



Review article

Seasonal variation in elemental composition of certain red algae from Southeast coast of India

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[Accepted: 22 December 2020]

Abstract: Three species of red algae belonging to the class Rhodophyceae viz. *Amphiroa fragilissima*, *Centroceras clavulatum* and *Gracilaria canaliculata* were collected from seven localities in the southeast coast of India. The collected red algae were analysed for elemental composition (Al, B, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn) using inductively coupled plasma atomic emission spectroscopy (ICP - AES) from May 2018 to April 2019 at three months interval. The seasonal variation in the elemental composition of the three red algae species showed that most of the minerals were found to accumulate during the summer season followed by pre-monsoon season. This could perhaps be due to the ambient concentration of these minerals were high during these seasons; thereby facilitating their uptake by seaweeds. The accumulation factor of certain ions by the algae were also discussed in this paper.

Keywords: Elemental composition - Inductively coupled plasma - Atomic emission spectroscopy - Seaweed - Southeast coast.

[Cite as: K Murugaiyan (2020) Seasonal variation in elemental composition of certain red algae from Southeast coast of India. *Tropical Plant Research* 7(3): 715–719]

INTRODUCTION

Seaweeds are the marine macro algae which play an important role in the marine ecosystem functioning as primary producers that provide food shelter to various aquatic organisms. From time immemorial marine algae have been considered as a food of delicacy and used as a part of diet. The use of marine algae as food for human, animals and aquaculture purposes is based on their high nutritive value arising from the richness of biochemical constituents and elements. Seaweeds are rich in minerals and trace elements like Magnesium (Mg), Iron (Fe), Potassium (K), Iodine (I), Manganese (Mn) and Chromium (Cr) at level much greater than those found in land vegetables. Like other plants seaweeds contain various organic and inorganic substances that include minerals, trace elements, protein, carbohydrate, lipids etc. which are beneficial for living beings (Kuda *et al.* 2002). They constitute important natural resources for fertilizers and play an important role in agricultural & horticulture (Fan *et al.* 2011, Bierman 2013, Cordel 2013, FAO 2013). Marine algae have been reported to contain more than sixty elements (Silas *et al.* 1987) of these about 21 elements are essential for the metabolic process in algae, whereas others do not any important metabolic roles. Devika (2015) studied nutrient composition of microalgae and its application in food industries. There is good evidence that C, H, O, N, P, S, K, Ca, Mg, Fe, Cu, Zn, Mn, and Mo are required by all algae, although S, K and Ca, can be replaced to some extent by other elements. Generally, essential as well as non-essential elements are accumulated in the tissues of algae to concentration above their levels in seawater. The elements such as C, H, O, N, P, S, Na, K, Ca and Mg are generally present in marine algae in high amounts. They are known as macro minerals, whereas the other elements, which are present in relatively low levels, are called micro minerals or trace elements. Hemavijayan (2015) evaluate the phytochemical estimation and mineral analysis of selected brown seaweeds from mullor coast. Manivannan *et al.* (2008) to analyse the mineral composition of seaweeds such as Chlorophyceae, Phaeophyceae, Rhodophyceae from Mandapam, Southeast Coast of Tamil Nadu. Reeta & Kulandaivelu (1999) studied the seasonal variation in the elemental composition of *Gracilaria* species of Gulf of Mannar, Tamil Nadu coast. Many studies have been made on the mineral distribution of Indian Marine algae also. However,

most of these studies are confined to a few coastal regions like Gujarat, Maharashtra, Goa, Mandapam etc. Information on the elemental composition of marine algae of southeast coast of India is meagre. The present study was made on the seasonal variation in the mineral composition of selected dominant red marine macro algae were studied for a period of one year (from April, 2018 to March, 2019) at three months intervals.

MATERIALS AND METHODS

Sample collection

Eight stations namely Pamban, Mandapam Seniappa-Dharga, Kilakarai, Ervadi, Valinokkam, Tharuvaikulam and Tuticorin in Coast of India were selected for the present investigation. At each station algal samples were collected during low tide period from the intertidal region 0.5 m, 1.0 m, 1.5 m and 2.0 m depth along 3 line transects (100 m intervals) using 1.0 m² metal quadrat perpendicular to sea shorts. The seaweed within the 1.0 m² quadrat were collected manually by scraping, hand picking and skin diving and also by employing small canoe. The collected algal samples were washed thoroughly in seawater to remove epiphytes and sand particles. Then the samples were kept in polythene bags and tagged for further studies. The collected marine algae were identified by referring the literatures published on identification of seaweeds by Rao (1970, 1972, 1987, Kalimuthu *et al.* 1992). Then the samples were dried at room temperature followed by hot air over at 40°C. After drying in oven the samples were powdered. The powdered samples were used for estimation of minerals.

Minerals analysis

The mineral content was estimated following the method of Farias *et al.* (2002). To 0.2 g dried powdered sample in a dry beaker 10 ml of di-acid mixture (5:2 of Nitric acid and Perchloric acid) was added. The contents of beaker were allowed to stand for 12 hours for cold digestion. The beakers were then kept on a hot plate and the contents were digested by increasing the temperature. The digestion was continued till the content become colourless. Then 5 ml of 2% nitric acid was added. The digested material was filtered through Whatman No. 1 filter paper. The filtrate was collected and made upto 20 ml. The filtrate thus obtained was suitably diluted and fed in to Inductively Coupled Plasma Spectrophotometer Perking Emler Optical Emission Spectrophotometer Optima 3400 PV (ICP-OES) using vinlab 32. The mineral content Aluminum (Al), Boron (B), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Magnesium (Mg), Manganese (Mn), Nickel (Ni), Lead (Pd) and Zinc (Zn) were analyzed.

RESULT AND DISCUSSION

Elemental analysis made on the seaweeds collected during summer of 2018 in *Amphiroa fragilissima* (L.) J.V. Lamouroux showed that it contain 12 different elements like Al, B, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn. Among these Magnesium (529.1±45.96 µg g⁻¹ of DW) was in abundant and cadmium found to be very limited to 0.38±0.63 µg g⁻¹ DW. Whereas *Centroceras clavulatum* (C.Agardh) Montagne analysed under ICP - OES composed of twelve different elements such as Al (610.4±40.83 µg g⁻¹ of DW) > mg (462.9±23.06 µg g⁻¹ of DW), > Fe (413.8±38.90 µg g⁻¹ of DW) > B (50.85±3.99 µg g⁻¹ of DW), > Mn (26.65±2.90 µg g⁻¹ of DW) > Cu (7.21±0.98 µg g⁻¹ of DW), > Cr (5.07±0.89 µg g⁻¹ of DW) > Pb (3.42±0.81 µg g⁻¹ of DW) > Zn(3.4±0.95 µg g⁻¹ of DW), > Ni (2.08±0.35 µg g⁻¹ of DW) > Co (0.7±0.05 µg g⁻¹ of DW) > Cd (0.33±0.16 µg g⁻¹ of DW). *Gracilaria canaliculata* (Kützing) Sonder contained Mg (324.1±22.09) > Fe (292.4±34.09) > Al (200.5±10.93) > Mn (55.49±3.09) > B (30.73±2.94) > Cr (13.48±1.92) > Pb (6.22±0.51) > Cu (5.36±0.89) > Zn (5.29±0.91) > Ni (4.83±0.85) > Co (1.36±0.76) > Cd (0.61±0.18) (Table 1). From these result, it could be clearly understood Al, Mg, Fe are major element in these species.

During the pre-monsoon period of 2019 there was notable amount of changes found in these three species and their elemental composition. Firstly in *Amphiroa fragilissima* there were 12 elements recorded. They were Mg (518.2±48.02) > Fe (100.5±9.01) > Al (95.8±7.09) > Mn (28.65±2.90) > B (8.53±0.88) > Cr (6.58±0.92) > Pb (4.2±0.96) > Cu (3.35±0.27) > Zn (3.22±0.27) > Ni (1.72±0.23) > Co (1.18±0.87) > Cd (0.33±0.2) (Table 2). In the case of *Centroceras clavulatum* there were 12 different elements. They include Mg (323±18.09) > Fe (282.3±12.97) > Al (190.2±12.67) > Mn (55.45±4.76) > B (30.62±2.34) > Cr (13.40±1.95) > Pb (6.21±0.37) > Zn (5.28±0.60) > Cu (5.25±0.34) > Ni (4.73±0.86) > Co (1.25±0.49) > Cd (0.52±0.29). When analysing *Gracilaria canaliculata* using ICP-OES in the pre-monsoon period. Magnesium (Mg) was the major elements (146.92±8.43). From these results, it could be clearly understood that magnesium, Aluminium (Al) & Iron (Fe) were found in major composition of these three red algal species (Table 2).

The next phase of the finding was carried out during post-monsoon of 2018. Which was vital period for the

growth of seaweeds. During this period *Amphiroa fragilissima* contain 12 different elements in the following order Mg > Fe > Al > Mn > B > Cr > Cu > Cd > Zn > Ni > Co > Pb. While, in the case of *Centroceras clavulatum* the order of elements were Fe > Mg > Al > B > Mn > Co > Cr > Co > Pb > Zn > Ni > Cd. As in the order Iron is major composition this species. In canalculated the major proportion of elements are magnesium followed by Iron (Fe), and Boron (B). The elemental composition of this species was little change when compared with other 2 species during monsoon period. Post-monsoon was the final part of the year. During this period also, these three species were chosen for the experimentation. It was observed that there were least change in the mineral accumulation in all the three species studied (Table 3).

Table 1. Mineral analysis of three species of red algae of Gulf of Mannar region during summer season ($\mu\text{g g}^{-1}$ dry weight of sample) (May 2018 to April 2019).

S.N.	Elements	Name of the species		
		<i>Amphiroa fragilissima</i> (L.) J.V. Lamouroux	<i>Centroceras clavulatum</i> (C.Agardh) Montagne	<i>Gracilaria Canaliculata</i> (Kützing) Sonder
1	Al	97.68±7.93	610.4±40.83	200.5±10.93
2	B	9.17±0.61	50.85±3.99	30.73±2.94
3	Cd	0.38±0.063	0.33± 0.16	0.61±1.18
4	Co	1.29± 0.71	0.7±0.05	1.36±0.76
5	Cr	7.36±0.96	5.07±0.89	13.48±1.92
6	Cu	3.42±0.73	7.21±0.98	5.36±0.89
7	Fe	100.6±7.89	413.8±38.90	292.4±34.09
8	Mg	529.1±45.96	462.9±23.06	324.1±22.09
9	Mn	29.67±2.39	26.65±2.90	55.49±3.09
10	Ni	1.89±0.53	2.08±0.35	4.83±0.85
11	Pb	4.69±0.86	3.42±0.81	6.22±0.51
12	Zn	3.75±0.89	3.4±0.95	5.29±0.91

Table 2. Mineral analysis of three species of red algae of Gulf of Mannar region during pre-monsoon season ($\mu\text{g g}^{-1}$ dry weight of sample) (May 2018 to April 2019).

S.N.	Elements	Name of the species		
		<i>Amphiroa fragilissima</i> (L.) J.V. Lamouroux	<i>Centroceras clavulatum</i> (C.Agardh) Montagne	<i>Gracilaria Canaliculata</i> (Kützing) Sonder
1	Al	95.18±7.09	190.2±12.67	73.05±5.78
2	B	8.53±0.88	30.62±2.34	25.65±2.14
3	Cd	0.33± 0.2	0.52±0.29	0.15± 0.58
4	Co	1.18±0.87	1.25±0.49	9.10±0.38
5	Cr	6.58±0.92	13.40±1.95	4.31±0.58
6	Cu	3.35±0.27	5.25±0.34	6.25±0.64
7	Fe	100.5±9.01	282.2±12.97	84.06±5.86
8	Mg	518.2±48.02	323±18.09	146.92±8.43
9	Mn	28.65±2.90	55.45±4.76	41.25±3.97
10	Ni	1.72±0.23	4.73±0.86	1.40±0.52
11	Pb	4.2±0.96	6.21±0.37	6.78±0.58
12	Zn	3.22±0.27	5.28±0.60	6.12±0.75

Table 3. Mineral analysis of three Red Algae species of Gulf of Mannar region during post-monsoon season ($\mu\text{g g}^{-1}$ dry weight of sample) (May 2018 to April 2019).

S.N.	Elements	Name of the species		
		<i>Amphiroa fragilissima</i> (L.) J.V. Lamouroux	<i>Centroceras clavulatum</i> (C.Agardh) Montagne	<i>Gracilaria Canaliculata</i> (Kützing) Sonder
1	Al	92.52±7.90	59.0±7.6	6.43±0.11
2	B	9.15±0.67	57±4.67	19.15±1.97
3	Cd	3.2±0.53	0.28±0.98	0.47± 0.57
4	Co	1.31±0.87	1.7±0.77	0.71±0.85
5	Cr	7.25±0.38	4.98±0.25	6.19±0.28
6	Cu	3.4±0.58	6.99±0.81	4.95±0.38
7	Fe	100.2±0.45	490.3±38.08	61.12±5.93
8	Mg	490.5±32.07	453.4±30.68	169.5±13.78
9	Mn	21.15±2.89	21.92±2.72	43.05±3.95
10	Ni	2.14±0.39	1.17±0.27	1.12±0.69
11	Pb	4.52±0.59	1.53±0.36	2.86±0.76
12	Zn	2.99±0.19	1.98±0.75	2.99±0.69

Higher accumulation of Mg and Fe was mostly observed in seaweeds during summer season, it may be explained here that the accumulation elements in situ was more due to the reduction in osmoregulation activities usually affected by the increase in salinity. The enhanced bio-accommodation of most of the elements in seaweed during summer and pre-monsoon could perhaps be due to the ambient concentration of these elements was high during these season, thereby facilitating their uptake by the seaweeds, seasonal variation in mineral content in seaweeds may be related to growth rates and metabolic process (Myklestad *et al.* 1978, Eide *et al.* 1980, Munda & Hudnik 1991), reported quick uptake of elements and slow uptake during winter, during summer and ecological implications are important in metal uptake by seaweeds (Kremer & Munda 1982). The present study was concurred with the earlier studies and the bioaccumulation of mineral composition of seaweeds were very according to several factors such as surrounding seawater, age of the plant, period of species collection, geographical area, seasons, environmental, physiological fluctuations and species specificity (Mabeau & Fleurence 1993, Kaehler & Kennish 1996). It also depends upon the pH, salinity and dissolved oxygen of the system (Styron *et al.* 1976, Soundaria Rani *et al.* 2018).

Mineral composition of seaweeds varies according to several factors such as surrounding seawater, age of the plant, period of species collection, geographical area, season, environmental, physiological fluctuation and species specificity. In the present study, the seasonal distribution of mineral concentration of 40 species of algae showed relatively high values during summer as well as pre-monsoon season when compared to other seasons during the period from April 2018 to March 2019. Some species which was studied for biochemical content in all the season but not available in some season which are avoided for easy interpretation. The high concentration of the mineral contents during the period summer and pre-monsoon would be related to the lean summer flows and increase in evaporation rate. Further, the seasonal variation of elements in marine algae are brought about by precipitation during summer while dislocation during monsoon season.

CONCLUSION

The result obtained in all the four seasons of the year (2019) such a summer, pre-monsoon, monsoon & post-monsoon were separately tabulated. Further, all the values were correlated with each other (Table 1–3). The seasonal distribution of mineral concentration in all the three red algal species frequently studied was characterized to the relatively high during summer as well as pre-monsoon season as compared to the other seasons over the sampling periods (2018 to 2019). The high concentration of mineral content during that period (2018 to 2019). The high concentration of mineral content during the periods of summer and pre-monsoon was found to be related to the lean summer flows and increase in evaporation rate (Devi *et al.* 1996).

ACKNOWLEDGEMENTS

The author thanks to the authority of Annamalai University for providing laboratory facilities and also thanks to University Grant Commission for providing fund for carry out the research work.

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