Chapter - IV

ORGANOCHLORINE PESTICIDES IN WATER AND SEDIMENTS

4.1 BACKGROUND

Over the last 50 years, the increasing global use of toxic synthetic pesticides has seriously affected human health, environmental hazards and agricultural sustainability. Pesticide use is continuing to increase, especially in developing countries. It persists in the environment and many are dispersed globally as a result of drift, volatilization from soil and vaporization (Kurtz 1990). Pesticides have caused widespread contamination of soil, surface and ground water, marine and estuarine sediments, fog, rain, polar snow, mammals and even the bark of trees (Simonich and Hites 1995). Organochlorine pesticides such as hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), heptachlor, aldrin, chlordane, dieldrin, endrin, mirex are among the most persistent and globally distributed organic pollutants. These organic compounds are an anthropogenic origin and resist photolytic, chemical, and biological degradation. Being semi-volatile, they used to move long distances in the atmosphere, resulting in widespread distribution across the earth, including "remote areas" such as the Polar Regions (Allen-Gil et al 1997).

The pesticides transport can occur in three ways: i) movement in the vapour phase; ii) surface runoff; iii) leaching. The tropical warm temperature favour evaporation from earth surface. Among them surface runoff can contribute maximum load from the non point source through streams and canals. Hence, the logic is to dictate that the concentration will be highest near the point of release and decline with distance. Relatively mobile organochlorine compounds have the exception with the distance because of their tendency to partition for easy movement (James 2000). These persistent organic compounds such as HCH isomers, DDT and its metabolites are the

predominant chemical contaminants found along the Indian coast (Sarkar et al 2008) and were reported in major rivers (Rajendran and Subramanian 1997; Zhou et al 2006; Leong et al 2007; Imo et al 2007; Ma et al 2007; Ize-Iyamu et al 2007; Kannel et al 2007; Poolpak et al 2008; Doong et al 2008 and Kaushik et al 2008).

Organochlorine pesticide (OCPs) residues are an important potential component of chemical pollutants used extensively for agriculture and sanitation purposes in India as these are comparatively cheap and effective. These persistent organic compounds such as HCHs, DDTs and its metabolites are the predominant chemical contaminants found around the globe and thus constitute both alluring and grave areas of scientific research (Sarkar et al 2008). Pesticides are indispensable in modern agriculture, their use or misuse may lead to serious surface and ground water contamination. Pesticides enter the soil and ground water by direct treatment or being washed off from plant surfaces during rainfall. Depending on the phenotype and density of the plant type, it is estimated that an average of 35-50% of the plant protection material is deposited on soil immediately after spraying. The behaviour of pesticide in soil and ground water involves persistence, movement and metabolism. The formation of residues in soil mainly depends on water solubility and the binding capacity of both organic and inorganic constituents of soil. The major health effects due to pesticide are neuropathy headache, memory loss, jaundice, respiratory, depression, breathlessness and birth defects that occur through food chain (Sinha et al 1995; Lu et al 2000).

The use of these pesticides, especially DDT and HCH has therefore been either banned or restricted in several countries including India. Although there is a general decline in residue levels, the ban or restricted use has not completely eliminated the residues of these compounds and their metabolites from the environment (Bhatnagar et al 1992; Bhattacharya et al 2003). India is one of the major producer and consumer of organochlorine pesticides, particularly dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexanes (HCHs) for agriculture and public health programs. Even in

the 1990s, more than 70% of the gross tonnage of pesticides used in agricultural applications in India consisted of formulations which are banned or severely restricted in the east and west (Gupta 1989; Shetty 2001; Subramanian et al 2007).

Consumption of insecticide in agriculture has been increased more than 100% from 1971 to 1994-95. For instance, insecticide consumption in India, which was to the tune of 22013 tons, has increased to 51755 tons by 1994-95 (Fig 4.1) (www.indiastat.com). The Indian pesticide industry with 82,000 MT productions for 2005-06 is ranked second in Asia (behind China) and twelfth on global market. According to Green Peace report, India is producing 90,000 metric tons of pesticides as the largest industry in the whole of Asia. India as most of the rivers pass through agricultural fields, they are subjected to contamination with different pesticides used for crop protection (http://www.greenpeaceindia.org/nopesti.htm). Higher levels of HCH are being reported to occur in Indian marine water and it is estimated that about 25 tons of organochlorines produced have been already transported to the sea (Mohapatra and Saha 2000).

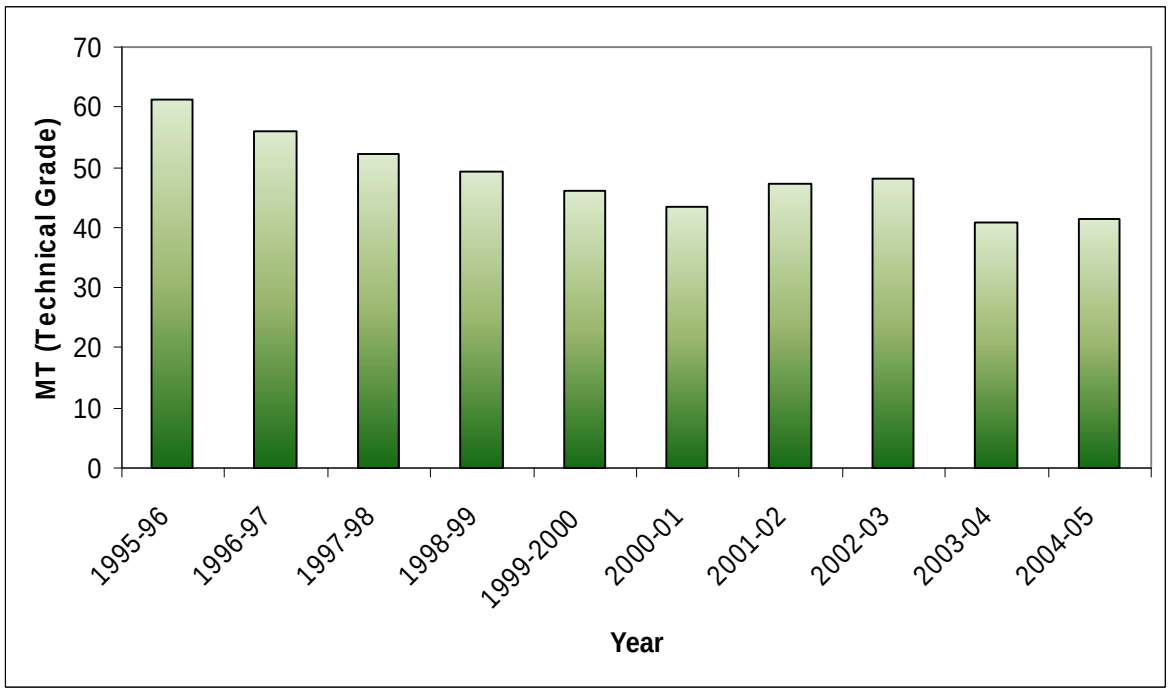

Figure 4.1. Consumption of pesticides in India (1995 to 2005)

(Source: DPPQ & Faridabad).

Apart from the US, India is the only country which has applied more than 100,000 tons of DDTs since its formulation, mainly in its agricultural and malarial control programmes until it was banned for agricultural use in 1989 (Kannan 1995). Even though usage of technical HCH was finally banned completely in 1977 (Kannan 1997), the Government of India is encouraging its replacement with Lindane (γ-HCH), an isomer which has all the hazardous properties of HCH. Even though DDT has been banned for agricultural use, India has sought exemption under stockholm convention for use of 10,000 tons of DDT for restricted use in the public health sector (Lallas 2001). The national malaria program (NAMP) used 3750 tons of DDT in the year 2001 in rural and semi-urban areas for residual spraying (Gupta 2004).

4.2 GLOBAL DISTRIBUTION

The information on the residues of persistent organochlorine pesticides (POPs) in the environmental media - air, freshwater, seawater, sediments and soil as well as the tendencies for their elimination in regional and global aspect is analyzed. The adverse effects for the living organisms as a result of bioaccumulation and biomagnifications of those substances in the tissues are outlined. Pesticides are transported from the field to the surface water mainly by the process of runoff. Although numerous factors affect runoff, and therefore pesticide concentrations in surface water, many of these factors such as soil type, stream channel network, land use, and landscape remain virtually unchanged over time and thus reduce essentially to constants for a given watershed. In such cases, the temporal and spatial changes of pesticide concentrations in surface water are primarily dependent on two major environmental variables, both of which are very well documented: precipitation and pesticide use. Precipitation determines the total amount of runoff water, and pesticide use represents the source of contamination. The surface transport of pesticides and their runoff to the river depends on factors like slope, texture and porosity of soil, intensity of rainfall, erosivity of rainwater, erodibility of soil, water table and solubility and polarity of pesticides (Vassilev 2006). Since water of rivers and canals is used for drinking purposes in India, it becomes

imperative to study the extent and magnitude of these restricted or banned pesticides in these water bodies.

The strongest evidence for the global dispersion of POPs in the environment is their accumulation in living organisms, plants, water organisms, terrestrial animals. Very high concentrations of DDT were found in some terrestrial and water plants like pine needles (Eriksson et al 1989). Pollution of rivers and fresh water lakes with pesticides is strongly influenced by the hydro-geological regime of water courses and the presence of suspended solids. It is reasonable to analyze water samples paralelly for dissolved content and content on suspended solids. Very often after stormy rains and floods high levels are registered because of elevated amount of suspended soil particles. The highest mean levels of organochlorine pesticide in rivers and lakes are detected in developing countries. DDT and its metabolites, as well as HCHs in concentrations up to and about 0.1mg l^{-1} are the most frequently found substances. In the developing countries of Africa, South America, South Asia detectable amount of wide spectrum of pesticides like endosulfan, dieldrin, heptachlor, chlordan, HCB, atrazine has been found. It is not surprising having in mind their popular use in the past, but may be still in present days in some regions. The presence of DDT and lindane are most often reported for European countries. In conclusion, except in cases of accidents, the highest levels in freshwater are reported from the regions of Africa, South America, India and South-east Asia where some persistent chemicals are still in use for vector control and probably in agriculture. The global trend is declining of registered values in natural water compared with 70's and 80's (Vassilev 2006).

Seawater is the final receivers of land based pollution sources and through the sea currents is realised the global transport of some pollutants in the world ocean. Generally, the content of pollutants in coastal water is much greater than this in open seawater. The coastal water are polluted by discharges of sewage and industrial effluents and rivers, whereas the major sources of pollution in open sea are atmospheric

depositions. The presence of persistent and hydrophobic chemicals in seawater is important because of the possibilities for bioaccumulation and biomagnifications through food web. The worldwide consumption of pesticide is about two million tons per year, of which 24% is consumed in the USA alone, 45% in Europe and 25% in the rest of the world. The usage of pesticides in India is only 0.5 kg ha^{-1}, while in Korea and Japan; it is 6.6 and 12.0 kg ha^{-1}, respectively (Chauhan and Singhal 2006). Among the various pesticides used in India, 40% of all the pesticides used belong to organochlorine class of chemical pesticides (FAO 1994; Gupta 2004; FAO 2005).

Global transports of persistent organic pollutants (POPs) have caused serious environmental concern (Table 4.1). In remote regions such as the Arctic and the Antarctic, POPs have been observed with high concentrations (Wania and Mackay 1993). Far away from source regions, many POPs, especially organochlorine pesticides (OCPs), have been detected, e.g., HCB in barks (Simonich and Hites 1995) and α-(-) HCH in seawater (Iwata et al 1993a; Wania and Mackay 1996). Long-range transport in the atmosphere is the most important global transport path for POPs. In warm regions, POPs tend to evaporate into the atmosphere and are transported long distances in the atmosphere before ending up on cold surfaces in the polar region. Similar to Polar Regions, low temperatures in mountainous regions could also allow high mountains to act as cold condensers for POPs in the atmosphere and play important roles in the global transport of POPs (Blais et al 1998). Recent studies on organochlorine pesticides in the air of the Mt. Everest region is the evident for such transports (Li et al 2006). A survey on global plant biomass has found that low-latitude and high-altitude regions had the highest HCB concentrations (Calamari et al 1991). High concentrations of organochlorine compounds in fish and lake sediment of Canadian Rocky Mountains have also been reported (Donald et al 1998).

Several reports are available for the occurrence of pesticides in various environmental compartments. Recently, four hexachlorocyclohexanes isomers in eight

plant species growing in an industrial premise have been reported having high concentrations in *Withania somnifera* (L) *Dunal* and *Solanum torvum* (Abhilash et al 2007 & 2008). Tanabe et al (1991); Takeoka et al (1991) evaluated the transport of HCHs from land to sea in a paddy field and adjoining estuarine systems in southern India and found out that major portion of the HCHs used is removed to the air and contribute both to the regional and global pollution. A series of studies from other workers showed the existence of various pesticides in samples of air (Pillai 1986; Ramesh 1989; Iwata et al 1994 and Rajendran et al 1999), Water (Sarkar and Gupta 1989; Ramesh et al 1990; Misra and Bakre 1994, Rehana et al 1996, Agrawal 1999, Aleem 2005, Amaraneni 2006; Fatima and Ahmad 2006), Soil and sediments (Ramesh et al 1991; Iwata et al 1994; Khans et al 1999 and Bhattacharaya et al 2003), Wildlife including dolphins, sharks and mussels (Tanabe 1993; Subramanian et al 1999; Tanabe 2004 and Shankar et al 2006), Fish (Singh 2008), Birds (Tanabe 1998), Food stuffs (Lal et al 1989; John et al 2001; Kumari et al 2006; Bhanti and Taneja 2007 and Venkateshwarlu et al 2007) from India.

4.3 PESTICIDE POLLUTION IN INDIAN RIVERS

The use of the pesticides in India started only after the independence and the first plant to produce a pesticide (BHC) on a commercial basis was set up in 1952, while the first public-sector DDT plant came into existence in 1955 (Jalees and Vemuri 1980). When, DDT was imported for malaria control and BHC used for low cost control. India started pesticide production with manufacturing plant for DDT and benzene hexachloride (BHC), (HCH) in the year 1952. In 1958, India was producing over 5000 metric tons of pesticides. Currently, there are approximately 145 pesticides registered for use, and production has increased to approximately 94,000 metric tons Ministry of Chemicals and Fertilizers (MoCF 2005-06). The agricultural sector consumes about 67% of the pesticides produced; the remainder is used in public health programmes. Within the agricultural sector, a few crops like cotton, paddy, vegetables and fruits account for two-thirds of consumption.

The consumption pattern of pesticides in India is also very different from the rest of the world. In India, insecticides account for 76% of the total domestic market while herbicides and fungicides have a significant higher share in the global market (Lal 2007). Several researchers (Agarwal et al 1986; Ramesh et al 1990; Rehana et al 1995; Rajendran and Subramanian 1997 & 1999; James 2000; Malik et al 2009; Begum 2009) report the pesticide pollution and their impact on Indian rivers. The present study seeks to identify and quantification of OCPs concentration in both water and sediment samples of the entire Tamiraparani river to assess the impacts of agricultural inputs on the river system.

4.4 SOURCES OF PESTICIDE IN TAMIRAPARANI RIVER BASIN

Agriculture sector is a very important part of the Indian economy and greatly contributes to overall food needs of the country and provides domestic industry with agricultural raw materials. It promotes industrial development through expanding the market for industrial goods such as pesticides, chemical fertilizers, equipment and machineries. Pesticides are generally recognized as significantly benefiting our ability to meet the worlds need for abundant, safe and affordable food and fiber. Pesticides reach the soil environment by direct and indirect application from aerial and ground applications. The main processes potentially affecting the ultimate fate of pesticides in soils are retention by soil materials (involving adsorption/ de-sorption processes), transformation processes (biological and chemical degradation), and transport through soil, atmosphere, surface water or ground water (van der Hoff and van Zoonen 1999).

Table 4.1 Global distribution of organochlorine (ng l^{-1} and ng g^{-1})

Location	ΣDDT		ΣHCH	Aldrin	Dieldrin	Endrin	Reference
Yangtse river, China	(W)	0.21-4.50	0.18-1.41	0.04-1.27	-	BDL-0.14	Xu et al., (2000)
River Wuchuan, Southeast China	(W)	53.45 - 163	15.46 - 111.0	5.38 - 49.62	1.78 - 21.14	1.90 - 26.38	Zhang et al., (2002a)
	(S)	0.47 - 2.14	0.21 - 3.85	0.02 – 0.87	0.03 – 0.24	0.02 – 0.13	
Buffalo river, South Africa	(W)	-	60 ± 0.0001	10 ± 0.005	10 ± 0.003	-	Awofolu and Fatoki (2003)
	(S)	$3.5x10^3$±5.4	$4.6x10^3$±20.2	-	-	$2.0x10^3$±15.0	
Minjiang river estuary, Southeast China	(W)	40.61-233.5	52.09-515.0	5.25-53.17	5.39-74.03	13.37-101.3	Zhang et al., (2003)
	(S)	1.57-13.06	2.99-16.21	0.47-2.23	0.67-1.79	0.27-2.43	
Qiantang river, East China	(W)	0.80 - 97.54	0.79 - 202.8	0.23 - 103.9	<0.15 - 42.06	<0.10 - 28.46	Zhou et al., (2006)
	(S)	8.64 - 100.2	19.74 - 152.1	0.36 - 19.56	<0.15 - 28.40	<0.16 - 52.37	
Northeastern part of Sa˜o Paulo	(W)	0.02 – 0.6	0.02 – 0.58	0.005 – 0.006	0.005 – 0.005	<0.005 – 0.005	Rissato et al., (2006)
State, Brazil	(S)	0.05 – 0.92	0.12 – 11.01	<0.04 – 0.23	0.05 – 0.96	<0.05 – 0.25	
Sediments and water from Lake	(W)	0.23 - 1.76	0.75 - 1.61	-	-	-	Darko et al., (2008)
Bosomtwi, Ghana	(S)	15.06 - 31.92	2.03 - 13.94	0.30 - 0.46	0.20 - 0.46	-	
River Nile at Rosetta Branch, Egypt	(W)	>0.01	>0.01	>0.01	>0.01	>0.01	Ahmed et al., (2008)
	(S)	>0.01	>0.01	>0.01	>0.01	>0.01	
Saiburi river, Thailand	(W)	0.40-203.1	0.20-0.36	-	-	0.06-1.10	Samoh and Ibrahim (2008)
Gao-ping river, Taiwan	(W)	0.44 - 1.88	5.02 - 8.62	<0.05 – 9.59	<0.12 – 1.42	<0.22 – 0.97	Doong et al., (2008)
Gomti River, India	(W)	BDL-74.98	1.63-368.7	<0.1-77.93	<0.05-22.45	<0.05-4.25	Malik et al., (2009)
	(S)	1.63-368.7	BDL-155.17	<0.1-10.89	<0.05-1.65	<0.05-11.96	
Tamiraparani river,	(W)	0.31 - 0.72	0.12 - 0.78	<0.02 - 1.02	<0.03 - 7.53	<0.02 - 58.0	Present Study
India	(S)	37.8 - 857.4	0.12 - 472.4	<0.02 - 562.4	<0.03 - 1693	-	

W: Water sample S**:** Sediment samples

The paddy is traditionally cultivated in Sankarankoil, Tirunelveli, Tenkasi, Sencottah, Ambasamudram and Nanguneri taluks in this province. Cereal, gingelly and black gram are being cultivated in the dry tracts of this basin mainly in Sivagiri and part of Sankarankoil taluks. Cotton is being cultivated mainly in Sankarankoil. The total geographical area of the basin was 5869 km^2 and cropped area accounts for about 20.91% of the total area. Forestlands cover about 17.62% of the total land. A significant portion (48.06%) of the land falls under the category of 'non available for cultivation' and 'fallow lands'. The land utilization pattern in Tirunelveli district forest lands (18%), non available for cultivation (18%), other uncultivated lands (13%), fallow lands (30%), cropped area (21%). The river Tamiraparani is one of the perennial rivers in South India, which is being intensively utilized (>90%) for agricultural purposes. The irrigated land occupies 48% by direct irrigation (34,934 ha) and rest 52% by indirect method through numerous tanks, which is available in the river basin (IWS 1988).

4.4.1 Organochlorine pesticides in water

The concentration of 17 organochlorine pesticide residues in surface water samples of the present studies are ranged from 2.5 to 79.9 ng l^{-1}. (Table 4.2) illustrate the results of water sample analysis, and it can be seen that the concentrations of DDTs and other OCPs were much higher than that of HCHs. Fig 4.2 shows the distribution pattern of total OCPs residues in water for three seasons sample along the river. It clearly reveals that the OCPs residues in monsoon and summer season were much higher than other two sampling seasons. This could be due to some OCPs are released from non point sources and subsequent leaching processes during monsoon period throughout the basin and intense agriculture practices in summer season followed by Southwest monsoon in the upper region. Higher concentrations of OCPs in upstream (S3 and S7) province are probably resulted during monsoon season from farmland runoff (Tenkasi) along with untreated municipal waste directly mixing into the river flow. At the same time lower concentration of OCPs in the Servalar areas explains

dense forestation with less agriculture practice and midstream province (S15) influenced by man made damming activities resulting subsequent soil deposition lead to decrease in pesticides load. The highest concentrations of 58.0 ng/l was observed at Papanasam lower dam (S3) site during monsoon season reveals the fact that it receive water from Western Ghats region where rubber cultivation dominates and used organochlorine insecticides. The organochlorine pesticide under different trade names of DDT are listed as anofex, cezarex, chlorophenothane, clofenotane, dicophane, dinocide and zerdane etc.,) aldrin (ENT 15949 (compound 118), HHDN, octalene, OMS 194) and dieldrin (ENT 16225 (compound 497), HEOD, alvit, octalox, OMS 18, quintox) (http://www.inchem.org/documents/hsg/hsg/hsg021.htm). In the downstream area of Eral (S17) and Punnakayal (S21), locations are also witnessed higher concentrations of OCPs for all the seasons as a result of collective down flow loads. In the four sampling periods, the highest concentration of HCHs in the river was 0.78 ng l^{-1} in (S15) during premonsoon, 7.53 ng l^{-1} for dieldrin (S7) during monsoon and 58.0 ng l^{-1} for endrin (S3) during monsoon season (Table 4.2). This elevated concentration is comparable with other Indian and World river.

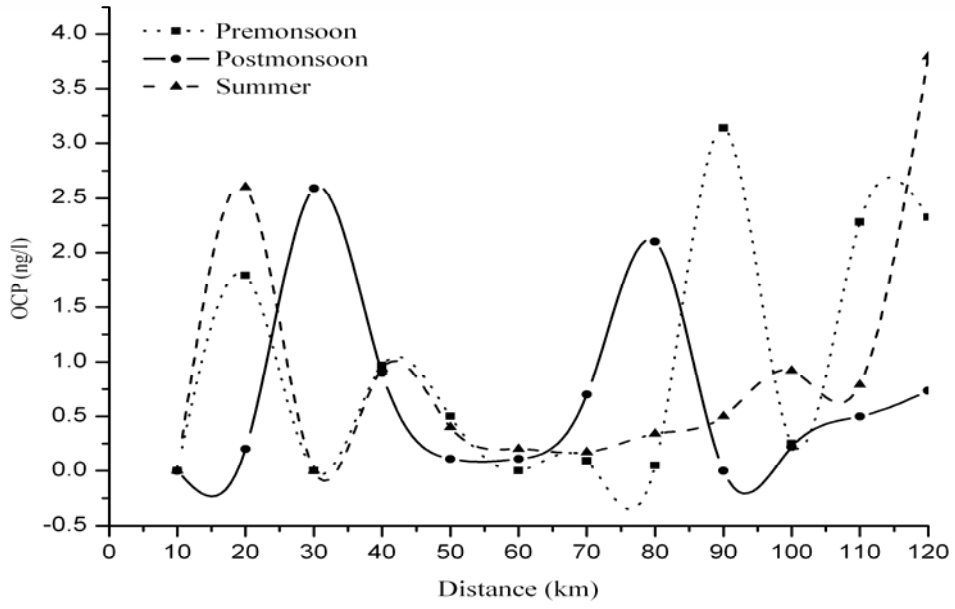

Figure 4.2 Spatial distributions of ΣOCPs in water samples

Other OCPs including aldrin, endrin, dieldrin, heptachlor, trans-Chlordane, cis-Chlordane and mirex were found small amounts in all sampling sites and seasons. Specifically, endrin and dieldrin were found in most of the locations for water as well as sediment samples. Dieldrin was widely used as an effective insecticide around the world until the middle 1970s, mainly for the control of soil pests, like termites, grasshoppers, locusts, beetles, textile pests, and for the treatment of seeds. Additionally it has also been used to control vectors of tropical diseases, including malaria, yellow fever and again used for industrial purposes to protect electric and telephone cables and to preserve timber materials etc., (DeJong 1991). In the study region dieldrin is effectively used as soil insecticide, especially for perennial crops, such as palm, and banana. Also, aldrin and dieldrin were used to control termites in houses by direct soil injection in the past (ATSDR 2002). Aldrin is rapidly converted to dieldrin in the environment. The sum of all sites aldrin concentrations were in the minimum and maximum ranges of <0.02 to 4.0 ng l^{-1} in different seasons and the same trend was observed for dieldrin in the range of 1.4 – 12.7 ng l^{-1}. The present results showed that these compounds were probably originated from the above said industrial and public health practices. Pesticides pollution of surface water on agriculture use has been well documented around the world in recent years. But there is limited data is available for these 17 OCPs and hence the presence study is the holistic approach towards comparison of Tamiraparani results with Indian and other world rivers.

The heptachlor concentration were ranged between <0.06 to 2.10 ng l^{-1} during monsoon and <0.06 to 0.47 ng l^{-1} during postmonsoon season. Heptachlor is metabolized to heptachlor epoxides in the soils, plants and animals, which are more stable in biological systems. In this study, heptachlor concentration is relatively lower than that reported by Zhang et al (2002a) for Pearl river estuary (2.83 – 294.0 ng l^{-1}). Similarly, the levels of ΣHCH (0.12 to 0.78 ng l^{-1}) were also found lower than Pearl river estuary (Zhang et al 2002b) and Minjiang river estuary (Zhang et al 2003). Contrary the residual levels of aldrin and dieldrin were considerably higher (<0.02 to

4.0 ng l^{-1} and 1.4 – 12.7 ng l^{-1}) than Malik et al (2009). Aldrin has been used as a soil insecticide to control root worms, beetles and termites. Dieldrin has been used in agriculture for soil and seed treatment as well as for control of mosquitoes and tsetse flies (Jensen 1983). Other uses for dieldrin include veterinary treatments for sheep, wood treatment against termites and mothproofing of woolen products (ATSDR 1989). Endrin has been used as an agricultural insecticide on tobacco, apple trees, cotton, sugar cane and grain, as well as to control rodents and birds (ATSDR 1997). Based on the water samples analysis for four seasons, the river basin is polluted in the order of endrin > dieldrin > aldrin > ΣDDT > heptachlor > mirex > cis-Chlordane > ΣHCH > HCB > trans-Chlordane.

4.4.2 Residual levels in sediments

The total OCPs concentrations in sediments were varied from 1534.4 to 3839.7 ng g^{-1} –dry weight (dw). Table 4.3 and Fig 4.3 illustrate the distribution statistics of surface sediments for three sampling seasons. The concentrations in sediments sample during summer season was in the range of 0.12 to 472.4 ng g^{-1} -dw for ΣHCHs (α-, β-, γ-HCH), 20.5 to 56.2 ng g^{-1} -dw for DDTs (p,p′-DDT, o,p′-DDT, p,p′-DDD, o,p′-DDD, o,p′-DDE), 12.6-421.5 ng g^{-1} -dw for other ΣOCPs (HCB, heptachlor, aldrin, trans-chloradane, dieldrin, mirex). Concentrations of ΣDDTs and its isomer were much higher than those of ΣHCHs. The same situation is evidenced for water samples. This trend is consistent with the fact that the amount of technical DDT used was significantly higher than that of HCHs in the river basin. The status of OCPs contamination in sediments was compared with other world rivers. Among the Indian rivers, the levels of DDTs and other OCPs in sediments of Tamiraparani river ranked considerably higher (0.12 to 472.4 ng g^{-1} for HCHs, 37.8 to 857.4 ng g^{-1} for DDTs). In the present study, the ΣDDT concentrations higher than those reported for Minjiang river estuary (1.6 –13.1 ng g^{-1} -dw; (Zhang et al 2003); Haihe and Dagu drainage rivers (0.32–80.18 ng g^{-1} –dw; 3.60–83.49 ng g^{-1} - dw (Yang et al 2005) and Taiwan rivers (0.21–8.81 ng g^{-1} -dw; Doong et al 2002). Among the DDT metabolites, o,p′-DDE,

p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT and p,p′-DDT were ranged from <0.02 to 34.9 ng g^{-1}; <0.01 to 82.77 ng g^{-1}, <0.02-50.2 ng g^{-1}, <0.01-30.4 ng g^{-1}, <0.01-252.7 ng g^{-1} and <0.01-460.8 ng g^{-1} -dw, respectively. The sediments residue levels of o,p′-DDT and p,p′-DDT are higher than those reported for Qiantang river (0.28–9.61 ng g^{-1}; Zhou et al (2006).

In this study, p, p′-DDD and p, p′-DDT was the maximum percentage of DDT metabolite detected in the both water and sediments. The dominance of parent compound over their degradation products (metabolites) in the sediments suggested the recent use of DDT. The ΣHCH concentrations in sediments were two fold higher than Minjiang river (Zhang et al 2003) and are comparable with river Kaveri, India (4.35 – 158.4 ng g^{-1} -dw; Rajendran and Subramanian (1999); Qiantang river, East China (9.23 –152.1 ng g^{-1}, Zhou et al 2006) and Dagu drainage river (33.24 – 141.03 ng g^{-1}, Yang et al 2005). HCB is a widespread contaminant that has entered the environment through their past production and its formation as a by-product of a variety of chlorinated compounds. In aquatic systems, HCB is persistent in sediment and tends to accumulate in the tissues of organisms. In these river sediments the concentrations of HCB are ranged between and <0.05 to 19.5 ng g^{-1} -dw and are relatively higher than (0.14 – 3.96 ng g^{-1}) Yangtse river (Xu et al 2000) and trans-Chlordane and cis-Chlordane concentrations are ranged between and <0.01 to 20.0 ng g^{-1} -dw and <0.01 to 93.6 ng g^{-1} –dw. The chlordane isomers are not frequently presented most of the sites for all four seasons in the river. It is notable that in India chlordane is completely banned on manufacturing, import and export (IPEP 2006).

Table 4.2 Average concentration of OCPs (ng l^{-1}) in surface water samples (n=48)

Pesticide	Premonsoon		Monsoon		Postmonsoon		Summer	
	Range	Mean ± S.D	Range	Mean ± S.D	Range	Mean ± S.D	Range	Mean ± S.D
α-HCH	<0.01	-	<0.01	-	<0.01	-	<0.01- 0.12	0.25 ± 0.00
β-HCH	<0.05	-	<0.05	-	<0.05	-	<0.05	-
HCB	<0.05	-	<0.05- 0.24	0.24 ± 0.00	<0.05	-	<0.05- 0.25	0.15 ± 0.13
γ-HCH	<0.06 - 0.78	0.78 ± 0.00	<0.06	-	<0.06	-	<0.06	-
Heptachlor	<0.06 - 0.33	0.31 ± 0.04	<0.06 - 2.10	1.12 ± 0.85	<0.06- 0.47	0.09 ± 0.00	<0.06- 0.60	0.24 ± 0.21
Aldrin	<0.02	-	<0.02 - 1.48	0.34 ± 0.54	<0.02 - 1.02	0.48 ± 0.41	<0.02 - 0.25	0.16 ± 0.09
Trans-Chlordane	<0.01	-	<0.01	-	<0.01	-	<0.01 - 0.21	0.21 ± 0.00
o,p'-DDE	<0.02 - 0.07	0.07 ± 0.00	<0.02 - 0.29	0.16 ± 0.09	<0.02 - 0.14	0.11 ± 0.06	<0.02 - 0.04	0.04 ± 0.01
cis-Chlordane	<0.01 - 0.25	0.16 ± 0.71	<0.01	-	<0.01 - 0.49	0.24 ± 0.23	<0.01 - 0.42	0.2 ± 0.19
Dieldrin	<0.03 - 2.28	1.59 ± 0.51	<0.03 - 7.53	1.07 ±2.20	<0.03 - 1.98	1.02 ± 0.84	<0.03 - 0.56	0.23 ± 0.16
p,p'-DDE	<0.01 - 0.02	0.02 ± 0.00	<0.01 - 0.29	0.22 ± 0.09	<0.01	-	<0.01 - 0.10	0.08 ± 0.03
o,p'-DDD	<0.02 - 0.05	0.05 ± 0.00	<0.02 - 0.37	0.06 ± 0.11	<0.02 - 0.22	0.09 ± 0.08	<0.02 - 0.04	0.03 ± 0.01
Endrin	<0.02	-	<0.02 - 58.0	58.002 ± 0.00	<0.02	-	<0.02 - 3.01	2.42 ± 0.83
p,p'DDD	<0.01- 0.2	0.89 ± 0.00	<0.01- 0.28	0.21 ± 0.96	<0.01- 0.33	0.17 ± 0.14	<0.01 - 0.17	0.11 ± 0.06
o,p'DDT	<0.01	-	<0.01 - 0.31	0.31 ± 0.00	<0.01 - 0.14	0.14 ± 0.00	<0.01 - 0.18	0.09 ± 0.08
p,p'DDT	<0.01	-	<0.01	-	<0.01- 0.38	0.37 ± 0.00	<0.01	-
Mirex	<0.01 - 0.7	0.47 ± 0.32	<0.01 - 0.47	0.39 ± 0.11	<0.01- 0.17	0.13 ± 0.06	<0.01 - 0.15	0.11 ± 0.05
ΣHCH[a]	0.12 - 0.78	0.78 ± 0.00	0.12	-	0.12	-	0.12 - 0.13	0.25 ± 0.00
ΣDDT[b]	0.02 - 0.38	0.12 ± 0.16	0.306 - 0.72	0.50 ± 0.16	0.21- 0.50	0.33 ± 0.15	0.09 - 0.36	0.23 ± 0.12
ΣOther OCP[c]	0.61 - 7.94	0.17 ± 3.22	0.236 - 58.0	13.32 ± 22.32	0.567 - 3.05	1.23 ± 1.16	0.21 - 4.84	1.15 ± 1.6
ΣOCP[d]	0.51 -10.88	4.06 ± 5.91	2.527 - 79.91	41.21 ± 54.71	1.663 - 6.5	4.08 ± 3.42	0.13 - 8.04	3.06 ± 4.33

BDL - Below detectable limit

ΣHCH [a] = α-HCH + β-HCH + γ-HCH

ΣDDT [b] = o,p'-DDE + p,p'-DDE + o,p'-DDD + p,p'DDD + o,p'DDT + p,p'DDT

Σother OCP [c] = HCB + Heptachlor + aldrin + trans-Chlordane + cis-Chlordane + dieldrin + endrin + mirex

ΣOCP [d] = Σ HCH + ΣDDT + Σother OCP

Table 4.3 Average of concentration of OCPs (ng g^{-1} -dw) in surface sediment samples (n=48)

Pesticide	Premonsoon		Monsoon		Postmonsoon		Summer	
	Range	Mean ± S.D	Range	Mean ± S.D	Range	Mean ± S.D	Range	Mean ± S.D
α-HCH	<0.01	-	<0.01	-	<0.01	-	<0.01	-
β-HCH	<0.05 - 114.4	114.4 ± 0.00	<0.05	-	<0.05	-	<0.05	-
HCB	<0.05	-	<0.05	-	<0.05	-	<0.05 -19.5	19.50 ± 0.00
γ-HCH	<0.06	-	<0.06	-	<0.06 - 240.2	240.00 ± 0.00	<0.06 - 472.4	386.90 ± 120.92
Heptachlor	<0.06 - 75.2	72.2 ± 0.00	<0.06 - 102.8	56.80 ± 65.03	<0.06	-	<0.06 - 57.3	56.00 ± 1.84
Aldrin	<0.02	-	<0.02 - 562.4	375.65 ± 264.10	<0.02	-	<0.02 - 18.4	18.40 ± 0.00
Trans-Chlordane	<0.01 - 20.0	20.0 ± 0.00	<0.01	-	<0.01 - 12.6	10.50 ± 3.30	<0.01 - 6.3	6.30 ± 0.00
o,p'-DDE	<0.02 - 2.1	2.10 ± 0.00	<0.02 - 23.6	18.90 ± 6.65	<0.02 - 34.9	18.63 ± 15.23	<0.02 - 7.7	5.13 ± 2.24
cis-Chlordane	<0.01 - 24.0	14.90 ± 9.70	<0.01 - 93.6	69.43 ± 24.72	<0.01	-	<0.01	-
Dieldrin	<0.03 - 179.4	77.35 ± 69.12	<0.03 - 1693	906.53 ± 693.41	<0.03	-	<0.03 -121.8	84.30 ± 21.83
p,p'-DDE	<0.01- 4.5	4.50 ± 0.00	<0.01 - 82.77	82.70 ± 0.00	<0.01-14.7	13.55 ± 1.63	<0.01	-
o,p'-DDD	<0.02 - 18.4	12.45 ± 8.41	<0.02 - 50.2	30.55 ± 27.79	<0.02 - 50.2	35.95 ± 20.58	<0.02 - 15.8	11.24 ± 3.16
Endrin	<0.02	-	<0.02	-	<0.02	-	<0.02	-
p,p'DDD	<0.01 - 30.4	23.90 ± 9.19	<0.01	-	<0.01 - 23.8	23.80 ± 0.00	<0.01 -17.4	12.87 ± 3.96
o,p'DDT	<0.01 - 12.4	12.40 ± 0.00	<0.01 - 252.7	165.13 ± 80.92	<0.01 - 16.4	16.40 ± 0.00	<0.01 - 22.3	20.20 ± 2.97
p,p'DDT	<0.01	-	<0.01 - 460.8	285.80 ± 162.60	<0.01 - 214.5	214.50 ± 0.00	<0.01 - 44.9	44.90 ± 0.00
Mirex	<0.01 - 26.9	22.53 ± 4.62	<0.01- 68.9	64.88 ± 6.24	<0.01 - 88.5	40.19 ± 22.39	<0.01- 78.7	48.35 ± 42.92
ΣHCH[a]	0.12 - 114.4	114.4 ± 0.00	0.12	-	0.12 - 240.2	240.00 ± 0.00	0.12 - 472.4	386.90 ± 120.92
ΣDDT[b]	2.1 - 47.8	18.38 ± 18.71	37.8 – 857.4	306.88 ± 361.13	16.4 ± 214.5	68.26 ± 74.71	20.5 - 56.2	40.12 ± 12.93
ΣOther OCP[c]	20.0 - 309.4	103.38 ± 117.17	208.3 - 2719.6	984.68 ± 1182.2	31.5 - 281.3	184.33 ± 133.94	12.6 - 421.5	207.79 ± 287.80
ΣOCP[d]	91.7 - 519.9	241.0 ± 239.20	1534.4 - 3938.7	2737.0 ± 1700.8	240.2 - 409.6	400.9 ± 156.53	200.6 -1454.6	709.16 ± 659.62

BDL - Below detectable limit

ΣHCH [a] = α-HCH + β-HCH + γ-HCH

ΣDDT [b] = o,p'-DDE + p,p'-DDE + o,p'-DDD + p,p'DDD + o,p'DDT + p,p'DDT

Σother OCP [c] = HCB + Heptachlor + aldrin + trans-Chlordane + cis-Chlordane + dieldrin + endrin + mirex

ΣOCP [d] = Σ HCH + ΣDDT + Σother OCP

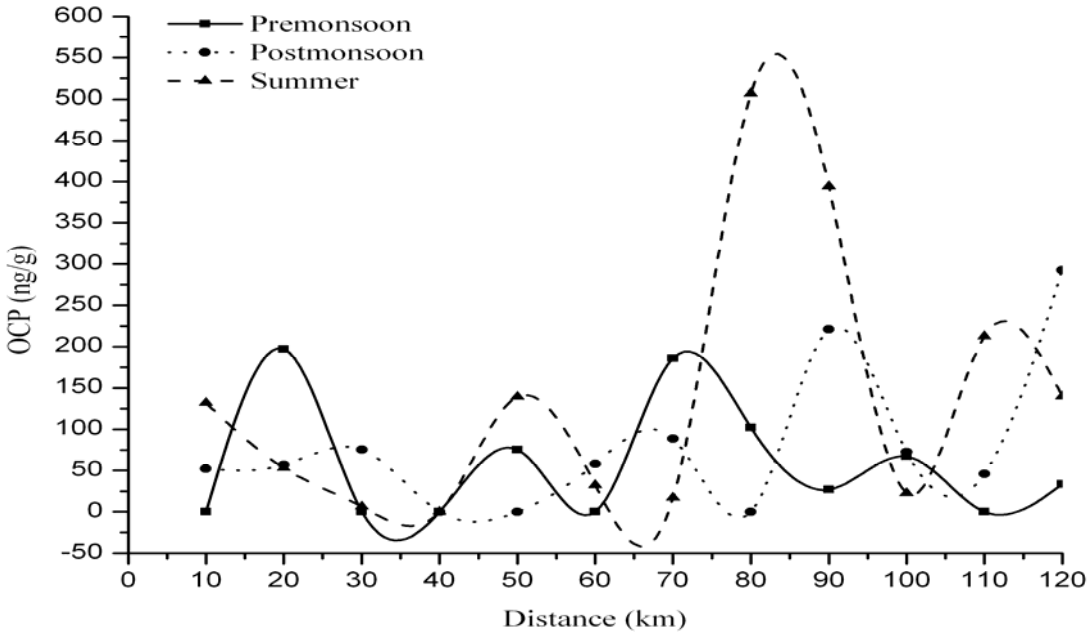

Figure 4.3 Spatial distributions of ΣOCPs in sediments

4.4.3 Spatial and temporal distribution of OCPs in sediments

The two highest concentrations of total OCPs including DDT, endrin and dieldrin were found in stations S13 and S17 during monsoon season, which is agreed with the distribution pattern of surface water. It may be due to similar chronological input and source of OCPs in this region. The third highest concentration is observed at Punnakayal station (S21), located in the end part of river before confluence to estuary region. As a whole, OCPs concentrations in downstream were higher than that of upstream in the sediments are well explanatory with heavy rainfall in association with water leaching processes and adsorption and re-suspension in the sediment environment could cause for source and sink for pollution material. For some OCPs, chemical transformation and microbial decomposition may occur, e.g. DDT is transforming to DDE and δ-HCH to α-HCH. However, complete mineralization of organochlorine compounds does not usually take place either or is an extremely slow process (Falandysz et al 2001). The differing composition of DDT metabolites and HCH

isomers in the environment could indicate their different sources of contamination (Yang et al 2005). The present result revealed that the concentrations of HCHs and DDTs differs in physiochemical and biosolubility properties, with HCHs having higher water solubility than DDTs, vapour pressure and biodegradability and lower lipophilicity and particle affinity as compared to DDTs (Loganathan and Kannan 1994) owing multi level entry of contaminants and non biodegradability and hence persistent nature in the environment. Mirex has observed most of the sampling sites and also the same pattern were obtained during all four sampling seasons. It is mainly used as a stomach insecticide, usually formulated into baits, for the control of ants, especially fire ants and harvester ants. We could conclude that, mirex are recently used for agricultural purposes in the river basin, whereas, it is not registered pesticide in India (IPEP 2006).

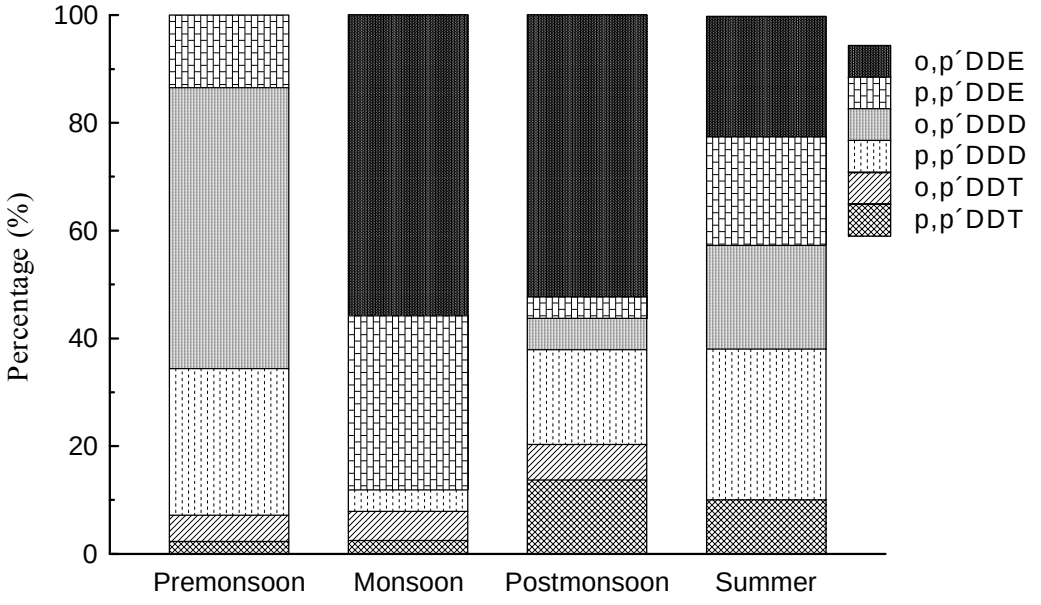

Figure 4.4 Fractionation of DDTs in sediment samples

The percentage composition of DDT isomers measured in the sediment samples with reference to four different seasons are o,p´-DDE: 32.7%, o,p´-DDD: 19.3%, p,p´-DDD: 19.3%, p,p´-DDE: 17.2%, p,p´-DDT: 7.13%, o,p´-DDT: 4.23% (Fig. 4.4) with the dominance of the parent compound over their degradation products

(metabolites) in the sediments suggests for the recent use of DDT along with degradation of DDT used earlier. It is evident that India has banned DDT for agricultural use in 1989, although it is still used in the public health sectors for malaria control (UNEP 2003). The relative concentration of the parent DDT compound and its metabolites, DDD and DDE, can be used as indicative indices for assessing the possible pollution sources. Since DDT can be biodegradable under aerobic condition to DDE and under anaerobic condition to DDD (Bossi et al 1992), the ratio of (DDE+DDD)/DDTs are less than 0.5 could be thought us it is subjected for long term weathering (Doong et al 2002). Fig. 4.5 shows the relationship between the (DDE+DDD)/DDTs and DDD/DDE in the surface sediments collected for monsoon and summer season. Ratios of (DDE+DDD)/DDTs were in the range of 0.1 to 0.86 with most values being less than 0.5 (Fig 4.5). This indicates that in the river sediments, source of DDT contamination is from the aged and weathered agricultural soils with signature of recently used DDT in Tamiraparani river catchment area.

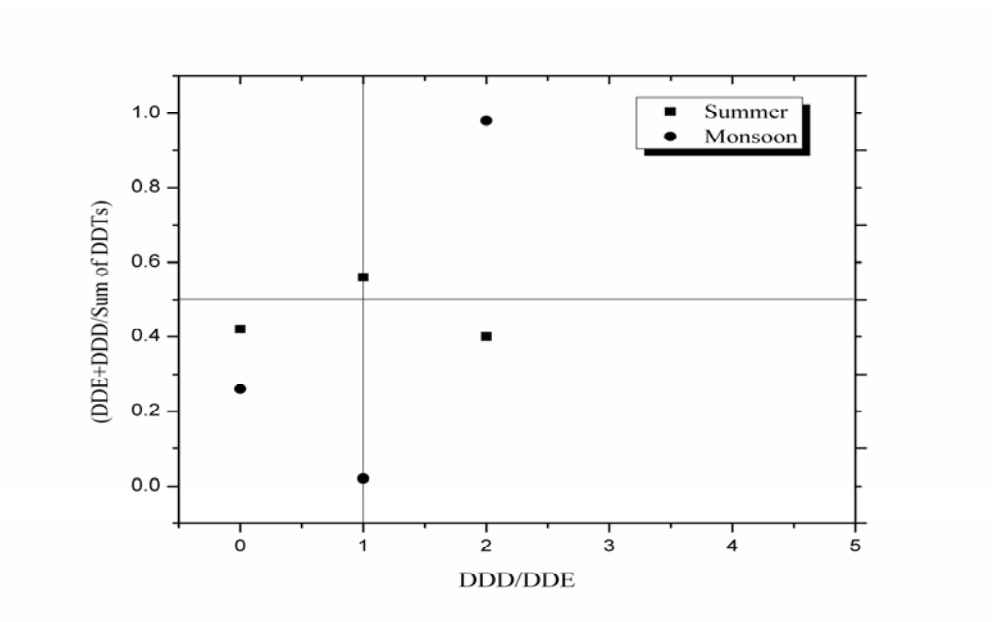

Figure 4.5. DDTs metabolite ratio in sediment samples

In order to assess any adverse effect of persistent organic pesticides (POPs) contamination in the freshwater quality, criteria of maximum residue limit (MRL) by

Food and Agricultural Organisation (FAO) and WHO recommended certain limits for aldrin (0.1-180 µg l^{-1}), chlordane (1.5-6.0 µg l^{-1}), dieldrin (0.1-1.8 µg l^{-1}) and DDT (1.0 µg l^{-1}). Also the levels of endrin, heptachlor, HCB, mirex are even in low concentration could cause toxic to fish, aquatic invertebrates and phytoplankton (IPEP 2006). In the present study the concentration levels of aldrin, chlordane, dieldrin, DDT were well below FAO/WHO values for all the sites and endrin, heptachlor, and mirex are recorded as trace amount in most of the sites and this may contribute the freshwater ecosystem of Tamiraparani river to toxic sources and sink.