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Aldrin Contamination in Ennore Estuary and Coastal Waters of Chennai, East Coast of India

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The Ennore estuary and nearby coastal area is a typical environment in Chennai, East coast of India which was studied for presence of aldrin concentration in the coastal water. Samples were collected semi-diurnally from Ennore estuary and Chennai coast for 48 h. The concentration was determined by gas chromatography with electron capture detector. The aldrin concentration in Ennore estuary varied from 4.82 ± 0.13 to 21.88 ± 1.18 ng/L and 9.49 ± 0.28 to 52.75 ± 2.04 ng/L during the high and low tides respectively. In the nearby coastal waters, the concentration varied from 2.24 ± 0.24 to 4.51 ± 0.19 ng/L and 3.14 ± 0.13 to 5.32 ± 0.30 ng/L during the high and low tides respectively. There is a significant ($P < 0.000$) spatial variation of aldrin concentration in the Ennore estuary during low tide, while during high tide, the spatial variation in the concentration is altered and more or less uniform among the first 4 sites (WQE-1 to WQE-4). This indicated that the tide influences aldrin concentration as well as change in the spatial spreading. However, in Chennai coast, the spatial variation in aldrin concentration is very minimal at low tide whereas in high tide, concentration became uniform in all the sites except WQC-6. In both Ennore estuary and Chennai coast, between high and low tides showed significant ($P < 0.05$) difference in aldrin concentrations except WQC-2 in Chennai coast.

Keywords: Organochlorine, Aldrin, Chennai coast and Ennore estuary.

INTRODUCTION

Pesticides are organic (some synthesized and some extracted from plants such as nicotine) and inorganic chemicals (*e.g.* synthesized from inorganic salts of arsenic compounds), used to combat agricultural pests. These compounds are characterized by their toxicity, relatively high volatility, as well as by their capacity to interfere with cell biochemistry when accumulated in organic tissues. In the human body, pesticides may cause acute anemia, bone structure disorders, teratogenic and embryologist diseases, *etc*.[1,2].

In the Indian context, there are currently 179 pesticides registered for use in India; 30 others have been banned, while seven are restricted, including DDT, aldrin, chlordane and heptachlor were banned in September, 1996; while DDT is in restricted use since July, 1989. Dieldrin came in restricted use since May, 1990 and was banned completely in July, 2003. Endrin was banned in May, 1990 while HCH in April, 1997. Use of endosulfan and methoxychlor has been permitted while HCB was never registered as a pesticide[3].

In this diversity of pesticides, organochlorine pesticides (OCPs) are ubiquitous environmental organic micro-pollutants[4,5]. Although their production, usage and disposal to the environment have been regulated or prohibited in most western countries since the 1970s, organochlorine pesticides are still very important pesticides used in many developing countries, especially in south Asia, middle Asia, South America and Africa. In recent decades, many investigation reports have been documented that these contaminants might be transported widely through atmosphere and eventually pollute all over the world. Such a worldwide spread and transition is expected to affect the current status of global contamination and pose a threat to human beings and wildlife, particularly marine mammals[6-10]. Some organochlorine pesticides are highly resistant to degradation by biological, photochemical or chemical means. They are also liable to bioaccumulation and are prone to long range transport[11]. These are also typically characterized as having a lower water solubility and high lipid solubility[12]. However, organochlorine pesticides are ubiquitous environmental pollutants in the global ecosystem due to their lipophilicity and persistency, they accumulate along the food chain[13,14]. Aldrin was one of the major pesticides in India till 1996. Though the use of aldrin was banned after 1996 their effects on the soil and aquatic animals are still persistent due to their less solubility. Aldrin contamination in the water body has the potential to damage the aquatic species to a greater extent and it also has the ability to extent its hands in damaging the life of birds and humans through contact with water bodies. Therefore it is very important to study about the contamination of the aldrin in the environment.

In recent years there was no proper studies on the Ennore estuary and Chennai coasts about the aldrin contamination. Therefore the study was made to understand the contamination of aldrin in the surface water of the Ennore estuary and coastal waters and it was presented in this paper. The water samples were extracted and analyzed by capillary gas chromatography coupled with electron capture detector (GC-ECD) for the confirmation of organochlorine pesticides.

Study area

Chennai coast: Chennai coastal zone covers a stretch of approximately 30 km length from Adyar river in the south to Ennore estuary in the north. The area is bound by the latitude 13°0'N and 13°15'N and longitude 80°15'E and 80°21'E. Nearly 98.2 % of the land area is used for industrial, residential and commercial purposes. The majority of wastewater is disposed of in Adyar river, Cuvum river and Buckingham canal outlets. Apart from these major disposal sites, a number of domestic and industrial wastewater sites are prevalent along the coastal zone of the north Chennai. A number of refineries, thermal power plants, chemical rubber and fertilizer industries are located along the Chennai coastal zone. The wastewaters from all these industries and residential zones are finally directed to the coastal waters of Chennai. Therefore, Ennore, Chennai Harbour, Cuvum and Adyar estuaries have been identified as most important areas[15] on the basis of (1) location of industrial effluents discharge along the coast, (2) location of municipal sewage dumping areas and (3) location of dredging activated areas, for monitoring the levels of pollutants.

Ennore estuary: Ennore coast receives untreated sewage from Royapuram sewage outfall, treated and untreated industrial effluents from Manali industrial belt, which houses many chemical industries like fertilizer, oil refineries, sugar, chemicals *etc*. Apart from this, it receives fly ash and thermal discharges from the nearby Ennore Thermal Power Station. In addition to that, fishing and navigational activities take place in the area. The dredging activities in Ennore area result in changes in the landscape, sediment transport and dust pollution to the coast by quarrying process[16].

EXPERIMENTAL

Sample collection: In this study, the intention was to determine the persistence of the compounds under local conditions. Samples were collected semi-diurnally during the period of 48 h. The total 13 samples were collected from the two high and low tides of Ennore estuary and Chennai coastal area, comprises 7 sites in estuary and 6 sites in coast (Fig. 1).

Water samples were collected from the surface using clean Amber glass container (2.5 L capacity). The amber glass bottle was washed thoroughly using distilled water and *n*-hexane before sampling. Samples were collected from both the high and low tides and stored[17] in the freezer at +4 °C, which was extracted within 24 h.

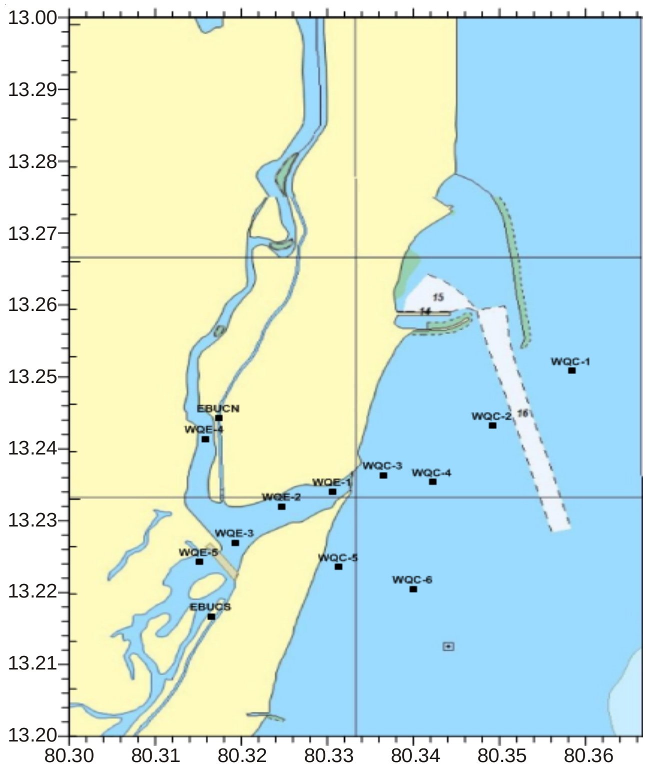

Fig. 1. Map showing the sampling location along the Chennai coast and Ennore estuary of East coast of India

The working standards with the concentration of 10, 30, 50 and 80 ng/L were prepared using individual pesticide stock standard of aldrin (5 mg/mL) (Accu standard, USA). All stock and working standards solution were stored[18] in a light protected freezer -20 °C.

All the solvents and reagents employed in this study was an HPLC grade of *n*-hexane and dichloromethane (Merck, Germany) and the deionized water synthesized using ultra pure water system (TKA, Germany).

Sample preparation: The collected water samples were extracted by liquid-liquid extraction (LLE) method[19]. The solvent was evaporated using a rotary evaporator (BUCHI R-215, Switzerland) until it condense to a 1 mL residual solution. The residual solution was dissolved in 5 mL *n*-hexane solution and analyzed[20,21].

For qualitative and quantitative interpretation of results, a concentration of 100 ng/L aldrin was used as an internal standard to know the condition of instrument and the accuracy of the results[20].

Sample analysis: Gas chromatograph (Shimadzu GC-2014 series) equipped with electron capture detector (^{63}Ni-ECD) was used for analysis. Gas chromatograph separations were performed on a capillary column Rtx-5 with 0.25 µm film thickness; 30 m length; 0.25 mm inner diameter (Restek, USA). The gas chromatograph operating condition was; injection temperature 250 °C, detector temperature 320 °C and carrier gas (Nitrogen) with the flow rate of 34 mL/min. The gas chromatograph temperature program conditions for the analysis on organochlorine pesticides were initial oven temperature 150 °C heated to 300 °C by a temperature ramp of 10 °C min^{-1} which was hold for 2 min. in 300 °C. The hexane extracted water samples was analyzed twice by GC-ECD.

Calibration curves were prepared using the working standard which was prepared from the stock solution. The peak areas of the corresponding analyte were plotted against the calibration and concentration and the regression coefficient was $R^2 = 0.9964$. The retention times obtained for the aldrin is 6.64 min.

Before sample analysis, relevant standards were analyzed to check column performance, peak height, resolution and the limits of detection. With each set of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention time[22].

The qualitative identification of the aldrin was performed by comparing the relative retention times (RRT), with respect to the internal standard, for each peak in the chromatogram of the real sample to those (RRTs) in the chromatogram of the aldrin.

The quantitative determination was carried out by using the relative peak areas and relative concentrations. Then, the average concentration calculated for the four runs of each sample was given as the final result.

To evaluate the whole analytical procedure, the recovery percentage of aldrin was determined by spiking known concentrations of aldrin with selected samples. The recoveries of aldrin were ranged from 72.9-96.3 % in both estuary and coastal water samples.

RESULTS AND DISCUSSION

The mean concentration of aldrin in the water samples of the Ennore estuary during the high tide varied from 4.82 to 21.88 ng/L and during the low tide, the concentration varied from 9.49 to 52.75 ng/L (Table-1, Fig. 2). The high concentration of aldrin was found at the site EBUCS during both high and low tides. The high concentration at this site might be associated with the input of pollutants from the urban runoff, agricultural runoff and industrial discharge.

The mean concentration of aldrin in the water samples of the nearby coastal water during the high tide varied from 2.24 to 4.51 ng/L and during the low tide varied from 3.14 to 5.32 ng/L (Table-2, Fig. 2). The high concentration was detected at the site WQC-3 in both the high and low tide water samples. The WQC-3 station was located at the mouth of the estuary. The pollution load from the estuary entering the coastal waters due to the influence of tide could be attributable for the high concentration of aldrin in this site.

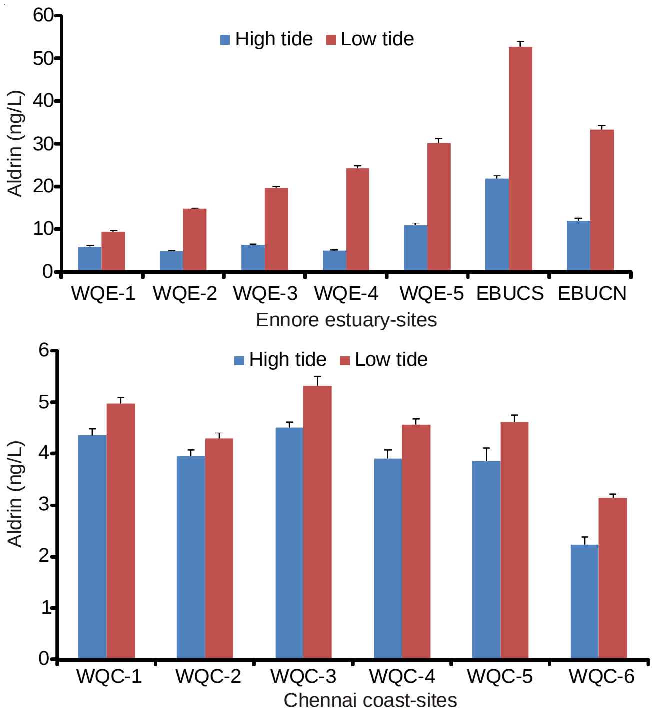

Fig. 2. Aldrin concentration in Ennore estuary and Chennai coastal waters, East coast of India

A significant spatial variation ($P < 0.000$) in the aldrin concentration in Ennore estuary was observed during the periods of low and high tides (Table-1). However, during high tide, the concentration of aldrin was found to be uniform among the first four sites (WQE-1 to WQE-4). Greater differences in aldrin concentration during low tides could be because of the geographic position of the sites that are located more towards the locations in which industrial effluents mixes with the sea water. In Chennai coast, the aldrin concentration is minimal spatial variations at low tide, while during high tides, except one site (WQC-6), all the other sites had uniform concentration of aldrin (Table-2). This could be attributed to water currents in both low tide as well as high tides. It is important to note that in both Ennore estuary and Chennai coast, both the high tide and low tide periods showed significant ($P < 0.05$-0.000) differences between them in aldrin concentration except for a site (WQC-2) in Chennai coast.

The results are compared with previously reported organochlorine pesticide concentration in other estuaries and marine systems around the world. The concentration of aldrin in

TABLE-1
CONCENTRATION OF ALDRIN DURING HIGH AND LOW TIDE PERIOD IN THE SURFACE WATER OF ENNORE ESTUARY

Site	Locations	Aldrin (ng/L, mean)		F-value	Level of significance
		High tide	Low tide		
WQE-1	13°14'02.5711"N, 80°19'50.2803"E	5.96c#	9.49f$	262.29	0.000
WQE-2	13°13'55.1770"N, 80°19'29.1770"E	4.82c#	14.78e$	2854.7	0.000
WQE-3	13°13'37.0028"N, 80°19'09.4659"E	6.28c#	19.64d$	2393.6	0.000
WQE-4	13°14'28.9689"N, 80°18'56.7361"E	4.97c#	24.29c$	1117.8	0.000
WQE-5	13°13'27.2347"N, 80°18'54.4617"E	10.91b#	30.16b$	301.48	0.000
EBUCS	13°13'00.0600"N, 80°18'59.5200"E	21.88a#	52.75a$	514.8	0.000
EBUCN	13°14'39.5022"N, 80°19'02.6378"E	11.94b#	33.35b$	366.7	0.000
	F -value	222.77	394.08		
	Level of significance	0.000	0.000		

Different letter(s) on the same column indicates significant differences; Different symbol on the same row indicates significant differences

TABLE-2
CONCENTRATION OF ALDRIN DURING HIGH AND LOW TIDE PERIOD IN THE SURFACE WATER OF CHENNAI COAST

Site	Locations	Aldrin (ng/L, mean)		F-value	Level of significance
		High tide	Low tide		
WQC-1	13°15'02.9400"N, 80°21'30.3000"E	4.36a#	4.98ba$	13.59	0.01
WQC-2	13°14'35.5800"N, 80°20'57.0600"E	3.96a#	4.31c#	5.61	NS
WQC-3	13°14'10.7400"N, 80°20'11.4000"E	4.51a#	5.32a$	15.44	0.01
WQC-4	13°14'07.2600"N, 80°20'31.9800"E	3.92a#	4.58b$	11.43	0.01
WQC-5	13°13'24.7200"N, 80°19'52.8000" E	3.86a#	4.62bc$	6.88	0.05
WQC-6	13°13'17.1600"N, 80°20'09.9600"E	2.24b#	3.14d$	32.49	0.001
	F-value	25.53	39.08		
	Level of significance	0.000	0.000		

Different letter(s) on the same column indicates significant differences; Different symbol on the same row indicates significant differences

Ennore estuary and nearby coastal waters were lower than the Haibo river estuary (n.d – 70.43 ng/L) in China and Nestos river estuary (n.d – 68 ng/L) in Greece, but higher than those reported in the Chukchi sea (1.5-1.8 ng/L)[7] and Daliao river estuary (3.4-25.8 ng/L) in China[23]. The concentration of aldrin in the study site was also within the prescribed limits set by United States of Environmental Protection Agency (USEPA) (1.3 μg/L for marine water)[24].

Conclusion

The present studies revealed that Ennore estuary and nearby coastal areas in East Coast of India were contaminated by aldrin. Agricultural runoffs, industrial waste water and sewage discharge are reasons for the persistent level of aldrin. The study results show that although concentration of aldrin in the aqueous phase were lower than the previous study conducted globally and the standards set by USEPA, they are slightly higher in some sites of the estuary. The tidal cycles also play an important role affecting the aldrin concentration in the aqueous samples. Though the use of aldrin was banned in the field of agriculture, still traceable amounts are used in the form of pest killers in residential and commercial areas. This usage is one of the reasons for the presence of aldrin in the aqueous phase of the environment. Further studies are required to monitor the aldrin concentration in the sediment samples and biological samples to evaluate their long term harmful effects to the environment and to identify its persistent nature in the environment.

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