentration of total DDT in marine fishes in Hong Kong markets ranged between 2.30 ng/g and 1018 ng/g and the higher concentration was recorded in *Snubnose pompano* (Cheung *et al.*, 2007). It has been reported that carnivorous fishes normally contain the highest lipid content as they are the top consumers in the food chain and will accumulate more POPs such as DDT due to its lipophilic nature, though factors such as size, age and species will also affect the rates of their bioaccumulation (UNEP, 2002). The maximum permissible value of DDT in fishery products set by China's National Environmental Protection Agency (NEPA) is 1000 ng/ g wet weight based on 23 g/ day of fish consumption rate (Zhou and Wang, 2004).

Organochlorines (OCs) such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), were measured in 26 species of seafood commonly consumed by the Korean population. PCBs and DDTs were the predominant contaminants with

concentrations from 0.2 to 41 ng/g wet wt and from < 0.04 to 37 ng/g wet wt, while CHLs (<0.01- 1.9 ng/g wet wt), HCB (<0.004–1.0 ng/g wet wt), and HCHs (<0.02– 0.4 ng/g wet wt) were 1- 2 orders of magnitude lower than the concentrations of PCBs and DDTs. The dominant PCBs and OCPs were PCB 153, 187, 138, and 118 and *p,p'* DDE, HCB, *p,p'* DDT, and *p,p'* DDD, respectively. Dietary intakes of OCs for the general population, males, and females were estimated at 69, 78, and 60 ng/kg body weight/week, respectively. Mackerel, Tuna, and Hairtail were the main contributors to the dietary intakes of OCs. Among the eight age groups investigated, infants <2 years had the highest dietary exposure to OCs. Hazard ratios of non-cancer risk of all of the OCs were less than one, while the lifetime cancer risks of PCBs and DDTs were all greater than one for Korean populations (Moon *et al.*, 2009). Hence the presence of organochlorine residues and its toxic effects on humans as well as other organisms has to be viewed with concern.

2.3 Indian Status

Reports are available in plenty indicating the presence of OCP in a variety of commercial fish species in many countries (Itawa *et al.*, 1993; Kannan *et al.*, 1995; Grobler *et al.*, 1996; Pastor *et al.*, 1996; Fairey *et al.*, 1997; Anon, 1998; Spiric and Saisic, 1998; Chan *et al.*, 1999; Monirith *et al.*, 1999; Cleeman *et al.*, 2000; Zhulidov *et al.*, 2000 and Jabbar *et al.*, 2001). Compared to this only few reports are available on the presence of pesticide residues in fish from Indian waters (Radhakrishnan *et al.*, 1986; Radhakrishnan and Antony, 1989; Radhakrishnan, 1994; Kannan *et al.*, 1995; Das *et al.*, 2002; Karuppiah *et al.*, 2005 and Muralidharan *et al.*, 2009) and birds (Muralidharan, 1993; Muralidharan *et al.*, 2009; Dhananjayan *et al.*, 2010 and Dhananjayan *et al.*, 2011). These studies have provided information on the contamination status of persistent organochlorine pesticide residues in the environment.

Fish have been selected for monitoring because they concentrate pollutants in their tissues directly from water and also through diet, thus enabling the assessment and transfer of pollutants through the pelagic food web (Bruggeman, 1982). They generally exhibit a low metabolism for organochlorines and consequently should reflect the levels of pollution in the aquatic environment (Muir *et al.*, 1990) and they occupy different

habitats in the same ecosystem and have different feeding behaviors, thus offering the potential to study the influence of environmental and biological factors in the bioaccumulation of pollutants (Porte and Albaiges, 1993).

Venugopalan and Rajendran, (1984) studied the pesticide residues in fish samples obtained from Vellar Estuary of South India adjoining the Bay of Bengal including the Grey or Striped Mullet *Mugil caphalus* L. (Perciformes: Mugilidae), Therapon or Targetfish *Therapon jarbou* (Forsskal) Klunzinger (Perciformes: Terapontidae), Spine Foot *Siganus javus* L. (Perciformes: Siganidae), and the catfishes *Mystus gulio* Hamilton (Siluriformes: Bagrinae) and *Arius* (Tachysurus) sp. (Siluriformes: Ariidae). Residue concentrations were in the following ranges (ng/g ww): Σ DDT, 0.4 to 89.27; lindane, 0.05 to 4.64 and endosulfan, 0.02 to 2.47. Between DDT and its metabolites, *p,p'* DDE was the dominant degradation product. There was no significant variation in the concentration of various pesticides between fish species and they observed no obvious variations in pesticide concentrations between herbivorous and carnivorous fish species. They studied the toxicity of these pesticides under laboratory conditions and found that the order of toxicity was DDT > lindane > endosulfan. *M. cephalus* was more sensitive than *M. gulio* to all three pesticides.

Shailaja and Sen Gupta, (1989) measured HCHs and DDTs in various fish species collected from different regions of the seas around peninsular India. However, the concentration of the isomers of HCHs was too low to be quantified. The concentration of total DDT was found to be in the range of 8.1- 204 ng/g (dry wt) and the mean concentration level was 59.2 ng/g. They observed highest amount of total DDT residue burden (344.7 ng/g) from the estuarine regions followed by the coastal varieties from that of 23 fish species. Among the metabolites of DDT, DDE constituted a major proportion.

Kannan *et al.* (1992) reported no change in the residue level of most of the organochlorine pesticides except DDTs, implying a continuous input of certain organochlorine contaminants from Eastern European Countries. The residues of heptachlor epoxide, aldrin and dieldrin in canned cod-liver from the southern Baltic Sea were 3.9-4.4, 6.7-8.3 and 50-60ng/g. The annual intake of OCs such as heptachlor epoxide,

aldrin and dieldrin from cod liver were 0.44, 0.77 and 5-9 μg/ person/ annum respectively. The intake of persistent OCs from such contaminated sea food might be of toxic concern. He also reported that the dietary intake of aldrin and dieldrin in India were greater than those of other organochlorines through the sea foods.

Karunagaran *et al.* (1994) reported the concentration of HCH and *p,p'* DDE residues in eight species of edible fish comprising carnivorous, herbivorous and planktivoruos collected from landing centers of Kanyakumari. Total HCH concentration ranged between 4.2 ng/g in *Sardinella longiceps* and 23.1 ng/g in *Scomberomorus guttatus.* The lowest concentration of *p,p'*--DDE was recorded in *Scomberomourus guttatus* (0.11 ng/g) and the highest (2.2 ng/g) in *Nemipterus japonicus.* The residual concentrations in fishes were well below the tolerance levels prescribed for fish products in India (DDT, 7 ug/g) (*Anonymous,* 1990), FAO/WHO (HCH 0.2 - 0.5 ug/g and DDT 2.5 ug/g) and USFDA (DDT 5 ug/g).

Food stuffs collected from different regions in India were analyzed for the presence of aldrin, dieldrin and heptachlor. Significant high levels of food contamination with aldrin and dieldrin were evident throughout India. The contribution of dairy products to the dietary intake of HCH, aldrin and dieldrin were 70, 87 and 87 % respectively. Moreover the concentration of these organochlorines in a few dairy products were above the maximum residue limits (MRLs) set forth by the FAO/ WHO (Kannan *et al.*, 1995).

Kumari *et al.* (1996) reported total HCH and total DDT in soils and pond water of Haryana, India. The values of total HCH in soil and pond water ranged from 0.048 μg/g to 0.162μg/g and 2.2 μg/g to 9.0 μg/g respectively. Total DDT concentration varied from below detectable level to 0.045 μg/g in soil samples and below detectable level to 2.7 μg/g in pond water.

The major contribution to the dietary intake of aldrin and dieldrin were dairy products which contributed 70 and 87 % of the total intake respectively. The ADI of aldrin and endosulfan are 4,450 ng/person. The average daily intake of aldrin and endosulfan were 1.04 μg and 0.61 μg in small fishes. The WHO has recommended the per capita

consumption of fish to be 11 kg in India (www.fao.org/fishery/country/sector/FJ-CP_IN/en).

Sarkar *et al.* (1997) reported the concentration of total DDT, total HCH and dieldrin in sediments of both Offshore and Estuaries of West Coast of India. They ranged from 1.47 ng/g to 25.17 ng/g, 0.85 ng/g to 7.87 ng/g and 0.70 ng/g to 3.33 ng/g in West coast estuaries and 1.14 ng/g to 17.59 ng/g , 0.10 ng/g to 6.20 ng/g and 0.20 ng/g to 1.41 ng/g in offshore sediment respectively. In the East Coast of India the total DDT of marine sediment ranged from 0.02 ng/g to 0.78 ng/g and dieldrin 0.05ng/g to 0.51 ng/g.

Shailaja and Nair, (1997) pointed out a strong influence of the feeding habit and habitat of the fish on the residue levels of OCs. They recorded highest total DDT concentration in two carnivore species, Barracuda (*Sphyraena acutipinnis*) and Shark (*Scoliodon sorrakowah*) from the Arabian Sea and suggested a rapid dissemination through the water column of the pesticides entering the northern Arabian Sea in the monsoon season. They had also established that the liver generally accounted for the highest level of total DDT on a wet wt. basis, followed by the gills while, on a lipid basis, the residue content in the muscle was the highest among the different fish tissues.

A study conducted by Sarkar *et al.* (1988) reported varying levels of chlorinated pesticide residues in marine sediments of Bay of Bengal; total DDT ranged between 0.02 µg/g and 0.78 µg/g and aldrin and dieldrin from 0.02 µg/g to 0.53µg/g and 0.05µg/g to 0.51 µg/g respectively.

A monitoring study by Kole *et al.* (2001) reported endosulfan and hexachlorocyclohexane residues in market fish samples available in and around Calcutta. The results showed that more than 50 % of 235 samples analyzed during 1993- '94 to 1997- '98 were contaminated with endosulfan residues in the range of 0.01 to 1.41 ug/g. About 16 % of the samples were above the maximum residue limit (MRL) of endosulfan (0.2 ug/g) prescribed for meat on fat basis (FAO/ WHO 1978). More than 80 % of 157 samples tested positive for HCH residues in the overall range of 0.01 to 9.72 ug/g. The extent of contamination was, therefore, much higher by HCH than that of endosulfan residue. About 38 % of the samples were above the legal limit (0.5 ug/g) of HCH (FAO, 1983). The

majority of the contaminated samples were in the range of 0.21 to 2.00 ug/g of HCH residues.

Jabber *et al.* (2001) reported organochlorine pesticide residues in muscle samples of *Lates calcarifer, Liza subviridis* and *Cynoglossus cynoglossus*, collected during October-December (dry season) 1996 and May- July (wet season) 1997 from the Ganges estuary. The organochlorine residues were more in the muscle of *Lates calcarifer* because of its carnivorous food habit, and lowest in *Liza subviridis,* a herbivorous fish. Among the nine organochlorine pesticides residues analysed, only dieldrin and heptachlor residues in *Lates calcarifer* exceeded the FAO/WHO (1993) recommended permissible limit.

Studies by Jayakumar, (2001) showed the presence of heavy metal contaminants in select fresh water fishes of commercial importance in Coimbatore. The studies done by Vijayan et al. (2004) have extensively reported the organochlorine pesticide residues in the inland wetland fishes of India respectively and have assessed their suitability for human consumption. Similar study has been carried out by Dhananjayan and Muralidharan, (2010) in the inland wetland fishes of Karnataka.

Amaraneni and Pillala, (2001) reported maximum concentration of cyclodiene pesticides residues in fish tissues from Kolleru lake (endosulfan - 76.5 µg/g, dieldrin - 1.9 µg/g). It is also reported that endosulfan at concentration of 1 ppb are toxic to freshwater fish (Brown, 1979). Concentrations of persistent organochlorine residues were measured in economically important fish of the River Ganges from different locations in Bihar. The contamination pattern of organochlorines in fishes from several locations was Dichlorodiphenyltrichloroethanes (DDTs) > Hexachlorocyclo- hexanes (HCHs) > aldrin > endosulfan. The average wet weight concentrations in the muscles of fishes were DDTs, 13.6 to 1665.9 ng/g; HCHs, 115.8 to 1206.8 ng/g; aldrin, 3.1 to 86.1 ng/g; and endosulfan 2.9 to 74.5 ng/g. The study indicated that organochlorine contaminants are still entering the Ganges river system, and suggested that the human population that consumes contaminated fish from the river may be at risk from those contaminants (Kumari *et al.*, 2001).

Considering different feeding habits, Pandit *et al.* (2001) studied accumulation of OCPs in the muscle tissues of different fin fishes and shell fish (prawn) from Alibagh and Mumbai, west coast of India. They observed predominance of α and γ HCH which reflected the use of technical grade HCH in India. They detected low concentration of OCPs in comparison to other temperate countries suggesting a lower accumulation in tropical fish which could be due to rapid volatilization and degradation of these compounds in the tropical environment. Also, the higher temperature in the tropics could enhance the elimination rate of chemicals from fish due to the influence of temperature on their respiratory requirements, as the biological half-lives of compounds such as HCH and DDT are shorter at high temperature. A monitoring study by Singh and Gupta, (2002) between 1997 and 2000 reported the presence of pesticide residues in different sources of drinking water of Jaipur, India.

Das and Das, (2004) observed positive correlation between total organochlorine residues and the percentage of fat content in muscle of River Shad *Hilsa ilisha* from the south patches of the Bay of Bengal. Pesticide residues were found to be higher in the muscle of larger fishes as they content more fat than the smaller ones (Stout, 1980 and Gregoriades *et al.*, 1991).

A study conducted by Babu Rajendran, (2005) in the coastal waters of Bay of Bengal reported the concentration of total PCB to be range between 1.93 ppt and 4.46 ppt and total DDT between 0.13 ppt and 0.44 ppt. In sediment the concentration of total PCB and total DDT ranged from 19.9 pg/g to 6570 pg/g and 0.04 pg/g to 0.8 pg/g respectively. Sarkar and Sen Gupta, (1990) reported the total DDT, γ HCH and dieldrin concentration to range from 15.81 ng/l to 444 ng/l, 0.26 ng/l to 9.4 ng/l and not detectable value to 50.98 ng/l respectively in central West Coastal water of India.

The presence of varying levels of cyclodiene insecticide residues were reported in Varanasi during South West monsoon and North West monsoon (Singh *et al.*, 2006). About 83 % of the South West monsoon samples showed the presence of Aldrin. While the percentage occurrence of dieldrin, heptachlor, Heptachlor epoxide and γ chlordane were 8.3, 25, 29 and 54 % respectively.

Pandit *et al.* (2006) carried out a study of multi-compartment monitoring of residue levels of organochlorine pesticides in coastal marine environment of Mumbai. The concentration of total HCHs and total DDT in seawater varied from 0.16 to 15.92 ng/l and 3.01 to 33.21ng/l respectively. Among HCH isomers, γ HCH contributed almost 55 % to the total HCH. The concentration of total HCHs and total DDT in different marine species varied from 0.87 ng/g to 33.73 ng/g and 0.38 to 34.1 ng/g respectively.

Muralidharan et al. (2009) reported the organochlorine pesticide residues in ten species of fishes caught at Cochin and Rameshwaram coast, and sold in Coimbatore, Tamil Nadu, India. A total of 389 fishes analyzed showed varying levels of residues of HCH, DDT, endosulfan and dieldrin. Among the ten species comparatively high concentrations of pesticide residues were recorded in *Sardinella longiceps, Carangoides malabaricus, Chlorophthalmus agassizi, Saurida tumbil* and *Rastrelliger kanagurta*. Only four species of fishes showed monthly variation in residue levels and there was no significant correlation between the body size and residue levels in the tissue. About 22 % of the fishes exceeded the Maximum Residue Limits (MRL) of total HCH prescribed by FAO/ WHO for fish products. The calculated dietary intake of total HCH through consumption of the above referred species also exceeded the maximum ADI limits prescribed for human consumption.

The study carried out in the agricultural soils of North India by Kumar *et al.* (2011) have recorded the average concentration of OCPs of about 37.67 ± 0.33 ng/g (dry weight-DW) while HCHs alone accounted for 93 % followed by DDT (4.27 %) and endosulphan (2.51 %). The α/γ ratio of HCH (< 0.01- 8.64) reflects the use of technical as well as lindane formulations. The ratio of *p,p'* DDT/ *p,p'* DDE (0.16) and *o,p'* DDT/ *p,p'* DDT (< 0.01) indicates the contamination of soils with the past use of technical DDT. The contamination of soils is a matter of concern but is not alarming because the observed levels were lower than those given by the Canadian soil quality guidelines.

A study was conducted on selected vegetables from West Bengal to assess the level of organochlorine pesticide residues by Mukherjee *et al.* (2011). In this study, the concentration of total OCPs was ranged between, <0.01- 65.07 µg/kg with average of 9.67

± 2.34 µg/kg (wet wt.). The concentration of total DDT, total HCH, aldrin, dieldrin and heptachlor was 3.49 ± 0.93 µg/kg, 2.07 ± 0.53 µg/kg, 1.32 ± 0.65 µg/kg, 1.36 ± 1.18 µg/kg and 1.80 ± 0.4 µg/kg (wet wt) respectively. Isomer composition was determined from the observed concentrations to identify the possible contamination sources. Ratio of α HCH/ γ HCH varied in the range of 0 - 5.69 with mean value of 0.76 which reflects the usage of technical HCH and lindane. The ratio of *p,p'* DDT/ Σ DDTs, DDTs/ Σ DDT, DDE + DDD)/ Σ DDT, and DDT/ DDE was 0.30, 0.50, 1.17 and 1.97 respectively, indicating DDT contaminations from biotransformation and transported depositions. The observed residue levels of OCPs were below maximum residue limits (MRLs) indicating minimal risk to the consumers. The study indicates the use of lindane as well as technical formulation of the HCH in the study area and, contamination of these vegetables with DDTs. This may be due to transportation of pollutants from nearby human settlement areas, where pesticides used for public health aspects.

A survey of persistent organochlorine pesticides residues in some Streams of the Cauvery River, Karnataka by Begum *et al.* (2009) showed that all the samples contained at least one of the pesticide residues analysed (α HCH, β HCH, γ HCH, δ HCH, *p,p'* DDT, *p,p'* DDE, *p,p'* DDD and endosulphan). Maximum Concentration of *p, p'* DDE pesticide residue (0.96 µg/l) was found in water. Maximum Concentration of β HCH pesticides residue (82.22, 80.45 and 79.23 µg/ kg) was found in sediments in. However the concentration of all the pesticides residues was maximum in sediments except one sampling site which is away from all pollution sources. Maximum concentration of β HCH pesticides residue (74.34 µg/l) was found in shrimp *Caridina* sp. and in fish species the maximum concentration of pesticide residue (α HCH - 54.23 and β HCH 44.68 µg/kg) was found in fish *Etroplus suratensis*. This may be attributed to the pollution from agricultural activities throughout the year. These results demonstrate an accumulation of pesticides residues through food chain (from soil-water-sediments-microbes-crop fish-human) which is a serious matter of concern.

The concentrations of organochlorine contaminants, DDT and HCH, have been determined in human breast milk from Dibrugarh and Nagaon districts of Assam state, North-East India done by Mishra and Sharma, (2011) showed that the mean levels of total

DDT were 3210 ng/g lipid wt. and 2870 ng/g lipid wt. and total HCH were 2720 ng/g lipid wt. and 2330 ng/g lipid wt. in Nagaon and Dibrugarh respectively. There was no significant difference in the levels of investigated pollutants between the two districts. Significant differences in ADI (Average Daily Intake) for total DDT were found between the two districts. In addition, a positive correlation was observed between OCP levels in breast milk and age of mothers. Based on OCP levels in human breast milk, the ADI by the infants has been estimated. It has been found that high daily intake of DDTs and HCHs by the infants exceeded the TDI (Tolerable Daily Intake) which implied that infants of the region are potentially at high risk by these contaminants.

The recent study on the contamination levels and spatial distribution of organochlorine pesticides in soils from India showed substantially higher concentrations of these pesticides in the surface soils of the area. In addition, the levels were found highest among the soil levels from various parts in India reported so far. Such higher levels are due to intense application of DDT and HCH for control of vector borne diseases in this malaria endemic region and for agricultural purposes to increase crop yield. The ratio of α/γ HCH and DDT/ (DDE + DDD) indicated that these pesticides were applied in large quantities from the past decades till recently due to low cost, high effectiveness and lack of suitable alternatives. Highest HCH and DDT concentrations in soils of paddy fields indicate high HCH consumption in rice crop but illegal use of DDT in paddy fields cannot be denied. In addition, the higher pesticide levels in soil system in high water table areas pose a risk of ground water contamination and subsequently the drinking water supplies (Mishra *et al.*, 2011).

Studies conducted over a period of time on the distribution of OCPs in many environmental components particularly fishes clearly show the status of organochlorine contamination. In India, although the studies on the levels of organochlorine contaminants in fishes are carried out, they are not oriented towards assessing the impact on human health. Hence there exists a gap in relating the organochlorine residues in fishes to the impacts on human beings through consumption. This indicates the need for launching a large scale investigation on organochlorine pesticide residues in fishes in order to evaluate their suitability for human consumption.

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1 Study Area

Coimbatore is an important industrial town in South India. It is located between 10^0 55' and 11^0 10' N, and 77^0 50' and 76^0 50' E at an approximate altitude of 470 m. Coimbatore is the second largest city by population (0.93 million; Census of India 2011) in Tamil Nadu. The city is a major textile and engineering hub of South India, hence called as Manchester of South India. Coimbatore is situated in the extreme west of Tamil Nadu, near the state of Kerala. It is surrounded by mountains on the west, with reserve forests. The eastern side of the district is predominantly dry. The entire western and northern part of the district border the Western Ghats with the Nilgiri biosphere as well as the Anaimalai and Munnar ranges. The consumption of marine fishes in Coimbatore city is based on the supply from the major coastal towns of South India such as Cochin, Rameshwaram, Kanyakumari, Vijayawada, Mangalapuram and Chavakkad. Of which Cochin and Rameshwaram (Figure 3.1) contribute the maximum (90 %) to the local market (Muralidharan *et al.*, 2009). Hence the study was restricted to only fishes of these two locations.

3.1.1 Cochin

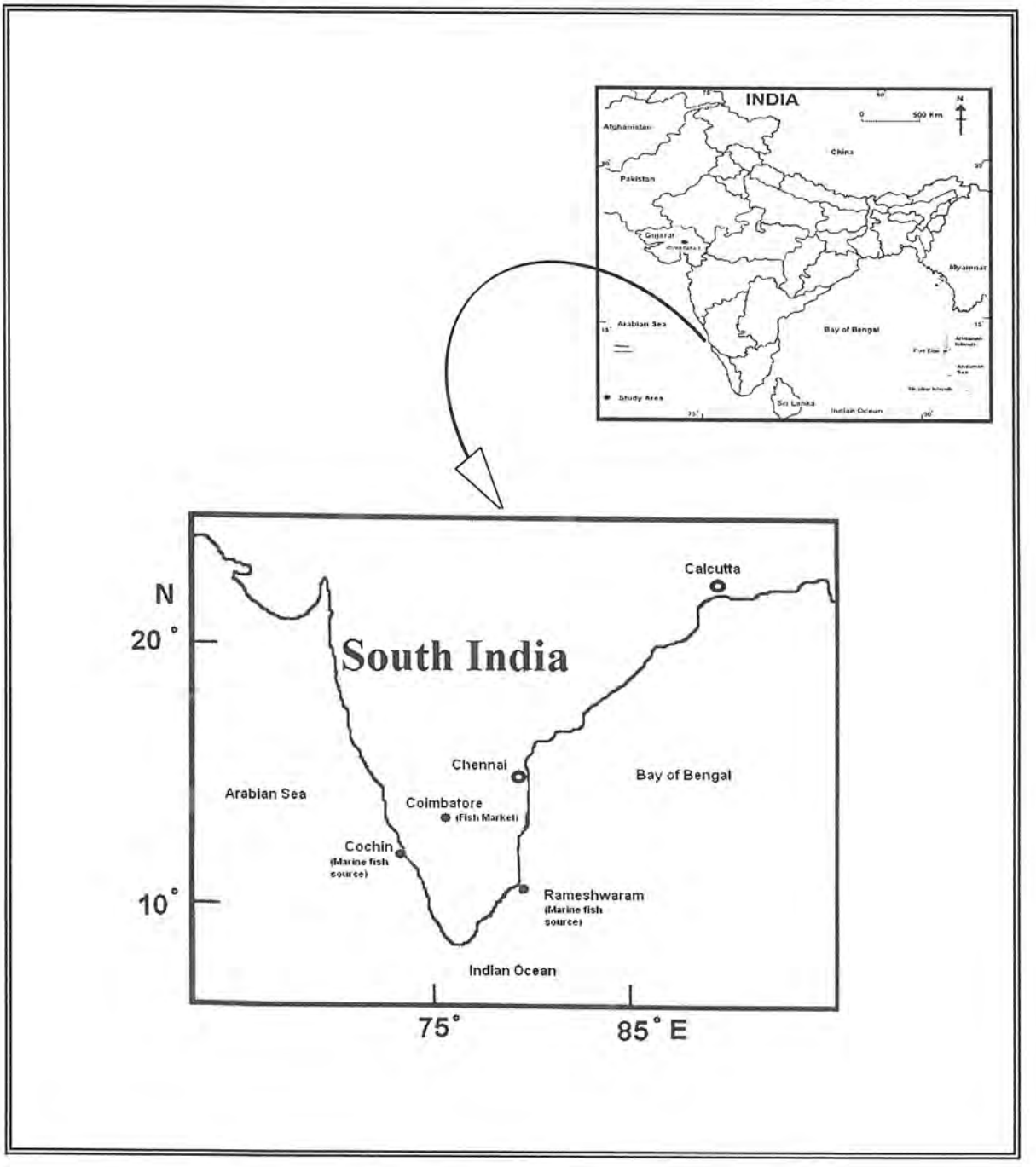
Cochin is located on southwest coast of India at 9° 58′N - 76°13′E / 9.967°N - 76.217°E, spanning over an area of 94.88 km^2 in Kerala which ranks fourth in the country's total marine fish supply. To the west lies the Arabian Sea and to the east is the urbanized region in the rest of the mainland area. Much of Cochin lies at sea level, with a coastline of 48 km. Cochin features a tropical monsoon climate. Average annual rainfall is 3,228.3 mm, with an annual average of 132 rainy days. Annual temperatures range between 23 and 31 ^{0}C (73 - 88 ^{0}F) with the record maximum being 38 ^{0}C (100 ^{0}F), and record minimum 17 ^{0}C (63 ^{0}F). The coasts of Kerala are endowed with brackish water lagoons interconnected with natural and man - made canals as also 41 rivers outfalls. This coastal area does receive effluents from industries, domestic, automobiles and oil spills. There are about 300 large and medium scale industries and 1,66,000 small scale industries, most of them are located

in the coastal area. Of these 250 large and medium scale industries and 5000 small scale industries do pollute the environment significantly (Sharma, 2000). The effluent load is estimated at 0.15 million metric tonnes per day. Port and defense activities also contribute to the contaminant load. Approximately five million tonnes of oil enter the Arabian Sea each year (ESCAP, 1995). Oil pollution from shipping and offshore oil rigs is also a concern.

3.1.2 Rameshwaram

Rameshwaram, the coastal town situated at 9°17'N - 79°18'E / 9.28°N - 79.3°E on the east coast of Tamil Nadu is the gate way to Sri Lanka. It is about 330 km from Coimbatore. It has an average elevation of 10 meters. The island spread over an area of 61.8 km^2 happens to be in the shape of a conch. It has dry tropical climate, with average annual rainfall of 94 cm, mostly from North East monsoon (October to January). Maximum temperature ranges around 35 ^{0}C. Highest ever temperature recorded at Pamban station is 37 ^{0}C and lowest is 17 ^{0}C. Industries such as sea food processing, leather processing, petro and agrochemicals, cement, mining and automobile are the major sources of pollution along the coastal line of Chennai, Ennore, Cuddalore, Avadayankoil and Tuticorin of Tamil Nadu and Karaikal of Puducherry (Sharma, 2000). Spillage from oil transport and waste from aquaculture farms are increasingly posing threats to coastal water quality. Approximately, 0.35 million metric tonnes/ day of effluent generated through these industrial establishments are let into the sea. The Bay of Bengal receives around 400,000 tonnes of effluent from similar sources (Sharma, 2000).

Figure 3.1 Map showing study sites and regular supply towns of marine fishes to Coimbatore



3.2 Sample Collection

A preliminary survey was conducted throughout the Coimbatore city to assess the market potential of marine fishes. Based on the survey, it was found that Ukkadam market acts as a hub for collection/reception of fishes from all the landing centres across the country and subsequently distributes throughout the city. The survey results showed that about 12 tonnes of marine fishes were sold in the market daily.

The samples from the market were collected from October 2004 to September 2006, i.e., two years which falls into eight quarters with three months being one quarter (October to December 2004 - Quarter 1; January to March 2005 - Quarter -2; April to June 2005- Quarter 3; July to September 2005 - Quarter - 4; October to December 2005 - Quarter 5; January to March 2006 - Quarter- 6; April to June 2006- Quarter 7; July to September 2006- Quarter- 8).

A minimum of three and maximum of 10 individuals belonging to seven species of fishes, namely Indian Mackerel (*Rastrelliger kanagurta)*, Japanese Threadfin Bream (*Nemipterus japonicus*), Oil Sardine (*Sardinella longiceps*), Great Barracuda (*Sphyraena barracuda*), Malabar Travelly (*Carangoides malabaricus*), Tongue Sole (*Cyanoglossus macrolepidotus*) and King Seer (*Scomberomonus commerson*) received at the market from Cochin and Rameshwaram were collected during each Quarter. All the seven species of marine fishes were selected on the basis of human consumption and availability throughout the year in Coimbatore Fig 3.2, Table 3.1.

Totally 716 fishes were collected during the study period. On collection samples were cleaned of external dirt, labeled and packed in clean polythene bags, transported to the laboratory over ice. The samples were stored at -20 ^{0}C deep freezer till the dissection was carried out. Morphometric measurements such as body length and weight were recorded soon after collection and sex of the fish was identified in all possible samples. Common name, length, weight, the major food items and the feeding habits of the fishes are given in the Table 3.1.

PLATE 1- FISHES INCLUDED IN THE STUDY

A). Malabar Travelly *Carangoides malabaricus*

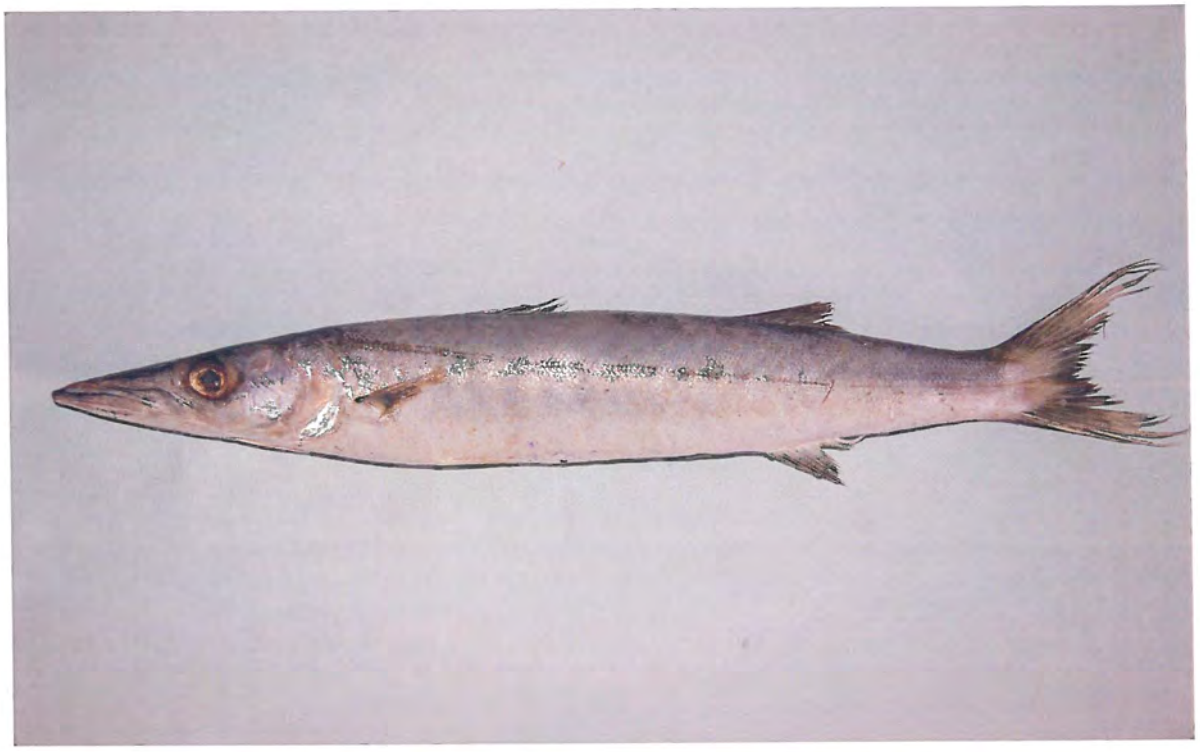
B). Tongue Sole *Cynoglossus macrolepidotus*

C). Japanese Threadfin *Nemipterus japonicus*

D). Indian Mackerel *Rastrelliger kanagurta*

E). Oil Sardine *Sardinella longiceps*

F). King Seer *Scomberomorus commerson*



G). Great Barracuda *Sphyraena barracuda*

H). View of Coimbatore fish market

Table 3.1 Details of fishes collected from Cochin and Rameshwaram coast between 2004 and 2006

S. No	Common Name	Scientific Name	Number of Fishes		Length (cm) Mean ± SD	Weight (g) Mean ± SD	Major food items*
			Cochin	Rameshwaram			
1	Malabar Travelly	*Carangoides malabaricus*	35	30	22.2 ± 1.9	143.9 ± 30.8	Crustaceans, small squids and fishes
2	Tongue Sole	*Cynoglossus macrolepidotus*	40	47	23.6 ± 5.0	98.8 ± 55.9	Benthic invertebrates
3	Japanese Threadfin Bream	*Nemipterus japonicus*	77	64	18.4 ± 3.1	73.4 ± 30.7	Small crustaceans, small fishes and invertebrates
4	Indian Mackerel	*Rastrelliger kanagurta*	69	61	22.1 ± 1.7	120.1 ± 30.9	Phytoplankton, zooplankton, shrimps and fishes
5	Oil Sardine	*Sardinella longiceps*	75	80	16.5 ± 1.3	37.3 ± 7.2	Phytoplankton, and small crustaceans
6	King Seer	*Scomberomorus commersonii*	43	31	49.5 ± 11.9	1134.4 ± 872.3	Anchovies, Clupeids, Carangids, Squids, Penaeoid
7	Great Barracuda	*Sphyraena barracuda*	33	31	36.1 ± 7.5	247.2 ± 140.5	Fishes, Cephalopods and Shrimps
Total			**372**	**344**			

*Source: www.fishbase.org

A questionnaire survey was conducted from about 325 families across the city to assess the consumption pattern of the marine fishes. The survey aimed at collecting information on preference of species, family size, frequency of consumption etc., in order to estimate the daily dietary intake of the study species by the local people. The format of the survey form-1 is given below (Muralidharan *et al.,* 2009).

SALIM ALI CENTRE FOR ORNITHOLOGY AND NATURAL HISTORY

Coimbatore - 641 108

SURVEY FORM - 1

SURVEY ON THE CONSUMPTION PATTERN OF MARINE FISHES IN COIMBATORE

Name and address of the respondent	:	Mr. P. Karthikeyan
Occupation	:	Business
Income	:	Rs. 16000/ Month
Family size	:	4
Number of members who eat fish in a family	:	4
Frequency of fish consumption	:	Once in a week
Amount of fish purchase	:	1.25 Kg
Place of fish purchase	:	Ukkadam
Most preferred fish	:	

Indian Mackerel		Japanese Threadfin		Bream Oil Sardine	✓
Great Barracuda		Malabar Travelly		Tongue Sole	
King Seer	✓				

Reasons for species specific preference : Taste [✓] Cost [✓] Health benefits [ ]

Other information, if any : Nil

Date: 10. 08. 2004

Name of the Surveyor: P. Jayanthi

3.3 Sample Processing

3.3.1 Sample Dissection

Fish samples were taken out from the deep freezer, thawed, cleaned in tap water and scales were sloughed off. Muscle tissue was dissected between the pectoral fin and vent of the fish, minced into smaller pieces and a subsample was taken from the homogenate. About 10 g of the homogenate was weighed using a top loading electronic balance (Mettler AE420) and transferred to clean specimen vials and stored at -20 °C in freezer. Although the vital organs such as gill, kidney and liver are sensitive to organochlorine accumulation, muscle forms the major edible portion in the fish. Therefore muscle tissue alone was analyzed, as one of the objectives is to also determine the dietary intake by the human.

3.3.2 Grinding and Desiccation

About 10 g of the muscle tissue of each sample was taken and mixed with 40 g of anhydrous sodium sulphate. Then it was ground to get a homogenous mixture. The homogenous mixture was then loaded into cylindrical thimble sheet and desiccated over night to remove excess moisture from the sample.

3.3.3 Soxhlet Extraction

The desiccated samples were extracted in soxhlet apparatus for seven hours using 250 ml of hexane and dichloromethane mixture (1:1). The obtained extract was then condensed to a specific aliquot of 5 ml by using the Roto-flask Evaporator (Buchi- R 210). The aliquot was then subjected to acid digestion by adding 2 ml of sulphuric acid. This procedure was carried out to remove the lipid content from the aliquot which may interfere with the chemical analysis.

3.3.4 Column Cleanup

The extracted and acid digested sample aliquot was then purified by column clean up procedure. This involved use of a glass column (25 cm length, 1 cm internal diameter) packed with slurry of silica gel in hexane (60 - 120 mesh). The sample aliquot was placed onto the column and eluted with 100 ml of hexane. The eluant was collected, then

condensed to 1 ml with the Roto - flask Evaporator and stored at a -20^{0}C deep freezer till the gas chromatography analysis. All the chemicals used in the process were of pesticide residue analysis grade obtained from E - Merck, India.

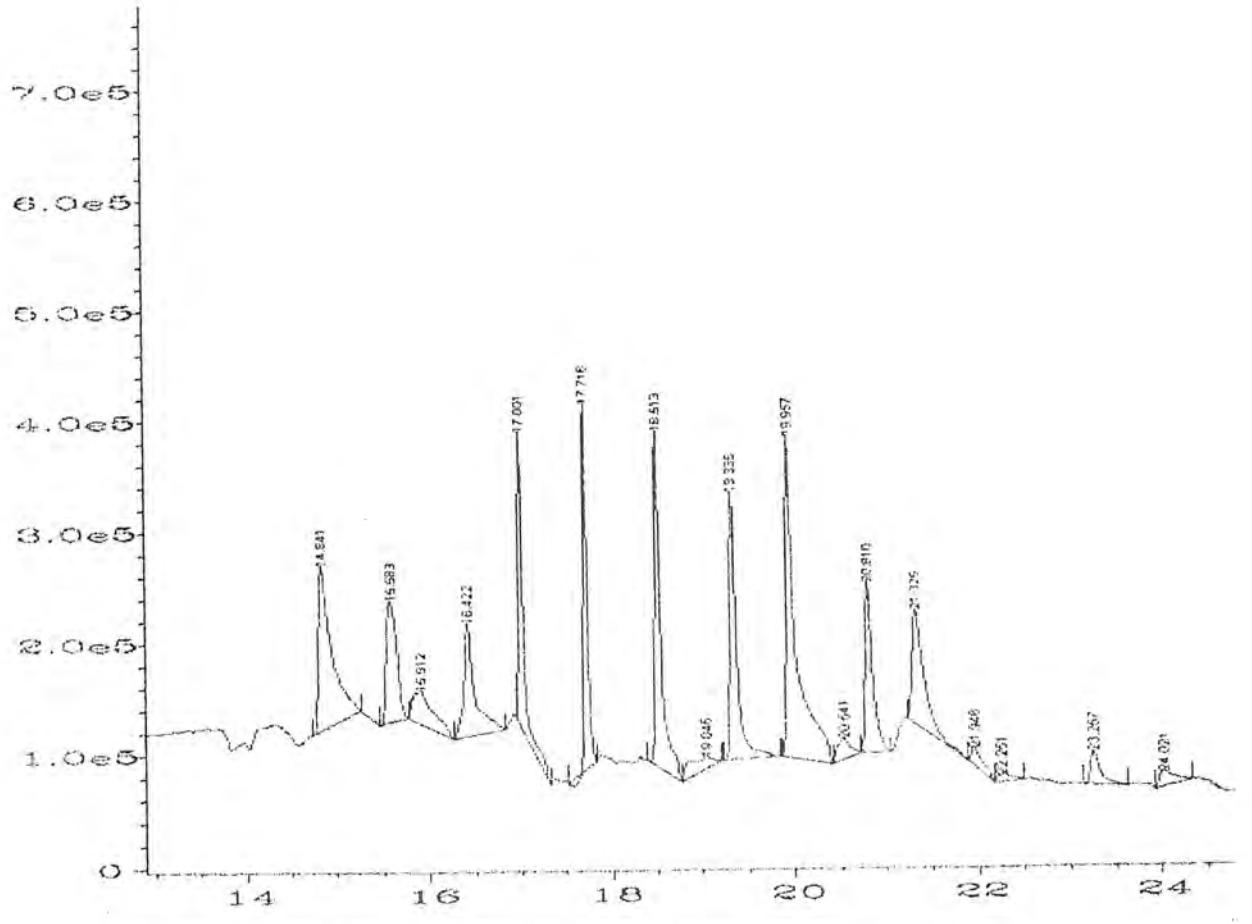
3.4 Chemical analyses

The processed samples were analyzed with Hewlett Packard – 5890 series II Gas Chromatograph equipped with Ni^{63} ECD and DB-608 fused silica capillary column (30 m x 0.32 mm x 0.5 µm) coated with 35 % phenyl methyl polysiloxane. The Chromatographic conditions were as follows.

Detector	:	300 ^{0}C
Injector	:	200 ^{0}C
Oven Temp Program	:	180 ^{0}C – 3 minutes
		4 ^{0}C/min to 260 ^{0}C - hold 15 minutes.
Carrier gas	:	Nitrogen flow 1 ml/ min.

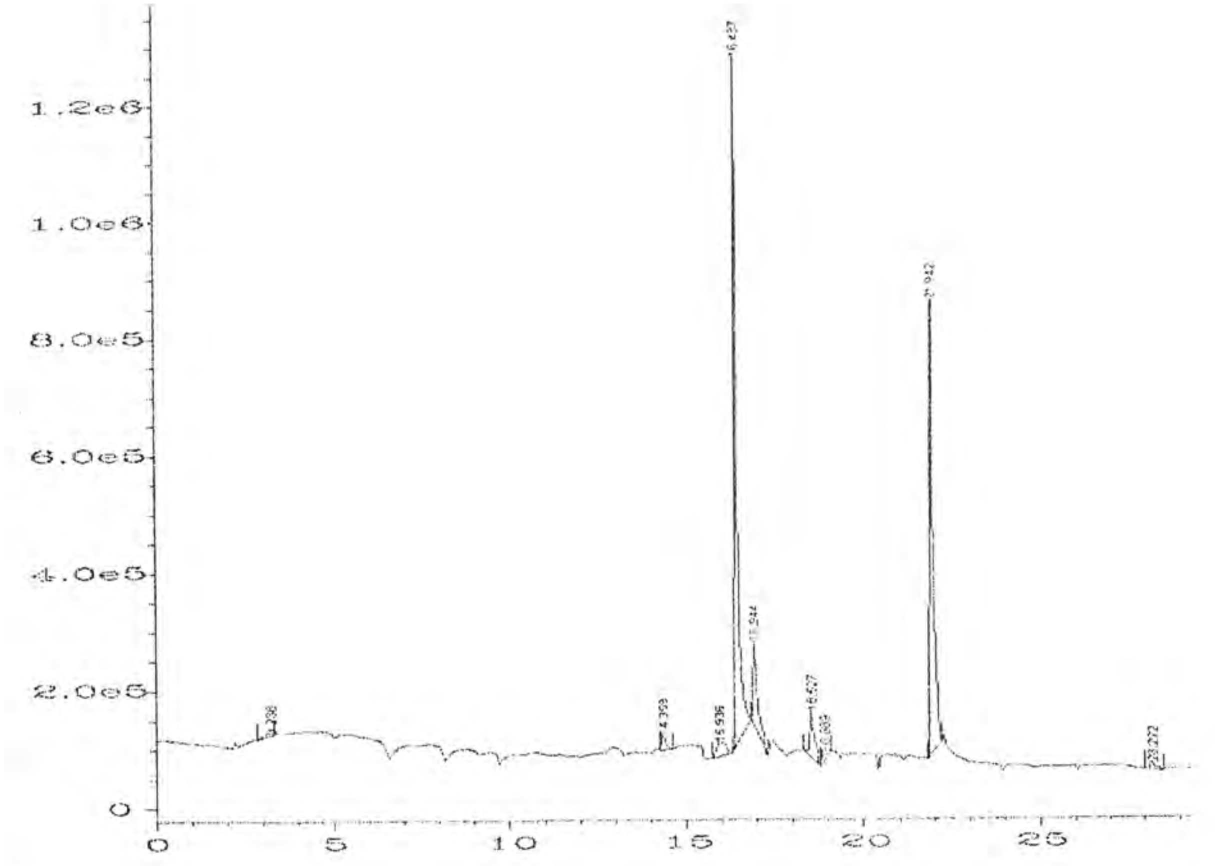
All the samples were analyzed for 13 OC pesticide residues namely, α HCH, β HCH, γ HCH, δ HCH, *p,p'* DDT, *p,p'* DDE, *p,p'* DDD, α endosulfan, β endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide, and dieldrin. An equivalent mixture, provided by Dr. Ehrenstorfer Laboratories (Germany) was used as the standard Fig 3.3 (i) & (ii). The limit of detection for all the OC pesticide residues was 1 ppb. The concentration of the individual compounds in each sample was calculated from the peak area of the sample to that of the corresponding external standard. Recoveries of the compounds from fortified samples (100 ppb) ranged from 95 % to 100 % and the results were not corrected for percent recovery and further expressed as ppb in wet weight basis.

Analyses were run in batches of 10 samples plus four quality controls which includes reagent blank, matrix blank, QC check sample and random duplicate sample (one each). The methodology followed was also counter checked with Tamil Nadu Agricultural University, Coimbatore.



Ret Time	Area	Type	Width	Ref#	ng/ul	Name
14.641	1491081	BB	0.138	1	0.0100	a-HCH
15.583	[illegible]	BB	0.117	1	0.0100	g-HCH
16.422	469487	BB	0.184	1	0.0100	b-HCH
17.001	[illegible]	BB	0.136	1	0.0100	d-HCH
17.716	1015836	BB	0.057	1	0.0100	Heptachlor
18.513	978543	BB	0.046	1	0.0100	Aldrin
19.335	1356973	BB	0.065	1	0.0100	Heptachlor epoxide
19.957	2277230	BB	0.266	1	0.0100	o,p'DDE
20.610	1161185	BB	0.072	1	0.0100	Endosulfan a
21.325	2166852	BB	0.102	1	0.0100	p,p' DDE
23.207	176119	BB	0.122	1	0.0100	Dieldrin
24.021	654180	BB	0.081	1	0.0100	Endosulfan b
24.940	927054	BB	0.126	1	0.0100	Endrin
25.207	151185	BB	0.124	1	0.0100	o,p' DDT
25.207	208570	BB	0.101	1	0.0100	Endrin aldehyde
24.021	153084	BB	0.146	1	0.0100	Endosulfan sulfate

Fig. 3.3 (i) Standard chromatogram of 16 individual organochlorine pesticides calibrated in GC-ECD



Ret Time	Area	Type	Width	Ref#	ng/ul	Name
14.841	* not found *			1		a-HCH
15.563	* not found *			1		g-HCH
15.936	454158	BB	0.214	1	0.00797	b-HCH
16.437	6217681	BB	0.075	1	0.0700	d-HCH
16.944	1204655	BB	0.114	1	0.0116	Heptachlor
17.718	* not found *			1		Aldrin
18.527	749319	BB	0.123	1	0.00541	Heptachlor epoxide
16.889	159168	BB	0.169	1	0.00637	p,p'DDD
19.335	* not found *			1		Endosulfan a
19.957	* not found *			1		p,p' DDE
20.541	* not found *			1		Dieldrin
20.810	* not found *			1		Endosulfan b
21.525	* not found *			1		Endrin
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	p,m' DDT
23.217	* not found *			1		Endrin aldehyde
24.021	* not found *			1		Endosulfan sulfate

Not all calibrated peaks were found

Fig. 3.3(ii) Sample chromatogram of individual organochlorine pesticides quantified in GC-ECD

3.5 Statistical analyses

Analysis of variance (ANOVA) was used to test the differences in organochlorine residues among the species and quarters of both the locations, i.e., Cochin and Rameshwaram. Student T-test was employed to understand the level of variations in the residues present in the samples received from Cochin and Rameshwaram. Spearman's rank correlation was applied to evaluate the correlation between the chemical concentrations and the size of fish as well as with the chemical concentrations and sex of the fish.

About 30 outliers, out of all the samples were excluded from the statistical analysis. All the data sets were normalized with log transformation and subjected to statistical analysis using statistical software-SPSS Student Version 11. All the statistical results were presented in the results section.

RESULTS

4. RESULTS

Totally 716 marine fishes comprising seven species, namely *Carangoides malabaricus, Cynoglossus macrolepidotus, Nemipterus japonicus, Rastrelliger kanagurta, Sardinella longiceps, Scomberomorus commersonn* and *Sphyraena barracuda* received at Coimbatore market (Ukkadam) from Cochin and Rameshwaram were included in the study. All the samples were collected between October 2004 and September 2006 (2 years) which comprised eight quarters with one quarter having a span of three months. The samples were analyzed for residues of a set of persistent organochlorine pesticides, namely α HCH, β HCH, γ HCH, δ HCH, *p,p'* DDT, *p,p'* DDE, *p,p'* DDD, α endosulfan, β endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide and dieldrin. The sum of residues of all the pesticides detected in a sample is referred as the total organochlorine pesticide residue or load of the sample. The residue data are elucidated under different subheadings to explain the variations in the individual organochlorine pesticide residues among the species as well as their spatial and temporal variations.

4.1 Detection percentage of individual organochlorine pesticides

All the fishes analyzed, had residues of one or more pesticides, although some of them were at below detectable limit (BDL) i.e., below 1ng/g. In other words, the frequency of detection of residues in the samples was 100 %. However individual isomer or metabolite varied in their frequency of occurrence. These variations were perceived when samples were considered irrespective of sampling locations, quarters and species.

Among the organochlorines analyzed, HCH isomers namely, α HCH, β HCH, γ HCH and δ HCH were detected in 57 %, 58 %, 52 % and 60 % respectively. The detection frequency of DDT metabolites were in the order of 40 % for *p, p'* DDT, 36 % for *p,p'* DDE and 32 % for *p,p'* DDD. Among the cyclodiene group, α endosulfan, β endosulfan and endosulfan sulfate were detected in 48 %, 43 % and 16 % of samples, whereas heptachlor, heptachlor epoxide and dieldrin were detected at 48 %, 64 % and 48 % of samples respectively.

4.2 Spatial variation in the levels of organochlorine residues among various species of fishes studied

The term spatial variation refers to the difference observed among the individual organochlorine residues between two landing centres, namely Cochin and Rameshwaram, from where fishes were received at Coimbatore market. Residue levels of individual organochlorines in fishes had considerable variations between namely Cochin and Rameshwaram. The residue levels reported in this section in all the species are irrespective of sampling seasons. The data are presented in Fig 3(i-vii).

4.2 (i) *Carangoides malabaricus*

Residues of HCH isomers, namely α, β, γ and δ HCH in *Carangoides malabaricus* were higher in the fishes of Rameshwaram than Cochin except β HCH. However, the variations are not significant ($P > 0.05$). Residues of *p,p'* DDT was higher (2.91 ± 1.73 ng/g) in *Carangoides malabaricus* received from Cochin than Rameshwaram (1 ± 0.6 ng/g). Levels of all the other metabolites of DDT were below the detection limit in *Carangoides malabaricus* received from both the locations. Residues of all cyclodiene group pesticides were less than the detection limits in the samples received from Cochin. Residue levels of α endosulfan and heptachlor in the fishes received from Rameshwaram were 1 ± 0.37 and 1.17 ± 0.51 ng/ g respectively fig 4.2. (i).

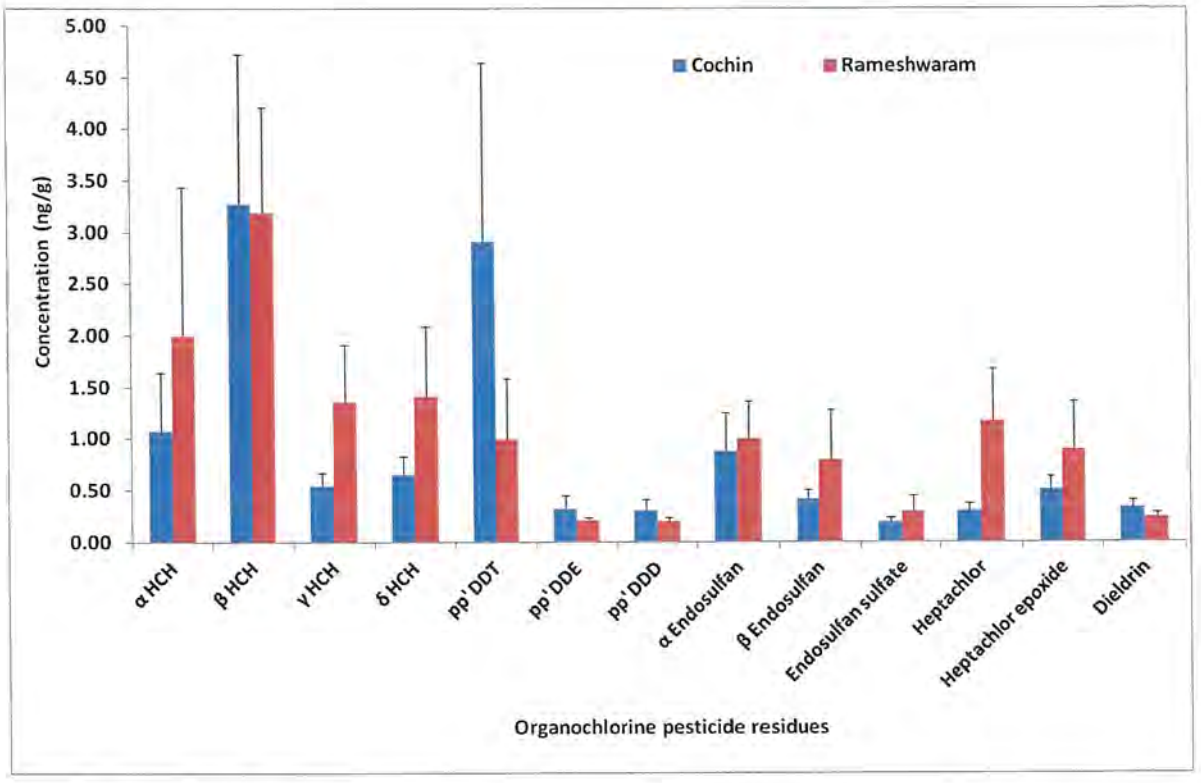


Fig 4.2 (i) Levels of organochlorine pesticide residues in *Carangoides malabaricus* collected from Cochin and Rameshwaram

Of all the OC pesticides in *Carangoides malabaricus*, levels of only heptachlor were significantly different between Cochin and Rameshwaram ($P<0.05$; F value – 9.6).

4.2 (ii) *Cynoglossus macrolepidotus*

Among the residues of HCH isomer in *Cynoglossus macrolepidotus*, β HCH (5.3 ± 1.8 ng/g) and γ HCH (1.1 ± 0.6 ng/g) were higher in concentration in the fishes received from Rameshwaram than in the fishes from Cochin. (β HCH: 2.6 ± 0.9 ng/g and γ HCH :1.6 ± 0.1 ng/g). In contrast the α HCH and δ HCH residues were maximum in the fishes received from Cochin (1.5 ± 0.06 ng/g and 1.2 ± 0.4 ng/g) when compared to Rameshwaram fishes whose concentrations were 1.4 ± 0.6 ng/g and below the detection limit respectively. Variation of β HCH ($P<0.05$; F value – 13.3) and δ HCH ($P<0.05$; F value – 5.1) were found to be statistically significant.

When residues of DDT metabolites were considered, residues of *pp'* DDT was higher in the Rameshwaram fishes (4.2 ± 1.5 ng/g) than the fishes received from Cochin (3.9 ± 1.2 ng/g). Levels of the other DDT metabolites namely *p,p'* DDE and *p,p'* DDD from both the locations were below the detection limits. All the other pesticides belonging to cyclodiene group such as endosulfan, heptachlor and dieldrin had levels below detection limits in the fishes of both Cochin and Rameshwaram fig. 4.2. (ii).

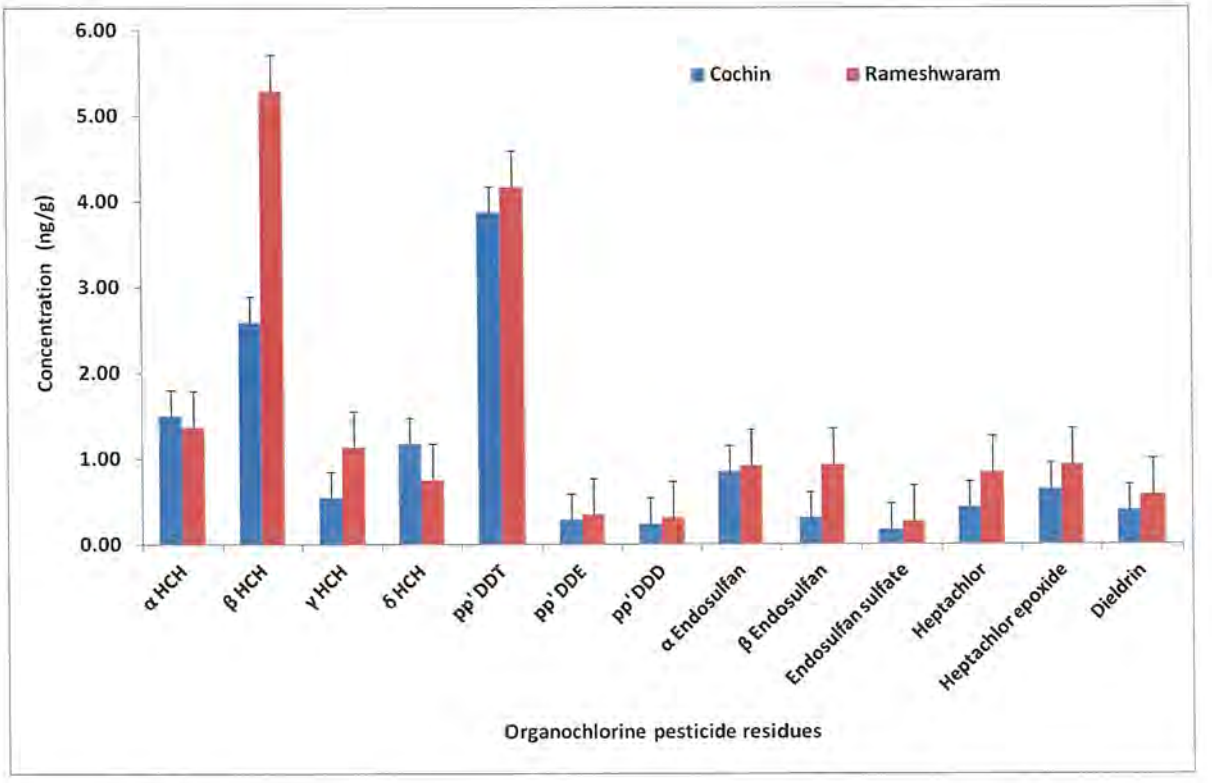


Fig 4.2 (ii) Levels of organochlorine pesticide residues in *Cynoglossus macrolepidotus* collected from Cochin and Rameshwaram

4.2 (iii) *Nemipterus japonicus*

Residues of HCH in *Nemipterus japonicus* was the maximum in fishes from Rameshwaram than Cochin. Of all the isomers of HCH, β HCH in the fishes of Rameshwaram was the highest concentration (7.1 ± 2.0 ng/g) followed by α HCH (2.05 ± 0.97 ng/g), whereas in the fishes of Cochin were 5.1± 1.6 ng/g (β HCH) and below the detection limit (α HCH). Similarly the δ HCH residues were higher in Rameshwaram fishes (1.13 ± 0.23 ng/g)

while it was below detection limits in the fishes of Cochin. However the variation in δ HCH residues between the two locations alone were statistically significant ($P<0.05$; F value – 2.5). In contrast, although γ HCH had greater concentration (1.5 ± 0.5 ng/g) in Cochin fishes than Rameshwaram fishes (1.2 ± 0.4 ng/g), the variation was not statistically significant ($P > 0.05$).

Among the metabolites of DDT, concentration of *p,p'* DDT in the fishes of Rameshwaram (5.3 ± 1.0 ng/g) was significantly different ($P < 0.05$; F value - 11.3) from the fishes of Cochin (3.2 ± 0.9 ng/g). Residue levels of other metabolites of DDT (*p,p'* DDE and *p,p'* DDD) in the fishes of both the locations were below detection limits. Among the cyclodiene pesticide residues, only α endosulfan residues in the fishes from Cochin and heptachlor in the fishes of Rameshwaram were detected at a concentration of 1.3 ± 0.4 ng/g and 1.2 ± 0.3 ng/g respectively. The heptachlor epoxide residues were below the detection limits in fishes of Cochin. All the other residues in both the location were below the detection limits fig. 4.2. (iii).

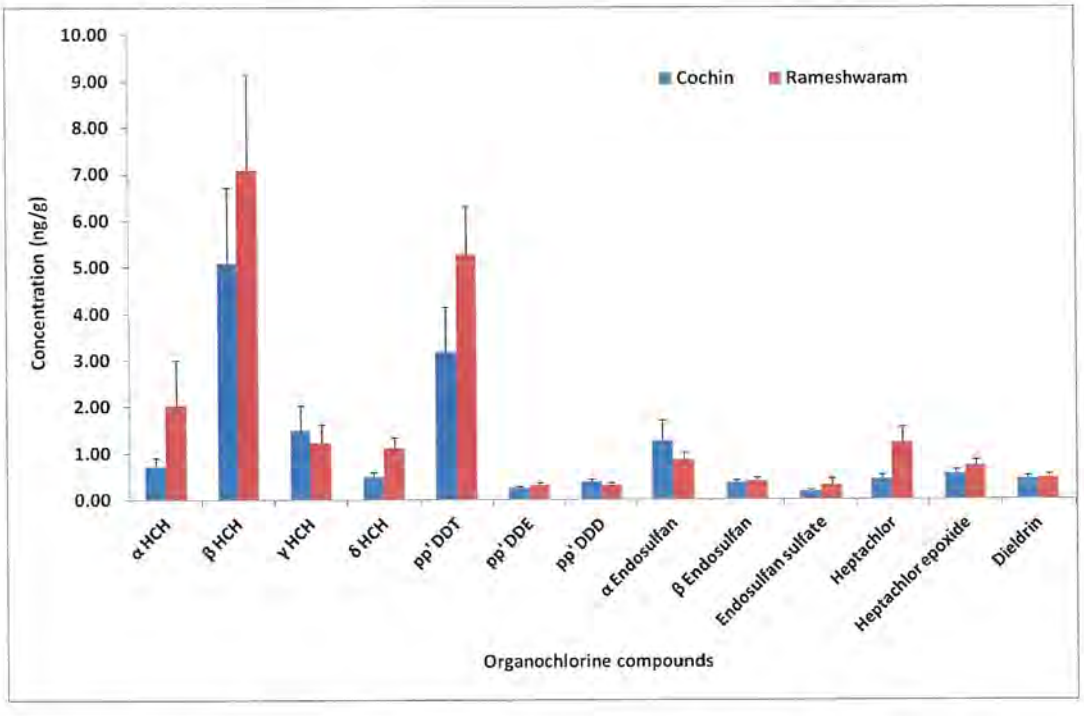


Fig 4.2 (iii) Levels of organochlorine pesticide residues in *Nemipterus japonicus* collected from Cochin and Rameshwaram

4.2 (iv) *Rastrelliger kanagurta*

In *Rastrelliger kanagurta*, residues of only α HCH and β HCH were at detectable levels among all the HCH isomers. The concentration of α HCH was 1.2 ± 0.5 ng/g in the fishes received from Cochin and below the detection levels in the fishes received from Rameshwaram. The β HCH residue levels were in the order of 8.2 ± 2.2 ng/g and 2.2 ± 0.8 ng/g in the fishes received from Cochin and Rameshwaram respectively. The variation in β HCH residues between the two locations was found to be statistically significant ($P< 0.05$; F value – 12.0). The other isomers of HCH, namely γ HCH and δ HCH were below detection levels in the fishes from both the locations.

Similar to HCH isomers, among the DDT metabolites, only *p,p'* DDT residues were at detectable levels. Concentration of *p,p'* DDT was higher (4.03 ± 1.05 ng/g) in Cochin fishes than the concentration recorded in Rameshwaram fishes (2.35 ± 0.77ng/g). The variations in the concentrations were observed to be statistically significant ($P< 0.05$; F value – 9.0). The residues of other DDT metabolites in both the locations were at below detection limits.

When Cyclodiene group of pesticides is concerned, only α endosulfan residues in the fishes of Cochin (1.3 ± 0.3 ng/g) were at detection levels. All the other cyclodiene residues were below the detection levels. Residues of α endosulfan in the fishes of Cochin were significantly varying with the concentration in the fishes of Rameshwaram ($P< 0.05$; F value – 26.6) fig. 4.2. (iv).

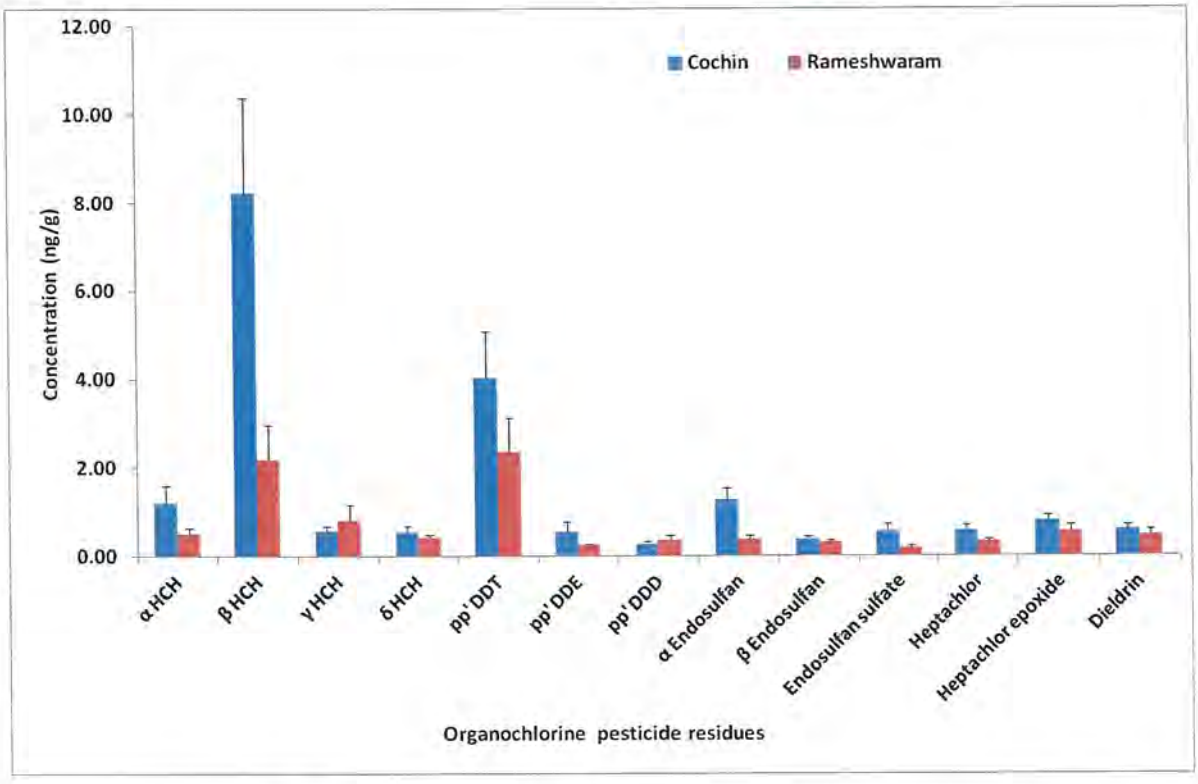


Fig 4.2 (iv) Levels of organochlorine pesticide residues in *Rastrelliger kanagurta* collected from Cochin and Rameshwaram

4.2 (v) *Sardinella longiceps*

In *Sardinella longiceps*, the average concentration of α HCH was 1.77 ± 0.54 and 1.97 ± 0.7 ng/g in the fishes of Cochin and Rameshwaram respectively. Regarding β HCH residues, while the average concentration in the fishes of Cochin was 7.56 ± 3.05 ng/g. In the fishes of Rameshwaram, it was 6.39 ± 2.3 ng/g and the variation was not very much different. Residues of γ HCH were about 1.37 ± 0.5 ng/g in Cochin fishes and it was below the detection limit in the Rameshwaram fishes. Residues of δ HCH in the fishes were below the detection limit in both the locations.

Among the DDT metabolites in *Sardinella longiceps,* the concentration of *p,p'* DDT in the fishes received from Cochin was lower (2.44± 0.6 ng/g) than the concentration (3.25 ± 0.81 ng/g) in the fishes received from Rameshwaram. The other DDT metabolites namely *p,p'* DDE and *p,p'* DDD were at below detection levels.

The cyclodiene pesticide residues in all the fishes received from Cochin were below detection Heptachlor residues. The concentrations of Heptachlor and Heptachlor epoxide in the fishes of Rameshwaram were 1.06 ± 0.4 ng/g and 1.54 ± 0.2 ng/g respectively. Of all the OCP residues recorded in both the locations, the variation in the concentrations were not statistically significant (P>0.05) fig. 4.2. (v).

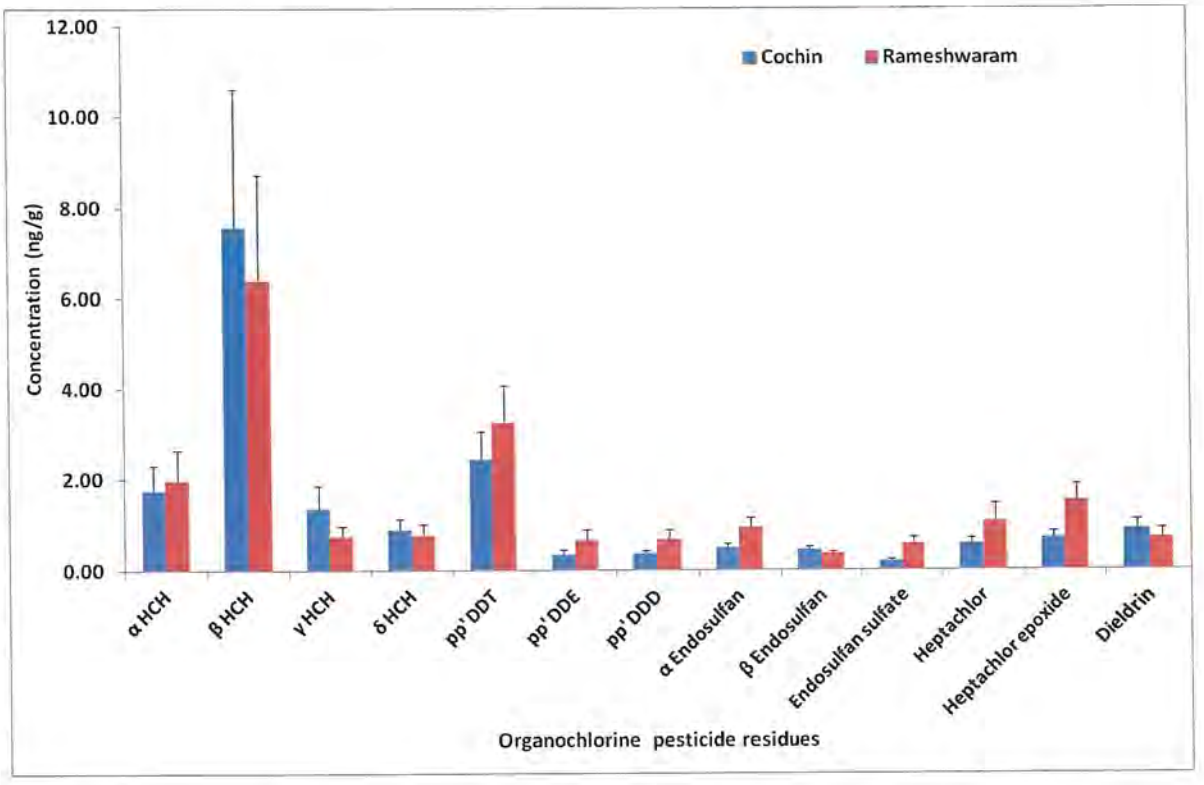


Fig 4.2 (v) Levels of organochlorine pesticide residues in *Sardinella longiceps* collected from Cochin and Rameshwaram

4.2 (vi) *Scomberomorus commersonn*

Residues of all the HCH isomers in *Scomberomorus commersonn* were at below detection limit except β HCH, which recorded a concentration of 9.1 ± 3.9 ng/g in the fishes collected from Cochin and it was about 2.53 ± 0.7 ng/g in the fishes collected from Rameshwaram. The variation was found to be statistically significant (P<0.05; F value -7.1).

Similar to HCH isomers, all the DDT metabolites were at below detection limit except *p,p'* DDT, which recorded a concentration of 7.8 ± 2.0 ng/g in the fishes collected from Cochin and it was about 4.08 ± 1.9 ng/g in the fishes collected from Rameshwaram. Variations were not statistically significant (P>0.05).

Among the Cyclodiene residues, α endosulfan recorded higher concentration (2.8 ± 1.3 ng/g) in the fishes received from Rameshwaram than the fishes collected from Cochin (1.75 ± 0.7 ng/g). The same pattern in concentration was observed for β endosulfan in the fished collected from Cochin (1.41 ± 0.7 ng/g) and Rameshwaram (1.56 ± 0.9 ng/g). Endosulfan sulfate residues were 1.83 ± 1.1 ng/g in the fishes collected from Rameshwaram and it was below the detection limits in the fishes collected from Cochin. The variations observed among the endosulfan residues were not statistically significant (P>0.05).

Further, the heptachlor and heptachlor epoxide residues were about 1.13 ± 0.4 ng/g and 1 ± 0.2 ng/g in the fishes collected from Cochin respectively. The variation in heptachlor epoxide residues in the fishes of Cochin, when compared with Rameshwaram fishes was found to be statistically significant (P<0.05; F value- 3.3) fig 4.2. (vi).

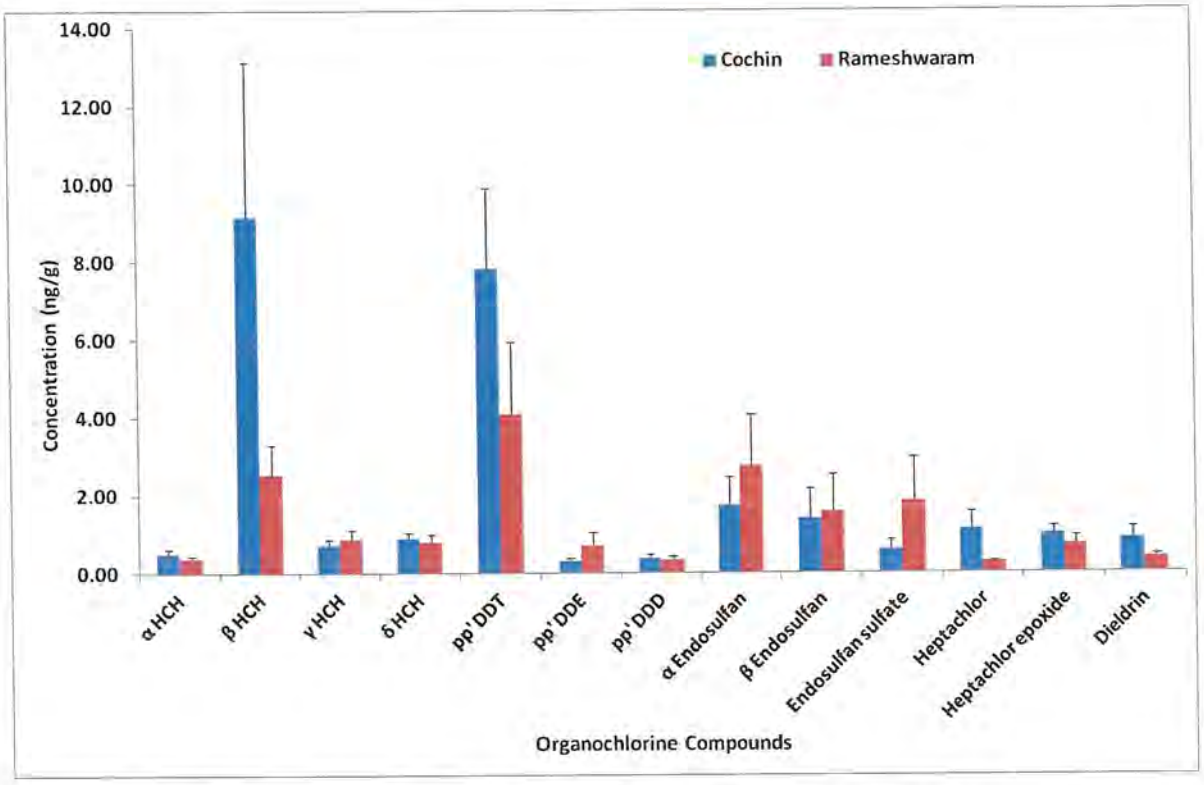


Fig 4.2 (vi): Levels of organochlorine pesticide residues in *Scomberomorus commersonn* collected from Cochin and Rameshwaram

4.2 (vii) *Sphyraena barracuda*

The average concentrations of β HCH (9.04 ± 4.3 ng/g) and α HCH (2.1 ± 1.14 ng/g) residues in *Sphyraena barracuda* were found to be higher in the fishes collected from Rameshwaram than that of Cochin, where the concentrations were 6.1 ± 1.5 ng/g and 1.96 ± 0.9 ng/g respectively. The Residues of γ HCH residues in the fishes collected from Cochin was about 1.4 ± 0.83 ng/g, whereas it was below detection limit in Rameshwaram fishes. Although only β HCH and γ HCH residues were relatively high, the variation in the concentration between the two locations were not statistically significant (P>0.05).

When DDT metabolites were considered, only *p,p'* DDT residues were at detectable levels. The concentrations were higher in the fishes of Cochin (4.3 ± 1.4 ng/g) than in the fishes of Rameshwaram (2.3 ± 0.9 ng/g). The other DDT metabolites were at below detection

limit in the fishes collected from both the locations. The recorded variations were not statistically significant ($P > 0.05$).

Cyclodiene pesticide residues in *Sphyraena barracuda* were all at below detection limit, except α endosulfan which was 1.2 ± 0.4 ng/g in Cochin fishes and below detection limits in Rameshwaram fishes fig. 4.2. (vii).

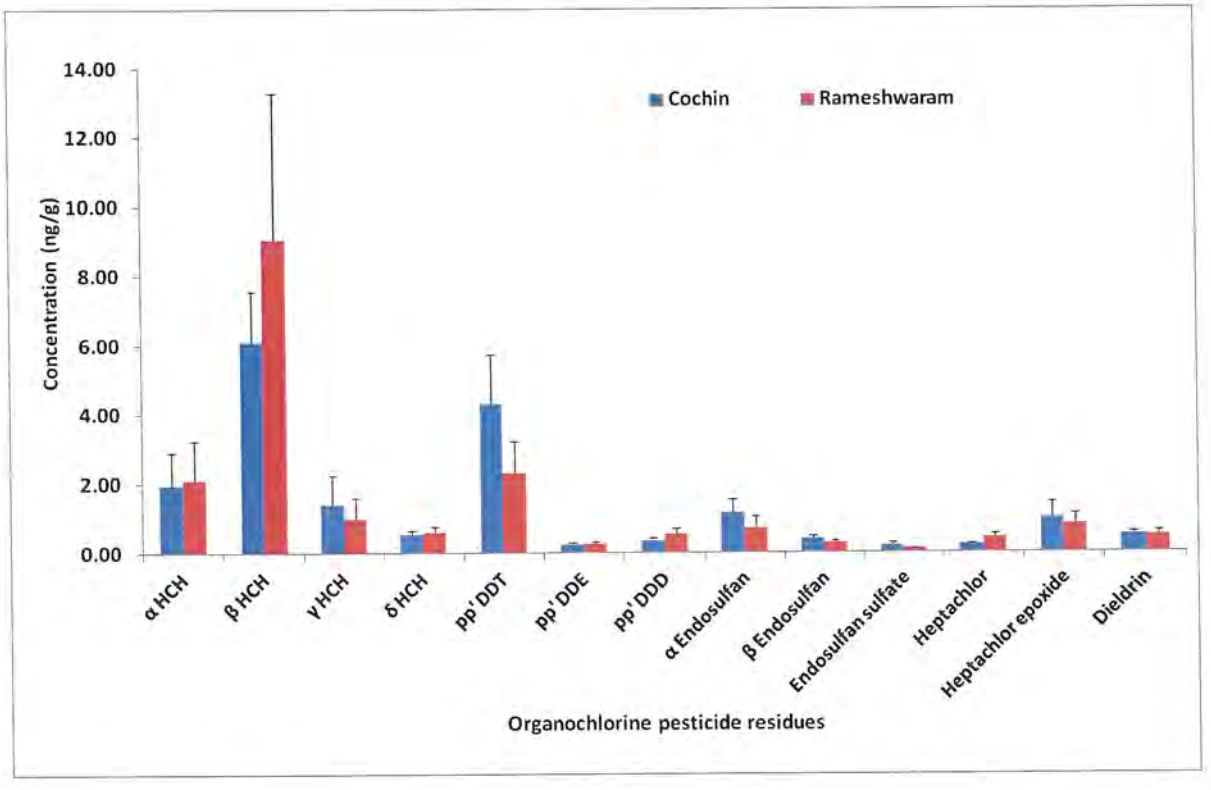


Fig 4.2. (vii) Levels of organochlorine pesticide residues in *Sphyraena barracuda* collected from Cochin and Rameshwaram

4.3 Temporal variation in the levels of organochlorine residues among various species of fishes studied between October 2004 and September 2006.

The term temporal variation refers to the difference observed in the residue levels of individual organochlorine among eight quarters in all the seven species of fishes included in the study.

During the study period (October 2004 - September 2006) there were eight quarters as detailed below;

Quarter I	-	October to December 2004
Quarter II	-	January to March 2005
Quarter III	-	April to June 2005
Quarter IV	-	July to September 2005
Quarter V	-	October to December 2005
Quarter VI	-	January to March 2006
Quarter VII	-	April to June 2006
Quarter VIII	-	July to September 2006

4.3 (i) *Carangoides malabaricus*

Concentration of total HCH in *Carangoides malabaricus* was the maximum in VII quarter (20.8 ng/g) and minimum in IV quarter (below detection limit). While there was a decreasing trend from I quarter (7.5 ng/g) to IV quarter, subsequently towards the VIII quarter, the concentration showed an increasing trend. The variation in concentration of the total HCH residues in quarter VII was significantly varying ($P < 0.05$; F Value - 10.5) with all the other quarters. Similarly the concentration of total HCH residues in quarter VI was significantly varying ($P < 0.05$; F Value - 10.5) with that of IV and III quarter respectively.

Pattern of variation in total DDT concentration was similar to that of total HCH. It varied between 14.9 ng /g (quarter VI) and below detection limits (quarter II). The total DDT residue concentration showed a sharp rise and fall among quarter V (1.7 ng/g), quarter VI (14.9 ng/g) and quarter VII (3.9 ng/g). The variation in total DDT residues was significant among quarter I, III VI and quarter VII ($P < 0.05$; F Value – 4.9).

Among the cyclodiene group of pesticides, total Endosulfan residues were the highest in VI quarter (7.3 ng/g) and lowest in II quarter (below detection limit). Heptachlor epoxide and dieldrin residues were relatively low (below detection limit) in all the except VI (1.7 ng/g) and VII quarters (2.8 ng/g). The cyclodiene residues in the fishes collected during all the other quarters were below the detection limits, fig 4.3. (i).

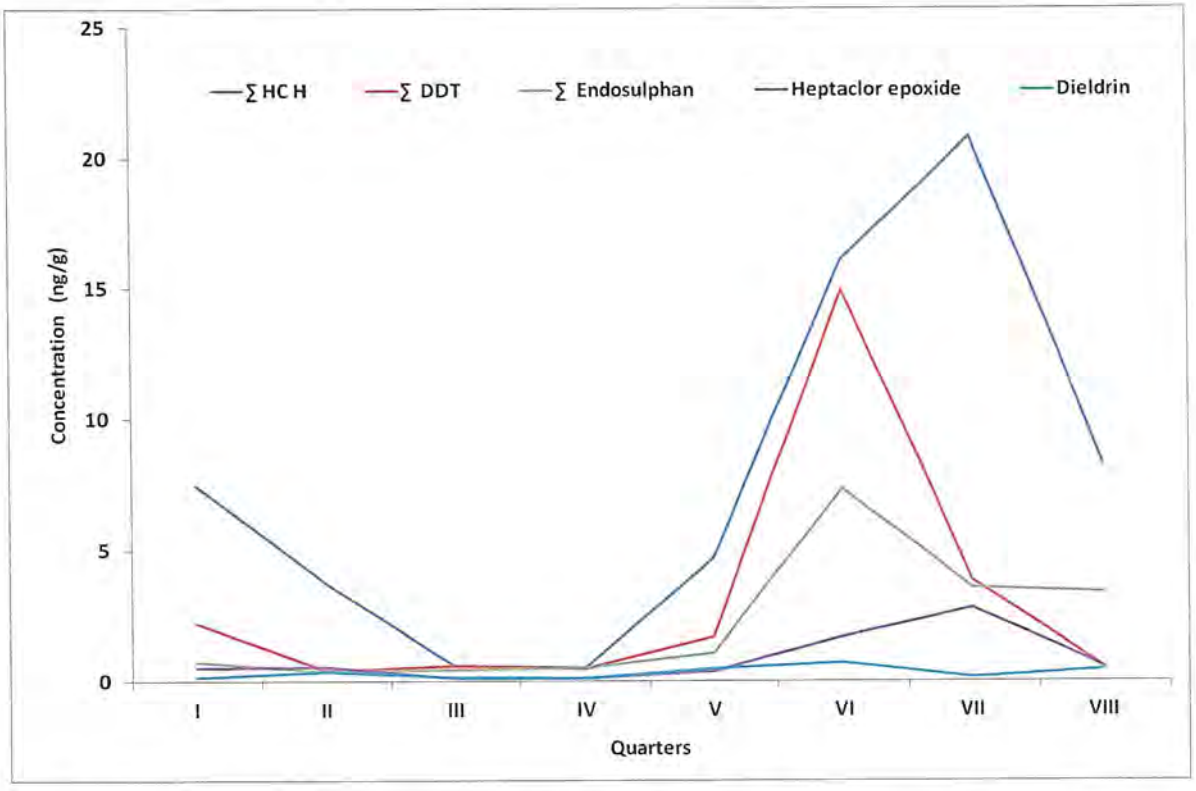


Fig 4.3 (i) Variation of organochlorine pesticide residues in *Carangoides malabaricus* among various quarters

4.3 (ii) *Cynoglossus macrolepidotus*

The concentration of total HCH residues in *Cynoglossus macrolepidotus* during the I and III quarter was 1.9 ng/g. During II quarter the residue lowered a little 1.7 ng/g. It raised towards the V quarter (5.2 ng/g) and came down during the VI quarter (4.7 ng/g). Subsequently the HCH concentration raised and reached the maximum of 23. 9 ng/g during VIII quarter. Although there were variations in concentration of HCH among all the quarters studied, the variation between quarters VII and VIII was significant ($P<0.05$; F Value – 6.8).

When DDT metabolites were considered, the concentrations were below detection limit from I to IV quarter. But it was on a steady rise from V (3.2 ng/g) to VII quarter (12.8 ng/g). However the concentration of total DDT decreased to 5.8 ng/g during the VIII quarter. Similar to HCH the variation of DDT residues were significantly different between VII and first four quarters ($P<0.05$; F Value – 5.3).

Among the cyclodiene group of pesticides, residues of the total endosulfan were below detection limit in the I, II and IV quarters. It showed a decreasing trend from VI quarter (3. 3 ng/g) to VIII quarter (1.3 ng/g). Heptachlor residues in *Cynoglossus macrolepidotus* was below detection limit in the fishes collected during I, II, III, IV and VIII quarters. During quarter V, VI and VII the residues of heptachlor epoxide were 1.8 ng/g, 1.2 ng/g and 1.3 ng/g respectively. Dieldrin residues in *Cynoglossus macrolepidotus* were below the detection limit in all the quarters except VIII quarter which recorded about 1.3 ng/g. (Fig 4-ii). The cyclodiene residues in *Cynoglossus macrolepidotus* were not significantly varying among the quarters. ($P>0.05$), fig 4.3. (ii).

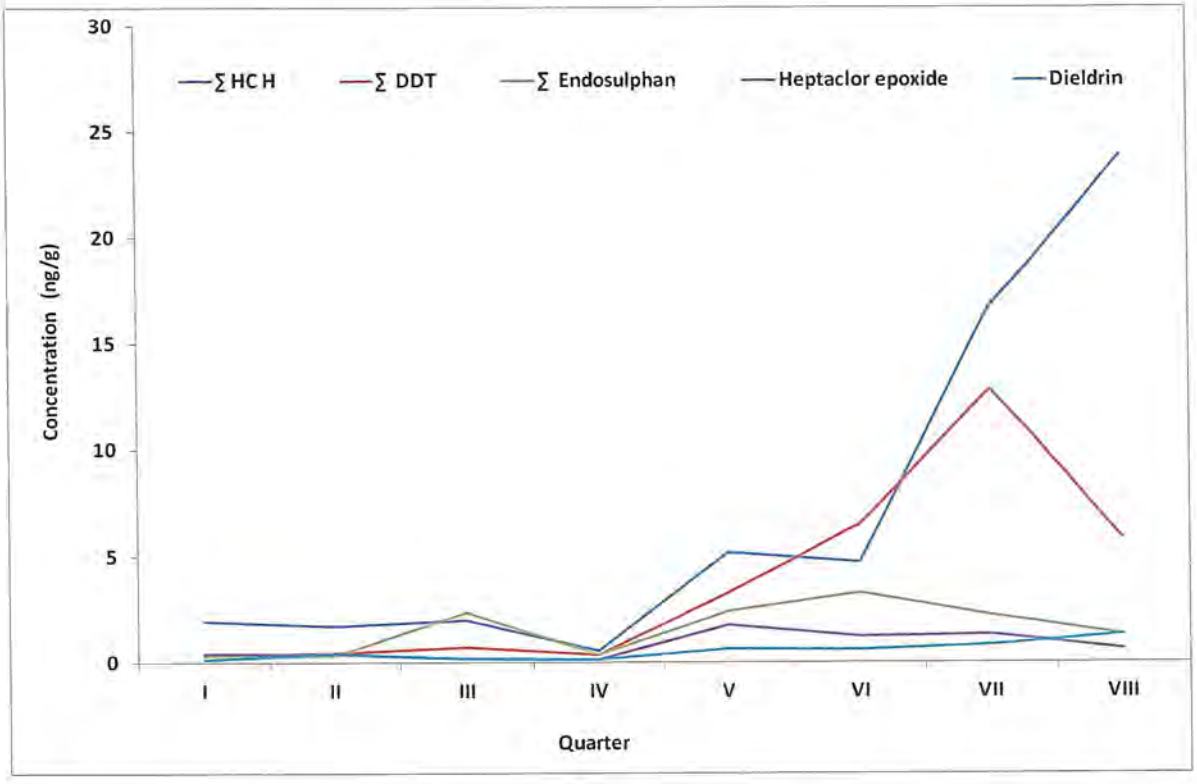


Fig 4.3 (ii) Variation of organochlorine pesticide residues in *Cynoglossus macrolepidotus* among various quarters

4.3 (iii) *Nemipterus japonicus*

Nemipterus japonicus showed varying pattern in total HCH residues across the quarters. The fishes collected in the I quarter recorded 10.8 ng/g of total HCH and decreased to 1.1 ng/g during III quarter. However concentration further raised from 2.3 ng/g in the IV quarter to 23.5 ng/g in the VII quarter and came down to 19.7 ng/g towards the VIII quarter. Concentration of total HCH residues in the VII and VIII quarter was found to be significantly higher than that of the residues recorded during the first four quarters ($P < 0.05$; F Value – 9.3).

When DDT metabolites were considered, the concentration raised from 1.3 ng/g (quarter I) to 6.8 ng/g (quarter II). Further it lowered to 1.8 ng/g in the III quarter and subsequently increased from 2.3 ng/ g in the IV quarter to 9.8 ng/g in the VII quarter. However, it decreased to 4.1 ng/g in the VIII quarter. The pattern of variation of DDT

metaboloites was quite similar to that of the HCH residues. But the variation in total DDT residues recorded in I, III and IV quarters were significantly different with that of the VI quarter ($P < 0.05$; F Value – 3.8).

Residues of total endosulphan belonging to cyclodiene group of pesticides in *Nemipterus japonicus* did not show any pattern of variation. It was below the detection limit during I, III and VIII quarters. The concentration was nearly equal in the II quarter (3.7 ng/g) and VI quarter (3.3 ng/g). Similarly the concentration was in the range of 1.1 ng/g, 1.4 ng/g and 1.7 ng/ g during IV, V and VII quarter respectively. Hence there was not any significant variation in the residues among the quarters. The other cyclodiene residues such as heptachlor epoxide and dieldrin were at below detection limit in all the quarters except the VI quarter which recorded about 1 ng/g of dieldrin residues, fig 4.3. (iii).

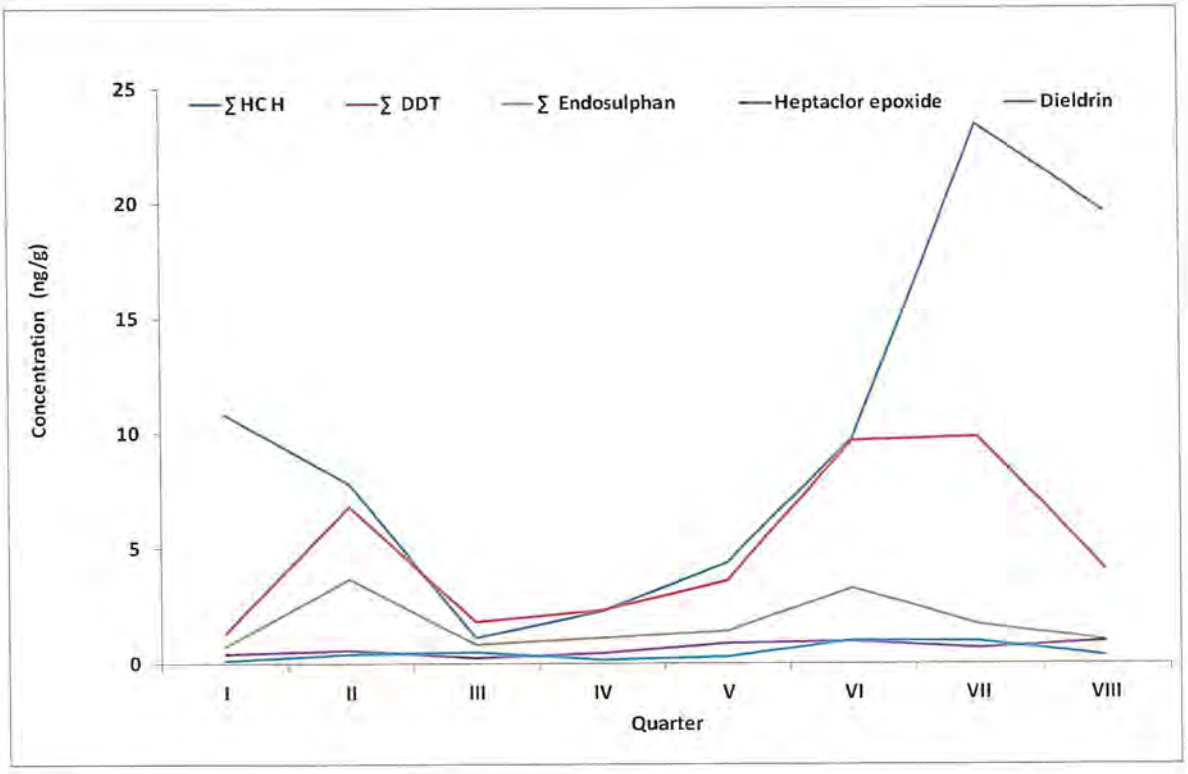


Fig 4.3 (iii) Variation of organochlorine pesticide residues in *Nemipterus japonicus* among various quarters

4.3 (iv) *Rastrelliger kanagurta*

The total HCH residues in *Rastrelliger kanagurta* were on the decreasing trend from I to III quarter (10.3 ng/g - 1.9 ng/g) and similarly from IV to VI quarter (13.3 ng/g - 2.5 ng/g). The level of concentration was sharply raised to about 23.5 ng/g during quarter VII and decreased to 7.9 ng/g towards the VIII quarter. The decreasing trend observed between the VII and VIII quarter was found to be significant ($P< 0.05$; F Value - 5.8).

Unlike total HCH, total DDT residues did not follow an increasing or a decreasing trend across various quarters. The residues recorded in quarter I was 1.7 ng/g and it raised to about 10 ng/g in the II quarter, only to decrease to 4.4 ng/g in the III quarter and 1.8 ng/g in the IV quarter. The minimum was 1.4 ng/g in quarter VIII. The variation in the concentration of DDT residues recorded in *Rastrelliger kanagurta* among different quarters was not significant ($P<0.05$, F value - 4.8).

Total endosulfan residues belonging to cyclodiene group were at below detection levels in all the fishes collected during the quarters I, IV and VIII. The levels recorded in quarter II (1.8 ng/g) and quarter VI (2.0 ng/g) were at closer range. The highest endosulfan residue (3.5 ng/g) was recorded during quarter V. Variations observed were found to be significant ($P< 0.05$; F Value - 4.3). Residues of other cyclodienes, namely heptachlor epoxide and dieldrin were not significant and below the detection levels in all the quarters except quarter VI and quarter V during which it was 1.3 ng/g (heptachlor epoxide) and 1.2 ng/g (dieldrin) respectively , fig 4. 3. (iv).

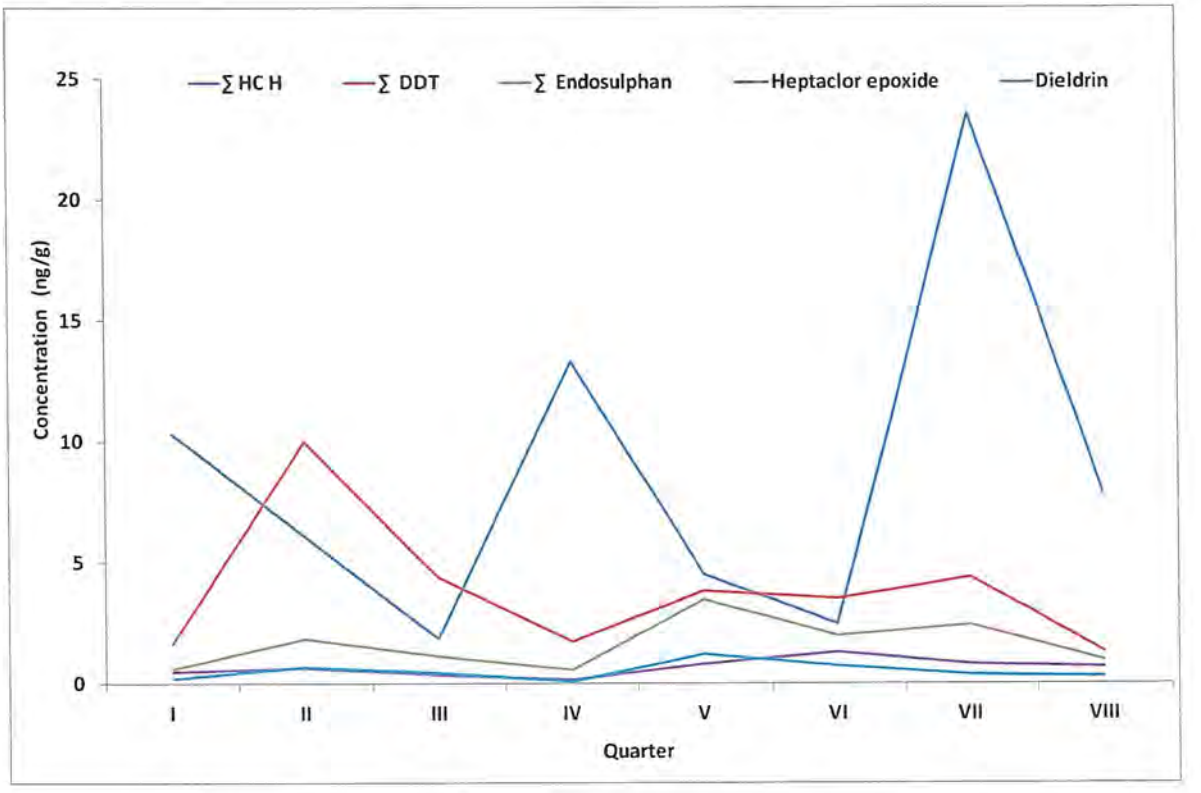


Fig 4.3 (iv) Variation of organochlorine pesticide residues in *Rastrelliger kanagurta* among various quarters

4.3 (v) *Sardinella longiceps*

Total HCH residues in *Sardinella longiceps* during I and II quarter were at comparable levels (14.9 ng/g and 14.3 ng/g). Similarly residues were also at comparable levels among quarter VII (23.2 ng/g) and VIII (23. 4 ng/g). Residues were below detection level during quarter IV and increased to 5.6 ng/g in quarter V and decreased to 3.9 ng/g in quarter VI. The total HCH residues recorded in *Sardinella longiceps* during quarter II, VII and VIII were observed to vary significantly with that of the residues recorded during quarter III and IV ($P<0.05$; F Value – 5.9).

Similar to HCH, the DDT residues in *Sardinella longiceps* were around 5 ng/g in quarter VI and VIII, while quarter III and IV had around 1.5 ng/g. The levels of DDT residues during quarter II, V and VI were 2.9, 6.5 and 7.0 ng/g respectively. It was below detection limit

during quarter II. DDT residues in quarter V was significantly varying from that of quarter II, III and IV. Similarly the variation was significant between quarter IV and VII ($P<0.05$; F Value – 4.9).

Among the cyclodiene group, total endosulfan residues recorded were around 1 ng/g in all the quarters except VIII quarter (2.4 ng/g). Similarly heptachlor epoxide residues were below detection limit in all quarters except I, V and VII which was around 1.7 ng/g. Dieldrin residues were also below detection limit in all the quarters except quarter II and IV which were 1.0 ng/g and 1.9 ng/g respectively. The variation in the cyclodiene residues recorded in *Sardinella longiceps* were not statistically significant ($P>0.05$), fig 4.3. (v).

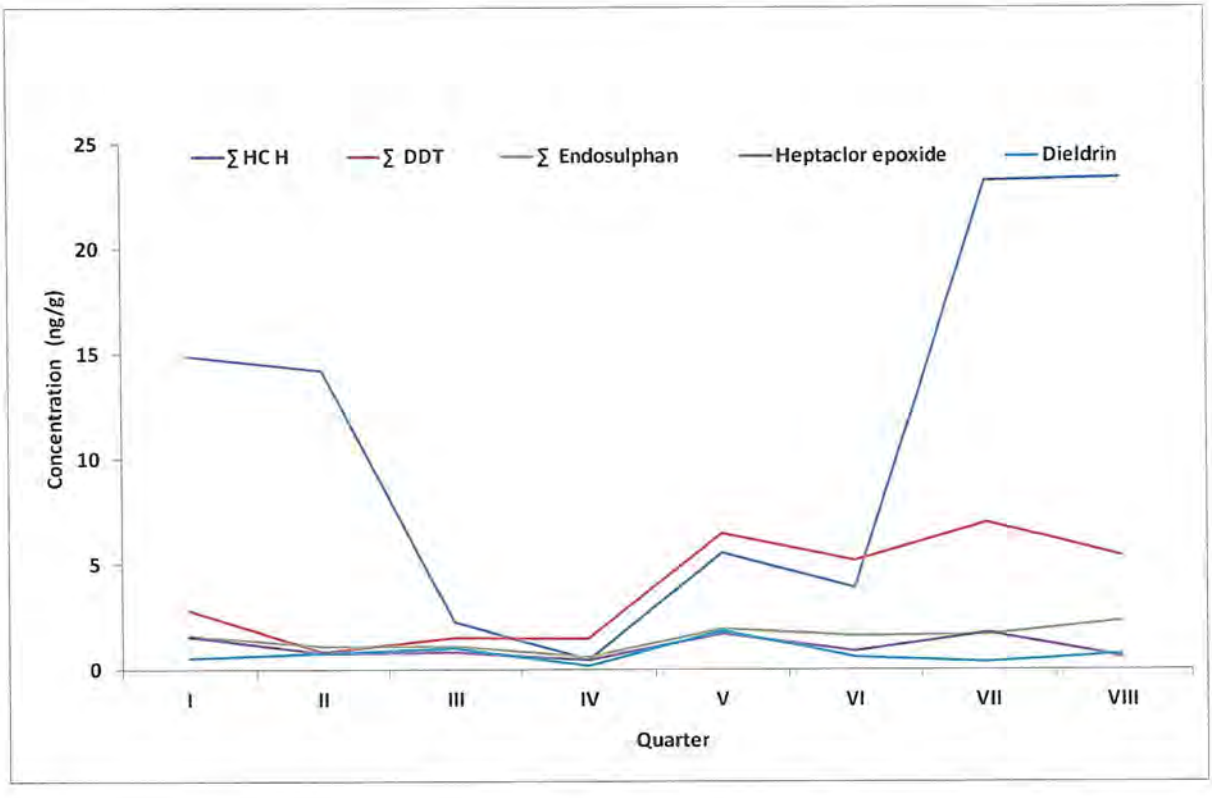


Fig 4.3 (v) Variation of organochlorine pesticide residues in *Sardinella longiceps* among various quarters

4.3 (vi) *Scomberomorus commersonn*

Scomberomorus commersonn showed a different pattern of temporal variation with the maximum concentration of total HCH (36.1 ng/g) during the II quarter. The ranges of the residue levels were around 4.3 ng/g to 6.4 ng/g in all the other quarters except quarter VIII in which the fishes recorded of 9.6 ng/g total HCH. This variation was found to be significant ($P<0.05$; F Value - 3.7). Interestingly the DDT residues in *Scomberomorus commersonn* were on the continuous rise from I to VIII quarter. The concentration raised from 2.2 ng/g to 12.6 ng/g except a minor fall during the III quarter (1.87 ng/g). However, the increasing trend of DDT residues across the quarters was not found to be significant ($P>0.05$).

Among the cyclodiene group, total endosulfan residue pattern was more or less similar to that of total HCH with high concentration (15.7 ng/g) recorded in the fishes collected during quarter II, while the minimum was below detection limit in quarter I. The concentrations in the fishes were on the rise from quarter III to V (1.0 ng/g - 8.1 ng/g). The level came down to 2.9 ng/g during quarter VI and raised to 6.9 ng/g during quarter VIII. Hence the total endosulfan residues were found to vary significantly among quarters ($P<0.05$; F Value - 3.6). Heptachlor residues in the fishes were below detection limit in all quarters except quarter III, V and VI which recorded around 1.5 ng/g. Dieldrin residues were also below detection limit except III quarter which recorded 2.6 ng/g. However, the variations in heptachlor epoxide and dieldrin residues among the quarters were not statistically significant ($P>0.05$), fig 4.3. (vi).

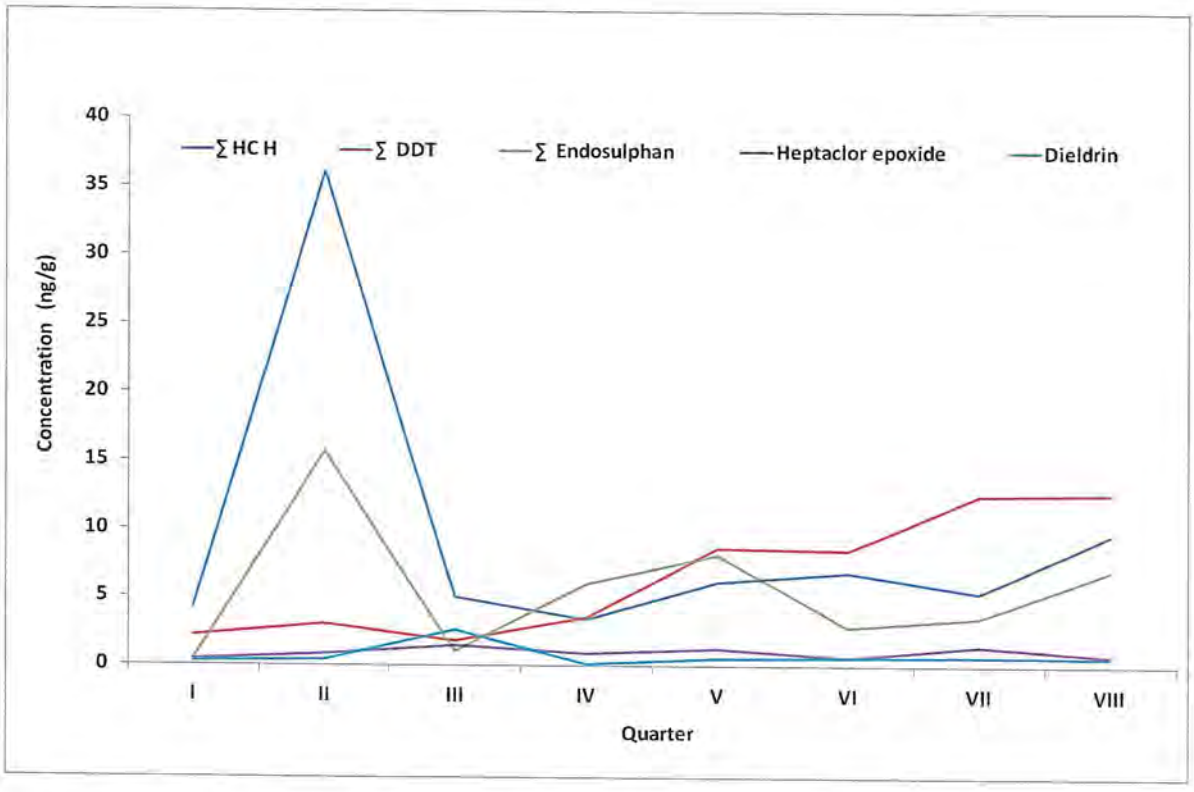


Fig 4.3 (vi) Variation of organochlorine pesticide residues in *Scomberomorus commersonn* among various quarters

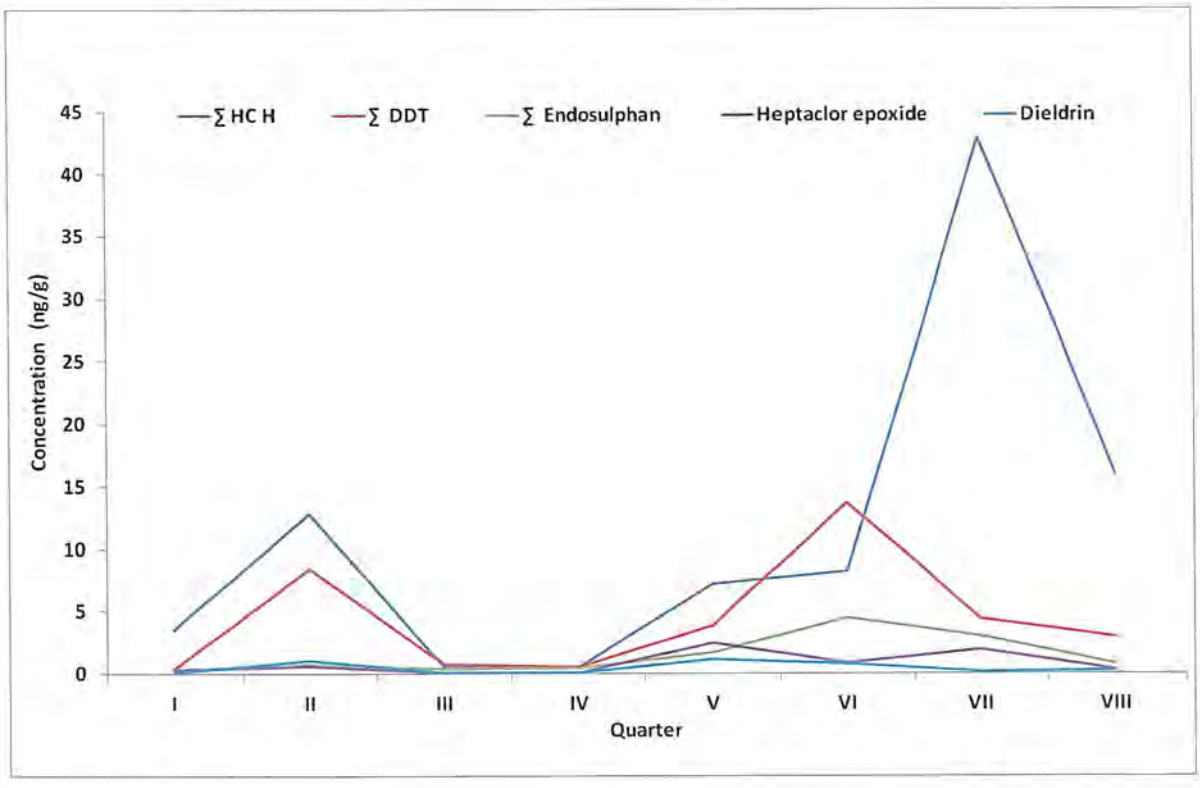
4.3 (vii) *Sphyraena barracuda*

Sphyraena barracuda recorded the maximum concentration of total HCH (42.8 ng/g) during quarter VII which is significantly higher than all the other species, but fell to 15.9 ng/g during quarter VIII, while it was below the detection limit during quarter III and IV. During I and II quarter, the fishes recorded 3.6 and 12.8 ng/g respectively. Levels during V and VI quarter were 7.2 ng/g and 8.2 ng/g respectively. The total HCH residues during quarter VII varied significantly with the residues in all the other quarters ($P<0.05$; F Value – 11.4).

Total DDT residues in *Sphyraena barracuda* were below detection level during quarter I, III and IV. DDT residues were at a concentration of 8.4 ng/g in quarter II. Similar to HCH, further the levels of DDT residues varied in the remaining quarters. The levels recorded were 3.8 ng/g in quarter V, 13.6 ng/g in quarter VI, 4.4 ng/g in quarter VII and 2.9 ng/g in

quarter VIII. The variation in total DDT residues in quarter VI was significantly varying with the residue levels in quarter IV, I, III and VIII ($P<0.05$; F Value – 5.8).

The cyclodiene group of pesticides showed a similar pattern of variation among themselves. The maximum concentration of total endosulfan during VI quarter 4.5 ng/g followed by 3.0 ng/g during VII quarter and 1.7 ng/g during V quarter. These levels were significantly varying ($P<0.05$; F Value – 7.8) with that of the levels recorded during I quarter. Heptachlor epoxide residues were higher in concentration (2.5 ng/g) in the fishes collected during quarter V followed by 1.9 ng/g during quarter VII. But it did not vary significantly ($P>0.05$). Variation in dieldrin residues in the fishes were not significant and were in the order of 1.2 ng/g in V quarter and 1.1 ng/g during II quarter. The cyclodiene residues in the fishes collected during all the other quarters were below detection limit, fig 4.3. (vii).



4.3 (vii) Variation of organochlorine pesticide residues in *Sphyraena barracuda* among various quarters

4.4 Variation in organochlorine pesticide residues among the different species of fishes received from Cochin and Rameshwaram

The Organochlorine pesticides referred in the present study comprise 13 individual compounds. These compounds vary in their residue levels among different species of fishes. The variations in concentration of the compounds have been explained in the following section and expressed in table 4.4.(i). Apart from this, the composition pattern of HCH isomers (α HCH, β HCH, γ HCH and δ HCH), DDT metabolites (*p,p'* DDT, *p,p'* 'DDE and *pp'* DDD), endosulfan metabolites (α endosulfan, β endosulfan and endosulfan sulfate) and heptachlor metabolites (heptachlor and heptachlor epoxide) have also been reported through fig. 4.5.(i)-(iv).

HCH isomers

4.4 (i) α HCH

The α HCH is one of the primary isomers of HCH. Among the seven species of fishes, *Sphyraena barracuda* recorded the maximum mean concentration (11.3 ± 2.5 ng/g). Similarly the average concentration in *Sardinella longiceps* was 10.7± 2.1 ng/g. The mean α HCH residues recorded in the other species such as *Carangoides malabaricus, Cynoglossus macrolepidotus, Nemipterus japonicus, Rastrelliger kanagurta* and *Scomberomorus commersonn* were 6.6± 1.7, 7.2 ± 1.5, 9.5 ±1.5, 7.5 ± 1.4 and 8.4 ± 2.4 ng/g respectively. The residues of α HCH among the different species of fishes did not vary significantly (P>0.05; table 4.4. (i)).

4.4 (ii) β HCH

The mean concentration of β HCH was the highest in *Scomberomorus commersonn* (7.1 ± 1.4 ng/g) followed by *Nemipterus japonicus* (4.8 ± 0.7 ng/g) and *Cynoglossus macrolepidotus* (4.6 ± 1.0 ng/g). *Carangoides malabaricus* recorded the minimum mean concentration of 2.6±1.0 ng/g, the mean residues in the other species such as *Rastrelliger kanagurta* (4.0 ± 0.7 ng/g), *Sardinella longiceps* (3.9 ± 0.6 ng/g) and *Sphyraena barracuda* (4.0 ± 0.9 ng/g) were the same. Similar to α HCH, the residues of β HCH among the different species of fishes does not vary significantly (P>0.05; table 4.4. (i)).

4.4 (iii) γ HCH

The mean concentration of γ HCH was more or less the same in all the species (1.5 ± 0.2 ng/g - 1.7± 0.3 ng/g), except *Scomberomorus commersonn* (4.8 ± 1.0 ng/g). While the minimum concentration of γ HCH was 1.4 ± 0.3 ng/g in *Sphyraena barracuda*, overall variation among the species studied, did not vary significantly (P> 0.05; table 4.4. (i)).

4.4 (iv) δ HCH

When compared to the other isomers of HCH, δ HCH recorded low levels of residues. Among the seven species of fishes, the highest mean concentration was found in *Sardinella longiceps* (1.1± 0.2 ng/g). The mean concentrations in all the other species were very low i.e., < 1 ng/g. The δ HCH residues also did not vary significantly among the species (P>0.05; table 4.4. (i)).

4.4 (v) *p,p'* DDT

Among the DDT metabolites, the mean residue levels of *p,p'* DDT were less than 1 ng/g in all the species. However, the maximum range of concentration was in *Sardinella longiceps* (13.2 ng/g) followed by *Scomberomorus commersonn* (11.7 ng/g). of all the species *pp'* DDT residues were significantly varying between *Carangoides malabaricus* and *Nemipterus japonicus* (P<0.05; F value – 2.23; table 4.4. (i)).

4.4 (vi) *p,p'* DDE

Similar to *p,p'* DDT, the mean *p,p'* DDE residues in all the species were less than 1 ng/g. The maximum detected level was in *Sphyraena barracuda* and *Nemipterus japonicus* (1 ng/g). However, the variations observed among the species were not statistically significant (P>0.05; table 4.4. (i)).

4.4 (vii) *p,p'* DDD

The highest range of concentration of pp, DDD was found in *Sardinella longiceps* (0.53 ng/g) and the range was between below detection limit and 10.1 ng/g. While the level of DDD in other species of fishes was between 2 and 4 ng/g, the variation among the species studied was not statistically significant (P>0.05; table 4.4. (i)).

4.4 (viii) α Endosulfan

Residues of α-Endosulfan were the highest in *Scomberomorus commersonn* (2.2 ± 0.7 ng/g). It was followed by *Nemipterus japonicus* with a mean concentration of 1.1± 0.2 ng/g. The other species namely, *Carangoides malabaricus, Cynoglossus macrolepidotus, Rastrelliger kanagurta* and *Sardinella longiceps* recorded the mean concentration less than 1ng/g. However the residue levels were not varying significantly among the species (P>0.05; table 4.4. (i)).

4.4 (ix) β Endosulfan

β Endosulfan residue levels showed similar trend as that of α endosulfan. The maximum mean concentration was recorded in *Scomberomorus commersonn* (1.5 ± 0.6 ng/g) while the higher end of the range was 29.7 ng/g. Although the mean concentration was less than 1 ng/g, the maximum in *Carangoides malabaricus* and *Cynoglossus macrolepidotus* was about 13.6 ng/g and 21.8 ng/g respectively. The variations observed among the species were not statistically significant (P>0.05; table 4.4. (i)).

4.4 (x) Endosulfan sulfate

The mean endosulfan sulfate residues were also higher in *Scomberomorus commersonn* (1.1±0.3 ng/g). The other species have recorded the residues below the detection limit. These residues were found to vary significantly between *Scomberomorus commersonn* and *Sphyraena barracuda.* (P<0.05; F Value – 2.1; table 4.4. (i)).

4.4 (xi) Heptachlor

Although all the species recorded less than 1ng/g of heptachlor residues, the range maximum was higher in *Sardinella longiceps* (22.9 ng/g). The maximum range of residues in *Carangoides malabaricus, Cynoglossus macrolepidotus* and *Nemipterus japonicus* were around 11 ng/g to 15 ng/g respectively. The variations observed among the species were not statistically significant (P>0.05; table 4.4. (i)).

4.4 (xii) Heptachlor epoxide

The highest mean concentration of heptachlor epoxide (1.1 ± 0.3 ng/g) was detected in *Sardinella longiceps*. All the other species recorded the residues below the detection limit. The variations observed among the species were also not statistically significant (P>0.05; table 4.4. (i)).

4.4 (xiii) Dieldrin

The mean dieldrin residues were less than 1 ng/g in all the species studied. However, the range was found to be wide in *Sardinella longiceps* (BDL - 13.6 ng/g) followed by *Scomberomorus commersonn* (BDL - 11.7 ng/g).The residues did not vary significantly among the species (P>0.05; table 4.4. (i)).

Table 4.4 (i) Mean Concentrations (Mean ± SE ng/g) of residues of organochlorine pesticides among various species of fishes. (BDL - Below Detection Limit)

Species	*Carangoides malabaricus*	*Cynoglossus macrolepidotus*	*Nemipterus japonicus*	*Rastrelliger kanagurta*	*Sardinella longiceps*	*Scomberomorus commersonn*	*Sphyraena barracuda*
N	63	84	136	125	144	74	60
α HCH	6.6 ± 1.7	7.2 ± 1.5	9.5 ± 1.5	7.5 ± 1.4	10.7 ± 2.1	8.4 ± 2.4	11.3 ± 2.5
β HCH	2.6 ± 1.0	4.6 ± 1.0	4.8 ± 0.7	4.0 ± 0.7	3.9 ± 0.6	7.1 ± 1.4	4.0 ± 0.9
γ HCH	1.7 ± 0.4	1.7 ± 0.4	1.7 ± 0.3	1.6 ± 0.2	1.5 ± 0.2	4.8 ± 1.0	1.4 ± 0.3
δ HCH	BDL	BDL	BDL	BDL	1.1 ± 0.2	BDL	BDL
p,p' DDT	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p' DDE	BDL	BDL	BDL	BDL	BDL	BDL	BDL
p,p' DDD	BDL	BDL	BDL	BDL	BDL	BDL	BDL
α Endosulfan	BDL	BDL	1.1 ± 0.3	BDL	BDL	2.2 ± 0.7	BDL
β Endosulfan	BDL	BDL	BDL	BDL	BDL	1.5 ± 0.6	BDL
Endosulfan sulfate	BDL	BDL	BDL	BDL	BDL	1.1 ± 0.5	BDL
Heptachlor	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Heptachlor epoxide	BDL	BDL	BDL	BDL	1.1±0.3	BDL	BDL
Dieldrin	BDL	BDL	BDL	BDL	BDL	BDL	BDL

4.5 Composition pattern of various isomers and metabolites of organochlorine compounds detected in different species of fishes studied

The organochlorine compounds, namely HCH, DDT, endosulfan and heptachlor exist in various isomeric and metabolic forms, which are explained as follows;

4.5 (i) HCH composition

Among the seven species of fishes studied, predominant occurrence of α HCH with more than 50 % of composition was observed in all the species of fishes. The maximum contribution was in *Sphyraena barracuda* (65 %). The contribution of β HCH was comparatively less with the highest contribution being in *Scomberomorus commersonn* (32 %). The contribution of γ HCH towards the total HCH residues was around 10-15 % among the species. In the case of δ HCH, the contribution towards the total HCH residues were the lower than the other isomers in all the species. It accounted for only 2-5% of the total HCH load. Thus the overall pattern of HCH residues showed the predominance of α HCH isomer contributing towards the total HCH load fig 4.5.(i).

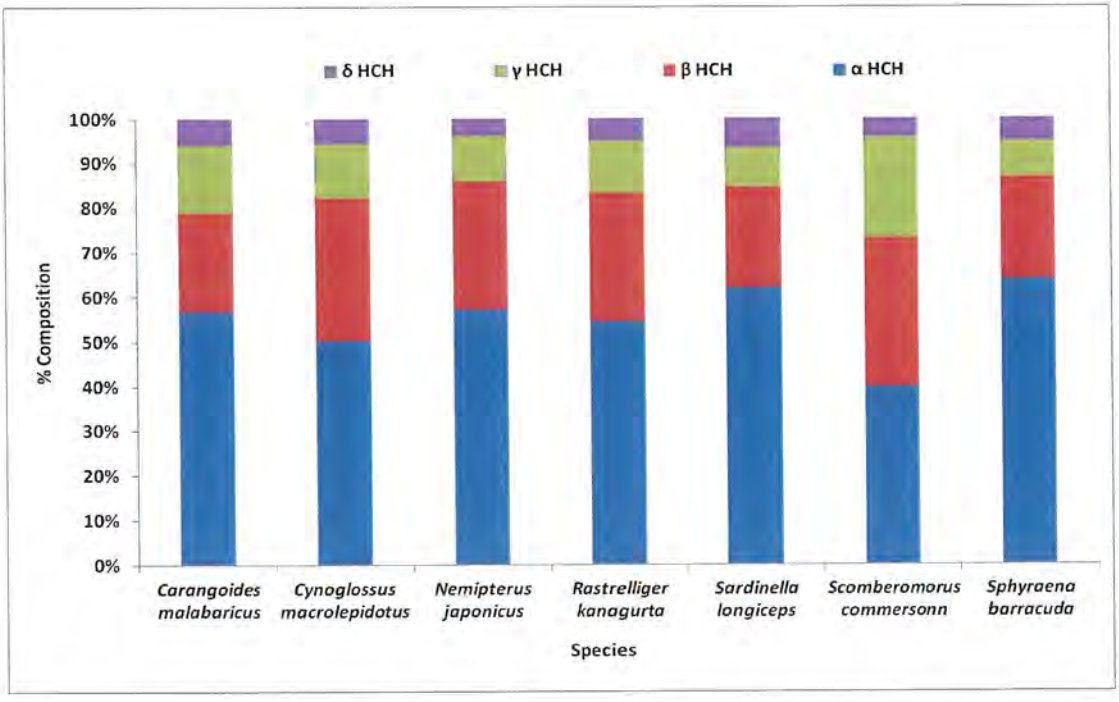


Fig 4.5 (i) Composition pattern of HCH residues among various species of fishes

4.5 (ii) DDT composition

Among the DDT metabolites, *p,p'* DDT was found to be the predominant contributor towards the total DDT residues in all the species of fishes. The maximum contribution of *p,p'* DDT was found in *Cynoglossus macrolepidotus, Scomberomorus commersonn* and *Sardinella longiceps* (42 %). The contribution of *pp'* DDE metabolites in all the species were around 20- 30 % with the highest being in *Sardinella longiceps.* Among all the metabolites, *p,p'* DDD was the least contributed in all the species. However it is also comparable with the *p,p'* DDE's contribution.

The overall pattern of DDT residues showed higher contribution of *p,p'* DDT residues towards the total DDT residues, fig 4.5. (ii).

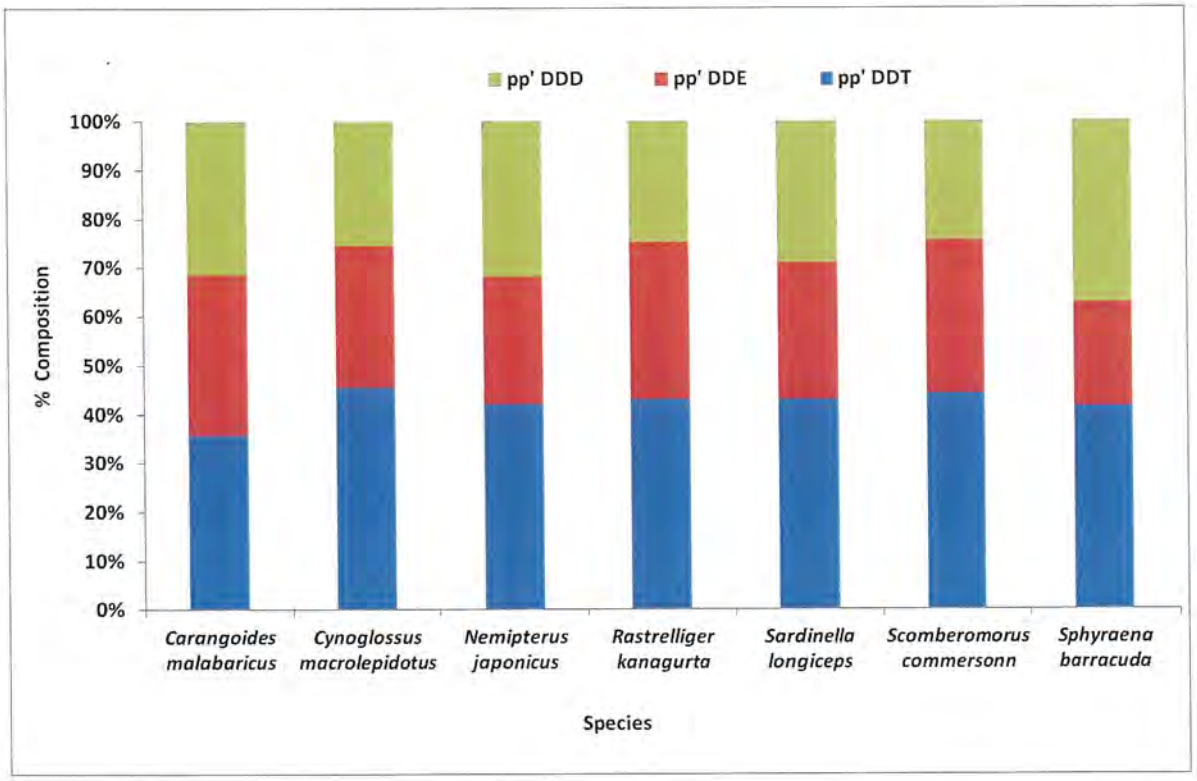


Fig 4.5 (ii): Composition pattern of DDT residues among various species of fishes

4. 5 (iii) Endosulfan composition

Among the endosulfan metabolites, the contribution of α endosulfan was the maximum. The contribution ranged from 47 % in *Sardinella longiceps* to 65 % in *Scomberomorus commersonn*. However, the composition of β endosulfan residues was only between 20 % and 40 % in all the species studied. Endosulfan sulfate residues contributed the minimum which was around 15 % in all the species.

Thus α endosulfan was the primary contributor to the total endosulfan residues in all the seven species of fishes studied fig 4.5. (iii).

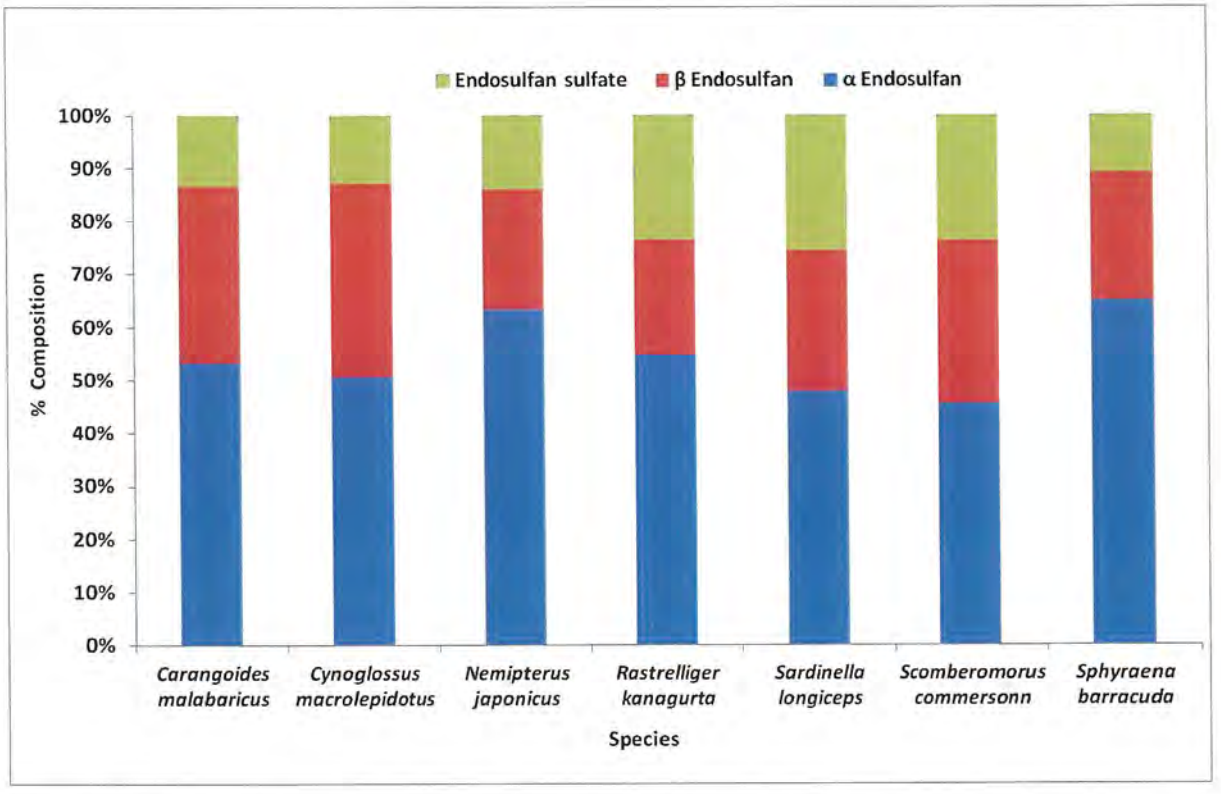


Fig 4.5 (iii) Composition pattern of endosulfan residues among various species of fishes

4. 5 (iv) Heptachlor composition

Among the heptachlor metabolites, the highest contribution of heptachlor epoxide was found to occur in all the species except *Nemipterus japonicus* and *Carangoides malabaricus*, with the maximum being 78 % in *Sphyraena barracuda*. In *Rastrelliger kanagurta* and *Nemipterus japonicus*, the contribution of heptachlor and heptachlor epoxide was 50% each. On the whole, heptachlor epoxide contributed to the maximum to the total heptachlor in all the species fig 4.5. (iv).

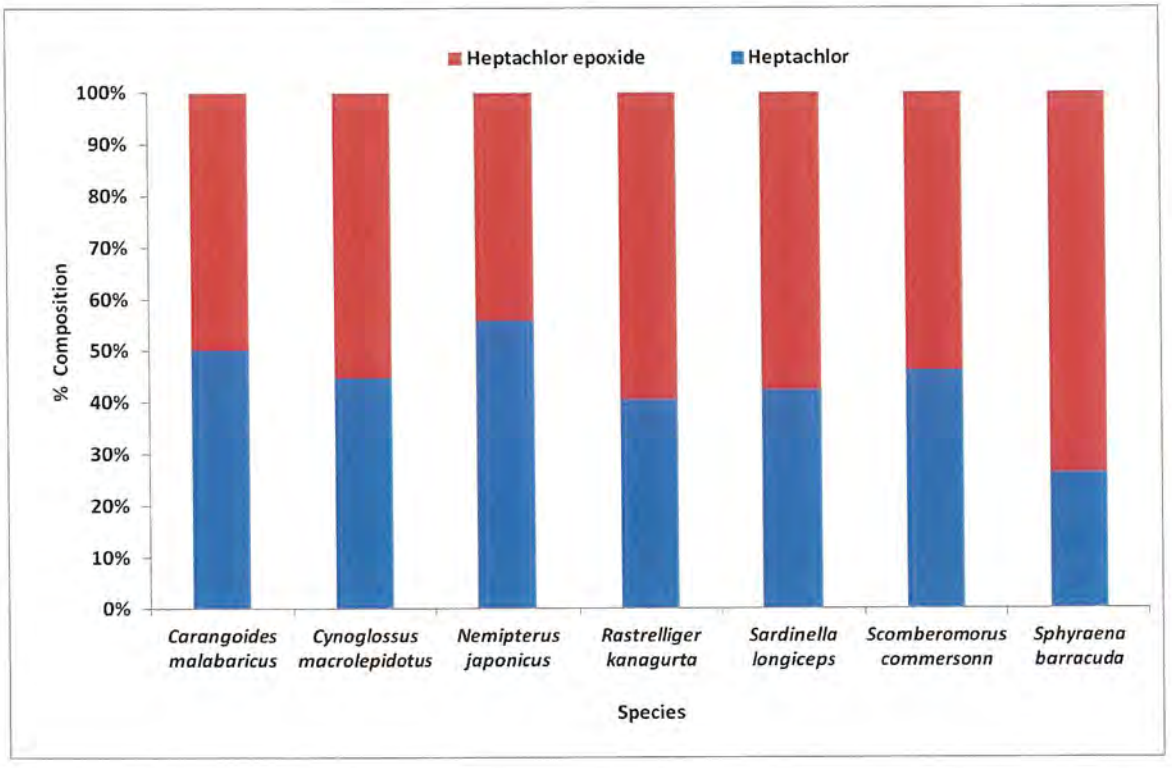


Fig 4.5 (iv) Composition pattern of Heptachlor composition residues among various species of fishes

4.6 Total load of organochlorine residues among the different species of fishes studied

The total organochlorine load refers to the sum of all the individual organochlorine residues detected in each species of fishes received from Cochin and Rameshwaram. The residues reported in this section are considered irrespective of the quarters during which the fishes were collected.

The overall load of total OC residues among the seven species of fishes received from both Cochin and Rameshwaram is shown in fig4.6.(i).

Among the seven species of fishes received from Cochin, *Scomberomorus commersonn* recorded the maximum organochlorine concentration load (29.12 ± 4.93 ng/g) followed by *Rastrelliger kanagurta* (21.14 ± 3.01 ng/g). The minimum load among the species was in *Carangoides malabaricus* (12.87 ± 3.92 ng/g). The other species namely *Cynoglossus macrolepidotus, Nemipterus japonicus, Sardinella longiceps* and *Sphyraena barracuda* recorded 14.69 ± 2.4 ng/g, 17.05 ± 2.58 ng/g, 19.77 ± 3.93 ng/g and 20.8 ± 3.52 ng/g of residues respectively.

Among the seven species of fishes received from Rameshwaram, *Nemipterus japonicus* had the highest load of total OC (24.13 ± 2.87 ng/g) followed by *Sardinella longiceps* (23.14 ± 3.65 ng/g). The lowest load was in *Rastrelliger kanagurta* (10.37 ± 1.55 ng/g). *Carangoides malabaricus, Cynoglossus macrolepidotus, Scomberomorus commersonn* and *Sphyraena barracuda* recorded 16.40 ± 5.47 ng/g, 20.59 ± 4.20 ng/g, 18.8 ± 3.48 ng/g and 20.24 ± 4.82 ng/g respectively.

The overall picture shows total OC residue load was the maximum in Rameshwaram for all the species except *Scomberomorus commersonn* and *Nemipterus japonicus. Sphyraena barracuda* recorded almost similar load with respect to both the locations. The statistical analysis of the total organochlorine residues among the species was significant between *Carangoides malabaricus* and *Scomberomorus commersonn* ($P < 0.05$; F value – 2.21).

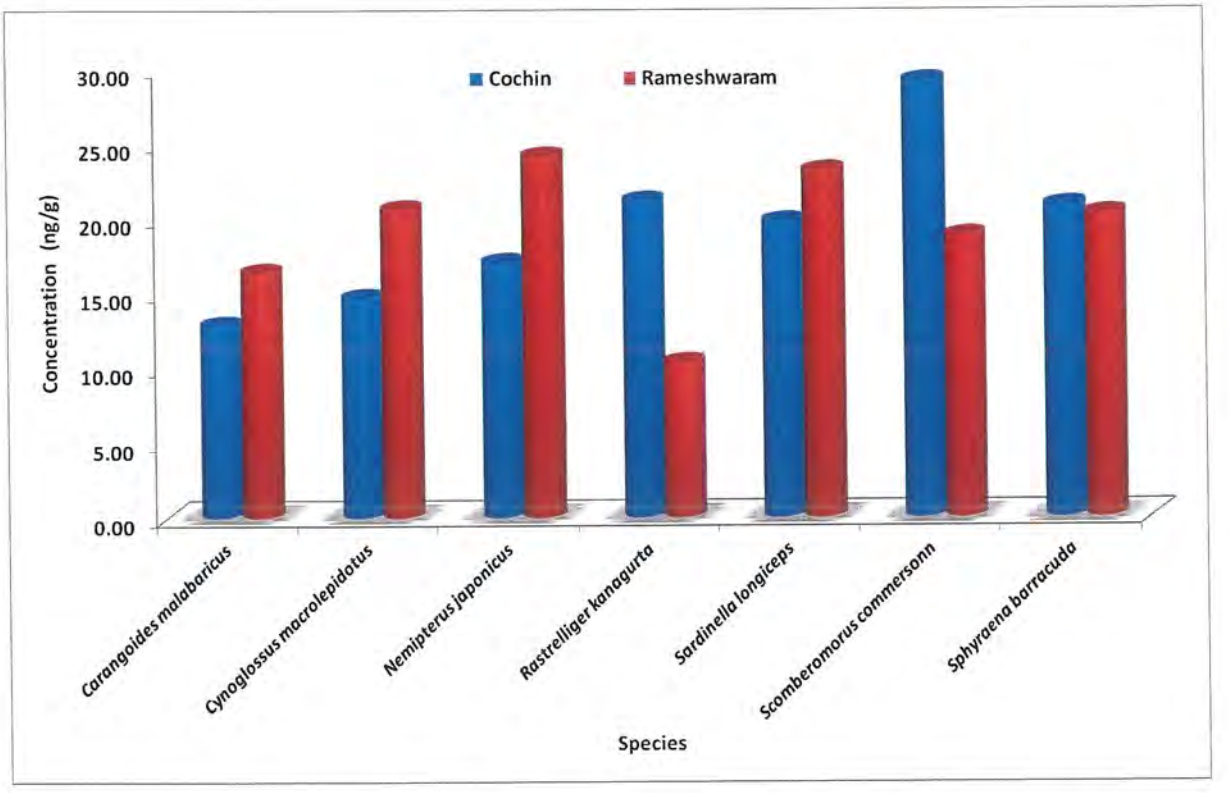


Fig 4.6 (i) Total Organochlorine pesticide load (ng/g) among the species of fishes received from Cochin and Rameshwaram

4.7 Correlation studies

An attempt was made to assess the correlation statistically between the organochlorine residues and the size of the fishes. The statistical tests revealed that a stronger positive correlation ($P<0.05$) existed between the organochlorine residues and the size (i.e., length and weight) for all the species of fishes except *Sardinella longiceps* and *Sphyraena barracuda* (Table 4.7).

Table 4.7 Correlation between the length of the fishes and the total organochlorine residues

S. No	Species	Total OC (Mean ± SD)	Length (cm) (Mean ± SD)	Weight (g) Mean±SD	r value	P value	Significance at 0.05 level
1	*Carangoides malabaricus*	14.23±26.61	22.2±1.9	143.9±30.8	0.37	0.01	S
2	*Cynoglossus macrolepidotus*	17.79±22.77	23.6±5.0	143.9±30.8	0.43	0.00	S
3	*Nemipterus japonicus*	20.28±22.55	18.4±3.1	98.8±55.9	0.23	0.02	S
4	*Rastrelliger kanagurta*	16.14±20.39	22.1±1.7	73.4±30.7	0.26	0.01	S
5	*Sardinella longiceps*	19.13±28.06	16.5±1.3	120.1±30.9	0.04	0.8	NS
6	*Scomberomorus commersonn*	23.57±20.09	49.5±11.9	37.3±7.2	0.80	0.03	S
7	*Sphyraena barracuda*	22.49±23.11	36.1±7.5	1134.4±872.3	0.24	0.22	NS

Correlation test between the sexes (all the species pooled together) and the organochlorine residues did not reveal any relation. In addition to that the test performed between the male and female fishes of individual species also did not show any significant correlation for all the species of fishes studied.

DISCUSSION

5. DISCUSSION

5.1 Selection of fish species

According to 1993 US EPA guidelines, the most important criterion for selecting target fish for contaminant monitoring programs and assessing human health concerns was that the species should be commonly consumed by the human beings in the study area and of commercial, recreational or subsistence fishing value. Two other criteria of major importance are that the species should have the potential to bioaccumulate high concentrations of chemical contaminants and have a wide geographic distribution. In the present study all seven fish species selected satisfied all the three above-referred criteria (Muralidharan *et al.,* 2009).

Although there are many studies on the levels of organochlorines (OC) in fishes in India, all are short term studies or one time sampling and hence they failed to explain the impact on consumers. Hence, there exists lacuna in spatio - temporal variations of OC pesticide residues in fishes in any given area. Moreover the pilot study done by Muralidharan *et al.,* (2009) in the same study area recommended the need for continuous monitoring of pesticide residues. Additionally most of the studies in India and worldwide (Shailaja and Nair, 1997; Mwevura *et al.*, 2002; Sankar *et al.*, 2006; Barasa *et al.*, 2008 and Sarkar *et al.*, 2008) also support the same fact. Hence, in the present study, select fish species were collected from Coimbatore market for a period of two years from October 2004 to September 2006 consisting of eight quarters; a period of three months was one quarter. This continuous monitoring exercise has provided information on the status of the organochlorine residues integrated over a period of two years.

5.2 Detection percentage of individual organochlorine pesticides

Marine fishes in the present study were analyzed for residues of a set of persistent organochlorine pesticides, namely α HCH, β HCH, γ HCH, δ HCH, *p,p'* DDT, *p,p'* DDE, *p,p'* DDD, α endosulfan, β endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide

and dieldrin. Out of 716 samples of fishes analyzed, it was found that no sample was free of residues. This emphasizes the fact that open seas play a role as a final sink for persistent toxic contaminants (Tanabe, 2000).

Among the organochlorines analyzed, HCH isomers such as α HCH, β HCH, γ HCH and δ HCH were detected in 57 %, 58 %, 52 % and 60 % of samples respectively. The detection frequencies of DDT metabolites were in the order of 40 % for *p,p'* DDT, 36 % for *p,p'* DDE and 32 % for *p,p'* DDD. Among the cyclodiene group, α endosulfan, β endosulfan, endosulfan sulfate and dieldrin were detected in 48 %, 43 %, 16 % and 48 % of samples whereas heptachlor and heptachlor epoxide were detected in 48 % and 64 % of samples respectively. However, the residue levels are considerably less when compared with the study done by Muralidharan *et al.* (2009). The declining trend of these residues was also reported by Babu Rajendran *et al.* (2005) and Chakraborty *et al.* (2010).

Although the use of the chlorinated pesticides has been curtailed, the chemical and physical stability of these compounds have resulted in their continuing presence in the environment and food chain (Sannino *et al.*, 1996). Inspite of being reported that the residue burden in fish has been observed to decline since the banning of many organochlorine insecticides in western countries (Murty, 1986), the presence is continued in fish from different regions of developing countries (Kole and Bagchi, 1995; WHO, 2000 and Dhananjayan and Muralidharan, 2011).

Despite the long time restriction or ban on the use of these organochlorine compounds, the contamination pattern in the present study may be attributed to the pollution from large number of industries, anthropogenic and agricultural activities, i.e., soil percolation, air drift or surface runoff, leaching, disposal of empty containers and manufacturing units throughout the year locally. Further, these OCPs end up in groundwater and their transformation products may remain for years (Mudiam *et al.*, 2011). The lipophilic nature of these pesticides is an added disadvantage. As the cell walls in human beings and fishes are also made of lipoproteins, the problem assumes a greater significance. Many

organic pesticides and trace elements are hydrophobic; that is, in aquatic environment they tend to be associated with sediment and biological tissues rather than dissolved in water. As a result, they can be biomagnified through food chains and produce harmful effects at every level (Muralidharan *et al.*, 2009). The results further demonstrate an accumulation of pesticide residues through food chain (from soil- water- sediments- fish- human) which is a serious matter of concern (Jeyaratnam, 1985; Igbedioh, 1991; Forget, 1993; Begum *et al.*, 2009; Muralidharan *et al.*, 2009 and Mudiam *et al.*, 2011).

5.3 Spatial variation in the levels of organochlorine residues among various species of fishes studied

The documentation of the residue pattern of 13 individual organochlorines in the commercially important marine fishes showed varying levels of these residues. The spatial variation observed for the individual organochlorine pesticide residue was not highly remarkable except a few. However, the variations in the concentration of the organochlorines among various species of fishes included in the study were compared with similar studies done elsewhere.

5.3 (i) *Carangoides malabaricus*

Residues of HCH isomers, namely α, β, γ and δ HCH in *Carangoides malabaricus* were higher in the fishes of Rameshwaram than Cochin except β HCH. The levels recorded in the present study were several folds higher than the levels reported by Sankar *et al.* (2006), in *Pamphia malabaricus* (0.94 ng/g) collected along the west coast. Similarly the γ HCH residues in *Pamphia malabaricus* in the above referred study were about 0.59 ng/g. The levels of α HCH, β HCH and γ HCH recorded in our study are higher than in the study referred above. More over the residues of the individual organochlorines in the inland waters and the freshwater biota along the east and west coast were found to have similar pattern of residues (Shailaja and Nair, 1997; Babu Rajendran *et al.*, 2005 and Sankar *et al.*, 2008).

Residues of *p,p'* DDT was higher (2.91 ± 1.73 ng/g) in *Carangoides malabaricus* received from Cochin than Rameshwaram (1 ± 0.6 ng/g). These levels were however comparable with the levels (1.1 ng/g) of DDT in *Epinephelus malabaricus* reported by Mwevura *et al.* (2002). The occurrence of DDT metabolites at high concentrations in the marine environment of the west coast of India is evidently documented by Pandit *et al.*(2006).

Of all the OC pesticide residues in *Carangoides malabaricus*, levels of only heptachlor were significantly different between Cochin and Rameshwaram. This could be attributed to the past usage pattern of heptachlor as an insecticide along the eastern coast of India (Verlecar *et al.*, 2006). The variations in the organochlorine residues could also be attributed to the feeding habit of *Carangoides malabaricus* which is a benthic feeder (Karunagaran *et al.*, 1994).

5.3 (ii) *Cynoglossus macrolepidotus*

Among the HCH isomers analysed in *Cynoglossus macrolepidotus*, α HCH was higher in fishes from Cochin (1.51 ± 0.61 ng/g) than from Rameshwaram (1.36 ± 0.56 ng/g). However, β HCH was significantly higher in Rameshwaram fishes (5.28 ± 1.82 ng/g) than the Cochin fishes (2.59 ± 0.88 ng/g). Similarly the γ HCH residues were also higher in Rameshwaram (1.13 ± 0.58 ng/g). These levels were found to be higher than the HCH residues in Lemon sole reported by Green and Knutzen (2003) in the Norwegian coast. They recorded a level of 0.03 ng/g of α HCH and 0.11 ng/g of γ HCH. When the levels were compared with the study done by Muralidharan *et al.* (2009) in the same species received from Rameshwaram, it is quite lower.

Similarly, residues of only *p,p'* DDT were at detectable levels and was higher in Rameshwaram fishes. The same trend was observed for DDT residues also. But when compared with the study of Green and Knutzen (2003) which recorded about 10.1 ng/g of DDT residues, the levels recorded in the present study are lower.

The mean total endosulfan residues in *Cynoglossus macrolepidotus* as reported by Muralidharan *et al.* (2009) was about 13 ng/g. When compared to this, the levels of total

endosulfan residues in the present study are several folds lower i.e., around 1.5 ng/g. This reduced level reflects the declining trend of these groups of chemicals in the east as well as west coast of India. However, the presence of detectable levels of chlorinated cyclodiene pesticide in marine ecosystem is due to their past use and continued atmospheric transport from remote regions (Muralidharan *et al.,* 2009). However, there exists a lacuna in the availability of information on the same species at different locations. Hence extensive comparison becomes difficult.

5.3 (iii) *Nemipterus japonicus*

Nemipterus japonicus in the present study recorded the maximum concentration of residues in the fishes of Rameshwaram than from Cochin, with 2.05 ± 0.97 ng/g of α HCH, 7.10 ± 2.03 ng/g of β HCH, 1.13 ± 0.23 ng/g of δ HCH, 5.27 ± 1.04 ng/g of *p,p'* DDT and 1.24 ± 0.33 ng/g of heptachlor.

The organochlorines analysed in 12 edible organisms from the Adriatic Sea, Italy had shown the presence of 0.96 ng/g of lindane in pelagic fish and 0.32 ng/g of β HCH in mackerel, whereas the same residues in pelagic fish (*Nemipterus japonicus*) are higher in the present study. But still the levels in both the studies were not above the MRL level for HCH isomers (Muccio *et al.,* 2002).

Among the isomers of HCH residues, δ HCH is found to vary significantly between Cochin and Rameshwaram only in *Nemipterus japonicus.* This could be certainly attributed to the feeding habit of the fishes. As *Nemipterus japonicus* belongs to demersal fishes which feed on the planktonic community in the surrounding water, the HCH residues in the biota have high variations between the east and west coast as reported by Sankar *et al.* (2006) and Babu Rajendran *et al.* (2005). However, the variations in HCH residues between the two locations were not relevantly significant.

Further, another study by Karunagaran *et al.* (1994) reported highest concentration of *p,p'* DDE in *Nemipterus japonicus* to be 2 ng/g which is lower than the levels recorded in the present study.

The heptachlor epoxide residues as reported by Muralidharan *et al.* (2009) were around 1 ng/g in all the fishes studied. The present study however has reported less than 1 ng/g of heptachlor residues. But still the range was as high as 77.66 ng/g in the bottom feeders such as *Nemipterus japonicus.*

5.3 (iv) *Rastrelliger kanagurta*

Among the organochlorine compounds analyzed in *Rastrelliger kanagurta,* only residues of β HCH, *p,p'* DDT and α Endosulfan were significantly varying between two locations. Organochlorines recorded in 12 edible organisms from the Adriatic Sea, Italy had shown 0.32 ng/g of β HCH in mackerel (*Rastrelliger kanagurta*) whereas the residues in the same species were higher (4.0 ± 0.7 ng/g) in the present study. But still the levels in both the studies were not above the MRL for HCH isomers (Muccio *et al.*, 2002).

Various organochlorines at different locations along the east and west coast of India, and their variation among locations along Indian coast were reported by Pandit *et al.* (2006). The study reported 25.09 ng/g, 5.70 ng/g and 5.36 ng/g of *p,p'* DDT, *p,p'* DDE and *p,p'* DDD in R*astrelliger kanagurta* respectively. The same species in the present study recorded the maximum of 5.62 ng/g of *p,p'* DDT, 14.39 ng/g of *p,p'* DDE and 4.2 ng/g of *p,p'* DDD. Higher residues of *p,p'* DDE indicate the metabolisation of DDT to DDE. However, the other species in the present study recorded higher concentrations of *p,p'* DDT. DDT, one of the most notorious pesticides of all time, is being used even today in India on a larger amount to control malaria, despite its ban in most other countries. Since malaria is still a serious health problem in different parts of our country, the present perception of DDT use is reasonable in India (Mishra *et al.*, 2012). This indicates the fresh input of DDT into the marine environment.

Mwevura *et al.* (2002) reported that the levels and occurrence of residues in biota seem to be governed by feeding habit, age and mobility of the biota. With reference to this statement, the species such as *Rastrelliger kanagurta* and *Sardinella longiceps* which are the benthic feeders, recorded high level of DDT residues in the present study than the other species. The residues recorded in the marine biota in the above referred study were also higher than the levels recorded in the present study. But the levels were below FAO/WHO maximum acceptable limits in fish and sea food (200 mg/kg f.w., FAO/WHO 1986) and Canadian maximum allowable limits in fish (500 mg/kg f.w., McDonald 1994). Further the spatial variations in organochlorines recorded in *Rastrelliger kanagurta* in the above referred studies (Mwevura *et al.*, 2002 and Pandit *et al.*, 2006) were not significant.

5.3 (v) *Sardinella longiceps*

Sardinella longiceps sampled in the present study did not show any significant variation in the organochlorines between the locations studied. However, it was comparable with a few studies available in Indian context.

On comparison with the study of Muralidharan *et al.* (2009), the residues were much lower in the fishes of both the locations of the present study and were comparable with the study of Pandit *et al.* (2006). The ratio of *p,p'* DDT to *p,p'* DDE greater than one in the present study also indicates the recent use of technical grade DDT, which is evidently supported. The DDT residues are found to occur more in the fishes having high fat content such as *Rastrelliger kanagurta,* which is almost coherent with the study of Muccio *et al.* (2002).

5.3 (vi) *Scomberomorus commersonn*

Individual OC residues, namely β HCH and heptachlor epoxide residues in *Scomberomorus commersonn,* varied significantly between the locations studied. These variations in among the species can be attributed to the lipid content of the fishes and also their feeding mode and mobility (Muccio *et al.*, 2002). The spatial variation of these compounds

could be due to metabolic activity influenced by various physical factors in the marine environment (Schmitt *and* Dethloff, 2000).

Residues of all the other compounds included in the present study were high. The DDT residues were found to be more in fishes with high fat content in *Scomberomorus commersonn*, as reported by Muccio *et al.* (2002). The variations among species was also attributed to fat content as explained by Karunagaran *et al.* (1994).

5.3 (vii) *Sphyraena barracuda*

The mean concentration of α HCH in *Sphyraena barracuda* analyzed in the present study ranged from 6.61 ng/g to 11.31 ng/g which were several folds higher than the levels reported by Sankar *et al.* (2006) in *Sphyreana jello* (0.04 ng/g) along the west coast. Similarly β HCH residues in *Sphyraena jello* in the above referred study were about 0.28 ng/g. All the levels of α HCH, β HCH and γ HCH recorded in our study was higher than the referred study. However the variations in the residues observed between the locations were not significant.

The levels recorded in the present study were more or less comparable with a few species referred as barracudas collected along the east coast by Karunagaran *et al.* (1994). The levels have been attributed to the feeding habit of the fishes. However the comparison could not be made very extensively due to lack of adequate studies in the referred species.

In addition to a very few studies available in Indian context for comparison, the spatial variation in the organochlorine residues in the present study shows the contamination status of the Indian marine environment along the east and west coast. The variation levels also agree with the residue pattern of organochlorines analysed in various samples such as marine water, sediments and biota. Thus the spatial variation of organochlorine residues in the marine fishes discussed in the present study fulfils the objective and gives a clear picture of the status of organochlorine residues.

5.4 Temporal variation in the levels of organochlorine residues among various species of fishes

The samples included in the present study were collected across eight quarters. Each quarter varied with their own physiographic and climatic conditions depending on the time scale. Generally these variations greatly influence the accumulation pattern of residues in the fishes. Hence the temporal variation observed for the total HCH, total DDT, total endosulfan, heptachlor epoxide and dieldrin in various species of fishes included in the present study have been discussed in the following section.

5.4 (i) Total HCH

The total HCH residues in *Carangoides malabaricus, Cynoglossus macrolepidotus, Nemipterus japonicus* and *Sardinella longiceps* had raised significantly during quarter VII and VIII. Similarly the residues in *Sphyraena barracuda* were high during quarter VII. The drastic rise of the residues during the VII and VIII quarter may be due to the use pattern of these chemicals across the coastal regions and its continued input into the marine environment (Babu Rajendran *et al.,* 2005). The residue pattern during these quarters resembled the pattern in sediment and water samples reported by Pandit *et al.* (2006) and Sarkar *et al.* (2005).

The temporal variation in total HCH residues observed in the above referred species during quarter VII and VIII may be partially attributed the higher magnitude of transportation of pollutants to the ocean waters. Sarkar *et al.* (1997) reported the concentration of various contaminants in the Indian marine environment was remarkably high during the post monsoon period. Supporting to this fact the quarter VII and VIII falls on the premonsoon season. However the temporal variation in the contaminant load influenced by several factors in also may result in the variation of residues (Sarkar *et al.,* 2008 and Muralidharan *et al.,* 2009).

The total HCH residues in *Rastrelliger kanagurta* were at varying levels across the quarters. These variations were significant during quarter I, IV and VII. The temporal variation in HCH residues observed in *Rastrelliger kanagurta* may be considered as the

combined effect of compound isomerisation and difference in contamination pattern of the coastal regions also may result in the variation of residues (Barasa *et al.,* 2008; Sarkar *et al.,* 2008 and Muralidharan *et al.,* 2009).

Scomberomorus commersonn showed a different pattern of temporal variation. It significantly varied in total HCH concentration of during the II quarter. However, it has been stated that the monsoonal rains during the II quarter as well as the pelagic feeding habit, high lipid content and the habitat of the fishes are the contributing factors for their variation in the organochlorine residues (Nayak *et al.,* 1995 and Shailaja and Nair, 1997). The temporal variation in HCH residues among the fishes is related to the volatilization and sedimentation coefficient reactions that are happening in the marine environment. This process is found to have a great influence over the isomerisation process of the HCH residues (Barasa *et al.,* 2008). However, in the current exercise, such informations were not gathered.

5.4 (ii) Total DDT

The total DDT residues in *Carangoides malabaricus, Cynoglossus macrolepidotus* and *Sardinella longiceps* had raised significantly during quarter VII. Similarly the residues in *Sphyraena barracuda* and *Nemipterus japonicus* were significantly high during quarter VII. Similar to HCH, the temporal variation in DDT residues can also be attributed to the post monsoonal input of the residues into the marine environment (Sarkar *et al.,* 1997 and Barasa *et al.,* 2008).

The temporal variation of DDT can also be attributed to the recent input of these residues into the environment and the change in Bioconcentration factor (BCF) of the fishes with relation to temperature. Thus the temperature fluctuation in water has a tendency to change the BCF of fishes and thereby the residue accumulation (Barasa *et al.,* 2008 and Muralidharan *et al.,* 2009).

The DDT residues in *Rastrelliger kanagurta* varied significantly during quarter II. There are studies which report higher dissemination rate of the DDT metabolites in the water during rainy and monsoonal seasons (Barasa *et al.*, 2008 and Sarkar *et al.*, 2008) Quarter II being a post monsoonal period, the occurrence of DDT residues may be due to higher bioaccumulation rate in the fishes (Sankar *et al.*, 2006).

DDT is likely to rapidly volatilize in the tropical environment (Wania and Mackay, 1993). The high temperatures prevailing in the tropics could also enhance the elimination rate of chemicals in the fish, as the biological half-lives of the semi volatile compounds such as DDT are short at high temperatures (Kannan *et al.*, 1995). However the present study has recorded significantly high levels of DDT residues during quarter VI and VII.

In the seawater and sediment samples the conversion of DDT is found to be very less, which can be attributed to the fresh input of DDT. The input of DDT into the marine environment may be due to its continuous usage in India even today on a larger amount to overcome malaria situation, despite of its ban in most of the countries (Mishra *et al.*, 2012). Hence, the temporal variation in DDT residues clearly indicates the behavior of DDT residues over time and its accumulation pattern in the marine fishes.

5.4 (iii) Cyclodiene pesticides

Among the cyclodiene group of pesticides only the total endosulfan residues were varied significantly during quarter V in *Rastrelliger kanagurta* and quarter VI in *Sphyraena barracuda* respectively. Similarly the endosulfan residues in *Scomberomorus commersonn* were significantly high during quarter II and V.

It has been reported that next to HCH and DDT, the residues found to be higher in the marine environment is endosulfan. The temporal variations in these may be due to the fresh input in to the marine environment through agricultural runoff and higher rate of influx of these contaminants in the marine environment (Sarkar *et al.*, 2008).

The endosulfan residues in fishes during the dry and wet seasons were considerably varying along the Indian Ocean coast in Kenya (Barasa *et al.*, 2008) which is concurrent with the present study.

The temporal variation of cyclodiene residues was not high when compared to the HCH and DDT residues. Moreover since these compounds recorded very low residues in the fish species studied.

The temporal variation in the organochlorine residues among the species was highly significant particularly for HCH and DDT residues. Certain uniform pattern of variation could be observed among the species. The striking fact in the temporal variation is the post tsunami effects which have resulted in food source. This effect subsequently perhaps reflected in reduction in the occurrence of organochlorine residues in the marine environment. As a result invariably all the species included in the present study have recorded low levels of organochlorine residues during the post tsunami period i.e., quarter III and IV. Due to lack of temporal studies on the residue pattern of the organochlorine pesticides, particularly on the east coast, extensive discussion becomes difficult. However, the temporal variation discussed above clearly indicates the behavior of the contaminants over time and their accumulation pattern in the marine fishes.

5.5 Variation in organochlorine pesticide residues among the different species of fishes received from Cochin and Rameshwaram

The seven species of marine fishes included in the current study were selected based on socio economical, physiological and toxicological criteria. These fishes were analyzed for the presence of 15 individual organochlorine pesticide residues. The information on the variation pattern of the individual organochlorines will give a better picture of the contamination pattern of these edible fishes. Hence, the variation in organochlorine residues among the species was examined.

5.5 (i) HCH isomers

Residues of HCH isomers namely, α HCH, β HCH, γ HCH, δ HCH were recorded at varying levels among the species included in the study. However the variation in all these isomers was not significant. However, the levels recorded in the present study were discussed in comparison with similar studies conducted elsewhere.

The levels of all the HCH isomers were around ten folds lower than the levels reported by Muralidharan *et al.* (2009) in the same species studied. These reduced levels could perhaps include declining trend of these groups of chemicals in the east as well as west coast of India.

Among the HCH isomers, α HCH is the primary isomer. The mean concentration levels of α HCH in the present study ranged from 6.61 ng/g to 11.31 ng/g which were several folds higher than the levels reported by Sankar *et al.* (2006), from Calicut, Kerala, in certain species of marine fish and shellfish namely, *Megalaspis cordyla* (0.16 ng/g), *Sphyraena jello* (0.04 ng/g) and *Trichiurus savala* (0.07 ng/g), *Pamphia malabaricus* (0.94 ng/g) and *Sepia* sp. (0.03 ng/g) respectively. The multi compartment monitoring of residue levels of OCPs in coastal marine environment of Mumbai, done by Pandit *et al.* (2006) had reported α HCH residues in the range of 0.87 mg/g to 5.3 mg/g in the marine biota. These levels, when compared with our study, having a range of < BDL to 173.8 ng/g were found to be several times lower. The presence of lower level of α HCH residue in the marine biota of Mumbai has been attributed to the tropical climate, which induces rapid volatilization. The high temperature was found to enhance the elimination rate of chemicals in fish, as the biological half lives of compounds like HCH were shorter at high temperature. This factor also lowers the residence time of the compounds in the environment (Wania and Mackay 1993).

In contrary to that α and β HCH in the species of the present study indicates the continuous input of these chemicals as well as their persistent nature and higher

accumulation capacity of the fishes. Most of the studies done in India as reviewed by Sarkar *et al.* (2008) show similar pattern as observed in the present study.

Among the isomers of HCH, β HCH has been reported as the most persistent isomer (ECO/OPS/OMS/1995). Although the variation was not significant the occurrence of β HCH in large number of samples indicates its persistent nature. The predominant occurrence of β-HCH, the most persistent form (Burke *et al.,* 2003), is due to the isomerisation of α and γ HCH into β HCH in seawater and sediment and also due to its high stability (Jensen, 1983). It was the compound with the highest concentration with its consequent accumulation in the fatty tissue of marine organisms and humans (Barkatina *et al.,* 2002).

Presence of high concentrations of β HCH has been reported in various biological components (Nayak *et al.,* 1995; Kumari *et al.,* 2001 and Kole *et al.,* 2001), and in human milk tested in Delhi (Nair *et al.,* 1996). Sankar *et al.* (2006) reported the β HCH residues in *Sphyraena jello* which were higher than the levels recorded in the same genus in the present study. Moreover, it is also reported that β HCH will accumulate 10 to 30 times more in fatty tissues than lindane (Heeschen, 1980). The review article by Sankar *et al.* (2008) reported the concentration levels of β and γ HCH residues in the sediments and fishes, which are similar to our study. An understanding of the environmental pathway is required to predict its environmental behavior. In this regard, the physical and biological factors contributing to the transport of α HCH and its conversion to β HCH is well explained by Li *et al.* (2002).

The γ HCH contributes to the major composition in the technical grade HCH used in India (Sarkar *et al.,* 2008). The presence of γ HCH in the fishes of the present study indicates its recent usage and input into the marine environment. Sankar *et al.* (2006) reported of 0.59 ng/g of γ HCH residues in *Pamphia malabaricus.* The ranges and mean concentration levels of γ HCH in both the studies were at comparable levels.

The levels of organochlorine pesticide residues in edible biota from coastal area of Dar es Salaam City has reported the presence of 1 ng/g, 0.5 ng/g and 0.8 ng/g of γ HCH in *Scylla serrata* from fresh water, *Epinephelus malabaricus* and *Scylla serrata* from marine water respectively. These levels were similar to the levels reported in our study. The levels and occurrence of residues in biota samples seem to be governed by feeding mode and mobility of the biota (Mwevura *et al.*, 2002). The organochlorines analysed in 12 edible organisms from the Adriatic Sea, Italy have shown the presence of 0.96 ng/g of lindane in pelagic fish and 0.32 ng/g of β HCH in mackerel, whereas the same residues in pelagic fish (*Nemipterus japonicus*) and mackerel (*Rastrelliger kanagurta*) were higher in the present study. But still the levels in both the studies were not above the MRL level for HCH isomers (Muccio *et al.*, 2002).

The recorded levels of γ HCH in the samples were comparable with the levels of lindane in frozen fishes and fish products meant for consumption in Republic of Belarus. The levels were well below the FAO limit of 2 mg/kg (Barkatina *et al.*, 2006). The highest levels in human milk were reported from India, this is likely to reflect the high usage of lindane and technical HCH in the country. (Burke *et al.*, 2003).

Barasa *et al.*, (2008) reported higher concentration of γ HCH in the sampled fishes suggesting higher rates of continued usage of technical HCH formulations for soil treatment, foliage application on fruit and nut trees, vegetables and ornamentals, timber and wood protection. He also adds that the transportation of pollutants to the ocean waters and subsequent bioaccumulation in marine fish samples would have occurred.

The ranges and mean concentration levels of δ HCH in the fishes studied by Pandit *et al.* (2006) were comparable with the present study. Mostly all the studies dealing with the organochlorine pesticide residues, particularly HCH isomers have recorded low levels of δ HCH residues. The poor stability of the δ HCH isomer is also considered as a factor contributing to its lower residues in the environmental components. Further, most of the studies do not deal with the concentration of δ HCH separately. Added to this fact,

technical grade HCH is being extensively used in India, and its environmental dissipation plays a major role in the occurrence of which is found to have lower composition of δ HCH residues in the marine environment (Sarkar *et al.*, 2008).

Thus the overall trend of HCH residues in the present study indicates a chronic accumulation. Though the levels are not alarming, it may be expected to create physiological changes in fishes as well as health effects in humans in a long run.

5.5 (ii) DDT metabolites

Similar to HCH, the residues of DDT metabolites, namely *p,p'* DDT, *p,p'* DDE and *p,p'* DDD in the present study were recorded at varying levels. Among the DDT metabolites studied, only *p,p'* DDT residues were varying significantly between *Carangoides malabaricus* and *Nemipterus japonicus*. The variation in *p,p'* DDT metabolites were attributed to higher fat content in *Carangoides malabaricus* and *Nemipterus japonicas* (Karunagaran *et al.*, 1994). Although the variations were not significant, the residue levels of DDT metabolites recorded in the present study were discussed in comparison with similar studies.

The residues of DDT metabolites recorded in the present study were 10 folds lower than the levels recorded by Muralidharan *et al.* (2009) in the same species of fishes. However, the ratio of *p,p'* DDT to *p,p'* DDE (>1) indicates the fresh input of these chemicals into the marine environment. This is because of its low cost and non availability of viable alternative, and hence the residues in the environment (Singh, 2001). Sankar *et al.* (2006) reported 0.2 ng/g of *p,p'* DDT in a marine fish species, *Saurida tumbil*. This level was highly similar to the levels in the species included in the present study. Moreover, the species of the present study, though different, has vast similarities to the species that was reported by Sankar *et al.* (2006). It has also been reported that with a high half life of 10 to 20 years (Sericano *et al.*, 1990). DDT undergoes degradation to DDE and DDD. The pattern of DDT compounds in the fishes indicates the availability or use of DDT in these areas is very limited but the metabolites of DDT are still in the environment.

The concentrations of *p,p'* DDT, in R*astrelliger kanagurta* along Indian coast as reported by Pandit *et al* (2006) is about 25.09 ng/g. The same species in the present study has recorded the maximum of 5.62 ng/g of *p,p'* DDT. However the other species included in the present study has recorded higher concentrations of *p,p'* DDT. This indicates the fresh input of DDT into the marine environment. But the exact area of use cannot be said for various reasons. The distribution of chemical species in a multiphase system is governed by physical and chemical properties such as vapor pressure, water solubility, octanol-water partition coefficients and bioconcentration factors (BCF). Despite the high quantity of consumption, HCH and DDT residues in fish in India are lower than those in the temperate countries suggesting a lower accumulation in tropical fish, which could be due to rapid volatilization of this insecticide in the tropical environment. The high temperature in the tropics also enhances the elimination rate of chemicals in fish as the biological half-lives of semi volatile compounds such as DDT are short at high temperatures (Pandit *et al.,* 2001).

The concentrations of *p,p'* DDT, *p,p'* DDE and *p,p'* DDD in R*astrelliger kanagurta* along Indian coast as reported by Pandit *et al.* (2006) is about 25.09 ng/g, 5.7 ng/g and 5.36 ng/g respectively. The same species in the present study has recorded the maximum of 5.62 ng/g of *p,p'* DDT, 14.39 ng/g of *p,p'* DDE and 4.2 ng/g of *p,p'* DDD respectively. The higher residue of *p,p'* DDE indicates the metabolisation of DDT to DDE. However, the other species, namely, *Sardinella longiceps* and *Scomberomorus commersonn* in the present study have recorded higher concentrations of *p,p'* DDT. DDT is being used even today on a larger amount in India to overcome malaria situation, despite of its ban in most of the countries (Mishra *et al.,* 2012). This indicates the fresh input of DDT into the marine environment.

The high frequency of occurrence of *p,p'* DDE is due to its past use along the coastline or the residues brought by rivers through runoff and erosion. Stefanalli *et al.* (2004) reported the presence of *p,p'* DDE levels up to 25 ng/g which was higher than the levels of the present study.

Concentrations of *p,p'* DDE found in our study are also lower than the levels reported in fishes of Ganges Estuary, Bangladesh (1-2 ppb) (Jabber *et al.*, 2001). The comparison with these studies clearly shows the declining trend of these chemicals in the Indian marine environment. However, it is now accepted that *p,p'* DDE may have sublethal impacts on reproduction and may cause genetic disorders in fishes (Landis *et al.*, 1997). Accordingly species namely, *Rastrelliger kanagurta* and *Carangoides malabaricus* of the present study have higher residue of *p,p'* DDE than *p,p'* DDT indicating the transformation process (Barasa *et al.*, 2008).

In the present study, concentration of *p,p'* DDD ranged from below detectable level to 10.13 ng/g. The OCP residues in different fishes obtained from different locations along the Indian Ocean coast of Kenya, showed less concentration of *p,p'* DDT than its metabolite, *p,p'* DDD. The higher concentration of *p,p'* DDD than those of *p,p'* DDE suggested anaerobic transformation of parent *p,p'* DDT. Since *p,p'* DDE is less toxic than *p,p'* DDT, the transformation of the parent compound probably represents a good protective mechanism in fish Barasa *et al.*, 2008).

The DDT and its metabolites are considered to be neurotoxins and endocrine modulating agents that cause cancer in laboratory animals (Sax, 1984). Sankar *et al.* (2006) had reported 0.13 ng/g of *p,p'* DDD in the marine fish *Saurida tumbil*. Similarly the other species such as *Megalospis cordyla, Ttrichirius savala, Johnieops dussumieri, Perna viridis, Pamphia malabaricus* and *Sepia* sp. had recorded the concentrations of 0.02 ng/g, 7.39 ng/g, 0.05 ng/g, 0.16 ng/g, 0.1 ng/g and 0.01 ng/g of *pp'* DDD respectively.

These levels were highly concordant to levels recorded in the species of fishes included in the present study. Moreover, the species of the present study, though different, have vast similarities to the species referred (Sankar *et al.*, 2006). But still these residues were not significantly varying among the species.

In marine biota, DDT is mostly converted into its metabolites, namely DDE and DDD, which could be due to its short biological half-life and it is more so in tropical regions. In the seawater and sediment samples the conversion of DDT was found to be very less (Sarkar *et al.,* 2008). Thus from the above facts, it is clear that the DDT and its metabolites (*p,p'* DDT, *p,p'* DDE and *p,p'* DDD) even after the ban in India, continues to exists in its coastal environment, particularly in fishes. But there is a clear declining trend over the years in the concentrations of DDT metabolites. The data also suggest the fresh input of DDT entering into the marine environment. This is because; DDT is still used for certain public health activities in India and also in a few other countries. Continued ecocoordinated monitoring is needed across regions to keep track of the notorious chemical's fate.

5.5 (iii) Cyclodiene pesticides

The Cyclodiene group of pesticides namely α endosulfan, β endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide and dieldrin were used mainly to control agricultural pests, insect born diseases and for termite control. The present study has recorded considerable concentrations of these pesticides. However, the variations in only endosulfan sulfate residues were significant between *Scomberomorus commersonn* and *Sphyraena barracuda*. These variations among the species can be attributed to the lipid content of the fishes and also the feeding mode and mobility of the biota (Muccio *et al.,* 2002).

Endosulfan residues in fishes during the dry and wet seasons were considerably varied along the Indian Ocean coast in Kenya (Barasa *et al.,* 2002). But the present study does not show any variation. The α endosulfan residues in the fishes of present study ranged between below detectable level to 31.81 ng/g in the fishes. These levels were higher than residues were certain fishes such as Boi, Black fish and prawn collected across the east and west coast of India (Pandit *et al* 2001). Sediment samples had also recorded about 0.05 to 1 ng/g in the same study.

Beta (β) Endosulfan residue levels showed similar trend as that of α Endosulfan. Venugopalan and Rajendran (1984) had reported 0.1 to 0.4 ng/g of endosulfan residues in the marine zooplanktons of Vellar estuary along the west coast. In terms of order of magnitude of contamination; they had also rated endosulfan to be the least. But in the species included in the present study, the higher concentrations of endosulfan were recorded in all the fish species analysed.

Mean total endosulfan residues in species, namely *Nemipterus japonicus, Sardinella longiceps, Carangoides malabaricus, Cynoglossus macrolepidotus* and *Rastrelliger kanagurta* as reported by Muralidharan *et al.* (2009) were 11, 19, 21, 5, 13 and 23 ng/g respectively. When compared to this, the levels of total endosulfan residues in the present study were several folds lower i.e., around 1.5 ng/g. These reduced levels are an indication to the declining trend of this group of chemicals in the east as well as west coast of India. However presence of detectable levels of chlorinated cyclodiene pesticide in marine ecosystem is due to their past use and continued atmospheric transport from remote regions. The Supreme Court of India vide its order dated May 13th 2011 has banned manufacture, sale, use and export throughout India. Hence it may be noted that in India, until very recently endosulfan was in use.

The mean endosulfan sulfate residues were significantly higher in *Scomberomorus commersonn* (1.14 ng/g) with the range being below the detection limit to 30.31 ng/g. Total endosulfan residues (α, β and endosulfan sulfate) detected in Salton Sea fish were comparatively lower and reflective of the present study (Reidel *et al.,* 2002). The recovery studies of different fat contented fishes as reported by Sun *et al.* (2003) showed higher recovery rates of endosulfan sulfate i.e. (266.5 %). This indicates that higher fat content in *Scomberomorus commersonn* might have attributed to the higher endosulfan concentration.

Among many species of fishes studied in Calicut region, only *Pamphia malabaricus* and *Sepia* sp. had recorded 0.02 and 0.12 ng/g of heptachlor residues respectively. These

levels were lower than the levels in the present study (BDL to 77.66 ng/g). Even the fresh water fishes such as *Itropus suratensis* recorded 0.07 ng/g of heptachlor while *Epinephelus* sp., *Latjanus revalatus* and *Mugil cephalus* recorded 0.1 ng/g, 0.06 ng/g and 0.25 ng/g of heptachlor epoxide respectively. Further heptachlor epoxide residues were higher than heptachlor residues which are similar to the present study (Sankar *et al.*, 2006).

Heptachlor and heptachlor epoxide residues in various species of fishes in lake Tanganyika ranged from non detectable levels to 12.3 ng/g and 14.1 ng/g respectively. These levels are found to be higher than the levels recorded in the present study though expressed in fat weight basis (Manirakiza *et al.*, 2002). The Salton Sea fish captured near shore had recorded heptachlor and heptachlor epoxide in a range of 0.12 ng/g and 0.07 ng/g to 0.13 ng/g respectively (Reidel *et al.*, 2002). These levels were several folds lower than the present study. However, the variations observed among the species were not statistically significant.

Heptachlor epoxide residues as reported by Muralidharan *et al.* (2009) were around 1ng/g in all the fishes they had sampled. The present study however has reported less than 1 ng/g of heptachlor epoxide residues. But still the levels were as high as 77.66 ng/g in bottom feeders, namely *Nemipterus japonicus*.

Although the referred pesticides are banned in India, residues of dieldrin, chlordane and heptachlor epoxide have been reported in various environmental components in India. It is to be noted that many pesticides which have been banned/ severely restricted in many countries of the world but are still being used in India.

Fishes such as Navaga, Bull trout, Cods and Herring from White sea had recorded about 0.73, 0.1, 0.07 and 0.72 ng/g of heptachlor epoxide residues and 0.52, 0.03, 0.05 and 0.17 ng/g of heptachlor residues respectively. Those levels were lower than the mean heptachlor residues recorded in the fishes of the present study. Incidentally species of

both locations have similar feeding habits (Muir *et al.*, 2003). The White fish of the Great lakes was found to contain 9.4 ng/g of heptachlor epoxide residues, which is higher than the mean residues recorded in the present study. (Gerstenberger *et al.*, 1997). However the variations observed among the species were not statistically significant (P> 0.05).

Nevertheless the presence of heptachlor and heptachlor epoxide clearly indicates that these chemicals are being used illegally somewhere and being transported through ocean current.

Dieldrin residues which ranged from BDL to 13.16 ng/g in the present study was higher than the levels (0.16 ng/g) recorded in *Megallospis cordyla* and also in the fresh water fishes such as *Platicephalus* sp. (0.09 ng/g) *Epinephelus* sp. (6.09 ng/g) and in *Lutjanus rivulatus* (0.31 ng/g) (Sankar *et al.*, 2006). Similar to the heptachlor epoxide residues, the range of Dieldrin residues recorded in the present study were higher than the levels reported in the study done by Muralidharan *et al.* (2009).

The study done by Mvewura *et al.* (2002) showed the presence of dieldrin residues at the average concentrations of 2.7 µg/kg fw in *Scylla serrata* and 1.26 µg/kg in *Glossgobius biocellalus*, whereas the other species have recorded at BDL levels. These levels of dieldrin residues were comparable with the present study. The presence of the residues only in two fishes was attributed to the larger size of the fishes.

Stefanalli *et al.* (2004) has estimated the dieldrin concentrations in the range of 0.63 ng/g to 1.17 ng/g in Mackeral, 0.18 ng/g to 0.35 ng/g in Anchovy, 0.21 ng/g to 0.46 ng/g in Red Mullet and 0.1 ng/g to 0.13 ng/g in Cod samples respectively. These levels were comparable to that of the mean dieldrin levels recorded in the present study.

In India, dieldrin and aldrin was banned in 1974 and 1994 respectively, whereas endrin and heptachlor was banned in 1996. Although these pesticides were banned in India, residues of dieldrin, chlordane and heptachlor epoxide have been reported in various

environmental components in India. (Kuruganti, 2004). Despite being banned long before, the occurrence of dieldrin residues in the marine fishes included in the present study should be viewed with concern. However only a very few studies have reported the

presence of dieldrin residues in marine biota. Hence extensive comparison for the occurrence of dieldrin residues becomes difficult.

The variation discussed in the context of individual organochlorines among the fish species reveals that most of the studies have focused only on documenting the residue levels. Only very few studies could explain the toxicological implications due to organochlorine pesticide residues. Hence the present study serves to fill up this lacuna by explaining the dietary intake levels of these organochlorine pesticides and associated health risks through consumption of the fishes.

5.6 Composition pattern of various isomers and metabolites of organochlorine compounds detected in different species of fishes studied

5.6 (i) HCH isomers

The overall pattern of HCH residues in the present study showed the predominance of α HCH contributing to the total HCH load The composition pattern of HCH isomers in the present study are similar to the one reported by Monirith *et al.* (1999) in Cambodia; with the α HCH being the dominant contributor to the HCH residues. It was reported that low residue levels of HCHs and higher α HCH composition in fish may suggest their atmospheric transport to Cambodia from other Asian countries (Monirith *et al.*, 1999).

Dave *et al.* (1996) pointed out that technical mixture of HCH is used in India even recently. A complete ban on the production and sale of HCH in India came into effect in April 1997 (Tomar and Parmar, 1998). Except for termite control in agriculture and buildings, the import, manufacture and use of lindane (γ HCH) is also restricted since August 2007 (The Gazette of India 2007). According to Li (1999) historically, the most

polluted continent by technical HCH is Asia, where the three most polluted countries, China, India and Japan are located. Predominance of α-isomer in environmental samples reflects the continuing use of technical mixtures of HCH (Doong *et al.*, 2002).

Higher levels of HCH were detected from human breast milk (Tanabe *et al.*, 1990 and Kalra *et al.*, 1994), fish (Kannan *et al.*, 1995), bird (Tanabe *et al.*, 1998) and drinking water (Kumari *et al.*, 1996) in India. Fish are also used as sentinel species for HCH contamination (Willett *et al.*, 1998). Muralidharan *et al.* (2009) have reported the predominant occurrence of the HCH residues in the marine fishes collected from the same locations. Considering that HCH is rapidly evaporated and widespread by the atmospheric transport (Wania and Mackay, 1993), HCH concentration found in Cambodian sample is likely to be reflected by the atmospheric transport from India through the south-west monsoon (Monirith *et al.*, 1999).

A survey of organochlorine contamination in wildlife from an agricultural watershed in southern India by Ramesh *et al.* (1992) showed the predominant occurrence of α HCH in fishes which is attributed to the contamination of marine environment due to the continuous use in India.

Global HCH transport is also evident in residues found in marine mammals and Arctic species. For example, residues in some Indians indicated recent exposure to technical HCH while contamination in Arctic wildlife shows global transport of HCHs. While isomer-specific residue concentrations do provide evidence for HCH transport and fate, there are still no clear correlations between isomer specific tissue concentrations and toxicological effect. Isomer differences could indicate different sources of contamination, different times of exposure or different mechanisms of uptake, metabolism, or storage by various species. Clearly, further research is necessary within and among species to understand the differential isomer tissue concentrations (Willett *et al.*, 1998).

5.6 (ii) DDT metabolites

The overall pattern of DDT residues showed higher contribution of *p,p'* DDT to the total DDT residues in the fishes presently studied. It is adequately evident that DDT breaks down gradually in to several different metabolites, of which DDE is the most stable and toxic. Strandberg *et al.* (1998), reported that the ratio of *p,p'* DDT/ *p,p'* DDE provides a useful index to know whether the DDT at a given site is fresh or aged. The ratio greater than 1 indicates the fresh input of DDT. The ratio of *p,p'* DDT/ *p,p'* DDE in the current study was found to be greater than 1 which indicates the fresh input of DDT in the Indian marine environment. Subsequently this has lead to the high occurrence of *p,p'* DDT in the marine fishes included in the present study. This is because DDT is still used for certain public health activities in India and also in a few other countries.

Similar observation of high *p,p'* DDT to total DDT ratio at the fishes of Calicut region has been reported by Pandit *et al.* (2006). The study by Shailaja and Nair (1996) has reported the primary DDT content in the zooplanktons along the west coast of India suggesting strongly the new inputs of DDT during that period. The same pattern of occurrence of DDT residues was observed in the current study. However similar studies on the east coast of India are lacking.

Similar to this Mwevura *et al.* (2002) has reported the high occurrence of *p,p'* DDT residues in the edible marine biota of Dar es Salaam city in Tanzania. Meng *et al.,* (2007) reported the predominance of *p,p'* DDT in the freshwater fishes and marine fishes of China. It has been suggested that the presence of current point sources of DDTs in the study areas, which may include intermittent production of DDT mixtures to satisfy export demand and the manufacture and use of dicofol technical products known to contain a large amount of DDT residues (Qiu *et al.,* 2004).

The composition pattern of DDT residues in the present study indirectly shows the usage and input into the Indian marine environment and there by bioaccumulation of these residues in the fishes. Hence the relative concentration of the parent compounds and their

metabolites are very useful in providing information on source and history of input to the environment and possible degradation pathways involved.

5.6 (iii) Endosulfan composition

In the present study α-endosulfan residues were the primary contributor to the total endosulfan residues in all the seven species of fishes. The α endosulfan residues have a tendency to convert to β endosulfan and endosulfan sulfate. The metabolites are highly toxic than the parent compound. The presence of various forms of residues indirectly indicates the occurrence of conversion of the parent compound. These facts have been reported in almost all the studies dealing with endosulfan residues.

The study by Sankar *et al.* (2006) had reported the presence of detectable levels of endosulfan residues in the fishes of Calicut region. Alarmingly high levels of endosulfan residues were observed in human blood and milk in a study in Kasargod in Kerala, India (Padma *et al.*, 2001 and Anon 2002). The presence of endosulfan residue in almost all the environmental samples indicates its current usage.

More than 120 nations across the world endorsed the endosulfan ban struck the deal on April 29, 2011 under the Stockholm Convention, an international treaty for controlling persistent organic pollutants. They after five days of negotiations in Geneva under the deal, most uses of endosulfan will cease in 2012. However, this organochlorine insecticide may be used on certain combinations of crops and pests until 2017. For example, endosulfan can continue to be used on cotton to control bollworms.

Some 18,000 to 20,000 tons of endosulfan are produced each year, according to the United Nations. India makes about 10,000 tons; China manufacturers some 5,000 tons; and Israel, Brazil, and South Korea produce the rest. The biggest users of this pesticide are India, Brazil and China with Argentina and the U.S. also consuming significant quantities.

(pubs.acs.org/cen/news/89/.../8919notw9.html). However, the endosulfan residues were found to be high in Asian countries when compared to developed countries.

Despite of this, The Supreme Court of India vide its order dated May 13th 2011 has banned manufacture, sale, use and export throughout India. Hence it may be noted that in India, until very recently endosulfan was in use. However, the studies explaining the primary contribution of α endosulfan residues related to the fresh input of the pesticides is lacking at Indian context. Hence the higher composition of α-endosulfan residues in the fishes of the current study indicates fresh input of these residues into the environment.

5.6 (iv) Heptachlor composition

In the present study, the heptachlor epoxide was predominant to contribute to the total heptachlor residues in all the species of fishes. Heptachlor is a chlorinated dicyclopentadiene insecticide that tends to persist in the environment and accumulates in the food chain. Although, heptachlor has been banned for manufacturer, use, import and export in India, (Kumar *et al.*, 2011) these pesticides are still persistent in environment and in biological samples where these may be associated with adverse effects (Mustafa *et al.*, 2010). Sankar *et al.* (2006) reported significantly higher levels of heptachlor epoxide compared to heptachlor, in the fishes caught at Calicut region, Kerala. Still the studies on heptachlor residues reported in India are very limited to explain its transformation process.

However, It has been stated that heptachlor epoxide, the converted metabolite of heptachlor was highly toxic than the parent compound. Heptachlor is converted to heptachlor epoxide and other degradation products in the environment. Heptachlor epoxide degrades more slowly and, as a result, is more persistent than heptachlor (Connell *et al.*, 2002). Heptachlor epoxide has been found in food crops grown in soils treated with heptachlor many years before. Both heptachlor and heptachlor epoxide adsorb strongly to sediments, and both are bioconcentrated in aquatic and terrestrial organisms. Because of the more persistent nature of heptachlor epoxide and its

lipophilicity, biomagnification of heptachlor epoxide in terrestrial food chains is significant (Hartley and Johnston 1983 and Cullen and Connell 1994).

Hence the higher contribution of heptachlor epoxide in the fishes of the present study evidently suggests the bioconcentration factor of these residues in the Indian marine environment. Though banned, the presence of higher amount of heptachlor epoxide should be viewed with toxicological concern.

5.7 Total organochlorine load among the species

The overall pattern of total organochlorine among the seven species of fishes collected between the two study locations, there is a declining trend in the residues with an earlier study (Muralidharan *et al.,* 2009) in the same locations.

In India, organochlorine pesticides (OCPs) especially DDT and HCH were used extensively till recently both for agricultural and sanitary purposes (Pandit *et al.,* 2001 and Kumar *et al.,* 2006). It is estimated that about 25,000 MT of chlorinated pesticides was used annually in India and DDT accounted over 40 % of this group (Mathur, 1993). Further substantial portions of applied pesticides are dissipated at the site of application through chemical and biological degradation processes. Still, a reasonable fraction of the OCPs residues reach the oceans through agricultural run-off, atmospheric transport and sewerage discharge (GESAMP, 1989).

Even though India occupies fourth position in terms of fish production, the per capita consumption of fish in India is only 4.8 kg/ year (http://www.st.nmfs.gov/st1/fus/us04 /08perita2004.pdf). India exports shrimp and fish to the world market and majority of the population along the coastal regions consume fish. The levels reported in the present study were concurrent with the study done by Sankar *et al.* (2006) on the fishes of Calicut region, Kerala. However the studies explaining the organochlorine pesticides in the marine fishes are limited at Indian context.

Hence the total organochlorine pesticide residues in the fish species studied explains the status of occurrence of these residues in Indian environment. Although the levels reported were found to be less, the chronic exposure to organochlorine pesticides in humans through the dietary intake of these fishes becomes significant.

SUITABILITY OF FISHES FOR HUMAN CONSUMPTION

6. SUITABILITY OF FISHES FOR HUMAN CONSUMPTION

6.1 Introduction

The present study involved analysis of organochlorine pesticide residues in select species of marine fishes collected from the market in Coimbatore. Seven species of fishes were selected on the basis of preference by people and their availability throughout the year. The core work of the present study was to assess these seven species of marine fishes for their suitability for human consumption on the basis of the organochlorine residues they contained.

The preceding chapters have explained the organochlorine residue levels in the marine fishes collected over a period of two years. Based on the residue data obtained, an attempt was made to assess the suitability for human consumption. For this purpose, an extensive survey was conducted in 325 families in Coimbatore city. The survey results were employed to arrive at the per capita consumption of the marine fishes in the city.

Based on the per capita consumption data and the organochlorine residue levels, dietary intake levels were calculated as explained by FAO/WHO 1991. The calculated dietary intake levels represent the quantum of organochlorine pesticides entering the human body through consumption of these seven species of fishes, selected for the present study. The levels were compared with the Allowable Dietary Intake (ADI) concentration levels proposed by various statutory agencies across the world. Apart from this, the maximum permissible residue limits of the pesticide residues proposed by International Regulatories and Advisories have also been compared with the residue levels documented in the present study.

6.2 Calculated Dietary Intake of pesticide residue through consumption of fish

Based on the questionnaire survey conducted in 325 families across the city, the average per capita consumption of marine fishes was estimated to be 47 g/day. The dietary intake concentration of the organochlorine pesticides was calculated by multiplying the

pesticide concentrations measured in each species of fish by the per capita consumption. The levels are expressed as μg/person/day in table 6.1 for all the seven species of fishes included in the study.

The calculated Dietary Intake of organochlorine pesticides through consumption of seven species of fishes included in the present study varied among themselves. Such variations could be noticed among isomers and metabolites as well. The dietary intake of α HCH (0.51 μg) and β HCH (1.88 μg) was higher through the consumption of *Sphyraena barracuda*. The lower input of α HCH and β HCH was through *Scomberomorus commersonn* (0.12 μg) and *Carangoides malabaricus* (0.81 μg). But through all the other species, levels of input of these residues were moderate. The highest intake of γ and δ HCH were through *Nemipterus japonicus* (0.34 μg) and *Carangoides malabaricus* (0.25 μg). The lowest intake of both these residues was through consumption of *Rastrelliger kanagurta* (0.17 μg and 0.12 μg) (Table 6.1).

Thus the dietary intake levels were not consistent among the four isomers of HCH in all the seven species of fishes studied. When total HCH was considered, the maximum intake was through consumption of *Sardinella longiceps* (2.68 μg) and minimum through *Carangoides malabaricus* (1.65 μg) (Table 6.1).

With reference to DDT residues, a uniform pattern was observed among the metabolites. The highest intake of *p,p'* DDT residues was through consumption of *Scomberomorus commersonn* (1.55 μg) and it was the lowest through *Carangoides malabaricus* (0.51 μg). Similarly the maximum intake of *p,p'* DDE and *p,p'* DDD residues was through *Sardinella longiceps* (0.13 μg). The minimum intake of *p,p'* DDE and *p,p'* DDD residues was through *Sphyraena barracuda* (0.06 μg) and *Carangoides malabaricus* (0.06 μg) respectively. When total DDT residues were considered, the highest input was through *Scomberomorus commersonn* (1.77 μg) and the lowest through *Carangoides malabaricus* (0.64 μg) (Table 6.1).

Among the cyclodiene group of pesticides, the dietary intake of all the three endosulfan metabolites (α, β endosulfan and endosulfan sulfate) as well as heptachlor was higher through the consumption of *Scomberomorus commersonn*. The calculated intake of

α, β endosulfan and endosulfan sulfate was 0.55 µg, 0.37 µg, 0.28 µg and 0.19 µg respectively. Similarly, the lowest input of β endosulfan (0.09 µg) endosulfan sulfate (0.04 µg) and heptachlor (0.08 µg) was through consumption of Sphyraena *barracuda* while the lowest input of α endosulfan (0.18 µg) was through *Sardinella longiceps*. The intake concentrations of heptachlor epoxide was at a different pattern with the maximum (0.28 µg) through *Sardinella longiceps* and minimum (0.16 µg) through *Nemipterus japonicus*. Dieldrin intake is higher through consumption of *Sardinella longiceps* (0.2 µg) and lowest through *Carangoides malabaricus* (0.07 µg) (Table 6.1).

When all the pesticides were considered together irrespective of species, β HCH contributed the maximum intake (1.41 µg) followed by *p,p'* DDT (0.92 µg) and *p,p'* DDE. *p,p'* DDD contributed the minimum (0.09 µg). Similarly when total intake was calculated, irrespective of species and pesticides, the overall intake was 4.31 µg/person/day through the consumption of marine fishes available in Coimbatore (Table 6.1).

Table 6.1: The Calculated dietary intake concentration (µg/person/day) of organochlorine residues through consumption of various species of marine fishes sold in Coimbatore market.

Species	α HCH	β HCH	γ HCH	δ HCH	*p,p'* DDT	*p,p'* DDE	*p,p'* DDD	α Endosulfan	β Endosulfan	Endosulfan sulfate	Heptachlor	Heptachlor epoxide	Dieldrin	Total OC
Carangoides malabaricus	0.37	0.81	0.22	0.25	0.51	0.07	0.06	0.23	0.15	0.06	0.17	0.17	0.07	3.14
Cynoglossus macrolepidotus	0.36	1.00	0.21	0.24	1.01	0.08	0.07	0.22	0.16	0.06	0.16	0.20	0.12	3.89
Nemipterus japonicus	0.33	1.50	0.34	0.20	1.03	0.07	0.09	0.27	0.10	0.06	0.20	0.16	0.12	4.47
Rastrelliger kanagurta	0.22	1.35	0.17	0.12	0.81	0.10	0.08	0.22	0.09	0.09	0.11	0.17	0.13	3.66
Sardinella longiceps	0.47	1.74	0.26	0.21	0.72	0.13	0.13	0.18	0.10	0.10	0.21	0.28	0.20	4.73
Scomberomorus commersonn	0.12	1.57	0.20	0.22	1.55	0.12	0.09	0.55	0.37	0.28	0.19	0.22	0.17	5.65
Sphyraena barracuda	0.51	1.88	0.30	0.14	0.83	0.06	0.11	0.23	0.09	0.04	0.08	0.23	0.12	4.62
Average Dietary Intake Concentration through fishes	0.34	1.41	0.25	0.20	0.92	0.09	0.09	0.27	0.15	0.10	0.16	0.20	0.13	4.31

6.3 Comparison with Allowable Daily Intake (ADI) Levels

It has been stated that no pesticide is approved for agricultural or any other use without an assessment of its potential human health implications. Hazard identification involves a series of in vitro and in vivo studies to define those biological properties of the chemical that could lead to adverse effects if the dose were sufficiently high. There are international guidelines for the conduct of studies used for risk assessment in order to ensure the reliability of the data. These guidelines for each compound have been stated as Allowable or Acceptable Daily Intake (ADI) concentrations which are derived from the complete safety database with the aim of defining a level of exposure one could be subjected to everyday throughout life. Hazard identification is primarily aimed at defining the potential adverse effects of the compound whereas hazard characterization is concerned with defining the dose or the concentration response relationships in order to establish intake levels that would be without significant health effects in exposed humans. (Renwick 2002).

The ADI levels have been established by various statutory agencies, such as FAO/WHO, USEPA, FDA, Health Canada. They come out with various inventories and guidelines for toxic chemicals such as organochlorine pesticides at stipulated time intervals. These guidelines serve as reference levels to assess the toxic effect particularly to humans through food.

The various ADI and permissible levels of different organochlorines have been presented in table 6.2 along with the average daily dietary intake concentration calculated from the present study. The comparison of the levels documented in the present study with that of the stipulated ADI levels, clearly indicates the contaminant burden of the marine fishes and input of residues into humans through consumption (Table 6.2).

The calculated levels of α HCH, β HCH and DDT residues were below the ADI limits prescribed particularly by IARC, WHO, USEPA and Health Canada. The same pattern existed for cyclodiene group also. The calculated concentration levels compared with the existing statutory guidelines show that all the organochlorine pesticide residues were

below the ADI limits with reference to the seven species of marine fishes included in the present study.

Most of the studies reporting the organochlorine input to humans through diet, done elsewhere in India and abroad have explained the chronic ill effects in humans. Fish consumption was considered as a major source of dietary OCP exposure and human body burden (Leng *et al.*, 2009). Hence the potential health threat from contaminants in fish should still be emphasized for the populations consuming large quantities of fish (Du *et al.*, 2012). Based on the human health point of view, an increased exposure of humans to organochlorine pesticides through foods in developing countries leads to increased risk of cancer (Kannan *et al.*, 1995). It has been stated that the high ADI levels reported by statutory agencies could be attributed to high pesticide application along with dietary habits, especially fish consumption or animal derived food-stuffs (Mishra and Sharma, 2011). Even though the present levels of organochlorines do not appear to be harmful to human, chronic exposure and increased per capita consumption may lead to deleterious effects.

Table 6.2: Comparison of calculated dietary intake concentration with the acceptable dietary intake (ADI) stipulated by various statutory agencies

Compound	ADI Limit (ng/g)	Agency	Year	Reference
α HCH	200 ng/g	European Union	2000	Di Muccio *et al.*, 2002
β HCH	100 ng/g	FDA	2001	Di Muccio *et al.*, 2002
γ HCH	300 ng/g	FDA	-	Barasa *et al.*, 2008
∑ HCH	18 µg/person	Health Canada	1996	Muralidharan *et al.*, 2009
p,p' DDT	5 ng/g	FDA	2001	Barasa *et al.*, 2008
∑ DDT	300 µg/person	IARC	1989	Muralidharan *et al.*, 2009
∑ Endosulfan	1 mg/ kg	European Union	2000	Di Muccio *et al.*, 2002
Heptachlor	450 µg/person	IARC	1989	Falandysz *et al.*, 2001
	50 ng/g	Tolerance limits of Germany	-	
Heptachlor epoxide	100 ng/g	Tolerance limits of Sweden		
∑ Heptachlor	0.3 ppm	FDA Action limit	2000	Santerre *et al.*, 2000
	200 ng/g	European Union	2000	Stefanalli *et al.*,2004
Dieldrin	6 µg/person	Health Canada	1996	Muralidharan *et al.*, 2009

6.4 Assessment on suitability for human consumption

Based on the questionnaire survey conducted in 325 families across the city, the average per capita consumption of marine fishes was estimated to be 47 g/day. The human consumption pattern was comparable with that of the South Korean population (50 g/day), (Moon *et al.,* 2009). However it was lower than the fish consumption rate (142.2 g/day) set by USEPA (2000). The dietary intake concentrations of the organochlorine pesticides were calculated by multiplying the pesticide concentrations which were measured in each species of fish by the per capita consumption. The levels were expressed as µg/person/day (Table 6.1). When calculated dietary intake concentration levels of various organochlorine pesticides in the marine fishes included in the present study were compared with various ADI limits, it has been inferred that all the seven species included in the study are prone to higher HCH and DDT contamination to a larger extent when they were compared to other residues. Though the levels were below the statutory guidelines, it is expected to create a chronic health effect in a long run.

The dietary intake concentration of HCH residues were the highest through consumption of *Sphyraena barracuda* (2.83 µg/person/day) followed by consumption of *Sardinella longiceps* (2.68 µg/person/day). The earlier study Muralidharan *et al.,* (2009) indicated the same trend with higher concentrations of HCH intake through consumption of *Sardinella longiceps* (31 µg).

The higher dietary intake concentration of DDT residues were through *Scomberomorus commersonn* (1.77 µg/person/day) and *Nemipterus japonicas* (1.19 µg/person/day). A study conducted by Vijayan *et al.,* (2004) also reported similar scenario in inland fishes of India. The study extensively documented the organochlorine pesticide residues in 1249 fishes belonging to 20 species from 115 wetlands spread over 14 states across India. It further reported higher dietary intake of DDT and HCH residues through consumption of fresh water fishes. Of all the fishes analyzed from various states, the fishes from few wetlands belonging to Assam, Gujarat, Maharashtra, Uttar Pradesh and West Bengal exceeded the maximum residue limits recommended for fish and wildlife by various statutory agencies. It was found that even 250 g of these fishes, in a week, was not safe for

human consumption. It has been stated that if the input of HCH and DDT to human being continues it may accumulate in tissues and even in mothers' milk (Burke *et al.*, 2003). And more recently, a report by Sun *et al.* (2005) suggested that although organochlorine pesticide, such as DDT and HCH, have been banned in China, the residues of such compounds still exists in the environment and cause food contamination. However, the dietary intake of cyclodiene residues was lower when compared to the dietary intake levels of HCH and DDT residues.

A similar study done by Mwevura *et al.* (2002) also showed the same pattern of residues in the marine biota of coastal Dar es Salaam city. The organochlorines analyzed in 12 edible organisms of Adriatic Sea, Italy by Muccio *et al.* (2002) reported the dietary intake concentrations of 126.3, 2.99 and 7.67 ng/person /day for DDT, γ HCH and dieldrin respectively which are comparable with the present study. However, the dietary intake levels in both the studies did not exceed the ADI limits.

Earlier studies conducted by Kannan *et al.* (1992) and Kumari *et al.* (2001) also reported high concentration of HCH in fish and food products and higher dietary intake through fishes. Although no major ill effects in man have been correlated with the levels of HCH, altered thyroid function was reported in women (Hagmar *et al.*, 2001). Apart from this carcinogenic and non carcinogenic health risks in humans have also been attributed through the dietary intake of organochlorine insecticides (Moon *et al.*, 2009, Du *et al.*, 2012).

The average dietary intake concentration of organochlorines irrespective of the species preference was estimated to be 4.31 µg/person/day. However, the higher dietary intake of organochlorine residues is mainly through *Scomberomorus commersonn* (5.65 µg/person/day) followed by *Sardinella longiceps* (4.73 µg/person/day). These are the species which are the most preferred and highly consumed by the local people. These fishes are rich in fat content and thereby accumulate higher quantum of organochlorine residues. Though the residue levels were low, if a person consumes 250g of these fishes in a week, the dietary intake concentration of organochlorine pesticides was about 30.05 µg through *Scomberomorus commersonn* and 25.16 µg through *Sardinella longiceps* and

chronic exposure to the organochlorine residues may lead to carcinogenic risk in humans (Moon *et al.,* 2009).

In India, although studies on the levels of organic contaminants in fishes are carried out, they are sporadic and not oriented towards assessing the impact on human health. Considering the increase and potential risks of marine fish consumption in India, systematic monitoring programs for organochlorines in seafood should be instituted. The present study clearly shows the need for continued monitoring. Formulation of guidelines in terms of MRLs and ADIs are especially is very much important for those compounds where no basic guidelines are available. Thus a framework of guidelines and statutory limits in Indian context to ensure food safety in India is the need of the hour.

SUMMARY AND CONCLUSION

7. SUMMARY AND CONCLUSION

- ✓ The current study has attempted to document the organochlorine pesticide residues in select species of commercially important marine fishes, received from Cochin and Rameshwaram, and sold at Coimbatore market.

- ✓ A total of 716 fish samples belonging to seven species, namely *Carangoides malabaricus, Cynoglossus macrolepidotus, Nemipterus japonicus, Rastrelliger kanagurta, Sardinella longiceps, Scomberomorus commersonn* and *Sphyraena barracuda* caught at Cochin and Rameshwaram were collected from the Coimbatore market. The samples were collected with regular intervals during the study period (October 2004 - September 2006) which fell into eight quarters, with three months being one quarter.

- ✓ All the samples were analyzed for 13 organochlorine pesticide residues, namely α HCH, β HCH, γ HCH, δ HCH, *p,p'* DDT, *p,p'* DDE, *p,p'* DDD, α endosulfan, β endosulfan, endosulfan sulfate, heptachlor, heptachlor epoxide and dieldrin in Gas chromatograph fitted with Electron Capture Detector by following standard protocol. All the results were expressed in ng/g at wet weight basis.

- ✓ A preliminary survey was conducted to assess the total marine fish sold in Coimbatore, common species available and their origin and to assess the consumption pattern of marine fishes. The study also documented the spatio-temporal variation in organochlorine residues among the fishes, and assessed the suitability of the fishes for human consumption.

- ✓ Analysis of variance (ANOVA) was used to test the differences in organochlorine residues among the species and quarters of both the locations, i.e., Cochin and Rameshwaram. Students t-test was employed to understand the significant variation in the residues present in the samples received from Cochin and Rameshwaram. Spearman's rank correlation was applied to evaluate the correlation between the

chemical concentrations and the size of the fish as well as with the chemical concentrations and sex of the fish.

- ✓ Among the organochlorines analyzed, HCH isomers namely α HCH, β HCH, γ HCH and δ HCH were detected at 57 %, 58 %, 52 % and 60 % respectively. The detection frequency of DDT metabolites were in the order of 40 % for *p,p'* DDT, 36 % for *p,p'* DDE and 32 % for *p,p'* DDD. Among the cyclodiene group, α endosulfan, β endosulfan and endosulfan sulfate were detected at 48 %, 43 % and 16 %, whereas heptachlor, heptachlor epoxide and dieldrin were detected at 48 %, 64 % and 48 % respectively.

- ✓ Among various species of fishes analysed, concentrations of α HCH was found to be high (11.3± 2.5 ng/g) in *Sphyraena barracuda*, followed by *Sardinella longiceps* (10.7 ± 2.1 ng/g) and *Nemipterus japonicus* (9.5 ± 1.5 ng/g). Concentrations of the β HCH (7.1 ± 1.4 ng/g) and γ HCH (4.8 ± 1.0 ng/g) were higher in *Scomberomorus commersonn.* Among the DDT metabolites, the mean residue levels of all the metabolites were less than 1 ng/g in all the species. However, the maximum concentration range of *p,p'* DDT was in *Sardinella longiceps* (13.2 ng/g) followed by *Scomberomorus commersonn* (11.7 ng/g).

- ✓ Among the cyclodiene pesticides, the higher concentration of endosulfan residues (α endosulfan 2.2 ± 0.7 ng/g, β endosulfan 1.5 ± 0.6 ng/g and endosulfan sulfate 1.1± 0.5 ng/g) were observed in *Scomberomorus commersonn.* However all the other cyclodiene pesticide residues were detected at lower concentrations. Of all the organochlorine pesticides only endosulfan sulfate residues varied significantly in *Scomberomorus commersonn* ($P< 0.05$).

- ✓ The spatial variation in the levels of organochlorines were found to be significant for β HCH, *pp'* DDT and α endosulfan residues ($P< 0.05$) in *Rastrelliger kanagurta.*

- ✓ Among the organochlorines analyzed, the total HCH residues in *Carangoides malabaricus, Cynoglossus macrolepidotus, Nemipterus japonicus* and *Sardinella longiceps* had raised significantly during quarter VII and VIII ($P<0.05$). The residues in *Rastrelliger kanagurta* were at significantly varying levels during quarter I, IV and VII ($P<0.05$).

- ✓ The total DDT residues in *Carangoides malabaricus, Cynoglossus macrolepidotus* and *Sardinella longiceps* had varied significantly (P< 0.05) during quarter VII. Similarly the residues in *Sphyraena barracuda* and *Nemipterus japonicus* were significantly high (P< 0.05) during quarter VII. The DDT residues in *Rastrelliger kanagurta* varied significantly (P< 0.05) during quarter II.

- ✓ Among the cyclodiene group of pesticides, only the total endosulfan residues varied significantly (P< 0.05) during quarter V in *Rastrelliger kanagurta* and quarter VI in *Sphyraena barracuda* respectively.

- ✓ A stronger significant positive correlation (P< 0.05) was found to exist between organochlorine residues and the size (i.e., length and weight) of all the species of fishes except *Sardinella longiceps* and *Sphyraena barracuda.* The correlation test between the sexes (all species pooled together) and organochlorine residues did not show any significance. In addition to that the test performed between the male and female fishes of individual species also did not show any significant correlation for all the species of fishes studied.

- ✓ Based on the results of the human consumption survey, it has been estimated that the daily per capita consumption of marine fishes in Coimbatore city is 47 g/ day. The concentration of organochlorine residues recorded in each species of marine fishes was multiplied by daily intake of fishes to calculate dietary intake levels of organochlorine residues through consumption of marine fishes.

- ✓ Based on this, the average dietary intake concentration of organochlorines irrespective of the species preference was estimated to be 4.31 µg/person/day. However, the higher dietary intake of organochlorine residues is mainly through *Scomberomorus commersonn* (5.65 µg/person/day) followed by *Sardinella longiceps* (4.73 µg/person/ day). These are the species which are the most preferred and highly consumed by the local people. These fishes are rich in fat content and thereby accumulates higher quantum of organochlorine residues.

- ✓ The calculated input levels when compared with the existing statutory guidelines (Health Canada, 1996; European Union 2000 and FDA 2000 and 2001) show that all the organochlorine pesticide residues were below the ADI limits with reference to the marine fishes included in the present study.

- ✓ The residue levels of all the OC pesticides currently investigated, when compared with earlier studies conducted in the same study area, appear to be less. Similarly within two year period also, the levels appear to be showing a declining pattern.

- ✓ Hence, the bioaccumulation of persistent organochlorine pesticide residues in the edible marine fishes, appear to be not alarming. Despite declining trend, the levels reported were found to be higher than that of the developed countries. However, considering the fact that there is some amount of fresh input of OC to the marine environment from different sectors, the situation should be viewed with concern. Further it is emphasized that strict regulations on pesticide use and regular monitoring of the environmental residue levels in select components is essential.

- ✓ The findings of the study have been compared with various guideline values proposed by international statutory bodies such as FDA (2000 and 2001), Health Canada (1996) and European Union (2000). Hence there is a strong need for formulation of guidelines in terms of MRLs and ADIs in Indian context.

- ✓ Organic farming methods together with Integrated Pest Management will help a long way in combating the pesticide residues in the human diet in the years ahead. Along with organic farming better pest management strategies and formulation of the guidelines are very much essential to address the pesticide residues in the environment.

REFERENCES

8. REFERENCES

Abhilash PC and Singh N (2009). Pesticide use and application: An Indian Scenario. *Journal of Hazardous Materials* 165(1-3): 1- 12.

Aguilar A (1984). Relationship of DDE/ DDT in marine mammals to the chronology of DDT input into the ecosystem. *Canadian Journal of Fisheries and Aquatic Sciences* 41: 840- 844.

Aktumsek A Kara H Nizamlioglu F and Dinc I (2002). Monitoring of OC pesticides residues in Pikeperch, *Stizostedion Lucioperca* L. In Beysehir Lake (Central Anatolia), Selcuk University, Turkey. *Environmental Technology* 23(4): 391- 394.

Allen GR Hoese DF Paxton R Randall JK Russell BC Starck II WA Talbot FH and Whitley GP (1976). Annotated checklist of the fishes of Lord Howe Island. *Records of the Australian Museum* 30(15): 365- 454.

Amaraneni SR and Pillala RR (2001). Concentration of residue in tissues of fish from Kolleru lake in India. Department of inorganic and analytical chemistry, School of Chemistry, Andhra University, John Wiley and Sons, *Environmental Toxicology* 16: 550- 556.

Angulo P Keach JC Batts KP and Lindor KD (1999). Independent predictors of liver fibrosis in patients with nonalcoholic steatohepatitis. *Hepatalogy,* 30: 1356- 1362.

Anon (1998). Fish and fish products hazards and control guide. US Food and Drug Administration. Center for Food Safety and Applied Nutrition Rockville, MD, USA.

Anon (2002). Final Report of the Investigation of Unusual Illnesses allegedly produced by endosulfan exposure in Padre village of Kasaragod District (N. Kerala); National Institute of Occupational Health, Indian Council for Medical Research, Ahmedabad, India.

Anonymous (1990). Prevention of food adulteration rules (1955). Government of India, New Delhi). 111.

Babu Rajendran R Venugopalan VK and Ramesh R (1999). Pesticide residues in air from coastal environment, South India. *Chemosphere* 39: 1699- 1706.

Babu Rajendran R Imagawa T Tao H and Ramesh R (2005). Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. *Environment International* 31: 503- 512.

Barakat AO Kim M Qian Y and Wade TL (2002). Organochlorine pesticides and PCB residues in sediments of Alexandria harbour, Egypt. *Marine Pollution Bulletin* 44: 1421- 34.

Barasa MW Shem O Wandiga Joseph OL (2007). Seasonal variation in concentrations of organochlorine pesticide residues in tropical estuarine sediments along the Indian Ocean Coast of Kenya. *Marine Pollution Bulletin* 54: 1962- 1989.

Barkatina EN Pertosovsky AL Murokh VI Kolomiets ND Shulyakovskaya OV Venger ON and Makarevich VI (1999). Organochlorine pesticide residues in basic food products and diets in the republic of Belarus. *Bulletin of Environmental Contamination and Toxicology.* 63: 235- 242.

Barkatina EN Pertsovsky AL Murokh VI Kolomiets ND Shulyakovshaya OV Veretennikova ND and Venger ON (2002). Determination of organochlorine pesticides in human adipose tissue in Minsk, Republic of Belarus. *Bulletin of Environmental Contamination and Toxicology.* 69: 30- 34.

Barron MG Stehly GR Hayton WL (1990). Pharmacokinetic modeling in aquatic animals I. models and concepts. *Aquatic Toxicology,* 17: 187- 212.

Begum A Harikrishna S Khan IA (2009). Survey of persistent organochlorine pesticides residues in some Streams of the Cauvery River, Karnataka, India. *International Journal of ChemTech Research* 1(2): 237- 244.

Bhattacharya A Sarkar SK and Bhattacharya A (2003). An assessment of coastal modification in the low-lying tropical coast of northeast India and role of natural and artificial forcings. Proceed of the International Conference on Estuaries and Coasts, Hangzhou, China. 9-11:158- 165.

Borga K Gabrielsen GW Skaare JU (2001) Biomagnification of organochlorines along a Barents Sea food chain. *Environmental Pollution* 113: 189- 198.

Botello AV Rueda-Quintana L Díaz-González G and Toledo A (2000). Persistent Organochlorine Pesticides (POPs) in coastal lagoons of the subtropical Mexican Pacific. *Bulletin of Environmental Contamination and Toxicology* 64(3): 390- 397.

Bright DA Grundy SL and Reimer KJ (1995). Differential bioaccumulation of non-ortho-substituted and other PCB congeners in coastal Arctic invertebrates and fish. *Environmental Science and Technology* 29: 2504- 2512.

Britto APX Bruning IMRA and Moreira I (2002). Chlorinated pesticides in mussels from Guanabara Bay, Rio de Janeiro, Brazil. *Marine Pollution Bulletin* 44: 71- 81.

Brown AWA (1979). Ecology of pesticides. Wiley-Inter Science Publication. New York: 179.

Brown DW Mccain BB Horness BH Sloan CA Tilbury KL and Pierce SM (1988). Status correlations and temporal trend of chemical contaminants in fish and sediments from selected sites on the Pacific coast of USA. *Marine Pollution Bulletin* 37: 67- 85.

Bruggeman WA (1982). Bioaccumulation and transformation of dichlorophenyls in fish. In: Hutzinger O (ed). *The handbook of environmental chemistry* : 29- 47.

Buchman MF (1999). NOAA Screening Quick reference Tables, NOAA HAZMAT report 99-1, Seattle WA, Coastal protection and restoration division, National Oceanic and Atmospheric Administration *p* 12.

Burgeot T Bocquene G Porte C Dimeet J Santella RM Garcia de la Parra LM Pfhol-Leszkowicz A Raoux C and Galgani F (1996). Bioindicators of pollutant exposure in the northwestern Mediterranean sea. *Marine Ecology Progress Series* 131: 125- 141.

Burke ER Holden AJ Shaw IC Suharyanto FX and Sihombing G (2003). Organochlorine residues in human milk from primiparous Women in Indonesia. *Bulletin of Environmental Contamination and Toxicology* 71: 148- 153.

Chakraborty P Zhang G Li J Xu Y Liu X Tanabe S Jones KC (2010). Selected organochlorine pesticides in the atmosphere of major Indian cities: levels, regional versus local variations and sources. *Environmental Science and Technology,* 44: 8038- 8043.

Chan HM Chan KM and Dickman M (1999). Organochlorines in Hongkong fish. *Marine Pollution Bulletin.* 39: 351–356.

Chen SJ Luo XJ Mai BX Sheng GY Fu JM Zeng EY (2006). Distribution and mass inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in sediments of the Pearl River Estuary and the northern South China Sea. *Environmental Science and Technology* 40: 709- 714.

Cheung KC Leung HM Kong KY Wong MH (2007). Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong and their health risk assessment. *Chemosphere* 66: 460- 468.

Cleeman M Riget F Paulsen GB Klungsoyr J and Dietz R (2000). Organochlorines in Greenland marine fish, mussels and sediments. *Science of the Total Environment* 245: 87- 102.

Codex (1996). Codex Alimentarius. Joint FAO/ WHO Food Standard Programmes. Vol. 2B. Residues in Food. FAO /WHO, Rome.

Connell DW (1990). Bioaccumulation of xenobiotics compounds. CRC Press, Florida.

Connell DW Miller G and Anderson S (2002). Chlorohydrocarbon pesticides in the Australian marine environment after banning in the period from the 1970s to 1980s. *Marine Pollution Bulletion* 45: 78- 83.

Council of the European Communities (1980). Council directives of 15 July 1980 relating to the quality of water intended for human consumption (80/778/EEC). *Official Journal of the European Communities* 229: 11- 29.

Covaci A Gheorghe A Voorspoels S Maervoet J Steen Redeker E Blust R and Schepens P (2005). Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt River (Belgium): analytical aspects and depth profiles. *Environment International* 31: 367- 375.

Cullen MC and Connell DW (1994). Pesticide bioaccumulation in cattle. *Ecotoxicology and Environmental Safety* 28: 221- 231.

Das B Khan YSA Das P and Shaheen SM (2002). Organochlorine pesticide residues in catfish, *Tachysurus thalassinus* (Ruppell, 1835), from the south patches of the Bay of Bengal. *Environmental Pollution*. 120: 255- 259.

Das B and Das P (2004). Organochlorine pesticide Residues in water, sediments and muscle of river Shad, *Hilsa ilisha* (Hamilton 1822) from the south patches of Bay of Bengal. *Bulletin of Environmental Contamination and Toxicology* 72: 496- 503.

Dave PP (1996). India: A generics giant. *Farm Chemicals International* 10: 36- 37.

David M Mushigeri SB and Philip GH (2003). Alterations in the levels of ions in tissues of freshwater fish *Labeo rohita* exposed to Fenvelarate. *Pollution Research* 22(3): 359- 363.

De Mora S Villeneuve JP Sheikholeslami MR Cattini C and Tolosa I (2001). Organochlorinated compounds in Caspian Sea sédiments. *Marine Pollution Bulletin*. 48: 30- 43.

Dhananjayan V and Muralidharan S (2010). Levels of organochlorine pesticide residues in blood plasma of various species of birds from India. *Bulletin of Environmental Contamination and Toxicology* 85: 129- 136.

Dhananjayan V and Muralidharan S (2010). Organochlorine pesticide residues in Inland Wetland fishes of Karnataka, India and their implications on human dietary intake. *Bulletin of Environmental Contamination and Toxicology* 85: 619- 623.

Dhananjayan V Muralidharan S Ranapratap S (2011). Organochlorine pesticide residues in eggs and tissues of house sparrow, *Passer domesticus,* from Tamil Nadu, India. *Bulletin of Environmental Contamination and Toxicology* DOI 10.1007/s00128-011-0414-9.

Dickman MD and Lengu KMC (1998). Mercury and organochlorine exposure from fish consumption in Kong Hong. *Chemosphere* 37: 991- 1015.

Doong RA Lee CY and Sun YC (1999). Dietary intake residues of organochlorine pesticides in foods from Hsinchu, Taiwan. *The Journal of AOAC International.* 82(3): 677- 682.

Du ZY Zhang J Wang C Li L Man Q Lundebye AK Froyland L (2012). Risk-benefit evaluation of fish from Chinese markets: Nutrients and contaminants in 24 fish species from five big cities and related assessment for human health. *Science of the Total Environment* 416: 187- 199.

ECO/OPS/OMS (1995). Alfa-y beta-hexa chlorocyclohexanes (Alfa-y beta- HCH's). Guia para la salud y la seguridad. Mexico.53: 34.

ESCAP (1995). Asian and Pacific ministerial conference in preparation for the world summit for social development: proceedings (ST/ESCAP/1475).

Everaarts JM Van Weerler EM Fisher CV and Hillegrand MTJ (1996). Polychlorinated biphenyls and cyclic pesticides in sediments and macro-invertebrates from coastal regions of different climatological zones. International Atomic Energy Conference, July 1-5, 1996, Vienna, IAEA-SM/343- 345.

Fairey R Tabersk K Lamerdin S Johnson E Clark RP Downing JW Newman J and Petreas M (1997). Organochlorines and other environmental contaminants in muscle tissues of sport fish collected from San Francisco Bay *Marine Pollution Bulletin.* 12: 1058-1071.

Falandysz J Strandberg L Puzyn T and Gucia M (2001) Chlorinated cyclodiene pesticide residues in blue mussel, crab and fish in the Gulf of Gdansk, Baltic Sea. *Environmental Science and Technology* 35: 4163 - 4169.

Falandysz J Wyrzykowska B Warzocha J Barska I Wesołowskab AG and Szefer P (2004). Organochlorine pesticides and PCBs in perch *Perca fluviatilis* from the Odra/Oder river estuary, Baltic Sea. *Food Chemistry* 87(1): 17- 23.

FAO/ WHO (1978). Acceptable daily intake, residue limits and guide line levels proposals at joint committee meeting food and agriculture organization of the United Nations. World Health Organization 23 pp.

FAO (1983). Compilation of legal limits for hazardous substances in fish and fishery products. Food and Agriculture Organization of the United Nations, Rome, Italy.

FAO/WHO (1986). Maximum limits for pesticide residues. Codex Alimentarius Vol. XIII, Second Eds, Rome.

FAO/WHO (1991). Pesticide residues in food- 1991 evaluations. Part II. Toxicology. World Health Organization, WHO/PCS/92.52, Geneva.

FAO/WHO (1993). Pesticide residues in food- 1993 evaluations. Part II. Toxicology. World Health Organization, WHO/PCS/94.4, Geneva.

FAO/WHO (2000). Maximum residue limits in Codex Alimentarius. Vol-2B.

Faroon O Jones D and de Rosa C (2001). Effects of polychlorinated biphenyls on the nervous system. *Toxicology and Industrial Health* 16: 305- 333.

Fiedler H (2007). Stockholm convention on POPs: Obligations and implementation. In the fate of persistent organic pollutants in the environment. 3-12.

Fillmann G Readman JW Tolosa I Bartocci J Villeneuve JP Cattini C and Mee LD (2002). Persistent organochlorines residues in sediments from the Black Sea. *Marine Pollution Bulletin* 44: 122- 133.

FishBase (2007). /www.fishbase.org/serach.phpS.

Forget G (1991). Pesticides and the third world. *Journal of Toxicology and Environmental Health* 32: 11-31.

Forget G (1993). Balancing the need for pesticides with the risk to human health. In: Impact of Pesticide Use on Health in Developing Countries. Eds Forget G, Goodman T and De Villiers A, IDRC, Ottawa, p. 2.

Fowler SW (1987). PCB and the environmental Mediterranean marine ecosystem. In: Waid JS (ed) PCB and the environment, CRC Press, Florida: 209- 239.

Gerstenberger SL Gallinat MP and dellinger JA (1997). Polychlorinated Biphenyl congeners and selected organochlorine in lake superior fish, USA. *Environmental and Toxicological Chemistry* 16(11): 2222 -2228.

GESAMP (1989). The atmospheric input of trace species to the world ocean. GESAMP Reports and Studies, No. 38.

Glasby GP and Roonwal GS (1995). Marine pollution in India: an emerging problem. *Current Science*. 68: 495–497.

Government of India (2001). Tenth five-year plan: 2002-2007. Planning commission of India, New Delhi. 513 - 566. http://planningcommission.nic.in/plans/planrel/fiveyr/welcome.html.

Gregoriades GE Vassilopoulou V and Stergiou KI (1991). Multivariate analysis of organochlorine pesticide in red mullet from Greek Waters. *Marine Pollution Bulletin* 22: 297-241.

Grobler DF Badanhorst JE Kempster PL (1996). PCBs, chlorinated hydrocarbon pesticides and chlorophenols in the Isipingo Estuary, Natal, Republic of South Africa. Marine Pollution Bulletion. 32(7): 572- 575.

Gupta PK (2004). Pesticide exposure - Indian scene. *Toxicology*. 198: 83- 90.

Hagmar L Rylander L Dyremark E Klasson-Wehler E Erfurth EM (2001). Plasma concentration of persistent organochlorines in relation to thyrotropin and thyroid hormone levels in women. *International Archives of Occupational and Environmental Health* 74: 184 -188.

Halsall CJ Bailey R Stern GA Barrie LA Fellin P Miur DCG Rosenberg B Rivinsky FY Kononov EY and Pastukhov B (1998). Multi- year observations of organohalogen pesticides in the Arctic atmosphere. *Environmental Pollution*. 102: 52- 62.

Hao L Senthil Kumar K Sajwan KS Li P Peck A Gilligan M and Pride C (2009). Accumulation of polychlorinated biphenyls in fish collected from St. Simon's estuary, Brunswick, Georgia, USA. *Organohalogen Compounds*. 71: 170- 173.

Harding GC LeBlane RJ Vass WP Addison RF Hargrave BT Pearre Jr Dupuis A and Brodic PF (1997). Bioaccumulation of polychlorinated biphenyls in marine pelagic food web. *Marine Chemistry*. 56: 145- 179.

Hayes WJ and Laws ER (1991). Hand book of Pesticide Toxicology, Academic press, New York.

Hazarika R (2003). A study of neurotoxicity of BHC in relation to residual accumulation on the brain tissue of *Heteropneustes fossilis* (Bloch). *Journal of Environmental Biology.* 24: 77- 80.

Hazarika R and Das M (1998). Toxicological impact of BHC on the ovary of the Air-Breathing Catfish *Heteropneustes fossilis* (Bloch). *Bulletin of Environmental Contamination and Toxicology* 60: 16- 21.

Hedgecott S (1994). Prioritization and standards for hazardous chemicals. In: Calow P (ed). Handbook of Ecotoxicology, Blackwell Scientific Publications, London. 2: 368-393.

Heeschen W (1980).ToksikologischebewertungvonHCH-ruckstanden.Keil Milchwirtsch. Forchungsber 32: 151- 155.

Hesselberg RJ Hickey JP Nortrup DA and Willford WA (1990). Contaminant residues in the bloater of Lake Michigan, 1969-1986. *Journal of Great Lakes Research* 16:121-129.

Holland PT Hickey CW Roper DS and Trower TM (1993). Variability of organic contaminants in Inter- tidal sand flat sediments from Manukau harbour, New Zealand. *Archives of Environmental Contamination and Toxicology.* 25: 456 - 463.

Hong H Xu L Zhang L Chen JC Wong YS and Wen TS (1995). Environmental fate and chemistry of organic pollutant in sediment of Xiamen and Victoria harbors. *Marine Pollution Bulletin.* 31: 229- 64.

Hong SH YIm UH Shim WJ Oh JR and Lee IS (2003). Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. *Marine Pollution Bulletin.*46: 244- 53.

Horrigan L Robert SL and Walker P (2002). How sustainable agriculture can address the environmental and human health harms of industrial agriculture. *Environmental Health Perspective* 110: 445- 456.

http://www.cseindia.org accessed on 10th Nov. 2011.

http://www.st.nmfs.gov/st1/fus/us04 /08perita2004.pdf

http://www.teri.res.in/teriin/news/terivsn/issue31/pesticid.htm accessed on 10th November 2011.

Hussen A Westborn R Megersa N Mathiasson L and Bjorklund E (2007). Selective pressurized liquid extraction for multi-residue analysis of organochlorine pesticides in soil. *Journal of Chromatography A.* 1152: 247- 253.

Igbedioh SO (1991). Effects of agricultural pesticides on humans, animals and higher plants in developing countries. *Archives of Environmental Health* 46: 218.

Indian Pesticides Industry (2011). Credit analysis and research limited *p.*84.

Itawa H Tanabe S Sakai N and Tatsukawa R (1993). Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environmental Science and Technology* 26: 1080-1098.

Iwata H Tanabe S Sakai N Nishimura 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. *Environmental Pollution* 85:15- 33.

Jabber SMA Khan YSA and Rahman MS (2001). Organochlorine pesticide residues in the muscles of three fishes from the Ganges Estuary, Bangladesh. *International Journal of Ecology and Environmental Sciences* 27: 111-116.

Jacinto GS (1997). Preliminary assessment of marine pollution issues in the east Asian region at the end of the millennium. *Tropical Coasts.* 4: 3-7.

Jayakumar R (2001). Levels of heavy metal in commercial freshwater fishes of Coimbatore. M. Phil thesis submitted to Bharathiar University.

Jensen AA (1983). Chemical contaminant in human milk. *Residue Rev.* 89:1-128.

Jeyaratnam J (1985). Health problems of pesticide usage in the third world. *British Journal of Industrial Medicine* 42: 505- 506.

Johansen HR Alexander J Rossland OJ Planting S Lovik M Gaarder PI Gdynia W Bjerve KS and Becher G (1996). PCDDs, PCDFs and PCBs in human blood in relation to consumption of crabs from a contaminated Fjord area in Norway. *Environmental Health Perspective* 7: 756- 764.

Joint Meeting on Pesticide Residues (1998). JMPR Evaluations 1998-Part II. Toxicological Report.

Kalra RL Singh B Battu RS (1994). Organochlorine pesticide residues in human milk in Punjab, India, *Environmental Pollution.* 85: 147–151.

Kannan K Tanabe S and Tatsukawa R (1995). Geographical distribution and accumulation features of organochlorine residues in fish in tropical Asia and Oceania. *Environmental Science and Technology.* 29: 2673- 2683.

Kannan K Tanabe S Ramesh A Subramanian A and Tatsukawa R (1992). Persistent organochlorine residues in food stuffs from India and their implication on human dietary exposure. *Journal of Agricultural and Food Chemistry* 40: 518- 524.

Karunagaran VM Babu S Rajendran SB and Subramanian AN (1994). Organochlorine insecticide (HCHs and *p,p'*-DDE) residues in fishes from Kanyakumari (8º04'N, 77º36'E). *Indian Journal of Marine Sciences* 23:182-18.

Karuppiah S Subramanian A and Obbard JP (2005). Organochlorine residues in Odontocete species from the southeast coast of India. *Chemosphere.* 60(7): 891–897.

Kendall R Dickerson R Gisey J Suk W (1998). Principle and process of evaluating endocrine disruption in wild life. *Pensacola*: SETAC Press, pp. 491.

Klumpp DW Huasheng H Humphrey C Xinhong W and Codi S (2002). Toxic contaminants and their biological effects in coastal waters of Xiamen, China. I. organic pollutants in mussels and fish tissue. *Marine Pollution Bulletin* 44: 752-760.

Kole RK and Bagchi MM (1995). Pesticide residues in the aquatic environment and their possible ecological hazards. *Journal of the Inland Fisheries Society of India* 27:79-89.

Kole RK Banerjee H and Bhattacharya H (2001). Monitoring of Market fish samples for endosulfan and hexachlorocyclohexane residues in and around Calcutta. *Bulletin of Environmental Contamination and Toxicology* 67: 554- 559.

Kumar A Dayal P Shukla G Singh G and Joseph PE (2006). DDT and HCH residue load in mother's breast milk: a survey of lactating mother's from remote villages in Agra region. *Environmental International* 32: 248- 251.

Kumar B Kumar Garg R S Goel G Mishra M Singh SK Prakash D and Sharma SC (2011). Persistent organochlorine pesticides and polychlorinated biphenyls in intensive agricultural soils from North India. *Soil and Water Research* 6(4): 190- 197.

Kumari A Sinha RK Gopal K and Prasad K (2001). Dietary intake of persistent organochlorine residues through Gangetic fishes in India. *International Journal of Ecology and Environmental Sciences* 27:117-120.

Kumari B Singh R Madan VK Kumar R and Kathpal TS (1996). DDT and HCH compounds in soils, ponds and drinking water of Haryana, India. *Bulletin of Environmental Contamination and Toxicology* 57:787-793.

Laden F Neas LM Spiegeiman D Hankinson Se Willet WC and Ireland K (1999). Predictions of plasma concentrations of DDE and PCBs in a group of U.S Women. *Environmental Health Perspective* 107:75-81.

Leng JH Fujio K Wang PY Nakamura M Nakata T Wang Y (2009). Levels of persistent organic pollutants in human milk in two Chinese coastal cities, Tianjin and Yantai: influence of fish consumption. *Chemosphere* 75: 634- 639.

Leyva-Cardoso DO Ponce-Velez G Botello AV and Diaz-Gonzalez G (2003). Persistent organochlorine pesticides in costal sediments from Petacalco Bay, Guerrero, Mexico. *Bulletin of Environmental Contamination and Toxicology* 71: 1244- 1251.

Li YF (1999). Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Science of the Total Environment* 232: 121-158.

Locke MA Zablotowicz RM and Gaston LA (1995) Fluometuron interactions in crop residue managed soils pp. 55-58 In: Kingery, WL and Beuhring N (eds.) *Conservation farming: A Focus on water quality.* Mississippi Agriculture Forestry Experiment Station Special Bulletin 88 -7.

Long ER Macdonald DD Smith SL and Calder FD (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management. 19(1): 81- 97.

Manirakiza P Akimbamijo O Cavaci A Adediran SA Cisse I Fall ST and Schepens P (2002). Persistent chlorinated pesticides in fish and cattle fat and their implications for human serum concentrations from the Sene-Gambian region. *Journal of Environmental Monitoring* 4: 609- 617.

Marchand MD Vas and Dursma EK (1976). levels of PCBs and DDTs in mussels from the NW Mediterranean Coast. *Marine Pollution Bulletin* 7: 65-69.

Martin MA Malek MA Amin MR Khatoon J Rahman MS and Rahman M (1993). DDT residues in dried fish of Bangladesh. International Atomic Energy Agency, Dhaka.

Mathur SC (1999). Future of Indian pesticides industry in next millennium. *Pesticide Information* 24(4): 9-23.

McDonald DD (1994). A review of environmental quality criteria and guidelines for priority substances in the Fraser river basin. Department of environment, Canada. 1-58.

Minh TB Nakata H Watanabe M Tanabe S Miyazaki N Jefferson TA Prudente M and Subramanian A (2000). Isomer-specific accumulation and toxic assessment of polychlorinated biphenyls, including coplanar congeners in cetaceans from the North Pacific and Asian coastal waters. *Archives of Environmental Contamination and Toxicology.* 39:398-410.

Minh TB Kunisue T Yen NTH Watanabe M Tanabe S Hue ND and Qui V (2002). Persistent organochlorine residues and their bioaccumulation profiles in resident and migratory birds from North Vietnam. *Environmental Toxicology and Chemistry.* 21: 2108- 2118.

Mishra K and Sharma RC (2011). Assessment of organochlorine pesticides in human milk and risk exposure to infants from North-East India. *Science of the Total Environment* 409: 4939–4949.

Mishra K Sharma RC Kumar S (2012). Contamination levels and spatial distribution of organochlorine pesticides in soils from India. *Ecotoxicology and Environmental Safety* (76): 215– 225.

Monirith I Nakata H Tanabe S and Tana TS (1999). Persistent organochlorine residues in marine and freshwater fish in Cambodia. *Marine Pollution Bulletin.* 38(7): 604-612.

Monirith I Nakata H Watanabe S Takahashi S Tanabe S and Tana TS (2000). Organochlorines contamination in fishes and mussels from Cambodia and other Asian countries. *Water Science and Technology* 42(7-8): 241-252.

Monirith I Ueno D Takahashi S Nakata H Sudaryanto A and Subramanian AN (2003). Asia-Pacific mussel watch: Monitoring contamination of persistent organochlorine compounds in coastal waters of Asian countries. *Marine Pollution Bulletin* 46: 281-300.

Moon HB Kim HS Choi M Yu J and Choi HG (2009). Human health risk of polychlorinated biphenyls and organochlorine pesticides resulting from seafood consumption in South Korea, 2005-2007. *Food and Chemical Toxicology* 47:1819-25.

Muccio DA Stefanelli P Funari D Barbini A Generalli T Pelosi P Girolimetti S Amendola G Vanni F and Muccio DS (2002). Organochlorine pesticides and Polychlorinated biphenyls in 12 edible marine organisms from Adriatic Sea, Italy, spring 1997. *Food additives and contaminants* 19(12): 1148- 1161.

Mudiam MKR Pathak SP Gopal K and Murthy RC (2011). Studies on urban drinking water quality in a tropical zone *Environmental Monitoring and Assessment* Mar 17, 2011.1-9.DOI 10.1007/s10661-011-1980-3.

Muir D Norstom RJ and Simon M (1990). Organochlorine in arctic marine food chains: accumulation of specific polychlorinated biphenyl's and chlordane related compounds. *Environmental Science and Technology* 22: 1071-1079.

Mukherjee DP Kumar B Kumar S Mishra M Gaur R Prakash D Singh SK and Sharma CS (2011). Occurrence and distribution of pesticide residues in selected seasonal vegetables from West Bengal. *Archives of Applied Science Research* 3(5): 85-93.

Muralidharan (1993). Aldrin poisoning of Sarus Cranes *(Grus antigone)* and a few granivorous birds in Keoladeo National Park, Bharatpur, India. *Ecotoxicology* 2:196-202.

Muralidharan S Dhananjayan V and Jayanthi P (2009). Organochlorine pesticides in commercial marine fishes of Coimbatore, India and their suitability for human consumption. *Environmental Research.* 109:15-21.

Murty AS (1986). Toxicology of Pesticides to Fish, CRC Press, Inc, Florida.

Mwevura H Othman OC and Mhehe GL (1999). Organochlorine pesticide residues in Msimbazi and Kazinga rivers and the marine shoreline environment of Dar es Salaam. In: proceeding of the international inaugural conference of the Tanzania chemical society, Dar es Salaam, Tanzania: 106-119.

Mwevura H Othman OC and Mhehe GL (2002). Organochlorine pesticide residues in edible biota from the coastal area of Dar es Salaam city. *Western Indian Ocean Journal of Marine Sciences* 1:91-96.

Nagava R Nirakava H and Hori T (1995). Estimation of 1992-1993 dietary intake of organochlorine and organophosphorus pesticides in Fukuoka Japan. *Journal of AOAC International* 78: 921- 929.

Nair A Mandapati R Dureja P and Pillai MKK (1996) DDT and HCH load in Mothers and their infants in Delhi, India. *Bulletin of Environmental Contamination and Toxicology* 56: 58- 64.

Nakagava R Nirakava H and Hori T (1995). Estimation of 1992-1993 dietary intake of organochlorine and organophorous pesticides in Fukuoka Japan. *Journal of AOAC International* 78: 921-929.

Nandita B Vidyasaga K and Loganathan BG (2009). Congener specifies analysis and toxic evaluation of PCB congeners in sediment and fish samples from lower Tennessee river, Kentucky, USA. *Organohalogen Compounds.* 71: 615-619.

Nayak AK Raha R Das AK (1995). Organochlorine pesticide residues in middle stream of the Ganga river, India. *Bulletin of Environmental Contamination and Toxicology* 54: 68- 75.

Newell AJ Johnson DW and Allen LK (1987). Niagara river biota contamination project: fish flesh criteria for piscivorous wildlife. New York Department of Environmental Conservation, Division of fish and wildlife, Albany, technical report 3: pp 182.

Niethammer KR White DH Baskett TS and Sayre MW (1984). Presence and biomagnifications of OC chemical residues in Oxbow Lakes of northeastern Louisiana *Archives of Environmental Contamination and Toxicology.* 13: 63-74.

Olsson A Valters K and Burreua S (2000). Concentration of organochlorine substances in relation to fish size and tropic position. *Environmental Science and Technology.* 34: 4878- 4886.

Padma SV Mishra R Johnson S (2001), Analysis of Samples from Padre Village from Kasargod District of Keralam for Endosulfan Residues (Pollution Monitoring Laboratory- Pesticide Residue Monitoring Study CSE/PRM-1/2001). Centre for Science and Environment, New Delhi.

Pandelova M Henkelmann B Roots O Simm M Jarv L Benfenati E and Schramm KW (2008). Levels of PCDD/F and dioxin-like PCB in Baltic fish of different age and gender. *Chemosphere* 71: 369- 378.

Pandit GG and Sahu SK (2001). Gas exchange of OCPs across the air–water interface at the creek adjoining Mumbai Harbour, India. *Journal of Environmental Monitoring* 3:635-638.

Pandit GG Mohan Rao AM Jha SK Krishnamoorthy TM Kale SP and Raghu K (2001). Monitoring of organochlorine pesticide residues in the Indian marine environment. *Chemosphere.* 44(2): 301-305.

Pandit GG Sahu SK Sharma S Puranik VD (2006). Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai. *Environmental International* 32: 240 – 243.

Pastor D Boix J and Albaiges J (1996). Bioaccumulation of organochlorine contaminants in three estuarine fish species. *Marine Pollution Bulletion* 32: 257-262.

Phoung PK Son CPN Sauvain JJ and Tarradellas J (1998). Contamination by PCBs, DDTs and heavy metals in sediments of Ho Chi Minh city's canals, Vietnam. *Bulletin of Environmental Contamination and Toxicology*. 60: 347-354.

Picer M and Picer N (1991). Long term trends of DDTs and PCBs in sediment samples collected from the Eastern Adriatic Coastal waters. *Bulletin of Environmental Contamination and Toxicology*. 47: 864- 873.

Porte C and Albaiges J (1993). Bioaccumulation pattern of hydrocarbons and polychlorinated biphenyl's in bivalves, crustaceans and fish. *Archieves of Environmental Contamination and Toxicology*. 26: 273-281.

Prudente M Tanabe S Watanabe M Subramanian A Miyazaki N Suarex P and Tatsukawa R (1997). Organochlorine contamination in some Odontoceti species from the North Pacific and Indian Ocean. *Marine Environmental Research*. 44: 415-427.

Psenner R (1989). Chemistry of high mountain lakes in siliceous catchments of the Central Eastern Alps. Aquatic Sciences. 51: 108–128.

Qiu X Zhu T Li J Pan H Li Q Miao G and Gong J (2004). Organochlorine pesticides in the air around the Taihu Lake, China. *Environmental Science and Technology*. 38: 1368-1374.

Radhakrishnan AG and Antony PD (1989). Pesticide residues in marine fishes. *Journal of Fisheries Technology* 26: 60- 61.

Radhakrishnan AG Antony PD Mukundan MK and Stephan J (1986). On the use of mussels as a pollution indicator. In: Proceedings of National seminar on mussel watch, Cochin, pp. 13- 14.

Radhakrishnan AG (1994). Organochlorine pesticide residues in farmed prawn (*Penaeus monodon*), oyster (*Crassostrea madrasensisi*) and mussel (*Perna viridis*). In: Proceedings of the symposium nutrients and bioactive substances in aquatic organism. Society of fisheries technologists (India), Cochin, p.266.

Rajendran RB Imaganwa T Tao H and Ramesh R (2005). Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. *Environmental International* 31: 503- 512.

Ramesh A Tanabe S Kannan K Subramanian AN Kumaran PL and Tatsukawa R (1992). Characteristic trend of persistent organochlorine contamination in wildlife from a tropical agricultural watershed, South India. *Archives of Environmental Contamination and Toxicology* 23: 26- 36.

Rekha Naik SN and Prasad R (2006). Pesticide residue in organic and conventional food-risk analysis. *Journal of Chemical Health and Safety* 13:12- 19.

Richard EJ (1976). DDT metabolism in microbial system. *Residue reviews.* 61:1-28.

Riedel R Schlenk D Frank D and Costa B (2002). Analysis of organic and inorganic contaminants in salton sea fish. *Marine Pollution Bulletin.* 44: 403- 411.

Ross GL (2004). The public health implications of polychlorinated biphenyls (PCBs) in the environment. *Ecotoxicology and Environmental Safety,* 59: 275- 291.

Ruiz X and Llorente GA (1991). Seasonal variation of DDT and PCB accumulation in muscle of Carp (*Cyprinus carpio*) and Eels (*Anguilla anguilla*) from the Ebro Delta, Spain. *Vie et Milieu* 41: 133–140.

Sankar TV Zynudheen AA Anandan R Nair PGV (2006). Distribution of organochlorine pesticides and heavy metal residues in fish and shellfish from Calicut region, Kerala, India, *Chemosphere* 65: 583–590.

Sannino A Mambriani P Bandini M and Bolzoni L (1996). Multiresidue methods for determination of organochlorine insecticides and polychlorinated biphenyl congeners in fatty procssed foods. *Journal - Association of Official Analytical Chemists.*79: 1434- 1446.

Santerre CR Ingram R Lewis GW Davis TJ Lane LG Grodner RM Wei CI Bush PB Xu DH Shelton J Alley EG and Hinshaw JM (2000). Organochlorines, Organonophosphates and Pyrethroids in channel Catfish, Rainbow Trout and Redswamp Cray fish from Aquaculture. *Journal of food Science* 65 (2): 231-235.

Sarkar A and Sen Gupta R (1988). Chlorinated pesticide residues in marine sediments. *Marine Pollution Bulletin* 19(1): 35- 37.

Sarkar A and Sen Gupta R (1990). Evaluation of the levels of organochlorine pesticide residues in the sediment, water and marine organisms from the seas around India. Proc. IX international symposium on medical oceanography, at Carrefour Universitaire Maditerraneen, NICE, France, 22-24 Oct., Sec: Ecological Impact of Pollution.

Sarkar A Nagarajan R Chaphadkar S Pal S and Singbal SYS (1997). Contamination of organochlorine pesticides in sediments from the Arabian Sea along the West Coast of India. *Water Reseach* 31(2):195-200.

Sarkar SK Bhattacharya BD Bhattacharya A Chatterjee M Alam A Satpathy KK and Jonathan MP (2008). Occurrence, distribution and possible sources of

organochlorine pesticide residues in tropical coastal environment of India: An overview. *Environmental International.* 34:1062–1071.

Sax NI (1984). Dangerous properties of Industrial materials, Sixth edition, Van Nostren Rein hold, New York. p. 2580.

Schantz S Gasior D Polverejan E McCaffrey R Sweeney A Humphrey H and Gardiner J (2001). Impairments of memory and learning in older adults exposed to polychlorinated biphenyls via consumption of Great Lakes fish. *Environmental Health Perspective* 109: 605-601.

Schmitt CJ (1990). U.S. fish and wild life service, National Fisheries Contaminant Research Center, Columbia, Missouri, Twenty- Eight Hanford symposium on health and the environment: 5-14.

Schmitt CJ Zajicek JL and Peterman PL (1990). National contaminant biomonitoring Program: Residues of organochlorine in fresh water fishes of the United States, 1976 -1984. *Archinves of Environmental Contamination and Toxicology.* 19: 748- 782.

Schmitt CJ and Dethloff GM (2000). Biomonitoring of environmental status and trends program: Scheduled methods for monitoring chemical contaminants in aquatic ecosystems. US Geological Survey, Biological resources division, Columbia, MO, Information and technology report USGS/BRD/ITR-2000-0005, 81 pp.

Schmitt CJ and Bunck CM (2004). Persistent environmental contaminants in fish and wildlife. National Biological Service: 1-9.

Sericano JL Wade TL Atlas FL and Brooks JM (1990). Historical perspectives on the environmental bioavailability of DDT and its derivatives to Gulf of Mexico Oysters. *Environmental Science and Technology.* 24:1541-1548.

Sericano JL Wade TL Jackson TJ Brooks JM Tripp BW Farrington HW Mee LD Readman J Villeneuve HP and Goldberg ED (1995). Trace organic contamination in the America: An overview of the US national status and trends and the International 'Mussel Watch' Programme. *Marine Pollution Bulletin* 31: 214-225.

Sericano JK Wade TL Jackson TJ Brooks JM Tripp BW Farrington HW Mee LD Read man JW Villeneuve HP and Goldberg ED (1995). Trace organic contamination in the Americas: An overview of the US national status and trends and the international, mussel watch programmed, *Marine Pollution Bulletin* 31: 214-225.

Shailaja MS Sen Gupta R (1989). DDT residues in fishes the eastern Arabian Sea. *Marine Pollution Bulletin* 20: 620- 630.

Shailaja MS and Sen Gupta R (1990). Residues of dichlorodiphenyltrichloroethane and metabolites in zooplankton from the Arabian Sea. *Current Science.* 59: 929- 931.

Shailaja MS and Nair M (1997). Seasonal differences in organochlorine pesticide concentrations of zooplankton and fish in the Arabian Sea. Marine Environmental Research 44: 264- 274.

Sharma VK (2000). Environment problem of coastal areas in India, Book well press, New Delhi. 201-216.

Shegunova P Klanova J and Holoubek I (2007). Residues of organochlorinated pesticides in soils from Czech Republic. *Environmental Pollution.* 146: 257- 261.

Shelepchikov AA Brodsky ES Feshin DB and Mir-Kadirova EY (2009). Organic contaminants in the Moscow region. *Organohalogen Compounds* 71: 439– 443.

Simonich SL and Hites RA 1995. Global Distribution of Persistent Organochlorine Compounds. *Science* 269: 1851-1854.

Singh RP (2001). Comparison of organochlorine pesticide levels in soil and ground water of Agra, India. *Bulletin of Environmental Contamination and Toxicology* 67: 126-132.

Singh B and Gupta A (2002). Monitoring of pesticide residues in different sources of drinking water of Jaipur, India. *Bulletin of Environmental Contamination and Toxicology* 69: 49- 53.

Singh SK Raha P and Banerjee H (2006). Banned organochlorine cyclodiene pesticide in ground water in Varanasi, India. *Bulletin of Environmental Contamination and Toxicology* 76: 935 - 941.

Singh K Malik A Sinha S (2007). Persistent organochlorine pesticide residues in soil and surface water of Northern Indo-Gangetic alluvial plains. *Environmental Monitoriong Assessment* 125 (1): 147- 155.

Solomon GW and Weiss PM (2002). Chemical contaminants in breast milk: time trends region variability. *Environmental Health Perspective* 110: 339- 347.

Spiric A and Saisic S (1998). Monitoring Chlorinated pesticides and toxic elements in tissues of food producing animals in Yugoslavia. *Journal of AOAC International.* 81(6):1240-44.

Stefanelli P Muccio DA Ferrarra F Barbani DA Generali T Pelosi P Amendola G Vanni F Muccio DS Ausili A (2004). Estimation of intake of organochlorine pesticides and

chlorobiphenyls through edible fishes from the Italian Adriatic Sea during 1997. *Food Control.* 15: 27-38.

Stein JE Collier TK Reichert WL Casillas E Hom T and Varanasi U (1993) Bioindicator of contaminant exposure and sublethal effects in benthic fish from Puget Sound, WA, USA. *Marine Environmental Research.* 35: 95-100.

Stout V (1980). Organochlorine residues in fish from the Northwest Atlantic Ocean and Gulf of Mexico. *Fisheries Bulletin US* 78: 51- 58.

Strandberg B Van Bavel B Bergqvist PA Broman D Ishaq R and Naf (1998). Occurrence, sedimentation and spatial variations of organo contaminants in settling particulate matter and sediments Northern part of the Baltic Sea. Environmental Studies (CEMS), Ehime University Japan.

Sun P Basu I Blanchard P Backus SM Brice KL Hulting ML and Hites RA (2003). Temporal and spatial trends of atmospheric toxic substances near the great lakes: IADN results through 2003. Environment Canada and the United States Environmental Protection Agency, Chicago IL.

Sun SJ ZhaoJH Koga M Ma YX Liu DW Nakamura M Liu HJ Horiguchi H Clark GC Kayama F (2005).Persistent organic pollutions in human milk in women from urban and rural areas in northern China. *Environmental Research* 99: 285- 293.

Tanabe S Iwate H and Tatsukawa R (1994). Contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Science of the Total Environment* 154:163-77.

Tanabe S (2000). Asian developing regions: Persistent organic pollutants in the seas. In: Sheppard, CRC (Eds,) Seas at the Millennium: An Environmental Evaluation. Elsevier Science. Amsterdam. pp. 447-46.

Tanabe S Prudente MS Kan-arireklap S and Subramanian A (2000). Mussel watch; Marine pollution monitoring of butyltins and organochlorines in coastal waters of Thailand, Philippines and India. *Ocean and Coastal Management* 43: 819- 839.

Tashiro S and Matsumura F (1978). Heptachlor is metabolized into heptachlor epoxide in humans and animals. *Archives of Environmental Contamination and Toxicology* 7:113-127.

Temple SA and Weins JA (1989). Bird populations and environmental changes: can birds be bio-indicators? *American Birds.* 43: 260- 270.

The Gazette of India (2007). Part II-Sec. 3(ii), No. 1051, REGD. No. D.L-33004/99, Ministry of Agri., Department of Agriculture and Co-operation, August 29, 2007.

Tomar SS and Parmar BS (1998). Adieu organochlorine pesticides. *Journal of Pest Science* 10: 1–13.

Tsigouri AD and Tyrpenou AE (2000). Determination of organochlorine compounds (OCPs and PCBs) in marine fish oil and fish liver oil by capillary Gas Chromatography and Electron Capture Detection. *Bulletin of Environmental Contamination and Toxicology* 65: 244- 252.

UNEP (2002). Global report on regionally based assessment of persistent toxic substances, UNEP chemicals, Geneva, Switzerland.

van Den Berg M Birnbaum LS Denison M De Vito M Farland W Feeley M Fiedler H Hakansson H Hanberg A Haws L Rose M Safe S Schrenk D Tohyama C Tritscher A Tuomisto J Tysklind M Walker N and Peterson RE (2006). The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences* 93: 223- 241.

van der Oost R Goksoyr A Celander M Heida H Vermeulen NPE (1996). Biomonitoring of aquatic pollution with Fera Eel (*Anguilla anguilla*) - II. Biomarkers: pollution-induced biochemical responses. *Aquatic Toxicology*. 36: 189-222.

van der Oost R Opperhuizen A Satumalay K Heida H and Vermeulen NPE (1996) Biomonitoring aquatic pollution with feral eel (*Anguilla anguilla*). I. Biota–sediment ratios of PCBs, OCPs, PCDDs and PCDFs. *Aquatic Toxicology,* 35: 21- 46.

Van Oost dam J Gilman A Dewailey E Usher P Whitely B Kunhlein H Neve S Walker H Feely TM Jerome V Kwavnick B (1999). Human health implications of environmental contaminants in Arctic Canada: A review, *Science of the Total Environment.* 230 (1-3):1-82.

Vassilopoulo V and Georgakopoulous-Gregoriades E (1993). Factors influencing the uptake of organochlorines in red mullet (*Mullus barbatus*) from a gulf of Central Greece. *Marine Pollution Bull*etin 26: 285-287.

Venugopalan VK and Rajendran N (1984). Pesticide pollution effects on marine and estuarine resources. DAE Research Project Report, Parangipetti. India: Centre for Advanced Study in Marine Biology, Annamalai University p.1-316.

Verlecar XN Pereira N Desai SR Jena KB and Snigdha (2006). Marine pollution detection through biomarkers in marine bivalves *Current Science* 91(9): 10.

Vijayan VS Prasad SN Vijayan L and Muralidharan S (2004). In: Inland wetlands of India - Conservation priorities (pp. XXIV + 532).

Villeneuve JP Carvalho FP Fowler SW and Cattini C (1999). Levels and trends of PCBs, chlorinated pesticides and petroleum hydrocarbons in mussels from the NW Mediterranean Coast: comparison of concentration in 1973/1974 and 1988/1989. *Science of the Total Environment* 57-65: 237-238.

Wang X Wang D Qin X and Xu X (2008). Residues of organochlorine pesticides in surface soils from college school yards in Beijing, China. *Journal of Environmental Sci*ences 20: 1090-1096.

Wania F and Mackay D (1993). Global fractionation and cold condensation of volatile organochlorine compounds in Polar Regions. *AMBIO* (*Advanced Nanostructured Surfaces for the Control of Biofouling*) 22:10 - 8.

Wania F and Mackay D (1996). Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology.* 30: 390-396.

Wayne G Robin LA Geoffrey MB and Matthews (1997). Design and analysis of multispecies toxicity tests for pesticide registration *Ecological Applications* 7: 1111-1116.

Weseloh DV Ewins PJ Struger J Mineau P Bishop CA Postapalsky S and Ludwig JP (1995). Double-crested cormorants of the Great Lakes: changes in population size, breeding distribution and reproductive output between 1913 and 1991. *Colonial Waterbirds* 18: 48- 59.

White DH and Stickel LF (1975). Impacts of chemicals on waterfowl reproduction and survival. Transactions of the first International Waterfowl symposium: 132-142.

WHO (1979). DDT and its derivatives. WHO, New York.

WHO (1984). Guidelines for drinking water quality. II: 190-218.

WHO - World Health Organization (1993). Polychlorinated biphenyls and terphenyls (Second edition). *Environmental Health Criteria.* Geneva.140: pp 682.

WHO (2000). Public health impact of pesticides used in agriculture. World Health Organization, WHO-UNEP, Geneva. p. 88.

Wienmeyer SN Mulhrn BM Ligas FJ Hensel RJ Mathisen JE Robards FC and Postapalsky S (1972). Residues of organochlorine pesticides, polychlorinated biphenyl's, and mercury in Bald Eagle eggs and changes in shell thickness, 1969 and 1970. *Pesticide Monitoring* 6: 50-55.

Willett K Ulrich EM and Hites RA (1998). Differential toxicity and environmental fates of hexachlorocyclohexane. *Environmental Science and Technology* 32: 2197-2207.

Winger PV Schultz DP and Johnson WW (1990).Environmental contamination concentration in biota from the lower Savannah River. Geogria and South Carolina. *Archives of Environmental Contamination and Toxicol*ogy 19: 101-107.

www. fao.org/fishery/country/sector/FJ-CP_IN/en

www.indiastat.com accessed on January 27, 2012.

www.st.nmfs.gov/st1/fus/us04 /08perita2004.pdf)

Yamada H Takayanagi K Tateishi M Tagata H and Ikeda K (1997). Organotin compounds and polychlorinated biphenyls of livers in squid collected from coastal waters and open oceans. *Environmental Pollution.* 96: 217-226.

Yassi A Kjellström T de Kok T and Guidotti TL (2001). Basic environmental health. Oxford: University Press: 291-2.

Zhou HY and Wong MH (2004). Screening of organochlorines in freshwater fish collected from Pearl River Delta, People's Republic of China. *Archives of Environmental Contamination and Toxicology* 46: 106-113.

Zhou JL Maskaoui K Qui YW Hong HS and Wang ZD (2001). Polychlorinated biphenyls congeners and organochlorinated insecticides in the waters and sediments of Daya Bay, China. *Environmental Pollution* 113: 373–384.

Zhulidov AV Roberts RD Headley JV Liber K Zhulidov DA Zhulidova OV and Pavlov DF (2000). Levels of DDT and hexachlorocyclohexane in Burbot (*Lota lota* L) from Russian Arctic rivers. *Science of the Total Environment* 292: 231- 246.

ANNEXURE

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Organochlorine pesticides in commercial marine fishes of Coimbatore, India and their suitability for human consumption

Subramaniyan Muralidharan *, Venugopal Dhananjayan, Palaniyappan Jayanthi

Ecotoxicology Division, Sálim Ali Centre for Ornithology and Natural History, Coimbatore 641 108, TN, India

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ABSTRACT

Organochlorine pesticide residues were determined in 10 species of fishes caught at Cochin and Rameshwaram coast, and sold in Coimbatore, Tamil Nadu, India. Species were selected on the basis of their regular availability throughout the year and commercial value. A total of 389 fishes were analyzed for organochlorine residues and their suitability for human consumption was evaluated. Results show varying levels of residues of hexachlorocyclohexane (HCH), DDT, heptachlor epoxide, endosulfan and dieldrin. Among the 10 species, high concentration of pesticide residues were recorded in *Sardinella longiceps*, *Carangoides malabaricus*, *Chlorophthalmus agassizi*, *Saurida tumbil* and *Rastrelliger kanagurta*. The variation in total organochlorine residues among species and between places was not significant ($P > 0.05$). Only five species of fishes showed monthly variation in residue levels and there was no significant correlation between the body size and residue levels in the tissue. About 22% of the fishes exceeded the maximum residue limits (MRL) of total HCH prescribed by FAO/WHO for fish products. The calculated dietary intake of total HCH through consumption of *C. malabaricus*, *C. agassizi* and *S. longiceps* exceeded the maximum acceptable dietary intake (ADI) limits prescribed for human consumption. The present study recommends continuous monitoring of environmental contaminants in marine fishes to assess the possible impact on human health.

1. Introduction

Organochlorines continue to be the potential group of chemicals used in control of agricultural pests and vectors of diseases like malaria (David et al., 2003), even though many new broad spectrum pesticides have been developed in recent years. Moreover, the lipophilic nature, hydrophobicity and, low chemical and biological degradation rates of organochlorine pesticides have led to their accumulation in biological tissues and subsequent magnification of concentration in organisms progressing up in the food chain (Swackhamer and Hites, 1988). Pollution by persistent chemicals is potentially harmful to the organisms at higher trophic levels in the food chain. The aquatic organisms like fish are able to accumulate several fold higher concentration of pesticide residues than the surrounding water (Siddiqui et al., 2005). It has been found that greater than 80% of the total intake of pesticide residues in human beings is through the food chain (Martinez et al., 1997; Trotter and Dickerson, 1993). Studies have also related the presence of organochlorine residues in breast milk and consumption of contaminated fish, and their role in alteration of thyroid function (Fitzgerald et al., 2001; Hagmar et al., 2001). It has been reported that considerable amount of organochlorine pesticide residues find their way into humans through consumption of contaminated marine fishes (Mwevura et al., 2002).

India is now both the largest manufacturer and consumer of pesticides in South Asia. Despite the proliferation of different types of pesticides, organochlorines such as hexachlorocyclohexane (HCH) and DDT still account for two-thirds of the total consumption in the country (Kumari et al., 2001) for agriculture and public health purposes. Due to the human and environmental risks associated with the use of such pesticides, they have been banned in several countries but are still used in India (Mathew, 1993). In India as most of the rivers pass through agricultural fields, they are subjected to contamination with different pesticides used for crop protection. Higher levels of HCH are being reported to occur in Indian marine waters and it is estimated that about 25 tonnes of organochlorines produced have been already transported to the sea (Mohapatra and Saha, 2000).

In India there are many studies on the presence of organochlorine residues in aquatic system; water and fishes (Sarkar et al., 2003), soil and ground water (Singh, 2001), water (Muralidharan, 2000) and water, sediment and fishes (Vijayan and Muralidharan, 1999). Studies done by Kole et al. (2001) reported the presence of endosulfan and HCH residues in fishes sold at Calcutta market. Karunagaran et al. (1994) documented the presence of

* Corresponding author. Fax: +91 422 2657088.
E-mail address: ecot_mur@yahoo.com (S. Muralidharan).

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organochlorine (HCH and *p,p'*-DDE) residues in fishes collected from the landing sites of Kanniyakumari coast. But information available on the daily intake of persistent organochlorine pesticide residues through fishes to human beings are limited (Kumari et al., 2001; Vijayan et al., 2004). The present study was aimed at assessment of OCPs in selected species of marine fishes sold in Coimbatore market; documentation of the variation in the magnitude of contamination among months and between locations; and evaluation of the potential exposure to human through the consumption of these fishes.

2. Materials and methods

2.1. Study area and sample collection

Coimbatore is an important industrial town in the South of India. It is located between 10°55′and 11°10′N, and 77°50′ and 76°50′E at an approximate altitude of 470 m. The population of Coimbatore as per the 2001 census of India is 0.9 million. The supply of fresh water fishes is from various wetlands within the city and nearby, whereas marine fishes come from both the southwest and east coast of India. The present study is focused on marine fishes collected from Cochin and Rameshwaram and sold in Coimbatore (Fig. 1).

A preliminary survey was conducted to assess the total marine fish sold in Coimbatore, the common species available and their origin. Ukkadam is the major fish market in Coimbatore where from the fishes are distributed throughout the city. Altogether around 10 tonnes of marine fishes are sold in the city every day (Esha Mathew, 2004). All the samples were collected from this market for the current study. Although more than 20 species come to this market, only 10 species are sold here on a regular basis. Hence, only those 10 species of fishes were collected on monthly basis between January and May 2004. The common name, size, weight and the major food items of species included in the study are given in Table 1. Totally 389 fishes were selected at random, cleaned off external dirt, labeled and packed in clean polythene bags, transported on ice to the laboratory and stored in deep freezer at −20 °C till the dissection was carried out. Morphometric measurements such as body length and weight were recorded at the collection spot. A questionnaire survey was also conducted comprising 325 families covering entire Coimbatore. Information on preference of the species, age of the person and frequency of consumption was collected in order to estimate the daily dietary intake of the study species by the local people.

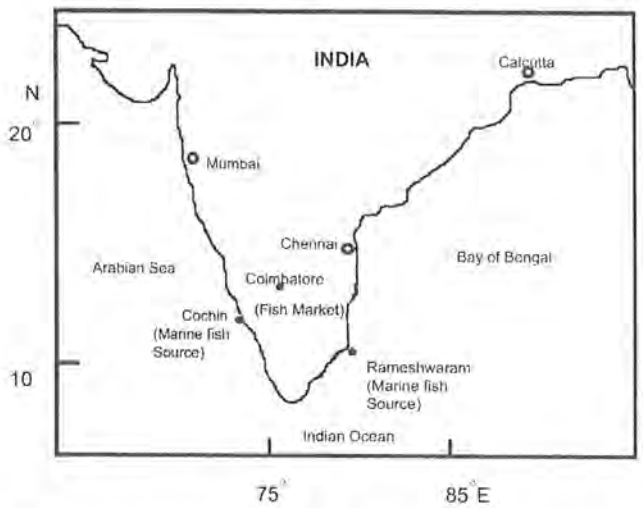

Fig. 1. Map showing the regular supply sites of marine fishes to Coimbatore.

2.2. Sample processing

Although the vital organs such as gill, kidney, liver are sensitive to pesticide accumulation, muscle forms the major edible portion in the fish. Therefore, muscle tissue alone was analyzed as the objective is to determine the dietary intake to human body. The fish samples were taken out from the deep freezer, thawed, cleaned in tap water, and scales sloughed off. Muscle tissue was dissected between the pectoral fin and vent of the fish, minced into smaller pieces and a subsample was taken from the homogenate. About 10 g of muscle tissue was weighed, ground with anhydrous sodium sulphate and the mixture was packed in a thimble (Whatman), and desiccated overnight prior to extraction. The desiccated thimble was loaded in a Soxhlet extractor and extracted with 250 ml of pesticide grade hexane (Merck) for 6 h. The extract was condensed in a rotary flask evaporator to a specific aliquot (5 ml). The aliquot was then subjected to acid treatment by adding 2 ml of concentrated sulphuric acid then neutralized with saturated sodium hydroxide solution. Further the sample was cleaned by placing on a glass column packed with silica gel (60–120 mesh) and eluted with 250 ml of hexane. The eluate was again condensed in a rotary flask evaporator and stored in deep freezer at −20 °C till the gas chromatography analysis.

2.3. Chemical analysis

Samples were analysed with Hewlett-Packard 5890 Series II gas chromatograph equipped with Ni^{63} electron capture detector (ECD) and DB-608 fused silica capillary column (30 m × 0.32 mm × 0.5 μm) coated with 35% phenyl methyl polysiloxane. Chromatographic conditions were as follow: detector 300 °C; injector 250 °C; oven temperature was programmed as 180 °C 3 min; 4 °C/min to 260 °C 15 min. All the samples were analysed for alpha-hexachlorocyclohexane (α-HCH), β-HCH, δ-HCH, lindane (γ-HCH), heptachlor epoxide (HE), dieldrin, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD, α-endosulfan, β-endosulfan and endosulfan sulphate. An equivalent mixture provided by Dr. Ehrenstorfer Laboratories (Germany) was used as the standard. The concentrations of the individual compounds were quantified from the peak area of the sample to that of the corresponding external standard.

Recoveries of the compounds from fortified samples (50 ppb) ranged from 94% to 103% and the results were not corrected for per cent recovery and the results were expressed in wet weight basis. Analyses were run in batches of 10 samples plus four quality controls (QCs) including one reagent blank, one matrix blank, one

Table 1
List of fishes included in the study

Common name	Scientific name	N	Mean ± SD		Major food items[a]
			Size (cm)	Weight (g)	
Cochin					
Perch	*Chlorophthalmus agassizi*	30	19.6 ± 1.7	62.2 ± 19	Small crustaceans, small fishes and invertebrates
Japanese threadfin	*Nemipterus japonicus*	48	14.5 ± 3.0	46.5 ± 28	Small crustaceans, small fishes and invertebrates
Oil sardine	*Sardinella longiceps*	44	15.5 ± 1.4	32.9 ± 9.2	Phytoplankton, and small crustaceans
Lizard fish	*Saurida tumbil*	50	19.9 ± 1.9	56.3 ± 17	Crustaceans, small squids and fishes
Husky catfish	*Tachysurus maculatus*	34	20.9 ± 2.6	82.0 ± 32	Small crustaceans, small fishes and invertebrates
Rameshwaram					
Malabar trevelly	*Carangoides malabaricus*	39	17.8 ± 1.7	84.7 ± 32	Crustaceans, small squids and fishes
Tongue sole	*Cynoglossus macrolepidotus*	40	23.1 ± 2.5	98.8 ± 46	Benthic invertebrates
Pig-faced bream	*Lethrinus conchyliatus*	27	25.8 ± 13	88.4 ± 22	Small crustaceans, small fishes and invertebrates
Jew fish	*Otolithes cuvieri*	30	21.4 ± 2.5	98.6 ± 28	Benthic invertebrates
Indian mackerel	*Rastrelliger kanagurta*	47	22.5 ± 1.5	115.7 ± 22	Phytoplankton, zooplankton, shrimps and fishes
Total		389			

[a] *Source*: FishBase (2007).

QC check sample and one random sample in duplicate. The minimum detection limit for all the compounds analysed was 1 ppb.

2.4. Statistical analysis

Analysis of variance (ANOVA) was used to test the differences in organochlorine residues among species, months and between places. The mean was calculated from the detectable values and the value below detectable limit was considered as zero. Spearman's rank correlation was applied to evaluate the correlations between chemical concentrations and the size of each fish species. All these calculations were performed using statistical software, SPSS Student version 10.

3. Results

Among the organochlorines analyzed, HCH was the most frequently detected (98%) and the frequency of occurrence among its isomers ranged between 64% and 87%. One or more derivatives of DDT were detected in 66% of fishes. Among the cyclodiene pesticides, HE was detected in 69%, dieldrin in 38% and total endosulfan in 66% of the samples analyzed.

3.1. Variation in organochlorine residues among a few species of marine fishes of Cochin coast

Significant variations ($P<0.05$) in organochlorine residues were observed only in *Sardinella longiceps*, a herbivore which recorded the highest mean concentration of β-HCH (562 ppb). The lowest concentration of β-HCH was detected in *Nemipterus japonicus* (203 ppb). The concentrations of α- and γ-HCH were more or less equal in most of the samples while δ-HCH recorded less than 10 ppb in all the fishes except *S. longiceps* (17 ppb) (Table 2). The *p,p'*-DDT and its metabolites *p,p'*-DDD and *p,p'*-DDE did not show any significant variation ($P>0.05$) among the species. The maximum average concentration of *p,p'*-DDT was detected in *S. longiceps* and *N. japonicus* (9 ppb), while the minimum was in *Chlorophthalmus agassizi* (3 ppb). The higher concentration of *p,p'*-DDE was recorded in *Saurida tumbil* (25 ppb) followed by *S. longiceps* (14 ppb), while the lowest was in *C. agassizi* (1 ppb). In the case of *p,p'*-DDD, the maximum was in *S. longiceps* (24 ppb) and the minimum in *C. agassizi* (2 ppb) (Table 2). Similarly among the cyclodiene pesticides (endosulfan, HE and dieldrin), endosulfan was found to be the maximum in *S. longiceps* (21 ppb) and the minimum in *C. agassizi* (11 ppb). The maximum average concentration of HE was recorded in *S. longiceps* (8 ppb) followed by *N. japonicus* (5 ppb) and the minimum in *C. agassizi* (1 ppb). The mean concentration of dieldrin ranged from 1 ppb in *C. agassizi* to 5 ppb in *N. japonicus* (Table 2). Of the five species of fishes received from Cochin, *S. longiceps* and *C. agassizi* showed the highest concentrations of OCPs, while *N. japonicus* showed the lowest.

3.2. Variation in organochlorine residues among a few species of marine fishes of Rameshwaram coast

Five species of fishes, namely *Carangoides malabaricus*, *Cynoglossus macrolepidotus*, *Lethrinus conchyliatus*, *Otolithes cuvieri* and *Rastrelliger kanagurta* were analyzed for OCPs (Table 3). Among the isomers of HCH, β-HCH recorded the maximum, similar to that of the fishes of Cochin. The maximum mean concentration of β-HCH was observed in *C. malabaricus* (534 ppb) and the minimum in *L. conchyliatus* (196 ppb). The highest amount of

Table 2
Mean (±SE) concentration of organochlorine residues (ppb, wet wt.) in marine fishes collected from Cochin coast

Compound	*Chlorophthalmus agassizi*, $N=30$		*Nemipterus japonicus*, $N=48$		*Sardinella longiceps*, $N=44$		*Saurida tumbil*, $N=50$		*Tachysurus maculatus*, $N=34$	
α-HCH	27±10	(27)	9±1	(43)	40±8	(41)	22±8	(44)	17±4	(30)
γ-HCH	45±30	(22)	12±4	(40)	41±9	(40)	14±4	(38)	11±3	(28)
β-HCH	407±166	(22)	203±60	(41)	562±129	(38)	354±111	(45)	235±71	(24)
δ-HCH	2±1	(14)	6±2	(34)	17±5	(38)	4±1	(36)	3±1	(15)
p,p'-DDT	3±1	(10)	9±6	(17)	9±2	(26)	4±2	(20)	4±2	(12)
p,p'-DDE	1±0.5	(17)	4±3	(24)	14±9	(32)	25±23	(25)	3±1	(15)
p,p'-DDD	2±1	(9)	6±4	(16)	24±13	(20)	3±1	(12)	5±2	(6)
Heptachlor epoxide	1±0.6	(8)	5±3	(28)	8±2	(28)	3±1	(28)	3±2	(8)
∑Endosulfan	11±1	(17)	19±8	(34)	21±4	(32)	14±2	(39)	14±5	(17)
Dieldrin	1±0.6	(9)	5±3	(19)	4±1	(24)	1±0.4	(21)	3±1	(11)

SE, standard error of the mean; number of samples with quantifiable residues are shown in parentheses.

Table 3
Mean (±SE) concentration of organochlorine residues (ppb, wet wt.) in marine fishes collected from Rameshwaram coast

Compound	*Carangoides malabaricus*, $N=39$		Cyanoglossus macrolepidotus, $N=40$		Lethrinus conchyliatus, $N=27$		Otolithes cuvieri, $N=30$		Rastrelliger kanagurta, $N=47$	
α-HCH	32±12	(35)	22±7	(32)	13±5	(19)	35±10	(29)	34±9	(45)
γ-HCH	22±8	(30)	10±2	(36)	10±3	(21)	14±4	(27)	28±10	(36)
β-HCH	534±206	(31)	222±67	(29)	196±87	(17)	322±100	(21)	325±74	(38)
δ-HCH	2±0.4	(23)	3±1	(24)	6±3	(11)	2±1	(18)	5±1	(34)
p,p'-DDT	2±0.5	(15)	5±2	(16)	10±7	(15)	7±4	(11)	8±2	(23)
p,p'-DDE	1±0.3	(13)	3±1	(17)	6±4	(11)	1±0.2	(16)	5±2	(29)
p,p'-DDD	1±0.2	(7)	2±1	(10)	14±13	(3)	1±0.1	(7)	10±3	(20)
Heptachlor epoxide	1±0.1	(17)	3±1	(15)	6±5	(6)	<DL		4±1	(27)
∑Endosulfan	5±1	(28)	13±2	(28)	22±10	(13)	8±1	(16)	23±3	(36)
Dieldrin	<DL		2±1	(16)	6±5	(6)	<DL		2±1	(21)

SE, standard error of the mean; number of samples with quantifiable residues are shown in parentheses.

α-HCH was detected in *O. cuvieri* (35 ppb) followed by *R. kanagurta* (34 ppb) and the lowest was in *L. conchyliatus* (13 ppb). In the case of γ-HCH, the maximum was recorded in *R. kanagurta* (28 ppb) and minimum in *C. macrolepidotus* and *L. conchyliatus* (10 ppb). Among the metabolites of *p,p'*-DDT, the *p,p'*-DDD was found to be the maximum in *L. conchyliatus* (14 ppb) followed by *R. kanagurta* (10 ppb), while it was the minimum in *C. malabaricus* and *O. cuvieri* (1 ppb). *p,p'*-DDT was the maximum in *L. conchyliatus* (10 ppb) and minimum in *C. malabaricus* (2 ppb). Concentration of *p,p'*-DDE ranged from 1 ppb in *C. malabaricus* and *O. cuvieri* to 6 ppb in *L. conchyliatus* (Table 3). Among the cyclodiene pesticides, total endosulfan levels were higher than the rest with the highest (23 ppb) in *R. kanagurta* and the lowest in *C. malabaricus* (5 ppb). The residues of HE were found to be the highest in *L. conchyliatus* (6 ppb) and lowest in *C. malabaricus* (1 ppb). Dieldrin concentrations ranged from below detection limit in *O. cuvieri* and *C. malabaricus* to 6 ppb in *L. conchyliatus* (Table 3). Of the five species of fishes received from Rameshwaram, *C. malabaricus* and *R. kanagurta* found to be highly contaminated with organochlorine residues, while *C. macrolepidotus* the least.

3.3. Variation in total organochlorine residues among species, months and between locations

Among the 10 species of marine fishes analyzed, the total organochlorine load was the highest in *S. longiceps* (740 ± 24 ppb), and lowest in *N. japonicus* (279 ± 8 ppb) (Fig. 2). The variation in organochlorine load among species was significant. The monthly variations in total organochlorine residues were significant ($P<0.05$) only in *C. agassizi*, *S. longiceps*, *Saurida tumbil*, *C. malabaricus* and *R. kanagurta* (Table 4). Length of the species negatively correlated with total organochlorine residues except *Tachysurus maculates*, but not significant ($P>0.05$).

4. Discussion

4.1. HCH and its isomers

Concentrations of HCH recorded in the present study are twofold greater than the other organochlorine residues measured

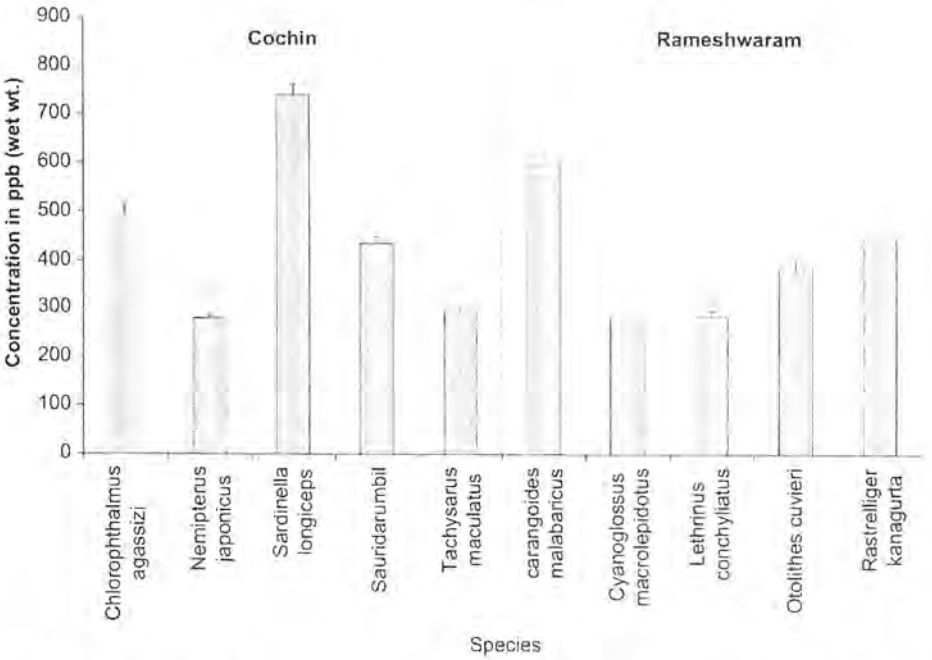

Fig. 2. Total organochlorine ± SE (ppb, wet wt.) load in various species of marine fishes received from Cochin and Rameshwaram.

Table 4
Total organochlorine pesticide residues ± SE in various species of fishes collected during 2004 at Cochin and Rameshwaram Coast, India

Species	*N*	January	February	March	April	May	Anova *P*-value
Cochin							
Chlorophthalmus agassizi	30	26 ± 10	1123 ± 458	334 ± 215	NA	NA	S
Nemipterus japonicus	48	261 ± 165	153 ± 66	110 ± 54	229 ± 175	636 ± 199	NS
Sardinella longiceps	44	105 ± 74	1560 ± 299	1360 ± 369	170 ± 71	852 ± 313	S
Saurida tumbil	50	66 ± 37	1175 ± 457	135 ± 56	162 ± 91	642 ± 382	S
Tachysarus maculatus	34	253 ± 173	374 ± 148	128 ± 103	NA	533 ± 176	NS
Rameshwaram							
Carangoides malabaricus	39	52 ± 44	1979 ± 746	189 ± 61	NA	116 ± 37	S
Cyanoglossus macrolepidotus	40	182 ± 106	498 ± 179	77 ± 31	NA	368 ± 211	NS
Lethrinus conchyliatus	27	415 ± 246	264 ± 140	155 ± 131	NA	NA	NS
Otolithes cuvieri	30	68 ± 38	638 ± 231	451 ± 226	NA	NA	NS
Rastrelliger kanagurta	47	201 ± 132	649 ± 211	689 ± 293	687 ± 184	29 ± 5	S

NA, not available; S, significant ($P<0.05$); NS, not significant.

and high enough to cause deleterious impact on the ovarian histology of the exposed fishes (Hazarika and Das, 1998). Although the production of technical HCH is being phased out, the annual production of γ-HCH in India increased from 40 metric tonnes in 1996–97 to 250 metric tonnes in 1997–98. It was also reported that residues of HCH persist in the environment, concentrate in the crops, continue to be detected in the food chain (Nigam and Siddiqui, 2001) and accumulate in human tissues and fluid due to their lipophilic nature and excreted in breast milk (Snedekers, 2001). The predominance of occurrence of β-HCH, the most persistent form (Burke et al., 2003), is due to the isomerization of α- and γ-HCH into β-HCH in seawater and sediment and also due to its high stability (Jensen, 1983). Presence of high concentrations of β-HCH has been reported in various biological components (Nayak et al., 1995; Kumari et al., 2001; Kole et al., 2001), and in human milk tested in Delhi (Nair et al., 1996). Moreover, it is also reported that β-HCH will accumulate 10–30 times more in fatty tissues than lindane (Heeschen, 1980).

The average concentration of total HCH (alpha, beta, gamma and delta) recorded in *S. longiceps* in the present study is 150 times higher than the concentrations reported in the same species (4.2 ppb) collected during 1990 from the landing centers of Kanniyakumari, India (Karunagaran et al., 1994). Although similar information on other species is lacking, the concentrations of total HCH reported here are greater than those reported elsewhere, regardless of species.

4.2. DDT and its derivatives

Although DDT is banned for use in agriculture in India, it continues to be used for public health purposes. This is because of its low cost and non-availability of viable alternative, and hence the residues in the environment (Singh, 2001). Ratio of *p,p'*-DDT to total DDT was lower than that of metabolite *p,p'*-DDE in *S. longiceps* and *S. tumbil*. The high frequency of occurrence of *p,p'*-DDE can be due to its past use along the coastline or the residues brought by rivers through runoff and erosion. Moreover, the conversion of *p,p'* DDT to *p,p'*-DDE could be due to the activity of the mixed function oxygenase enzyme through metabolic functions. The bioconcentration factor also plays a major role in this conversion (Wang and Simpson, 1996). Since bioconcentration factor mainly depends on food chain transfer and the feeding habits of the individual, it can be well established that the higher level of *p,p'* DDE in *S. tumbil* and *S. longiceps* is due to their feeding habits. DDT levels reported in *C. malabaricus* in the present study are higher than the levels reported in *Epinephelus malabaricus* (1.1 ppb) collected from Indian Ocean coastline, which have the similar feeding habit (Mwevura et al., 2002). Further another study by Karunagaran et al. (1994) reported the highest concentration of *p,p'*-DDE in *N. japonicus* to be 2 ppb which is lower than the levels recorded in the present study. Concentrations of *p,p'*-DDE found in our study are comparable with the levels reported in fishes of Ganges Estuary, Bangladesh (1–2 ppb) (Jabber et al., 2001).

4.3. Cyclodiene insecticides

The presence of chlorinated cyclodiene pesticide in marine ecosystem is partly due to their past use and continued atmospheric transport from remote regions. It may be noted that endosulfan is being widely used in India. The concentrations of dieldrin detected were comparable with the levels reported in fishes of Baltic Sea (Falandysz et al., 2001). Among the cyclodiene group of pesticides, concentrations of endosulfan were lower than the levels reported in Calcutta (Kole et al., 2001). These levels are also lesser than the levels that could produce histopathological changes in exposed gills (Khare et al., 2002). Similarly, concentrations of HE in the present study were lower than the concentrations reported (110 ppb) in the fishes of the Ganges Estuary, Bangladesh (Jabber et al., 2001).

4.4. Total organochlorine load among the species, months and between locations

The higher load of total organochlorine residues in *S. longiceps* seems to be influenced by its feeding mode. This species is a pelagic fin fish which feeds on sediments, phytoplankton especially diatoms (Table 1). Sarkar and Gupta (1987) had reported high levels of organochlorine residues in sediments of the Arabian Sea along the central west coast of India from where samples for the present study were collected. Hence, it is logical to presume that the contaminants from the sediments ultimately found their way into the marine fishes. The total organochlorine load was lower in *N. japonicus* which feeds on crustaceans and invertebrates. Since, the species from the study locations were not similar, the comparison could not be made.

The monthly variation in organochlorine residues in *C. agassizi*, *S. longiceps*, *S. tumbil*, *C. malabaricus* and *R. kanagurta* may be due to the temporal difference in the contaminant load. Although, negative correlation between length of the species and total organochlorine residues was observed, it was not significant. On the contrary the *Tachysurus maculates* showed positive correlation. Similar correlation was reported in *Anguilla anguilla* collected from Vaccares lagoon, France (Roche et al., 2000). Species-specific differences and lipid content of the fishes also influence the variation in accumulation pattern of organochlorine residues among the species.

4.5. Suitability for human consumption

Based on the questionnaire survey and interviews conducted in 325 families in Coimbatore city, the average per capita consumption was estimated at 47 g/day. The dietary intake of organochlorine was calculated by multiplying the pesticide concentrations measured in each species of fish by the per capita consumption.

The greatest exposure in humans to total HCH is through consumption of *S. longiceps* (31 μg) followed by *C. malabaricus* (28 μg), while it would be the lowest through *L. conchyliatus* and *N. japonicus* (11 μg) (Table 5). The results should be of great concern, because *S. longiceps* is wildely consumed by local people. Among the 10 species included in the current study, three of them, namely *S. longiceps*, *C. malabaricus* and *C. agassizi* measured elevated concentrations of HCH isomers. Thus, the daily dietary intake of total HCH through consumption of these species of fishes would exceed the acceptable dietary intake (ADI) of 18 μg/day as reported by Health Canada (1996), while through *S. tumbil*, *R. kanagurta* and *O. cuvieri* the intake concentration would be equal to the ADI limit. The intake of other chemicals is within acceptable limits for human consumption. Maximum permissible dietary intake concentration of 300, 6 and 450 μg/person/day were prescribed for total DDT (IARC, 1989), dieldrin (Health Canada, 1996) and endosulfan (IARC, 1989), respectively (Table 6). Consumption of as little as 47 g of these fishes in a single day will bring in organochlorine pesticides exceeding the statutory limits for human health. A study conducted by Vijayan et al. (2004) also reported similar scenario in inland wetland fishes of India. About 22% of individual of all the species exceeded the tolerance limit of 200–500 ppb of total HCH (FAO/WHO, 1989) permitted for fish products (Tables 2 and 3). If the input of HCH to human

Table 5
The calculated dietary intake concentration (μg/person/day) of organochlorine residues through consumption of various species of marine fishes

Name of the fish	HCH				∑HCH	Heptachlor epoxide	*p,p'*-DDT	*p,p'*-DDE	*p,p'*-DDD	∑DDT	Dieldrin	∑Endo sulfan
	α	γ	β	δ								
Carangoides malabaricus	1.5	1.0	25	0.1	28	0.0	0.1	0.0	0.0	0.1	0.0	0.2
Chlorophthalmus agassizi	1.3	2.1	19	0.1	23	0.1	0.1	0.1	0.1	0.3	0.1	0.2
Cynoglossus macrolepidotus	1.1	0.5	10	0.1	12	0.1	0.2	0.1	0.1	0.5	0.1	0.5
Lethrinus conchyliatus	0.6	0.5	9	0.3	11	0.3	0.5	0.3	0.6	1.4	0.3	0.9
Nemipterus japonicus	0.4	0.6	10	0.3	11	0.2	0.4	0.2	0.3	0.9	0.2	1.0
Otolithes cuvieri	1.6	0.6	15	0.1	18	0.0	0.3	0.0	0.0	0.4	0.0	0.2
Rastrelliger kanagurta	1.6	1.3	15	0.3	18	0.2	0.4	0.2	0.4	1.1	0.1	1.2
Sardinella longiceps	1.9	1.9	26	0.8	31	0.4	0.4	0.7	1.1	2.2	0.2	1.0
Saurida tumbil	1.0	0.7	17	0.2	18	0.1	0.2	1.2	0.1	1.5	0.1	0.4
Tachysurus maculatus	0.8	0.5	11	0.1	12	0.2	0.2	0.1	0.2	0.6	0.1	0.7
Average dietary intake concentration through fishes	1.2	1.0	16	0.2	18	0.2	0.3	0.3	0.3	0.9	0.1	0.6

Table 6
Comparison of calculated dietary intake concentration with the acceptable dietary intake (ADI) stipulated by various statutory agencies

Pesticides	The calculated dietary intake concentration through consumption of fishes in the present study (μg/person/day)	Allowable limits by various statutory agencies (μg/person/day)
∑-HCH	18	18[a]
∑-DDT	0.9	300[b]
∑-Endosulfan	0.6	450[b]
Dieldrin	0.1	6[a]

[a] Health Canada (1996).
[b] IARC (International Agency for Research on Cancer (1989)).

being continues, it may accumulate in tissues and even in mothers' milk.

And more recently, a report by Sun et al. (2005) suggested that although organochlorine pesticide, such as DDT and HCH, have been banned in China, the residues of such compounds still exists in the environment and cause food contamination. The prevalence of HCH in fishes confirms its higher consumption (more than 70%) in India (Nair et al., 1996). Earlier studies conducted by Kannan et al. (1992) and Kumari et al. (2001) also reported high concentration of HCH in fish and food products and higher dietary intake through fishes. Although no major ill effects in man have been correlated with the levels of HCH, altered thyroid function was reported in women (Hagmar et al., 2001).

5. Conclusion

Invariably all the species studied had uniformly high concentrations of HCH than previously measured in fish from these areas, while concentrations of other pesticides varied. Although the species collected varied between Rameshwaram and Cochin, the level of contamination did not significantly vary ($P>0.05$). HCH and its isomers had higher frequency of occurrence than the rest of the chemicals analyzed. Of all the species, the greatest concentrations of pesticides were recorded in *S. longiceps* and the lowest in *N. japonicus*. One of the noteworthy findings of this study is *S. longiceps* is the most preferred species by the local people and hence the levels of contamination in it should be viewed with great concern. It was observed that 22% of fishes exceeded the MRL for total HCH residues prescribed for fish products. Regarding the potential risk for human health, the calculated dietary intake of HCH in *S. longiceps*, *C. malabaricus* and *C. agassizi* exceeded the ADI limits proposed by Health Canada (1996) for human consumption. Even though the present levels of organochlorines do not appear to be harmful to human, chronic exposure may lead to deleterious effects.

In India, although studies on the levels of organic contaminants in fishes are carried out, they are sporadic and not oriented towards assessing the impact on human health. The present study clearly shows the need for continued monitoring. Formulation of guidelines in terms of MRLs and ADIs are especially important for those compounds where no basic guidelines are available.

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References

Burke, E.R., Holden, A.J., Shaw, I.C., Suharyanto, F.X., Sihombing, G., 2003. Organochlorine residues in human milk from primiparous women in Indonesia. Bull. Environ. Contam. Toxicol. 71, 148–153.

David, M., Mushigeri, S.B., Philip, G.H., 2003. Alterations in the levels of ions in tissues of freshwater fish *Labeo rohita* exposed to fenvalerate. Pollut. Res. 223, 359–363.

Esha Mathew, 2004. Are the marine fishes of commercial importance available in Coimbatore safe for public consumption in the perspective of heavy metal contamination? M.Sc., Thesis, Bharathiar University, Coimbatore.

Falandysz, J., Strandberg, L., Puzyn, T., Gucia, M., 2001. Chlorinated cyclodiene pesticide residues in blue mussel, crab, and fish in the gulf of Gdansk, Baltic Sea. Environ. Sci. Technol. 35, 4163–4169.

FAO/WHO (World Health Organization), 1989. Guidelines for Predicting Dietary Intake of Pesticide Residues. Geneva, p. 24.

FishBase, 2007. <www.fishbase.org/serach.php>.

Fitzgerald, E., Hwang, S.-A., Deres, D.A., Bush, B., Cook, K., Worswick, P., 2001. The association between local fish consumption and DDE, mirex, and HCB concentrations in the breast milk of Mohawk women at Akwesasne. J. Exposure Anal. Environ. Epidemio. 11, 381–388.

Hagmar, L., Rylander, L., Dyremark, E., Klasson-Wehler, E., Erfurth, E.M., 2001. Plasma concentration of persistent organochlorine in relation of thyrotropin and thyroid hormone levels in women. Int. Arch. Occup. Environ. Health 74, 184–188.

Jazarika, R., Das, M., 1998. Toxicological impact of HCH on the ovary of the air-breathing catfish *Heteropneustes fossilis* Bloch. Bull. Environ. Contam. Toxicol. 60, 16–21.
ealth Canada, 1996. Provisional Tolerable Dietary Intake (PTDI), Values Presently used by Contaminants Toxicology Section. Food Directorate, Ottawa, Ontario, Canada.
Heeschen, W., 1980. Toksikologische bewertung von HCH-ruckstanden. Keil Milchwirtsch. Forchungsber 32, 151–155.
IARC (International Agency for Research on Cancer), 1989. Overall evaluation of carcinogenicity: an updating of IARC monograph. Monogr. Eval. Carcinog. Risks. Hum., 1–42.
Jabber, S.M.A., Khan, Y.S.A., Rahman, M.S., 2001. Organochlorine pesticide residues in the muscles of three fishes from the Ganges Estuary, Bangladesh. Int. J. Ecol. Environ. Sci. 27, 111–116.
Jensen, A.A., 1983. Chemical contaminant in human milk. Residue Rev. 89, 1–128.
Kannan, K., Tanabe, S., Ramesh, A., Subramanian, A., Tatsukawa, R., 1992. Persistent organochlorine residues in food stuffs from India and their implication on human dietary exposure. J. Agri. Food Chem. 40, 518–524.
Karunagaran, U.M., Babu, S., Rajendiran, R.B., Subramanian, A.N., 1994. Organochlorine insecticides HCH, and *p,p'*-DDE residues in fishes from Kanniyakumari 8°04'N, 77°36'N. Indian J. Mar. Sci. 23, 182–183.
Khare, S., Singh, S., Mehrotra, A., 2002. Histophathological changes in the gills of *Nandus nandus* induced by endosulfan and carbaryl. Nat. Environ. Pollut. Technol. 11, 1–4.
Kole, R.K., Banerjee, H., Bhattacharya, H., 2001. Monitoring of market fish samples for endosulfan and Hexachlorcyclohexane residues in and around Calcutta. Bull. Environ. Contam. Toxicol. 67, 554–559.
Kumari, A., Sinha, RK., Gopal, K., Prasad, K., 2001. Dietary intake of persistent organochlorine residues through gangetic fishes in India. Int. J. Ecol. Environ. Sci. 27, 117–120.
Martinez, M.P., Angulo, R., Pozo, R., Jodral, M., 1997. Organochlorine pesticides in pasteurized milk and associated health risks. Food Chem. Toxicol. 35, 621.
Mathew, G.A., 1993. Pesticide registration application and formulation in India. Pestic. Inf., 1–15.
Mohapatra, B.C., Saha, C., 2000. Pesticides in aquatic environment. In: Aquatic Pollution and Management, first ed. Central Institute of Freshwater Aquaculture, pp. 29–53.
Muralidharan, S., 2000. Organochlorine residues in the waters of Keoladeo national park, Bharatpur, Rajasthan. Bull. Environ. Contam. Toxicol. 65, 35–41.
Mwevura, H., Othman, O.C., Mehe, G.L., 2002. Organochlorine pesticide residues in edible biota from the coastal area of Dar es Salaam city. J. Mar. Sci. 1, 91–96.
Nair, A., Mandapati, R., Dureja, P., Pillai, M.K.K., 1996. DDT and HCH load in mothers and their infants in Delhi, India. Bull. Environ. Contam. Toxicol. 56, 58–64.
Nayak, A.K., Raha, R., Das, A.K., 1995. Organochlorine pesticide residues in middle stream of the Ganga river in India. Bull. Environ. Contam. Toxicol. 540, 68–75.
Nigam, U., Siddiqui, M.K.J., 2001. Organochlorine insecticide residues in dairy milk samples collected in Lucknow, India. Bull. Environ. Contam. Toxicol. 66, 678–682.
Roche, H., Buet, A., Jonot, O., Ramade, F., 2000. Organohchlorine resiues in European eel (*Anguilla anguilla*), crucian carop (*Carassius carassius*) and catfish (*Ictalurus nebulosus*) from vaccares lagoon (French national nature reserve of Camargue) effects on some physiological parameters. Aquat. Toxicol. 48, 443–459.
Sarkar, A., Gupta, R.S., 1987. Chlorinated pesticide residues in sediments from the Arabian Sea along the central west coast of India. Bull. Environ. Contam. Toxicol. 39, 1049–1054.
Sarkar, U.K., Basheer, V.S., Singh, A.K., Srivastava, S.M., 2003. Organochlorine pesticide residues in water and fish samples: first report from rivers and streams of Kumaon Himalayan region, India. Bull. Environ. Contam. Toxicol. 70, 485–493.
Siddiqui, M.K.J., Anand, M., Mehrotra, P.K., Sarangi, R., Mathur, N., 2005. Biomonitoring of organochlorines in women with benign and malignant breast disease. Environ. Res. 98, 250–257.
Singh, R.P., 2001. Comparison of organochlorine pesticide levels in soil and ground water of Agra, India. Bull. Environ. Contam. Toxicol. 67, 126–132.
Snedekers, M., 2001. Pesticides and breast cancer risk: a review of DDT, DDE and Dieldrin. Environ. Health Perspect. 109, 35–47.
Sun, S.J., Zhao, J.-H., Koga, M., Ma, Y.-X., Liu, D.-W., Nakamura, M., Liu, H.J., Horiguchi, H., Clark, G.C., Kayama, F., 2005. Persistent organic pollutions in human milk in women from urban and rural areas in northern China. Environ. Res. 99, 285–293.
Swackhamer, D., Hites, R.A., 1988. Occurrence and bioaccumulation of organochlorine compounds in fish from Siskiwit lake, Isle Royale, Lake Superior. Environ. Sci. Technol. 22, 543–548.
Trotter, W.J., Dickerson, R., 1993. Pesticide residues in composite milk collected through the US pasteurized milk network. J. AOAC Int. 76, 1220.
Vijayan, V.S., Muralidharan, S., 1999. Pesticide contamination in district Nilgiris with special reference to select species of Avifauna. Project Report, Ministry of Environment and Forest, Govt. of India, by Salim Ali Centre for Ornithology and Natural History, Coimbatore.
Vijayan, V.S., Prasad, S.N., Vijayan, L., Muralidharan, S., 2004. In: Inland Wetlands of India—Conservation Priorities, Salim Ali Centre for Ornithology and Natural History, Coimbatore, pp. XXIV+532.
Wang, J.S., Simpson, K.L., 1996. Accumulation and depuration of DDTs in the food chain from Artemia Brook Trout (*Salvelinus fontinalis*). Bull. Environ. Contam. Toxicol. 56, 888–895.