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CHEMICAL STUDIES ON INDIAN SEAWEEDS

I. Mineral Constituents*

BY V. KRISHNA PILLAI

(*Central Marine Fisheries Research Station, Mandapam Camp*)

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INTRODUCTION

THERE is practically no reference which gives a complete account of the mineral constituents of the commercial seaweeds and their relationship with the organic constituents or on the ionic exchanges taking place between the algæ and the surrounding water. The early attempts to utilize seaweeds for the manufacture of potash and iodine provide some data on the amounts of these elements and their seasonal variations in particular species. Work on British seaweeds has shown (Chapman, 1950) that the changes in the iodine content are nearly directly proportional to the potash and that the amount of these nutrients in the living plant varies from month to month.

Webb (1937) carried out a spectrographic analysis of three algæ (*Ulva lactuca, Fucus serratus* and *Saccorhiza bulbosa*) and obtained values for sodium, potassium, calcium, magnesium, strontium, barium, boron, molybdenum, aluminium, manganese, iron, copper, lead, etc. Cornec (1919) detected silver, arsenic, cobalt, copper, manganese, zinc, bismuth, tin, barium, molybdenum, gold, antimony, titanium and uranium in marine plants. The analysis was done by spectroscopic methods and was purely qualitative. The species analysed have not been given. Jones (1922) estimated the arsenic content of eleven species of British seaweeds and obtained a value of 125 mg./kg. in *Laminaria digitata*. Later Williams and Whetstone (1940) also made studies on the distribution of arsenic in marine algæ. Meulan (1932) studied the molybdenum content of several species of algæ and reports a figure of 0·16 mg./kg. dry weight. Igelsrud, Thompson and Zwicker (1938) give the range of boron content in a few seaweeds as between 4·2 and 14·9 mg./kg. dry material. Even some of the rare earth elements have been detected in *Laminaria cloustoni* by Servigne and Tchakirian (1939), who found about 5 mg./kg. of Pr, Nd and Sm. Accumulation of radium in algæ has been observed by Wiesner (1938) analysing more than

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20 species of algæ of both fresh- and salt-water origin. Oy (1940) discusses in detail the physiological importance of iron, copper, manganese and boron and estimates these elements in several species of seaweeds, *viz.*, *Laminaria* spp., *Fucus serratus* and *Fucus vesiculosus*.

An analysis of a dry seaweed meal has been reported by Beharrell (1942), and in 1941 Wilson and Fieldes estimated spectrographically eighteen of the minor elements in *Macrocystis pyrifera*. Black and Mitchell (1952) in a detailed study have reported the cobalt, nickel, molybdenum, iron, lead, tin, zinc, manganese, barium, copper, chromium, titanium, rubidium, silver, vanadium, lithium and strontium contents of the following species of brown algæ: *Pelvetia canaliculata*, *Ascophyllum nodusum*, *Fucus serratus*, *Laminaria digitata* and *Laminaria cloustoni*; in certain cases the fronds and stipes have been separately analysed. In this work an attempt has been made to study the seasonal variations in the trace element contents of particular species; and the data obtained show positive variation in the concentration of the trace elements investigated. The authors also have correlated the trace element content of the surrounding sea-water with that of the seaweeds and have established that trace elements accumulate to a very great extent in the seaweeds.

The foregoing review bears out that the chief concept in the existing literature on the subject of the chemical composition of seaweeds is variation in the individual species with the condition of the surrounding water, with depth and with seasons. But the entire work referring as it does to the seaweeds of temperate regions leaves the subject untouched so far as the seaweeds of the tropical waters are concerned.

EXPERIMENTAL

In the present communication a preliminary account is given on the seasonal changes in the chemical composition of 11 species of seaweeds common to the Indian coast. The species studied are:

1. *Chætomorpha linum* Kutz. 2. *Enteromorpha intestinalis* Link.	Chlorophyceæ
3. *Gracilaria lichenoides* (L.) Harv. 4. *Chondria dasyphylla* (Woodw.) Ag. 5. *Acanthophora spicifera* (Vahl.) Boerg. 6. *Laurencia papillosa* (Forssk.) Grev. 7. *Hypnea musciformis* (Wulf.) Lamour. 8. *Sarconema filiforme* (Sond.) Kylin. 9. *Sarconema furcellatum* Zan.	Rhodophyceæ

10. *Rosenvingia intricata* (J. Ag.) Boerg.) } Phæophyceæ
11. *Padina australis* Hauck.

Among these *Chætomorpha linum*, *Gracilaria lichenoides*, *Hypnea musciformis* and *Rosenvingia intricata* form a floating association while the others are attached forms. The samples were collected from Palk Bay near Mandapam. The littoral area is shallow and is fringed by a coral reef, the dead coral masses and fragments providing a firm substrate for the attachment of the algæ. The Bay being sheltered permits a floating association as well. The first collection of the algæ was made in April 1952, and subsequently once in a month until March 1953. By selecting the above species for investigation it was felt that the characteristic differences between different species in the same group could be studied. Since almost all the seaweeds (both floating as well as attached forms) were available throughout the year the changes in their composition during different stages of growth could also be studied.

The fresh samples after removal of sand and calcareous particles were thoroughly washed in fresh-water and left for drying in the sun. The atmospheric temperature was sufficiently high for proper drying of the samples. A few species like *E. intestinalis*, *G. lichenoides*, *L. papillosa* and *P. australis* were analysed in the fresh condition with a view to study the changes in the water-soluble minerals in them.

Methods of Analysis

For the estimation of water-soluble constituents known quantities of the seaweed, after superficial washing in distilled water, is ground to a paste with acid-washed sand adding distilled water to requirement. The paste and the washings are centrifuged and the clear extract taken. The process is repeated three times and the combined extracts are made upto a known volume.

Estimation of total minerals.—For each estimation the ash obtained from 2 grams of the dry seaweed are used in the case of the major elements sodium, potassium, calcium, magnesium, and chlorine. As against this about 10 to 20 grams of the seaweed will be required for the estimation of trace elements. The methods employed in the analysis of the above constituents are the same as reported in an earlier communication (Krishna Pillai, 1955).

With a view to understand the form in which the two elements Mn and B exist in the different seaweeds, a series of analysis were conducted on representative collections of young and mature specimens of all the 11 species mentioned above.

The results of analysis on the water-soluble constituents of the 4 species of seaweeds are tabulated in Tables I to VI. The moisture, ash, sodium, potassium, calcium, magnesium and chlorine of the different species collected during the various months are represented in Graphs 1 to 11. The seasonal variations in the trace element contents of the seaweeds are given in Tables VII to XIV.

TABLE I

Water-Soluble Minerals in Seaweeds Collected during June 1952

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
A. spicifera	0·03	0·07	0·04	0·03	0·26
	(0·32)	(0·18)	(0·42)	(0·38)	(3·06)
L. papillosa	0·05	0·08	0·04	0·04	0·26
	(0·42)	(0·61)	(0·29)	(0·31)	(2·10)
S. furcellatum	0·08	0·05	0·02	0·02	0·28
	(0·56)	(0·31)	(0·16)	(0·15)	(1·80)
P. australis	0·12	0·14	0·05	0·08	0·22
	(0·78)	(0·93)	(0·32)	(0·50)	(1·40)

TABLE II

Water-Soluble Minerals in Seaweeds Collected during August 1952

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
G. lichenoides	0·03	0·11	0·04	0·04	0·42
	(0·20)	(0·81)	(0·28)	(0·28)	(2·80)
P. australis	0·14	0·14	0·12	0·07	0·40
	(0·75)	(0·76)	(0·65)	(0·41)	(2·20)

TABLE III

Water-Soluble Minerals in Seaweeds Collected during September 1952

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
L. papillosa	..	0·05 (0·41)	0·04 (0·31)	..	0·15 (1·30)
S. furcellatum	..	0·05 (0·40)	0·06 (0·51)	..	0·22 (1·81)

TABLE IV

Water-Soluble Minerals in Seaweeds Collected during October 1952

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
G. lichenoides	0·04	0·10 (0·75)	0·04 (0·30)	0·02 (0·16)	0·45 (3·70)
L. papillosa ..	0·10 (0·88)	0·09 (0·82)	0·07 (0·61)	0·03 (0·29)	0·25 (2·00)
P. australis	0·21 (1·28)	0·15 (0·90)	0·09 (0·50)	..	0·39 (2·40)

TABLE V

Water-Soluble Minerals in Seaweeds Collected during December 1952

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
E. intestinalis	0·04 (0·58)	0·05 (0·63)	0·02 (0·28)	..	0·08 (1·25)
G. lichenoides	0·02 (0·23)	0·21 (2·01)	0·04 (0·40)	..	0·20 (2·00)
L. papillosa	0·15 (1·16)	0·11 (0·70)	0·04 (0·31)	..	0·32 (2·40)

TABLE VI

Water-Soluble Minerals in Seaweeds Collected during February 1953

Values expressed as percentage on wet weight. (Figures in brackets are values on dry weight as calculated from wet weight)

Name of Species	Na	K	Ca	Mg	Cl
G. lichenoides	0·03	0·18	0·02	..	0·55
	(0·20)	(1·25)	(0·11)		(3·84)
E. intestinalis	0·06	0·05	0·04	0·03	0·14
	(0·73)	(0·61)	(0·51)	(0·41)	(1·70)

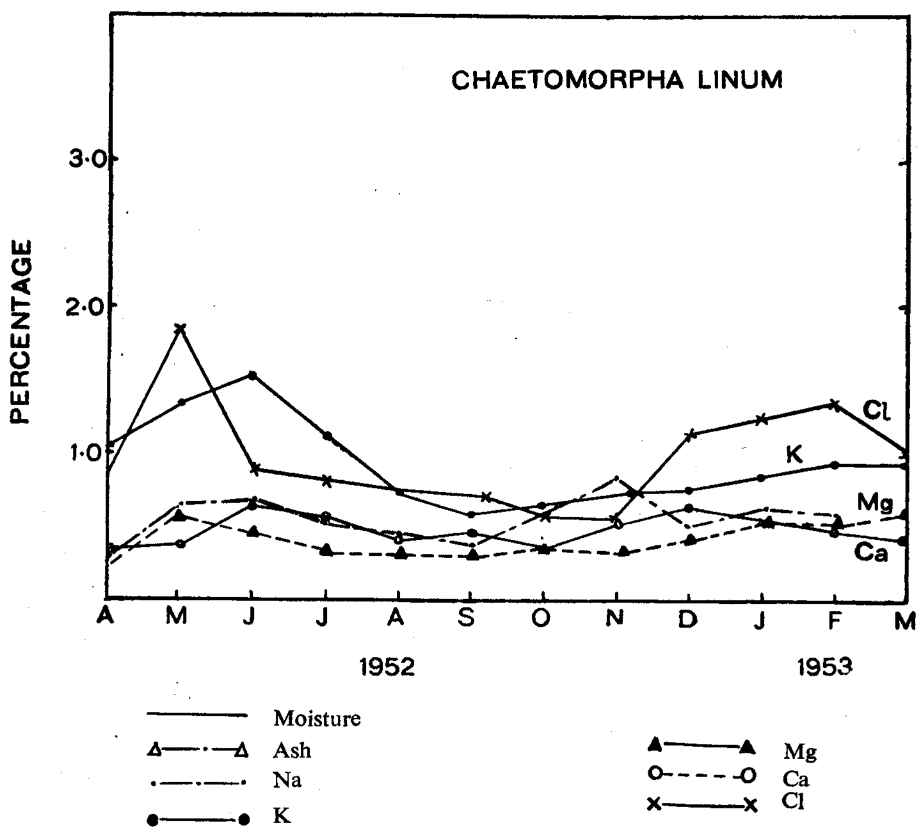


FIG. 1

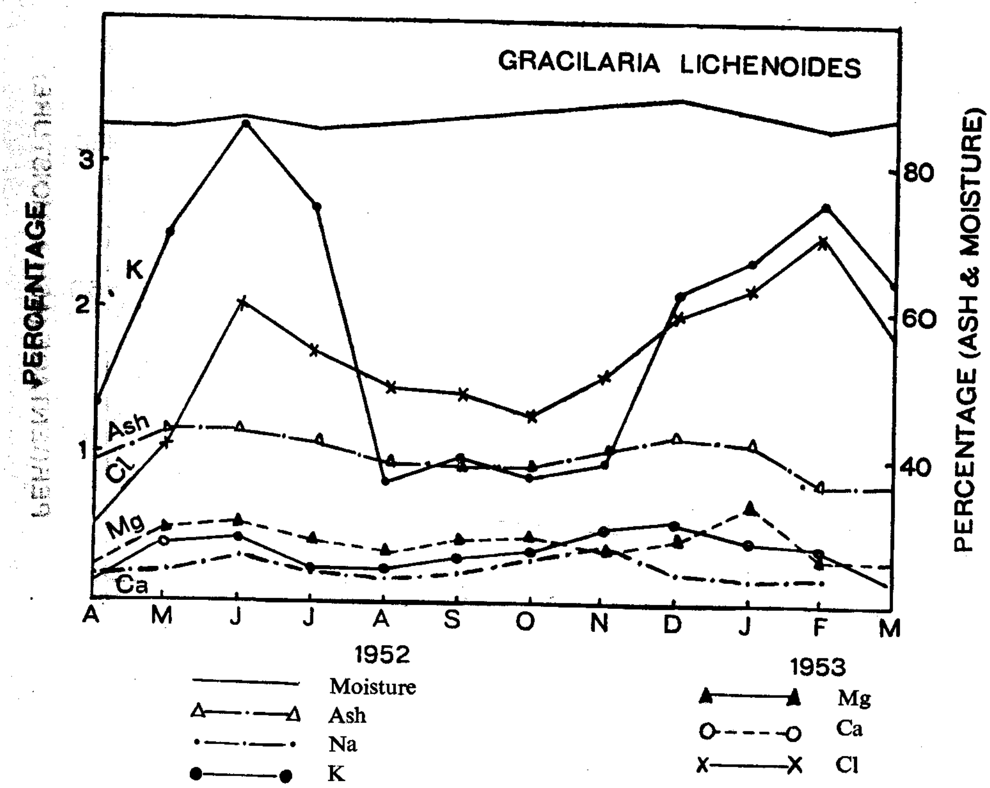


FIG. 2

TABLE VII

Trace Elements in Seaweeds Collected during April 1952
(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	42·0	5·0	46·0	1·0	trace	32·0	13·0
G. lichenoides ..	70·0	3·0	112·0	2·8	0·08	115·0	26·0
C. dasyphylla ..	126·0	2·6	73·0	trace	trace	74·0	20·0
E. intestinalis ..	38·5	trace	38·0	1·6	0·06	34·0	10·0
A. spicifera ..	140·0	trace	40·0	4·3	trace	79·0	25·0
L. papillosa ..	160·0	1·8	91·0	1·0	trace	39·5	24·0
H. musciformis	196·0	3·2	69·0	4·0	0·10	98·7	43·0
S. filiforme ..	83·0	2·4	95·0	3·7	0·10	86·4	24·0
S. furcellatum ..	76·0	2·0	56·0	1·8	0·07	99·0	32·0
R. intricata ..	129·0	4·0	240·0	1·8	0·06	123·0	15·0
P. australis ..	237·0	1·4	46·0	2·0	0·10	79·0	28·0

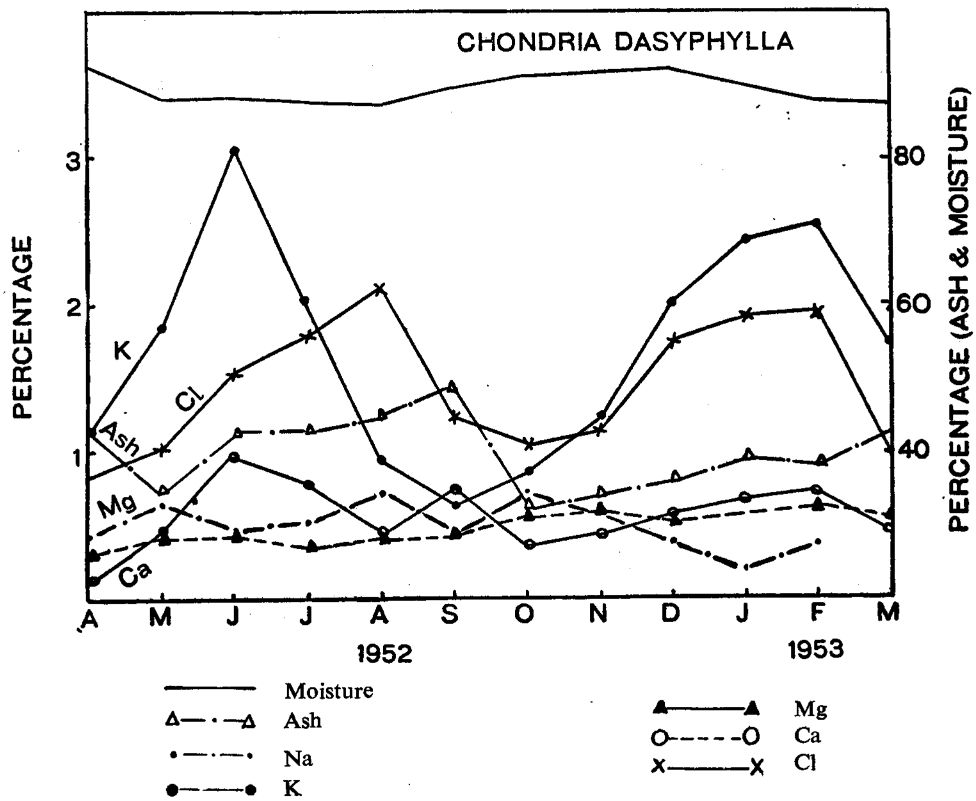


FIG. 3

TABLE VIII

Trace Elements in Seaweeds Collected during May 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	112·0	3·8	..	trace	trace	64·0	18·0
G. lichenoides ..	..	5·0	trace	1·8	0·08	123·0	19·0
C. dasyphylla ..	144·2	trace	87·0	1·6	trace	96·0	16·0
E. intestinalis ..	126·0	1·5	30·0	1·2	trace	58·0	18·0
A. spicifera ..	128·8	10·0	trace	3·1	trace	88·0	15·0
L. papillosa ..	190·4	5·0	trace	3·6	..	60·0	15·0
H. musciformis	210·0	9·0	180·0	3·8	0·08	60·0	26·0
S. filiforme ..	65·0	6·5	63·0	1·9	0·08	96·0	20·0
S. furcellatum ..	70·0	30·0	200·0	2·0	trace	74·0	28·0
R. intricata ..	119·0	5·0	575·0	7·0	0·05	264·0	12·0
P. australis ..	259·0	trace	195·0	11·0	0 08	246·0	28·0

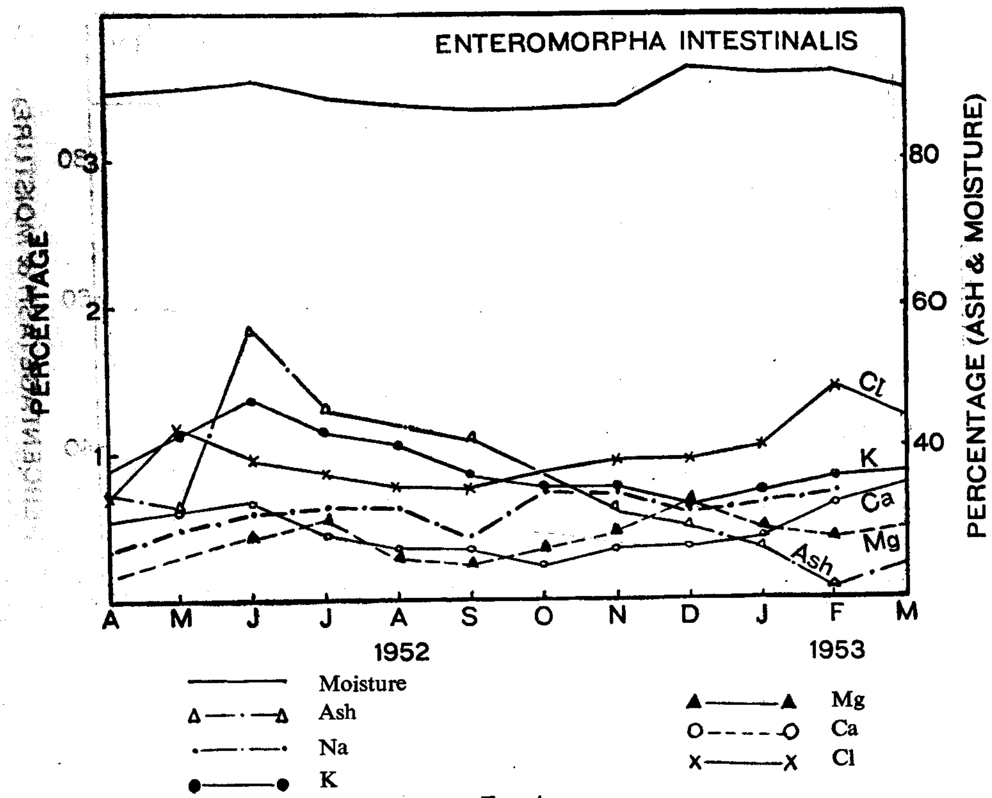


FIG. 4

TABLE IX

Trace Elements in Seaweeds Collected during June 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	100·8	5·0	35·0	2·7	0·05	72·0	16·0
G. lichenoides ..	79·8	4·6	163·0	10·4	0·20	108·0	59·0
C. dasyphylla ..	112·0	6·0	140·0	8·0	0·10	72·0	37·0
E. intestinalis ..	86·4	2·2	80·0	4·5	0·10	41·0	21·0
A. spicifera ..	87·5	3·5	20·0	2·2	0·06	76·0	7·0
L. papillosa ..	129·5	Nil	85·0	4·6	0·06	24·0	14·0
H. musciformis ..	185·2	5·0	135·0	8·0	0·10	12·0	28·0
S. filiforme ..	85·6	2·0	187·0	7·3	0·10	56·0	20·0
S. furcellatum ..	80·5	1·8	..	9·4	0·05	160·0	58·0
R. intricata ..	136·5	0·8	181·0	7·4	0·06	30·0	26·0
P. australis ..	251·6	11·2	208·0	11·0	0·08	186·0	40·0

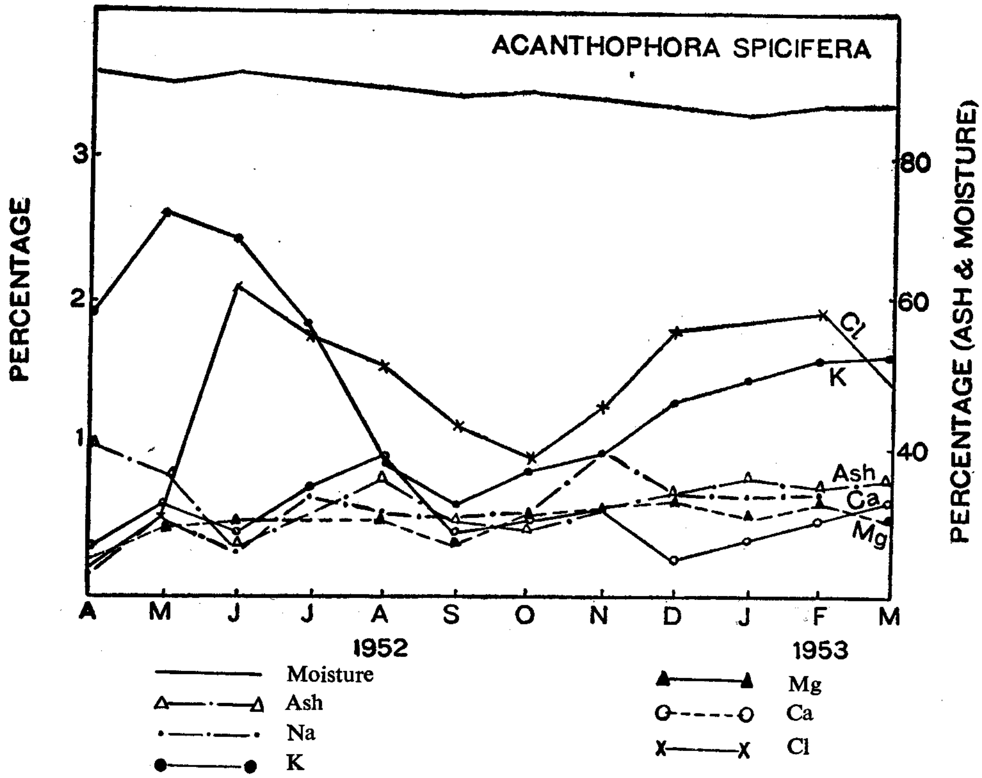


FIG. 5

TABLE X

Trace Elements in Seaweeds Collected during August 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	198·0	4·0	210·0	4·4	trace	..	..
G. lichenoides ..	70·0	10·0	550·0	12·8	0·24	119·0	65·0
C. dasyphylla ..	186·0	6·0	155·0	8·5	0·10	90·0	34·0
E. intestinalis ..	103·0	..	130·0	6·0	0·08	..	28·0
A. spicifera ..	105·0	12·0	85·0	2·8	0·06	90·0	17·0
L. papillosa ..	140·0	3·8	240·0	4·4	0·05	trace	11·0
H. musciformis	172·0	Nil	195·0	7·5	0·09	trace	24·0
S. filiforme ..	103·0	trace	160·0	..	0·12	..	33·0
S. furcellatum ..	63·0	Nil	390·0	8·6	0·08	357·0	65·0
R. intricata ..	214·0	1·1	140·0	..	0·06	32·0	23·0
P. australis ..	315·0	2·5	450·0	9·0	0·10	212·0	37·0

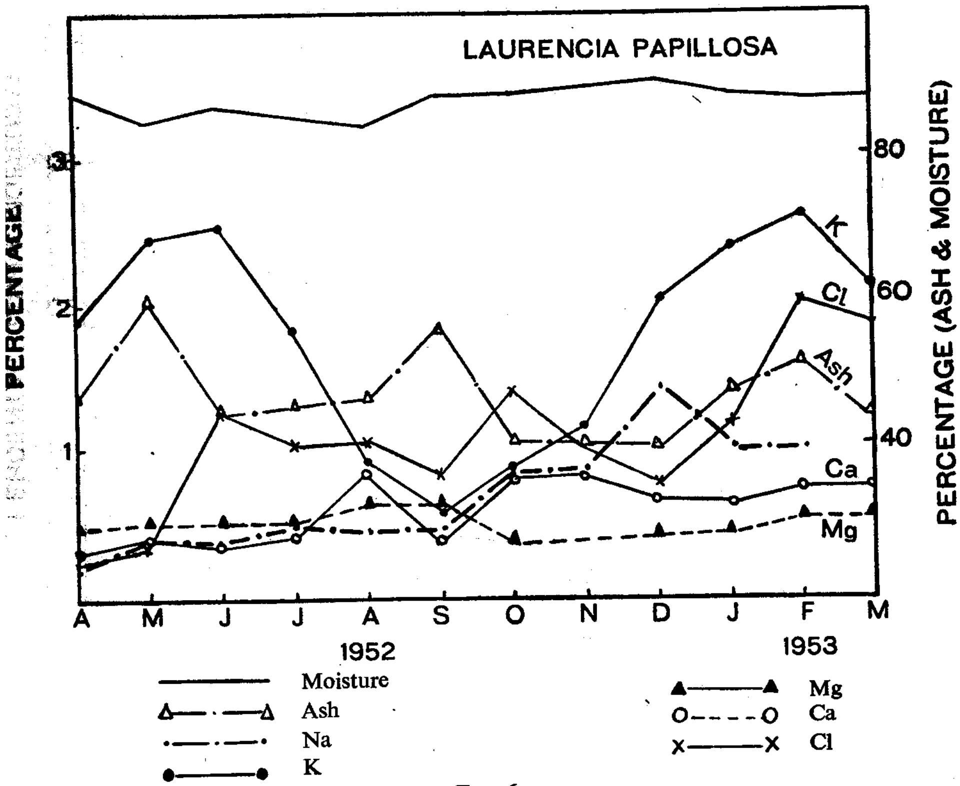


FIG. 6

TABLE XI

Trace Elements in Seaweeds Collected during September 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	217·0	4·0	385·0	1·2	0·08	Nil	30·0
G. lichenoides ..	280·0	..	149·0	..	0·10	63·0	60·0
C. dasyphylla ..	248·5	1·0	82·5	1·0	0·08	..	68·0
E. intestinalis ..	78·0	..	64·0	..	..	15·0	44·0
A. spicifera ..	210·0	3·8	60·5	Nil	trace	Nil	52·0
L. papillosa ..	140·0	2·5	104·5	1·6	trace	Nil	trace
H. musciformis	186·5	trace	173·1	3·0	..	14·0	43·0
S. filiforme ..	143·0	4·0	..	..	0·06	..	37·0
S. furcellatum ..	35·0	2·4	85·0	2·6	0·10	23·0	54·0
R. intricata ..	208·0	trace	165·0	2·6	trace	164·0	20·0
P. australis ..	372·0	trace	140·0	3·0	trace	153·0	29·0

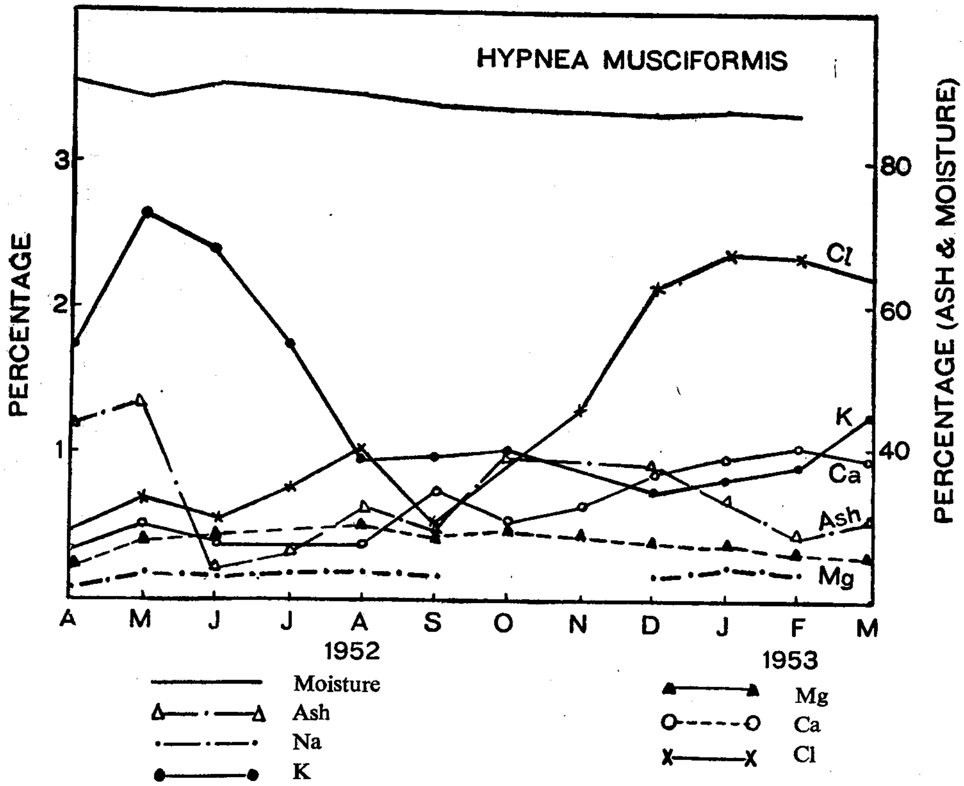


FIG. 7

TABLE XII

Trace Elements in Seaweeds Collected during October 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	88·0	1·8	..	..	trace	14·0	..
G. lichenoides ..	196·0	5·0	171·0	4·0	0·12	125·0	65·0
C. dasyphylla ..	292·4	7·5	82·5	2·5	0·09	60·0	..
E. intestinalis ..	140·0	trace	87·4	..	..	32·0	..
A. spicifera ..	280·0	12·0	51·3	2·0	trace	20·0	70·0
L. papillosa ..	378·0	3·5	93·5	3·5	Nil	18·0	50·0
H. musciformis	280·0	5·0	104·0	6·5	0·05	24·0	50·0
S. filiforme ..	196·0	2·4	65·4	3·9	trace	56·0	..
S. furcellatum ..	140·0	2·6	73·6	6·2	0·10	116·0	30·0
R. intricata ..	224·0	trace	115·5	4·3	trace	263·0	..
P. australis ..	504·0	trace	123·4	4·8	Nil	275·0	..

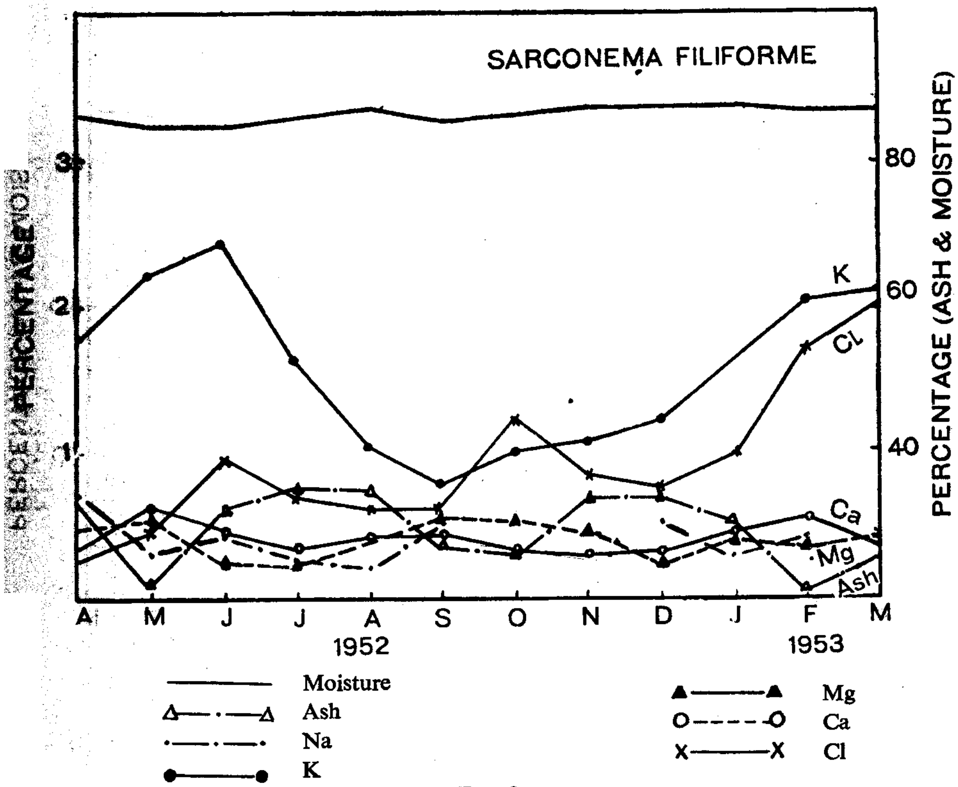


FIG. 8

TABLE XIII

Trace Elements in Seaweeds Collected during December 1952

(Values given as milligram per kilogram of air-dried material)

Name of Species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	90·0	..	..	3·0	0·10	10·0	29·0
G. lichenoides ..	112·0	5·0	200·0	14·3	0·12	175·0	76·0
C. dasyphylla ..	350·0	6·0	175·0	2·4	0·16	98·0	46·0
E. intestinalis ..	110·0	2·5	55·0	..	0·05	30·0	30·0
A. spicifera ..	126·0	1·5	40·0	2·6	trace	29·0	14·0
L. papillosa ..	164·0	3·8	97·5	3·0	0·05	40·0	26·0
H. musciformis	112·0	2·5	55·0	7·0	0·05	84·0	46·0
S. filiforme ..	70·0	2·5	93·0	4·8	0·10	107·0	53·0
S. furcellatum ..	..	..	55·0	2·3	0·09	212·0	40·0
R. intricata ..	165·0	Nil	76·0	5·0	trace	449·0	32·0
P. australis ..	273·0	Nil	136·0	3·4	0·10	500·0	30·0

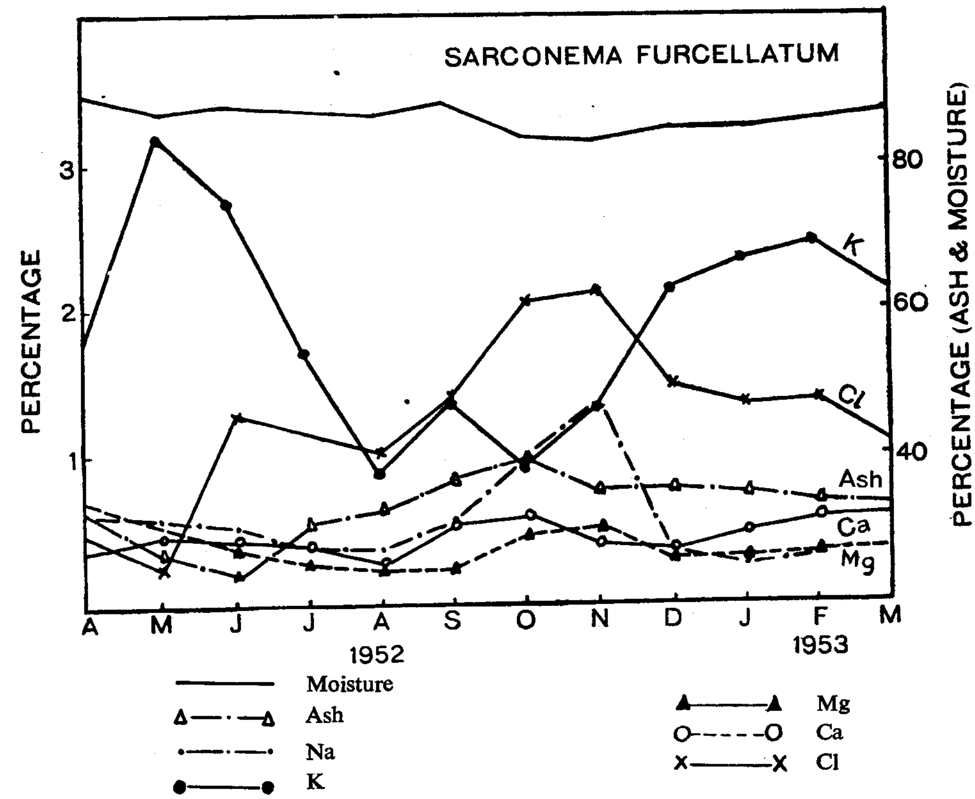


FIG. 9

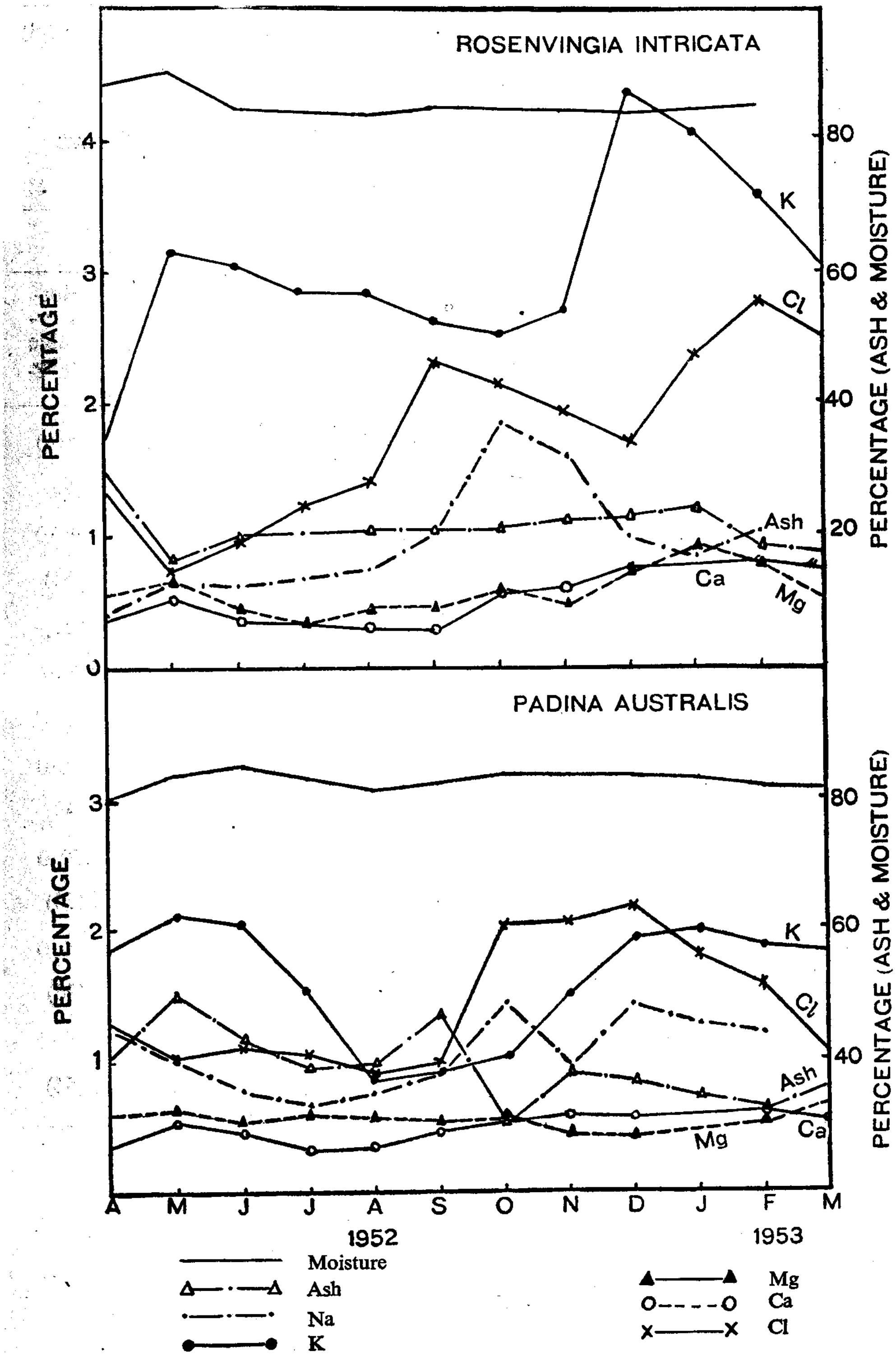
TABLE XIV

Trace Elements in Seaweeds Collected during February 1953

(Values given as milligram per kilogram of air-dried material)

Name of species	Fe	Cu	Mn	B	Mo	I	Zn
C. linum ..	124·0	2·3	275·0	1·6	0·10	24·0	18·0
G. lichenoides ..	189·0	5·6	168·0	6·4	0·16	208·0	83·0
C. dasyphylla ..	308·0	9·0	36·5	4·0	0·16	96·0	48·0
E. intestinalis ..	86·0	1·3	58·0	3·0	0·08	29·0	14·0
A. spicifera ..	..	trace	55·0	1·8	0·05	63·0	46·0
L. papillosa ..	140·0	trace	137·5	2·0	0·05	137·0	55·0
H. musciformis	..	2·7	..	5·0	0·05	100·0	80·0
S. filiforme ..	140·0	2·0	142·4	Nil	0·10	98·0	64·0
S. furcellatum ..	..	..	..	..	0·12	198·0	57·0
R. intricata ..	210·0	..	105·0	3·8	0·08	430·0	31·0
P. australis ..	231·0	..	165·0	1·9	0·10	470·0	44·0

FIG. 10



B2

FIG. 11

The total, as well as cold water and hot water-soluble manganese and boron contents of the seaweeds are given in Tables XV and XVI respectively.

TABLE XV

Partition of Manganese in Seaweeds during Different Stages of Growth

(Figures in brackets are percentages in total Mn)

Name of Species	Mature Specimen			Young Specimen		
	Total mg./kg.	Cold-water-soluble Mn mg./kg.	Hot-water-soluble Mn mg./kg.	Total mg./kg.	Cold-water-soluble mg./kg.	Hot-water-soluble mg./kg.
G. lichenoides ..	550·0	170·0 (31)	200·0 (36·4)	200·0	120·0 (60)	120·0 (60)
C. dasyphylla ..	155·0	65·0 (42)	75·0 (48)	175·0	90·0 (51)	95·0 (54)
E. intestinalis ..	130·0	..	..	55·0	..	..
A. spicifera ..	85·0	15·0 (18)	15·0 (18)	40·0	20·0 (50)	20·0 (50)
L. papillosa ..	140·0	35·0 (25)	40·0 (28·5)	97·5	42·5 (48)	46·0 (49)
H. musciformis ..	195·0	40·0 (21)	50·0 (26)	100·0	65·0 (65)	70·0 (70)
S. furcellatum ..	390·0	40·0 (10)	60·0 (15)	55·0	15·0 (27)	20·0 (36)
P. australis ..	450·0	150·0 (33)	150·0 (33)	113·4	55·4 (48)	60·4 (54)

TABLE XVI

Partition of B in Seaweeds

(Figures in brackets indicate percentages on total B content)

Name of Species	Mature Specimens Total mg./kg.	Mature Specimens Cold-water-soluble mg./kg.	Mature Specimens Hot-water-soluble mg./kg.	Young Specimens Total mg./kg.	Young Specimens Cold-water-soluble mg./kg.	Young Specimens Hot-water-soluble mg./kg.
G. lichenoides ..	12·8	0·90	0·94	4·0	0·38	0·42
		(7·0)	(7·3)		(9·5)	(10·5)
C. dasyphylla ..	8·5	0·68	0·67	2·5	0·26	0·24
		(8·0)	(7·9)		(10·4)	(9·6)
E. intestinalis ..	6·0	0·35	0·41	..	..	..
		(5·8)	(6·8)			
A. spicifera ..	2·8	0·24	0·28	2·0	0·21	0·21
		(8·5)	(10·0)		(10·5)	(10·5)
L. papillosa ..	4·4	0·45	0·44	3·5	0·30	0·33
		(10·2)	(10·0)		(8·6)	(9·4)
H. musciformis ..	7·5	0·50	0·55	6·5	0·70	0·70
		(6·7)	(7·5)		(10·8)	(10·8)
S. furcellatum ..	8·6	0·60	0·62	4·3	0·39	0·42
		(7·0)	(7·2)		(9·0)	(9·8)
P. australis ..	9·0	0·94	0·95	4·8	0·46	0·46
		(10·4)	(10·6)		(9·6)	(10·0)

DISCUSSION OF RESULTS

From an examination of the fresh seaweed samples immediately after bringing them to the laboratory it was observed that those collected between the months of March and July were fully mature and fruiting. Collections made after August were a mixture of fruiting and young specimens, the proportion of young plants increasing until December when the collections were found to contain only non-fruiting young plants.

Black (1948) has shown beyond doubt that marked seasonal variations in chemical composition occur mainly in the fronds, where most photosynthesis takes place, while seasonal variations in the stipes are only very little. It is not logical, he has pointed out, to expect vast changes in the chemical composition of stipes which being perennial are unlike the annually formed fronds. In the present study four of the eleven species taken up are members of a floating association, others are plants of small stature, while the two green species, *viz.*, *Chætomorpha linum* and *Enteromorpha intestinalis* are filamentous forms; and in all of them the thallus lacks differentiation into stipes and fronds.

Tables I to VI give the amounts of the major ions, *viz.*, sodium, potassium, calcium, magnesium, and chlorine, present in the different seaweeds in water-soluble form during the different months of collection. The figures given in the tables represent the quantities of the various elements in the ionic form in the cell fluids of the seaweeds. Unfortunately the data on the seasonal variations in the ionic composition of the water-soluble portion of all the seaweeds considered here could not be gathered and to this extent the data presented are not complete. However they are sufficient to show the distinctive characteristics of each species studied in regard to the manner of absorption of elements.

In Tables I to VI, figures are also given for sodium, calcium, magnesium and chlorine on the dry basis as calculated from values obtained from the wet materials. In order to understand the mechanism of absorption of elements by the algæ the values thus obtained by calculation are compared with those from the analyses of the dry algæ. As may be seen from tables moisture content of the species taken up for study varies between 85 to 92%. Most of this water is not in the combined form but in a free state which may be driven out of the cells by prolonged exposure to the atmosphere. It can be assumed that as the moisture content is so high the volume of the cell fluids will be somewhere about 80 to 90 c.c. per 100 gram of the material. This large amount of water in the algæ may be absolutely necessary for the transport of nutrients from the outer medium to the cells.

Selective Absorption of Individual Elements

It is widely accepted and proved by different workers that the elements present in sea-water have a constant proportion to each other and that this factor undergoes only very little change with zones and seasons. If the absorption of these elements from the water by the seaweeds were a simple process of sea-water getting into the cell walls the amounts of the elements present in the cell fluids would have borne the same proportions as found in natural sea-water. From an examination of the tables it may be seen that the proportion of the elements in the water and in the water-soluble portion of the seaweeds differ widely. This indicates that selective absorption of ions is taking place in the algæ. The ratios between Na and Cl in sea-water collected from the Palk Bay area is about 6: 11 (unpublished data). This is in good agreement with the generally accepted ratio between the two elements as given by Harvey (1928). But in the water-soluble portion of the algæ examined in the present series the value for the above ratio works out differently. In the case of *A. spicifera* collected in June 1952 (Table I), the ratio between Na and Cl is 266: 2553, while the corresponding values for *L. papillosa* and *S. furcellatum* collected during the same months are 516: 2644 and 845: 2788 respectively. This indicates less absorption of sodium as compared to that of chlorine in the species mentioned above, all of them belonging to the group Rhodophyceæ. It can also be seen that even with individual species there is a variation in the ratio between the two ions absorbed. An exception is, however, found in the case of *P. australis*. The ratios between the two ions in the water-soluble portion of this brown alga are found to be 1214: 2232, 1371: 4035 and 2112: 3946 during the months of June, August and October respectively. These values closely resemble the ratio given for normal sea-water, and hence indicate that the alga shows preference to Na ion unlike the Rhodophyceæ mentioned above. Similarly in the Chlorophyceæ, *E. intestinalis*, the ratio does not vary much from that in sea-water. The low absorption noticed in the case of Rhodophyceæ is more evident in the agar-bearing species, particularly in *G. lichenoides*.

Absorption of Potassium, Calcium and Magnesium

From the data presented in the tables it is evident that potassium and calcium are found in high concentrations in the algæ. In certain cases as for example in *P. australis* collected in June 1952, the amount of potassium present in the water-soluble portion of the alga is more than half of the amount of chloride, whereas in sea-water the ratio between the two ions (Cl: K) is roughly about 1: 55. Comparing the amounts of the three ions K, Ca and Mg absorbed by the algæ it can be noticed that potassium and calcium are absorbed to a greater extent than magnesium, the intensity varying with the type of algæ. This is again added proof that the elements present in the algæ are not in similar proportions as they exist in sea-water, for in sea-water the quantity of magnesium is more than the other two elements. Thus in the seaweeds there is greater absorption of potassium and calcium while the absorption of Cl is not quite proportional to these. The ionic equilibrium between the cell fluid and the external medium is, probably, kept up by greater absorption of SO_4 by the algæ.

Comparison of the over-all ionic composition of the seaweeds (as shown in the graphs) and the calculated values given in Tables I to VI show the following: The chloride values as calculated are, in all cases, higher than the values obtained from the actual analyses of the dry algal samples. This is explained by the fact that a portion of the chloride is lost during incineration. The results also indicate that all the chloride absorbed by the algæ are in an ionic form and not in organic combination. In the case of sodium also the amount found in the ionic form in the water-soluble portion is equivalent to the total quantity found in the entire algæ. It has to be assumed that these elements do not come under the group of " essential nutrients ". Sodium and chlorine are present in the form of soluble salts in the sea-water from which the algæ have to absorb certain " essential nutrients "; and naturally to keep up the osmotic balance a certain amount of the sodium and chloride ions also will be absorbed. In the present series of analyses no evidence has, therefore, been obtained as to prove the value of Na as a nutrient in the algæ. It can, however, be observed that Na acts as conserver of potassium, as an inverse relationship has been found to exist between the Na and K contents in certain species of the seaweeds.

It has already been indicated that accumulation of K takes place in the algæ. But it may also be seen that absorption of K is greater in the young and growing plants collected during December and subsequent months. This is in agreement with the findings of early workers in regard to land plants. Evidently potassium also does not undergo any stable organic combination in the seaweeds as almost the entire amount of potassium in the seaweeds exists in the water-soluble form. Janssen and Bartholomew (1929) working on the potassium supply in higher plants have observed that potassium acts as catalyst in the synthesis of carbohydrate, without itself undergoing combination. It has to be assumed that a similar role is played by the element in seaweeds also.

In the case of calcium and magnesium it is observed that only a portion of the total amount is present in the water-soluble inorganic form in all the species studied. The proportion of the water-soluble inorganic form is maximum in the young plants collected in December, the amount becoming less and less as the weeds grow and attain maturity. This suggests that a certain amount of Ca and Mg absorbed by the plants is used up in the organic complex of the seaweeds. Evidence has been given by other workers (Chapman, 1950) showing that agar and algin exist in the form of Ca and Mg compounds. Studies conducted on higher land plants also bring to light the importance and function of these elements. Presence of calcium regulates the entry of antagonistic ions in the cells. Mg, on the other hand, plays an important direct part in the synthesis of chlorophyll. In the seaweeds Ca and Mg may have these functions also besides their function in the synthesis of carbohydrates.

Variations in the Inorganic Elements in the Different Seaweeds with Seasons and Different Growth Stages

Moisture content.—The moisture content of the seaweeds follows the same pattern in all the species with slight exceptions in certain cases. The maximum moisture content is found in samples collected during November-December. At this period the samples obtained were all young and non-fruiting. The rise in the moisture content starts from August-September, reaches a maximum in December (Figs. 1 to 11), is followed by slow decrease in the values giving the minimum in April-July. This change appears to follow the growth changes in the seaweeds rather than the changes in the seasons. New growth of the algæ starts with the few light showers in August, more rapid growth taking place after the moderate rains in October. In *C. linum* the maximum moisture content was 91·2% in May, with the minimum value in December. The behaviour of the above green species is found to be different from that of the other species. This may be due to the fact that the alga is obtained as drift weed and the sample may not be representative of the growth during the month in which it is collected. The maximum and minimum moisture content of the other algæ are as follows: *G. lichenoides* 89·3% in December and 84·9% in August; *E. intestinalis*, 92·8% in December and 86·6% in September; *A. spicifera* 92·0% in June and 86·0% in January; *H. musciformis* 86·0% in February and 91·0% in June; *L. papillosa* 93·0% in December and 84·0% in August; *S. filiforme* 88·0% in December and 85·0% in June; *S. furcellatum* 89·0% in April and 83·0% in November.

Ash.—The ash content of the algæ taken up for study do not seem to undergo wide variations except in the case of *R. intricata* which belongs to the group of Phæophyceæ. As the place of collection is near the equatorial line there is no marked change between summer and winter so much so that the activity of the plants will be more or less the same throughout the year. Hence there is no likelihood of marked changes in the mineral contents of the seaweeds unlike that observed in the case of seaweeds of the temperate regions (Black, 1948). This author records a maximum ash content of 43% in the fronds of the sub-littoral seaweeds of Scotland in the month of May and a minimum of 13% in November. But in the present experiments the values are higher especially in regard to the minimum ash content; and the differences between the minimum and the maximum values are very low.

The total ash content in *C. linum* is maximum in May (39·7%) and minimum in December (28·0%); *G. lichinoides* 43·4% in May and 36·2% in February; *C. dasyphylla* 48·4% in September and 32·0% in October; *E. intestinalis* 57·4% in June and 21·6% in February; *A. spicifera* 41·3% in April and 27·8% in June; *L. papillosa* 61·6% in May and 40·0% in December; *S. filiforme* 34·8% in July and 20·6% in February; *S. furcellatum* 39·0% in October and 24·0% in June; *R. intricata* 29·4% in April and 16·0% in May, and *P. australis* 50·0% in May and 30·0% in October.

Except for the floating association species, and *S. furcellatum* the seaweeds show maximum ash content in samples collected in May and the minimum in those collected in the months of October to January. This period corresponds with the two fairly distinct growth stages of the algæ.

It may also be observed that in certain cases there are two maximum and two minimum values for the ash contents, and of these only the more conspicuous are given above. Thus for example *G. lichenoides* exhibits a maximum ash content of 43·4% in May followed by a minimum value of 38·6% in October. Another maximum (42·8%) appears in December followed again by a minimum (36·2%) in February. Such a phenomenon is also observed in *C. dasyphylla*, *A. spicifera*, *L. papillosa*, *H. musciformis* and *S. furcellatum*. This may normally be taken to mean that growth of the algæ is swift, that they attain maturity within a period less than 12 months and that fresh growth takes place more than once in an year in most cases; but as no distinct regularity is seen in the data gathered the above facts cannot be definitely proved. At the same time if only the more distinct and regular changes are taken into consideration they will agree with the findings of other workers, like Black (1948) who observes that the fronds of *Lainaria* sp. are annual features.

Distinct minima in the Na, K, Ca, Mg and Cl contents are found between the months of August and September, the amounts increasing afterwards from December to May or June and giving the maxima in one of these months. This indicates increased absorption of the elements during the early stages of growth of the plants after the rainy season with considerably limited growth during the latter part of the summer by which time the algæ attain maturity and disappear.

It is also seen from Figs. 1 to 11 that the changes in the absorption of potassium is more marked than any other element. In certain species especially *R. intricata* which belongs to the group of brown seaweeds the potassium content increases to 4·4% of the dry matter.

Trace Element Content of the Algæ

In the present series of experiments only manganese, iron, molybdenum, copper, iodine, zinc and boron have been studied. The results obtained for these elements in eight monthly collections are given in Tables VII to XIV. The quantities of the algæ collected during the intervening months were not sufficient for a complete analysis. However the data obtained give a conclusive idea of the seasonal changes in these constituents.

(i) *Iron.*—There is considerable difference between the three groups of alga, Chlorophyceæ, Phæophyceæ and Rhodophyceæ in regard to their iron contents. The iron content of the Chlorophyceæ is comparatively lower than that of the other two groups, the Phæophyceæ containing the maximum (Table XII). Besides this there are also differences in the iron contents of individual species in the same group. *C. linum* contains a maximum of 217 mg. Fe./kg. in September while the quantity falls down to 42 mg. Fe/kg. in April. In *E. intestinalis*, the other Chlorophyceæ investigated, the iron content varies from 140 mg. in October to 38·6 mg. in April. In regard to the Rhodophyceæ, the variation in iron content in the agar-bearing species, *G. lichenoides*, *C. dasyphylla*, *H. musciformis*, *S. filiforme* and *S. furcellatum*, is most marked, in all instances the values reaching the maxima during September to October. This contrasts with the variations in the major ions in our series of seaweeds, which showed minimum values during the months of August, September and October.

The highest value for iron content obtained in the present studies is 504 mg./kg. in the case of *Padina australis* in October, while much higher values (2040 mg. for *Pelvetia canaliculata*, 3380 mg. for *Fucus spiralis*, 1150 mg. for *Ascophyllum nodusum* and 1260 mg. for *Laminaria digitata*) have been recorded by Black and Mitchell (1952). However it is evident that the algæ require iron for its growth and metabolism.

(ii) *Copper.*—The amount of copper present in the algæ is comparatively lower than that reported by workers like Oy (1940) and Black and Mitchell (1952). In some of the collections copper was absent or present only in traces; and in such of those collections where the presence of copper was detected and estimated no definite regularity was observed so that a seasonal correlation could not be obtained. The maximum copper content (12·0 mg./kg.) was found in *A. spicifera* during August and October (Tables X and XII). In the case of the green species, *C. linum* and *E. intestinalis*, the variation of the copper content is only between 1·8 mg. and 5·0 mg./kg. dry weight. In most of the collections of *L. papillosa* copper is present only in traces while in *G. lichenoides* a maximum of 10 mg. is found in August.

(iii) *Manganese*.—Manganese shows wide variations in the species studied. In all the cases the maximum values are obtained in the collections taken in August and the minimum in April. The increase is more marked in the red species of seaweeds, especially in those containing agar. *G. lichenoides* shows a manganese content of 550 mg./kg. during August. This value is quite comparable to the figures given by other workers. Oy (1940) records a manganese content of 100 to 130 mg./kg. in the Fucaceæ, *F. vesiculosus* and *F. serratus* and Black and Mitchell (1952) recorded a maximum of 800 mg./kg. in *F. serratus* collected in January, while in the Laminariaceæ examined by them the usual range recorded is between 30 and 160 mg./kg. Comparing these values it can be observed that the manganese content in the Indian seaweeds is greater than that of the temperate species examined by the above authors. It is found that almost 60% of the total manganese exists in the water-soluble form in the young plants (Table XV) while in the mature and fruiting plants the quantity of water-soluble manganese comes down to 30%. There is practically very little difference between the cold and hot water-soluble portions in any one of the algæ.

(iv) *Boron*.—The variation in the boron content of the seaweeds follow the same course as manganese, giving maximum values in August. In the brown species the maximum value obtained is 9·0 mg./kg. of dry seaweed while in the greens the values are still less. As in the case of manganese the agar-bearing Rhodophyceæ contain the maximum amount of boron (12·8 mg. B in *G. lichenoides*, 7·5 in *H. musciformis* and 8·6 in *S. furcellatum*). Igelsrud, Thompson and Zwicker (1938) record values between 4·2 and 14·9 mg. B/kg. in marine algæ examined by them, while Oy (1940) found up to 100 mg./kg. in Fucaceæ. Unfortunately Black and Mitchell do not seem to have analysed the seaweeds for their boron contents. In studying the partition of the element in the seaweeds it has been observed that only a very small quantity, generally between 10 and 14%, exists in the water-soluble portions of the algæ examined (Table XVI).

(v) *Molybdenum.*—The usual range of molybdenum has been found to be between 0·05 and 0·1 mg./kg., but a maximum value of 0·24 has been found in *G. lichenoides* collected in August. Here again the quantity varies from month to month and from species to species giving maximum values in the month of August. Much higher values for the molybdenum content of brown seaweeds have been given by Black and Mitchell (1952) and these values usually vary between 0·03 and 1·3 mg./kg.

(vi) *Iodine.*—The two species of Chlorophyceæ examined contained the lowest amounts of iodine, some of the collections containing no iodine at all. The red species show very wide variations among themselves in regard to iodine content, species like *A. spicifera* and *L. papillosa* giving the least values. The agar-bearing seaweeds show comparatively higher iodine contents but these are quite moderate and much lower than the iodine contents of the two brown species. In all these cases the maximum values were recorded in February while the minimum were recorded in August, except in the case of *S. furcellatum* which gave maximum value (357 mg. I/kg.) in August. The values obtained for these Indian seaweeds are, however, lower than that reported by Black (1948 *a*, *b*; 1949) who recorded between 0·1 and 1·0% iodine in the dry matter of the brown seaweeds.

(vii) *Zinc.*—Not much seasonal variation is found in the zinc content of the seaweeds though a slight increase is observed in the collections made in February. But the variations between the zinc content of the different species are quite apparent—the green forms giving the least values while the red species *G. lichenoides* and *H. musciformis* contain the maximum zinc content. On an average the zinc content varies between 10 and 80 mg./kg. and this is in agreement with the values reported by Black and Mitchell.

SUMMARY

A study of the seasonal variations in the mineral contents of eleven species of seaweeds common to the Palk Bay area has been made. The species studied belong to the three major groups, Chlorophyceæ, Rhodophyceæ and Phæophyceæ.

The data on the water-soluble constituents indicate that selective absorption of particular elements takes place in the algæ resulting in the accumulation of that element. There is evidence that some of the elements like Na and Cl absorbed by the algæ remain almost completely in the inorganic form. Among the major elements the absorption of potassium is found to be the maximum especially in the brown seaweeds.

It is observed that almost all the elements estimated vary not only with species but with seasons and different growth stages of the plants. An

effort has been made to determine the growth stage of the plants by microscopic examination and to correlate with the variations in the chemical constituents. The variations in the dry matter, ash, Na, K, Ca, Mg, Cl, etc., in all the eleven species, have been studied and their significance in the growth cycle of the plants discussed. Similarly the amounts and variations of some of the trace elements in the algæ have also been studied. Phæophyceæ contain the maximum amount of iron, while Chlorophyceæ contain the least. The amount of iron varies considerably with species but in all cases the maximum quantity is found in the mature plants. Copper is present only in small quantities. Manganese, boron and molybdenum are found more in the agarophytes like *G. lichenoides* and reach a maximum in mature plants collected in July to August. As against this the iodine content is found to be maximum in collections made in February when the plants are young and non-fruiting.

An attempt has also been made to follow the partition of the two important trace elements, Mn and B, in the different seaweeds. It is found that in the young plants a major portion of the Mn exists in a water-soluble form while the percentage decreases as the plant grows. In regard to boron only very small quantities are found in the water-soluble form irrespective of whether the plant is mature or young.

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REFERENCES

Chapman, V. J. .. "*Seaweeds and Their Uses*," Methuen & Co., London, 1950.

Webb, D. A. .. "Spectroscopic analyses of marine invertebrates with specia reference to the composition of their environment," *Sci Proc. Roy. Dublin Soc.*, 1937, **21**, 505–39.

Cornec, E. .. "Spectrographic studies of the ash of marine plants," *Comp Rend. Acad. Sci., Paris*, 1919, **168**, 513–14.

Jones, A. J. .. "The arsenic content of some of the marine algæ," *Pharm Jour.*, 1922, **109**, 86–87.

Williams, T. and Whetstone, R. E. "Arsenic distribution in soils and its presence in certai plants," *Tech. Bull. U.S. Dept. Agri.*, 1940, **732**, 1–20.

Meulan, H. Ter. .. "Distribution of molybdenum," *Nature*, 1932, **130**, 966.

Igelsrud, I., Thompson, T. and Zwicker, B. M. G. "Boron content of sea-water and of marine organisms," *Amer. Jour. Sci.*, 1938, **35**, 47–63.

Servigne, M. and Tchakirian, A. .. "Sur la presence d'elements des terres rares dans les Algeus *calcaires* (*Lithothamnium calcareum*)," *Comp. Rend. Acad. Sci., Paris*, 1939, **209**, 570–72.

Wiesner, R. .. "Determination of radium content of marine algæ," *Sitzber. Akad. Wiss. Math.-Naturw. Klasse.*, 1938, Abt. II *a*, **147**. 512–18.

Oy, E. .. "Content of iron, copper, manganese and boron in seaweeds," *Tidsskr. Kemi. Bergv.*, 1940, **20**, 114–17.

Beharrell, J. .. "Seaweed as a food for livestock," *Nature*, 1942, **149**, 306–07.

Wilson, S. H. and Fieldes, M. .. "Minor elements in a seaweed (*Macrocystis pyrifera*)," *New Zealand Jour. Sci. Tech.*, 1941, **23**, 47 B–48 B.

Black, W. A. P. .. "The seasonal variations in chemical composition of some of the sub-littoral seaweeds common to Scotland," *Jour. Soc. Chem. Ind.*, 1948 *a*, **67**, 165–72.

——— .. "Seasonal variation in chemical composition of the littoral seaweeds common to Scotland," *Ibid.*, 1948 *b*, **67**, 355–57.

——— .. "Seasonal variations in chemical composition of littoral seaweeds common to Scotland. Part II," *Ibid.*, 1949, **68**, 183–89.

——— and Mitchell, R. L. "Trace elements in the common brown algae and in seawater," *Jour. Mar. Biol. Assn., U.K.*, 1952, **30**, 575–84.

Krishna Pillai, V. "Observations on the ionic composition of blue-green algæ, growing in saline lagoons," *Proc. Nat. Inst. Sci.*, 1955, **21**, 90–102.

Harvey, H. W. .. "*Biological Chemistry and Physics of Seawater*," Cambridge, 1928, p. 36.

Janssen, G. and Bartholomew, R. P. "The translocation of potassium in tomato plants and its relation to their carbohydrate and nitrogen distribution," *Jour. Agri. Res.*, 1929, **38**, 447–65.