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SEASONAL VARIATION IN BIOCHEMICAL AND ELEMENTAL COMPOSITION OF SOME MARINE ALGAE OF MANDAPAM, SOUTHEAST COAST OF INDIA

K. Murugaiyan And K. Sivakumar*

Dept. of Botany, Periyar Govt. Arts College, Cuddalore-607001 (Tamil Nadu) India.
*Dept. of Botany, Annamalai University, Annamalai Nagar-608002 (Tamil Nadu) India.

Abstract

Seasonal variation in growth, biochemical and elemental composition of Hypnea valentiae, Acanthophora spicifera, Laurencia papillosa, Enteromorpha compressa and Caulerpa recemosa were observed for one year from April, 2016 to March, 2017. In general, peak growth and biomass of these algae occurred during the period of pre monsoon (June-August) and post monsoon (January - March) 2016-17. The maximum values in these algae varied from 12.5 to 13.2% for protein, 13.0 to 13.3% for carbohydrate and 10.3 to 12.0% for lipid. Further Seaweed was subjected SEM-Energy Dispersive spectroscopic analysis and quantified the minerals such as Na, Mg, Si, S, Cl, K, Ca, Mn, P, Fe, Zn and Cr between April, 2016 to March, 2017. Seasonal distribution of elemental composition in the seaweeds showed that most of the minerals were in the values peak during summer followed by post-monsoon and monsoon seasons.

Key words: Seaweed, Seasonal Variation,.Marine Algae

Introduction

Studies on the biochemical constituents such as protein, carbohydrate and lipid in green and brown marine algae have been carried out from different parts of Indian coast (Dave and Parakh, 1975; Dhargalkar *et al*., 1980; Sumitra Vijayaraghavan *et al*., 1980; Dave *et al*., 1987; Parekh and Chauhan, 1987; Sobha *et al*., 1988; Chennubhotla *et al*., 1990; Reeta *et al*., 1990; Kumar, 1993; Kaliaperumal *et al*., 1994; Ganesan and Kannan, 1994. The seasonal changes in protein, carbohydrate and lipid contents of five economically important seasweeds Hypnea valentiae, Acanthophora spicifera, Laurencia papillosa, Enteromorpha compressa and Caulerpa racemosa in relation to their growth behaviour. The chemical and spectral analysis of phycocolloid of Porphyra vietnamensis were estimated by Madhaiyan and Rajasulochana, 2012. Mohan Narasimharao and Prayagamurty carried out the phytochemical analysis of labophora variegata from visakhapatnam coast 2012. Raju Saranam *et al*., (2015) studied, seaweed distribution and diversity on the intertidal rocks at Nochiyurani Coast of gulf of mannar. Kaliaperumal and chennubhotla, (2015) studied marine algae of Andrapradesh. Chennbhotla, Rao and Kaliyaperumal, (2015) concluded some adverse factors / affected on the diversity and distribution of marine macro algae along the Indian coasts. Sarojini *et al*., (2013) studied diversity and distribution of marine algae on Visakapatnam coast). Only very few of these studies were mode on the seasonal changes of biochemical constituents. Seasonal changes in elemental composition were studied for a period of one year from April, 2016 to March, 2017. Further, the seaweeds were subjected to Energy Dispersive spectroscopic analysis and the results of these studies are discussed in this paper.

***Author for correspondence :** E-mail: murugaiyan66@gmail.com

Materials and Methods

Plants of Hypnea valentiae (Turner) Montagne, *Acanthophora spicifera* (Vahl) Boergesen and *Laurencia Papillosa* (C.Agardh) Greville, *Enteromorpha compressa* (Linnaeus) Lees and *Caulerpa racemosa* (Forsskal) J. Agardh from Mandapam (Fig. 2) were collected at fortnightly intervals for one year from April, 2016 to March, 2017. The materials were collected randomly from 10 to 12 quadrats of 1.0 m^2 area in the intertidal and subtidal region upto 0.5m depth. The wet weight for all these algae were taken whereas the height of 50 plants were taken randomnly. The samples were brought to the laboratory cleaned thoroughly in fresh water followed by distilled water, dried in oven at 60-70°C, pulverised and sieved. The dried powder was used for estimating the protein carbohydrate and lipid.

The protein estimation was followed by (Lowry *et al*.,). Carbohydrate was analysed by phenol-sulphuric acid method of Dubois *et al.,* (1956). The lipid was extracted by Folch *et al*., (1957) and estimated by sulphospho-vanillin method (Barnes *et al*., 1973). Materials for each of H.valentiae, A.specifiera and L.papillosa collected in different months were mixed and phycocolloid was estimated following the method of Ji Ming Hou, (1995). Sample was taken, cut into small pieces and washed with fresh water. Then it was boiled at 60-70°C, with 300ml of 5% KOH solution for one hour. It was filtered with 80 mesh bolting silk and the filtrate was neutralised with dilute hydrochloric acid. Then 300ml distilled water was added and heated at 85°C for 2 hours. Again it was filtered in hot condition using 80 mesh bolting silk cloth. The filtrate was cooled at room temperature, cut into strips and freeze-thawed. The values were expressed as percentage in dry weight basis. Further vegetative part of these five algal species of 2-3mm size were fixed in 3% glutaraldehyde for scanning electron microscopic studies. Then they were dehydrated through a graded series of alcohol with 12-15mm interval at 4°C upto 70%. Dehydrated in 90% and 100% of alcohol at room temperature for 2-3 hours. Finally, the dehydrated samples were treated with critical point drier (CPD). They were mounted on a stub and coated with gold. They were examined using JOEL JSM-56010 LV with INSA-EDS. They were examined in at the central sophisticated instrumentation laboratory, Department of Physics, Annamalai University, Annamalai Nagar, Tamil Nadu. Physico - chemical parameters of seawater were analysed using water and soil analysis kid model 1160-E.

Results and Discussion

Physico-chemical parameter such as atmospheric temperature, surface seawater temperature, salinity, pH and DO are presented in table 1 to 4. The seasonal variation in surface water temperature and air temperature invariably showed high values during pre-monsoon and low in post monsoon. The air temperature

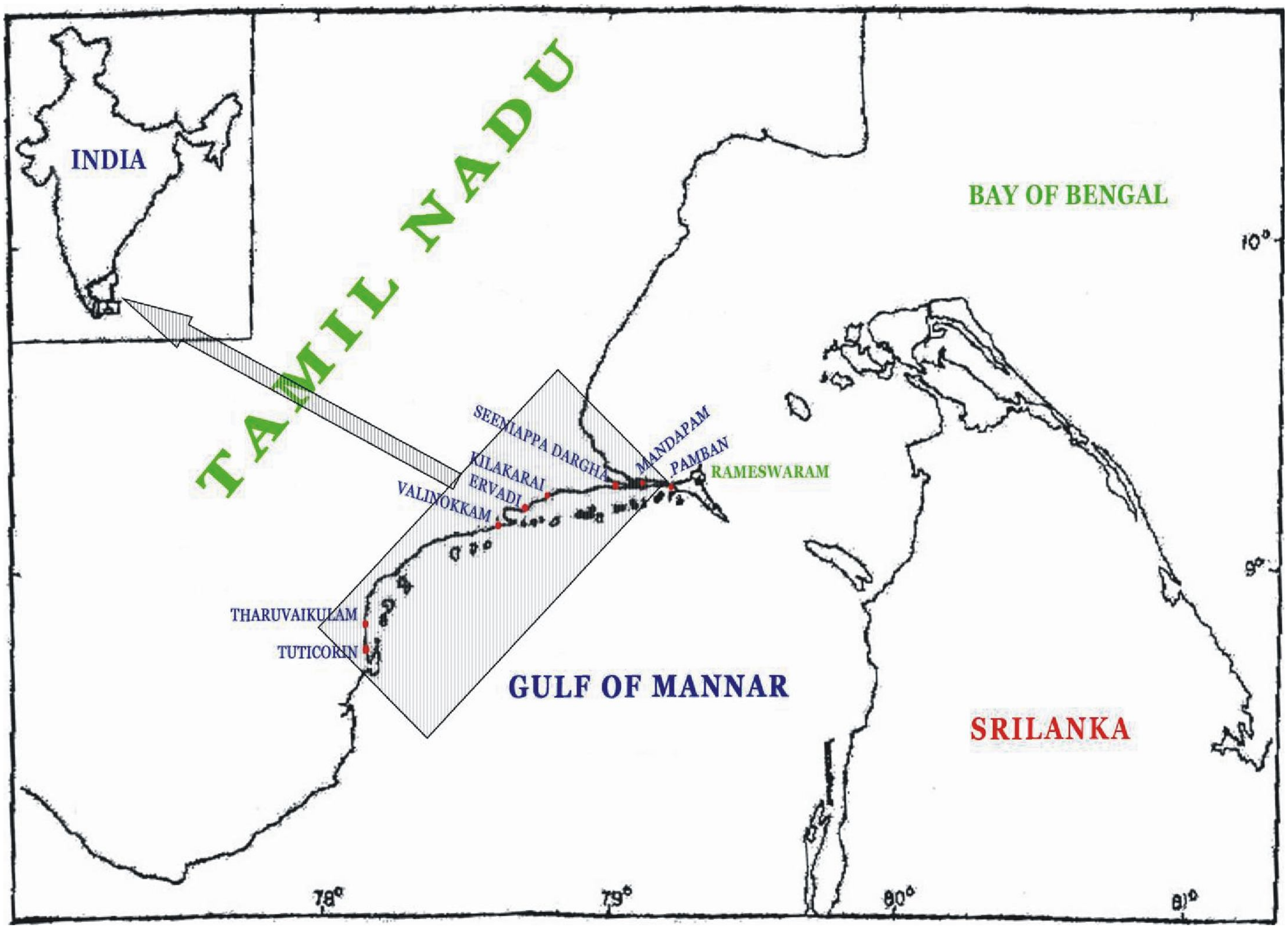

Fig.1: Map showing South East Coast of India.

Table 1: Protein content (% dry wt) in marine algae of Mandapam Coast (April 2016 - March 2017).

Month	Seaweed				
	H. valentiae	A. spicifera	L. papillosa	E. compressa	C. racemosa
April - 2016	-	13.2	12.0	-	12.0
May	-	13.2	11.8	13.0	12.0
June	11.8	12.4	12.8	12.8	11.8
July	11.8	12.1	12.6	12.6	12.3
August	12.0	12.1	12.9	12.4	12.0
September	12.6	12.7	12.8	12.2	12.5
October	12.5	12.8	12.9	12.4	12.5
November	12.5	12.0	11.8	12.2	12.0
December	12.7	12.5	12.0	12.4	12.0
January 2017	12.0	12.0	12.0	12.0	12.2
February	12.3	12.6	12.3	12.4	12.1
March	11.9	13.0	12.1	12.0	-

varied from 33.6 to 36.0°C. The surface seawater temperature varied from 33.1 to 34°C. The salinity of seawater showed high values during summer and low in monsoon period. The salinity varied from 33 to 34.2%o. The pH of seawater was high during summer and pre monsoon season. The pH varied from 7.1 to 7.5. The Dissolved Oxygen varied from 4.1 to 4.7 ppm with high value during post monsoon season.

Data collected on the seasonal changes in growth, biomass and elemental composition of H.valentiae A.specifera and L.Papillosa. In H valentiae, minimum biomass of 408g f.wt/m^2 in December and maximum biomass of 3240g f.wt/m^2 in August were obtained. Plants with minium height of 2.2cm in March and maximum height of 8.6 cm in June were observed. The biomass of A.spicifera varied from 856g fr.wt/m2 in July to 2272g fr.wt/m^2 in October. The mean height of plants varied from 4.2cm in January to 8.3cm in August. In L.papillosa, the biomass ranged from 260 to 1280g fr. wt/m2 during November and August respectively. Plants with minimum growth of 2.7 cm in January and maximum growth of 5.3 cm in May were recorded. Data collected on the seasonal variation in the biomass of *E.compressa* and *C.racemosa.*

Acanthophora spicifera (Vahl) Boergesen
Caulerpa racemosa (Forsskal) J. Agardh
Enteromorpha compressa (Linnaeus) Nees
Hypnea valentiae (Turner) Montagne
Laurencia papillosa (C. Agardh) Greville

Fig. 2: Morphology of Studied Marine Algae.

Table 2: Carbohydrate content (% dry wt) in marine algae of Mandapam Coast (April 2016 - March 2017).

Month	Seaweed				
	H. valentiae	A. spicifera	L. papillosa	E. compressa	C. racemosa
April-2016	-	13.2	13.0	-	12.0
May	-	12.4	12.1	13.0	12.6
June	12.4	12.4	12.4	12.4	12.4
July	12.1	11.8	12.9	12.4	12.4
August	11.8	11.6	12.8	12.6	13.0
September	12.0	12.4	12.9	12.4	12.8
October	11.6	12.3	13.3	12.0	12.8
November	13.0	11.8	12.0	12.2	12.8
December	12.4	11.8	12.6	12.0	12.8
January 2017	11.8	11.7	12.8	11.8	12.2
February	12.0	12.0	12.5	11.6	12.4
March	12.0	12.1	12.0	12.2	12.0

The biomass of *E.compressa* was low (128g fr.wt/m^2) in june and high (1064gfr.wt/m^2) in March. *C.racemosa*, the minimum and maximum values for biomass were 566 and 1980g fr.wt/m2 during the month of December and May respectively. The seasonal variation observed in protein, carbohydrate and lipid contents of the five algae are given in Tables 1to 3 respectively. In, general, there was no much seasonal variation in these biochemical constituents in all the algae. The protein content varied from 11.4% to 13.2% in carbohydrate from 11.6 to 13.3% and lipd from 8.9 to 12.0%. The estimated phycocolloid values were: 11.3% in *H.valentiae*, 60% in *A.spicifera* and 8.1% in *L.papillosa*.

Analysis of the different elemental composition of the five seaweeds using SEM- EDS was carried out during the different seasons from April, 2016 to March, 2017.

Table 3: Lipid content (% dry wt) in marine algae of Mandapam Coast (April 2016 - March 2017).

Month	Seaweed				
	H. valentiae	A. spicifera	L. papillosa	E. compressa	C. racemosa
April - 2016	-	10.4	9.8	-	9.0
May	-	10.0	9.6	10.3	9.8
June	10.0	10.6	10.8	9.6	9.0
July	9.6	10.8	10.0	9.8	9.8
August	9.8	10.8	10.5	9.2	10.0
September	11.4	10.0	9.6	9.8	10.0
October	11.6	11.0	9.0	9.0	10.5
November	10.0	10.2	9.2	9.6	9.6
December	11.0	10.6	9.0	9.4	9.8
January - 2017	11.5	10.4	9.2	9.2	9.0
February	11.6	10.5	9.4	9.6	9.0
March	11.4	12.0	8.9	9.0	-

The experiment was conducted for four seasons *i.e.* summer, pre monsoon, post monsoon, monsoon. The result of the study showed distinct variation in the elemental composition of the seaweeds analysed. The percentage composition of various elements was in the following order in different seaweeds. Hypnea valentiaeCa>Mg>Cr>Na>Zn>P>S>Fe>Cl >Si>K>Mn; *A.spicifera* -Ca>Si>Zn>Mg >S>Cr>Mn>Cl>P>Na>Fe>K; *G. E.compressa*-Ca>Mg>Si>Na>Cl>S>Cr >Zn>Mn>Fe> K; *C-racemosa* -Ca>Cl >Mg>P>Cr>Zn>Na>Fe>P>Mn>S>K and L. Papillosa - Ca>Cl>P>Si>Fe>Cr >Zn>Na>Mg >K (Tables 4-7).

Seaweeds collected during post - monsoon showed maximum contribution of calcium. They were ranging between 23.92 ± 0.30 to 39.54 + 0.37 total weight. Minimum values varied among species during monsoon period. In *E.compressa* lowest values were obtained for phosphorus (1.39 ± 0.06), *H. Valentiae* Mn (1.34 ± 0.06), *A. Specifera,* Cr (1.61 ± 0.07), *L.Paillosa* S (2.08 ± 0.0) and *C. racemosa,* (!.82 ± 0.07) Table 4 to 7.

In the present investigation, maximum stature and biomass of the five algae were recorded during the periods from June to August and January to March. This findings were generally accorded with the observations of Umamaheswara Rao, (1972) on the growth of *Enteromorpha compressa,* brown and red algae of Gulf of Mannar and Palk Bay. There was no marked seasonal variation in the protein, carbohydrate and lipid contents of these five algae studied. The values obtained for these biochemical constituents in the present study agree with the values obtained for the same species growing at Mandapam area (Parekh and Chauhan, l987; Chennubhotla *et al.*, 1990; Reeta *et al.*, 1990). Tuticorin (Kumar, 1993; Ganesan and Kannan, 1994). Goa coast (Sumitra Vijayaraghavan *et al.,* 1980; Solimabi *et al.,* 1980), Maharashtra coast (Dhargalkar *et al.,* 1980), Gujarat coast (Dave and Parekh, 1975; Parekh arid Chauhan, 1987; Dave *et al.*, 1987) and Lakshadweep (Kaliaperumal *et al.*, 1994).

Distribution of minerals such as Ca and Cl is high in the selected species of seaweeds in the study area. Significantly higher concentration of elements such

Table 4: Elemental composition of seaweeds using SEM-EDS during summer (April-June 2016).

Seaweed	Minerals (wt %)												
	Na	**Mg**	**Si**	**S**	**Cl-**	**K**	**Ca**	**Mn**	**P**	**Fe**	**Zn**	**Cr**	**Total**
Hypnea valentiae	11.14 ±0.11	27.96 ±0.15	4.63 ±0.09	4.10 ±0.09	3.60 ±0.07	2.44 ±0.06	41.38 ±0.20	1.50 ±0.07	-	3.22 ±0.08	-	-	99.97 ±0.18
Acanthophora spicifera	5.40 ±0.14	12.71 ±0.10	19.20 ±0.08	11.43 ±0.13	-	-	41.70 ±0.20	6.82 ±0.08	2.73 ±0.07	-	-	-	99.99 ±0.23
Enteromorpha compressa	13.36 ±0.52	17.25 ±0.25	11.66 ±0.21	6.65 ±0.14	10.33 ±0.10	1.71 ±0.13	34.01 ±0.22	2.23 ±0.07	1.16 ±0.04	1.60 ±0.17	-	-	99.96 ±0.24
Caulerpa racemasa	8.47 ±0.11	15.27 ±0.19	14.84 ±0.16	5.43 ±0.07	17.42 ±0.19	1.48 ±0.06	25.13 ±0.20	3.81 ±0.08	5.64 ±0.12	2.47 ±0.75	-	-	99.96 ±0.12
Laurencia Papillosa	7.94 ±0.09	4.65 ±0.07	11.0 ±0.09	-	20.93 ±0.14	3.67 ±0.08	32.85 ±0.22	-	13.05 ±0.10	-	-	5.88 ±0.07	99.97 ±0.20
Values are expressed as the mean± SD; n=3.													

Table 5: Elemental composition of seaweeds using SEM-EDS during premonsoon (July - Sep 2016).

Seaweed	Minerals (wt %)												
	Na	**Mg**	**Si**	**S**	**Cl-**	**K**	**Ca**	**Mn**	**P**	**Fe**	**Zn**	**Cr**	**Total**
Hypnea valentiae	9.06 ±0.12	23.13 ±0.18	2.90 ±0.09	3.71 ±0.08	3.04 ±0.08	2.44 ±0.06	33.36 ±0.19	-	3.92 ±0.08	4.25 ±0.11	4.83 ±0.08	11.77 ±0.11	99.97 ±0.18
Acanthophora spicifera	2.20 ±0.07	10.02 ±0.35	18.79 ±0.08	8.86 ±0.11	31.3 ±0.29	-	31.3 ±0.29	4.81 ±0.08	2.94 ±0.07	1.86 ±0.06	10.90 ±0.13	3.85 ±0.07	99.99 ±0.23
Enteromorpha compressa	10.64 ±0.11	13.14 ±0.15	10.95 ±0.18	8.93 ±0.08	29.10 ±0.22	1.71 ±0.13	29.10 ±0.22	1.75 ±0.07	1.93 ±0.07	1.62 ±0.06	4.06 ±0.05	6.38 ±0.06	99.96 ±0.24
Caulerpa racemasa	6.24 ±0.13	11.40 ±0.11	12.42 ±0.13	3.10 ±0.04	21.89 ±0.19	1.48 ±0.06	21.89 ±0.19	3.54 ±0.04	4.93 ±0.08	6.70 ±0.14	5.07 ±0.10	5.86 ±0.11	99.96 ±0.24
Laurencia Papillosa	5.92 ±0.12	4.44 ±0.15	9.71 ±0.08	3.57 ±0.05	27.33 ±0.22	3.67 ±0.08	27.33 ±0.22	6.10 ±0.10	9.71 ±0.08	5.60 ±0.10	7.75 ±0.08	-	99.97 ±0.20
Values are expressed as the mean± SD; n=3.													

Table 6: Elemental composition of seaweeds using SEM-EDS during monsoon (October - December 2016).

Seaweed	Minerals (wt %)												
	Na	**Mg**	**Si**	**S**	**Cl-**	**K**	**Ca**	**Mn**	**P**	**Fe**	**Zn**	**Cr**	**Total**
Hypnea valentiae	8.95 ±0.11	22.60 ±0.17	2.52 ±0.04	3.67 ±0.08	2.82 ±0.03	1.91 ±0.06	33.17 ±0.23	1.81 ±0.06	3.99 ±0.09	3.86 ±0.08	4.52 ±0.09	10.13 ±0.14	99.95 ±0.15
Acanthophora spicifera	2.14 ±0.10	9.53 ±0.08	17.98 ±0.13	8.66 ±0.12	3.82 ±0.07	1.39 ±0.08	29.26 ±0.31	4.34 ±0.08	2.64 ±0.09	1.44 ±0.06	12.46 ±0.11	6.31 ±0.04	99.99 ±0.23
Enteromorpha compressa	10.47 ±0.11	13.08 ±0.11	10.90 ±0.08	8.80 ±0.09	9.06 ±0.10	1.49 ±0.05	28.92 ±0.20	2.53 ±0.04	1.10 ±0.04	1.60 ±0.06	3.96 ±0.07	8.06 ±0.07	99.96 ±0.24
Caulerpa racemasa	6.11 ±0.13	11.32 ±0.13	10.81 ±0.09	2.93 ±0.08	16.41 ±0.19	2.09 ±0.05	21.16 ±0.17	4.50 ±0.08	4.93 ±0.07	5.15 ±0.06	6.61 ±0.08	7.94 ±0.12	99.96 ±0.24
Laurencia Papillosa	5.10 ±0.11	3.87 ±0.11	9.14 ±0.12	2.62 ±0.06	19.36 ±0.17	2.80 ±0.09	25.77 ±0.23	1.30 ±0.07	9.87 ±0.12	8.97 ±0.07	5.45 ±0.11	5.71 ±0.08	99.97 ±0.20
Values are expressed as the mean± SD; n=3.													

as Ca, Mg and K is encountered in the various type of seaweeds during summer and post-monsoon periods which reflect the capacity of these seaweed to accumulate more amount of elements during these seasons. The concentration of Na was also found to be high during summer and pre-monsoon seasons which coincides with peak period of growth (Jayasankar and Kulandaivelu, 1999). Moreover, differences in element concentration of seaweeds in the study area, during the various seasons might be related not only to different mineral level in ambient water but also due to different ecological conditions such as tidal range, temperature and salinity (Munda and Hudnik, 1991).

In general, bioaccumulation of the elements in the seaweeds depends upon the pH, salinity, dissolved O_2 and the osmotic potential of the system (Styron *et al.*,

Table 7: Elemental composition of seaweeds using SEM-EDS during post monsoon (January - March 2017).

Seaweed	Minerals (wt %)												
	Na	Mg	Si	S	Cl-	K	Ca	Mn	P	Fe	Zn	Cr	Total
Hypnea valentiae	10.70 ±0.14	26.40 ±0.32	3.15 ±0.06	3.77 ±0.11	3.04 ±0.08	2.15 ± 0.06	38.67 ±0.06	1.34 ±0.06	-	3.08 ±0.11	4.73 ±0.08	2.93 ±0.09	99.96 ±0.24
Acanthophora spicifera	3.73 ±0.08	11.41 ±0.14	18.68 ±0.16	11.81 ±0.13	3.20 ±0.10	-	39.54 ±0.37	5.18 ±0.12	2.59 ±0.98	-	2.84 ±0.06	1.61 ±0.07	99.96 ±0.31
Enteromorpha compressa	12.36 ±0.16	16.70 ±0.12	10.76 ±0.10	5.93 ±0.09	9.86 ±0.13	1.92 ±0.07	30.67 ±0.29	1.96 ±0.06	1.39 ±0.06	1.85 ±0.06	4.61 ±0.07	1.95 ±0.05	99.96 ±0.18
Caulerpa racemasa	7.10 ±0.08	13.64 ±0.05	13.65 ±0.11	4.75 ±0.07	16.03 ±0.14	1.82 ±0.07	23.92 ±0.30	3.18 ±0.04	6.09 ±0.14	1.94 ±0.08	2.73 ±0.07	5.10 ±0.08	99.95 ±0.17
Laurencia Papillosa	6.84 ±0.12	4.27 ±0.06	9.83 ±0.13	2.08 ±0.10	19.74 ±0.29	3.10 ±0.08	2996 ±0.30	-	11.56 ±0.19	-	6.69 ±0.07	5.90 ±0.21	99.97 ±0.29
Values are expressed as the mean± SD; n=3.													

1976). Marine algae exhibit high content of ash (De Boer, 1981) mainly due to the presence of Na, K, Ca and Mg cations (Fe and S will be of minor importance). Higher accumulation of Mg and Fe was mostly observed in seaweeds during summer season. It may be explained that the accumulation of elements *in situ* was more due to the reduction in osmoregulation activities usually affected by the increase in salinity. Though the silicon and chloride concentrations in ambient water exceeded those of other elements, the accumulation in seaweeds was very low and the most preferred being Ca, Mg and Na. This is probably is due to the fact that Ca and Mg are the predominant occupants of the uptake binding sites of the seaweeds which would inhibit accumulation of silicon and chloride by their competition for binding sites (Foster, 1976). The elements constituents of the cell wall of three species of *Sargassum* were reported by Sundari and Selvaraj, (2009) using SEM-EDS.

The enhanced bioaccumulation of most of the elements in seaweeds during summer and pre-monsoon seasons could be due to the following reasons : (i) ambient concentration of these elements was high during these seasons thereby facilitating their uptake by the seaweeds (ii) seasonal variation in mineral content in seaweed may be related to growth rates and metabolic process (Munda and Hudnik, 1991). Myklestad *et al.*, (1978) and Eide *et al.*, (1980) reported quick uptake of elements during summer and slow uptake during winter and (iii) ecological implications are important in metal uptake by seaweeds (Kremer and Munda, 1982). This was evident as dissolved oxygen and pH of the water samples during various seasons in the present study showed the variations of correlation between various elements in the seaweeds. The present findings showed maximum values of oxygen during summer and minimum during the winter. The higher values of oxygen during summer (April-June) are associated with the rise in seaweed population (Bhatt and Negi, 1985). These observations were in agreement with those of Chan, (1989) that the seasonal variations of the mineral concentration in aquatic biota may be due to seasonal fluctuation in tissue mass and changes in physico-chemical characteristics of the surrounding water.

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