Indian J. Fish., 58(2) : 75-83, 2011

Assimilative capacity of Cochin inshore waters with reference to contaminants received from the backwaters and the upstream areas

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ABSTRACT

Assimilative capacity of inshore waters off Cochin was assessed using data on hydrography, photosynthetic pigments, primary productivity, dissolved nutrients and trace metals collected over a period of three years (April 2003 - October 2006) from selected stations spreading over the source to the sink. Assimilative indices for Cochin estuary and inshore waters off Cochin were worked out and a scale of safe, desirable, caution or critical was attributed with regard to different parameters based on the score. The results revealed that in the estuary, total suspnded solids (TSS) and cadmium have reached critical levels and lead have attained levels of cautiion. Similarly, in the Cochin inshore waters, cadmium have reached critical levels while copper and lead have attained levels of caution.

Keywords: Assimilative capacity, Coastal pollution, Cochin inshore waters, Industrial contaminants, Primary production, Trace metals, Water quality

Introduction

Assimilative capacity is defined as the ability of an area to maintain a "healthy" environment and to accommodate the contaminants it receives. Cochin inshore areas along the south-west coast of the Arabian Sea receives water, sediment and silt from the extensive Vembanad Lake system at Ernakulam (Cochin barmouth) and at Munambam (Azheekode barmouth), discharged from the lower reaches of Periyar River. The urbanization, industrialization and related anthropogenic activities produce a large quantity of sewage and effluents laden with toxic contaminants that are discharged into the Cochin barmouth through the backwaters. More than 240 industrial units operating in Edayar village of Eloor panchayath make this part of the river into a cesspool of chemical pollutants. The volume of industrial effluents from Eloor- Kalamasery belt is about 2.6 million litres per day (Menon *et al.,* 2000; Greenpeace, 2003), much of which is discharged directly into the Periyar River from where it is emptied into Cochin backwaters. Frequent instances of fish kill along this belt especially during the south-west monsoon is a common affair (Unnithan *et al.,*1977; Greenpeace, 2003).

Cochin backwater (300 sq. km) is a positive estuarine system spreading from lat. 9^{O} 40' N - 10^{O} 12' N and long. 76^{O} 10' E - 76^{O} 30' E, receiving freshwater discharge from three major rivers of Kerala namely, Periyar, Muvattupuzha and Chalakudy (Sankaranarayanan *et al*., 1986). The common contaminants of Cochin backwaters are acids, alkalis, suspended solids, fluorides, free ammonia, insecticides, dyes, trace metals and radioactive nuclei (Lakshmanan *et al.,* 1987; Menon *et al*., 2000). The effluents from Ambalamugal located 16 km east of Cochin, which is an industrial complex with a giant fertilizer plant and an oil refinery, are discharged into Chitrapuzha which ultimately flows into the Cochin backwaters.

Mercury dissolved in offshore surface waters along the north-east coast (Kaladharan *et al*., 1990) and that of west coast of India (Kaladharan *et al*., 1999) indicate certain hotspots which are attributed to the runoff and river discharge. Variable distribution of dissolved nutrients in Cochin backwaters was studied by Lakshmanan *et al.* (1987). Considerable work on primary productivity in Cochin backwaters has been done by Qasim *et al.* (1969), Qasim (1973; 1979), Gopinathan *et al.* (1984) and Kaladharan *et al.* (1990). Environmental deterioration taking place in Cochin backwaters has been addressed by Gopalan and Nair (1975); Unnithan *et al.* (1977); Qasim and Madhupratap (1979) and Gopalan *et al.* (1983). Seasonality in the distribution of heavy metals in marine sediment as well as in certain finfishes and shellfishes of inshore waters of Cochin were addressed by Nair and Nair (1986) and Kaladharan *et al.* (2005).

As river water mixes with seawater at the estuary, metals and other contaminants may be lost or transformed from soluble form to the sediments by flocculation or to the plankton and macrophytes by adsorption and bioaccumulation (Bardovsky, 1964; Salomons, 1989) and finally get assimilated. The present communication attempts to assess the assimilative capacity of inshore waters of Cochin adjoining the Cochin backwaters which has been experiencing a lot of anthropogenic pressures during the last few decades.

Materials and methods

Sampling sites

Monthly data collected on water quality parameters such as trace metals as well as other contaminants, chlorophyll pigments and primary production from 11 sampling sites for a period of three years (April 2003 – October 2006) were used for the present study. Coordinates of the sampling sites covering the sea, estuary and backwaters were recorded using a hand held GPS (Garmin, Model Etrex) and plotted in a map as shown in Fig. 1.

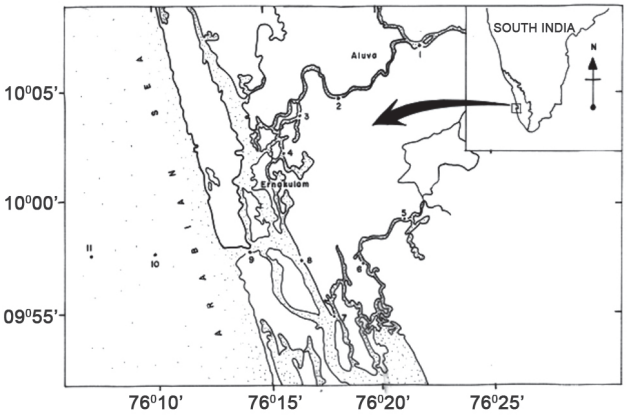

Fig. 1. Map showing the location of study sites

Station 1 is located at Thottumugham near Aluva which is a comparatively clean station in the upstream area of Cochin backwater system of Periyar River and is referred as BW. Stations 2- 4 are areas grouped as BW1 spread over northern part of Cochin backwater that receives effluents from Edayar industrial belt which is flocked by more than 230 chemical factories and industries manufacturing or processing fertilizers, chemicals, bioacids, metals, rutile, catalysts, dyes, tyres, machine tools, soaps, detergents, radioactive materials, pesticides, petroleum products, aviation fuels, rayon pulps *etc*. Stations 5-7 are grouped as BW2 which receives effluents from Ambalamugal unit of FACT and Cochin Refinery which are located at the southern part of Cochin backwaters. Stations 8 and 9 are in the estuary adjoining the Cochin Shipyard Ltd. and the Willingdon Island and are grouped as estuary. Stations 10 and 11 are located in the inshore areas along the ship channel at 10 m and 20 m depths respectively and are grouped as sea.

Methods

Water samples in duplicate, preferably during the morning hours, were collected using a PET Nansen reversing bottle (Hydrobios, Germany) onboard RV *Cadalmin* from the estuary (Stn. 8 and 9) as well as from the sea (Stn. 10 and 11) and using a clean plastic bucket on a small canoe from the backwaters (Stn. 1-7). Upon collection, samples were transferred to clean polythene bottles in an ice box and transported to the laboratory for analyses. Sea surface temperature (SST) was measured *in situ* with a bucket thermometer (0.5 ^{O}C accuracy). Sea bottom temperature (SBT) was measured from the reversing thermometer attached to the Nansen water sampler. The hydrogen ion concentration (pH) and salinity of the water was also measured *in situ* using multiparameter meter (WTW LF320, Germany).

Standard procedures were adopted for estimating ammonia, Ammonia biological oxygen demand (BOD) and total suspended solids (TSS) from water samples collected (APHA, 1998). Dissolved nutrients such as nitrate, nitrite, silicate and phosphate, chlorophyll pigments (glass fibre filters 0.45 µ Whatman), dissolved oxygen and primary productivity were determined according to standard procedures (Strickland and Parsons, 1968; Parsons *et al.,* 1984). Water samples were filtered (through 0.45 µ GF/C filters, Whatman) and trace metals such as cadmium, copper, lead, and zinc (µg l^{-1}) were determined from water samples directly by using anode stripping voltametry technique following the methods of Anoop *et al.* (2007). Briefly, total dissolved Zn, Cd, Pb and Cu were estimated using Differential Pulse Anodic Stripping Voltammetry (DPASV) by adding 10 ml sample and 1 ml acetate buffer in a Teflon cell. The concentrations of these metals were simultaneously measured by addition of mixed metal standards using Dosimat. The detection limit for Zn, Cd, Pb and Cu were 500, 50, 50 and 50 ppt respectively. A hanging drop electrode was used as working electrode and potential was measured against potassium chloride reference electrode and an auxiliary platinum electrode. The results presented are blank corrected. The accuracy of the analytical procedure was checked using certified reference material BCR e 403 (Community Bureau of Reference). The recovery was 99% for all metals studied, which was estimated by measuring standard spiked samples.

Box and whisker plot showing median (centre value), lower, upper quartiles (minimum and maximum values respectively) for different parameters were generated using the SPSS 13 software. Analysis of variance (ANOVA) test was utilized to study the effect of sampling zones, season and year on different environmental parameters.

To find out the level of assimilation over space and time, the data collected were analysed by zones such as river (BW) backwater (BW1 and BW2), estuary and sea (inshore region) as well as by season.

Results

Hydrography

Salinity (Fig. 2) in the backwater region was higher (3.8 ppt) than river (BW) and lower than estuary (22.64 ppt) and sea (31.12 ppt) as expected. Among the backwater areas, Edayar region (BW1) was less saline than the Ambalmugal region (BW2) during the south-west monsoon as well as premonsoon months and in the estuary during the postmonsoon months (Fig. 2). Dissolved oxygen levels in the inland (river and backwaters), estuary and seawater did not show much variation (Table 1). The river (BW) and backwater regions (BW1 and BW2) were characterized by acidic pH (6.64). However, the estuarine and sea regions were alkaline (7.42 and 7.69, respectively). During the premonsoon months, the water pH in all the regions remained higher than the monsoon and

Table 1. Mean values of certain water quality parameters from inland (river and backwaters), estuary and sea regions of Cochin inshore areas for computing assimilative factors

	TSS (mg l^{-1})	BOD (mg l^{-1})	NH_3 (µg at l^{-1})	PO_4 (µg at l^{-1})	NO_2 (µg at l^{-1})	SiO_3 (µg at l^{-1})	Zn (µg l^{-1})	Cu (µg l^{-1})	Cd (µg l^{-1})	Pb (µg l^{-1})
Inland	24.89	2.13	28.42	11.09	0.98	91.65	115.48	1.92	2.33	2.68
Estuary	55.42	1.73	2.70	1.51	0.43	33.75	29.48	2.03	0.47	2.69
Sea	41.36	1.58	0.75	0.79	0.37	14.07	23.20	1.46	0.53	3.17

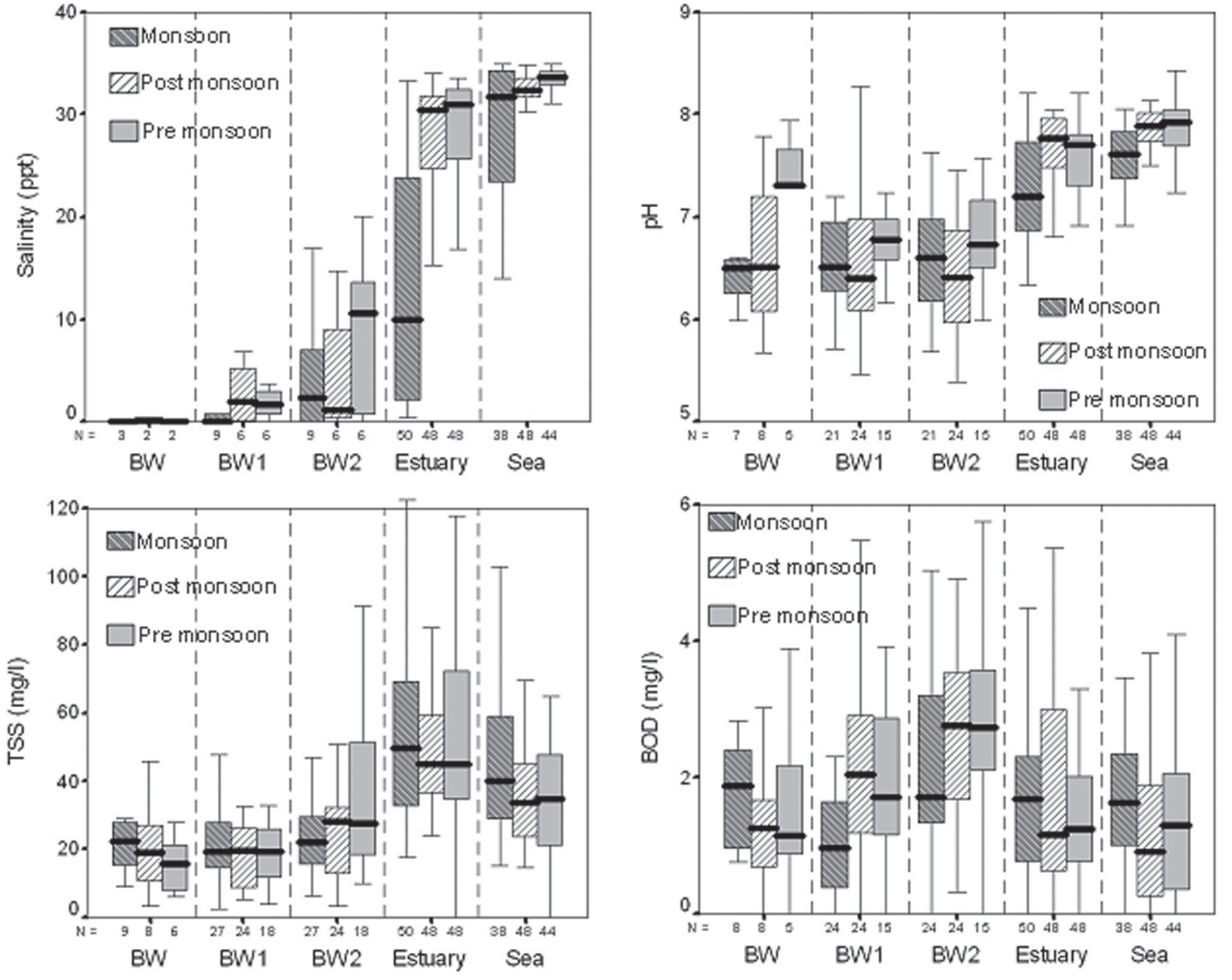

Fig. 2. Box and whisker plot showing median (centre value), lower, upper quartiles and the smallest and greater values for salinity, water pH, TSS and BOD at different sampling zones, covering three seasons (N = Number of samples)

postmonsoon months (Fig. 2). Reduction in pH during the monsoon months was quite conspicuous in the estuary as well as in sea. Whereas in both the backwaters (BW1 and BW2), pH values were higher during monsoon than the post monsoon season.

Water temperature in both estuarine and inshore areas showed similar trend during the three seasons without much variation. Biological oxygen demand (BOD) levels were well within the safe limits in the three domains, however, remained higher (2.13 mg l^{-1}) in the backwaters (Table 1). Considerable increase in BOD levels during monsoon period over the non monsoon periods could be observed from estuarine stations (1.67 mg l^{-1}), marine stations (1.67 mg l^{-1}) and in riverine stations (1.89 mg l^{-1}) than the backwater stations (Fig. 2).

Total suspended solids (TSS) ranged from 24.88 mg l^{-1} in the inland to 55.42 mg l^{-1} in the estuary and 41.36 mg l^{-1} in the sea region (Table 1). Values of TSS (Fig. 2) were higher in river, estuary and sea during monsoon than the non-monsoon season. However, backwaters adjoining Ambalamugal (BW2) registered higher mean values of TSS during premonsoon (31 mg l^{-1}) and postmonsoon (33 mg l^{-1}) seasons than during the monsoon months (Fig. 2).

Chlorophyll and primary productivity

Mean values of photosynthetic pigment Chl *a* in the river and backwater regions showed a mean of 1.14 mg m^3, whereas the same in the estuary was 0.91 mg m^3 and in the sea was 0.43 mg m^3. Except the inshore region, all the domains registered higher levels of chlorophyll *a* pigments during premonsoon months than the monsoon and postmonsoon season. In the inshore waters, maximum concentration of Chl *a* was recorded during monsoon season. Among all the regions, BW2 adjoining Ambalamugal area recorded maximum concentration of Chl *a* (Fig. 3).

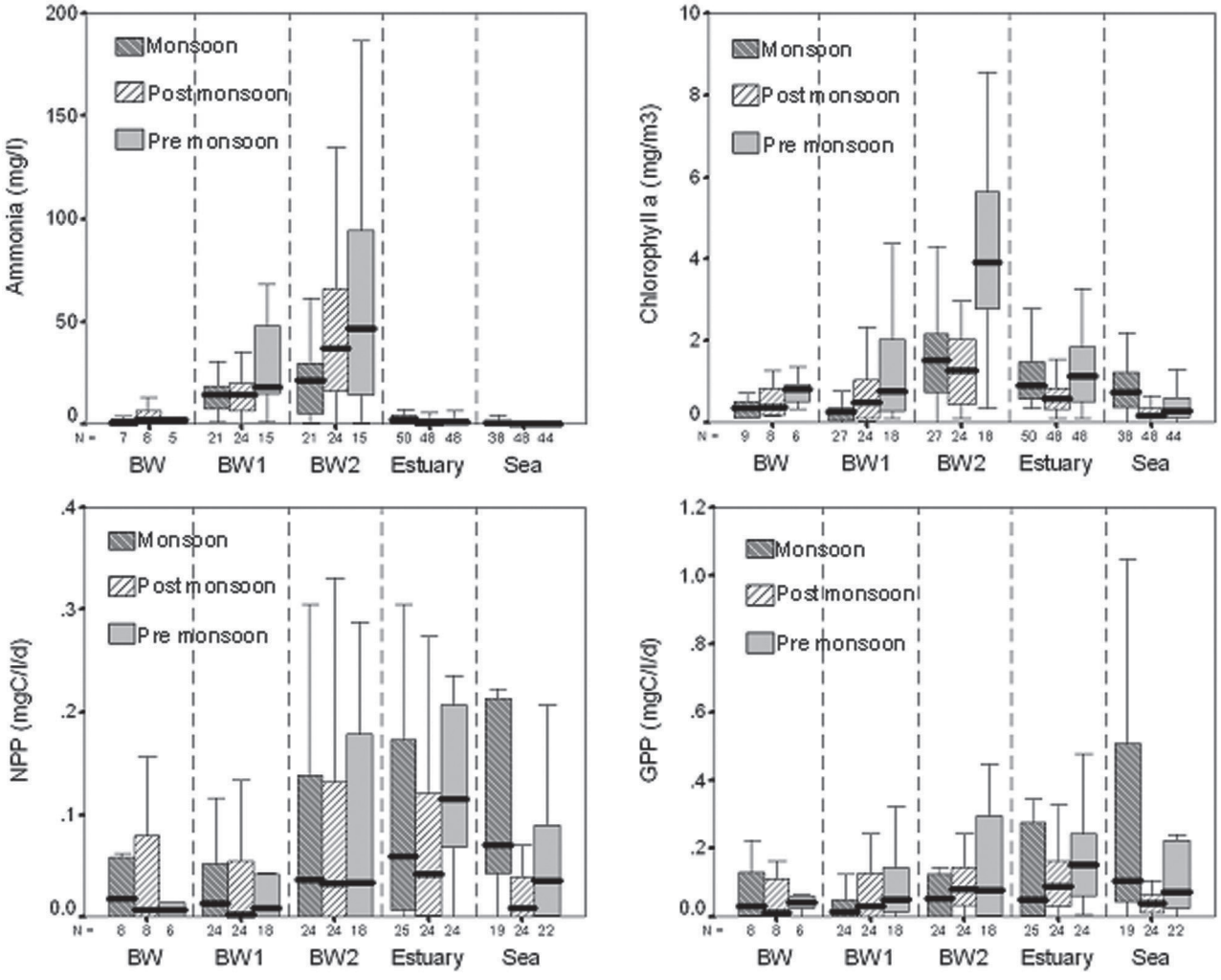

Fig. 3. Box and whisker plot showing median (centre value), lower, upper quartiles and the smallest and greater values for ammonia, chlorophyll *a* and productivity (net and gross) at different sampling zones, covering three seasons (N = Number of samples)

The estuary recorded higher levels of gross primary productivity (GPP) as well as net primary productivity (NPP) than the inland regions. Monsoon season registered maximum GPP in sea and minimum in BW1 (Fig. 3). Premonsoon season recorded maximum GPP (0.175 mg C l^{-1} d^{-1}) in the estuary and minimum of 0.063 mg C l^{-1} d^{-1} in both river as well as in BW1 (Fig. 3). NPP also followed almost similar trend during the three seasons.

Dissolved nutrients

Ammonia also followed similar trend showing highest values (28.42 µg at l^{-1}) in the backwaters, and the lowest (0.75 µg at l^{-1}) in the inshore areas indicating assimilation in the estuary as well as in the inshore regions (Table 1). Ammonia levels remained higher in BW2 than the inshore area as well as the river (BW) (Fig. 3). BW1 and BW2 registered peak levels of ammonia during the premonsoon months, whereas the estuary and the inshore regions encountered peak levels of ammonia during the monsoon months (Fig. 3).

Phosphates showed a mean of 11.09 µg at l^{-1} in the inland regions, 1.51 µg at/l in the estuary and 0.79 µg at l^{-1} in the sea (Table 1). In the backwaters, BW2 registered maximum level especially during the premonsoon season (Fig. 4). Estuary and sea regions showed minimum levels of PO_4 during postmonsoon season and the river station (BW) had very negligible levels of (Fig. 4). Nitrite levels also showed a trend similar to phosphates with 0.98 µg at l^{-1} in the inland, 0.43 µg at l^{-1} in the estuary and 0.37 µg at l^{-1} in the inshore waters (Table 1) and maximum concentration in BW2 and the maximum levels were observed during the postmonsoon season (Fig. 4).

Nitrates and silicates registered maximum concentration in inland regions and exhibited gradual decline towards inshore waters registering minimum levels (Table 1) in the sea. Their levels attained maximum during monsoon season. However, their levels remained low during premonsoon season for nitrates and during the postmonsoon months for silicates (Fig. 4).

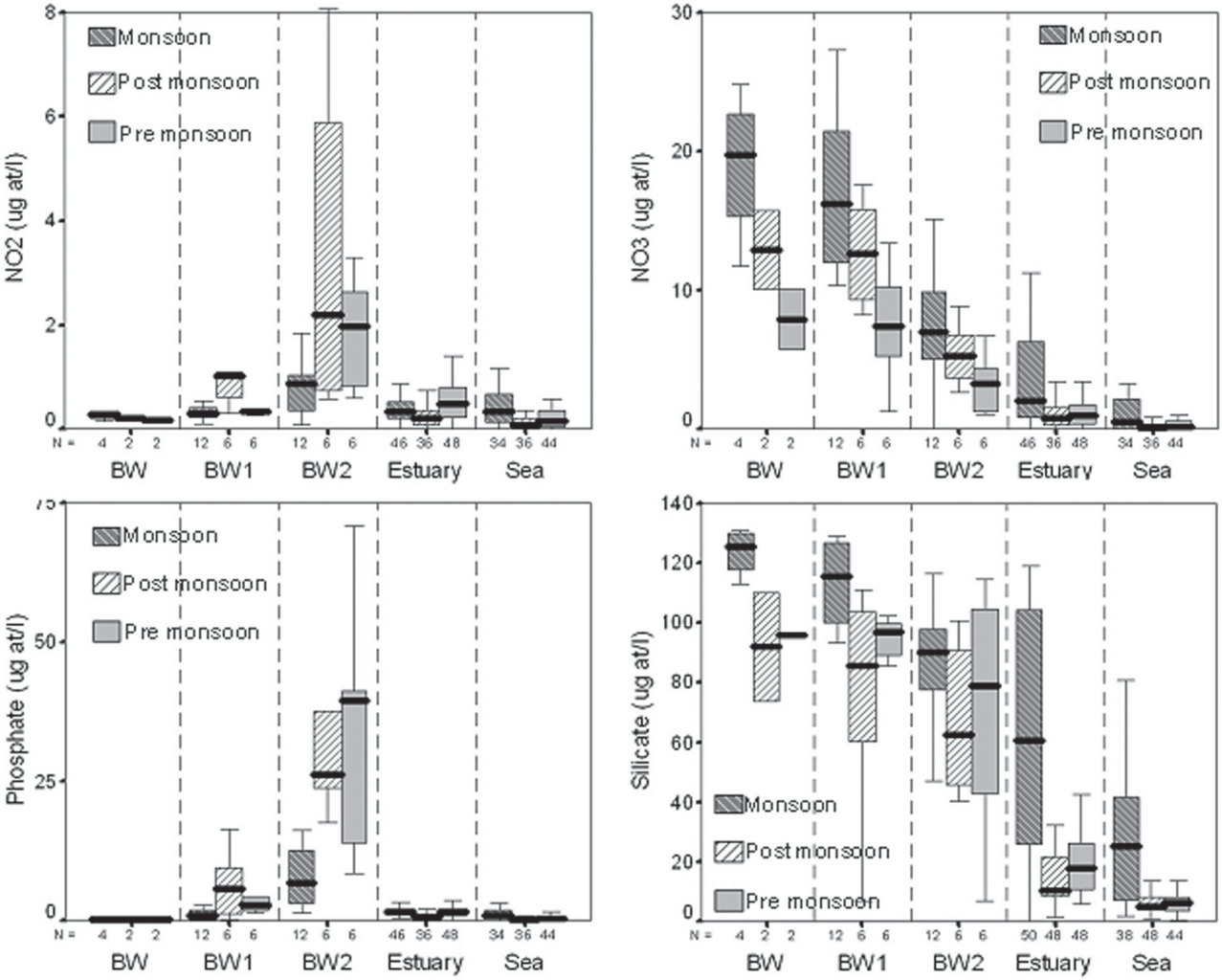

Fig. 4. Box and whisker plot showing median (centre value), lower, upper quartiles and the smallest and greater values for nutrients (nitrite, nitrate, phosphate and silicate) at different sampling zones, covering three seasons (N = Number of samples)

Metals

Mean values of trace metals such as Zn and Cd recorded higher levels in river and backwaters (Zn: 115 µg l^{-1} and Cd: 2.33 µg l^{-1}) than in estuary and in the inshore area (23.2 µg l^{-1} and 0.53 µg l^{-1} respectively). Whereas, copper registered highest value (2.03 µg l^{-1}) in the estuary followed by backwaters (1.92 µg l^{-1}) and sea (1.46 µg l^{-1}). Unlike other metals, Pb concentration remained higher in the sea (3.17 µg l^{-1}) than in the estuary and in the backwaters (Table 1).

Cadmium concentration among the backwater stations remained higher in BW2 than in BW. Monsoon as well as postmonsoon months registered maximum inflow of Cd into the estuary and to the inshore waters than during the premonsoon months (Fig. 5). Copper remained higher in backwaters of Edayar region (BW1) especially during monsoon season, whereas backwaters of Ambalamughal region (BW2) showed very low levels as equal to that of river (BW) stations (Fig. 5). Seasonal fluctuation in the distribution of Pb was not significantly evident in any of the regions (Fig. 5). Zinc also remained higher in BW1 region and the postmonsoon season accounted for maximum concentration (Fig. 5).

Summary of results of multi-way analysis of variance (ANOVA) showing the influences of sampling zone, year and season of sampling as measured by F-ratio and level of significance (p) are shown in Table 2. Significant differences were observed in values of most of the parameters between the sampling zones, except for the parameters such as NPP, and lead. Significant differences were also observed in values of most of the parameters between the years of sampling, except for the parameters such as pH, NH_3, Chl *a*, zinc, copper and cadmium. For sampling seasons, significant differences were observed in values of most of the parameters, except for TSS, BOD, NH_3, NO_2, PO_4, GPP, NPP, zinc, copper and cadmium.

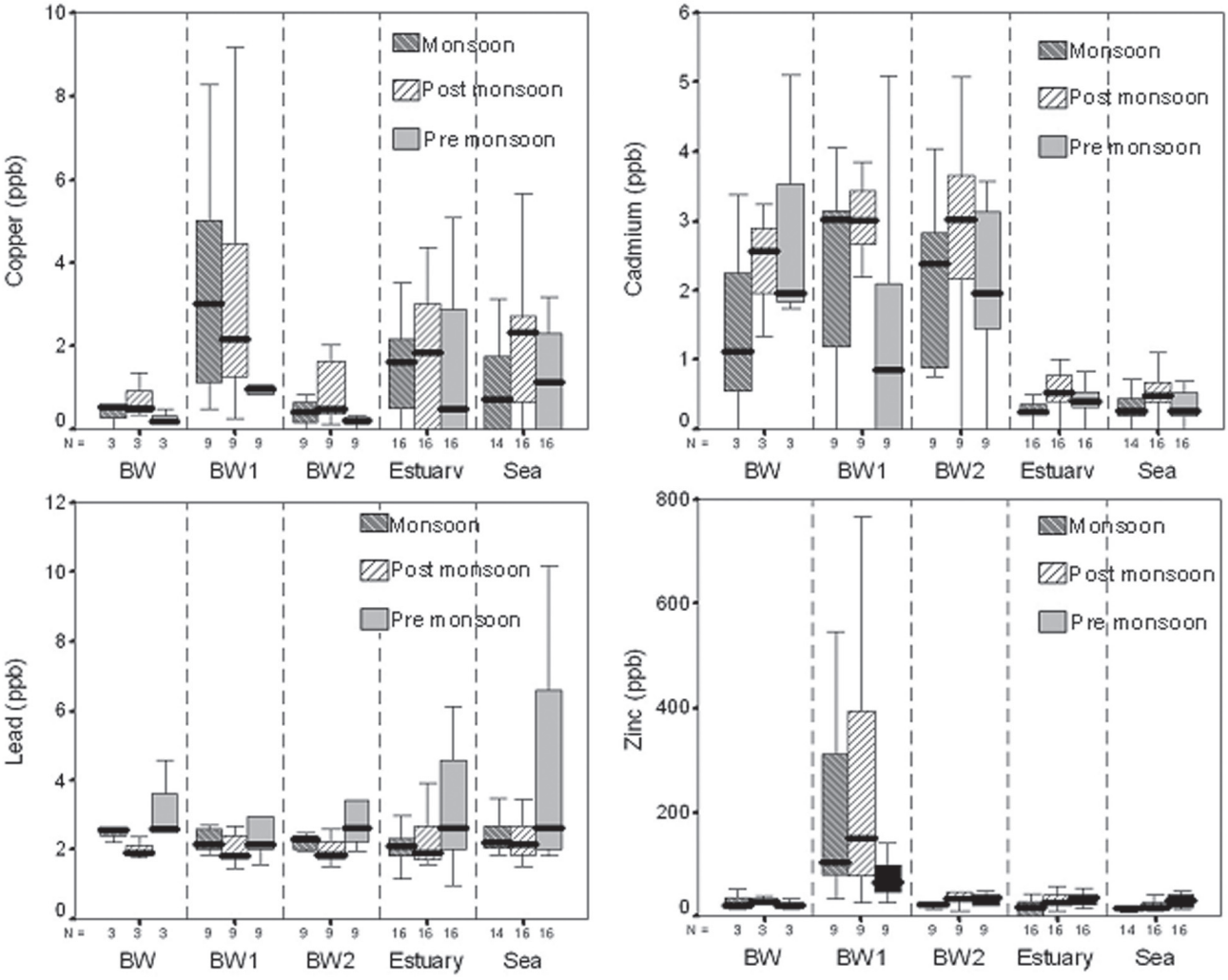

Fig. 5. Box and whisker plot showing median (centre value), lower, upper quartiles and the smallest and greater values for trace metals (copper, cadmium, lead and zinc) at different sampling zones, covering three seasons (N = Number of samples)

Table 2. Assimilative factors of various contaminants for estuary and the inshore waters of Cochin

Assimilation Factor	TSS	BOD	NH_3	PO_4	NO_2	NO_3	SiO_3	Zn	Cu	Cd	Pb
Estuary	2.23	0.81	0.09	0.14	0.44	0.2	0.37	0.26	1.06	2.0	1.0
Sea	0.75	0.91	0.28	0.5	0.86	0.39	0.42	0.79	0.72	1.13	1.18

Discussion

Cochin backwaters joining the receive effluents from the upstream and seawater from the inshore areas through intrusion at different magnitudes in different seasons. Our results (Fig. 2) indicate that among the backwater regions, Edayar region (BW1) is less saline than that of Ambalamughal region (BW2) during the SW monsoon season as well as premonsoon months and the other way round during the postmonsoon months indicating possibly that the intrusion of seawater in BW2 and river runoff is more towards BW1 region than BW2. Intrusion of seawater is felt upto Kalamaserry (Sankaranarayanan *et al.,* 1986) more than 12 km away from the barmouth. Increase in water pH (Fig. 2) in both the backwater systems during the monsoon over the postmonsoon period also indicates possible transport of industrial effluents or contaminants through runoff at higher rate during monsoon. Maximum load of TSS in the estuary accumulated from both the backwater systems (BW1 and BW2) as depicted in Fig. 2 is indicative of initiation of assimilation process in the estuary and its completion in the inshore waters.

The trace metal distribution in the coastal environments, to a great extent is influenced by freshwater inflow (Riley and Chester, 1971) and terrestrial contamination and anthropogenic inputs (Kremlin and Petersen, 1984). Cochin backwater is known to contain higher concentration of almost all trace metals during premonsoon and postmonsoon (Nair *et al*., 1990). Premonsoon months registered maximum levels of dissolved nutrients as well as maximum concentration of chlorophyll pigments in the backwaters especially BW2 region (Fig. 3 and 4; Table 1) which might be due to large volumes of effluents released prior to the onset of monsoon. Very high level of PO_4 especially in BW2 alone (Fig. 4) may be due to the inputs from the fertilizer factory near the Ambalamughal area which is subsequently utilized by the water hyacinth population.

The type of effluents/ contaminants especially in the case of metals in BW1 region is considerably different from that of BW2 region as evidenced from the results presented. The metal Pb is found unassimilated in the inshore waters as well as in the estuary. It is felt that Pb levels are added from the inshore waters released possibly through anthropogenic activities such as mechanized fishing, shipping and port activities. However, metals such as Zn and Cu originate from the backwaters and get assimilated in the inshore waters along the estuary.

Table 3. Summary of results of multi-way analysis of variance (ANOVA) showing the influences of sampling zone, year and season of sampling as measured by F-ratio and level of significance (p)

Parameters	Sampling zone		Year		Season	
(Main effects)	F- ratio	p	F- ratio	p	F- ratio	p
Salinity	90.77	0.0000	23.26	0.0000	28.32	0.0000
DO	7.36	0.0000	4.89	0.0024	15.12	0.0000
pH	35.66	0.0000	3.33	0.0197	14.00	0.0000
TSS	26.20	0.0000	14.92	0.0000	1.17	0.3112
BOD	5.02	0.0006	6.80	0.0002	1.86	0.1564
NH_3	63.23	0.0000	1.56	0.1976	0.99	0.3727
NO_2	18.27	0.0000	4.12	0.0070	0.03	0.9690
NO_3	124.54	0.0000	13.09	0.0000	21.67	0.0000
PO_4	70.95	0.0000	7.19	0.0001	0.48	0.6212
SiO_3	77.66	0.0000	19.62	0.0000	48.98	0.0000
Chla	14.56	0.0000	1.45	0.2271	5.53	0.0043
GPP	3.87	0.0044	12.98	0.0000	3.92	0.0210
NPP	2.99	0.0193	11.35	0.0000	3.53	0.0305
Zn	12.95	0.0000	1.11	0.2927	1.75	0.1771
Cu	6.27	0.0001	1.98	0.1612	2.72	0.0693
Cd	25.88	0.0000	0.14	0.7058	2.54	0.0820
Pb	0.53	0.7112	14.31	0.0002	12.29	0.0000

The higher levels of trace metals observed during the non-monsoon months than the monsoon may be attributed to the concentration of these metals in the stagnant water during the non-monsoon months (Holmes, 1986). However, Ouseph (1987) felt that the increased levels of metals during the premonsoon season may be due to the intrusion of seawater. Higher levels of Zn in the effluents from the industrial complex situated at Edayar (Saraladevi *et al.,* 1979) may hold good for the higher concentrations of Zn in BW1. Rajendran and Kurian (1986) pointed out that, overall seasonal pattern of heavy metal load in water was not evident in Cochin backwaters. However, Lakshmanan *et al*. (1987) reported marked seasonal variation in distribution of dissolved nutrients from Cochin backwaters due to the inputs received from industrial units and through land runoff. Marginally higher concentrations of Cu during monsoon than the premonsoon and postmonsoon period were observed by Mohapatra and Rangarajan (2000). Kumaraguru (1980) in the Vellar estuary and Killi backwaters of South India, noticed a trend similar to this. Senthilnathan and Balasubramanian (1998) observed distinct seasonal pattern, in the distribution of trace metals with higher level of Cd, Pb and Zn during monsoon and lower levels in summer season.

The observation on primary productivity during the monsoon season is agreeable with that of Madhupratap (1987) that intense organic production in Cochin backwaters coincides with the retreat of SW monsoon. The settling of organic matter in the coastal water bodies facilitates biogenic association of metals in the remaining seasons. Hence it may be considered that the geochemical behavior of the estuary is controlled by the anthropogenic forces, whereas the inshore areas remained free from contaminants as the metals are rapidly removed by coastal currents and biogenic association (Madhupratap, 1987) or get assimilated. The process of metal assimilation in the inshore water is facilitated by flocculation induced by salinity, chelation accelerated by humic substances (Bordovsky, 1964) and utilization or bioaccumulation by flora and fauna (Lakshmanan and Nambisan, 1979; Krishnakumar *et al*., 1990). Humified organic matter, existing in coastal waters either as particulate or as dissolved form is collectively known as humic substances and they are considered natural chelators (Saphiro, 1964) and the inhibitor of toxic effects of certain pollutants (Ying *et al.,* 1996; Barbera *et al.,* 1997).

From the results presented, assimilative factor for estuary (ratio between concentration of contaminants in estuary and their concentration in the backwaters BW1 and BW2) as well as the inshore waters (ratio between concentration of contaminants in the inshore waters (sea) and their concentration in the estuary) were calculated for each contaminant.

Assimilative factor thus computed from our study for each parameter was indexed at 0.5 unit interval as safe (<0.5), normal (>0.5 - <1), caution (>1- 1.5) and critical (>1.5 - 2) based on the level of assimilation. An assimilative factor for a particular input within 0- 0.5 indicates that inputs received either in the estuary from the upstream backwater areas or in the inshore areas from the estuary are completely assimilated and hence considered safe, which revealed that in the Cochin estuary TSS and Cadmium have reached critical levels while copper and lead have reached cautionable levels. Similarly in the Cochin inshore waters cadmium and lead have attained level of caution.

Acknowledgements

The authors are grateful to the Director, CMFRI, Cochin for the encouragement received and to the crew of RV *Cadalmin* for offering field support.

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Date of Receipt : 14.01.2010
Date of Acceptance : 18.04.2011