Seasonal variations in halides in marine brown algae from Porbandar and Okha coasts (NW coast of India)

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Seasonal variation of halides and their ratios were estimated in three brown algae, namely *Cystoseira indica*, *Sargassum tenerrimum* and *S. johnstonii* from Porbandar and Okha coasts. Halides were found to be higher in early stages of growth. The Br:F ratio was higher in reproductive stage indicating that algae tend to accumulate Br compared to F during this stage than at early and senescent stages; though Br level in ambient medium is not a limiting factor. Matrix analysis of DPEF (differential percentage of enrichment factor) of halides shows that the tissue concentration of each halide was independent of other halides accumulation. The extent of bioaccumulation could be related to intrinsic property such as \( \times \) spec (spectroscopic electronegativity) of each halide. The \( \times \) spec was found to control the relative enrichment of elements (halides).

From the available data on Indian marine algae, the stoichiometric relationship of iodine with respect to the bulk constituents was found to be 7900:531:16:1 for C:N:P:I which differs from that of Redfield ratio.

Halides except iodide are the major anions in seawater and their constancy in composition in relation to chloride and to other major elements is well established\(^1\). However, the physiological significance of F is not known in marine algae whereas the role of other halides is well established\(^2\). There could be seasonal variations in halides content in the same species associated with different stages of growth cycles and also due to the environmental parameters which could influence the accumulation of halogenated compounds in marine algae. The present study is on variations in halides content in relation to phenology of brown macro algae along with the halide ratios, which gives an insight into the biogeochemical behaviour of halides in algae.

Materials and Methods

Three species of brown marine algae, namely *Cystosera indica* (Thivy et Doshi) Mairh, *Sargassum tenerrimum* J. Ag. and *Sargassum johnstonii* Setchell and Gardner (Phaeophyceae/Fucales) were collected from intertidal regions of Porbandar (lat. 21°38' N; long 69°37' E) and Okha (lat. 22°28' N; long 69°05' E) for a 12 months period (Oct. 1982 - Sept. 1983). Algal samples were cleaned of extraneous material, shade dried, ground to powder and used for analysis. Detailed analytical methodology was given elsewhere\(^3\). In brief, halogen compounds in the samples were converted to alkali halides by treating with alkali salts. Fluoride was estimated by ion-selective electrode method. Chloride was estimated argentimetrically. Bromine was estimated colorimetrically after extracting it into chloroform phase. Iodine was estimated titrimetrically against standard sodium thiosulphate. Differential percentage of enrichment factors, \( \left[ \frac{(enrichment \, of \, X) - (enrichment \, of \, Y)}{(enrichment \, of \, X)} \right] \times 100 \), were calculated by the equation given by Kesava Rao & Indusekhar\(^4\). Spectroscopic electro- negativity (\( \times \) spec) values were taken from Allen\(^5\).

Results and Discussion

F, Cl, Br and I contents of marine algae (Fig.1) were more during Oct./Nov. the period of early growth. Algal species having the second fruiting stage (*S. johnstonii*) showed high values of these ions during April/May. During other months the pattern was not clear. The individual contents of halides during different stages of algal growth from both the places, were in the order, Cl > Br > I > F. However, the CF, concentration factor (content of an element in algae normalised to that of seawater concentration) of the above elements was in the decreasing order of I > F, Br > Cl (Fig.2). The values of DPEF during their phenological stages of algae were in the decreasing order of I over Cl, I over Th (sum of four halides), I over Br, I over F, F over Cl, F over Th, Br over Cl, Br over Th and F over Br. Thus iodine has been preferentially accumulated throughout the phenological stages of marine algae than other halides.

Br:F ratio was marginally higher during fruiting stages than that of early and senescent stages (Fig.3)
whereas Br:I and Cl:F ratios showed irregular distribution in all the algal species.

No report is available on the seasonal variation of F except in green marine algae. In the present study it is observed that F content more or less follows the ash content pattern i.e. the total minerals content. Higher Cl, Br and I in marine algae during early growth is in agreement with earlier reports on brown marine algae. Vinogradov and Saenko et al. noted that seaweed species growing at greater depths possess higher amounts of I content in their tissue. This trend was not seen in the present study as both C. indica and S. tenerrum were collected at middle and lower parts of the intertidal zone of Okha and Porbandar respectively.

Br:F ratio in seawater is constant whereas it varies in marine algae. During the reproductive stage its value is higher than that of early and senescent growth stages (Fig.3) as Br is essential for reproduction in certain marine algae. In younger tissues halides’ enrichment is more and decreases subsequently with age. During the reproductive stage contribution of juvenile parts towards the total plant biomass is less. It is probable that the relative accumulation of Br might be higher than F, by the moderately old tissues which comprise most part of plant biomass that leads to higher Br:F ratio during reproductive stage.

Oceanographically consistent data on nutrient type distribution of I has been documented. Coupled with the Redfield ratio, a stoichiometric relationship for iodine with respect to nutrients is reported to be 357:22.7:1 (N:P:IO₃). Therefore, in seawater the Redfield ratio with respect to iodate could be 2400:357:22.7:1 (C:N:P:IO₃). Data on nutrients gave the mean values for C, N, P in Indian marine algae, respectively of 31.04, 2.43, 0.16% dry
wt. If the above ratio normalised to total iodine content\(^8\) (415 mg. kg\(^{-1}\)), the Redfield relationship can be extended to 7900:531:16:1 (C:N:P:I) for marine algae. The deviation from the Redfield ratio might be due to the fact that marine algae prefer iodine in the form of iodide rather than iodate form. Intertidal position of habitat also may affect the Redfield ratio in marine algae as is noted in the bulk nutrients\(^11\).

Matrix analysis of DPEF shows no significant relationship with any of the halides with respect to accumulation of other halides. Thus individual halide ion accumulation seems to be independent of other halides' presence. But the extent of biomagnification is an intrinsic property of individual halides. It is reported that CF of elements in algae are related to geochemical properties (residence time) as well as periodic functions (electronegativity and ionisation potential) of elements\(^8,12-14\). The above properties are two-dimensional periodic functions. In a periodic group where elements exhibit almost similar geochemical behaviour, 3-dimensional periodic functional property would be useful to evaluate the relative accumulation rates among similar elements. Therefore in the present study \(\chi\) spec (a 3-dimensional periodic function) values were utilised to compare geochemical reactivity of halides in terms of their DPEFs. A significant negative correlation between \(\chi\) spec ratios and relative enrichment factors (Table 1) is observed. The related equation for total marine algae from a large data base is, log \((\text{DPEF of } X \text{ over } Y) = 3.61-6.75 \log (X_{\text{spec}}/Y_{\text{spec}})\). In conformity with this, \(\chi\) spec ratios show positive correlation with \(\tau\) ratios (\(p < 0.01\)). Validity of the former equation has been tested with the latter relationship by correlating the actual \(\tau\)
Table 1—Least square fitting parameters for differential percentage enrichment of halides in marine algae in relation to their x spec ratios and r, residence time (a—intercept; b—slope; r—correlation coefficient; P—level of significance)

<table>
<thead>
<tr>
<th>X axis (log)</th>
<th>Y axis (log)</th>
<th>a</th>
<th>b</th>
<th>r</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cystoseira indica</td>
<td>DPEF</td>
<td>3.34</td>
<td>-7.71</td>
<td>-0.791</td>
<td>&lt;0.01</td>
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<tr>
<td>(Porbandar)</td>
<td></td>
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</tr>
<tr>
<td>x spec ratio</td>
<td>DPEF</td>
<td>3.48</td>
<td>-6.73</td>
<td>-0.744</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sargassum tenerimm</td>
<td>(Porbandar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x spec ratio</td>
<td>DPEF</td>
<td>3.31</td>
<td>-7.57</td>
<td>-0.763</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cystoseira indica</td>
<td>DPEF</td>
<td>3.47</td>
<td>-6.87</td>
<td>-0.747</td>
<td>&lt;0.1</td>
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<tr>
<td>(Okha)</td>
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<td></td>
</tr>
<tr>
<td>x spec ratio</td>
<td>DPEF</td>
<td>3.55</td>
<td>-5.62</td>
<td>-0.61</td>
<td>—</td>
</tr>
<tr>
<td>Sargassum johnstonii</td>
<td>DPEF</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>x spec ratio</td>
<td>DPEF</td>
<td>3.47</td>
<td>-6.67</td>
<td>-0.729</td>
<td>0.1</td>
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<td>Phaeophyceae algae</td>
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<td></td>
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<tr>
<td>(mean of 3 species)</td>
<td>DPEF</td>
<td>3.61</td>
<td>-6.75</td>
<td>-0.751</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>x spec ratio</td>
<td>DPEF</td>
<td>1.47</td>
<td>1.64</td>
<td>0.994</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>* Calculated from Kesava Rao*</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>** Actual r ratio</td>
<td>** Cal. r ratio</td>
<td>1.47</td>
<td>1.64</td>
<td>0.994</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>x spec versus r for halides</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>** x spec ratio</td>
<td>r ratio</td>
<td>-2.36</td>
<td>0.45</td>
<td>0.993</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

* F value is not considered in calculating the r ratio and p spec ratio with respect to I since F being the first element in the halogen's group.

*** Calculated values were derived from the Eq(3) which in turn derived from Eqs (1 and 2)

\[
\log (\text{DPEF of } X \text{ over } Y) = 3.61 - 6.75 \log \left(\frac{X_{x \text{ spec}}}{Y_{x \text{ spec}}}\right) \text{ (1)}
\]

\[
\log \left(\frac{r_X}{r_Y}\right) = -2.36 + 0.45 \log \left(\frac{X_{x \text{ spec}}}{Y_{x \text{ spec}}}\right) \text{ (2)}
\]

\[
\log \left(\frac{r_X}{r_Y}\right) = -2.12 - 0.07 \log \left(\text{DPEF of } X \text{ over } Y\right) \text{ (3)}
\]

DPEF values were calculated from the present data on CF's and substituted in Eq(3) for calculating the calculated log \(\left(\frac{r_X}{r_Y}\right)\)

![Graph showing Br:F ratios in different life stages of marine algae](image)

Fig. 3—Br:F ratios in different life stages of marine algae (1—Cystoseira indica, Porbandar; 2—Sargassum tenerimm, Porbandar; 3—Cystoseira indica, Okha; 4—Sargassum tenerimm, Okha; 5—Sargassum johnstonii, Okha and 6—mean)

values ratio and expected r values ratio \((P < 0.01,\
Table 1)\). Therefore, it seems that the geochemical principle, r and chemical reactivity function such as x spec control or affect the relative enrichment of elements with special reference to halides. Therefore x spec will give a better picture for understanding the distribution of periodicity of elements in environmental samples.

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References

3 Kesava Rao Ch, Studies on seasonal variations in the important chemical constituents of some seaweeds and seawater along the Saurashtra coast, Ph.D. thesis, Bhavnagar University, India, 1987.


7 Vinogradov A P, The elementary chemical composition of marine organisms, (Sears Foundation for Marine Research, Yale University, New Haven) 1953, 647.


