1.1 General Introduction

In modern society, thousands of chemicals (both organic and inorganic) are in common use (industrial, medicinal purposes etc) and depending on their life cycle (extraction, manufacturing, transport, use and disposal) finally reach the estuarine and coastal systems through a number of pathways. Many of these compounds enter the aquatic environment via non point sources (eg. agricultural or urban storm water runoff), but a number of them are discharged from point sources such as wastewater treatment plants, which were not designed to deal with the ever increasing diversity of organic compounds that pass through their treatment units (Sujatha et al., 1993; Thomson, 2002; Dsikowitzky et al., 2014). These wastes discharges accompanying complex contaminants either directly enter the estuaries or the coastal areas; but, in many cases, they enter into the freshwater bodies and finally enter the ocean margins. The toxic character of many such compounds has been known for decades; however, in other
cases, it has taken considerable effort, both on the analytical side and on the toxicological assays, to determine that even at extremely low concentrations they cause harmful effects. Consequently, the residing bottom sediments are also recognized as an excellent temporary or long-term sinks for many types and classes of anthropogenic contaminants (OCIs, PAHs, PCBs, Trace metals etc).

According to the World Resource Centre, coastal habitats alone account for approximately 1/3 of all marine biological productivity, and estuarine ecosystems (i.e., salt marshes, sea grasses, mangrove forests) are among the most productive regions on the planet (EPA, 1990). Rapidly growing populations and expanding urbanization and land development are exerting escalating pressures on coastal ecosystems worldwide. Therefore, the study on coastal sediments becomes an important step in mapping the possible pollution sources and exposure pathways which would facilitate pollutants’ bioavailability to sediment dwelling organisms and their toxicological effect. Thus, a comprehensive insight into the effects of chemicals in the environment requires assessments ancillary to toxicology such as the fate of the chemical in the environment, and toxicant interactions with abiotic components of ecosystems. These assessments necessitate elucidating the adverse effects of chemicals that are present in the environment and predicting any ill/toxic effects of chemicals before they are discharged into the environment. Therefore, the Queen of Arabian Sea (Cochin), Kerala, the aquatic system under consideration is where the present research work focuses on the residual concept pertaining to OCIs,
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which are widely used/manufactured in the nearby areas of metropolitan city of Cochin and is their ultimate receiver.

1.2 Physiographical Features of the Study Area

The State of Kerala, which is a narrow strip of land lies on the south western part of Peninsular India with a 560 Km long coast and an average width of 80 Km, lying between Arabian Sea on the west and Western Ghats, a continuous mountain chain on the east. Topography of the area covers altitudes ranging from below mean Sea level to above ~2600 m the area of in Western Ghats. It is characterised by 44 short and swift flowing monsoon fed perennial rivers, which originates from the Western Ghats and 41 of them drain into either estuaries or the Arabian Sea. The most conspicuous feature of this coast is that the wide spread distribution of estuaries and lagoons are thought to be the remnants of the receding Sea. The area has a tropical humid climate with a temperature range of 13 to 42° C and an average rainfall of 3000 mm (Krishnan Nair, 1996; Soman, 1997; Menon et al., 2000).

The study area, the Cochin Estuary (Lat. 9° 30’ -10° 10’ N and Lon. 76° 15’ - 76° 25’E) situated in the central part of Kerala extends between the cities of Azhikode in the north and Alleppy in the south, running parallel to the Arabian Sea. It is generally wide (0.8-1.5 Km) and deep (4-13 m) towards south but becomes narrow (0.05-1.5 Km) and shallow (0.5-3 m) in its northern part. Six rivers: Pamba, Achankovil, Manimala, Meenachil, Periyar and Muvattupuzha with their tributaries, along with several canals, bring large volumes of freshwater into the estuary. Tidal intrusion from the Arabian Sea (tidal range avg. 1m) contributes a regular flow of salt water,
which diminishes considerably towards the head of the estuary (Madhuprathap, 1987; Balachandran et al., 2008). Among these rivers, Periyar (in the north) and Muvattupuzha (in the south) have an active influence in controlling the salinity of the estuarine system.

1.3 Behaviour and Fate of Trace Organic Contaminants in the Environment

In the natural environment, all chemicals are subject to physical, chemical and biological processes that can act on their chemical structure causing degradation and eventual removal or a considerable reduction in the potential for harmful effects. However, some chemicals do not break down or slowly break down in the environment. In addition, degradation processes might lead to the production of nondegradable by-products. These substances are known as persistent chemicals and are long-lived under prevailing environmental conditions. Moreover, hydrosphere acts as a major reservoir for persistent organic pollutants, they enter into the environment via many pathways, including:-

- Direct application for pest and vector control.
- Urban and industrial waste water discharges.
- Runoff from non-point sources.
- Leaching through soil.
- Aerosol and particulate deposition rainfall.
The issue that arises in these circumstances is whether the presence of the residual concentrations of these contaminants represents a risk to man and to biota.

Persistent organic pollutants (POPs), a group of xenobiotic lipophilic pollutants, are semi volatile, bio accumulative, persistent and toxic in character (Jones and de Voogt, 1999). They can be deposited in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff, and other means. Because POPs have low water solubility, they bond strongly to particulate matter in aquatic sediments (Leppanen, 1995). As a result, sediments can serve as reservoirs or ‘sinks’ for POPs. When sequestered in these sediments, POPs can be taken out of circulation for long periods of time. If disturbed, however, they can be reintroduced into the ecosystem and food chain, potentially becoming a source of local, and even global, contamination. Although the occurrence of POPs at elevated levels is of great environmental concern, the regional and global significance of the problem has received increased attention in the last decades (UNECE, 1998; UNEP, 2001). They have been reported to cause variety of effects including immunologic, tetratogenic, carcinogenic, reproductive and neurological problems in organisms (Kodavanti et al., 1998) and are of considerable concern to human and environmental health (Anupama and Sujatha, 2012). Moreover, POPs work their way in biomagnifications via the food chain by accumulating in the body fat of living organisms and becoming more concentrated as they move from one trophic creature to another. Ecological magnification in organisms through the food chain appears to be the most harmful environmental effect resulting
from the general usage of organochlorine insecticides. Sediment-dwelling animals therefore have a greater risk of accumulating toxic substances than pelagic animals, because they are exposed to all possible accumulation routes (Leppänen, 1995). Sharpe and Mackay (2000) estimates that benthic organisms attain about 95% of their accumulated contaminants from the sediment.

In the POPs, ‘Pesticides’ (lat. *pestis* – pest and *cedeo* – destroy) are the group of anthropogenic compounds that have been used in agriculture and households for several decades to control pests, diseases, and insect-borne diseases (e.g., malaria, dengue, encephalitis, and filariasis). Based on the applications, they can be divided into herbicides, insecticides, fungicides, rodenticides, molluscicides, acaricides, nematocides, aphicides and ovicides (Biziuk et al., 1996). OCIs are mainly synthetic organic insecticides and may also be named as ‘chlorinated hydrocarbons’ or ‘chlorinated insecticides’. Representative compounds in OCIs are DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride etc. Some persistent pollutants, including several pesticides, traverse to a long distance through air and in water over several hundred miles, and so even wildlife and people living far away from where these substances are used are under significant threat. These persistent organic compounds such as HCH and DDT isomers are the predominant chemical contaminants found along the Indian coast and thus constitute both alluring and vital areas of scientific research (Pandit et al., 2001; Kumar et al., 2006).

Apart from the OCIs, other important toxic pollutant categories are PAHs and PCBs. Among these, polycyclic aromatic hydrocarbons (PAHs) are
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a class of ubiquitous organic compounds with two to seven condensed aromatic rings. Overall 16 PAHs are considered by the USEPA as priority micropollutants because of their carcinogenic and mutagenic properties. They occur naturally as incomplete combustion products of organic compounds and enter into the aquatic environments via oil spills, waste discharge, runoff etc. Even though they are biodegraded in soils and water within weeks to months, the metabolites are more toxic and may last for long time. In marine ecosystem, PAHs can undergo degradation by photo oxidation in the superficial water layer. Polychlorinated biphenyls (PCBs) are another class of POPs and are among the most important industrial contaminants in marine ecosystems. Theoretically, they are 209 PCB congeners with one to ten chlorine atoms bound to the phenyl rings. They are very resistant to decomposition and have an excellent insulating property as well as a high heat absorbed capacity. Their properties have led to many industrial applications but also make PCBs one of the major environmental pollutant classes. PCBs, the commonly considered key representatives of the industrial pollutants are extensively used in electrical transformers and capacitors as heat transfer fluids and in consumer products (Harrad et al., 1994). They enter the environment through dispersion from their identifiable and specific place of use or from incineration and land fill sites etc.

1.4 A Perusal on Organochlorine Insecticide Pollution Status in the Indian Scenario

Presently, India is considered as the largest pesticides producing country in Asia and 12th largest in the world with 90,000 tons of annual pesticide production (Khan, 2010). Furthermore, India is involved in the
manufacturing, use and export of OCIs such as DDTs and HCHs on large scale (Pozo et al., 2011). Both industrial and agricultural sources would contribute significant amount of these contaminants to the environment through seepage, disposal and evaporation (Tolosa et al., 2010). Although substantial fractions of applied pesticides are dissipated at the site of application through chemical and biological degradation processes. Besides, a reasonable fraction of the OCIs’ residues reaches the oceans through agricultural run-off, atmospheric transport and effluent discharge (GESAMP, 1989). Since OCIs are known for their persistence, toxicity and bioaccumulation characteristics, there is a concern about their impact on the marine environment. Despite the fact that 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. The determination and quantification of those compounds existing in water and sediment may indicate the extent of aquatic contamination and the accumulation characteristics in the aquatic ecosystems (Sujatha et al., 1994; Pandit et al., 2001; Kumar et al., 2006).

There is a scarcity of literature on pesticide residues in air and seawater around India. A study by Babu Rajendran et al., (1999) reported that, higher concentration of HCHs (1.45-35.6 ng/m³) and DDTs (0.16-5.93 ng/m³) were detected in the tropical coastal atmosphere from India. Highly populated and agricultural areas along the Indian coastal length were found contaminated with higher levels of OCIs as endorsed by Zhang et al., (2008). Chakraborty et al., (2010) reported that higher concentration of Chlordane, DDTs, HCHs and Endosulfan were detected in the cities of
Mumbai, Bangalore, New Delhi, Kolkata, Chennai and Agra during passive air sampling campaigns. The authors suggested that higher concentrations of γ-HCH were found in Kolkata which indicated widespread use of lindane in India. Devi et al., (2011) reported the seasonal variations and emissions of HCHs and DDTs in various places in India, and the higher concentrations were found in the rural and urban sites during warmer season.

A study by Shailaja and Sen Gupta, (1989) reported that isomers of HCH, aldrin, dieldrin and DDT were detected in water samples collected from different regions of the Indian Ocean, in which total DDT was found to be present in significant level. Moreover, distribution of different chlorinated compounds along the central West Coast of the Arabian Sea reported by Shailaja and Sarkar, (1992) concluded that γ-HCH and the cyclodiene compounds-aldrin and dieldrin were found more consistently in seawater samples than compounds of the DDT family. Contamination by DDT and HCH residues in several rivers of South India was reported by Ramesh et al., (1990a) and Rajendran and Subramanian, (1997). They observed erratic trends in DDT residue concentrations in waters of the river like Vellar, Kaveri and Coleroon and in the Pichavaram mangrove wetland. The authors attributed low residue concentrations in water to high surface water temperatures, which resulted in a high rate of vapourization of pesticides. In southwest coast of India, Sujatha et al., (1994) evaluated the concentration of OCIs in the Cochin backwaters, in which the total DDT concentration was as high as 54.4 µg/l and the predominant metabolite was pp'DDE. Moreover, the total HCH concentration was as high as 1.1 µg/l in the Cochin Estuary due to premonsoonal accumulation of pesticides (Sujatha et al., 1993). OCIs show
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a wide variation in their concentration level in various sampling sites of CES. The riverine nature and acidic pH of the upper estuary combined with the industrial effluents from a pesticide manufacturing plant accounted for the very high concentrations of pesticides. Levels in the mid-estuarine region reflected the prominent influence of agricultural run-off (Sujatha et al., 1993). Furthermore Sujatha et al., (1999) concluded that contamination by Endosulfan isomers varying seasonally, with premonsoon loading always being higher (about two fold greater) than post-monsoon loading, and unnoticeable level throughout the monsoon period. Pandit et al., (2002) reported the elevated concentration of DDT and its metabolite, DDE in the seawater samples from west coast of India. Also, the presence of DDT and HCH isomers can be attributed to the use of these insecticides in agricultural and anti-malaria sanitation activities which have been carried out throughout the country. Recently Dsikowitzky et al., (2014) reported that the highest contamination by HCH isomers, endosulfan, hexachlorobenzene and DDT-metabolites were detected in the water and surface sediment samples collected from the industrial area of CES.

There are only a few studies on the fate and behaviour of OCIs in marine sediments (Sarkar and Sen Gupta, 1985; Sarkar and Sen Gupta, 1986; Shailaja and Sarkar, 1992; Rajendran and Subramanian, 1997; Sarkar et al., 1997; Rajendran and Subramanian, 1999; Senthilkumar et al., 1999; Pandit et al., 2002; Guzzella et al., 2005; Sarkar et al., 2008) from Indian waters. The authors recognise that the stability and fate of the pesticides in sediment samples were influenced by pH, salinity and exchangeable cations. Sarkar and Sen Gupta, (1988a,b) estimated the residues of OCIs in
sediments from the Bay of Bengal in the following order: op′-DDE > pp′-DDE > pp′-DDT > op′-DDD > pp′-DDD > op′-DDT. Among the isomers of DDT, both pp′-DDE and op′-DDE, were consistently found high, and explains the degradation of DDT to DDE in the coastal sediments. The unevenness in pesticide residue concentrations was attributed to the presence of numerous rivers along the east coast of India including the Hugli, Mahanadi, Vamsodhara, Godavari, Krishna, Pennar and Palar Rivers. All these rivers transport copious amount of agricultural discharges containing persistent organic pollutants including organochlorine insecticides and dumped into the Bay of Bengal. Sarkar and Sen Gupta, (1991) recorded the residue levels of OCIs in sediment samples off the west coast of India in the Arabian Sea and delineated in the following order: DDT > HCH > aldrin > dieldrin. According to the study by Ramesh et al., (1992) a large amount of technical HCHs were detected in the sediments from western part of Kolkata, along with the high concentrations found in biota. Sarkar et al., (1997) observed the prevalence of ΣDDT and dieldrin in estuarine sediments of the Arabian Sea areas compared to offshore sediments. Their overall assessment revealed that Zuari and Kali estuaries are the most susceptible to DDT as compared to other estuaries. In the east and west coast of India, residues of HCH and DDT metabolites were detected in majority of the surface sediment samples. The predominance of α- and β-HCH reflects the use of technical grade HCH in India Pandit et al., (2001). Moreover, the study infers that significant concentrations of DDE in coastal sediments to the presence of various kinds of marine benthic organisms which accelerate the biodegradation process and the alkaline nature of marine systems which is highly favourable for such types of
transformations. In eastern coastal part of India, Guzzella et al., (2005) reported that a wide range of spatial variations of various OCIs in the surface sediments of the Hooghly estuary including Sunderban mangrove wetland, can be supposed to the use of these insecticides in agriculture as well as anti-malaria sanitary activities in these regions. Sarkar et al., (2008) reported that occurrence of organochlorine pesticide residues in core sediments of Sunderban wetland ecosystem. Prevalent nature of DDT and its metabolites were detected in all sediment samples, but the concentration of individual metabolites showed differences, which revealed an irregular pattern, either top to bottom or vice versa, reflecting non-homogenous input of these compounds.

Wide variations of OCI residues have been reported in the zooplankton samples from Indian coastal waters. Kureishy et al., (1978) reported the presence of DDT, HCH along with unidentified compounds in the eastern Arabian Sea. DDD was the major metabolite detected in most of the samples off the Saurashtra Coast, Gujarat in the northern Arabian Sea (Kannan and Sen Gupta, 1987). Toxicity studies on zooplankton (Venugopalan and Rajendran, 1984; Rajendran and Venugopalan, 1988) indicated that DDT was more toxic than either lindane or endosulfan. Moreover, study by Shailaja and Sen Gupta, (1990) confirmed the metabolic activity of DDT in zooplankton.

Bivalves have been widely accepted and used as sentinel organisms to monitor the concentration of pollutants in coastal marine environments. Venugopalan and Rajendran, (1984) detected pesticide residues in three species of molluscs (the oyster Crassostrea madrasensis and the clams
Meretrix casta and Katalysia opima) collected from Vellar Estuary of South India adjoining the Bay of Bengal. The mean pesticide residues in these three species were 3.4 ng/g ww for DDT, 0.8 ng/g ww for lindane and 0.42 ng/g ww for endosulfan. The authors also studied the toxicity of DDT, lindane and endosulfan using the same three species of molluscs and the order of toxicity was found to be DDD>endosulfan>lindane and the sensitivity of the bivalves was in the order: C. madrasensis >K. opima >M. casta. Ramesh et al., (1990b) measured the concentrations of OCIs residues in green-lipped mussels Perna viridis L. (Mollusca: Bivalvia) collected from nine locations along the South Indian Coast, which includes the east and west coasts covering the Bay of Bengal and the Arabian Sea, respectively. Mussels collected from the west coast had higher levels of DDT, suggesting the use of DDT for vector control in urban locales and it eventually dispersed into the aquatic niche. However, in Porto Novo and Pondicherry harbours on the east coast and Suratkal on the west coast, HCH levels were slightly higher than DDT, which is indicative of the use of HCH for agricultural purposes in the nearby areas Ramesh et al., (1990b). However, an overall uniform concentration of pesticide residues was observed in the bivalves from Indian coastal waters.

Fish have been selected for environmental pollution monitoring studies because they concentrate pollutants in their tissues directly from water and through diet enabling the assessment and transfer of pollutants through the pelagic food web (Bruggeman, 1982). A study by Venugopalan and Rajendran, (1984) revealed that there was no significant variation in the concentration of OCIs among fish species collected from Vellar Estuary.
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. Shailaja and Nair, (1997) established that the liver generally accounted for the highest level of total DDT, followed by the gills among the different fish tissues. Pandit et al., (2001) studied accumulation of OCIs in the muscle tissues of different fin fishes and shell fish (prawn) from Alibagh and Mumbai, west coast of India. They observed predominance of \( \alpha \)- and \( \gamma \)-HCH which reflected the use of technical grade HCH in India. A high concentration of HCH in biota was also reported near the industrialized cities such as Mumbai (Monirith et al., 2003). The data on the distribution of OCIs in fishes is important not only for ecological reasons, but also because of their impact on human health.

Despite being banned, OCI concentrations remain higher in the environment due to illegal use, re-emission from soils and glaciers, terrestrial runoff and atmospheric deposition. A regular monitoring, assessment and reporting machineries should be implemented in accordance with appropriate environmental policies, laws and regulations. The Government and other related agencies should educate farmers and agriculture managers on Good Agricultural Practices (GAP). Furthermore, national and international monitoring programs helped to understand the relationship between the over use of chemicals in the environment.

1.5 Aim and Scope of the Study

Cochin Estuary, one of the largest tropical estuaries of India is facing gross pollution problems following the release of untreated effluents from
industries and domestic sectors. The developmental activities in and around the estuarine system have added to the complexities and environmental dilemmas in this coastal niche. For a long period, there were no pollution control regulations and the untreated effluents including those from heavily polluting industries were being discharged into the aquatic niche. As a result of careless disposal practices, they have become major pollutant in many areas of CES. Thus understanding the transport, distribution and characterization of Persistent Organic Pollutants (POPs) in the sediments of the estuaries is a challenging area of research for environmental chemists, because of their resistance to degradation has resulted the presence globally as contaminants in the environment. The increasing importance assigned to pesticide compounds like organochlorins and the tendency to deal with them as a generic group in regulatory actions, is imperative that the nature and profile of their distribution be assessed quantitatively and rigorously. A greater tendency shown by OCIs for bioaccumulation and biomagnifications in the food chains is due to their resistance to chemical and biological decay. In the absence of any authentic reports on the status of contamination by these toxicants in the sediments of this estuary, there exists a lot of uncertainty about even the orders of magnitude in which these substances present in the aquatic niche. This investigation will provide the baseline data on these xenobiotics being freely used in this part of the Indian sub-continent. Most of the earlier research contributions were based on one-time or seasonal sampling during a year, from the areas known for environmental pollution. An approach based on the analysis of OCI residues in sediments collected over a considerable time period can provide a clue for a change in environment and such studies are limited. The findings of this
research work constitute the first judicious base line data set for the OCI residues in the sediments of CES.

The objectives of the present study are:

- To investigate the spatial and temporal variability of
  - a) Biogeoorganic constituents &
  - b) Organochlorine Insecticides (OCIs) in the surface sediments of CES.

- To assess the Biogeochemical parameters in the core sediments of CES

- To evaluate the distribution pattern of OCIs in specific core sediments of the aquatic system.

In order to fulfil these objectives, the research was carried out by adopting suitable scientific approaches and methodologies are well presented in the 2nd Chapter.
1.6 References


Balachandran, K. K., Reddy, G. S., Revichandran, C., Srinivas, K., Vijayan, P. R., Thottam, T. J., 2008 Modelling of tidal hydrodynamics for a tropical ecosystem with implications for pollutant dispersion (Cochin estuary, Southwest India), Ocean Dynam., 58, 259–273.


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GESAMP., 1989. The atmospheric input of trace species to the world ocean. GESAMP, Rep Stud.38.


contamination in wildlife from a tropical agricultural watershed, South India. Arch Environ Contam Toxicol. 23 (1):26–36.


