Accumulation of Organic Pollutants in Aquatic Organisms from Ennore Estuary, Chennai, India

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(Received: 26 December 2011;

Accepted: 5 November 2012)

AJC-12366

The coastal waters of the maritime states are under the constant threat of pollution from a number of sources. Many economically important marine fishes and invertebrates are depending upon these regions for habitat and food. The present study focused on assessing the levels of organic pollutants in aquatic organisms, viz., fishes, prawn, crab and clams in the polluted stretch of Ennore estuary, southeast coast of India and to find out the relation between the organic pollutants and lipid profiles. After a field survey, six edible species were selected and caught from the polluted stretch of the estuary. Following USEPA 8280 procedure, the samples were processed and analyzed for organic pollutants by HRGC/LRMS. Presence of pollutants such as polycyclic aromatic hydrocarbons, phthalates and polymers shows the degraded environmental quality in the Ennore estuary. Mud crab is found to contain maximum pollutant accumulation followed by blood clams. The organic contamination in the selected aquatic animals indicates the possibility of high health risks for their consumers.

Key Words: Biota, Ennore, Pollution, Persistent organic pollutants, Sediment.

INTRODUCTION

Persistent organic pollutants (POPs) are toxic chemicals that adversely affect human health and the environment around the world. Persistent organic pollutants are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. Persistent organic pollutants can be deposited in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff and other means. Because persistent organic pollutants have low water solubility, they bond strongly to particulate matter in aquatic sediments. As a result, sediments can serve as reservoirs or "sinks" for persistent organic pollutants. When sequestered in these sediments, persistent organic pollutants 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. Humans can be exposed to persistent organic pollutants through diet, occupational accidents and the environment (including indoor). Exposure to persistent organic pollutants, either acute or chronic, can be associated with a wide range of adverse health effects, including illness and death¹. Stockholm convention (2004) aims to protect human health and the environment from the effects of persistent organic pollutants with a range of control measures to reduce and, where feasible, eliminate persistent organic pollutants releases, including emissions of unintentionally produced persistent organic pollutants such as dioxins.

The aquatic species, red swamp crayfish (*Procambarus clarkii*) and black bass (*Micropterus salmoides*) from Lake Naivasha, Kenya were analyzed for organochlorine and organophosphorus pesticide residues. The higher fat content in black bass accounted for the significantly higher residue concentrations of lindane, dieldrin, β -endosulfan, aldrin and organophosphate². Zhang and Jiang³ studied polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCBs) in the muscle of four species. A preliminary assessment in China's Pearl River Delta showed that organo chlorine pesticide contamination in the delta was particularly serious and might pose a threat to the health of the marine inhabitants⁴. According to a study conducted in Greenland fjord system, Norway, it was found that the concentration of PCDD/Fs was declined with increasing trophic levels⁵. The average dioxin concentration in the edible part of unprocessed fish are between 0.008 and 0.792 pg dioxin per gram of fresh weight, maximum concentration of 2.885 pg/g fresh weight had been measured in Herring from the Baltic Sea⁶. The estimates of intake through fish and shellfish accounted for *ca.* 45-70 % of total dietary intake in each age group⁷. The bottom feeder fishes were found to accumulate more dioxin and furan because of their association with adsorbed contaminants. In most aquatic organisms 2,3,7,8-substituted PCDD and PCDF congeners were found. Ikemoto *et al.*⁸, elucidated the biomagnification profiles of persistent organic pollutants through a tropical aquatic food web of

Vietnam of the persistent organic pollutants analyzed, dichlorodiphenyltrichloroethane and its metabolites were the predominant contaminants with concentrations. Doong *et al.*⁹, had positively correlated the polychlorinated biphenyl concentrations to the organic contents of the sediment particles. Trace amounts of persistent organic pollutants in estuarine sediments from Gaoping river were detected.

Investigation on the aquatic organisms is imperative to assess the environmental degradation of the estuary as well as the coast. The present study provides the information about the organic pollution in aquatic organisms. The data can be used as a baseline to monitor the estuaries and coast in future. The aquatic organisms considered for the study are the major source of food for the local people. Hence, it is essential to assess the environmental dangers and risks posed to human health in Ennore to take mitigation measures.

EXPERIMENTAL

Ennore estuary is situated in north of Chennai, India and facing the sea in the east between north latitude 13°14' and east longitude 80°20'. The average depth in the estuary rarely exceeds 2-5 m. Nearby Manali industrial complex has more than 25 major industries, including the coal based Ennore Thermal Power Station, North Chennai Thermal Power Station (NCTPS), Foundry, Fertilizer, Sugar, Chemicals, Refineries, *etc.*, generating about 21000 m³/day quantity of trade effluent. North Chennai Thermal Power Station draws freshwater from the Ennore Estuary and lets out hot coolant water into the Buckingham Canal and discharges toxic flyash, in the form of slurry, into the lagoon system. Wide variety of products manufactured by different industries in Ennore result in the discharge of various types of pollutants to the environment. The water bodies from the surroundings discharge treated/untreated industrial effluents, urban sewage, thermal effluents, *etc.* through Ennore estuary to the nearby coast. The construction of the Ennore Satellite Port has choked the mouth of the Ennore estuary, so continuous dredging is being done. This estuary is hence expected to contain elevated levels of trace metals, dissolved organic matter and all kind of anthropogenic pollutants relative to the open sea environment.

Sampling strategy: Field survey regarding the aquatic species available in the Ennore estuary was done and also the organisms that are available in the polluted stretch in particular were identified. After interaction with fishermen, fish vendors and the local residents, six species were selected on the basis of consumption by the local people. The species were caught by traversing through a boat from the outlet of Ennore Thermal Power Station till the estuarine mouth that joins the sea. The collected species were immediately stored in an ice box for preservation *viz.*, White prawn (*Penaeus indicus*), Mud crab (*Scylla serrata*), Blood clams (*Anadara granosa*), Mullet fish (*Mugil cephalus*), Jarpua terapon (*Terapon jarpua*), Indian oil Sardine (*Sardinella longiceps*).

The sample was prepared for analysis within 24 h of collection. In all the species collected, only the edible parts used for human consumption were taken for analysis. In case of fish samples, the head, tail, fin and scales were removed, before grinding them. For prawn, the outer shell was removed.

The fleshy part was collected in crab and clams, leaving behind the exoskeleton. The clams were immersed in hot water till the outer shell opened. Each species was then grinded to a fine paste. Sodium sulphate was then added to it and then homogenized. The samples were stored under refrigeration until extraction. Samples were analyzed for organic pollutants following USEPA 8280A¹⁰ using high-resolution gas chromatography/low-resolution mass spectrometry. The lipid content was determined because of the high affinity of persistent organic pollutants towards lipids.

RESULTS AND DISCUSSION

Organic pollutants in aquatic animals: Table-1 shows the lipid content in the aquatic organisms. Among the selected organism Mud crab and Indian oil sardine has the least lipid level and the highest level of lipid content, respectively followed by *Jarpua terapon*.

TABLE-1
LIPID CONTENT IN AQUATIC ORGANISMS

S. No.	Aquatic organism		Lipid content (1 g of sample) (g)
	Common name	Scientific name	
1	White prawn	<i>Penaeus indicus</i>	0.0377
2	Mud crab	<i>Scylla serrata</i>	0.0010
3	Blood clams	<i>Anadara granosa</i>	0.0359
4	Grey mullet	<i>Mugil cephalus</i>	0.0295
5	Indian oil sardine	<i>Sardinella longiceps</i>	0.1419
6	Jarpua terapon	<i>Terapon jarpua</i>	0.1356

The HRGC/LRMS results of aquatic organism samples confirm the accumulation of the following three groups of organic compounds in the species: Polycyclic aromatic hydrocarbons, phthalates, polymers.

The organic pollutants detected, vary in concentrations for each aquatic organisms. Table-2 illustrates the various organic pollutants and their concentrations with respect to their lipid level. Quantity of pollutants present in lipid was calculated by dividing the concentration of pollutants by the amount of lipid present in one gram of the sample.

Polycyclic aromatic hydrocarbons (PAHs) and phthalates are found to be dominant among the species. Polycyclic aromatic hydrocarbons are found in the highest level in the Mud crab followed by White prawn. In the latter, polycyclic aromatic hydrocarbon is the only pollutant group present. In Jarpua terapon, polycyclic aromatic hydrocarbon concentration is higher than phthalate group present. Anthracene, 9-methyl-, 9H-fluorene, 2-methyl-, 1,1'-biphenyl,3-methyl-, bi phenyls, 1,1'-biphenyl,3,4'-dimethyl-, are the polycyclic aromatic hydrocarbon compounds detected in the samples.

As individual concentration, phthalates or plasticizers are dominant in the biological samples tested. Among the phthalates 1,2-benzenedicarboxylic acid, diisooctyl ester is frequently found. Phthalic acid, butyl hexyl ester, bis(2-pentyl) ester, di-n-octyl phthalate are the other phthalates detected. Phthalates occur in relatively higher concentration than polycyclic aromatic hydrocarbon, *vice-versa* is observed while considering the lipid levels of the organism. In spite of the low lipid level, Mud crab shows the maximum amount of total organic pollutants, followed by Blood clams. This could be

TABLE-2
ORGANIC POLLUTANTS IN AQUATIC SAMPLES

Aquatic organism	Organic pollutants	Group	Concentration (mg)	Concentration of pollutants/lipid content (mg/g)
White prawn	1,1'-Biphenyl,3,4'-dimethyl-Bi phenyls	PAH	0.017	0.45
		PAH	0.095	2.52
Mud crab	Di-n-octyl phthalate	Phthalates	0.15	150
	Anthracene,9-methyl-	PAH	0.03	30
	9H-Fluorene,2-methyl-	PAH	0.03	30
Blood clams	1,2-Benzenedicarboxylic acid, diisooctyl ester	Phthalates	0.45	12.53
Grey mullet	Phthalic acid, bis(2-pentyl) ester	Phthalates	0.05	1.69
Jarpua terapon	1,2-Benzenedicarboxylic acid, diisooctyl ester	Phthalates	0.039	0.28
	1,1'-Biphenyl,3-methyl-	PAH	0.112	0.83
Indian oil sardine	1,5- Hexadien-3-ol	Polymers	0.43	3.03
	1,2-Benzenedicarboxylic acid, diisooctyl ester	Phthalates	0.5	3.52
	Phthalic acid, butyl hexyl ester	Phthalates	0.07	0.49

due to their close association with the sediments. Phthalates are recorded in the highest concentration in Mud crab. 1,2-Benzenedicarboxylic acid, diisooctyl ester is the phthalate that is frequently present in the samples. It is found to be maximum in blood clams, followed by *Jarpua terapon* and Indian oil sardine. Blood clams and Grey mullet contain only phthalates.

1,5-Hexadien-3-ol is the only compound of the polymer group detected. It is found in Indian oil sardine alone. It is a cross linking agent which is used for adding strength to polymers. It is used as an insulating substance in wires and many electrical appliances which get released due to high temperature and radiations.

Polycyclic aromatic hydrocarbons in the aquatic environment are derived largely from inputs of petroleum and its products, from sewage effluents, runoff and atmospheric deposition from the incomplete combustion of organic matter. Industrial activities such as metal smelting and the electrolytic production of aluminium also release polycyclic aromatic hydrocarbons into rivers, estuaries and inshore waters. Coastal waters additionally receive substantial amounts of polycyclic aromatic hydrocarbons from products such as ascreosote, coal tar and coal tar pitch which are used as preservatives and antifouling agents. Phthalates represent a large class of chemicals that are widely used in commercial products. 1,2-Benzene dicarboxylic acid, diisooctyl ester has low water solubility hence binds to the sediment or enters the food chain immediately. Polymers are commonly used in thousands of products as plastics, elastomers, coatings and adhesives. They make up about 80 % of the organic chemical industry.

Conclusion

Presence of organic pollutants such as polycyclic aromatic hydrocarbons, phthalates and polymers in aquatic animals shows the degraded environmental quality in the Ennore estuary. The lipid levels of Indian oil Sardine and *Jarpua terapon* are relatively higher than other aquatic animals. Mud crab is found to contain maximum pollutant accumulation followed by blood clams. Polycyclic aromatic hydrocarbons show varying ability to induce cancer and it is difficult to identify the structural

features associated with their carcinogenic activity. Some environmental transformation products of polycyclic aromatic hydrocarbons may react directly with DNA, causing mutations and possibly cancer, without the need for metabolic activation. The health effects of phthalates include decreased sperm counts, increased birth defects in male sex organs and an increased chance of breast cancer. Phthalates may cause birth defects, also damage the liver, kidneys and reproductive system. As the selected aquatic organisms show the organic contamination, the possibility of high health risks exists for their consumers.

ACKNOWLEDGEMENTS

The author thanks Dr. Anbu Munuswamy, Scientist, National Institute for Interdisciplinary Science and Technology and Priya Dharshini, G.R. for their technical help rendered in sample analysis.

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