Effect of Seasonal Variations of Selected Heavy Metals in Water and Grey Mullet (*Mugil cephalus)* Fish Tissues from Negombo Estuary.

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Abstract

Heavy metal pollution is of particular concern as they have deleterious effects on biota through mobilization and accumulation in various tropic levels. Industrial pollution and domestic solid waste dumping are considered as the major pollution sources of the Negombo estuary. The different localities within the estuary are polluted at different rates due to changes in input levels. The objectives of this study were to assess the seasonal variations of heavy metal levels in water (rainy and non rainy periods) and fish tissues in selected sites. Four sampling sites were selected along the estuary. For this study, water and fish samples were collected from eight sampling locations along the north (n =2), south (n=2), west (n=2), east (n=2) regions during the one year study period from January to December 2014. The levels of Hg metals were analyzed by cold vapor atomic absorption spectrophotometer whereas the other metals were analyzed by flame furnace atomic absorption spectrophotometer. The results revealed that the average concentration of metals Pb, Cd and Hg in water were 0.01 to 0.005 ppm, 0.0 to 0.01 ppm and 0 to 0.013 ppm respectively. The detected average concentration of mercury in water was above the maximum permissible limits of the proposed tolerance limits for the discharge of industrial wastewater quality standards for Central Environmental Authority, (2001) Sri Lanka. This study showed that the concentrations (mg/kg) of metals in the fish tissues were (Pb) 0 to 0.3, (Cd) 0.35 to 1.104 and (Hg) 0.0005 to 0.05 mg/kg respectively. The mean concentration of Pb and Hg metal levels in fish were much below when compared to the international standard limits. The results showed that there is a significant differences of ($P < 0.05$) of Pb and Hg levels in fish tissues and also for all metals in water. The levels of heavy metals in water and fish tissue were higher in north region of the estuary due to the discharge of industrial effluents and domestic solid waste into the estuary. The seasonality in the heavy metal levels of water and fish tissue were observed with a peak periods from May and June to October and November, which apparently coincided with the South West monsoon and the onset of second inter monsoon of the island respectively.

Keywords : Heavy metals, Seasonal variations, Water, Fish tissues, Negombo Estuary

Background

Estuaries are highly sensitive aquatic ecosystems and regarded as one of the natural sinks for the transfer of industrial and urban pollutants (Roast *et al.,* 2001). The pollution of the aquatic environment with toxic and non toxic heavy metals has become a worldwide problem during recent years, because they are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000). Water pollution is one of the principal environmental and public health problems in Negombo estuary in Sri Lanka (Silva, 1996). Based on the levels of Hg, Pb and Cd in the fish, edible muscle of *Etroplus suratensis* and *Ambassis commersoni* fish species collected from the estuary was found to be safe for human consumptions (Indrajith *et al.,* 2008). However, Negombo estuary is located in west coast of Sri Lanka, is becoming polluted due to rapid industrialization and urbanization in the area (Silva, 1996). With changing environmental conditions under increasing anthropogenic influences, especially from municipal and industrial sources pollutants including heavy metals may enter the food chain, accumulate in organisms and affect their survival. The quality of this ecosystem has been degrading due to domestic solid waste and human activities. Anthropogenic activities continuously increase the amount of organic, inorganic and toxic substances in the environment, especially in aquatic ecosystem, which is growing at an alarming rate and has become an important worldwide problem (Malik, *et al.,* 2010). The edible fish species *Mugil cephalus* has a high economic value in Negombo estuary (Pethiyagoda, 1991). *Mugil Cephalus* constitutes some of the main fishes caught in the estuary, and they also serves as one of the main sources of protein diet for the community.

Research Problem

Industrial pollution and domestic solid waste dumping are considered as the major pollution sources of the Negombo estuary. Based on the pollution inputs into the estuary, it is considered that different localities within the estuary are polluted at different rates.The problem of pollution is attracting the attention of people around the estuary. The any measures of industries effluents and solid wastes are therefore a major problem for estuary aquatic species.

Objectives

The objectives of this study were to determine the seasonal variations (rainy and non rainy periods) of heavy metal levels of the lead (Pb), mercury (Hg) and cadmium (Cd) in water and edible fish (*Mugil cephalus)* tissues.

Research Methodology

Four sampling sites were selected for the study representing the main channels entering into the estuary. For this study, water and fish samples were collected from eight sampling locations along the north (n =2), south (n=2), west (n=2), east (n=2) regions during the one year study period from January to December 2014. Water quality and heavy metals levels were analyzed employing standard methods. Sites of the estuary which are subjected to effluent discharges from most of the industrial zones, the large number of boats anchoring areas and domestic wastewater and solid waste from houses were considered in this study. Sampling sites were categorized as North, South, East, and West estuary (Table 1). The sampling sites 1 were located in the north region of the estuary whereas the sites 2, 3 and 4 were located in the south, west and east region (Table 1).

Table 1: Description of study sites at Negombo Estuary

Section of the estuary	**Input sources (if any)**
Northern Estuary **Site 1**	Municipal solid waste, industrial effluents, urbanization, hotels, fishing harbor and boat repair stations and sewage outlets.
Southern Estuary **Site 2**	Two fresh water canals, Ekala industrial zone, sea plane landing site, various effluents in Hamilton canal outlet.
Western Estuary **Site 3**	Hotels, shrimp farm and fish processing industries.
Eastern Estuary **Site 4**	Katunayake industrial processing zone, hotels and housing scheme.

Analysis of water

Water samples were collected, acidified with 05mL nitric acid (APHA, 1998). After filtration through Whitman filter papers, 1mL of nitric acid was added and then aspirated directly into the Atomic Absorption Spectrophotometer for heavy metal determination (APHA, 1998) for three times.

Fresh fish samples (*Mugil cephalus*) were collected by using cast nets from the same sampling sites during the one year period from January to December 2014. Triplicate fish samples were collected on all sites. These tissues were washed with tap water followed by distilled water, then oven dried to constant weight at 105 ^{0}C. The dried fish tissues were crushed and powdered in an agate mortar, and then they were kept in polyethylene bottles for analysis. One gram (01g) portions of fish tissues were

digested by means of a microwave digestion after addition of nitric acid and hydrogen peroxide. The results were calculated in milligram per kilogram wet weight (mg/kg). Pb, Cd and Hg were tested using AOAC (2002). Mercury in the digested fish sample was analyzed using cold vapor Atomic Absorption Spectrophotometer.

Data were analyzed to generate mean ± STD, t-test and a one-way analysis of variance using Minitab program version 14.0. The significance level was tested at the $p < 0.05$.

Key Findings

Metal levels in water

The results revealed that the average concentration of metals Pb, Cd and Hg in water at four sampling sites of the estuary are presented in Table 2.

Table 2: The Mean ± STD Value of Selected Metals in Water (n=8)

Sites	Pb (ppm)	Cd (ppm)	Hg (ppm)
Site 1	0.026±0.002	0.015±0.003	0.013±0.001
Site 2	0.023±0.001	0.001±0.002	0.001±0.001
Site 3	0.005±0.003	0.0±0.0	0.004±0.003
Site 4	0.017±0.09	0.001±0.002	0.0±0.0

The concentration 04 lead (Pb) was fluctuated within a narrow range 0.005 to 0.026 ppm respectively (Table 2). The high Pb values were recorded in the site 1 (Table 2). The Cd exhibited a wide range of variation between 0.0 to 0.015 ppm. The highest Cd value was recorded at site 1 (Table 2). The detected average concentration of mercury in water was above the maximum permissible limits of the proposed tolerance limits for the discharge of industrial wastewater quality standards for Central Environmental Authority, (2001) in Sri Lanka. The limits of detection of water in Lead and Cadmium contents in water were below the standard limits defined for each element are 0.1 ppm, 0.1 ppm and 0.0005 ppm respectively (CEA, 2001).

Metal levels in Fish

Total metal levels in tissue of the fish (*Mugil cephalus)* are presented in four sampling sites of the estuary are presented in Table 3.

Table 3: Mean concentrations ± SD of heavy metal in muscles (mg/kg) of fish species (n=8)

Sites	Pb (mg/kg)	Cd (mg/kg)	Hg (mg/kg)
Site 1	0.157± 0.631	1.045 ± 0.283	0.03± 0.018
Site 2	0.30 ± 0.194	0.45 ± 0.280	0.0005 ± 0.0004
Site 3	0.25 ± 0.044	0.55± 0.480	0.001 ± 0.0005
Site 4	0.0 ± 0.0	0.35 ± 0.160	0.050 ± 0.046

The result indicated that measured metals in the edible muscle tissues ranged from (Pb) 0 to 0.3 (Cd) 0.35 to 1.104 and (Hg) 0.0005 to 0.05 mg/kg respectively. The highest levels of Cd were in the fish which were found at the sampling site 1. Whereas levels of Hg was highest in the site 4 located in the east region (Table 3). This study revealed that the concentrations (mg/kg) of Pb and Hg metal levels in fish were much below than international standard limits (FAO, 2006). The detected lead, mercury and cadmium contents in fish tissue were below the standard defined for each element < 0.5 mg/kg, < 0.05 mg/kg, and < 0.5 mg/kg, respectively (FAO, 2006). The monthly variations of in Pb and Cd metal concentrations in fish tissue were found during October and November, which correspond to second inter monsoon (Table 4).

Table 4: Mean concentrations ± SD of monthly variation of heavy metal concentration in muscles (mg/kg) of fish species

Months 2014	Pb (mg/kg)	Cd (mg/kg)	Hg (mg/kg)
January	0.157±0.631	0.06±0.006	0.03±0.002
February	0.3±1.940	0.45±0.040	0.0005±0.0004
March	0.25±0.044	0.55±0.050	0.001±0.0005
April	0.1±0.010	0.35±0.010	0.05±0.004
May	0.5±0.050	1.1±0.110	0.01± 0.005
June	0.5±0.050	0.43±0.040	0.09±0.008
July	0.1±0.010	1±0.190	0.04±0.003
August	0.003±0.002	0.008±0.065	0.01±0.002
September	0.03±0.002	0.09±0.008	0.04±0.002
October	0.4±0.030	1.6±0.190	0.08±0.007
November	0.6±0.060	1.4±0.150	0.09±0.010
December	0.03±0.003	1.2±0.350	0.05±0.045

North part of the estuary is connected to the sea mouth and mixing to sea water, through the levels of Pb, Cd and Hg in water in all sampling sites in this part were higher than other sites. Hence the levels of metals in the water and fish tissue of north region were noted to change throughout the year and this may have partly contributed to high accumulation in sediment of this area in comparison to the other sites. The sampling site 2 receives water mainly from the Dandugam oya and it carries various effluents from Ekala industrial zone (CEA, 1994).

Conclusion

The results indicated that the levels of toxic heavy metals as Pb, Cd and Hg in water were comparatively high in north region of the estuary. This study revealed that there were significant differences ($P < 0.05$) in Pb and Hg in fish tissues. Significant seasonal differences ($P < 0.05$) were observed for all metals in water. In North region of the estuary, the levels of heavy metals in water and fish tissue levels were higher due to the discharge of industrial effluents and domestic solid waste into the estuary.The seasonality in the heavy metal levels of water and fish tissue were observed with a peak periods from May and June to October and November, which apparently coincided with the South West monsoon and the onset of second inter monsoon of the island respectively.

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