

A study of trace metal levels in selected fisheries harbours in South and West coast of Sri Lanka

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Abstract

Trace metals generally enter into the harbour environment through atmospheric deposition, erosion or due to anthropogenic activities such as release of industrial effluents, domestic and harbour generated sewage and oil spills. The present study was carried out to assess the levels of several trace metals, namely, Hg, Pb, Cd, Cr, Zn, Cu and Ni, in harbour basin water from six selected fisheries harbours along the Southern and Western coasts of Sri Lanka. A total of 54 samples were collected covering the areas around the harbour jetty, harbour entrance and fuel stations during the period of June to December, 2011. The level of total Hg was analyzed by cold vapour atomic absorption spectrometry (CV-AAS) and the other metals by graphite furnace atomic absorption spectrometry (GF-AAS). The trace metal concentrations in fisheries harbour basin water (n=54) varied widely. The mean concentrations \pm SD (μ g/L) found in the study were Hg <0.16, Pb 0.40 ± 0.61 , Cd 0.06 ± 0.17 , Cr 0.49 ± 0.80 , Zn 13.60 ± 19.10 , Cu 4.68 ± 8.99 and Ni 5.80 ± 7.98 . These values are all well below the limits for estuary and harbour basin water guideline, set by European Union (EU) and the Food and Agriculture Organization (FAO).

Keywords: Fisheries harbours, Trace metals, Sri Lanka

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Introduction

Sri Lanka is a small tropical island in the Indian Ocean, off the Southern tip of India, with an Exclusive Economic Zone (EEZ) of 517,000 km². The fisheries sector plays an important role and contributes a significant income to the national economy. The total contribution of the marine fisheries sub-sector to the Gross Domestic Production (GDP) was 1.7% in 2010. The production from capture fisheries amounted to 332,260 MT in 2010 of which a total of 18,325 MT fish and fisheries products were exported (MOFAR, 2010). In Sri Lanka, at present 18 fisheries harbours are in operation while another two are under construction. Nearly all of the marine fish and aquatic products that are exported come through these fisheries harbours. Fisheries harbours are equipped with a range of facilities and act as an interface between the capture of fish and its consumption. The services undertaken by these harbours include handling, processing and marketing of the fish as well as supplying ice, fuel, freshwater and facilities to maintain and repair the fishing boats.

Environmental pollution is an increasingly important issue and received worldwide attention. Continuous growth in urban and rural activities around fisheries harbours can be expected to increase the pressure on the quality of harbour water. The capacity of the harbour to receive pollutants from point and non-point sources has not been investigated and there is a need to monitor this environment and protect it from further deterioration. Analysis of seawater is particularly important because the coastal region and oceans are often used as dumping areas of wastes. Trace metals are regarded as serious pollutants of the aquatic environment because of their toxicity, persistence, lack of biodegradability and tendency to concentrate in aquatic organisms (Lafabrie *et al.*, 2008). Therefore, reliable analytical data for trace elements in sea and harbour water are required to monitor environmental quality.

Trace quantities of many metals are important constituents of harbour basin water. Many of these metals are also classified as pollutants. The presence of any of these metals in excessive quantities hinders beneficial uses of the water because of their toxicity. In the marine environment, sediments act as an important reservoir for heavy metals, which is released into the water and accumulated in organisms (Omanovic *et al.*, 2006 and

Hashem *et al.*, 2007). Heavy metals are an ill-defined subset of elements that exhibit metallic properties, and include the transition metals, some metalloids, lanthanides, and actinides. The pollution of marine ecosystems is a worldwide problem (Bryan, 1976) and the situation is aggravated by the ability of these ecosystems to concentrate and accumulate some metals within food chains. Mercury, lead and cadmium are considered the most harmful pollutants in the marine environment. The presence of trace metals in seawater can also be a threat for the health of people consuming marine fish. Though, some of the metals such as Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, others such as Hg, Cd and Pb have no known physiological activity, but are proved detrimental beyond a certain limit (Kar *et al.*, 2008 and Indrajith *et al.*, 2008). In addition, Hg is the most ubiquitous of all the heavy metals, because it is the only metal that can exist in liquid form at ambient temperature, and it has the highest vapor pressure of all metals (Edson *et al.*, 2001). The serious effects of the accumulation of these heavy metals on health, reproduction, neurological disturbances and genetic malfunctions have been well documented (Kar *et al.*, 2008).

Due to the acute shortage of potable water in many fishery harbours, harbour basin water is often utilized during cleaning of fish, boats and utensils in port, and constitutes a potential source of contamination. The harbour water quality is heavily influenced by human activity not only within the harbour complex but in the surrounding environment. Effluents from runoff from land, sewage discharge, and toxic effluents from fuel storage areas and industries adversely affect the harbour environment.

Some of the methods reported for determination of heavy metal concentrations in seawater include inductively coupled plasma - mass spectrometry, inductively coupled plasma-atomic emission spectrometry, atomic absorption spectrometry (AAS) with flame or electro thermal atomization, electrochemical ultra-microelectrodes and anode stripping voltametry (Gabriela *et al.*, 2005). Seawater represents a challenging matrix to the analyst as metals of interest may occur at very low concentrations. Owing to extremely low concentrations of trace elements in seawater, in many of the methods it is necessary to pre-concentrate the sample prior to determination by AAS. The analytical task is further complicated by the presence of salts and solids in the sea water matrix,

which can produce large, rapidly changing background signals and the possibility of chemical interferences. The microwave accelerated digestion is designed to perform extraction using microwave heating with nitric acid. Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Cold Vapour Atomic Absorption Spectrometry (CVAAS) and microwave assisted sample digestion technique are valuable techniques for determination of trace elements in difficult matrices such as seawater. The use of fast Zeeman Effect background correction, flexible furnace programming, chemical modification of the sample, pressure and temperature control facility within digestion time ensures reliability of determinations.

According to the FAO and EU guidelines, harbour basins should be tested annually. However, in areas where monsoons are very active, it may be advisable to test at the peak of the dry season when effluent point discharges tend to remain concentrated in the water body and again during the wet season when agriculture run-off is considerable. Another critical period for harbours is the peak of the fishing season when the harbour is at its busiest and vessel-generated pollution is likely to be at its peak. The recommended limits of trace metals in harbour basin water is summarized below (Table 1).

Table 1. EU standards for estuary and harbour basin water.

Parameter	Maximum limit
Mercury ($\mu\text{g/L}$)	0.50
Cadmium($\mu\text{g/L}$)	5.00
Chromium (mg/L)	0.50
Copper (mg/L)	0.50
Lead (mg/L)	0.50
Nickel (mg/L)	0.50
Zinc (mg/L)	50.0
pH	6-9

The baseline information available on levels of trace metals in fisheries harbour basin water in Sri Lanka is very limited. The objectives of this study are to;

- Estimate the levels of total trace metals (Hg, Cd, Pb, Ni, Cu, Cr and Zn) in the selected fisheries harbour basin water.
- Provide base line data for trace metals that could be used for pollution monitoring of the study area in the future.

Materials and Methods

Collection of harbour seawater samples

In this study, six fisheries harbours in the Southern and Western coasts of Sri Lanka, namely, Tangalle, Puranawella, Mirissa, Beruwala, Mutwal and Negombo were sampled (Fig. 1).



Fig. 1. Locations of sampled fisheries harbours

Harbour basin water samples were collected into polypropylene bottles (1 L) using a Rutner sampler. During the period June-December 2011, nine samples were collected at each fisheries harbour – including harbour mouth, jetty and at the vicinity of fuel supply facilities. All the sample containers and glassware used in analyses were cleaned in the laboratory, as per the requirements of trace metal analysis. Temperature and pH of the water

were measured on site (HACH EC 20, Colorado, USA). Samples were stored in an ice box and transported to the analytical chemistry laboratory, Institute of Post-Harvest Technology, National Aquatic Resource Research and Development Agency (NARA).

Digestion of seawater samples

The water samples were digested, immediately after reaching the laboratory, with concentrated nitric acid using an automated, programmable digesting system (CEM-MARS-XP-1500+ microwave accelerated system CEM, Matthews, USA). The seawater

and nitric acid (Sigma-AR, Dorset, United Kingdom) added to each digestion tube was 45 ml and 5 ml respectively. The digestion process followed is shown in Table 2. All the seawater samples, reagent blanks and spiked samples were analysed in duplicates.

Table 2. Microwave heating program

Stage	Power		Ramp time (min:sec)	Pressure (psi-limits)	Temp (°C)	Stir	Hold time (min:sec)
	Level	%					
1	400 W	100	10:00	350	160	Off	0:00
2	400 W	100	10:00	350	170	Off	0:00

Analysis of seawater samples

Working standards for the analyses were prepared by diluting the stock standard solutions (1000 mg/L) of the elements obtained from Fluka (Switzerland) with de-ionized water. The overall acidity of the solution was kept to 10% with respect to nitric acid. The analysis of digests and standards were carried out using AAS (Varian AAS-240 FS instrument - Varian, Springvale, Australia). All metals, other than mercury were analyzed using a Varian Graphite Tube Atomizer (GTA-120). The analysis of Hg was based on cold vapor generation using the vapor generation accessory (Varian VGA 77) with SnCl₂ as the reductant.

Statistical analysis (ANOVA) of data to compare the levels of metals between harbours were carried out using IBM-SPSS 22.

Results and Discussion

The harbours, selected for the study are mostly located in areas that are popular tourist destinations, with extensive commercial activities and increasing population. The harbour-related activities include repairs, services and maintenance of boats and supply of fuel and ice. All these activities contribute to the pollution of harbour basin water.

The pH value and temperature of the selected harbour basin water were 7.46±0.28 and 29.3±0.7 °C respectively. According to the EU estuary and harbour basin water standards

(www.fao.org), the recommended pH range was 6-9. The pH of the studied harbour water is within the range.

The accuracy of the laboratory analyses for trace metals was determined by spiking samples of seawater and measuring their recovery. The results of these recoveries are shown in Table 3.

Table 3. Mean recovery value and limit of detection (LOD= mean+3 σ)

Metal	Hg	Pb	Cd	Cr	Cu	Ni	Zn
Recovery (%)	83.02	72.63	78.57	97.79	85.03	89.13	75.72
LOD	0.16	0.39	0.03	0.17	0.57	1.09	0.43

The trace metal concentration in seawater recorded at six fisheries harbours for seven trace metals are shown in Table 4. The results show that for each of the metals apart from mercury, the concentrations were significantly different between harbours ($p>0.05$).

Table 4. The average trace metal concentration ($\mu\text{g/L}$) in harbour seawater.

Fisheries harbour	Hg	Pb *	Cd *	Cr *	Zn *	Cu *	Ni *
Mirissa	<0.16	1.17 \pm 0.59	<0.03	0.19 \pm 0.26	3.21 \pm 4.24	11.41 \pm 12.26	8.18 \pm 11.68
Beruwala	<0.16	<0.39	<0.03	0.32 \pm 0.33	2.47 \pm 4.72	14.71 \pm 11.83	6.26 \pm 4.14
Negombo	<0.16	<0.39	<0.03	1.32 \pm 1.21	8.01 \pm 5.79	<0.57	<1.09
Mutwal	<0.16	<0.39	<0.03	0.21 \pm 0.29	11.49 \pm 14.34	<0.57	<1.09
Tangalle	<0.16	<0.39	0.30 \pm 0.31	0.27 \pm 0.28	20.15 \pm 6.09	0.89 \pm 0.79	2.17 \pm 3.36
Puranawella	<0.16	0.61 \pm 0.79	0.03 \pm 0.09	0.60 \pm 1.17	36.29 \pm 34.25	<0.57	17.70 \pm 2.51

*are statistically significant between each harbour, $p>0.05\%$

Total Mercury (Hg)

The total mercury levels of all six harbour basin waters were below the detection limits of 0.16 $\mu\text{g/L}$. Indrajith *et al.*, (2008), in an earlier study of the Negombo Lagoon water found that Hg was less than their detection limit of 10 $\mu\text{g/L}$. Total Hg represents the sum of all mercury species (gaseous, dissolved and bound to particulates and colloids) in water samples. Hg concentration in seawater has no consistent relationship with the water depth (Masakichi *et al.*, 1983). The main dissolved Hg species in the aquatic environment are elemental Hg (Hg_0), complexes of Hg (II) with various organic and

inorganic ligands, and organic Hg forms, mainly the mono-methyl-mercury and di-methyl-mercury (DMHg) (Horvat *et al.*, 2003). That study showed that seasonal variations of Hg speciation in oceanic waters are related to temperature, redox conditions, as well as to seasonal changes in productivity and the bioavailability of nutrients. The study of Ferrara *et al.*, (2003), showed that minimum total Hg concentration were found in surface water and at a depth of 100 m which are the point before and after the thermocline, with an increase at 20 m depth (Horvat *et al.*, 2003).

Cadmium (Cd)

The highest total concentration of Cd (0.30 µg/L) in harbour basin water was found in Tangalle. Whereas lower values were observed in Mirissa, Beruwala, Mutwal and Negombo Harbour, all below the detection limit of 0.03 µg/L. The average total Cd concentration in all harbours was 0.06 ± 0.17 µg/L. However, this value was 83 times lower than the limits set by the European Union. According to a published report, industrial and domestic wastes are considered to be the main source of cadmium in the marine environment. In an earlier study, the Cd level of Negombo lagoon water was below the detection limit of 2.1 µg/L (Indrajith *et al.*, 2008). There is no evidence that Cd is biologically essential to any organism, but its toxicity is well documented in the literature. Bio availability of metals like Cd, Cu and Zn are related with the activity of free metal ion rather than total metal concentration. For Cd, it is the CdCl₂ complex that is predominant in sea water. Salinity is therefore considered to be the overriding factor which can alter free Cd activity (Jenkins and Sanders, 1986).

Lead (Pb)

Lead and lead compounds are generally toxic pollutants with Lead (II) salts and organic lead compounds considered the most harmful in the environment. Seawater normally contains trace amounts of Pb (230 parts per trillion). Under normal conditions Pb does not react with water but when it comes in contact with moist air, it's reactivity with water increases. The highest total Pb level in the present study was observed in the Mirissa harbour basin water (1.17 µg/L) while in all the other harbour basin water - except Puranawella harbour (0.61 µg/L) - total Pb levels were below the detection limit of 0.39 µg/L. The mean total Pb concentration was 0.40 µg/L and it was 1250 times lower than

published EU limits. In the previous study by Indrajith *et al.*, (2008), in the Negombo Lagoon, the total Pb concentration was below their detection limit of 5.7 µg/L of water.

Chromium (Cr)

Chromium does not occur freely in nature. Cr compounds can be found in trace amounts in sea water and the level varies widely (Solai *et al.*, 2010). The mean total concentration of Cr in studied fisheries harbours was 0.49 µg/L and this was 1020 times lower than recommended EU limit. The highest total concentration was observed in the Negombo fisheries harbour (1.32 µg/L) and the lowest observed in Mirissa (0.19 µg/L).

Nickel (Ni)

Nickel is often present in agricultural soils situated near fossil fuel industries. Organic matter often adsorbs nickel, causing coal and oil to contain traces of the element. Nickel compounds may also be found in sludge, and in slugs and fly ash from waste incinerators. The concentration of Ni in the studied fisheries harbours ranged from below the quantification level (MQL) to 17.70 µg/L (MQL, minimum quantification level of Ni was 1.09 µg/L). The highest total concentration of Ni was found in the Puranawella fishery harbour (17.70 µg/L) and the lowest in Mutwal and Negombo fisheries harbours (<1.09 µg/L). Ni concentration found in our fisheries harbours was at least 86 times lower than the recommended EU estuary and harbour basin water standards (www.fao.org).

Copper (Cu)

High levels of Cu in sea water reveal anthropogenic input from coastal industries. The antifouling paints used for the sea water intake pipeline structure is one of the major sources of higher concentrations of copper (Solai *et al.*, 2010). High concentrations of copper leaching from the ship's antifouling paint have been reported in the Indian Ocean (Danielsson, 1980). Soluble Cu at higher concentration is toxic to aquatic life including fish, invertebrates and amphibians. Trace amounts of Cu, however, are essential for human health.

The highest total concentration of Cu (14.71 µg/L) was found in the Beruwala fishery harbour. Mean total value obtained was 4.68 µg/L, while values found at Negombo, Mutwal and Puranawella fisheries harbours were less than the detection limit of 0.57 µg/L. However, average value was 107 times lower than EU standards.

Zinc (Zn)

Zinc is naturally present in sea water but if the pH is close to neutral, Zn is insoluble. Solubility increases with increasing acidity as well as at pH above 11 (Solai *et al.*, 2010). The total Zn level at the fisheries harbours in the present study ranged from 2.47 to 36.29 µg/L; the highest concentration was observed in the Puranawella harbour (36.29 µg/L) and lowest in the Beruwala fishery harbour (2.47 µg/L). The EU limit is stated as 50 mg/L and our value average was 3676 times lower.

Table 5. Trace metal levels (µg/L) in harbour water in other studies

Location	Hg	Cd	Pb	Cr	Ni	Cu	Zn	Reference
Negombo Lagoon, Sri Lanka	<DL	<DL- 2.1	<DL- 5.7	0.9- 1.2	<DL- 7.4	<DL- 2.5	40.4- 180.4	Indrajith <i>et al.</i> , (2008)
Karachi Harbour, Pakistan	-	0.485	-	2.61	0.72	2.13	03.0- 24.3	Saleem, 2002
Kepez harbour of Canakkale, Turkey	-	73,800	93,900	-	-	-	-	Yilmaz, 2010
Offshore of Pondicherry and Veerampattanam, India	-	1.74	4.14	3.40	4.59	4.14	33.98	Solai <i>et al.</i> , 2010
Huraghada harbor, Egypt	-	0.6	-	2.5	0.2	3.1	6.1	Hashem <i>et al.</i> , (2007)
Belledune and Dalhousi harbor, Canada	-	-	1.49	-	-	-	-	Bourgoin, 1990
Philippos harbor, Greece	-	-	-	<3.9	<1.5	<15.8	82.	Georgakopoulos <i>et al.</i> , (2002)
Damietta harbor, Egypt	-	-	-	-	-	2.23- 10.75	-	Fargallah <i>et al.</i> , (2009)
Tolo Harbour, Hong Kong	-	-	-	-	-	-	38-94	Wong <i>et al.</i> , (1980)
El Khomssea, Libya	81	62	560	-	-	2820	380	Metwally and Fouad, 2008

DL – Detection Level

The values for trace metal concentrations of harbour water found in the present study are compared with previously published data in Table 5.

Conclusions

The present and earlier studies showed that the concentration of all the metals studied in several fisheries harbours in Sri Lanka were satisfactory and well below the European Union published standards for estuaries and harbour basin waters. It is important, however, to undertake continuous monitoring of trace metals of fisheries harbours and open seawater. Moreover, National Quality Standards for fishery harbour and open seawater should be formulated and regulated. The sewage treatment capacity should be upgraded and the disposal of waste into fishery harbours should be closely monitored in order to prevent pollution.

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