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Preliminary study on physico-chemical characteristics and determination of selected pollutants in Mirissa and Puranawella harbours, southern coast, Sri Lanka

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Abstract

Pollution caused by anthropogenic influence is one of the major problems in coastal areas. Mirissa and Puranawella harbours are situated along the southern coast of Sri Lanka where intensive fishing activities take place. Therefore, both of these harbors are thought to be affected by acute storage of pollutants including crude oil, raw fish particles and other waste products from fishing vessels and other harbour activites. This study was carried out to study physico-chemical characteristics (pH, temperature, salinity, alkalinity, dissolved solids, dissolved oxygen, biological oxygen demand, total phosphorous, nitrate, and nitrite) and to identify some pollutants (floatable grease and oil, Cd, Pb, Cu and presumptive coliforms) in the two harbours. Monthly samples of water and sediments from three selected sites in each harbour were taken during the period of March 2007 to July 2007. All samples were taken from the water surface, middle part of the water column and from the bottom of each site. Significant variations between sampling sites in Mirissa harbour were observed for pH, temperature, salinity, ortho-phosphorous, nitrate and nitrite ($P<0.05$). Salinity, suspended solids, ortho-phosphorous, biological oxygen demand, nitrate and nitrite varied significantly between the sites in Puranawella harbour ($P<0.05$). When considering two harbours suspended solid content, dissolved oxygen and Pb in water and sediments varied significantly between Mirissa and Puranawella harbours. Grease and oil were analysed during one sampling occasion from two harbours and it was observed that the bottom water consisted of relatively higher concentrations than that of surface layers at each site. Cu, Cd and Pb concentrations in water and sediments varied significantly from harbour jetty towards the open sea in two harbours except for Cd and Pb in water. Relatively higher values of coliforms and feacal coliforms, BOD, suspended solids and metals in water and sediment were observed near the jetty of the two harbours due to variation of the contamination level from harbour jetty towards the open sea.

Keywords: pollution, anthropogenic influance, heavy metals

Introduction

Estuarine and coastal marine waters continue to be the most threatened systems due to increasing human population nearby water sheds and increasing use of coastal resources. The most conspicuous impacts occur near metropolitan centres and in well developed regions such as Boston harbour, Baltimore harbour, San Diego harbour and Tampa bay in the coastal zones world wide (Alongi, 1998). Fishing harbours receive nontoxic solid wastes, toxic solid wastes, oil wastes, sewage effluents, fish offal, toilet wastes, canteen wastes etc. from fishing vessels and various activities in harbours. Most fishing boats in Sri Lanka do not have onboard sanitation devices and hence commonly release raw sewage into coastal water (personal communication with fishermen at studied areas). It is a fact that fishing harbours are generally named as hot spots for coliforms and other pathogens, aliphatic and aromatic hydrocarbons and heavy metals (Nixon *et al.*, 1986). Kennish (1997, 1998) has noticed that the use of antifouling paint, creosote and other chemical preservatives are toxic to organisms and change biotic communities and habitats. Dissolved organic nitrogen, inorganic nitrogen and phosphorus exist in seawater received from raw sewage or partially treated municipal waste water discharges (Kennish, 2001). Most chronic oil pollution in marine environments derives from fixed installations, petrochemical industries; municipal and industrial waste water and release of crude oil from fishing vessels and other marinas (Clarke *et al.*, 1990). However, microbes can degrade as much as 40% to 80% of oil in estuarine and marine environments

(Gloldberg, 1995). Heavy metals in sea water are derived from eruption of volcanoes, municipal and industrial discharges, leaching of antifouling paints, smelting operations, and different point and non point sources. Heavy metals can rapidly absorb to particulate matter and accumulate in bottom sediments in estuarine and coastal areas (Gage and Tyler, 1991). Since harbours are considered as shallow coastal embayment with poor water circulation, pollutants may remain there for a long period. However, via the process of accumulation, pollutants can harm other organisms in different coastal habitats.

This study was carried out to determine physicochemical characteristics and concentrations of selected pollutants in two fishery harbours in southern coast, Sri Lanka. Further, the variations of pollutants between two harbours and within the harbours were studied. Also, impact of boat anchorage on the water quality and potential threats to humans due to water quality deterioration were also investigated in this study.

Materials and Methods

Description of the harbours

Mirissa harbour (5° 5' - 5 ° 6' N; 80 ° 26' - 80 ° 27' E) was commissioned in 1966. It has land area of 1.54 ha and the basin area is 7 ha. The depth of the harbour varies between 2.5 and 3.0 m. The capacity of the harbour is for 250 vessels with 3.5 to 5.0 tons (Mallawatantri, 2005). Puranawella harbour (5 ° 56' N; 80 ° 35' E) was opened in 1982. It has a land area of 1.75 ha and the basin area is 11 ha. It provides facilities to 400 boats with 3.5 to 5.0 tons (Mallawatantri, 2005). Deterioration of the water quality within the harbours is more obvious and fishermen release crude oil and other raw materials to the harbour water when cleaning their vessels (personal communication with fishermen).

Sampling sites and study period

Three sampling sites were selected at known distances from the jetty towards the sea in each of the two harbours. Figures 1 and 2 indicate the sampling sites in Mirissa and Puranawella harbours respectively. The study period was from March 2007 to July 2007. Samples were taken on monthly basis and the samples were taken during 7.00 am - 10.00 am period.

Physico-chemical parameters

Water transparency and water depth were measured by using a 20 cm diameter secchi disc and a depth gauge respectively. Water temperature and pH at surface, middle and bottom of each sampling sites were measured using a battery operated meter (Leybold Didactic GMBH). Salinity and total alkalinity at surface, middle and bottom of each sampling sites were determined by titration methods (Strickland and Parson, 1969). Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD) were determined by Winkler`s method at the three layers of each sampling site (Bruckner, 2008). Total Dissolved Solids and Suspended Solids were determined by filtering 250 ml water and then oven-drying the filterate at 105 °C for 8 hrs.

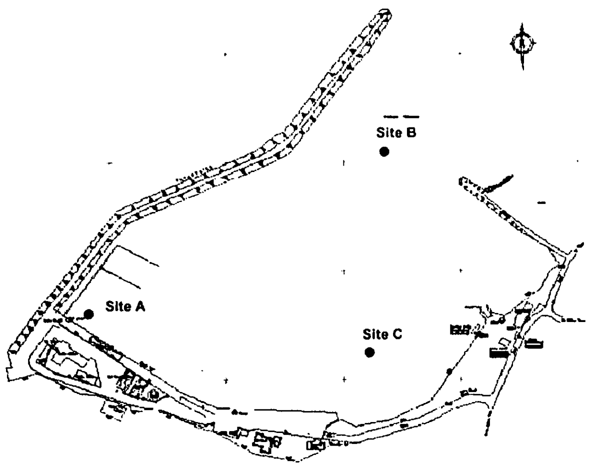

Figure 1: Sampling sites in Mirissa harbour (modified after Mallawatantri, 2005).

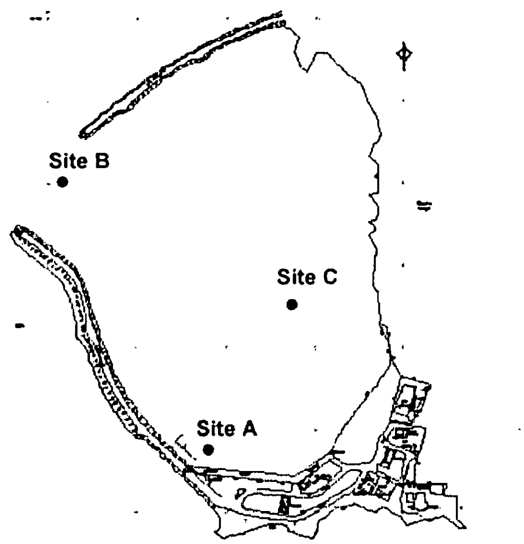

Figure 2: Sampling sites in Puranawella harbour (modified after Mallawatantri, 2005).

Total reactive phosphate and total phosphorous were determined by using ascorbic acid method (Mackereth

(1963). Nitrate was determined according to Strickland and Parsons (1972) after passing through a column of copperized cadmium metal (. Nitrite was determined according to the procedure described by Strickland and Parsons (1972). Floatable grease and oil content in 1L of water from each site were extracted using N-Hexane and then was quantified by gravimetric method. Copper, cadmium and lead concentrations in water and sediments from each site were determined using Atomic Absorption Spectrophotometer (Varian, 220). Sediment samples (0.5g) were digested using 5ml of Conc. HNO_3 and 2ml of H_2O_2 prior to use for metal analysis.

Microbial parameters

Water samples were ten times diluted and MacConkey broth and were used for determination of acid and gas production. Tubes which showed acid and gas production was considered as positive for presumptive coliform. Each positive MacConkey broth was subcultured in tubes with 5ml of BGB broth. Those tubes were incubated at 36^{0}C during 24 to 48 hours. BGB tubes which showed gas production were recorded as positive and confirmed for coliforms. Most Probable Number (MPN) table was referred and MPN of the coliform per 100ml of the sample was determined. Each presumptive positive tube was subcultured in tubes containing 5ml of BGB broth. After incubation at 44^{0}C during 24 to 48 hours BGB tubes were observed for gas production. The tubes with gas were recorded as positive for feacal coliform. MPN table was used to calculate *E. coli* in 100ml sample.

Statistical analysis

One way ANOVA tests were used to determine the variations of intra-site (surface, middle and bottom), inter-site (three sites in each harbour) and inter-location (two harbours) of physico-chemical parameters and selected pollutants during the study period. Post Hoc range tests and pairwise multiple comparisons were used to determine the variations of mean values within the three sampling sites. All statistical analyses were performed using SPSS software package.

Results

Physico-chemical parameters

Mean values of analysed physico-chemical parameters at the three layers (surface, middle, and bottom) at the three sites (site A, site B and site C) during the study period in Mirissa and Puranawella harbours are given in table 1. Physico-chemical parameters did not vary significantly with the layers of sampling at any sampling site in two harbours. Therefore, only the mean values of physico-chemical parameters at each site are shown in table 1.

Table 1 Mean values (±SE) of physico-chemical parameters in two harbours during the study period.

Parameter	Mirissa harbour			Puranawella harbour		
	Site A	Site B	Site C	Site A	Site B	Site C
Secchi depth (m)	2 ± .1	1.6 ± .0	1.5 ± .1	1.5 ± .1	1.5 ± .1	0.5 ± .0
Depth (m)	3	3	3	2.2	2.5	1.5
Temperature (^{0}C)	23 ± 2 *	27 ± 1 *	27 ± 1 *	27 ± 1	29 ± 1	26 ± 2
pH	8 ± 0*	7.6 ± .1*	8 ± 0*	8 ± 0	8 ± .1	7.6 ± .2
Salinity (ppt)	34 ± 1 *	36 ± 1 *	37 ± 1*	36 ± 1*	36 ± .3*	34.5 ± 1*
Alkalinity (mmol/l)	3.4 ± .1	3.4 ± .2	3.4 ± .1	3 ± .1	3 ± .1	3 ± .1
TDS (g/l)	33.5 ±1	33 ± 1	32.3 ± 1	33.7 ± .6	34 ± .6	32 ± .7
SS (g/l)	0.08 ± 0	0.05 ± 0	0.2 ± .1	0.3 ± 0*	0.2 ± .1*	0.3 ± 0*
DO (mg/l)	5.4 ± .3	6 ± .3	0.5 ± ..1	7 ± .6	7 ± .6	6 ± .3
BOD (mg/l)	3 ± 1	1 ± .3	3 ± .3	4 ± .3*	1.4 ± .2*	3 ± .3*
TotalP ×10^3 (mg/l)	5 ± 1	7 ± 1	6 ± 1	8 ± 1	5 ± 1	6.4 ± 1
OrthoP×10^3 (mg/l)	4.6 ± .1*	1 ± 0*	1.7 ± 0.1*	5.5 ± 1*	4 ± 1*	2.6 ± .4*
Nitrate (µg/l)	0.9 ± .1*	0.07 ± 0*	0.4 ± .1*	1 ± .1*	0.04 ± 0*	0.6 ± .1*
Nitrite (µg/l)	0.2 ± 0*	0.03 ± 0*	0.2 ± .1*	0.2 ± 0*	0.04 ± 0*	0.1 ± 0*

*: $p < 0.05$ (significant difference between sampling sites)

Water temperature, pH, salinity, ortho-phosphate, Nitrate and Nitrite varied significantly between sites A, B and C in Mirissa harbour ($p<0.05$). The highest values of water temperature (29^{0}C) at site B, salinity (39 ppt) at site C, ortho-phosphate (5 μg/l) at site A, Nitrate (1.3 μg/l) at site A and Nitrite (0.4 μg/l) at site C were observed in Mirissa harbour. Meanwhile, salinity, suspended solids, BOD, ortho-phosphate, Nitrate and Nitrite varied significantly between three sampling sites in Puranawella harbour ($p<0.05$). The highest values of salinity (37.6 ppt), suspended solids (0.43 g/l), BOD (5.46 mg/l), ortho-phosphate (8 μg/l), Nitrate (1.4 μg/l) and Nitrite (0.3 μg/l) were observed at site A which is near the jetty of Puranawella harbour.

However, only suspended solids and DO varied significantly between Mirissa and Puranawella harbours during the period of study ($p<0.05$).

Selected pollutants

Floatable grease and oil were analysed during only one sampling time due to unavoidable reasons. Concentrations of grease and oil (ppm) are given in table 2. Relatively higher concentrations of grease and oil were observed at bottom layers in both the harbours. Also, relatively higher grease and oil concentration was observed in Puranawella harbour than in Mirissa harbour.

Location	Site A		Site B	Site C	
	S	B	S	S	B
Mirissa	12	34	4	9	15
Puranawella	14	48	8	12	26

Table 2. Concentration of floatable grease and oil (ppm) in two harbours in May 2007. S denotes sufearce and B for bottom.

Mean concentrations of Cu, Cd and Pb at the three sampling sites in Mirissa and Puranawella harbours during months of sampling are given in table 3 and table 4 respectively. Since there were no significant variations between layers of sampling except for few cases mean concentrations at the three sites are included in table 3 and table 4. Cu and Cd concentrations in water of site A in Mirissa harbour varied significantly between surface, middle and bottom layers. Cu concentration in site A and Cd concentration in site B in Puranawella harbour varied significantly between surface, middle and bottom layers. According to Post Hoc multiple comparison tests metal concentrations in bottom layers show significant differences than in other two layers only at site A and site B ($p<0.01$). Therefore, the highest concentration of Cu (0.19 mg/l) and Pb (1.12 mg/l) in Mirissa harbour was observed at bottom layers in site A during May and June respectively. Similarly the highest concentration of Cu (0.22 mg/l) and Pb (1.16 mg/l) were observed at the bottom layers in site A and site B respectively in Puranawella harbour during May and June. Meanwhile, Cu, Cd and Pb concentrations varied significantly between the three sampling sites in Mirissa harbour ($p<0.05$). Post Hoc multiple comparison tests show that significant difference of metal concentrations in water from site A than in other two sites in both harbours. However, only Cu concentration varied significantly between site A, site B and site C in Puranawella harbour. Also, only the concentration of Pb in water varied significantly between Mirissa and Puranawella harbours

Table 3 Mean concentrations (±SE) of Cu, Cd and Pb in water (mg/l) at three sampling sites (A, B and C) in Mirissa harbour

Metal	March			May			June			July		
	A	B	C	A	B	C	A	B	C	A	B	C
Cu *	0.13 ± 0.00	0.10 ± 0.00	0.13 ± 0.00	0.17 ± 0.00	0.07 ± 0.01	0.11 ± 0.02	0.13 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.14 ± 0.00	0.07 ± 0.00	0.11 ± 0.01
Cd *	0.12± 0.00	0.10± 0.00	0.10 ± 0.00	0.16 ± 0.01	0.07 ± 0.01	0.07 ± 0.00	0.10 ± 0.00	0.12 ± 0.00	0.13 ± 0.00	0.12 ± 0.01	0.12 ± 0.00	0.01 ± 0.00
Pb *	0.90 ± 0.04	0.76± 0.00	0.68 ± 0.00	0.85 ± 0.05	0.87 ± 0.05	0.87 ± 0.05	1.1 ± 0.00	0.62 ± 0.01	0.96 ± .0.02	0.74 ± 0.01	0.66 ± 0.01	0.96 ± 0.01

*: $p<0.05$: significant difference between three sampling sites

Table 4 Mean concentrations (±SE) of Cu, Cd and Pb in water (mg/l) at three sites (A, B and C) in Puranawella harbour

Metal	March			May			June			July		
	A	B	C	A	B	C	A	B	C	A	B	C
Cu *	0.16 ± 0.02	0.05 ± 0.01	0.13 ± 0.03	0.18 ±0.01	0.06 ± 0.00	0.05 ± 0.01	0.16 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.19 ± 0.02	0.03 ± 0.00	0.13 ± 0.00
Cd	0.08 ± 0.00	0.08± 0.00	0.09 ± 0.00	0.12 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.09 ± 0.01	0.11 ± 0.02	0.10 ± 0.00	0.12 ± 0.00	0.13 ± 0.00	0.12 ± 0.00
Pb	0.92 ± 0.02	0.97± 0.01	0.92 ± 0.00	0.85 ± 0.02	0.73 ± 0.01	0.72 ± 0.01	0.99 ± 0.02	0.98 ± 0.08	1.15 ± 0.01	0.92 ± 0.03	0.98 ± 0.04	1.11 ± 0.02

*: $p < 0.05$ significant difference between three sampling sites

Mean concentrations of metals in sediments during the study period are given in tables 5 and 6 respectively for Mirissa and Puranawella harbours. Cu and Pb concentrations in sediments varied significantly between the three sampling sites in two harbours. According to Post Hoc multiple comparisons tests show that significant difference of Cu and Pb concentrations in sediments in site A than in other two sites in two harbours ($p<0.01$). Therefore, the highest concentration of Cu (0.19 mg/g dw) and Pb (0.23 mg/g dw) in sediments in Mirissa harbour and Pb (0.47 mg/g dw) in Puranawella harbour were observed near harbour jetty (site A). However, only concentration of Pb in sediment varied significantly between Mirissa and Puranawella harbours ($p<0.01$).

Microbial parameters

Most Probable Number of coliforms and feacal coliforms in site A, site B and site C in two harbours during the study period are given in table 7. The highest number of coliformr was observed near harbour jetty (site A) in two harbours. The number of coliforms at the site A and site C exceeded the recommended value (<100/100ml) by Central Environmental Authority (CEA) Sri Lanka. Also, feacal coliforms at the site A in two harbours exceeded the value recommended (<20/100ml) by CEA.

Table 5 Mean concentrations (±SE) of metals in sediments (mg/g dw) in Mirissa harbour during the study period

Metal	March			May			June			July		
	A	B	C	A	B	C	A	B	C	A	B	C
Cu *	0.16 ± 0.00	0.05 ± 0.00	0.07 ± 0.00	0.16 ± 0.00	0.06 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.04 ± 0.00	0.06 ± 0.00	0.19 ± 0.00	0.02 ± 0.00	0.08 ± 0.01
Cd	0.003 ± 0.000	0.004± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.003 ± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.004 ± 0.000	0.005 ± 0.000	0.004 ± 0.000	0.004 ± 0.000
Pb *	0.23 ± 0.00	0.07± 0.00	0.13 ± 0.03	0.22 ± 0.00	0.12 ± 0.00	0.17 ± 0.00	0.20 ± 0.00	0.09 ± 0.00	0.15 ± 0.00	0.22 ± 0.02	0.12 ± 0.00	0.43 ± 0.00

*: $p < 0.05$: significant difference between three sampling sites

Table 6 Mean concentrations (±SE) of metals in sediments (mg/g dw) in Puranawella harbour during the study period

Metal	March			May			June			July		
	A	B	C	A	B	C	A	B	C	A	B	C
Cu *	0.11 ± 0.00	0.04 ± 0.00	0.15 ± 0.00	0.10 ± 0.00	0.05 ± 0.00	0.15 ± 0.00	0.12 ± 0.00	0.07 ± 0.00	0.13 ± 0.00	0.15 ± 0.00	0.05 ± 0.00	0.34 ± 0.00
Cd	0.005 ± 0.00	0.003 ± 0.00	0.004 ± 0.00	0.003 ± 0.00	0.003 ± 0.00	0.004 ± 0.00	0.004 ± 0.00	0.004 ± 0.00	0.004 ± 0.00	0.004 ± 0.00	0.004 ± 0.00	0.004 ± 0.00
Pb *	0.40 ± 0.00	0.20 ± 0.05	0.33 ± 0.01	0.47 ± 0.01	0.34 ± 0.01	0.26 ± 0.00	0.25 ± 0.00	0.26 ± 0.00	0.11 ± 0.01	0.28 ± 0.01	0.19 ± 0.00	0.15 ± 0.00

*: $p < 0.05$: significant difference between three sampling sites

Table 7. Most Probable Number (MPN) of coliforms and feacal coliforms (in 100 ml) in two harbours

Month	MPN for coliforms in 100ml of original water					
	Mirissa harbour			Puranawella harbour		
	Site A	Site B	Site C	Site A	Site B	Site C
May	1800+	25	275	1800+	20	900
June	1800+	14	275	1600	25	900
July	1800+	25	900	1800+	70	550
	MPN for feacal coliforms in 100ml of original water					
May	35	3	14	275	5	17
June	20	2	12	250	4	14
July	25	2	11	250	2	17

Discussion

Significant variation of some physico-chemical parameters such as temperature, pH, salinity, ortho-phosphate, nitrate and nitrite in Mirissa harbour at the three sampling sites may reflects the changes of water quality at the sites. Since the depth of Mirissa harbour is around 3m, there may not be depth-wise variation in physico-chemical parameters. Water temperature in Mirissa harbour showed very low value (13.5 ^{0}C) at the site A during one sampling time because of unexpected cold wind during that sampling day. This exceptionally low temperature in site A would have brought about significant temperature variation between sites only in Mirissa harbour. Significant variations of salinity, suspended solids, BOD, ortho-phosphate, nitrate and nitrite between sampling sites in Puranawella harbour reflect the changes of water quality from harbour jetty towards the open sea. Also, relatively high suspended solids and BOD near the harbour jetty may be related to the excess amount of dumping of raw materials from boats and other harbour activities. Amount of suspended solids in Hikkaduwa fishery harbour was reported between 5.2 and 6.6 mg/l (De Alwis *et al.*, 1994). Suspended solids in both Mirissa and Puranawella harbours exceeded the reported value for Hikkaduwa harrbour. Also, BOD level near the harbour jetty (site A) in both harbours exceeded the quality standards for BOD of coastal water (< 4 mg/l) according to Sri Lanka Standard Institution and environmental quality standards (Central Environmental Authority, Sri Lanka). Therefore, it is important to consider about potential threats to human due to use of harbour water for different purposes such as washing fish and cleaning vessels. However, nitrate and nitrite concentrations in Mirissa and Puranawella harbours were lower than the reported values in Hikkaduwa harbour (Nitrate 1.2 – 18.4 µg/l and nitrite 0.11 – 3.8 µg/l respectively) (De Alwis *et al.*, 1994). Significant variation of suspended solids and DO between Mirrissa and Puranawella harbours may be related to the activities of two harbours including the effective area and number of boats anchorage in these harbours. However, the study was done during a short period of time and no replicate data are available for each sampling time to discuss temporal variation of physico-chemical parameters.

According to Subrahmayam and Ananthalashmi (1990), Cu concentration in water at surface and bottom layers were higher in harbours when compared to other coastal waters possibly due to vessel coating paints and other sources. Significant variations of Cu concentration in water and sediments between three sampling sites in both harbours were observed. Also, the highest concentrations of Cu and Pb were observed at bottom layers near the jetty of two harbours (site A), which may be due to contamination of vessel coating paints and fuel wastes including crude oil. The significant variation of Pb concentration in water between Mirissa and Puranawella harbours may be related to the number of boats anchorage in two harbours. The capacity of anchorage boats in Puranawella harbour (400) is relatively higher when compared to the number of boats in Mirissa harbour (250). Puranawella harbour is therefore more contaminated with fuel wastes than Mirissa harbour. Cd concentration in Visakhapuyam harbour in India was reported as 0.2 g/l and 0.5 g/l at surface water and at 6m depth respectively (Subrahmanyam and Ananthalakshmi, 1990). Cd concentration in water in both harbours was lower than the reported values in Visakhapuyam harbour in India. Concentrations of Cu, Cd and Pb in sediments in both harbours were lower than concentrations of these metals in some other harbours such as Satem, Boston, Portland and Saint John harbours world wide (Larsen *et al.*, 1992). The significant difference of Cu and Cd concentration in sediment between sampling sites in both harbours shows relatively higher concentrations near the harbour jetty than in open sea sampling sites. The impact of boat anchorage is reflected by the significant difference of Pb in sediments of two harbours. Higher number of boats in Puranawella harbour may be related to relatively higher Pb content in sediment. From the limited information about the oil content in water (as they were analysed during one sampling occasion in both harbours), relatively higher oil content is evident in Puranawella harbour than in Mirissa harbour. Feacal coliform counts were reported exceeding the recommended values near the jetty in both harbours and it may be related to high levels of suspended solids and BOD at those sites.

Conclusions

Physico-chemical characteristics were similar in both harbours except the observed significant differences of suspended solids and BOD. Also, water and sediment near harbour jetty were highly contaminated with suspended solids, metals, oil and feacal coliforms. Concentration of Pb in water and sediments varied significantly between both harbours and relatively higher values were observed in Puranawella harbour due to more fishing vessel anchorages in this harbour than in Mirissa harbour. In the present study however, the resilience capacity in water was not investigated. Therefore, further investigations are needed to study temporal variations of physico-chemical parameters and levels of pollutants in harbours.

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