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Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: A biomonitoring approach for pollution assessment

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ABSTRACT

Metal pollution in the marine coastline environment is an important topical issue in the context of ecological disturbance and climate change. Heavy metal contaminations (Cd, Cr, Cu, Mn, Ni, Pb and Zn) in seawater and surficial sediments, as well as macroalgal diversity, were determined in six different locations along the coast of the Gulf of Kutch in India. The marine coastline environment was found to be enriched with Cd and Zn in comparison to other metals. Significant ($p \leq 0.05$) inter-elemental positive-correlations were observed between Fe–Mn, Fe–Cu, Fe–Cr, Fe–Zn, Cr–Cu, Cu–Mn, and Cd–Zn, as well as negative-correlations between Cd–Pb, Ni–Pb, and Zn–Pb. Though genus specific macroalgal responses to heavy metal accumulation were significant, species specific response was insignificant ($p \leq 0.05$). The relative abundance of metals in macroalgae followed the order of Fe > Zn > Mn > Cu > Cd > Cr > - Ni > Pb. The high uptake of metals in green algae (*Ulva lactuca* and *Enteromorpha intestinalis*) and brown algae (*Padina gymnospora* and *Dictyota bartayresiana*) suggested that these algae may be used as potential biomonitors for heavy metal pollution. Three pollution indicators, Contamination Factor (CF), Enrichment Factor (EF) and Geochemical Index (I_{geo}) were calculated to determine the degree of metal pollution in the marine coastline and the contribution of anthropogenic influence.

1. Introduction

Heavy metal pollution in coastal zone is a serious issue leading to considerable environmental and ecological degradation (Gao and Chen, 2012; Zhang et al., 2009; Wang and Wang, 2007; Feng et al., 2004). Heavy metals, when found in high concentration in aquatic habitat, accumulate in different organisms, damaging their tissues and suppressing growth. Alternately, they may accumulate directly (into macroalgae, for example) or through the different trophic levels of the food chain, and ultimately affect human beings (Alkarkhi et al., 2009; Martins et al., 2004). Depending on macroalgal species, the metals exert their toxicity in the general order of Zn < Pb < Ag < Cd < Cu < Hg (Rai et al., 1981, Kangwe, 1999). Heavy metals have been found to deactivate proteins, denature enzymes, and disturb cell functions (Hall, 2002). They also elicit the production of free reactive oxygen species, which in turn impair the functions of proteins, lipids and DNA causing oxidative stress and ultimately cell death (Kannan and Jain, 2000).

In coastal ecosystem, metals exists in either dissolved state in the water column or get deposited on the sediment bed, depending upon the nature of the chemical species and physicochemical factors like pH, conductivity, salinity and organic matter (Lim et al., 2012; Hagan et al., 2011; Praveena et al., 2008). However, analysis of total metal content in water and sediment does not predict the toxicity of contaminants to biota (Aly et al., 2012; Wang et al., 2010; Rainbow, 2006). Hence, aquatic organisms are often used as both 'biomonitors' and 'bioindicators' of environmental pollution (Villares et al., 2002). Macroalgae are recognized as useful bioindicators for metal pollution in seawater due to their sedentary lifestyle, considerable biomass, and easy identification (Chaudhuri et al., 2007). Though several internal and external factors that determine metal uptake by macroalgae, they are still considered to provide qualitative information of metal contamination level and environmental quality of an area. A number of studies have been carried out across the globe using different species of seaweed as bioindicators of metal contamination (Conti and Cecchetti, 2003). In India, metal concentration in seaweeds have been used by various researchers to identify the pollution in Sundarban (Chatterjee et al., 2001); Pulicat lake (Kamala-Kannan et al., 2008) and the Andaman Islands (Nobi et al., 2010).

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The Gulf of Kutch, in the western part of India, is a luxuriant ecosystem with an abundance of marine organisms including micro and macroalgae. During the past decade, the region has become the center of industrial growth due to an economic growth in Gujarat (state of India), resulting in rampant and unchecked industrialization. Various types of industries including petroleum and petrochemicals-based plants, soda ash, cement, fertilizer industries, salt works, thermal power stations and ship-breaking operations are contributing to pollution build-up in the area. This, along with the ensuing urbanization, is rapidly changing the environmental and livelihood landscape of the coast, threatening a sensitive marine ecology consisting of mangroves, mud flats and coral reefs. Despite of a number of recent studies focusing on biodiversity in the Gulf of Kutch (Deshmukhe et al. 2000; Nair, 2002), the impact of increased anthropogenic stress on the coastal environment has not been studied in detail. An assessment of the heavy metal concentrations in this region is necessary to identify the vulnerability of these ecosystems to pollution as well as to compile baseline data for future monitoring.

The present study was carried out on the distribution pattern of heavy metals in seawater, sediments and the predominant macroalgae found in Gulf of Kutch. Furthermore, the study was to evaluate the potential threat (dissolved metals), probable threat (metals in sediments) and the actual threat (uptake by macroalgae and their role as a bioindicator).

2. Materials and methods

2.1. Study area

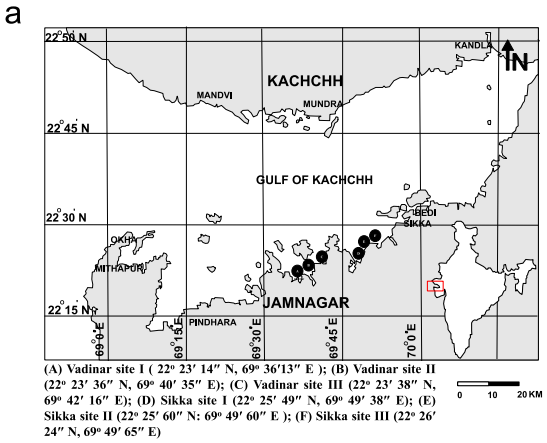
The Gulf of Kutch is geologically young and maximum depth within the gulf varies from 20 m at the head to 60 m in the outer regions fed by contributions from the Indus River (Chauhan et al., 2006). The coastal configuration is very irregular with numerous islands, creeks, bays and pinnacles. To determine the distribution of heavy metals in the area of Gulf of Kutch, we selected six sampling sites in two different regions, Vadinar and Sikka (Fig. 1a). These two locations were chosen because they have similar oceanographic conditions. Vadinar (situated at 22°28′ N and 69°43′ E) is impacted by occasional spillage during the unloading of large quantities of petroleum and its crude products (Vethamony et al., 2007). The principal pollution sources at Sikka (22°26′ N and 69°49′ E) are ship welding activities, and effluents from chemical industries, namely soda ash, sodium bicarbonate, caustic soda, cement, petrochemicals and fertilizers (Zingde and Anand, 1994). The waterways in Sikka are used for transportation of manufactured products. In addition, this region receives considerable discharge from a nearby thermal power plant, along with domestic waste.

2.2. Sample collection and preservation: Seawater, sediment and algae

Seawater, sediments and macroalgae were collected from Vadinar and Sikka for heavy metal analysis. Sampling occurred during summer 2011 in the months of April, May and June, due to the abundance of macroalgae in the study area during this season. Seawater samples were collected in polyethylene bottles after filtration using 0.45 μm cellulose acetate filters (Millipore) in field, and preserved by adding 50 percent (v/v) nitric acid (HNO_3) prior to transfer to the laboratory. Acidification was carried out to bring metal adsorbed on suspended particulate matter into the solution. All seawater samples were stored at 4 °C prior to analysis. Intertidal surface sediments (top 5 cm) were also collected from all six sampling sites. At each site, three discrete samples were taken within an area of approximately 10 m^2, and removed with a polyethylene scoop. Sediment fractions were transferred to polyethylene bottles and transported to the laboratory under cool conditions. Sediments were subsequently dried to a constant mass at 60 °C prior to further treatment. Algae were handpicked from substratum (mud and concrete surfaces) of the intertidal zone and placed into plastic bags for transfer to the laboratory in a low temperature refrigerator. Specimens were selected on the basis of their different morphological and physiological characteristics including size, shape (filamentous or not), color (Green, brown and red).

2.3. Estimation of environmental parameters

Electrical Conductivity (EC), pH, salinity, total dissolved solids (TDS) and of the seawater were measured onsite using a portable electrode (HACH). Salinity was measured using the Practical Salinity Scale.



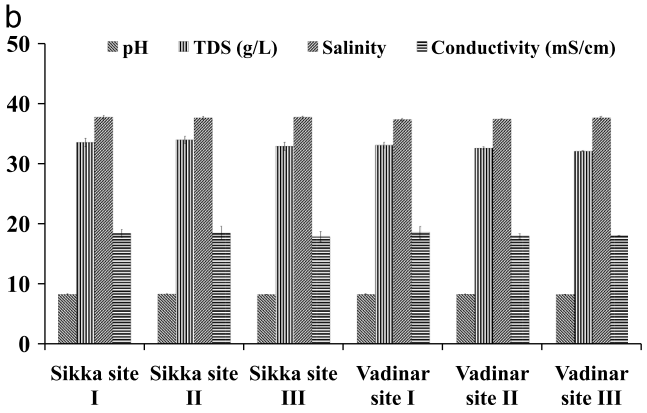


Fig. 1. (a) Sampling areas of Sikka and Vadinar, Gulf of Kutch, Gujarat, India. (b) Physico chemical parameters of seawater ($n=3$). Bar represents mean ± SE of $n=3$ ($p \leq 0.05$).

2.4. Identification of algae

Algal samples (0.5–1 kg) were cleaned immediately with local seawater from the sampling site followed by distilled water to remove any adhering impurities, sand debris and epiphytes. Algae were identified morphologically and microscopically based on comparisons with existing marine benthic seaweed literature (Jha et al., 2009).

2.5. Estimation of elemental (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) concentration of algae

Collected algal samples were freeze dried at −20 °C for 48 h, crushed and homogenized. The samples were stored at 4 °C until further analysis. Freeze dried and ground algal material (0.5 g) was weighed directly into a 75 ml glass digestion tube and cold digested in a fume cupboard overnight (16 h) with concentrated nitric acid (5 ml). The next morning the sample was heated using a temperature controlled digestion block (AI Scientific Block Digestion System AIM 500). Digestion blocks were programmed to slowly ramp to 140 °C over 8 h and then to maintain temperature. Sample digestion was continued at 140 °C until only a small residual liquid remained in each tube (≈ 1 ml). The tubes were subsequently removed from the digest block and allowed to cool to room temperature in the fume cupboard prior to dilution with 0.1% HNO_3 (20 ml). The samples were mixed thoroughly and filtered through 'Whatman No. 42' filter papers directly into plastic containers for storage prior to analysis. Each batch of digests included blanks, duplicates, spikes and CRMs at a rate of 5 percent. Samples were spiked with a multimix standard of heavy metals prior to digestion to give a concentration of 0.1 mg/l (200 μl of 10 mg/l standard in 20 ml).

Metal analysis was carried out using a Perkin Elmer Analyst 700 atomic absorption spectrometer equipped with a HGA graphite furnace and deuterium background corrector (Perkin Elmer part no. B3 001264, Pyrolytic-coated graphite tubes; Perkin Elmer AS-800 autosampler). The certified reference material used was 'Bush Branches and Leaves' (GBW07603) from the National Research Center for certified reference materials, China. Quality control using standard reference material was carried out to validate the assay performance (accuracy and precision: ± 5 percent).