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# Spatial Distribution of Polycyclic Aromatic Hydrocarbons in Ennore Estuary and Coastal Waters, Chennai, India

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Ennore estuary is one of the major polluted area in Chennai, India due to high pollution load from domestic waste, effluents discharge from petrochemical industries and refineries wastages. Polycyclic aromatic hydrocarbon (PAH) influence due to the petrochemical industries effluent and automobile vehicle transport, movement of ship and fisherman boats. The two rivers named Korattalaiar and Kosasthalaiyar are running along the farming and urban areas carrying all the pollutants, finally entering into the Ennore estuary. Therefore a short term study was conducted to estimate the prevailing concentrations of chrysene (polycyclic aromatic hydrocarbon) contaminants and to know the status of the pollutants. Sea water samples were collected semi-diurnally from Ennore estuary (7 sites) and Chennai Coast (6 sites) for 48 h. The collected samples were extracted by liquid-liquid extraction technique and analyzed by gas chromatography with flame ionization detector. The maximum and minimum mean concentration of chrysene in Ennore estuary during high and low tide was 8.13 and 1.43 mg $L^{-1}$ and 10.20 and 1.45 mg $L^{-1}$ respectively. The maximum and minimum mean concentration of chrysene in Chennai coastal waters during high tide and low tide was 1.49 and 0.77 mg $L^{-1}$ and 2.23 and 1.11 mg $L^{-1}$ respectively. A relatively high concentration of 10.20 ± 0.10 mg $L^{-1}$ chrysene was observed in the Buckingham Canal south. This high concentration of chrysene reported in this site due to the discharge of industrial effluents and domestic sewage. The results are showing significant variation spatial as well as temporally.

**Keywords: Hydrocarbons, Chrysene, Chennai coast, Ennore estuary.**

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), a group of stable chemical compounds, including two or more rings, are ubiquitous organic contaminants (xenobiotics) in the environment and belong to the group of persistent organic pollutant (POPs) and sixteen have been identified as priority pollutants by the U.S. Environmental Protection Agency (EPA) and the European Union (EU) [1]. They have relatively low solubility in water, but are highly lipophilic. Polycyclic aromatic hydrocarbons bind with ash and move long distances through air, especially those that are lighter, before those that are soluble get dissolved in rainwater and/or into rivers and groundwater sources [2,3]. When dissolved in water or adsorbed to particulate matter, polycyclic aromatic hydrocarbons can undergo photo decomposition when exposed to ultraviolet light from solar radiation [4].

Polycyclic aromatic hydrocarbons (PAHs) have become widespread environmental contaminants due to their occurrence in petroleum, coal, soot, air pollutants and cutting oils [5]. Although around a hundred polycyclic aromatic hydrocarbons are found in the environment in that only 16 compounds are possessing 2 to 6 aromatic rings, these are considered as priority compounds due to their toxicity, mutagenicity or carcinogenicity [6].

Polycyclic aromatic hydrocarbons are classified into two groups based on their physical, biological properties and its molecular weight. The polycyclic aromatic hydrocarbons depend upon molecular weight divided into two groups are high molecular weight (HMW) and low molecular weight (LMW) polycyclic aromatic hydrocarbons. The high molecular weight polycyclic aromatic hydrocarbons consist of 4-6 aromatic rings and are less readily bio-degraded by indigenous microorganisms, hence can persist in the aqueous environment by bio-accumulating in aquatic organisms like fish and mussels and are more carcinogenic [7]. The low molecular weight polycyclic aromatic hydrocarbons consists of 2-3 aromatic rings and although they are less carcinogenic also pose toxic effect to many aquatic organisms [8]. The polycyclic aromatic hydrocarbons composition of water and sediments can give some information about their sources and how they were derived. The largest concentration of low molecular weight

polycyclic aromatic hydrocarbons (*e.g.* acenaphthene, fluorene) most often occurs in sample matrices contaminated with naturally occurring polycyclic aromatic hydrocarbons (pathogenic and biogenic origins) while the polycyclic aromatic hydrocarbons from combustion processes (pyrolytic origin) often contain elevated concentrations of high molecular weight (*e.g.* phenanthrene, fluoranthene, pyrene) and fewer low molecular weight polycyclic aromatic hydrocarbons [9].

Chrysene is a symmetrical polycyclic aromatic hydrocarbon (PAH) consisting of four condensed benzene rings. It is formed through incomplete combustion of organic material and is a ubiquitous environmental contaminant [10]. The presence of chrysene in the environment is mainly due to human activities like intensive of fisheries, shipping and boat activities. A relatively low solubility in seawater will promote the adsorption of chrysene to particulate material, followed by sedimentation [11]. Polycyclic aromatic hydrocarbons and their halogenated forms are also chemically stable and due to their liphophilic nature they can easily penetrate biological membranes and accumulate in organisms. Many studies have shown that polycyclic aromatic hydrocarbons are toxic to fish and other aquatic organism. The accumulation of such pollutants in the fish can be transferred to the human food chain [12]. Polycyclic aromatic hydrocarbons potentially contribute to many diseases including cancer, damage to the reproductive system, disrupted endocrine and immune systems and neurobehavioral effect [13].

Chennai is one of the major metropolitan cities and it is situated in southeastern coast of Indian peninsular. Chennai is a coastal city, still having remnants of high sea levels in the geological past in the form of back waters, filled lagoons *etc*. Groundwater forms an important component of the water supply to the city, as the piped water supply is inadequate to meet the requirements [14]. Ennore coast consists of alluvial tracts and beach dunes, tidal flats and Estuary in the eastern part. Ignore comprises of lagoons, with salt marshes and backwaters, which are submerged under water during high tide and form an arm of the sea opening in to the Bay of Bengal [15].

Ennore estuary receives treated and untreated industrial effluents from Manali industrial belt, which houses many industries like fertilizer, oil refineries, chemicals, *etc*. Apart from this, it receives fly ash and thermal discharges from the nearby Ennore Thermal Power Station and North Chennai Thermal Power Station. Ennore estuary is connected with the Buckingham canal, which is polluted by urban sewage and industrial effluents and wastes generated by innumerable slum dwellers who live along its banks [16].

The present study was made to understand the contamination of chrysene in the surface water of the Ennore estuary and near coastal waters. The sea water samples were extracted and analyzed by capillary gas chromatography coupled with Flame ionization detector (GC-FID) for the confirmation of chrysene (polycyclic aromatic hydrocarbon).

## EXPERIMENTAL

**Sample collections:** Water samples were collected from total 13 selected sites (Fig. 1) on the Ennore estuary (7 sites) and near coast (6 sites) during two high and low tides. Water samples were collected from the surface and stored in clean

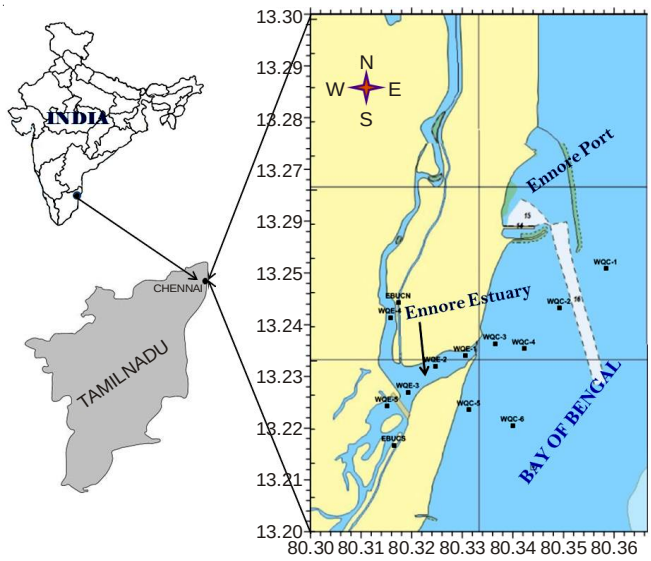


Fig. 1. Map showing the sampling location along the Ennore estuary and coastal water, Chennai, India

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 semi-diurnally for 48 h and stored in the freezer at +4 °C, which was extracted within 24 h [17]. The sampling apparatus and glassware were precleaned with *n*-hexane.

The calibration standards with the concentration of 1, 3, 6, 9 and 12 mg $L^{-1}$ were prepared using individual polycyclic aromatic hydrocarbon stock standard of chrysene (1 g) (ACROS Organics, USA). All stock and working standards solution were stored in a light protected freezer 4 °C [18].

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).

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 and analyzed [12].

For qualitative and quantitative interpretation of results, a concentration of 100 μg $L^{-1}$ chrysene 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 flame ionization detector (FID) 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 GC operating conditions; injection temperature 280 °C, detector temperature 330 °C and carrier gas (nitrogen) with the flow rate of 25.6 mL/min. The GC temperature program conditions for the analysis on polycyclic aromatic hydrocarbons were initial oven temperature 50 °C heated to 300 °C by a temperature ramp of 25 °C $min^{-1}$ up to 200 °C and 15 °C $min^{-1}$ which was hold for 10 min in 300 °C. The *n*-hexane extracted water samples were analyzed twice by GC-FID.

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 $R^2$ = 0.9972 [6]. The retention times obtained for the chrysene is 15.12 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 [21].

The quantitative determination was carried out by using the relative peak areas (RPA) and relative concentrations (RC). 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 chrysene was determined by spiking the known concentrations of chrysene with selected samples. The recoveries of chrysene were ranged from 83.00-97.90 % in both estuary and coastal water samples.

## RESULTS AND DISCUSSION

The mean concentration of chrysene in the water samples of the Ennore estuary during the high tide varied from 1.43 to 8.13 mg $L^{-1}$ and during the low tide the concentration varied from 1.45 to 10.20 mg $L^{-1}$ (Table-1, Fig. 2a). The high concentration of chrysene was found at the site Buckingham canal south (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, petrochemical and industrial discharge.

The mean concentration of chrysene in the water samples of the nearby coastal water during the high tide varied from 0.77 to 1.49 mg $L^{-1}$ and during the low tide varied from 1.11 to 2.23 mg $L^{-1}$ (Table-2. Fig. 2b). The high concentration was detected at the site water quality coastal (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 chrysene in this site.

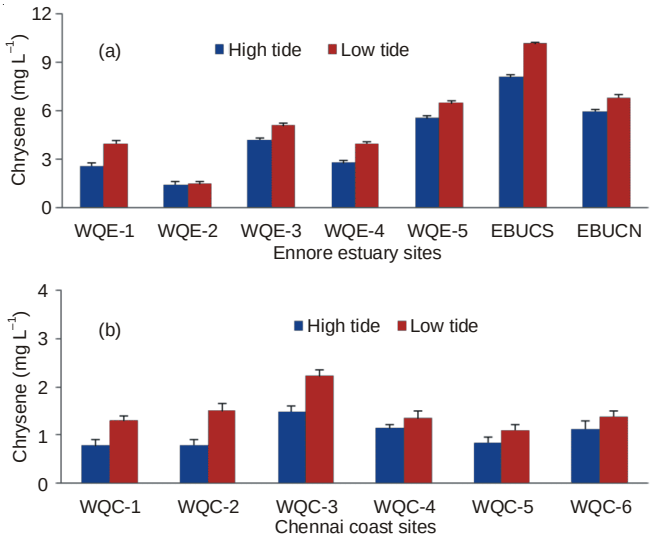


Fig. 2. Spatial and tidal variation of polycyclic aromatic hydrocarbon in terms of chrysene concentration (mean + SD) in (a) Ennore estuary and (b) Chennai coastal water, East Coast of India

A significant spatial variation ($P < 0.000$) in the chrysene concentration in Ennore estuary was observed during the periods of low and high tides (Table-1) except at one site water quality estuary (WQE-2). However, during high tide, the

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

| Site | Locations | Chrysene (mg $L^{-1}$) | | F-value | Level of significance |
|---|---|---|---|---|---|
| | | High tide (n = 4) | Low tide (n = 4) | | |
| WQE-1 | 13°14'02.5711"N, 80°19'50.2803"E | 2.57 | 3.99 | 143.11 | 0.000 |
| WQE-2 | 13°13'55.1770"N, 80°19'29.1770"E | 1.43 | 1.45 | 0.05 | 0.830 |
| WQE-3 | 13°13'37.0028"N, 80°19'09.4659"E | 4.19 | 5.10 | 158.91 | 0.000 |
| WQE-4 | 13°14'28.9689"N, 80°18'56.7361"E | 2.78 | 3.98 | 167.04 | 0.000 |
| WQE-5 | 13°13'27.2347"N, 80°18'54.4617"E | 5.56 | 6.50 | 131.48 | 0.000 |
| EBUCS | 13°13'00.0600"N, 80°18'59.5200"E | 8.13 | 10.20 | 842.62 | 0.000 |
| EBUCN | 13°14'39.5022"N, 80°19'02.6378"E | 5.98 | 6.82 | 77.226 | 0.000 |
| | F-value | 1212.21 | 1959.55 | – | – |
| | Level of significance | 0.000 | 0.000 | – | – |

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

| Site | Locations | Chrysene (mg $L^{-1}$) | | F-value | Level of significance |
|---|---|---|---|---|---|
| | | High tide (n = 4) | Low tide (n = 4) | | |
| WQC-1 | 13°15'02.9400"N, 80°21'30.3000"E | 0.77 | 1.29 | 40.63 | 0.000 |
| WQC-2 | 13°14'35.5800"N, 80°20'57.0600"E | 0.80 | 1.50 | 64.86 | 0.000 |
| WQC-3 | 13°14'10.7400"N, 80°20'11.4000"E | 1.49 | 2.23 | 90.28 | 0.000 |
| WQC-4 | 13°14'07.2600"N, 80°20'31.9800"E | 1.14 | 1.35 | 6.69 | 0.041 |
| WQC-5 | 13°13'24.7200"N, 80°19'52.8000" E | 0.85 | 1.11 | 14.76 | 0.008 |
| WQC-6 | 13°13'17.1600"N, 80°20'09.9600"E | 1.13 | 1.39 | 7.57 | 0.033 |
| | F-value | 23.99 | 43.71 | – | – |
| | Level of significance | 0.000 | 0.000 | – | – |

concentration of chrysene was found to be uniform among the sites except at one site (WQE-2) due to hot water discharge from power plant unit. Greater differences in chrysene 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 mixed with the sea water. In Chennai coast, the chrysene concentration is shown minimal spatial variations at all sites had uniform concentration (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 chrysene concentration except in Ennore estuary (WQE-2).

The results are compared with previously reported polycyclic aromatic hydrocarbons concentration in other estuaries and marine systems around the world. The concentration of chrysene in Ennore estuary and nearby coastal waters are showed higher than the Southern Caspian sea coastal region (0.003-0.0518 mg $L^{-1}$) [12], Yesilirmak Estuary in Turkey (0.0013-0.0061 mg $L^{-1}$) [22], Eastern Coast in Thailand (0.0001-0.0125 mg $L^{-1}$) [23] and Lagos Estuary in Nigeria (0.0207-0.192 mg $L^{-1}$) [13].

## Conclusion

The study reviewed clearly the chronic polycyclic aromatic hydrocarbons contamination is evident in the Ennore estuary. In the Ennore estuary contamination of polycyclic aromatic hydrocarbons originated from oil spill and leakage from boats, vehicular exhaust emission, discharge from municipal and industrial wastewater and runoff. It indicates that surface water received polycyclic aromatic hydrocarbons from different anthropogenic sources are known to responsible for the presence of polycyclic aromatic hydrocarbons in surface water, their occurrence cannot always be related to a particular source. It is also concluded that polycyclic aromatic hydrocarbons can easily spread and be transported across the globe *via* water bodies like Ennore estuary and its near coastal waters.

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