



## Baseline

## Distribution of trace metals in surface seawater and zooplankton of the Bay of Bengal, off Rushikulya estuary, East Coast of India



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## ARTICLE INFO

## Article history:

Received 28 March 2016

Received in revised form 24 June 2016

Accepted 28 June 2016

Available online 6 July 2016

## Keywords:

Zooplankton

Rushikulya estuary

Trace metals

Seawater

Bioaccumulation factor

## ABSTRACT

Concentrations of trace metals such as iron (Fe), copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni), manganese (Mn), lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), vanadium (V), and selenium (Se) were determined in seawater and zooplankton from the surface waters off Rushikulya estuary, north-western Bay of Bengal. During the study period, the concentration of trace metals in seawater and zooplankton showed significant spatio-temporal variation. Cu and Co levels in seawater mostly remained non-detectable. Other elements were found at higher concentrations and exhibited marked variations. The rank order distribution of trace metals in terms of their average concentration in seawater was observed as Fe > Ni > Mn > Pb > As > Zn > Cr > V > Se > Cd while in zooplankton it was Fe > Mn > Cd > As > Pb > Ni > Cr > Zn > V > Se. The bioaccumulation factor (BAF) of Fe was highest followed by Zn and the lowest value was observed with Ni. Results of correlation analysis discerned positive affinity and good relationship among the majority of the trace metals, both in seawater and zooplankton suggesting their strong affinity and coexistence.

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The coastal waters of most of the regions of the world ocean are under risk of pollution due to increase in coastal migration of human population and establishment of industries prompting excessive use of seawater and sea-based resources coupled with disposal of wastes (Buddemeier et al., 2002). Among several coastal pollution types, trace metal pollution had emerged as an important concern owing to the toxicity and persistency of metals for several decades in the environment through bioaccumulation–biomagnification (Yearley et al., 1998).

Trace metals enter into the marine environment from an array of sources ranging from atmospheric fall out to direct discharge of domestic wastes, industrial effluents, and land drainage. The fate of metals in the marine environment depends on their physical, chemical, and biological dispersal. The formation, consumption, sinking, and demineralization of organic matter regulate the biogeochemistry of trace elements in the marine environment (Donat and Bruland, 1995). In general, plankton (both phytoplankton and zooplankton) interact with dissolved and particulate trace metals of seawater through various processes such as adsorption, desorption, biological uptake, grazing, and microbial decomposition. Zooplankton play a key role in the biogeochemical cycling of trace metals in marine environment because of

their ubiquitous distribution and as intermediate links between the producer (phytoplankton) and consumers in food chains (Lee and Fisher, 1994). Studies relating to the distribution of trace metals in seawater and zooplankton in Indian coastal waters although are many (Table 1). However, reports on distribution of trace metals other than mercury along the Odisha coast are scanty (Rejomon et al., 2008). It is noteworthy to mention that coastal waters of Odisha, especially off Rushikulya estuarine region, are well recognized for hosting the mating process of migratory Olive Ridley sea turtles as well as for capture fisheries. Hence, studies on trace metal concentration in zooplankton and seawater of this ecosystem are very important.

The present study was carried out in the coastal waters of north-western Bay of Bengal, off the Rushikulya estuary (19° 22' 25"N, 85° 05' 30"E – 19° 24' 0"N, 85° 10' 50"E). Seawater samples were collected from three different stations (Fig. 1) using 1 l HDPE bottles during discrete months (April 2010–November 2011). Trace metal concentrations from these three locations were averaged for the present study. Zooplankton samples were collected using a plankton net (mouth: 0.11 m<sup>2</sup>; mesh: 120 μm). Each seawater sample was filtered through 0.45 μm acid-washed filter (Millipore) to separate them into dissolved and particulate fractions. The filtered seawater samples were stored for further analysis after acidifying with supra-pure HNO<sub>3</sub> adjusted to pH 2–3. Seawater samples were analyzed by diluting the sample 10-fold and fed to inductively coupled plasma mass spectrometer (ICP-

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**Table 1**

Trace metal concentrations in seawater (W) (in ppb) and zooplankton (P) (in ppm) in coastal and offshore waters.

Region		Fe	Co	Ni	Cu	Zn	Cd	Pb	Mn
North-western Bay of Bengal (Coastal) present study	W	4.47–13.71	BDL	1.46–3.56	BDL	0.10–3.55	0.01–0.30	1.39	0.72–7.34
	P	352–6388	0.21–0.65	1.50–3.10	2.64–14.38	16.96–1408	0.76–1.50	0.22–4.16	7.54–49.72
EEZ of Western Bay of Bengal (Coastal) <sup>1</sup>	W	0.78–3.28	0.032–0.168	0.021–0.124	0.44–1.98	0.92–2.84	0.012–0.048	0.108–0.723	
	P	1350–50,999	14.1–48.8	15.8–66.5	19.2–89.8	174–8162	8.2–49.4	1.4–21.1	
EEZ of Western Bay of Bengal (Offshore) <sup>1</sup>	W	1.21–2.77	0.008–0.121	0.021–0.081	0.22–1.61	0.78–1.88	0.017–0.035	0.113–0.491	
	P	1125–41,512	14.1–38.2	15.1–51.3	24.2–74.2	375–4233	9.2–34.2	1.5–16.2	
EEZ of the Bay of Bengal (Coastal) <sup>2</sup>	W	2.96–3.58	0.134–0.188	1.28–1.98	1.27–1.98	2.45–2.89	0.041–0.058	0.511–0.785	
	P	25,137–52,962	38.2–49.8	52.1–67.1	73.1–89.5	5800–8162	36.2–49.8	14.8–21.8	
EEZ of the Bay of Bengal (Offshore) <sup>2</sup>	W	1.24–2.79	0.045–0.124	0.034–0.088	0.48–1.68	0.88–1.92	0.018–0.042	0.114–0.496	
	P	1135–4556	13.8–24.8	14.8–34.4	22.8–35.3	357–785	9.3–18.8	1.5–7.7	
Southern Kerala coast (Cochin) <sup>3</sup>	W				3.46	13.06	0.17	1.99	6.61
	P				0.2	2.08	0.03	7.9	0.66
Southern Kerala coast (Alleppy) <sup>3</sup>	W				2.44	11.55	0.12	1.78	7.51
	P				0.32	0.62	0.01	2.69	0.13
Southern Kerala coast (Kayamkulam) <sup>3</sup>	W				0.62	5.64	0.14	1.86	6.17
	P				2.06	1.76	0.03	1.74	0.44
Southern Kerala coast (Neendakara) <sup>3</sup>	W				1.38	2.95	0.16	1.91	2.53
	P				2.7	6.03	0.08	1.01	2.71
Southern Kerala coast (Paravur) <sup>3</sup>	W				0.71	6.58	0.14	1.86	2.03
	P				1.11	2.73	0.05	1.19	4.22
Southern Kerala coast (Veli) <sup>3</sup>	W				1.28	9.45	0.14	1.86	11.12
	P				1.47	3.38	0.05	0.87	3.28
Coromandel Coast (Pulicate lagoon) <sup>4</sup>	W		110			11.925			
	P			7.85					
Coromandel Coast (Muttukadu) <sup>4</sup>	W				144		0.575		
	P					120.3			
Coromandel Coast (Cuddalore) <sup>4</sup>	W			6.875	98.6				
	P					118.25	0.275		
Coromandel Coast (Nagapattinam) <sup>4</sup>	W				153				
	P			14.75		120			
Bay of Bengal (off Visakhapatnam) <sup>5</sup>	W	2.81	0.1625	0.86	2.1	8.2	0.09	0.348	2.5
	P	50,962	34	54	78	7066	41	20	552
Bay of Bengal (off Chennai) <sup>5</sup>	W	2.81	0.129	0.612	1.29	8.09	0.04	0.2	1.4
	P	22,291	26	45	73	3379	18	7	438
Indian Ocean <sup>6</sup>	W								
	P	35.0–94.0	4	0.2–3.0	2.0–5.0	8–31			3.0–7.0

BDL: below detection limit.

<sup>1</sup> Rejomon et al. (2008).<sup>2</sup> Rejomon et al. (2010).<sup>3</sup> Robin et al. (2012).<sup>4</sup> Chinnaraja et al. (2011).<sup>5</sup> Paimpillil et al. (2010).<sup>6</sup> Sen Gupta and Qasim (1985).

MS) (Make: Agilent, Model: 7700 s) following the method outlined by Leonhard et al. (2002). Zooplankton samples were placed in a small nylon sieve and rinsed thoroughly with Milli-Q water for salt removal. Subsequently, the samples were oven dried at 65 °C and stored in vacuum desiccators for 48 h. The dried samples were powdered, digested in a microwave digestion system (Make: CEM, Model: MARS), and analyzed with ICP-MS. For each series of 10 samples, two analytical blanks were prepared in a similar manner to check for possible contamination. The metal concentrations in seawater are presented as ppb and in zooplankton as ppm. Instrument stability and data validity were ensured through acceptable range verification of calibration standards and control limit confinement of quality control parameters. The precision and accuracy of analysis were checked by replicate measurements of target metals in standard reference materials and spiked samples. The analyzed values obtained for the reference materials of seawater are in good agreement with the certified values (Table 2). Quality control of zooplankton analysis was ensured through spiking (recovery/sensitivity changes).

In order to determine the interrelationship between the trace metals, Pearson's correlation analysis was carried out with the aid of IBM SPSS 20.0. Further, bioaccumulation factor (BAF) was calculated to understand the bioaccumulation of trace metal in zooplankton. BAF is the ratio of metal concentration in an aquatic organism to its concentration in the ambient medium (Almeda et al., 2013; Bhattacharya et al.,

2014). The BAF of zooplankton in ambient medium was calculated as follows:

$$\text{BAF} = [\text{Metal Conc. in Zooplankton (ppm)}] \times 1000 / [\text{Metal Conc. in Seawater (ppb)}].$$

The distribution of trace metals in seawater depends upon their source of input and processes of physical, chemical, and biological dispersion. The entry of metals into the study area could mainly be from land drainage via the Rushikulya estuary because there is neither any heavy industry nor direct discharge of domestic wastes from any major city. The concentration of different metals are presented in Fig. 2.

Iron (Fe) is an essential element required by all eukaryotes as well as most prokaryotes and often limits phytoplankton growth in the ocean (Timmermans et al., 1998). In general, the concentration of Fe present in seawater is very low compared to the earth's crust. The chemical behavior and solubility of Fe in seawater strongly depends on the oxidation intensity within the system. During the study period, the Fe concentration present in seawater varied from 4.47 (April-10) to 13.71 ppb (January-11). Temporal variation showed the lowest concentration in April followed by June < August < September < November during 2010, while during 2011, its distribution pattern was November < August < April < January. Fe contents in zooplankton ranged from 352.14 (November-11) to 6388.02 ppm (April-11). In zooplankton, the concentration gradient was September < August < April < June < November during 2010 and November < August < January < April during 2011. The monthly variation

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