

Metal concentrations in seaweeds from KwaZulu-Natal, South Africa - a first report

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A survey of concentrations of selected metals in some common seaweeds from the KwaZulu-Natal coast was conducted. Samples of 40 seaweeds were collected from Palm Beach, Isipingo Beach and Mission Rocks and analysed for metals by X-ray fluorescence. High metal concentrations were found in a number of the seaweeds examined. *Stypocaulon funiculare* (Phaeophyta) and *Osmundaria serrata* (Rhodophyta) showed high levels of a wide range of metals and are recommended for further study as indicator species for metals in the marine environment of the KwaZulu-Natal coast.

Keywords: metals, seaweeds, macroalgae, South Africa, *Stypocaulon funiculare*, *Osmundaria serrata*.

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Introduction

Macroalgae are reportedly reliable indicators of metals in seawater because of their ability to accumulate these elements (Saenko *et al.* 1976; Zindge *et al.* 1976; Agadi *et al.* 1978; Philips 1980; Ho 1988; Ferletta *et al.* 1996). Seaweeds have several intrinsic advantages which make them suitable indicators in the marine environment, viz. they are sessile and can be used to monitor changes in metal levels over time, their size makes them readily identifiable and they are easily handled (Levine 1984). For a species to be a good indicator, it must be a bio-accumulator and its population size should be adequate to sustain regular sampling.

The literature reports six methods for metal analysis in seaweeds: atomic absorption spectrophotometry (Güven *et al.* 1992; Molloy & Hills 1996), electron microprobe X-ray analysis (Chung & Lee 1989), thermal neutron activation analysis (Güven *et al.* 1992), micro-PIXE (proton induced X-ray emission) imaging (Weiersbye *et al.* 1996), instrumental Neutron Activation analysis (INAA) (Vasquez & Guerra 1996) and X-ray fluorescence (XRF) (Bannatyne 1995). Metal concentrations in seaweeds from different parts of the world have been reported (Bryan & Hummerstone 1973, 1977; Fuge & James 1974; Haug *et al.* 1974; Morris & Bale 1975; Foster 1976; Eide *et al.* 1980; Bryan 1983; Forsberg *et al.* 1988). However, no such data are available for South African seaweeds. Due to the growing trends of informal settlement, urbanisation and industrialisation on the South African coastline, metal pollution of the marine environment is likely to increase and analysis of metal content in seaweeds may provide a useful monitoring tool for assessing metal pollution levels. Reservations on the validity of seaweeds as bio-indicators of metal levels in the environment have been expressed by Brown (1997).

This study examined the levels of metals found in commonly occurring seaweeds from Palm Beach (30°58'S; 30°17.5'E), a residential area surrounded by sugar cane farming, Isipingo Beach (29°58'S; 32°58'E) a relatively highly industrialised area, and Mission Rocks (28°1'S; 32°30'E), a low impact coastal reserve surrounded by a national park, in KwaZulu-Natal, South Africa. This paper is the first report to use XRF to study the levels of metals in seaweeds from KwaZulu-Natal.

Materials and Methods

Seaweed sample collection

Seasonally and locally abundant seaweeds were collected from the intertidal zone of Palm Beach, Isipingo Beach and Mission Rocks,

KwaZulu-Natal, on the east coast of South Africa in April 1995. Several large individual plants were collected in the field and pooled to provide a sample. Three replicate samples were taken. These were air-dried and sand, crustaceans and epiphytes were removed.

Isipingo Beach samples:

Phaeophyta- *Padina boryana* Thivy, *Ralfsia expansa* (J. Agardh) J. Agardh, *Sargassum incisifolium* (Turner) C. Agardh, *Stypocaulon funiculare* (Montagne) Kützing;

Rhodophyta- *Amphiroa ephedraea* (Lamarck) Decaisne, *A. bowerbankii* Harvey, *Arthrocardia carinata* (Kützing) Johansen, *Callithamnion stuposum* Suhr, *Cheilosporum cultratum* (Harvey) Areschoug, *C. sagittatum* (Lamouroux) Areschoug, *Galaxaura diessingiana* Zanardini, *Gelidium abbotiorum* R. Norris, *Hypnea spicifera* (Suhr) Harvey, *Jania verrucosa* Lamouroux, *Laurencia natalensis* Kylin, *Osmundaria serrata* (Suhr) R. Norris, *Plocamium corallorhiza* (Turner) J. Hooker and Harvey, *Prionitis nodifera* (Hering) Barton;

Chlorophyta- *Caulerpa filiformis* (Suhr) Hering, *C. racemosa* (Forsskål) J. Agardh, *Chaetomorpha antennina* (Bory de Saint-Vincent) Kützing, *Ch. linum* (O.F. Müller) Kützing, *Codium duthieae* P. Silva, *Halimeda cuneata* Hering, *Ulva rigida* C. Agardh, *Valonia macrophyssa* Kützing.

Palm Beach samples:

Phaeophyta- *Sargassum incisifolium*, *Stypocaulon funiculare*, *Stypopodium zonale* (Lamouroux) Papenfuss, *Zonaria tournefortii* (Lamouroux) Montagne,

Rhodophyta- *Galaxaura diessingiana*, *Gelidium abbotiorum*, *Hypnea spicifera*, *Osmundaria serrata*, *Prionitis nodifera*;

Chlorophyta- *Codium duthieae*, *Halimeda cuneata*, *Ulva rigida*.

Mission Rocks samples:

Phaeophyta- *Dictyopteris longifolia* Papenfuss, *Ecklonia radiata* (C. Agardh) J. Agardh, *Zonaria subarticulata* (Lamouroux) Papenfuss,

Chlorophyta- *Codium duthieae*.

The names and nomenclature of seaweeds are cited after Silva *et al.* (1996).

Table 1 Metal concentration ranges (ppm) in the 10 seaweeds showing the highest metal concentrations in this study

Metal	Metal concentration (ppm)									
	<i>Amphiroa ephedraea</i>	<i>Chaetomorpha antennina</i>	<i>Chaetomorpha linum</i>	<i>Halimeda cuneata</i>	<i>Stypocaulon funiculare</i>	<i>Hypnea spicifera</i>	<i>Osmundaria serrata</i>	<i>Prionitis nodifera</i>	<i>Sargassum incisifolium</i>	<i>Zonaria subarhculata</i>
As	< 24–45	37–78	37–81	66–119	102–120	36–83	900–1428	38–223	< 24–109	91–92
Ba	31–68	88–122	35–84	16–94	322–325	< 10–93	14–67	< 10–498	< 10–491	20–29
Co	< 9–13	< 9	< 9	< 9–14	< 9–29	< 9	< 9–12	< 9–13	< 9–12	< 9–11
Cr	26–31	< 9	< 9–12	17–21	143–168	< 9–20	35–148	< 9	< 9–19	25–28
Cu	< 2	< 2–45	< 2–10	< 2	< 2	< 2–17	< 2–35	< 2–16	< 2–18	< 2
Mo	< 2	< 2	< 2	< 2	< 2	< 2–119	< 2	< 2	< 2	< 2
Nb	< 3	< 3	< 3	< 3	< 3	< 3	< 3–5	< 3	< 3	< 3
Ni	20–24	< 9–11	< 9–26	< 9	104–107	11–33	< 9	< 9	< 9	< 9
Pb	< 10	28–53	28–53	< 10	18–23	< 10–61	70–75	25–61	< 10–12	< 10–15
Rb	< 3–31	22–50	35–45	42–73	50–58	31–51	581–799	35–210	25–36	357
Sr	1480–1615	175–525	1109	85–2427	43–406	1129–1739	23–380	1504–2100	107–1200	559–563
V	8–29	57–64	13–28	5–29	148–168	12–30	12–35	10–104	4–21	11–14
Y	< 3	< 3	< 3	< 3	29–38	< 3	< 3	< 3–25	< 3	< 3
Zr	< 6–26	69–1029	133–450	< 6–429	2774–3055	< 6–340	< 6–11	< 6–1771	< 6–142	31–38

X-ray fluorescence (XRF)

The clean air-dried samples were milled to a particle size of 75 µm in a carbon-steel geological mill (TS250 grinding mill, Dickie and Stockler, Johannesburg, South Africa). Following standard methods, six drops of 'liquid glue' [2% solution of mowiol (Hoechst, Krugersdorp, South Africa)] were mixed with 5 ml of each powdered seaweed and compressed in a pellet press. Five ml boric acid (Saarchem, Krugersdorp, South Africa) was added and the pellet was again compressed to form a bilayered pellet. Three pellets of each sample were prepared.

Each bilayered pellet was subjected to X-ray fluorescence (Philips PW1400, Holland) in order to determine the levels of metals (Tables 1 and 2). Cadmium and mercury could not be detected due to the nature of the detection tube used in this study. A multifactorial analysis of variance of the means, at the 95% confidence level, was used to compare metal levels among seaweeds.

Results and Discussion

Baseline values and variation of metal levels in different seaweeds

All seaweeds collected from KwaZulu-Natal contained detectable levels of various metals. The 10 seaweeds which showed the highest metal content are listed in Table 1. Table 2 lists the remaining seaweeds analysed in this study. There were no significant differences in the metal levels between seaweed species of the same genus collected at the same site (e.g. *Amphiroa bowerbankii* and *A. ephedraea*; *Caulerpa filiformis* and *C. racemosa*; *Chaetomorpha antennina* and *Ch. linum*) (Tables 1 and 2). However, metal ion levels varied greatly among seaweed species (Tables 1 and 2). This trend is in agreement with reports on Malaysian seaweeds (Ramachandran *et al.* 1994).

Nb, Co, Y, Mo, V, Rb, Zr and Ni concentrations in the tissues of seaweeds elsewhere in the world are not reported in the literature and are presented here for the first time (Tables 1 and 2).

Cu (< 2–87 ppm) and Sr (12–2882 ppm) were present in seaweed tissues at concentrations similar to those of algae from the Black Sea (Güven *et al.* 1992) and Malaysian seaweeds (Ram-

achandran *et al.* 1994). These authors reported levels of 3–10 ppm Cu and 77–1685 ppm Sr which they consider as high and indicative of industrial pollution in their respective marine environments.

Cr and Pb concentrations in seaweeds examined from KwaZulu-Natal (< 9–716 ppm and < 10–75 ppm respectively) were high compared with those in Malaysian seaweeds (1.0–21.5 ppm and 0.1–21.5 ppm respectively; Ramachandran *et al.* 1994).

Seaweeds with the highest Pb content were the rhodophytes *Osmundaria serrata*, *Hypnea spicifera* and *Prionitis nodifera*. This high concentration of Pb in the rhodophytes is similar to the findings of Ramachandran *et al.* (1994) and is reportedly ascribed to the phycocolloid, carrageenan in these algae which have a strong affinity for Pb.

Ba and As levels (< 10–498 ppm and < 24–1428 ppm respectively) reported in this study for seaweeds on the KwaZulu-Natal coast were high in comparison to corresponding concentrations reported for Black Sea algae (< 20 ppm and 3–48 ppm; Güven *et al.* 1992) which were considered to be indicative of a polluted environment.

Table 3 shows the seaweed species with the highest levels of individual metals. The red alga *Osmundaria serrata* contained the highest levels of As, Cr, Nb, Pb and Rb of all algae sampled in this study. The brown seaweed *Stypocaulon funiculare*, collected from Isipingo Beach, contained the highest levels of Cr, Co, Ni, V, Y and Zr (Table 3). The reason this alga may accumulate such a wide range of metals is that the thallus comprises tufted filaments which are basally compounded but apically free (Branch *et al.* 1994). The resultant large surface area, as well as the many closely packed branches entrap particles from the water and may allow metal uptake to occur more readily (Bannatyne 1995).

According to the assessments of Güven *et al.* (1992) and Ramachandran *et al.* (1994), the concentrations of As, Ba, Cr, Cu, Pb and Sr found in KwaZulu-Natal seaweeds are above the levels of these metals normally found in the marine environment. Of these As, Cr, Cu and Pb are reported industrial pollutants (Moore &

Table 2 Range of metal concentrations (ppm) in KwaZulu-Natal seaweeds

Metal concentration (ppm)										
Isipingo Beach										
Metal	<i>Padina boryana</i>	<i>Ralfsia expansa</i>	<i>Amphiroa bowerbankii</i>	<i>Arthrocardia carinata</i>	<i>Callitham- nion stu- posum</i>	<i>Cheilospo- rum cultra- tum</i>	<i>Cheilospo- rum saggit- tatum</i>	<i>Jania ver- rucosa</i>	<i>Laurencia natalensis</i>	<i>Plocamium corallorhiza</i>
As	38-43	36-49	< 24-40	< 24-18	< 24-55	68	< 24	< 24-43	142-168	223-342
Ba	116-133	56-118	17-63	23-84	52-151	89	20-57	20-110	62-101	19-143
Co	< 9-14	< 9	< 9	< 9-10	< 9-13	< 9	< 9-11	< 9	< 9-11	< 9-11
Cr	< 9	< 9-13	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9-11
Cu	< 2-19	< 2	< 2	< 2-22	< 2-73	16	< 2-14	< 2-87	< 2	< 2-12
Mo	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2-12
Nb	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Ni	< 9	< 9-26	< 9	< 9	< 9-17	< 9	< 9	< 9-13	11-14	< 9-22
Pb	23-26	< 10	< 10	< 10	< 10-25	< 10	< 10	< 10	< 10-16	< 10-27
Rb	29-36	12-25	11-25	< 3-19	22-53	49	< 3-25	< 3-25	111-125	169-235
Sr	126-422	1010- 1930	1578-1647	1442-1624	158-957	1537-1664	57-1410	291-783	1082-172	67-2240
V	22-40	18-21	7-14	5-13	25-79	34	9-16	3-27	13-39	23-48
Y	< 3	< 3	< 3	< 3	< 3-11	< 3	< 3	< 3	< 3	< 3-12
Zr	393-452	46-139	< 6-12	< 6-27	128-578	583	< 6-139	< 6-76	116-307	< 6-299

Metal concentration (ppm)									Mission Rocks		
Isipingo Beach									Mission Rocks		
Metal	<i>Caulerpa fliformis</i>	<i>Caulerpa racemosa</i>	<i>Valonia mac- rophysa</i>	<i>Gelidium abbottiorum</i>	<i>Codium duthieae</i>	<i>Ulva rigida</i>	<i>Osmunda- ria serrata</i>	<i>Hypnea spicifera</i>	<i>Dictyopteris longifolia</i>	<i>Ecklonia radiata</i>	<i>Codium duthieae</i>
As	< 24-40	29-68	31-85	61-144	134-139	< 24	1403-1428	53-76	43-47	68-76	74-80
Ba	< 10-59	48-198	79-88	< 10-69	26-38	< 10	< 10	< 10-56	< 10	< 10	< 10
Co	< 9	< 9-13	< 9-12	< 9-11	< 9	11-12	< 9-13	< 9	13-14	11-12	13-14
Cr	< 9	16-27	< 9-18	< 9	3-8	14-16	10-14	< 9	14-15	15-18	22-27
Cu	< 2	< 2-20	< 2-16	< 2	< 2	< 2	< 2	< 2-12	< 2	< 2	< 2
Mo	< 2	< 2	< 2	< 2	< 2	< 2	< 2-4	< 2	< 2	< 2	< 2
Nb	< 3	< 3	< 3	< 3	< 3	< 3	< 3-6	< 3	< 3	< 3	< 3-4
Ni	< 9	34-40	38-44	< 9	< 9	< 9	< 9	< 9-17	< 9	< 9	< 9-11
Pb	23-35	< 10-13	< 10	38-41	21-28	20-21	68-75	37-49	13-19	< 10-24	14-17
Rb	< 3-29	24-42	581-799	39-76	71-72	17-18	1109-1127	39-50	30-31	55-57	48-49
Sr	96-474	134-795	23-41	502-2882	166-171	123-126	37-44	43-209	1139-1153	1221-1231	143-147
V	8-38	19-104	23-62	14-79	16-24	10-12	11-12	13-21	10-11	11-13	17-20
Y	< 3	< 3-25	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Zr	16-198	161-1771	307-468	10-87	50-61	12-17	< 6-7	< 6-15	< 6-12	26-33	214-294

Table 2 Continued

Metal	Palm Beach								
	<i>Sargassum incisifolium</i>	<i>Zonaria tournefortii</i>	<i>Stypocaulon funiculare</i>	<i>Stypopodium zonale</i>	<i>Codium duthieae</i>	<i>Gelidium abbotiorum</i>	<i>Halimeda cuneata</i>	<i>Ulva rigida</i>	<i>Prionitis nodifera</i>
As	137–139	69–77	98–104	73–77	46–65	56–64	92–106	< 24–52	< 24
Ba	< 10	14–18	274–302	< 10	54–60	41–55	< 10	25–80	13–121
Co	11–12	11–12	11–23	13–14	< 9	10–12	< 9–14	< 9	< 9–18
Cr	15–19	22–26	121–154	55–62	< 9	25–26	14–21	< 9–13	< 9
Cu	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	21–49
Mo	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Nb	< 3	< 3	< 3	< 3	< 3	< 3–4	< 3	< 3	< 3
Ni	< 9	< 9	< 9	43–45	< 9	< 9	< 9	< 9–19	< 9
Pb	< 10–12	11–14	14–21	15–21	23–28	19–22	< 10	20–36	23–48
Rb	53–54	29–31	61–63	57–59	20–21	55–57	77–80	12–25	24–26
Sr	1107–1141	1655–1666	12–113	559–563	107–112	247–252	2442–2398	341–847	900–1300
V	12–13	18–20	120–132	12–14	13–20	26–27	14	4–17	10–14
Y	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3–5
Zr	< 6–7	254–272	1135–2132	31–38	16–23	219–300	52–63	< 6–46	< 6–578

As, Cr, Cu and Pb are reported industrial pollutants (Moore & Moore 1976) and their presence in the marine environment could

possibly be associated with industry along the KwaZulu-Natal coast. To confirm this further detailed studies need to be undertaken to determine metal accumulation in seaweeds over time, as well as to assess whether increased metal concentrations in sea-

Table 3 Seaweed species containing the highest levels of metals and the concentration range at which metals occur in selected seaweeds from KwaZulu-Natal

Metal	Range of metal concentrations in all seaweeds tested (ppm)	Species with highest metal concentration	Mean metal level (ppm) ± SE in seaweed with the highest metal concentration
As	< 24–1428	<i>Osmundaria serrata</i> (R)	1413 ± 13
Ba	< 10–498	<i>Prionitis nodifera</i> (R)	321 ± 270
Co	< 9–29	<i>Stypocaulon f?miculare</i> (P)	11 ± 7
Cr	< 9–168	<i>Stypocaulon funiculare</i> (P)	155 ± 13
Cu	< 2–87	<i>Jania verrucosa</i> (R)	48 ± 30
Mo	< 2–119	<i>Hypnea spicifera</i> (R)	42 ± 67
Nb	< 3–6	<i>Osmundaria serrata</i> (R)	5 ± 2
Ni	< 9–107	<i>Stypocaulon funiculare</i> (P)	105 ± 2
Pb	< 10–75	<i>Osmundaria serrata</i> (R)	73 ± 2
Rb	< 3–1127	<i>Osmundaria serrata</i> (R)	1118 ± 9
Sr	12–2882	<i>Gelidium abbotiorum</i> (R)	1654 ± 1191
V	< 3–168	<i>Stypocaulon funiculare</i> (P)	156 ± 11
Y	< 3–38	<i>Stypocaulon funiculare</i> (P)	33 ± 5
Zr	< 6–3055	<i>Stypocaulon funiculare</i> (P)	2929 ± 143

P = Phaeophyta; R = Rhodophyta; C = Chlorophyta

Table 4 Metal concentration ranges in seaweeds collected from Palm Beach, Isipingo Beach and Mission Rocks

Metal	Metal concentration (ppm)		
	Isipingo Beach	Palm Beach	Mission Rocks
As	< 24*–1428	< 24–1428	43–92
Ba	< 10–498	< 10–302	< 10–29
Co	< 9–29	< 9–23	< 9–14
Cr	< 9–168	< 9–716	14–28
Cu	< 2–87	< 2–49	< 2
Mo	< 2–12	< 2–119	< 2
Nb	< 3–6	< 3–5	< 3–4
Ni	< 9–107	< 9–45	< 9–11
Pb	< 10–75	< 10–75	< 10–24
Rb	< 3–1127	12–799	30–357
Sr	23–2882	12–2398	143–1231
V	3–168	4–132	10–20
Y	< 3–38	< 3–5	< 3
Zr	< 6–3055	< 6–2132	< 6–294

* lowest detection limit of the XRF n = number of seaweeds collected at the site

effluent along the coast. The data reported here are intended to provide a baseline for such future comparisons.

Effect of collection site on metal levels in seaweed tissues

Table 4 presents the concentration range of metals and found in seaweed tissues at the three sites investigated. Pb levels were higher in seaweeds from Palm Beach than those from Isipingo Beach and Mission Rocks (Table 4).

Conclusions

This study is the first report of metal levels to be found in some of the commonly occurring macroalgae from the coast of KwaZulu-Natal. The algae listed in Tables 1 and 2 occur in relative abundance in KwaZulu-Natal, for most part of the year and have the demonstrable ability to accumulate a range of metals. The two seaweeds that contained the highest levels of the majority of the metals tested in this study, were *Stypocaulon funiculare* (Co, Cr, Ni, V, Y and Zr), and *Osmundaria serrata* (As, Nb, Pb and Rb). It is suggested that these two seaweeds warrant further study as bio-indicators of metal levels in South African inshore waters.

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