



Baseline

Spatial budgetary evaluation of organochlorine contaminants in the sediments of Cochin Estuary, India



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ABSTRACT

This paper presents the first detailed investigation on the residual levels of organochlorine insecticide (OCI) concentrations in the Cochin estuarine sediment. It aims in elucidate their distribution and ecological impact on the aquatic system. Concentrations of persistent organochlorine compound (OC) were determined for 17 surface sediment samples which were collected from specific sites of Cochin Estuarine System (CES) over a period of November 2009 and November 2011. The contaminant levels in the CES were compared with other worldwide ecosystems. The sites bearing high concentration of organochlorine compounds are well associated with the complexities and low energy environment. Evaluation of ecotoxicological factors suggests that adverse biological effects are expected in certain areas of CES.

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Pesticides are synthetic organic chemicals used to control unwanted or harmful pests, such as insects and mites that feed on crops. The environmental pollution by organochlorine insecticides are one of the most important Persistent Organic Pollutants (POPs) and have been of great concern around the world owing to their chronic toxicity, persistence and bioaccumulation. They have been extensively studied over the last 30 years, because of their resistance to degradation which has resulted in its being an almost universal contaminant of the environment (Jones and Voogt, 1999; Laabs et al., 2002; Monirith et al., 2003; Mudiam et al., 2012; Akhil and Sujatha, 2012). Due to the careless disposal practices, they have become a major pollutant in many parts of the world. In aquatic environments, OCs get removed from the water column and adsorb onto the particulate matter, and finally deposit on to sediments. The persistent nature of these compounds in soil and water, can adversely affect the health of pedospheric (Kammenga et al., 2000) and aquatic biocoenoses and the quality of drinking water (Kumar et al., 1995; Akhil and Sujatha, 2012). A greater tendency shown by OCIs for bioaccumulation and biomagnification in the food chains is due to their resistance to chemical and biological decay (Badawy and Wahaab, 1997; Yamashita et al., 2000; Abbassy et al., 2003). Although the applications of OCIs have been banned in many developed countries, some developing countries are still producing and using these persistent pesticides because of their low cost and versatility in controlling various insects (Tanabe et al., 1994; Monirith et al., 2003).

The main objective of the study is to survey the contaminant levels, distributions and other sources of these OCIs in surface

sediments from CES and to assess their environmental impact in the ecosystem. Most of the earlier research contributions were based on one-time or seasonal sampling during a year, from the areas known for environmental pollution (Barakat, 2003; Khaled et al., 2004; Said et al., 2008). 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. A few reports are available on the residue analysis of conservative pesticides in CES (Sujatha and Chacko, 1991; Sujatha et al., 1993, 1994, 1999) but no studies concerning these persistent contaminants in sediment were reported. A broad spectrum of pesticides is used in India for agriculture as well as vector control programs and hence the impact of residues of these OCs on Indian coastal environments is of considerable interest.

Cochin Estuary, one of the largest tropical estuaries of India, is facing gross pollution problems due to the release of untreated effluents from industries and domestic sectors. The major polluting industries in the region include fertilizer plant, oil refinery, rare earth processing plant, minerals and rutilites plant, zinc smelter plant, insecticide manufacturing unit and organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the Cochin Estuary (Gopalan et al., 1983). Further, the construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline intrusion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation rate in the estuary (Menon et al., 2000). The development activities in and around Cochin Backwater 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 continuously discharged into the backwaters.

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Study area is divided into three zones viz South, Middle, and North (Fig. 1). The south zone is situated in the fresh water region and it originates from southern bough of Moovattupuzha. Major source of pollution is from agriculture runoff and it is less affected by industrial effluents (Station No 1–6). The middle zone is well regulated by a bund (namely Thannirmukham), which was constructed in order to prevent the salt water intrusion into the paddy fields. The bund remains open during monsoon season. This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion there by making cradle grounds for diverse types of flora and fauna. With the advent of ICTT project, this area has become a backbone for the economy of State of Kerala. Due to enhanced containerization, resulting in improved trade and economic growth, widespread activities like dredging, piling, along with anthropogenic inputs are increasing frequently (Station No 7–11). Finally north zone originates from the industrial locale of Periyar – the life line of Kerala. Large scale industries on the river bank discharge effluents directly into these waterways resulting in the accumulation of varying amounts of nutrients in the Periyar River (Station No 12–17).

Surface sediments (top 0–5 cm) were collected from seventeen locations of CES over a period of November 2009 and November 2011. This was performed using a stainless steel grab sampler used repeatedly (three to five times) at each station, followed by thorough mixing of collected sediment on an aluminum tray in order to obtain a more representative sediment sample. All samples were then transferred into well labeled hexane-rinsed glass jars and kept it in the ice chest boxes on board and during transportation. The samples were then stored at -20°C until the analysis.

About 5 gm of the sediment sample was accurately weighed and then extracted twice with 50 mL portions of 1:1 hexane-acetone

mixture (HPLC grade, Glaxo, Mumbai, India). The combined extract was subjected to a cleanup procedure involving elution through a Florisil column (60 cm \times 22 mm i.d) with 50 mL 1:1 hexane-acetone mixture. The extract was concentrated to about 5–6 mL by means of a rotary evaporator at $50\text{--}60^{\circ}\text{C}$ for further analysis. Separation and analysis of the OCIs were performed on a gas chromatograph (GC) (model 7890A, Agilent, Waldbronn, Germany) with a Ni-63 ECD and equipped with capillary column (HP-35, 30 m \times 0.320 mm \times 0.5 mm) using nitrogen as carrier gas (1.5 mL min^{-1}). The GC was calibrated with a standard solution of a pesticide mixture (Supelco, USA) prepared in HPLC grade n-hexane. Solvent blanks were used to confirm the absence of any pesticide residues. Analytical reproducibility was checked by replicate measurements. Identification and quantification of OCIs were accomplished by using reference solutions supplied by EPA (USA) and Supelco (USA). The following GC conditions were maintained: injection port temperature 250°C , detector temperature 350°C , oven temperature program: 110°C (5 min) at $5^{\circ}\text{C min}^{-1}$ to 190°C (2 min) at $15^{\circ}\text{C min}^{-1}$ to 280°C (10 min). $1\ \mu\text{L}$ of aliquot samples were injected onto the column. All data were subjected to strict quality control procedures, including the analysis of procedural blanks and spiked samples with each set of samples analyzed. None of the target compounds were detected in the procedural blanks for sediment samples. Spiked samples (10 ng of pesticide mix standard) were determined with good precision and high recoveries. Limit of detection (LOD) and relative standard deviation (RSD) of the analytical method for OCIs is as follows. The detection limit was lowest for aldrin (0.04 ng/g) and highest for endrin and 4,4'-DDT (0.19 ng/g), while the detection limit of other analytes lies within the range. The average recoveries ($n = 3$) for OCIs revealed an efficiency of $87\text{--}103\%$. The relative standard deviations (RSD) were below 5.0% and fall within the requirement criteria of US-EPA (Recovery: $70\text{--}130\%$, RSD is $<30\%$). The following organochlorine

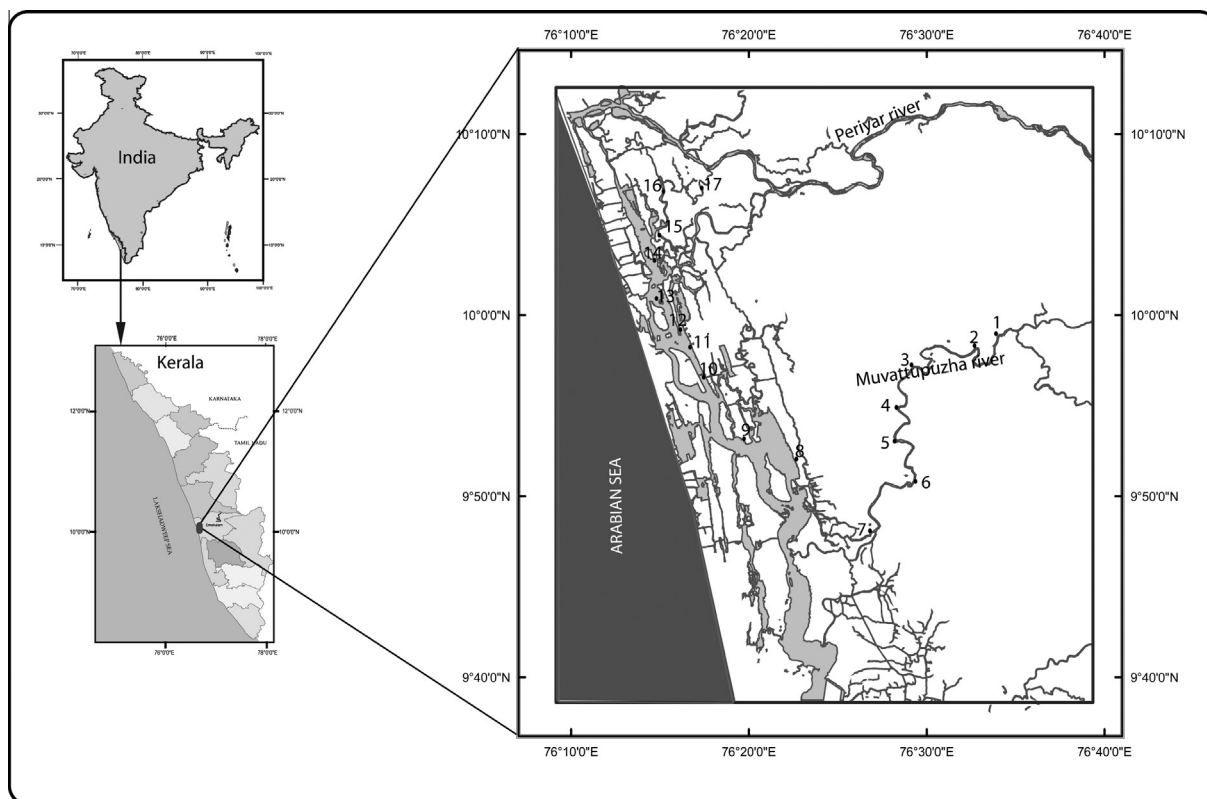


Fig. 1. Map of the study area and sampling sites.

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