

ESTIMATION OF ELEMENTS IN SEAWEEDS OF KARACHI COAST

*MUHAMMAD AFZAL RIZVI, **SHAZIA FAROOQUI &
***MUSTAFA SHAMEEL

*Bait al-Hikmah Research Institute, Karachi, Pakistan.

Abstract

Seaweeds are one of the econo-medicinal important living marine resources that belong to the primitive group of non-flowering plants, which grow submerged in intertidal, shallow, neritic waters upto 200 m depth in the sea. These marine benthic algae grow abundantly along the Karachi coast and show a wide range of structural organization, function and elemental distribution. Many species of green, brown and red seaweeds collected from Manora, Buleji and Paradise Point were analyzed for their elemental composition with the help of Perkin Elmer 3100 Atomic Absorption Spectrometer. Several significant elements e.g. Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Pb and Zn were detected quantitatively. The Ca, Fe, K, Mg and Na were found in large amounts (223.79-13129.56 ppm), Cr, Cu, Pb and Zn were present in small quantities (1.27-10.49 ppm), while Cd and Co were detected in extremely small amounts (0.39-1.10 ppm). The average quantity of Na was found to be the highest among these algae (13129.56 ppm), followed by K (11655.71 ppm) and Ca (4242.17 ppm). The average amounts of Cr (1.27 ppm) and Co (1.10 ppm) were quite low; Cd was detected in the lowest quantity (0.39 ppm).

Introduction

Pakistani coast inhabited a variety of marine algae. They have economical as well as medicinal properties. *Sargassum vulgare* contents Vit. A 78.23 ppm, Vit. B₂ 1682.59 ppm, Vit. "C" 5056.17 ppm and Folic acid 87.57 ppm, while *Hypnea musciformis* contents Vit. A 47.97 ppm, Vit. B₂ 773.99 ppm, Vit. "C" 8334.26 ppm and Folic acid 25.18 ppm (Kalharo & Usmani, 1990). *Enteromorpha compressa* and *E. prolifera* showed hypocholesterolemic and hypotensive activities (Ahmed & Perveen, 1993). *Iyengaria stellata* and *Spatoglossum asperum* showed highest activity against Tc (14.6 %) and LDL-c (28.3 %, 26.9 %) with an increase of 11.6-16.3 % in HDL-c respectively (Ara *et al.* 2000). *Ulva* spp. are reported to be a source of gelling polysaccharides of economic value (Anonymous, 2000). Algae concentrate minerals and trace elements from marine water, which are in an organic form (Chapman & Chapman, 1980). Seaweeds grow in a mineral rich medium. The numerous elements coming from the sea are Ca, Cl, Cu, I, Mg, Mn, Na, P, S and Zn (Jarvis, 1976). The green, brown and red algae have relatively high mineral contents (upto 38.9 %) e.g. Ca, K, Mg, Na and trace elements (Marderosian, 1972). The algal flora of India is considerably rich in Bromine, Iodine, Potash and Soda (Biswas, 1980). They show a wide range of organization, function and elemental composition. Brown algae accumulate strontium, *Sargassum* spp. from Gujarat coast contain 200-500 ppm iodine (Ahmad *et al.*, 1989). It seems that the tropical seaweeds tend to accumulate more Fe than Cu, Mn and Zn (Ganesan *et al.*, 1991). The variation of elements is attributed to environmental

**Hydrochemistry Laboratory, Hamdard University, Karachi-74600, Pakistan.

***Department of Botany, University of Karachi, Karachi-75270, Pakistan.

fluctuation in the form of availability of Ca, K, Mg and Na in seawater or it may be a function of metabolic activity within the cellular matrix of the seaweeds (Ilyas & Sukan, 1994). The marine algae such as *Ascophyllum nodosum*, *Fucus distichus*, *F. vesiculosus*, *Laminaria longicruris*, *Palmaria palmata* and *Ulva lactuca* were analyzed for metals such as As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. In general the health risks associated with concentration of these elements in the algae growing at the Gulf of Saint Lawrence were not very high. For regular consumers it would be preferable to use *Palmaria palmata* and *Ulva lactuca* in order to prevent potential problems. Algal consumption has beneficial health effects (Phaneuf *et al.*, 1999).

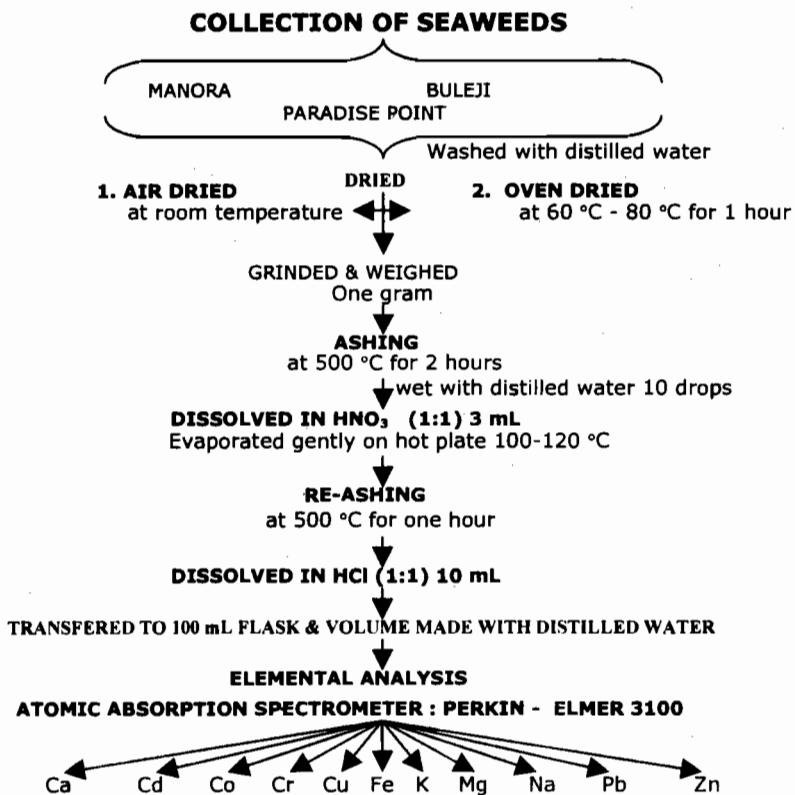
Karachi the capital of Sindh province and biggest city of Pakistan has a coastline of about 100 km at the northern boundary of the Arabian Sea. It includes beaches and numerous islands. The coastal waters around Manora, Sandspit, Hawkesbay, Buleji, Paradise Point, Pacha, Nathiagali and Cape Monze inhabit a variety of marine benthic algae (Shameel & Tanaka, 1992). Although a lot of work has been done on their taxonomy, distribution, morpho-ecological studies, phycochemistry and pharmacology but not much data is available in literature related to their elemental composition (Rizvi *et al.*, 2000). Studies were therefore carried out to examine the estimation of elements in marine algae on the coast of Karachi, Pakistan.

Materials and Methods

Collection of Marine Algae: Specimens of different species of marine algae were collected from sandy bays, large and shallow sand bottom flats, small and large pools with rocky or sandy bottom and at the rocky ledges on various coastal areas of Karachi, Pakistan *e.g.*, Manora, Buleji and Paradise Point during September 1997 to December 1998. The sub-littoral algae were picked up as drift material. The collected seaweeds were brought to the laboratory, where they were washed immediately with running water to remove epiphytes and attached debris and later by distilled water.

Reagents: The reagents used in the present investigation were HNO_3 (1 : 1). All glass were carefully cleaned and rinsed with distilled water.

Ashing and Digestion of the Seaweeds: The algal material was dried under shade at room temperature. The samples were dried in an oven at 60 - 80°C for 1 hour. They were then powdered through grinder and accurately weighed 1 g grinded sample into a porcelain crucible. Powdered samples were ashed at 500 °C in an oven to constant weight for 2 hours (Scheme I). The ash was cooled at room temperature, wet with 10 drops of distilled water and carefully dissolved in 3 mL HNO_3 (1 : 1). The sample in acid solution was then heated gently on a hot plate at 100-120 °C till nearly dry. The crucible was returned to muffle furnace and ashed again for 1 hour at 500 °C. It was then cooled and dissolved in 10 mL HCl (1 : 1), and the solution was filtered through Whatman filter paper into a 100 mL volumetric flask. The solution was now diluted to final volume with distilled water, mixed well and made ready for AAS reading (Jones, 1984).



Scheme I. Assay for the estimation of elements in Seaweeds

Elemental Assay: A flame atomic absorption spectrometer (AAS, Model Perkin - Elmer 3100, USA) was used for the purpose of estimating Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Pb and Zn. The various instrument parameters have been presented in(Table I). Instructions for instrument setting, calibration and assay for specific elements as laid down in the operational manual were strictly followed.

Table I. Instrument parameters.

| Elements | Symbol | Wave Length (nm) | Slit (nm) | Sensitivity (mg / L) |
|-----------|--------|---------------------|--------------|-------------------------|
| Calcium | Ca | 422.7 | 0.7 | 0.092 |
| Cadmium | Cd | 228.8 | 0.7 | 0.016 |
| Cobalt | Co | 240.7 | 0.2 | 0.078 |
| Chromium | Cr | 357.9 | 0.7 | 0.041 |
| Copper | Cu | 324.8 | 0.7 | 0.077 |
| Iron | Fe | 248.3 | 0.2 | 0.039 |
| Potassium | Kf | 766.5 | 0.7 | 0.043 |
| Magnesium | Mg | 285.2 | 0.7 | 0.008 |
| Sodium | Na | 589.0 | 0.2 | 0.012 |
| Lead | Pb | 283.3 | 0.7 | 0.079 |
| Zinc | Zn | 213.0 | 0.7 | 0.018 |

Recommended Flame: Air - Acetylene

Table II, Estimation of elements in seaweeds of Karachi coast.
(ppm)

| Seaweeds | Ca | Cd | Co | Cr | Cu | Fe | K | Mg | Na | Pb | Zn |
|---|-----------------|-------------|-------------|-------------|-------------|----------------|-----------------|-----------------|-----------------|--------------|---------------|
| Chlorophyta | 32312.5 | 1.84 | 5.92 | 8.65 | 9.3 | 2186.25 | 54855 | 12346.58 | 67977.5 | 23.47 | 33.93 |
| <i>Byssolys pennata</i> Lamour | 80800 | 3.15 | 3.15 | 9.925 | 12.9 | 3795 | 10855 | 6660 | 28535 | 43.875 | 37.425 |
| <i>Codium racemosum</i> (Forssk.) J. Ag. | 70300 | 2.2 | 2.2 | 12.525 | 11.25 | 2542.5 | 19625 | 764.5 | 155950 | 23.675 | 21.725 |
| <i>Codium taxifolium</i> (Vahl) C. Ag. | 14755 | 0.97 | 0.97 | 10.425 | 8.5 | 2840 | 15810 | 6870 | 110400 | 19.1 | 25.05 |
| <i>Codium tyongense</i> Burg. | 14730 | 1.92 | 1.92 | 2.825 | 5.65 | 862.5 | 231700 | 9605 | 169350 | 26.075 | 18.25 |
| <i>Enteromorpha intestinalis</i> (L.) Nees | 4745 | 0.5 | 3.67 | 23.325 | 14.0 | 2695 | 18590 | 13400 | 17470 | 19.6 | 81.55 |
| <i>Ulva lactuca</i> L. | 8545 | 2.3 | 3.05 | 1.85 | 7.125 | 382.5 | 32550 | 36900 | 25160 | 8.55 | 19.15 |
| Phaeophyta | 27351.6 | 2.67 | 6.16 | 7.81 | 9.7 | 673.5 | 68476.33 | 16836.33 | 36998.33 | 10.05 | 117.63 |
| <i>Cystoseira indica</i> (Thivy et Duth) Miah | 19050 | 3.95 | 5.12 | 4.7 | 8.125 | 249 | 118125 | 9425 | 80562.5 | 8.1 | 33.625 |
| <i>Padina tetrastrumata</i> Hawk | 46950 | 2.87 | 6.37 | 16.15 | 12.375 | 3105 | 26620 | 24500 | 20540 | 15.25 | 44.475 |
| <i>Sargassum vulgare</i> C. Ag. | 16055 | 1.2 | 7.0 | 0.18 | 8.6 | 1740 | 60666 | 14166 | 59012.2 | 6.8 | 274.8 |
| Rhodophyta | 12452.81 | 2.24 | 6.78 | 5.99 | 9.66 | 944.7 | 74821.87 | 12853.43 | 118226.8 | 13.57 | 26.83 |
| <i>Boerhaavia leptopoda</i> (J. Ag.) Kylin | 5055 | 2.9 | 8.05 | 3.4 | 13.6 | 499.5 | 65925 | 27040 | 201275 | 7.2 | 26.375 |
| <i>Champia compressa</i> Harv. | 10630 | 2.0 | 10.6 | 6.825 | 8.275 | 587.5 | 21475.0 | 7985 | 10885 | 22.55 | 15.05 |
| <i>Gracilaria corticata</i> (J. Ag.) J. Ag. | 11725 | 1.87 | 5.55 | 7.1 | 8.375 | 1105 | 114750 | 4380 | 26290 | 13.325 | 35.3 |
| <i>Hypnea musciformis</i> (Wulf) Lamour | 7977.5 | 1.97 | 5.1 | 2.325 | 6.675 | 230.5 | 62125 | 4930 | 129687.5 | 3.85 | 15.675 |
| <i>Hypnea valonioides</i> (Turn.) Mont. | 10150 | 2.7 | 7.75 | 10.625 | 11.625 | 1825 | 112937.5 | 15260 | 154187.5 | 14.1 | 29.925 |
| <i>Sargassum hercullatum</i> Zanard. | 7447.5 | 2.55 | 7.74 | 5.425 | 12.7 | 340.7 | 136375 | 19820 | 220187.5 | 16.05 | 20.775 |
| <i>Solenastrea rubra</i> (Grev.) Kylin | 14087.5 | 2.8 | 6.9 | 7.7 | 11.9 | 1900 | 70862.5 | 8462.5 | 184312.5 | 18.1 | 23.6 |
| Average amount | 4242.1 | 0.39 | 1.18 | 1.27 | 1.72 | 223.7 | 11655.71 | 2408.84 | 13129.86 | 2.77 | 18.49 |

Results and Discussion

Seventeen species of marine benthic algae were investigated, out of which six belonged to Chlorophyta, three to Phaeophyta and eight to Rhodophyta. The amounts all the elements estimated in these species have been presented in (Table II). Among these elements Ca, Fe, K, Mg and Na were found in large amounts (average between 223.79-13129.56ppm). *Gracilaria verrucosa* from the Izmir Bay was observed to be rich in Calcium showing a maximum value in August (Ilyas & Sukan, 1994). The values of Magnesium were present as low as 36.0 ppm in February. Iron was found in highest

concentration among the trace elements without any correlation with season, the maximum value (1702 ppm) was found in November and minimum as (521.48 ppm) in June (Ilyas & Sukan, 1994). The trace metal distribution in seaweeds of Indian Ocean has been reported (25.09-3420.56 ppm Mn, 128.09-1796.22 ppm Fe, 3.17-80.41 ppm Cu and 3.69-203.88 ppm Zn (Agadi *et al.* 1978). Iron was also found in large quantity, Cr and Zn in medium quantity and Co in small amount in several brown seaweeds of the Saronic Gulf, Greece (Kanas *et al.* 1991). In the present study the average quantity of Na was found to be the highest among these algae (13129.56 ppm), followed by K (11655.71 ppm) and Ca (4242.17 ppm), with an average amounts of Cr (1.27 ppm) and quite low amount Co (1.10 ppm). Cd was estimated in the lowest quantity (0.39 ppm). The concentration levels of Cd, Cr, Cu, Pb and Zn were also low. Their ranges in *Ptilota serrata* were 1.77-3.75 ppm in wet tissue weight and approximately 7.0-15.0 ppm dry tissue weight; Cu levels in *Polysiphonia urceolata*, *Phycodryis rubens* and *Laminaria saccharina* were similar to the concentration level in *Ptilota serrata* (Sears *et al.*, 1985). Sodium was found to be in highest amount in the Chlorophyta (67977.5 ppm) and Rhodophyta (118226.87 ppm) while K was estimated in highest quantity in Phaeophyta (68470.33 ppm) on the average. However, Cd was present in smallest amount in Chlorophyta (1.84 ppm), as compared to Phaeophyta (2.67 ppm) as well as Rhodophyta (2.24 ppm). Previously, Rizvi *et al.* (2000) determined the average amount of Co as 4.39 ppm, Cr as 1.91 ppm as well as Cd as 1.18 ppm in the seaweeds of Karachi coast.

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