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DISTRIBUTION OF HEAVY METALS IN *PADINA PAVONICA* (BROWN ALGAE), SEAWATER AND SEDIMENT OF TUTICORIN COAST, SOUTHEAST COAST OF INDIA

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Abstract

Distribution of heavy metals *viz*., zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), Chromium (Cr), cadmium (Cd) and lead (Pb) in water, sediments and marine algae using atomic absorption spectrophotometer at Tuticorin, Southeast Coast of India was studied during summer and monsoon season (2017-2018). Accumulation of heavy metals was observed in the order of sediments > Marine algae > seawater. In water, the order of heavy metals was found to be Mn>Fe>Cu>Zn>Cr>Cd>Pb and marine algae it was Fe>Mn>Zn>Cu>Cr>Cd>Pb. In water the highest recorded value among heavy metals was Mn. It varied from 498.78mg /1 to 514.23mg/1 and the lowest recorded value among metals was Pb and it varied from 0.0002mg/1 to 0.005 mg/1 in summer season. In sediments the highest recorded value among heavy metals was Mn and it varied from 724.9 mg/g to 820 mg/g and the lowest value among metals was Cd and it varied from 0.31mg/g to 0.0447 mg/g. In marine algae the highest recorded value among the heavy metals was Fe. It varied from 389.16 mg/g to543mg/g and the lowest value in metals was Cd, which varied from 0.49 g/g to 0.62 mg/g. Hence, in all three samples studied the metal concentrations showed significant variation in summer season at Tuticorin Coastal area, southeast coast of India.

Key words: Distribution, Heavy metal, Marine Algae, Marine Environment, *Padina pavonica*, Seawater, Sediment.

Introduction

Heavy metals are one of the most widespread and dangerous family of hazardous materials that can be encountered in natural and waste waters due to increasing development of industrial processes such as metal plating facilities, mining operations and tanneries (Odisa *et al*., 2016). Cr is among the most toxic and carcinogenic metal which is the powerful oxidizing agent. It has the potential to pass through cell membrane and reduces to reactive intermediates that attack DNA, protein and membrane lipids causing damage to the cellular integrity and function. Vu *et al*., 2016. In tuticorin untreated domestic sewage, industrial waste like fly ash from thermal power station and effluent from petrochemical industries are discharged into the sea. Tuticorin coastal water contains enormous amount of heavy metals stated by (Vekataraman Kumar and Anandhavalli Mahadevan, 1995). Pollution by heavy metals can be serious problem in aquatic habitats than by organic substances, because they cannot be degraded by natural process and persist in sediments from where they are released gradually into water. Studies on pollution effects on marine microalgae are very limited in India, though the tropical marine ecosystems are considered to be more sensitive to pollution (Murthy and Umamaheswara Rao, 2003). The effect of aquatic toxicity stated by Allen *et al*., 1980. Heavy metals contamination has become a global issue of concern due to their higher toxicities, nature of non-biodegradability, high capabilities in bio accumulation in human body and food chain and carcinogenicities to humans. Algae serve as good biosorbents due to their abundance in seawater and freshwater, cost effectiveness, reusability and high metal sorption capacities. Metal accumulation in fresh water algae stated by knauer *et al*., 1997.

Study on distribution of heavy metals in seawater is important to understand their role in various biogeochemical processes of the sea. Significant contributions have been made with reference to oceanic and coastal distribution of various heavy metals Govindasamy and Azariah, (1999). Studies reveal that heavy metals are biologically non-degradable and through food chain they may finally pass on to man Thomas and

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Jacquet, (1976). Numerous heavy metal studies have been made to understand the effect of metals on animals but relatively little attention has been paid to study the heavy metal accumulation on seaweeds. Hence, the present study was mainly aimed to assess the accumulation of heavy metals in the marine algae *Padina pavonica*. A similar study about Enteromorpha as a monitor for the determination of heavy metals in marine environment was done by Say *et al*., (1990). Summer and monsoon season considerable changes in the marine ecosystem by polluting the marine environment with high turbidity and also breaking the coastal vegetations (Kannan *et al*., 2005). With this view, the present study is aimed to determine the impact of on the accumulation of heavy metals in water, sediment and a marine algae *Padina pavonica* in Tuticorin coast, Southeast Coast of Tamil Nadu, India.

Materials and Methods

Water samples, sediments and *Padina pavonica* were collected in Tuticorin coastal areas fig. 1, during summer and monsoon period. Southeast coast of Tamil Nadu, on the Indian side Spreads along the latitude from 8°35' N to 9°25' N and along the longitude from 78°08' E to 79°30' E. Surface water samples were collected in pre cleaned and acid washed polypropylene bottles and were filtered in Millipore filter paper (mesh size 0.45). The samples were pre concentrated with APDC-MIBK extraction procedure (Brooks *et al.,* 1967)[3]. The resulting solution was aspirated to flame atomic absorption Spectrophotometer (Perkin-Elmer Model, 373) for the determination of Zn, Cu, Fe, Mn, Cr, Cd and Pb.

Sediment samples were collected in pre cleaned, acid washed PVC corer, transferred to clean polybags and transported to the laboratory. These samples were than washed with metal-free double distilled water and dried in hot air oven at 110°C for 5 to 6 hours and ground to powder in a glass mortar and stored in pre cleaned polythene bags. 500 mg of the sample was taken and digested with a mixture of 1 ml of concentration sulphuric acid (conc. H_2SO_4) 5 ml of concentration nitric acid (conc. HNO_3) and 2 ml of perchloric acid ($HClO_4$). A few drops of hydro fluoric acid (HF) were added to achieve complete digestion and the sample was filtered and made upto 25 ml with metal-free double distilled water for the estimation of Zn, Cu, Fe, Mn, Cr, Cd and Pb using flame atomic absorption spectrophotometer (Chester and Hughes, 1967).

The method explained by (Say *et al.,* 1986) was adopted for the analysis of heavy metals in alga *Padina pavonica species*. Healthy algae were removed carefully from their substrates and washed thoroughly with the

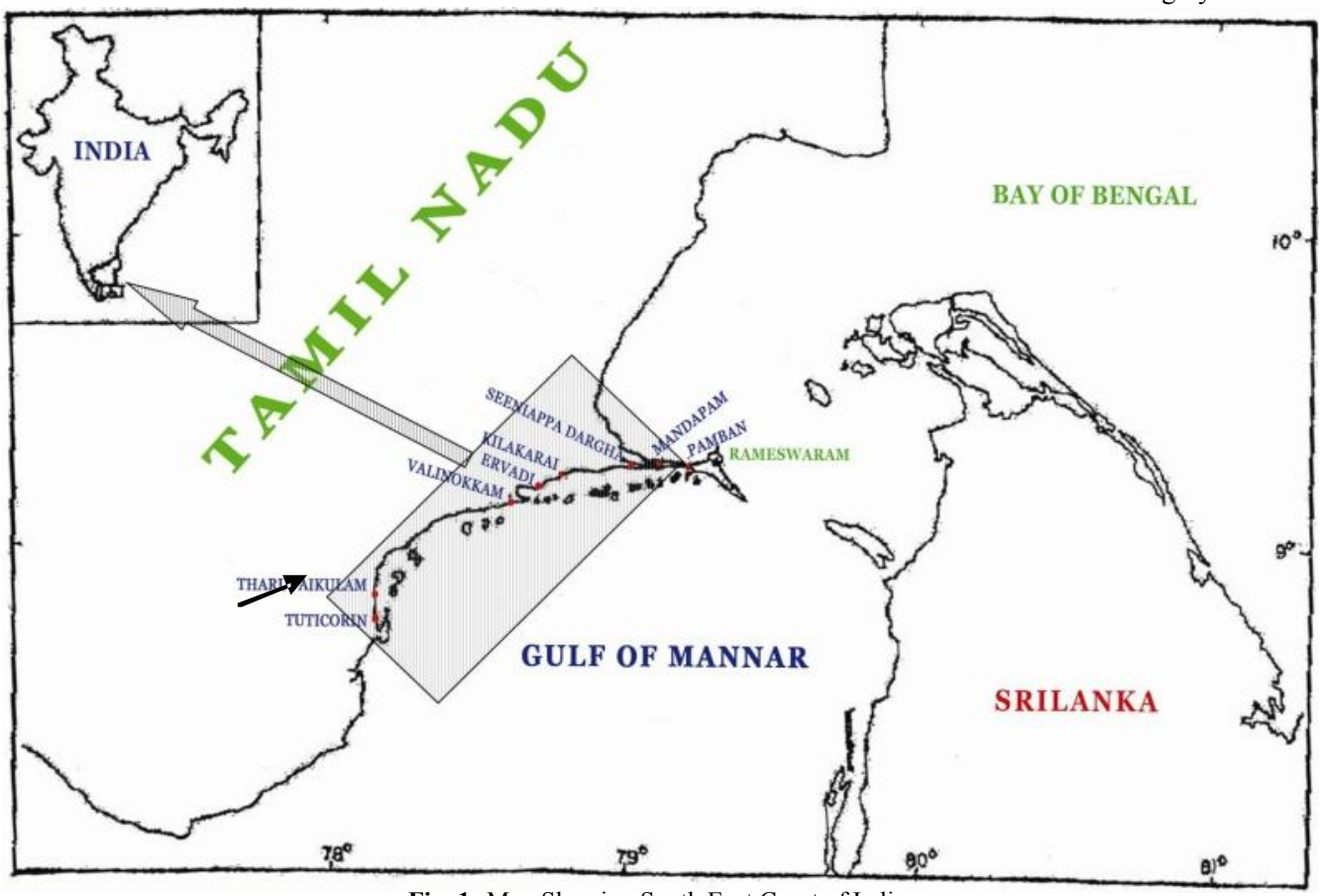

Fig. 1: Map Showing South East Coast of India.

Fig. 2: *Padina pavonica* (Linnaeus) Thivy.

sea water to remove sediments, debris and associated fauna. Cleaned algae were kept in polythene bags and transported to the laboratory in an icebox. Initially, they were washed under a jet of tap water before analysis. Washed material was then transferred to a dish containing metal-free double distilled water and washed thrice. 250mg of the dry weight sample was dried at 105°C and ground to powder and stored in pre cleaned polythene bag. The weighted sample was digested in 10ml of 2M HNO_3. The mixture was boiled, evaporated to near dryness and then resuspended in 10ml of 2M HNO_3. This was passed through a paper filter and made up to 25ml with metal free double distilled water and the solution was analysed for Zn, Cu, Fe, Mn, Cr, Cd and Pb using a standard atomic absorption spectrophotometer.

Results and Discussion

Variation in the accumulation of Zn, Cu, Fe, Mn, Cr, Cd and Pb in water, sediments and marine algae recorded at Tuticorin coast winter and summer are shown in the values of heavy metals observed in the three samples are given in table 1 to 3.

In water, the accumulation of heavy metals was observed in the order of MN>Fe>Zn>Cu>Cr>Cd>Pb.

Table 1: Heavy Metal Concentration ($\mu g.1^{-1}$) recorded in water samples of Tuticorin coast, monsoon and summer seasons (2017-2018).

S. No	Heavy metals (µg.1-1)	Monsoon	Summer
1.	Zn	49.210	52.480
2.	Cu	12.420	14.560
3.	Fe	296.300	314.250
4.	Mn	514.230	496.780
5.	Cr	6.940	7.210
6.	Pd	0.002	0.005
7.	Cd	0.050	0.100

Table 2: Heavy Metal Concentration ($\mu g.1^{-1}$) recorded in sediment sample of Tuticorin coast, monsoon and summer seasons (2017-2018).

S. No	Heavy metals (µg.1-1)	Monsoon	Summer
1.	Zn	8.000	9.600
2.	Cu	30.000	48.400
3.	Fe	270.000	128.500
4.	Mn	820.000	724.900
5.	Cr	0.920	1.54C
6.	Pd	ND	ND
7.	Cd	0.447	0.310

Highest recorded value among heavy metals was Mn which varied from 496.78mg/l to 514.23mg/l and the lowest recorded value among heavy metals was Pb which varied from 0.02mg/1 to 0.005mg/l. Except Mn, all the other metals (Zn, Cu, Fe, Cd, Cr and Pb) recorded higher concentrations during the summer season. This variation in metal concentrations is due to the impact heavy temperature caused large scale seawater inundation and the receding tidal waves carried into the sea, debris, anthropogenic wastes, adjacent terrestrial parts including plastic materials, domestic and shrimp farm, disposals from the nearby lands. Further, the heavy metals were higher in coastal waters due to the presence of major sources of metal pollution, intensive human activity and discharge of municipal waste and industrial effluents (Govindasamy and Azariah, 1999).

In sediments, the accumulation of heavy metals was found in the order of Mn>Fe>Cu>Zn>Cr>Cd>Pb. Zn, Cu and Cr recorded higher values whereas Fe, Mn and Cd recorded lower values in summer season. Concentration of Pb was not recorded, winter and summer. Highest recorded value among heavy metals was Mn, which varied from 724.9mg/g to 820mg/g. This variation in the heavy metal concentrations was due to the continuous stirring of sediments by the extreme physico-chemical properties.

In algae, the accumulation of heavy metals was found in the order of Fe>Mn>Zn>Cu>Cr>Cd>Pb. Like sediments, in Algae Zn, Cu, Cr recorded higher values whereas Fe, Mn and Cd recorded lower values in summer.

Table 3: Heavy Metal Concentration ($\mu g.1^{-1}$) recorded in *Padina pavonica* sample of Tuticorin coast, monsoon and summer seasons (2017-2018).

S. No	Heavy metals (µg.1-1)	Monsoon	Summer
1.	Zn	48.90	52.30
2.	Cu	26.50	49.56
3.	Fe	543.00	389.16
4.	Mn	302.00	209.40
5.	Cr	1.79	1.96
6.	Pd	ND	ND
7.	Cd	0.62	0.49

Pb was not recorded winter and summer. Higher recorded value among heavy metals was Fe. It varied from 389.16mg/g to 543mg/g and the lowest value in metals was Cd, which varied from 0.49mg/g to 0.62mg/g.

A similar result was obtained in the study on the effect of copper in seaweeds (Sornalakshmi *et al*., 2009). The increase in protein content might be a response to sequester of the heavy metal effect. Increase in the level of carbohydrate and lipid under heavy metal pollution stress has been observed in algae (Sornalakshmi *et al*., 2009, 2010)[14]. Algal from tuticorin coast were found to accumulate manganese in the range of 20-1077mgg^{-1} (Ganesan and Kannan, 1995). The metal Mg, Fe, Mn, Cu, NI, Zn, Cr and Pb showed high concentration and a variable distribution in seaweed species. This may be due to the variation of metal concentrations in seawater (Qari and Siddiqui, 2004, 2005).

Conclusion

The present study clearly shows significant variations in the accumulation of heavy metals in water, sediments and algae in summer. These variations in the marine environment are certainly brought about by coastal disaster as similar type of variation in the physico-chemical characters were observed in the coastal water quality of Dakshna Kannada coast (Reddy *et al.,* 2005)[11]. Heavy metals are essential micronutrients for growth, metabolism and enzymatic activities of various algae, cyanobacteria and other organisms. However, it is a proven inhibition of algal growth at higher concentrations. The present investigation clearly reveal a concentration dependent toxic effect of heavy metals on the specific growth rate, pigment content and the rate of primary production.

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