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Sodium, Potassium and Sulphate Composition in Some Seaweeds Occurring along the Coast of Gulf of Mannar, India

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Abstract: Minerals such as sodium (Na^+), potassium (K^+) and sulphate were analyzed in red, brown and green abundant seaweeds found along the Coast of Gulf of Mannar, India, during July 2005. A high mean amount of Na^+ was recorded in Chlorophyceae followed by Rhodophyceae and Phaeophyceae. The mean value of K^+ in the brown and red algae were higher when compared to green seaweeds. A less Na^+/K^+ ratio indicated high K^+ and low Na^+ in brown and red algae and a high Na^+/K^+ ratio in green seaweeds indicated high Na^+ and low K^+. The sulphate content was variable in the algae studied; the maximum concentration was found in red alga *Grateloupia lithophila* (162.8 mg g^{-1} alga dry wt.) and minimum in brown alga *Chnoospora implexa* (0.88 mg g^{-1} alga dry wt.).

Key words: Seaweeds, sodium, potassium, sulphate

INTRODUCTION

All the essential minerals are provided by seaweeds and these essential minerals may be some time absent from freshwater and food crops grown on mineral-depleted soils. Seaweeds contain 20-50% minerals in their dry weight (Kazutosi, 2002). This figure was obtained by burning off seaweed's organic material and weighing the remaining ash. The elements abundant in seaweeds include: potassium, sodium, calcium, magnesium, zinc, copper, chloride, sulfur, phosphorous, vanadium, cobalt, manganese, selenium, bromine, iodine, arsenic, iron and fluorine. Besides, seaweeds are rich in cell wall polysaccharides, vitamins and protein, of which brown algae tend to contain more minerals per unit weight than the red (Mabdau and Fleurence, 1993). Sodium, potassium and sulfur are found relatively in high quantities in marine algae and utilized directly for the cellular building blocks (De Boer, 1981). The mineral constituents of different species of marine algae around the world and Indian coast have been investigated (Rao Kesava, 1987; Rao Kesava and Indusekhar, 1987, 1989; Oza *et al*., 1983; Harold, 1977). The mineral constituents such as Ca, Na, K, P, Fe, Mn, Mg and Cl were analyzed in seaweeds (Rajasulochana *et al*., 2002; Vasanthi and Rajamanickam, 2003). The amount of K^+ was higher than Na, P and Cl contents in marine algae (Tewari and Rao, 1988). But in edible red seaweed *Porphyra vietnamensis* reported high Na and less K (Subba Rao *et al*., 2007). Though the seaweeds living in ocean containing predominantly Na and their salts, some seaweeds accumulated more K and their salts than Na. Potassium is an essential macronutrient required for the growth and metabolic activities of plants in general and seaweeds in particular. However, some seaweeds sequested more of Na^+ than K^+ (Dickson and Kirst, 1897). Sulphate is an important anion incorporated in commercially important cell wall hetero-polysaccharides of most of the seaweeds. The Gulf of Mannar located in the southeast coast of India declared as a biosphere reserve with an area of 10, 500 km^2 considered as biodiversity hot spot supported with 3600 species of corals, crustaceans, mollusks, fin fishes, seaweeds, sea grasses, mangroves and other marine animals. Seaweeds occurring abundantly in the 21 islands of this Gulf region are exploited for their commercial utilization (Kumaraguru, 2006). The present investigation was aimed to study the Na^+, K^+ and sulphate content in some red, brown and green seaweeds abundantly occurring along the coast of Gulf of Mannar, Rameswaram, Tamil Nadu, India and the proportion of Na^+ and K^+ was expressed as Na^+/K^+ ratio because it is a good index to indicate the level of Na^+ and K^+ salts in the seaweeds.

MATERIALS AND METHODS

Collection of material: Ten red seaweeds such as *Gelidiella acerosa* (Forsskal) J. Feldmann and G. Hamel, *Cheilosporum spectabile* Harvey, *Grateloupia lithophila* Boergesen, *Gracilaria corticata* var. *corticata*

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(J. Agardh) J. Agardh, *G. corticata* (J. Agardh) J. Agardh var. *cylindrica* Umamaheswara Rao, *G. canaliculata* Sonder (*G. crassa*), *G. pudumadensis* V. Krishnamurthy and Rajendran, *Hypnea valentiae* (Turner) Montagne, *Acanthophora spicifera* (Vahl) Borgesen and *Laurencia poitei* (Lamour.) Howe.; 10 brown seaweeds such as *Dictyota dichotoma* (Huds.) Lamour., *Stoechospermum marginatum* (J. Ag) Kuetz., *Padina boergesenii* Allender and Kraft, *Hydroclathrus clathratus* (C. Agardh) Howe., *Chnoospora implexa* J. Agardh, *Hormophysa cuneiformis* (J. Gmelin) P. Silva (*Hormophysa triquetra*), *Sargassum longifolium* J. Agardh, *Sargassum myriocystum* J. Agardh, *Sargassum wightii* Greville and *Turbinaria conoides* (J. Agardh) Kutzing; and 5 green seaweeds such as *Enteromorpha compressa* (Linn.) Nees, *Ulva lactuca* Linn., *Ulva reticulata* Forsskal, *Valoniopsis pachynema* (Martns) Boergsen and *Helimeda gracilis* Harvey ex J. Agardh were collected from the inter-tidal and sub-tidal regions along the Coast of Gulf of Mannar region during July 2005. After hand picking, the seaweeds were cleaned with seawater and then thoroughly with fresh water (3 to 4 times) to remove the extraneous matters such as associated fauna and pebbles. The samples were dried in shade for 5 days and then in an oven at 60°C for 12 h till getting constant weight. The algae were identified with the help of Check list of Indian Marine algae (Oza and Zaidi, 2001).

Flame photometric detection of sodium and potassium (Jackson, 1971): One gram of each dried seaweed sample was digested in 10 mL of triple acid mixture of H_2SO_4: HNO_3: HCl (9:3:1 v/v/v). Liquid ammonia was added into the digested sample to adjusted the pH 7 and the volume was made up to 100 mL by using distilled water. Then it was filtered through Whatman No.40 filter paper and the filtrates were stored in clean glass bottles till analysis made. The analysis of Na^+ and K^+ were done by using a Flame photometer (Elico, India) by selecting suitable filter against deionised water as a blank.

Estimation of sulphate (Verma *et al.*, 1977): The sulphate content of all seaweeds except 3 Red seaweeds (*Cheilosporum spectabile*, *Gracilaria crassa* and *G. pudumadensis*) and 3 Green (*Enteromorpha compressa*, *Ulva reticulata* and *Valoniopsis pachynema*) was made. One gram of each algal sample was subjected to 10 mL of triple acid mixture for digestion. To a 10 mL of aliquot prepared by triple acid mixture digestion, 1 mL of 6 M HCl followed by 5 mL of 70% sorbital solution and 1 g of $BaCl_2$. $2H_2O$ crystals were added. The content was shuck vigorously to dissolve the barium chloride and allowed to stand for at least 5 min. Then the turbidity of the suspension was read in a colorimeter at 470 nm, along with standards prepared in the same way and covering the sulphate concentration range 0-50 ppm. If the suspensions were left to stand for long time, it was advisable to shake the tubes gently before taking the reading. Triplicates were maintained for each experiment and mean values were expressed as mg g^{-1} alga dry wt.

Mean and Duncan Multiple Range Test (DMRT) were analyzed using SPSS14 statistical package and results expressed.

RESULTS

In the present study, analysis on Na^+ and K^+ content of 10 red, 10 brown and 5 green seaweeds; and sulphate content of all seaweeds except 3 red seaweeds (*Cheilosporum spectabile*, *Gracilaria crassa* and *G. pudumadensis*) and 3 green (*Enteromorpha compressa*, *Ulva reticulata* and *Valoniopsis pachynema*) occurring along the coast of Gulf of Mannar were made and the following results are recorded.

In the present study, 7 red seaweeds such as *Gelidiella acerosa*, *Cheilosporum spectabile*, *Grateloupia lithophila*, *Gracilaria corticata* var. *cylindrica*, *G. crassa*, *Hypnea valentiae* and *Laurencia poitei* were accumulated more Na than K, however the mean K content was higher than Na in the members of *Rhodophyceae* (Table 1). This is due to very high amount of 140.5, 119.12 and 114.54 mg g^{-1} dry wt. of K recorded in the red seaweeds such as *Gracilaria corticata* var. *corticata*, *G. pudumadensis* and *Acanthophora spicifera*, respectively. The mean Na/K ratio of red algae was 0.91. Unlike red algae, the ratio of Na/K in brown was decreased to 0.73 and this decrease in the mean value of Na/K ratio indicated as high K accumulation in brown seaweeds than in red (Table 2). Of the 10, 7 brown seaweeds contained more K than Na where as the rests were accumulated more Na. Based on the K^+ accumulation, the seven brown algae were arranged in decreasing order: *Sargassum longifolium*, *Turbinaria conoides*, *Stacheospermum marginatum*, *Padia boergesenii*, *Hydroclathrus clathratus*, *Dictyota dichotoma* and *Sargassum myriocystum*. Less Na/K ratio indicated high K and low Na content (Table 1, 2). A maximum amount of 121.41 mg g^{-1} alga dry wt. of K and 68.63 mg g^{-1} alga dry wt. of Na was recorded in *Sargassum longifolium* and *Turbinaria conoides*, respectively. Compared to red and brown, mean Na/K ratio was very high (1.79) in green seaweeds which indicate increasing level of Na^+ and decreasing level of K^+ (Table 1). Though a maximum Na^+ accumulation of 172.85 mg g^{-1} dry wt. was recorded in green alga *Valoniopsis pachyniema*,high proportionate accumulation of Na over K was observed in *Helimeda gracibis*, *Enteromorpha compressa*, *Valoniopsis*

Table 1: Na^+, K^+ and Na^+/K^+ ratio of seaweeds collected along the Coast of Gulf of Mannar, Rameswaram region, Tamil Nadu, India during July 2005 (*mg g^{-1} dry wt.)

Seaweeds	*Na^+	*K^+	Na^+/K^+ ratio
Red			
Gelidiella acerosa	22.87a	20.61b	1.10
Cheilosporum spectabile	96.59h	47.34f	2.04
Grateloupia lithophila	65.58g	38.18d	1.71
Gracilaria corticata var. *corticata*	43.21d	140.50j	0.30
Gracilaria corticata var. *cylindrica*	48.29e	56.19g	1.04
Gracilaria cannaliculata	36.09c	23.28c	1.55
Gracilaria pudumadensis	112.806	119.12i	0.94
Hypnea valentiae	17.79a	13.36a	1.33
Acanthophora spicifera	59.99f	114.54h	0.52
Laurencia poitei	47.78e	41.99e	1.13
Brown			
Dictyota dichotoma	27.96a	29.39a	0.95
Stoechospermum marginatum	61.00g	69.10g	0.88
Padina boergasenii	42.26c	49.63e	0.93
Hydroclathrus clathratus	31.52b	33.59b	0.93
Chnoospora implexa	55.92f	44.28d	1.26
Hormophysa triqetra	52.36e	50.77e	1.03
Sargassum longifolium	61.00g	63.76f	0.95
Sargassum myriocystum	55.92f	121.41h	0.46
Sargassum wightii	46.26d	35.88c	1.29
Turbinaria conoides	68.63	111.48	0.60
Green			
Enteromorpha comprssa	91.00d	33.59c	2.70
Ulva lactuca	25.92a	22.52b	1.15
Ulva reticulata	88.46c	50.39c	1.75
Valoniopsis pachynema	172.85e	116.06d	1.49
Helimida gracilis	34.06b	07.63a	4.46

Mean values not followed in the same letter significantly differed within the class of algae at 5 % level

Table 2: The mean Na^+, K^+ and Na^+/K^+ ratio of seaweeds collected along the Coast of Gulf of Mannar, Rameswaram region, Tamil Nadu, India during July 2005 (*mg g^{-1} alga dry wt.)

Seaweeds	*Na^+	*K^+	Na^+/K^+ ratio
Rhodophyceae (Red)	55.10b	60.51b	0.91
Phaeophyceae (Brown)	44.68a	60.92b	0.73
Chlorophyceae (Green)	82.46c	46.04a	1.79

Mean values not followed in the same letter significantly differed within the class of algae at 5% level

pachynima, *Ulva reticulata* and *U. lactuca* which was clearly indicated in Na/K ratio as an order of hierarchy (Table 1).

In the present study, sulphate content of 19 seaweeds such as red, *Gelidiella acerosa*, *Grateloupia lithophila*, *Gracilaria corticata* var. *corticata*, *Gracilaria corticata* var. *cylindrica*, *Gracilaria crassa*, *Acanthophora spicifera* and *Laurencia poitei*; brown, *Dictyota dichotoma*, *Stoechospermum marginatum*, *Padina boergeseni*, *Hydroclathrus clathratus*, *Chnoospora implexa*, *Hormophysa triquetra*, *Sargassum mariocystum*, *Sargassum longifolia*, *Sargassum wightii* and *Turbinaria conoides* and green *Ulva lactuca* and *Helimeda gracibis* was made. Generally two green algae contained high sulphate. However, of all the seaweeds studied, a maximum sulphate content was registered in red seaweed *Grateloupia lithophila* (168.2 mg g^{-1} dry wt.) while minimum sulphate content was recorded in brown seaweeds *Hormophysa triquetra*, *Chnoospora implexa*

Table 3: Sulphate content of seaweeds collected along the Coast of Gulf of Mannar, Rameswaram region, Tamil Nadu, India during July 2005

Seaweeds	Sulphate (mg g^{-1} alga dry wt.)
Red	
Gelidiella acerosa	6.190b
Grateloupia lithophila	168.200g
Gracilaria corticata var. *corticata*	3.540a
Gracilaria corticata var. *cylindrica*	106.200f
Gracilaria cannaliculata	53.100c
Acanthophora spicifera	88.500e
Laurencia poitei	79.700d
Brown	
Dictyota dichotoma	2.211b
Stoechospermum marginatum	45.110e
Padina boergesenii	2.650b
Hydroclathrus clathratus	23.000d
Chnoospora implexa	0.880a
Hormophysa triquetra	0.890a
Sargassum myriocystum	3.540b
Sargassum longifolium	61.100f
Sargassum wightii	20.910c
Turbinaria conoides	3.090b
Green	
Ulva lactuca	66.400b
Helimeda gracibis	17.700a

Mean values not followed in the same letter significantly differed within the class of algae at 5% level

and *Sargassum wightii* (0.88 mg g^{-1} dry wt.). Among the green seaweeds a high sulphate content of 66.4 mg g^{-1} dry wt. was recorded in *Ulva reticulata* (Table 3).

DISCUSSION

In the present study, 7 red algae were accumulated more Na than K, however the red algae *Gracilaria corticata* var. *corticata*, *G. pudumadensis* and *Acanthophora spicifera* contained high K as in 7 brown algae, whereas very high level of Na than K was recorded in green algae. As like in the present study, high potassium and low sodium were recorded in the brown algae *Macrocystis integerifolia* and *Nereocystis luetkeana* (Vinogradov, 1953; Sitakara and Tipnis, 1967). Bio-deposited concentration of elements such as Ca, K, Na, Mg, Mn and P showed high K and low Na in brown and red algae whereas high Na and low K were recorded in green seaweeds (Sivalingam, 1978). The salt inclusion and/or exclusion mechanisms in operation to avoid or tolerate the high salinity condition in marine organism. Accumulation of high concentration of Na as salt inclusion mechanism was toxic to biological systems. To lessen this toxic effect, Na was sequestered in side the vacuoles and the vacuolar osmotica was counter balanced by synthesizing non-toxic organic osmotic substances in the cytosol. Operation of this mechanism requires less expenditure of energy (Raven, 1980). High Na and low K recorded in green seaweeds in the present investigation may adopt the salt inclusion mechanism to withstand the saline condition. Most of the brown algae (7 out of 10) and few of the red algae (3 out of 7) accumulated more K than Na. This indicated that red and brown algae may sustain in seawater by operating Na exclusion mechanism. Active accumulation of K in their cell sap against osmotic gradient operating as salt exclusion mechanism at the expenditure of photosynthates and/or membranes with a lower permeability to (toxic) Na than K to lower the intracellular Na content below the (equilibrium) value from the interior negative membrane potential (Harold, 1977; Raven, 1980). Osmoregulation in marine algae are mainly maintained by Na^+ and K^+ pump operating between seawater and cell sap and the turgor pressure changes are caused by variable ionic composition of vacuoles (Eisler, 1980). Accumulation of more K than Na in brown and red algae against salt gradient of seawater indicated that they thrive in salinity by operating salt exclusion mechanism whereas high Na in green tolerate the salinity with salt inclusion principle. Variation in sodium, potassium, calcium and magnesium content observed among the different genera of seaweeds showed that high Na and low K were recorded in green seaweeds where as high K and low Na were recorded in brown and red algae (Ramavat *et al*., 1986).

Sulphate is an essential macronutrient required for the growth and development of algae. It is constituted in commercially important cell wall polysaccharides of red and brown seaweeds. However, Craigie (1990) reported low quality of agar in *Gracilaria* sp. due to high sulphate content. Studies of Craigie *et al*. (1984) and Cote and Hanisak (1986) showed that gel strength is one of the factors to determine the quality of agar which is inversely proportional to sulphate content. Carrageenans are highly sulphated polysaccharides found in some red seaweeds and its gel strength was inversely proportional to the sulphate content (Doshi *et al*., 1968; Ramalingam *et al*., 2003; Chandrasekhara and Kaladharan, 2003). The cell wall hetero-polysaccharide, fucoidan displaying various bioactivity mainly constituted with L-fucose sulphated at 2 and 4 position was extracted from brown algae (Percival and Ross, 1950; Black, 1954; Boisson-vidal *et al*., 1995). As like the earlier findings, in the present study, two green algae and some red and brown algae which are not potentially viable for the extraction of commercial cell wall hetero-polysaccharides (Agar, algin, carrageenan, fucoidan etc.,) contained high sulphate. So, those algae which are not commercially important for the extraction of cell wall polysaccharides but contained high sulphate recorded in the present study may opt as a source of sulphate.

CONCLUSION

Some algae contain high quantity of Na, K and Sulphate. Accumulation of more Na in majority of red seaweeds and a few brown seaweeds and accumulation of more K in few red seaweeds and majority of brown seaweeds shows that both groups sustaining in salinity by operating either Na inclusion and/or exclusion mechanism whereas all green seaweeds may defend salinity only by Na inclusion mechanism. Some red and brown algae are not commercially important for the extraction of cell wall polysaccharides sequestering high K and sulphate they may serve as a source of essential macronutrients (K and sulphate).

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