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SEASONAL VARIATION IN CHEMICAL CONSTITUENTS OF CERTAIN BROWN SEAWEEDS AND SEAWATER FROM SAURASHTRA COAST: II. MANGANESE, ZINC, COPPER, NICKEL, COBALT AND MOLYBDENUM

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ABSTRACT

Mn, Zn, Cu, Ni, Co and Mo contents have been estimated in seawater and three brown seaweeds *viz., Cystoseira indica* (Thivy *et* Doshi) Mairh, *Sargassum johnstonii* Setchell and Gardner and *S. tenerrimum* J. Ag. from Porbandar and Okha reefs of Saurashtra coast collected during October 1982 to September 1983. During the high biomass period a depletion in the metal content was observed in both Porbandar and Okha waters. Seasonal variations in trace metal content of seaweeds was found to be more related to phenological stages than to the ambient metal concentration, if the latter is not limiting the seaweed growth. The individual element accumulation throughout their life cycle was in the order of Mn > Zn > Cu > Ni > Co > Mo. Cumulative concentration factors (ratio between the total concentration of a metal in a seaweed and that in seawater during a particular period) in seaweeds exhibit distinct seasonal variations. A rapid increase in early growth to rapid biomass period is followed by more or less steady increase in other stages with age.

Key-words: Seasonal variation, seawater, seaweeds, trace metals, Saurashtra coast.

INTRODUCTION

The growth of a seaweed is a dynamic phenomenon and of cumulative effect of various factors. The uptake or tissue concentration of elements are mainly related to the growth quantum. The trace metal accumulations in seaweeds is a continuous uncontrolled process of biological uptake. As a result the level of an element in seaweed based on a single arbitrary analysis during its time scale of life is rather unreliable, unless the sampling at different phenological stages are accounted for. The absorption and accumulation of various elements by seaweeds are contingent upon the phenological stages as well as meteorological components. In this context, the elemental composition of seaweeds data based on seasonal variation would be meaningful.

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Brown seaweeds are being used in the coastal environment as metal pollution indicators (Phillips, 1977). Generation of data base of metal content of seawater and potential seaweed species that accumulate these metals and metal content in relation to their phenological stages is a prerequisite. In previous studies the trace metal content in different groups of seaweeds from single arbitrary analysis are reported (Rao and Indusekhar, 1986; Rao, 1986). In the present investigation, attempts have been made to monitor variations in Mn, Zn, Cu, Ni, Co and Mo contents with growth of 3 brown seaweeds *viz.*, *Cystoseira indica* (Thivy *et* Doshi) Mairh, *Sargassum johnstonii* Setchell and Gardner and *S. tenerrimum* J.Ag. and of seawater from Porbandar and Okha reefs of Saurashtra coast.

MATERIAL AND METHODS

Description of the sampling sites including their geographical location is same as that reported earlier (Rao and Indusekhar, 1986). Seawater samples filtered through membrane filter papers (pore size, 0.45 µ), preconcentrated through Chelex-100 resin were used for Mn, Zn, Cu, Ni, Co and Mo analyses by the atomic absorption spectrometer (Varian Techtron model AA-6) and colorimetry methods (Rao and Indusekhar, 1986; Rao, 1986).

The method of pretreatment of seaweed material prior to AAS and colorimetry analyses was also given in earlier work (Rao and Indusekhar, 1986; Rao, 1986). The acid digested samples were preconcentrated by running down through Chelex-100 resin column at an appropriate pH. Mn, Zn, Cu, Ni and Co were eluted with mineral acids and estimated with AAS. But Mo was eluted with 2N NH_4OH and estimated colorimetrically.

Precision of analysis determined from nine samples (each in duplicate) collected from Okha during October/November 1982 as percentages of coefficients of variation of Mn, Zn, Cu, Ni, Co and Mo are 4.2, 1.0, 1.2, 4.1, 3.1, 3.5 respectively in seawater and it is 6.3, 2.5, 2.7, 7.3, 5.2, 4.8 for *S. tenerrimum*.

Concentration factor (CF) was calculated by dividing the content of metal (dry weight basis) in seaweed by its concentration in seawater. Cumulative concentration factor was calculated by the ratio between the total concentration of metal in seaweed (dry weight basis) and seawater during a particular period.

RESULTS AND DISCUSSION

Seawater

High seaweed biomass was observed during post-monsoon months and in April and May as shown by earlier investigations (Murthy, Bhattacharya and Padia, 1978). During the above period relatively lower concentration of Zn, Cu, Ni, Co and Mo was observed in seawater of both the places. During monsoon and February-March relatively higher values

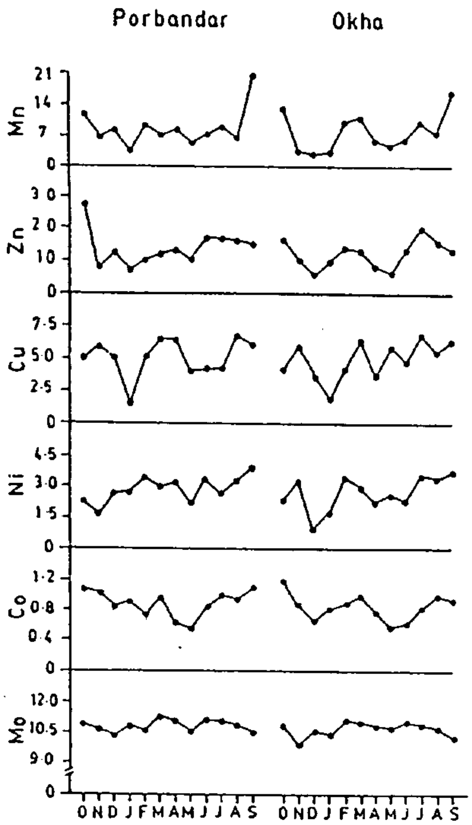

Fig.1. Monthly variation of trace metals content ($\mu g\ l^{-1}$) in seawater (average of 3 values)

were recorded. According to Bruland (1983) these trace metals are depleted in surface waters due to their uptake by organisms and are enriched in bottom waters due to the death and decay of these organisms. Rice and Windom (1982) observed that the decomposition of the seaweed detritus in an estuarine environment in general increases the trace metal concentration in ambient medium. It has been observed that most of the decomposition process of primary producers takes place in the coastal waters and the ambient medium is ultimately enriched with these trace metals during post-productive senescent period of primary tropic organisms (Fig.1).

Seaweeds

Metal concentration: Distinct seasonal variation was observed in trace metal content in seaweeds with low values during early and high values in the later growth stages. Two maxima and two minima values were recorded for trace metal concentration in *C. indica* and *S. johnstonii* as they have two reproductive stages in a year. *S. tenerrimum* with only one reproductive stage recorded only one maximum value. No distinct seasonal variation was found in trace metal CFs because of wide fluctuations. However, their cumulative CFs exhibited distinct seasonal variation. A rapid increase during October/November to January/February was followed by more or less a steady increase from March to August (Figs.2 & 3).

Seaweeds accumulate certain metals more than their body requirement (Eisler, 1981; Rao, 1987) the reason for such accumulation is not known. In the present study the concentrations of Mn, Zn, Cu, Ni, Co and Mo were 101-32, 23.4-9.4, 4.42-2.05, 2.38-0.73, 0.93-0.30 and 0.42-0.19 $\mu g.g^{-1}$ respectively in seaweeds during their maximum biomass period (November/December/January). However, maximum quantities were found usually during senescent growth (August/September/February) and the values for the above metals, *viz.*, Mn, Zn, Cu, Ni, Co and Mo respectively were 194-105, 46.7-23.0, 12.01-6.28, 3.80-2.75, 2.00-1.40 and 0.79-0.49 $\mu g.g^{-1}$. Eisler (1981) opines that high concentration of trace metals in the medium inhibit seaweed growth. How the seaweeds tolerate such a high quantity of trace metals which is of three orders magnitude of concentration in ambient medium is not yet known. It is possible that major part of the trace metal enter complexation with algal polysaccharides in cell walls and small amount is (actual requirement for biochemical budget) stored in vacuoles, granules and inter- and intra-cellular fluids (Weisner, 1962; Okelley, 1974; Manely and North, 1981). Liberation of free ions which are toxic, from such complexed form may not be possible during the life time of the seaweed.

Species specificity: In the present work, the seaweed species showed accumulation of Mn, Zn, Cu, Ni, Co and Mo in different quantities in a uniform trend wherein the quantities of elements either increased or decreased during every month. This corroborates the concept of species specificity (Saenko, Koryakova, Makienko and Dobrosmyslova, 1976). In *S. johnstonii* high content of Mn, Cu, Zn and Ni is recorded. Thus 'species specificity' of seasonal variation in metals content of seaweeds is characterised by high accumulation of certain elements and the increasing or decreasing trend of individual elements (Figs.2 & 3). The accumulation of trace metals in the above interesting phenomenon followed the Mn > Zn > Cu > Ni > Co > Mo every month.

Metal content and growth: Ishii, Iimura and Koyanagi (1979) investigated Fe content in *Sargassum horneri* in relation to the body size (height in cm). In the present study dry weight in grams was assumed as body size. Maximum biomass and low values for Mn, Zn, Cu, Ni, Co and Mo were observed during November/December and April/May and minimum values in October/November prior to the maximum biomass when the plants were in their early growth. Thus the maximum value period precedes the low value period. The present trend of low values in Mn, Zn, Cu, Ni, Co and Mo contents in the investigated seaweeds is comparable with the reported low values of Fe in *S. horneri* by Ishii, Iimura and Koyanagi, 1979) at its maximum biomass (maximum height in cm). But it is contrary to the observations made by Fujiyama and Maeda (1977) in *Porphyra* that Mn, Zn and Cu content is highest prior to fruiting stages and rapidly decreases in the period of maturity. The reported highest accumulation of trace metals in the hold fast implies that the older parts are rich in trace metal content (Phillips, 1977; Bryan, Langston, Hummerstone and Burt, 1985). Ishii, Suzuki and Koyanagi (1978) observed in *Sargassum thunbergi* that Mn, Co, Zn contents

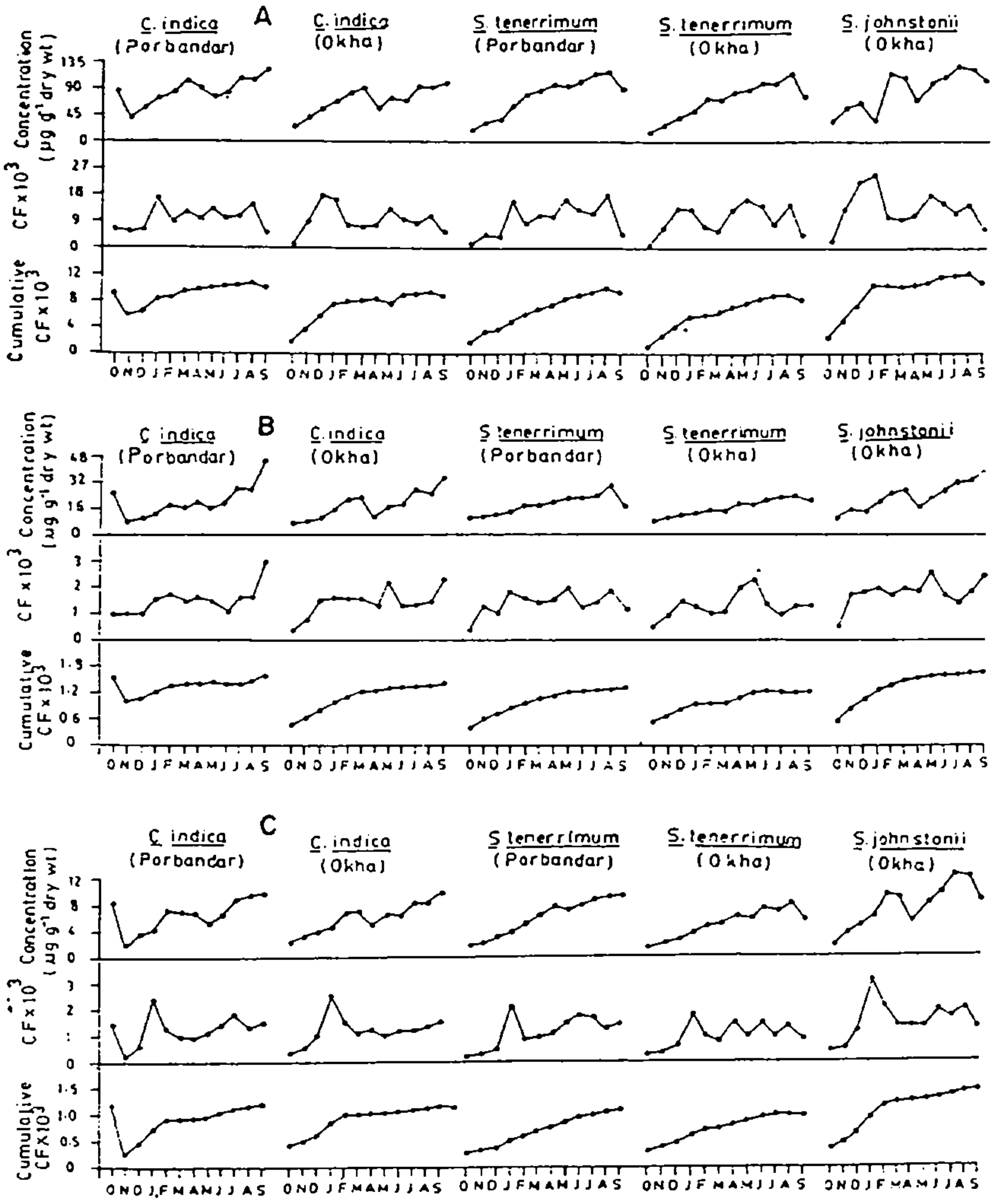

Fig.2. Monthly variations of Mn (A), Zn (B) and Cu (C) in seaweeds (average of 3 values)

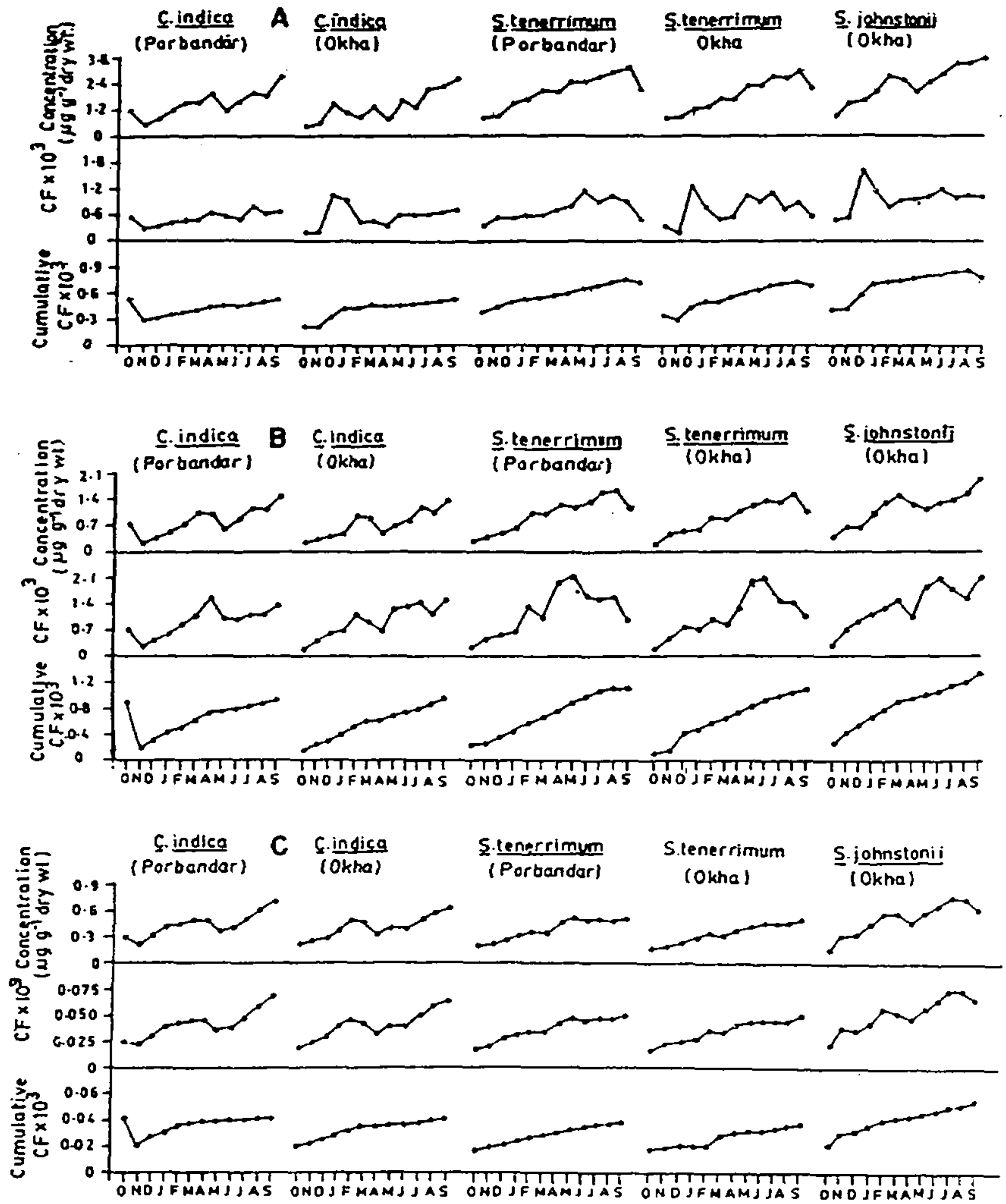

Fig.3. Monthly variations of Ni (A), Co (B) and Mo (C) in seweeds (average of 3 values)

gradually increased from January to March and then decreased from April to June during the six months period. Patel, Pawar, Balani and Patel (1980) observed similar trend in *S. tenerrimum* from Tarapur coast during December to May. They reported maximum values for Mn and Co during February-March when it bears fruiting bodies. However in the present study a gradual increase in accumulation (with some fluctuations) of Mn, Zn, Cu, Ni and Co in *S. tenerrimum* in both the places was observed during one year period of its life cycle.

Metal content and phenology: Towards the senescent period the proportion of the more exposed parts (older parts with high trace metal content) are predominant in biomass. The trace metal accumulation in seaweeds is either regular or irregular in its magnitude, but a continuous and irreversible process (Bonotto, Bossu, Nuyts, Kirchman, Mathot, Colard and Cinelli, 1983). As a consequence, gradual biodeposition is possible with the age. This is well supported by cumulative CFs data (Figs.2 & 3). In *C. indica* and *S. johnstonii* Mn, Zn, Cu, Ni, Co and Mo concentrations have increased from October/November to February. Thereafter the trace metal contents decrease followed by an increase, reaching maximum during August/September in the senescent period. Even though during the reproductive period trace metal content in the ambient medium is less than that of other stages (Fig.1), it is greater during the fruiting body formation than the earlier phases (Figs.2 & 3). Cumulative CFs data show a rapid increase during early growth to fruiting body formation stage. Therefore, this study indicates that the formation of fruiting bodies require enhanced uptake of Mn, Zn, Cu, Ni, Co and Mo and these results corroborate the earlier findings (Phillips, 1977).

The concentrations of Mn, Zn, Ni and Co in seawater at Porbandar are marginally higher than those at Okha. Their concentrations may not be a limiting factor for seaweed growth as these values are higher than those of the productive waters of the shelf (Topping, 1969; Chester and Stonner, 1974; Danielsson, 1980). Though the accumulation of these metals in seaweed is slightly higher at Porbandar than that at Okha its seasonal profiles at both the places are similar. *Fucus* was also reported (Fuge and James, 1973) to exhibit concurrent seasonal variations in polluted and non-polluted estuarine waters. However, the magnitudes of CFs are more for the high concentration ambient medium species than the low concentration ambient medium species. It is evident that the seasonal variations in trace metal content of seaweeds are more related to phenological stages than ambient metal concentration.

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