

Effect of soda ash industry effluent on bioaccumulation of metals by seaweeds of coastal region of Gujarat, India

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Received 25 August 2006; received in revised form 23 December 2006; accepted 28 December 2006

Available online 3 January 2007

Abstract

The bioaccumulation ability of five species of seaweeds to 15 metals was studied in the seawater polluted by the effluent of soda ash industry. The bioaccumulation of Al, Mn and Fe in these seaweeds increased continuously as distance increased from outfall. However, *Padina tetrastromatica* showed reverse trend. Quite a number of metals like Au, Co, Hg, Ni, Pb, Pt and Sn were not recorded from any species of seaweeds from all sampling stations. Cr was recorded in *Gracillaria acerosa* from control site only. Accumulation of Cu in *Gracillaria corticata* was maximum near effluent discharge point and least at control, whereas its accumulation in *P. tetrastromatica* was more at station with lower pollution (station-3) than higher polluted station (station-2). Seaweeds had different pattern of bioaccumulation to Cu and Ag under the influence of the effluent. The bioaccumulation of Cd in quite a number of species was in non-detectable range, however in case of red seaweed it was more under polluted condition and non-detectable in control. The biosequestering capacity of different seaweed to different metals and their suitability for bioremediation under the influence of effluent is discussed. Bioconcentration factor for different seaweed species from different distances from outfall has been computed and discussed.

The undiluted soda ash industry effluent is characterized by very high pH, density, settleable solids, total dissolved solids, ammonia and nitrate. The specific gravity, density, total suspended solids and total dissolved solids decreased continuously from undiluted effluent to seawater affected up to 1 km.

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Keywords: Soda ash industry; Bioaccumulation; Seaweeds; Pollution

1. Introduction

Metals occur naturally, and several of them are essential components of global ecosystems [1]. They are present in the environment with a wide range of oxidation states and coordination numbers, and these differences are related to their toxicity. Metals such as Cu and Zn are essential to life, whereas others such as Pb and Hg are not known to perform a useful biochemical function [2]. Environmental pollution by metals became extensive as mining and industrial activities increased in the late 19 and early 20 century. These pollutants, ultimately derived from a growing number of diverse anthropogenic sources

(industrial effluents and wastes, urban runoff, sewage treatment plants, boating activities, agricultural fungicide runoff, domestic garbage dumps and mining operations), have progressively affected more and more different ecosystems [1,3]. Heavy metals are usually present at low concentrations in oceanic surface waters and arrive there by atmospheric transport and upwelling. Higher levels occur in coastal waters because of river runoff. Close to urban centers, pollution is associated with sewage outlets, but levels are also elevated near extensive areas of industry [4–8]. Metal bioaccumulation by marine organisms has been the subject of considerable interest in recent years because of serious concern that high levels of metals may have detrimental effects on the marine organisms and may create problems in relation to their suitability as food for humans [9].

The soda ash industry near the study site manufactures soda ash by Solvay process [10]. It produces 40,300 tonnes of dense soda ash and 16,350 tonnes of sodium bicarbonate per annum; simultaneously it also generates 170,000 m³ effluent per day.

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The original effluent is diluted with seawater (to meet the pollution control standards) before discharging into the coastal waters [11]. The diluted effluent is discharged 500 m away from the coastline through a sub marine pipeline. The different species of seaweeds grow luxuriantly in this effluent affected region.

Considerable reports from the different parts of the world are available on the bioaccumulation of quite a number of heavy metals by different seaweeds under diversely stressed natural conditions [12–23]. However, the literature search did not reveal any published literature on the impact of soda ash industry effluent on the heavy metal biosorption by seaweeds. However, impact of chlor-alkali industry effluent, an effluent closely related to soda ash industry effluent, on the heavy metal content of seaweeds has been studied [24]. Very scanty information even at international level is available on the bioaccumulation capacity of the seaweeds for the noble metals like Ag and Au [14,25]. However, the authors are not aware of any reports on the biosorption of Pt by seaweeds. Therefore, it was thought desirable to study the effect of soda ash industry effluent on the heavy metal sorption capacity/pattern by seaweed flora in in situ conditions. The Gujarat coast of India, where the present study has been carried out, has quite a number of large chlor-alkali industries including soda ash industry. The objective of the present study is to understand whether the soda ash industry effluent has changed the sequestering capacity and accumulation pattern of the different heavy metals by different seaweeds in comparison with unpolluted condition.

2. Materials and methods

2.1. Description of experimental site

The soda ash industry effluent outfall is situated at latitude $20^{\circ}49'N$ and longitude $70^{\circ}28'E$. There is no source of pollutant other than soda ash industry near present study area. The first sampling station for seaweed was in the intertidal belt (region

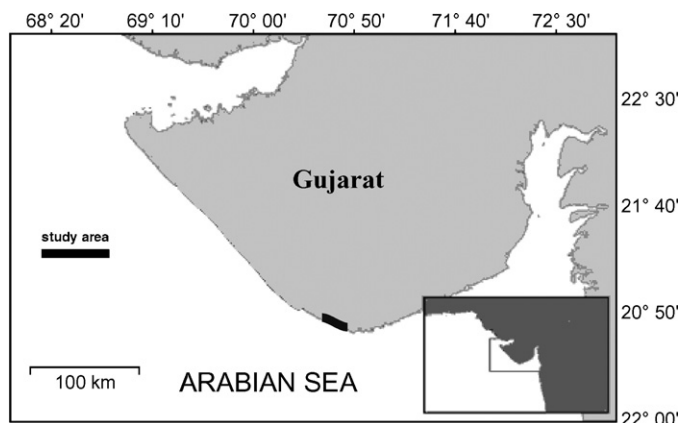


Fig. 1. Map showing study area.

which is exposed during low water tide) just in front of effluent outfall. The second, third and fourth stations were also situated in the intertidal belt of the coast at 1, 5 and 15 km away, respectively, in the down stream side of the effluent discharge point (Figs. 1 and 2). Station-4 situated at latitude $20^{\circ}43'N$ and longitude $70^{\circ}47'E$ and unpolluted by the effluent was considered as control. The effect of the said effluent decreases as we go down stream because of dilution due to sea current (as evidenced by seawater analysis, discussed later). Therefore, the control station was chosen almost 15 km away from the point, where the actual effluent is discharged through submarine outfall by the factory. There is no fresh water inflow at these stations and the tide pattern is semidiurnal. In fact, southwest region off Arabian Sea, where the experiment has been conducted, experiences biannual reversion of water movements due to prevailing monsoons. All the stations have hydrography of completely open reef. The seaweeds grow luxuriantly at almost all the stations. Even though the trace metal distribution in the coastal environment is to a great extent influenced by fresh water inflow, the areas of the current investigation do not show this effect. The seawater sam-

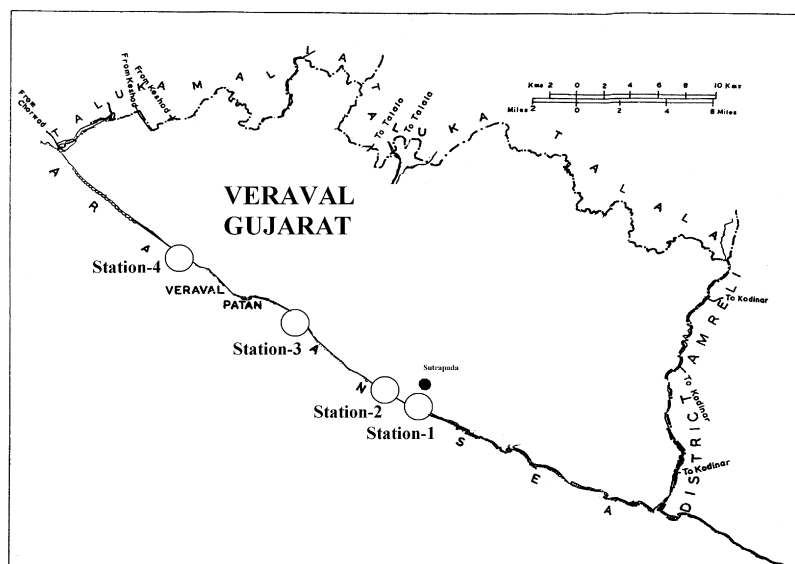


Fig. 2. Map showing effluent affected and control stations.

ples were collected from the sub tidal region in front of each station, while the diluted and undiluted effluents were collected from the factory premises. All the studies were performed during low water spring tides during last week of December 2003.

2.2. Sampling procedures, pretreatments and analysis of reference material

The samples of *Padina tetrastratica* Hauck., *Sargassum tenerrimum* J. Ag., *Gelidiella acerosa* (Forsk.) Feldman et Hamel, *Gracilaria corticata* J. Ag. and *Soleria robusta* (Grev.) Kylin, were manually collected from each station. The whole plants were cut above holdfast before collection. Only those species were collected which were found in appreciable quantity at all stations and at control. The seaweeds (fresh weight 2 kg) of same age and good health were collected randomly from the intertidal belt of each station. Each sample of seaweed was washed thoroughly three times with filtered seawater to remove dirt and other attached material and then they were rapidly rinsed in deionized water to remove adhere seawater. The samples were brought to the shore laboratory and spread on clean polythene sheet under shade and left for drying. The plants and animal epiphytes and other material attached to the plants were physically hand picked before drying. The dried material was packed in polythene bags and they were dried in air forced oven at 60 °C till constant weight. These samples were pulverized and sieved through 60 µm mesh sieve out of which 100 g pulverized samples were again dried at 60 °C and stored in desiccators for metal analysis. About 1 g (dry weight) of the pulverized sample of each species of seaweeds and standard reference material (SRM 2702 supplied by the National Institute of Standard and Technology, USA) were digested in microwave oven after 12 h of premineralization with 8 mL of ultra pure concentrated HNO₃ Merck Suprapur (Darmstadt, Germany). The solutions were filtered through Whatmann type 589/2 filters and diluted accurately to 25 mL volume with ultra pure deionized water. Such solutions were then analyzed for metal content by Inductively Coupled Plasma Spectrophotometer, model Perkin-Elmer Optima 2000 DV. The quality assurance of the result was controlled by the use of above said standard reference material. Precision of the analytical procedure was tested by treating 10 subsamples from one station. The following coefficients of variation were observed, Al 1.5%, Cr 1.1%, Mn 0.4%, Fe 1.6%, Cu 1.1%, Zn 1.3%, Ag 1.2% and Cd 1.3%.

Surface seawater samples were collected from the sub tidal water in front of each sampling station during the course of the study. Samples were filtered through acid-cleaned 0.45 µm membrane filters, stored in 1000 mL polypropylene bottles and frozen after the addition of nitric acid to adjust the pH between 4 and 5. The metals were determined by means of ICP-AES, using the standard addition procedure. The precision of the methodology expressed as standard deviation percentage was less than 12% for all metals except for Cr (26%).

All chemicals used in sample treatments were of ultrapure grade. Ultrapure water (Milli-Q System, Millipore) was used for all solutions. All glassware was cleaned prior to use by soaking in 10% HNO₃ for 24 h and rinsed with Milli-Q water. The standard

solutions of metals were prepared from stock standard solution of ultrapure grade supplied by Merck.

The physico-chemical constituents of effluent and seawater were estimated as per methods given below. Sodium and potassium were estimated by Flame Photometer (Model Evans Electro Selenium, EEL), where as calcium, magnesium, chloride and sulfate were estimated by the methods given by Mendham et al. [26]. The carbonate, bicarbonate and hydroxide were determined by the method described by Scott [27]. The total dissolved solids were estimated by the standard method [28]. The specific gravity was determined by specific gravity bottle method. All other remaining parameters were determined as per method described earlier [10,29].

2.3. Statistical analysis

The statistical analysis was performed in triplicate samples of effluent and effluent affected seawater. The physiochemical parameters were analyzed in the five replicates of the same sample for each parameter. The one-way ANOVA was analyzed by Microsoft Excel Software (Version 9.0.2720).

3. Results and discussion

3.1. Bioaccumulation of metals by seaweeds

The effect of soda ash industry effluent on bioaccumulation of metals in seaweeds is presented in Table 1. The bioaccumulation of Al, Mn and Fe in *G. corticata*, *S. tenerrimum*, *G. acerosa* and *S. robusta* (Mn not detected) increased continuously as distance increased from outfall. Therefore, concentration was maximum at control site ($p < 0.01$). However, *P. tetrastratica* showed reverse trend for these three metals. Au, Co, Hg, Ni, Pb, Pt and Sn were not recorded from any species of seaweeds from all sampling points including control. However, Cr was recorded in *G. acerosa* from control site only. The bioaccumulation of Cu and Ag showed different trends. Accumulation of Cu in *G. corticata* was maximum near effluent discharge point and minimum at control site where as its accumulation in *P. tetrastratica* was more at station-3 as compared to station-2. While in case of *S. tenerrimum* the lowest concentration was observed in control and highest at station-3 as compared to station-1 ($p < 0.01$). The concentration of Cu in *S. robusta* was less in control as compared to station-3. However, silver showed reverse trend in *G. corticata*, *P. tetrastratica* and *S. robusta*. The concentration of Ag in *S. tenerrimum* was maximum at station-2 whereas it was below detection limit at station-3. The bioaccumulation of Zn continuously increased in all the species of seaweeds as concentration of effluent decreased as well as in control site ($p < 0.01$). Bioaccumulation of Cd was seen in case of *G. corticata*, *G. acerosa* and *S. robusta* only under polluted conditions.

The bioconcentration of Al ranged from 0.83 mg g⁻¹ in *G. acerosa* to 7.6 mg g⁻¹ in *G. acerosa*, chromium from below detectable limits in all but one to 0.4 mg g⁻¹ in *G. acerosa*. While Mn varied from non-detectable quantity in *S. tenerrimum* and *S. robusta* to 0.250 mg g⁻¹ in *G. corticata*. Similarly concentration of iron ranged from 1.40 mg g⁻¹ in *S. robusta*

Table 1
Effect of soda ash industry effluent on the bioaccumulation of metals^a by seaweeds in in situ conditions (mg g⁻¹ dry weight)

Station	Name of seaweed species	Al	Cr	Mn	Fe	Cu	Zn	Ag	Cd
Station-1 [#]	<i>Gracilaria corticata</i>	2.170 ± 0.008	<0.02	0.140 ± 0.001	3.20 ± 0.01	0.115 ± 0.002	<0.05	0.060 ± 0.01	0.104 ± 0.002
Station-2	<i>Padina tetrastromatica</i>	2.240 ± 0.002	<0.02	0.090 ± 0.002	4.35 ± 0.06	0.111 ± 0.001	0.052 ± 0.001	0.190 ± 0.01	<0.01
	<i>Sargassum tenerrimum</i>	1.370 ± 0.006	<0.02	<0.01	1.95 ± 0.02	0.110 ± 0.002	<0.05	0.160 ± 0.006	<0.01
Station-3	<i>Padina tetrastromatica</i>	1.540 ± 0.001	<0.02	0.077 ± 0.001	3.87 ± 0.02	0.127 ± 0.001	0.055 ± 0.006	0.190 ± 0.003	<0.01
	<i>Sargassum tenerrimum</i>	1.50 ± 0.01	<0.02	0.017 ± 0.001	2.54 ± 0.01	0.128 ± 0.001	<0.05	<0.06	<0.01
	<i>Gelidium acerosa</i>	0.83 ± 0.01	<0.02	0.037 ± 0.003	5.70 ± 0.1	<0.040	0.077 ± 0.005	0.135 ± 0.001	0.151 ± 0.001
Station-4 (control)	<i>Soleria robusta</i>	0.946 ± 0.007	<0.02	<0.01	1.40 ± 0.007	0.098 ± 0.001	<0.05	<0.06	0.117 ± 0.002
	<i>Sargassum tenerrimum</i>	1.9 ± 0.1	<0.02	0.047 ± 0.005	3.03 ± 0.02	0.058 ± 0.001	1.100 ± 0.002	<0.06	<0.01
	<i>Gracilaria corticata</i>	3.6 ± 0.1	<0.02	0.250 ± 0.01	7.20 ± 0.2	0.107 ± 0.003	1.140 ± 0.001	0.154 ± 0.004	<0.01
	<i>Gelidium acerosa</i>	7.6 ± 0.3	0.4 ± 0.001	0.210 ± 0.001	13.20 ± 0.2	0.150 ± 0.009	0.920 ± 0.008	0.164 ± 0.003	<0.01
	<i>Soleria robusta</i>	1.430 ± 0.003	<0.02	<0.01	2.50 ± 0.09	0.090 ± 0.001	0.630 ± 0.001	0.182 ± 0.001	<0.01

^a Au (<0.1), Co (<0.02), Hg (<0.1), Ni (<0.05), Pb (<0.1), Pt (<0.1) and Sn (<0.2) in all the samples collected. [#] 'c' sign preceded by the figure indicates that the concentration of that particular metal is below detection limit.

[#] Near effluent discharge point.

to 13.20 mg g⁻¹ in *G. acerosa*, Cu from non-detectable quantity in *G. acerosa* to 0.150 mg g⁻¹ in *G. acerosa* and Zn from below non-detectable limit in *G. corticata*, *S. tenerrimum* and *S. robusta* to 1.140 mg g⁻¹ in *G. corticata*. The bioconcentration of Ag varied from non-detectable quantity in *S. tenerrimum* and *S. robusta* to 0.190 mg g⁻¹ in *P. tetrastromatica*, Cd concentration was below detectable limits in most of the species except in *G. acerosa* where it was found to be 1.51 mg g⁻¹. The results indicate that the highest percentage of different heavy metals were detected in *G. acerosa*, *G. corticata* and *P. tetrastromatica* (66.66, 22.22 and 11.11%, respectively). The soda ash industry effluent has significantly affected the metal sequestering capacity of most of the seaweeds. However, some species showed reverse trends.

3.2. Concentration factors of metals in seaweeds

Concentration factors (CF) were calculated for each metal and seaweed as the ratio of the mean metal concentration in the seaweed and its mean concentration in the seawater collected from the same station. Mathematically,

$$CF = \frac{C_s}{C_{sw}}$$

where C_s is the mean metal concentration in the seaweed and C_{sw} is the mean metal concentration in the seawater collected from the same station.

The influence of soda ash industry effluent on concentration factor of different species of seaweeds for different metal ions is depicted in Table 2. The reduction in CF of Al, at different distance from outfall over control, ranged from 22.97 in *S. tenerrimum* to 90.74% in *G. acerosa*, while that of Mn ranged from 40.85% in *G. corticata* to 82.71% in *G. acerosa*. Similarly the reduction in CF for Fe ranged from 16.17 in *S. tenerrimum* to 57.05% in *G. acerosa*, while for Zn it ranged from 5.45 in *P. tetrastromatica* to 91.6% in *G. acerosa*. However, for Ag reduction in CF varied from 17.68 in *G. acerosa* to 59.09% in *G. corticata*. The CF for Cu showed reverse trend, as the CF was more for seaweed growing in effluent affected region than control. The increase in CF (except *P. tetrastromatica* where it decreased) in these seaweed ranged from 6.52 in *S. robusta* to 120.69 in *S. tenerrimum*. The increase or decrease of CF for *P. tetrastromatica* at 1 km distance was calculated with reference to plants at 3 km distance, instead of control, as this seaweed was not recorded at control. An increase in concentration factor for Al, Mn, Fe and Ag ranged from 2.65 in silver to 81.48% in Al. However, Zn and Cu, showed reverse trend in this seaweed, as reduction in CF was observed at 1 km distance with reference to 3 km distance. It was not possible to calculate CFs in seaweed for other metals as these metals were below detection limit in seawater. The results indicate that maximum reduction in CF over control was observed in *G. acerosa* (75% metals) $p < 0.01$, followed by *G. corticata* (25%) $p < 0.05$.

The values for CF in different seaweeds for different metals showed different trends of variation. The trend in *G. corticata* was Fe > Al > Mn > Cu > Ag while in *P. tetrastromatica* it was Fe > Al > Mn > Ag > Cu > Zn. Similarly the trend for *S. tenerrimum*

Table 2
Impact of soda ash industry effluent on the bioconcentration factors of metals^{a,®} in seaweeds

Station	Name of seaweed species	Al	Cr	Mn	Fe	Cu	Zn	Ag	Cd
Station-1	<i>Gracilaria corticata</i>	17200 ± 568 (-46.31)	-	13900 ± 216 (-40.85)	322000 ± 2015 (-55.46)	2875 ± 133 (+7.48)	-	1050 ± 120 (-59.09)	10400 ± 202
Station-2	<i>Padina tetrastrumatica</i>	21300 ± 236 (+81.48)	-	8700 ± 324 (+12.98)	435000 ± 1093 (+12.40)	2775 ± 98 (-12.60)	1040 ± 23 (-5.45)	3200 ± 55 (+2.65)	-
	<i>Sargassum tenerrimum</i>	13100 ± 372 (-22.97)	-	-	195000 ± 909 (-35.64)	2850 ± 67 (+96.55)	-	2650 ± 41	-
	<i>Padina tetrastrumatica</i>	11750 ± 105	-	7700 ± 292	387000 ± 1567	3175 ± 97	1100 ± 50	3100 ± 88	-
Station-3	<i>Sargassum tenerrimum</i>	11450 ± 233 (-32.4)	-	1700 ± 87 (-63.83)	254000 ± 1055 (-16.71)	3200 ± 101 (+120.69)	-	-	-
	<i>Gelidium acerosa</i>	6400 ± 98 (-90.74)	-	3700 ± 54 (-82.71)	567000 ± 993 (-57.05)	-	1550 ± 31 (-91.60)	2250 ± 42 (-17.68)	15100 ± 111
	<i>Soleria robusta</i>	8600 ± 101 (-33.24)	-	-	140000 (-44.45)	2450 ± 99 (+6.52)	-	-	11700 ± 155
Station-4	<i>Sargassum tenerrimum</i>	16900 ± 434	-	4700 ± 66	303000 ± 1751	1450 ± 41	22000 ± 101	-	-
	<i>Gracilaria corticata</i>	32100 ± 721	-	23500 ± 367	723000 ± 2111	2675 ± 33	22800 ± 990	2600 ± 37	-
	<i>Gelidium acerosa</i>	68700 ± 829	20000 ± 411	21400 ± 297	1320000 ± 2965	3775 ± 68	18300 ± 857	2700 ± 46	-
	<i>Soleria robusta</i>	12800 ± 214	-	-	252000 ± 1200	2300 ± 51	12600 ± 657	3050 ± 71	-

(-) It is not possible to calculate concentration factors, as no metal is present in seawater. ^a Figures in parenthesis indicate increase/decrease of CFs (in percentage) over control or farthest distance from outfall. Minus or plus sign preceded by numbers indicates decrease or increase, respectively, over control or farthest distance from outfall. [®] Au (<0.1), Co (<0.02), Hg (<0.1), Ni (<0.05), Pb (<0.1), Pt (<0.1) and Sn (<0.2) in all the samples collected.

mum was Fe > Al > Cu > Ag, while that for *G. acerosa* it was Fe > Cd > Al > Mn > Ag > Zn. The similar trend for *S. robusta* was Fe > Cd > Al > Cu.

3.3. Physico-chemical characteristics of soda ash industry effluent

The physico-chemical characteristics of soda ash industry effluent and seawater affected by such effluent at different distances from outfall are given in Tables 3 and 4. The undiluted original effluent is characterized by very high pH (11.25), density (1.1007 kg L⁻¹), settleable solids (0.201 kg L⁻¹), total dissolved solids (0.163 kg L⁻¹) and nutrients like ammonia (562.22 μmol L⁻¹) and nitrate (187.50 μmol L⁻¹). The concentration of these parameters in diluted effluent was reduced by 6.59 for density to 66.14% for total dissolved solids. The pH of diluted effluent and seawater at near effluent discharge point were less than seawater pH while at other distances from outfall it was normal (8.08–8.34). The specific gravity, density, total suspended solids and total dissolved solids decreased continuously from undiluted effluent to seawater affected up to 1 km (*p* < 0.01). However, all these parameters had increasing trends (except total suspended solids) for station-2 onwards (up to station-4) (*p* < 0.05; Table 3).

The concentration of all studied parameters of soluble fraction of effluent was more (8.13–50.2%) in undiluted effluent than diluted effluent except magnesium, sulfate, bicarbonate, nitrate and nitrite where reverse trend was observed (283.78–1889.4% reduction). Clear trend of variation of different parameters of seawater was not observed from effluent discharge point up to control site as different parameters showed different trends at different distances (Table 4).

3.4. Relationships between different constituents of seaweeds

The results indicate that the bioaccumulation of Al, Mn and Fe metals increases in *G. corticata*, *S. tenerrimum*, *G. acerosa* and *S. robusta* as we proceed from station-1 to station-4 (*p* < 0.01). Similar trend has been observed in Zn with all the seaweed studied. An inverse correlation of heavy metal uptake like Cd with reference to Ca ion of the ambient water has been reported [30]. According to them the uptake of Cd is higher when Ca ion is less and vice versa. This correlates with above said data as the concentration of metals in these four species increased (Tables 1 and 4). The above said correlation has also been observed with reference to total dissolved solids of the seawater (Tables 1, 3 and 4). The authors feel that it is more logical to attribute this relationship, in highly complex effluent like soda ash industry effluent, to total dissolved solids rather than Ca alone. However, the present study does not support this conclusion for Cd as sequestering of Cd was more in *G. corticata*, *S. tenerrimum* and *S. robusta* at high degree of pollution as compared to control or less pollutant condition. It seems that mechanism of biosequestering of Cd by *G. corticata*, *S. tenerrimum* (Ag also) and *S. robusta* is different with respect to the above said three metals as higher accumulation was observed

Table 3
Physico-chemical quality of the soda ash industry effluent and effluent affected seawaters

Parameters/sample number	1 ^a	2 ^a	3 ^a	4 ^a	5 ^a	6 ^a
pH	11.25 ± 0.01	7.94 ± 0.01	7.53 ± 0.01	8.34 ± 0.01	8.08 ± 0.02	8.17 ± 0.01
Specific gravity	1.0713 ± 0.0005	1.0198 ± 0.0003	1.0174 ± 0.0001	1.0169 ± 0.0002	1.0176 ± 0.0003	1.0181 ± 0.0001
Density (g L ⁻¹)	1100.7 ± 0.1	1028.20 ± 0.09	1025.7 ± 0.2	1022.4 ± 0.1	1024.8 ± 0.1	1024.2 ± 0.1
Settleable solid (mL L ⁻¹)	210 ± 11	150.0 ± 12.1	–	–	–	–
Settleable solid (g L ⁻¹)	201 ± 3	160 ± 3	–	–	–	–
Total suspended solid (g L ⁻¹)	0.51 ± 0.01	0.31 ± 0.02	–	0.016 ± 0.002	0.014 ± 0.001	0.013 ± 0.001
Total dissolved solid (g L ⁻¹)	163 ± 7	55 ± 2	45.1 ± 0.6	44.7 ± 0.6	45.0 ± 0.7	46.0 ± 0.7

^a Sample-1, original undiluted effluent sample collected from factory premises; 2, original effluent diluted with sea water collected from the open channel coming from factory and before entering to submarine outfall pipeline; 3, sample of seawater collected from near effluent discharge point (down stream) from submarine outfall; 4, sample of seawater collected from 1 km away (down stream) from submarine outfall; 5, sample of seawater collected from 5 km away (down stream) from submarine outfall; 6, sample of seawater collected from 15 km away (down stream) from submarine outfall (control). Treated as control site for seaweed studies.

with species having higher Ca content and vice versa. In this case also a positive correlation was observed with total dissolved solids of the seawater at different stations. Different mechanisms for biosequestering of metals is described [1], which describes the differences of this activity to various metals in different seaweed. There are differences in between different species in terms of bioaccumulation of different metals which is to be contributed to the physiology of the seaweeds as well rather than effluent alone. However, the effect due to effluent is quite large comparing with the effect due to physiology of the seaweed.

The present study indicates that as highest concentration of different heavy metals were detected in agar yielding seaweeds like *G. acerosa* and *G. corticata* (Tables 2 and 3), therefore, these species may be cultivated in large scale in soda ash industry effluent area to remove heavy metals and plants nutrients especially nitrogen species (as soda ash industry effluent is rich in nitrogen species; Table 4). Based on his extensive research experience on cultivation biology of economically important seaweeds, Fei [31] believes that all cultivated seaweeds have actually played and are continuing to function as scavengers. The results also indicate that in addition to *G. acerosa* and *G. corticata*, *P. tetrastratica* can be used as scavengers for Al,

Mn, Fe and Ag from soda ash industry effluent affected seawater under natural condition. Similarly *S. tenerrimum* can also be used for scavenging Cu under such conditions as it is increased in CF ranged from 96.55 to 120.69%.

Sawidis et al. [20] states that the concentration of metals in the various seaweed species may reflect their morphology, those seaweeds having a larger surface area were found to have greater heavy metal content. However, in present study seaweeds with different morphology and surface area ranging from *Gelidiella* and *Gracilaria* (with cylindrical thin and flat branched fronds) to *Padina* and *Sargassum* (having thin lettuce like fronds and tree like fronds having stem, leaf like structure) has shown very high scavenging activity, although they are morphologically quite different. It seems that the high scavenging activity of particular seaweed is dependent on the nature of its cell membrane which greatly facilitates the movement of some metal ions to cells as compared to other metals. Different mechanism on entry of heavy metal to cell is described [1].

Species of *Padina* and *Sargassum* were reported to be the best species for biomonitoring and phytoremediation of Zn from coastal tropical environment [32]. However, the present study showed reverse trend as bioaccumulation of Zn in these genera

Table 4
Inorganic constituents of the soluble fraction of the soda ash industry effluent and effluent affected seawaters

Parameters/sample number	1 ^a	2 ^a	3 ^a	4 ^a	5 ^a	6 ^a
Total dissolved solids (g l ⁻¹)	163 ± 2	55.2 ± 0.8	45.1 ± 0.6	44.7 ± 0.3	45.0 ± 0.1	46.0 ± 0.2
Sodium (g L ⁻¹)	41 ± 2	23.5 ± 0.4	20.3 ± 0.1	19.6 ± 0.2	19.7 ± 0.2	19.7 ± 0.1
Potassium (g L ⁻¹)	4.6 ± 0.2	0.48 ± 0.03	0.29 ± 0.01	0.29 ± 0.01	0.37 ± 0.03	0.29 ± 0.01
Calcium (g L ⁻¹)	32.0 ± 2.1	2.6 ± 0.3	0.72 ± 0.01	0.80 ± 0.01	0.580 ± 0.008	0.600 ± 0.007
Magnesium (g L ⁻¹)	ND	1.030 ± 0.005	2.08 ± 0.05	1.14 ± 0.05	1.33 ± 0.02	1.34 ± 0.02
Chloride (g L ⁻¹)	82.4 ± 6.7	24 ± 1	19 ± 1	18 ± 1	19 ± 1	19 ± 1
Sulfate (g L ⁻¹)	0.740 ± 0.001	2.8 ± 0.8	1.6 ± 0.1	3 ± 1	3.0 ± 0.5	3.3 ± 0.6
Carbonate (g L ⁻¹)	240 ± 12	ND	ND	ND	ND	ND
Hydroxide (g L ⁻¹)	467 ± 15	ND	ND	ND	ND	ND
Bicarbonate (g L ⁻¹)	ND	20 ± 2	1.000 ± 0.001	1.050 ± 0.006	0.990 ± 0.001	0.850 ± 0.007
Ammonical-N (μmol L ⁻¹)	562 ± 10	192 ± 5	0.380 ± 0.001	0.380 ± 0.001	3.60 ± 0.01	0.700 ± 0.003
Nitrite-N (μmol L ⁻¹)	1.88 ± 0.01	37.4 ± 1.1	0.570 ± 0.001	7.8 ± 0.1	1.170 ± 0.001	0.722 ± 0.001
Nitrate-N (μmol L ⁻¹)	188 ± 1	32.90 ± 0.11	29.77 ± 0.01	29.03 ± 0.01	54.60 ± 0.01	8.0 ± 0.2
Phosphate-P (μmol L ⁻¹)	6.15 ± 0.01	3.08 ± 0.03	0.700 ± 0.005	2.2 ± 0.1	17 ± 1	0.600 ± 0.001

^a Sample-1, original undiluted effluent sample collected from factory premises; 2, original effluent diluted with sea water collected from the open channel coming from factory and before entering to submarine outfall pipeline; 3, sample of seawater collected from near effluent discharge point (down stream) from submarine outfall; 4, sample of seawater collected from 1 km away (down stream) from submarine outfall; 5, sample of seawater collected from 5 km away (down stream) from submarine outfall; 6, sample of seawater collected from 15 km away (down stream) from submarine outfall (control) treated as control site for seaweed studies.

were low. Probably in such cases species differences of the same genera may have different ability to concentrate same metal ion [19].

It is interesting to note that the bioconcentration of Ag and Au is very poor by seaweeds (Tables 1 and 2). The published reports on these two metals are also scanty, whereas no published literature available for Pt [16,33]. Our results indicate that Pt has not been reported either from seawater or seaweeds, probably the bioavailability of these metals might be due to their low polarity which hamper uptake [34].

Acknowledgements

The authors are thankful to Dr. P.K. Ghosh, Director, CSM-CRI, for providing facility and encouragements. They are also thankful to CSIR, New Delhi, for providing financial support. Sincere thanks are also due to Dr. S. Padmaja for her help during the course of revising this manuscript.

References

- [1] E. Pinto, C.S. Teresa, A.S.L. Maria, K.O. Oswaldo, D. Morse, C. Pio, Heavy metal induced oxidative stress in seaweeds, *J. Phycol.* 39 (2003) 1008–1018.
- [2] R. Allan, Mining and metals in the environment, *J. Geochem. Explor.* 58 (1997) 95–100.
- [3] G. Macfarlane, M. Burchett, Photosynthetic pigments and peroxides activity as indicators of heavy metal stress in the grey mangrove, *Avicennia marina* (Forsk.), *Vierh. Mar. Pollut. Bull.* 42 (2001) 233–240.
- [4] G. Wickfors, R. Ukeles, Growth and adoption of estuarine unicellular seaweed in media with excess copper, cadmium or zinc, *Mar. Ecol. Prog. Ser.* 7 (1982) 120–191.
- [5] S. Rebhun, A. Amotz, The distribution of cadmium between the marine seaweed *Chlorella stigmatophora* and seawater medium, *Water Res.* 60 (1984) 111–119.
- [6] M. Cotté-Krief, C. Guien, A. Thomas, J. Martin, Sources of Cd, Cu, Ni and Zn in Portuguese coastal waters, *Mar. Chem.* 71 (2000) 199–214.
- [7] A. Bu-Olayam, R. Al-Hassan, B. Thomas, M. Subrahmanyam, Impact of trace metals and nutrient levels on phytoplankton from the Kuwait coast, *Env. Int.* 26 (2001) 199–203.
- [8] B.K. Esser, A. Volpe, At-sea high resolution trace element mapping: San Diego bay and its plume in the adjacent coastal ocean, *Env. Sci. Technol.* 36 (2002) 2826–2832.
- [9] K.M. El-Moselhy, M.N. Gabal, Trace metals in water, sediments and marine organisms from the northern part of the Gulf of Suez, Red Sea, *J. Mar. Syst.* 46 (2004) 39–46.
- [10] A. Tewari, C. Raghunathan, Y. Khambhaty, R.N. Jadeja, Impact of soda ash industry effluent on biodiversity of epiphytic fauna of seaweeds, zooplankton and benthos of coastal region of Gujarat, *Proc. Natl. Acad. Sci. India 75B (IV)* (2005) 271–282.
- [11] Personal communication with plant authorities of soda ash industries.
- [12] M. Caliceti, E. Argese, A. Sfriso, B. Pavoni, Heavy metal contamination in the seaweeds of the Venice lagoon, *Chemosphere* 47 (2002) 443–454.
- [13] M.E. Conti, G. Cecchetti, A biomonitoring study: trace metals in seaweed and mollusks from Tyrrhenian coastal areas, *Env. Res.* 93 (2003) 99–112.
- [14] M. Ganesan, L. Kannan, Iron and manganese concentrations in seawater, sediments and marine seaweed of Tuticorin coast, southeast coast of India, *Indian J. Mar. Sci.* 24 (1995) 236–237.
- [15] M. Ganesan, R. Kannan, K. Rajendran, C. Govindasamy, P. Sampathkumar, L. Kannan, Trace metal distribution in seaweeds of the Gulf of Mannar, Bay of Bengal, *Mar. Pollut. Bull.* 22 (1991) 205–207.
- [16] X. Hou, X. Yan, Study on the concentration and seasonal variation of inorganic elements in 35 species of marine seaweed, *Sci. Total Env.* 222 (1998) 141–156.
- [17] A.S. Kalesh, S.M. Nair, Iron and manganese levels in marine macro seaweed from Karela, southwest coast of India, *Seaweed Res. Util.* 26 (2004) 99–116.
- [18] J.O. Muse, J.D. Stripeikis, F.M. Fernández, L. d’Huicque, M.B. Tudino, C.N. Carducci, O.E. Troccoli, Seaweeds in the assessment of heavy metal pollution in the Gulf of San Jorge, Argentina, *Env. Pollut.* 104 (1999) 315–322.
- [19] F. Riget, P. Johansen, G. Asmund, Baseline levels and natural variability of elements in three seaweed species from west Greenland, *Mar. Pollut. Bull.* 34 (3) (1997) 171–176.
- [20] T. Sawidis, M.T. Brown, G. Zachariadis, I. Sratis, Trace metal concentrations in marine macro seaweed from different biotopes in the Aegean Sea, *Env. Int.* 27 (2001) 43–47.
- [21] (a) V.G. Vardanyan, B.S. Ingole, Studies on heavy metal accumulation in aquatic macrophytes from Sevan (Armenia) and Carambolim (India) lake systems, *Env. Int.* 32 (2006) 208–218; (b) C.H. Lee, T.K. Ryu, M. Chang, J.W. Choi, Effect of silver, cadmium, chromium, copper, and zinc on the fertilization of the Northern Pacific asteroid, *Asterias amurensis*, *Bull. Env. Contam. Toxicol.* 73 (2004) 613–619.
- [22] R. Villares, X. Puente, A. Carballeira, Ulva and Enteromorpha as indicators of heavy metal pollution, *Hydrobiologia* 462 (2001) 221–232.
- [23] Y. Serfor-Armah, B.J.B. Nyarko, E.K. Osae, D. Carboo, S. Anim-Sampong, F. Seku, Rhodophyta seaweed species as bioindicators for monitoring toxic element pollutants in the marine ecosystem of Ghana, *Water Air Soil Pollut.* 12 (2001) 243–253.
- [24] A. Tewari, S. Thampan, H.V. Joshi, Effect of chlor-alkali industry effluent on the growth and biochemical composition of two marine macro seaweed, *Mar. Pollut. Bull.* 21 (1) (1990) 33–38.
- [25] H.T. Ratte, Bio-accumulation and toxicity of silver compounds: a review, *Env. Toxicol. Chem.* 18 (1) (1999) 89–108.
- [26] J. Mendham, R.C. Denney, J.D. Barnes, M. Thomas, Vogel’s Textbook of Quantitative Chemical Analysis, sixth ed., Pearson Education (Singapore) Pvt. Ltd., New York, 2002.
- [27] W.W. Scott, Standard Methods of Chemical Analysis, vol. 2, fifth ed., D. Van Nostrand Company Inc., New York, 1952.
- [28] L.S. Clesceri, W.E.F. Chair, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Waste Water, 20th ed., American Public Health Association, Washington, DC, 1998 (Part 5).
- [29] A. Tewari, H.V. Joshi, R.H. Trivedi, V.G. Sravan Kumar, C. Raghunathan, Y. Khambhaty, O.S. Kotiwar, S.M. Mandal, The effect of ship scrapping industry and its associated wastes on the biomass production and biodiversity of biota in situ condition at Alang, *Mar. Pollut. Bull.* 42 (2001) 325–328.
- [30] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green, red seaweed, *Chem. Eng. J.* 97 (2004) 249–255.
- [31] X. Fei, Solving the coastal eutrophication problem by large-scale seaweed cultivation, *Hydrobiologia* 512 (2004) 145–151.
- [32] G.M.A. Filho, C.S. Karez, L.R. Andrade, Y. Yoneshigue-Valentin, W.C. Pfeiffer, Effects on growth and accumulation of zinc in six seaweed species, *Ecotoxicol. Env. Saf.* 37 (1997) 223–228.
- [33] G. Blackmore, An overview of trace metal pollution in the coastal waters of Hong Kong, *Sci. Total Env.* 214 (1–3) (1998) 21–48.
- [34] J.R. Reinfeldt, S.I. Chang, Speciation and micro seaweed bioavailability of inorganic silver, *Env. Sci. Technol.* 33 (11) (1999) 1860–1863.