



Heavy metal accumulation in seaweeds and sea grasses along southeast coast of India

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ABSTRACT

Generally, heavy metals enter into the aquatic environment through atmospheric deposition, erosion of geological matrix or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes. The present study analyzed the concentration of seven elements (Cd, Cu, Mn, Ni, Pb, Zn and Hg) in eight seaweeds such as *Centrocerous clavutum*, *Sargassum wightii*, *Colpomenia sinosa*, *Spyridia hypnoides*, *Valoniopsis pachynema*, *Ulva reticulata*, *Gelidiella acerosa* & *Turbinaria ornata* and two seagrasses such as *Syringodium isoetifolium* & *Cymodocea serrulata* collected from three stations along southeast coast of India. Among the seaweeds, *S. hypnoides* could be effectively capable to uptake the heavy metals in Kanyakumari coast. *U. reticulata* recorded as less ability to absorb these heavy metals in Ervadi coast, whereas seagrasses *S. isoetifolium* and *C. serrulata* in Thondi station moderately absorbed the heavy metals. Since almost all the metals were tested and reported in these seaweeds and seagrasses species.

Keywords: Heavy metals, Seaweeds, Seagrasses, Southeast coast.

INTRODUCTION

The increasing significance of heavy metals disturbing the environment is especially evident in aquatic systems. Although most of the investigations have been made on microalgae and macrophytic algae and they are considered as valuable indicators because of their accumulation capacity [1]. Trace elements like manganese, copper, lead and zinc are present in very less quantities and are considered as the essential micro-nutrients for proper growth of the plants. It is well known that elements such as Cu, Mo, Ni, Cl and Zn are essential for plant growth in low concentrations [2]. Nevertheless, beyond certain threshold concentrations, these same elements become toxic for most plant species [3,4]. Certain plant species are capable of tolerating high concentrations of heavy metals and thus opened new possibilities to use these plants to remediate contaminated soils (phytoremediation). Many studies have been conducted to determine the toxic levels of heavy metals for certain plants, especially those metals considered as public health threats [2,5]. At the low concentrations some of the heavy metals excite some biological processes, but at threshold concentration these become toxic. Being non biodegradable, these metals accumulate at various tropic levels through food chain and can cause human health problems [6]. In humans, these metals hoard in living tissues and thus multiply the danger. Some metals cause physical distress while others may cause life-threatening illness, damage to vital body system, or cause other damages. Thus, it is very essential to control emission of heavy metals into the environment. Seaweeds are excellent agents of filtering the metals like zinc, cadmium, copper, nickel and iron and some potential carcinogens from seawater. They remove the toxic materials from the environment and accumulate in the body cell, which may be 4,000-20,000 times more than the surrounding water. The ability of algae to accumulate metals depends on a variety of factors such as the bioavailability of metals in the surrounding waters and their uptake capacity. The uptake of metals in seaweeds and seagrasses depends on the surface reaction in which metals absorbed through electrostatic attraction to negatives sites. This is independent of factors influencing

metabolism such as temperature, light, pH or age of the plant, but it is inclined by the virtual abundance of elements in the surrounding water [7]. In the present study, an attempt has been made to find the possibility of using the seaweeds and seagrasses as biomonitoring agents for assessing various heavy metals like Cd, Cu, Fe, Mn, Ni, Pb and Zn which are released from the industrial effluents, domestic sewage and seafood industries.

EXPERIMENTAL SECTION

Sampling Sites

Seaweeds were collected from three different stations along the southeast coast of India. Five species of seaweeds viz. *Centrocerous clavutum*, *Sargassum wightii*, *Colpomenia sinosa*, *Spyridia hypnoides* and *Valoniopsis pachynema* were collected from Station 1 (Kanyakumari - Lat. 08°04'N; Long. 77°36'E) and two species of seagrasses viz. *Syringodium isoetifolium* and *Cymodocea serrulata* were collected from Station 2 (Thondi - Lat. 09°44'N; Long. 79°02'E). Three species of seaweeds viz. *Ulva reticulata*, *Gelidialla acerosa* and *Turbinaria ornata* were collected from Station 3 (Ervadi - Lat. 9°15' N; Long. 78° 53'E).

Determination of metal concentration

After collection, seaweeds and sea grasses were thoroughly washed with seawater and tap water followed by distilled water to remove the epiphytes, sand and mud particles. They were allowed to shadow dry and then finely powdered by using mixer grinder. 1 g of the sample was weighed and digested in 100 ml glass beaker with concentrated nitric acid (20 ml) overnight. It was then mixed with 10 ml of concentrated nitric and perchloric acid (4:1) solution followed by evaporating the acid mixture by keeping the beaker on a hot plate 120°C for complete dryness. The residue was then made up to 20 ml solution by Milli-Q water with 20 % conc. nitric acid after filtering through No. 1 Whatman filter paper and then the metal concentrations were determined by using Inductively Coupled Plasma Optical Emission Spectrometer (Perkin Elmer, Optima 2100DV). All acids and chemicals were of analytical reagent grade. Laboratory glass wares were kept overnight in a 10% nitric acid solution and rinsed with de-ionized water and air dried before use.

Table 1. Operating parameters for the Inductively Coupled Plasma Optical Emission Spectrophotometer

Parameters	Conditions
Plasma capacity (w)	1300
Plasma flow rate (L min ⁻¹)	15
Nebulizer gas flow rate (L min ⁻¹)	0.8
Sample flow rate (mL min ⁻¹)	1.5

Table 2. Wavelength used for ICP-OES analysis for each metal

Element	Wavelength
Cd	228.802
Cu	324.752
Fe	238.204
Mn	259.372
Ni	231.604
Pb	220.353
Zn	213.857

Statistical analysis

Pearson Correlation Coefficient and one way ANOVA was employed for better understanding of relationship between the concentration of various metals with respect to different seaweeds and seagrasses.

RESULTS AND DISCUSSION

Environmental pollution has turn out to be a serious concern in both nationally and internationally. Among the various environmental pollutions, pollution of water resources is a matter of great anxiety. Water bodies get polluted with the accumulation of many pollutants including toxic metals. Major pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. Remediation of contaminated effluents before their discharge into water bodies is, therefore, a priority both in current environmental research and legislation [8]. In the present study, concentrations of Cd, Cu, Mn, Ni, Pb, Zn and Hg ($\mu\text{g g}^{-1}$) were determined in eight seaweeds such as *Centrocerous clavutum*, *Sargassum wightii*, *Colpomenia sinosa*, *Spyridia hypnoides*, *Valoniopsis pachynema*, *Ulva reticulata*, *Gelidialla acerosa* & *Turbinaria ornata* and two seagrasses such as *Syringodium isoetifolium* & *Cymodocea serrulata* which were collected from three stations along Southeast coast of India. Metals showed significant variations in concentration with respect to species and areas. According to Pearson Correlation Coefficient, the metals were significantly correlated to each other at each sampling area at 0.05 level. One way

ANOVA revealed that the concentration of metals was significantly varied with respect to different species ($P < 0.05$). Several possible mechanisms such as adsorption, intracellular compartmentalization of metals, chelation and secretion of extracellular exudates have been suggested for metal tolerance/resistance by algae [9,10,11,12]. The above said mechanisms make algae tolerant/resistant towards heavy metals present in the polluted water bodies and thus they may also have potential to remove/accumulate metal ions. In Kanyakumari station the Cd level was highly accumulated in *S. hypnoides* ($0.3 \pm 0.05 \mu\text{g g}^{-1}$) and no trace level was recorded in *C. clavatum* ($0.006 \pm 0.001 \mu\text{g g}^{-1}$). The Cu and Mn level was highly accumulated in *S. hypnoides* and lowest was recorded in *C. sinuosa* and *V. pachynema* respectively. In Ni and Pb are contain <1 ppm in all the seaweeds species studied. The Zn was highly recorded in *S. hypnoides* ($1.22 \pm 0.021 \mu\text{g g}^{-1}$) and lowest was recorded in *S. wightii* ($0.71 \pm 0.018 \mu\text{g g}^{-1}$) Table 3.

Table 3. Distribution of heavy metal accumulation in different seaweeds at Kanyakumari

Heavy metals	Station (1)	<i>C. clavatum</i>	<i>S. wightii</i>	<i>C. sinuosa</i>	<i>S. hypnoides</i>	<i>V. pachynema</i>
Cd	Kanyakumari	0	0.023 ± 0.015	0.006 ± 0.001	0.300 ± 0.050	0.034 ± 0.040
Cu		4.16 ± 0.080	3.17 ± 0.23	0.300 ± 0.10	6.55 ± 0.195	4.51 ± 0.121
Mn		2.42 ± 0.158	1.58 ± 0.072	2.86 ± 0.119	3.03 ± 0.018	0.62 ± 0.11
Ni		0.463 ± 0.63	0.803 ± 0.57	0.16 ± 0.034	0.452 ± 0.38	0.226 ± 0.24
Pb		0.26 ± 0.026	0.2 ± 0.026	0.3 ± 0.019	0.34 ± 0.04	0.25 ± 0.013
Zn		1.04 ± 0.039	0.71 ± 0.018	0.85 ± 0.026	1.22 ± 0.021	0.83 ± 0.083
Hg		0.01 ± 0.009	0.00	0.01 ± 0.001	0.01 ± 0.002	0.01 ± 0.001

In Ervadi station the concentration of Cd, Ni and Pb were recorded <1 ppm in *U. reticulata*, *G. acerosa* and *T. ornata* (seaweeds). The Cu and Mn were highly recorded in *G. acerosa* $1.04 \pm 0.024 \mu\text{g g}^{-1}$ and $11.38 \pm 0.752 \mu\text{g g}^{-1}$ and lowest recorded in *T. ornata* $0.31 \pm 0.019 \mu\text{g g}^{-1}$ *U. reticulata* $1.09 \pm 0.011 \mu\text{g g}^{-1}$.

Table 4. Distribution of heavy metal accumulation in different seaweeds at Ervadi

Heavy metals	Station (2)	<i>U. reticulata</i>	<i>G. acerosa</i>	<i>T. ornata</i>
Cd	Ervadi	0.024 ± 0.002	0.161 ± 0.022	0.138 ± 0.017
Cu		1.03 ± 0.017	1.04 ± 0.024	0.31 ± 0.019
Mn		1.09 ± 0.011	11.38 ± 0.752	2.5 ± 0.296
Ni		0.25 ± 0.029	0.54 ± 0.041	0.19 ± 0.041
Pb		0.42 ± 0.024	0.52 ± 0.030	0.2 ± 0.19
Zn		0.48 ± 0.066	1.24 ± 0.044	0.45 ± 0.049
Hg		0.00	0.01 ± 0.001	0.04

In Thondi station the Cu and Mn content was high ($5.09 \pm 0.042 \mu\text{g g}^{-1}$, $14.38 \pm 0.34 \mu\text{g g}^{-1}$) in *S. isoetifolium* and lowest level in *C. serrulata* ($3.84 \pm 0.127 \mu\text{g g}^{-1}$, $4.21 \pm 0.127 \mu\text{g g}^{-1}$). Whereas Zn was highly recorded in *S. isoetifolium* ($1.75 \pm 0.049 \mu\text{g g}^{-1}$) and low in *C. serrulata*, ($1.02 \pm 0.004 \mu\text{g g}^{-1}$). The metals such as Cd, Ni, Pb and Hg were recorded at <1 ppm in both the seagrasses (Table 5).

Table 5. Distribution of heavy metal accumulation in seagrasses at Thondi

Heavy metals	Station (3)	Sea grasses	
		<i>S. isoetifolium</i>	<i>C. serrulata</i>
Cd	Thondi	0	0.012 ± 0.003
Cu		5.09 ± 0.042	3.84 ± 0.127
Mn		14.38 ± 0.34	4.21 ± 0.11
Ni		0.18 ± 0.023	0.10 ± 0.024
Pb		0.3 ± 0.026	0.26 ± 0.022
Zn		1.75 ± 0.049	1.02 ± 0.004
Hg		0.00	0.03

Increasing industrialization, along with the desecration of effluent disposal norms, has caused heavy contamination of water bodies. Marine algae, seagrasses and other aquatic biota in the vicinity of industrial areas have been used to absorb the metals for gauging the level of pollution. In the present study, the heavy metal accumulation in eight different seaweeds in three different stations, in this concern accumulation of heavy metals in red algae affect several biological processes such as cellular metabolism and inhibition of photosynthesis [13] any how it was absorb the metal from the water and uphold it. These find a broad application in foods, pharmaceutical and cosmetic industries as gelling, thickening, emulsifying and stabilizing agents [14]. Sathya and Balakrishnan [15] have reported that Cd even at very low concentration can cause the physiological disturbance like protein, carbohydrate and pigment concentration. Copper is an essential micronutrient but when the concentration of copper will increase it will affect the photosynthesis and leads to depigmentation as well as it could be depressing the growth of algae. In the present study copper accumulation is very high among eight seaweeds and two seagrasses species. The high

level of copper accumulation indicates the lipid body of the plant cell. Different species of the algae revealed considerable difference in metal concentration, even taken from the different sampling sites [16]. Similarly tolerant concentration of Zn was tested in various seaweeds the brown seaweeds *Padina*, *Sargassum* and *Spyridia* were more tolerant, among them the brown seaweed absorbed highest level of Zn. The green algae *Ulva* and *Enteromorpha*, which presented similar responses to the increase in Zn concentration, were not tolerant to a concentration of 1000 mg liter⁻¹ [17]. In the present study, the Zn was moderately absorbed by the seaweeds and seagrasses. The ability to uptake of heavy metals in any one species of algae based upon cell wall polysaccharides [18]. It may be suggested that the variability of metal accumulation was probably the result of competition flanked by the metals to bind with such polysaccharides. The binding affinity of some polysaccharides to the various metals has been reported to be preferential [19]. Rashida qari [20] has reported that the red seaweed has more ability to uptake these metals (Fe, Mn, Cu, Ni, Zn, Cr & Pb) when compared to brown and green seaweeds. Seaweeds have regulated the uptake of these metals and hence it does not accumulate them to such a great extent. Previously Thangaradjou [21] has been reported that concentration of heavymetals (Mn, Al, Fe, Cr, Cu, Zn, Pb, Cd, Co and Ni) in eight different seagrasses *Enhalus acoroides*, *Halophila ovalis*, *Halophila ovata*, *Thalassia hemprichii*, *Cymodocea rotundata*, *halodule uninervis*, *Halodule pinifolia*, *Syringodium isoetifolium* among these species the Mn was maximum in all seagrasses and Co was found in minimum concentration which was coincide in the present report *S. isoetifolium* absorbed more Mn content. Vande and Groot [22] Bower [23] have been deliberated the metal uptake, translocation and effects in plants growing on naturally polluted and unpolluted sediments. Marine macro algae growing in polluted water were selected keeping in mind that algae of these habitats may have more metal removal potential since these have adapted themselves to grow in such environment. The bioaccumulation of metals by a plant depends on time of year as there are seasonal variations in growth and chemical composition influencing the pattern of accumulation in addition to variations in the activity concentrations in the environment. In the present study green, red and brown algae might be regarded as species dependent variation with respect to heavy metal assimilation.

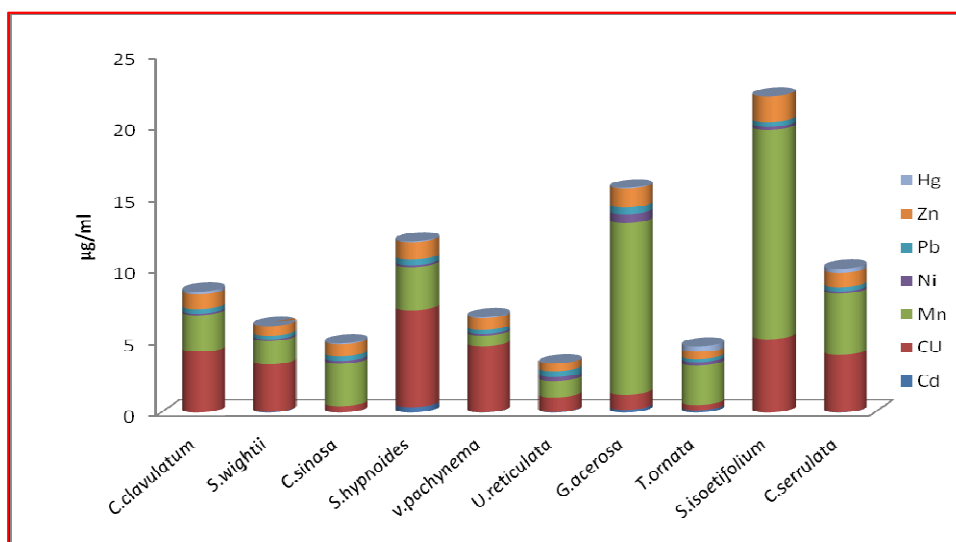


Fig1. Over all heavy metal accumulation in Seaweeds and Seagrasses

CONCLUSION

The need for an understanding of the kinetics of the accumulation of the metal in each species provides information on the time of period, reflected in the integrated measurement presented by the accumulated metal concentration. The study reveals that the level of Cd, Cu, Mn, Ni, Pb, Zn and Hg are moderate in Kanyakumari, Thondi and Ervadi stations. In the present study we suggested that red algae have more capacity to uptake of heavy metals when compare to green and red algae and moderate in seagrasses.

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REFERENCES

- [1] IM Munda, *Eutrofication und Truce Metal Cycling in Estuarine and Lagoons. Thessaloniki, Greece*, **1993**; pp. 455-65.
- [2] R Reeves; AJM Baker. Metal-accumulating plants. *Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment. John Wiley*, **2000**; pp.193–229.
- [3] M J Blaylock, JW Huang. *Phytoextraction of metals. 1st Edition, John Wiley*, **2000**; pp. 53–70.
- [4] S Monni; M Salemaa; N Millar. *Env. Pol.*, **2000**, 109, 221–229.
- [5] N Terry; G Banuelos. *Phytoremediation of Contaminated Soil and Water. Lewis Publishers, Inc.*, **2000**; 408 p.
- [6] M He; Z Wang; H Tang. *Wat. Res.*, **1998**, 32: 510-518.
- [7] ISanchez-Rodriguez; MA Huerta-Diaz; E Choumiline; O Holguin-Quinones; JA Zertuche-Gonzalez. *Env. Pol.*, **2001**, 114 (2), 145–160.
- [8] T A Davis; B Volesky; A. Mucci. *J. Water Res.*, **2003**, 37 : 4311-4330.
- [9] E Sandau; P Sandau; O Pulz; M Zimmermann. *Acta Biotechnol.*, **1996b**, 16; 103-119.
- [10] JL Gardea-Torresdey; JL Arenas; NMC Francisco; KJ Tiemann; R Webb. *J. Hazard. Sub. Res.*, **1998**, 1;1-18.
- [11] K Sufia; KP Sar; RK Asthana; SP Singh. *World J. Microbiol. Biotechnol.*, **1999**, 15; 599-605.
- [12] SK Mehta; JP Gaur. *Crit. Rev. Biotechnol.*, **2005**, 25; 113–152.
- [13] S Haritonidis; HJ Jager; HO Schwantes. *Angewandte Botanik. Berlin*, **1983**, 57, 311-330.
- [14] GA Towle, Carrageenan. In *Industrial Gums. 2nd edition*, ed. R. L. Whistler. Academic Press, San Diego, **1973**, pp. 83- 114.
- [15] KS Sathya; Balakrishnan KP. *Wat. Air. Soi. Pol.*, **1998**; 38, 283-297.
- [16] AG Davis, *Adv.Mar. Bio.*, **1978**, 15, 381-508.
- [17] M Gilberto; A Filho; CS Karez; LR Andrade; YY Valentin; WC Pfeiffer. *Eco. Env. Saf.*, **1997**, 37, 223-228.
- [18] RL Veroy; N Montano; MLB de Guzman; EC Laserna; GJB Cajipe. *Bot. Mar.*, **1980**, 23, 59-62.
- [19] AJP Hurlburt; Y Tanaka; SC Skoryna. *Bot. Mar.*, **1976**, 19, 327-328.
- [20] R Quari; A siddiqui. *Ind. J. Mar. Sci.*, **2010**, 39, 27-29.
- [21] T Thangaradjou; EP Nobi; E Dilipan; K Sivakumar; S. Susila. *Ind. J. mar.sci.*, **2010**, 39(1), 85-91.
- [22] DW Vande; AJ Groot. *Geol Mijnb.*, **1974**, 53; pp. 201–203.
- [23] PM Bower, HJ Simpson; SC Williams; YH Li. Heavy metals in the sediments of Foundry Cove, *Env. Sci. Tech.*, Cold Spring, New York. **1978**; 12, pp. 683– 687.