

Instrumental Neutron Activation Analysis Study of Elemental Concentrations in Some Species of Marine Algae from Different Regions of Libyan Coast

Ibrahim O. Abugassa¹ and Blaeid S. Dalim^{2,*}

¹Department of Neutron Activation Analysis, Tajoura Nuclear Research Center, Tajoura, Libya

²Department of Physics, El-Mergib University, Meslata, Libya

*Corresponding Author: biled_salemfarag@yahoo.com

Abstract

Algae are an ideal marine species to study responses to different environmental factors free from complications inherent in research with more complex higher plants. One of the advantages of environmental study using algae is the possibility to achieve and observe many generations during relative short time period. Algae materials have been used as ecological and environmental indicators to monitor and control in many fields of study such as freshwater and marine ecosystems, soil fertility, industrial applications, etc. It also has been shown that algal assemblages could be used as indicators of clean or polluted water. Previous studies proved high sensitivity of the most algae towards changing of environmental conditions, especially as consequences of water pollution. Algae respond rapidly and predictably to a wide range of pollutants and provide potentially useful early warning signals of deteriorating conditions and possible causes. Because of their nutritional needs and their position at the base of aquatic food web, algal indicators provide relatively unique information concerning ecosystem conditions compared with commonly used animal indicators. In most cases ecologically relevant signals of ecosystem changes are being provided that can be used to distinguish acceptable from unacceptable environmental conditions. Algal indicators are also a cost-effective monitoring.

Keywords: Algae; ecology; environment; Libyan coast.

1. Introduction

Marine algae are considered as important primary producers in the coastal region. Several marine algal species are being considered as raw material for various economically important products and this has resulted in their increasing demand [1]. Marine algal species also have been suggested to be the indicators of pollution [2]. Keeping in view the importance of marine algal species for direct or indirect human and cattle consumption, it is necessary to monitor the bioaccumulation of certain elements in these species. Algae also have been used to absorb excess nutrients from effluents, thereby reducing nutrient pollution in lakes

and streams [3]. It also has been shown that algal assemblages could be used as indicators of clean or polluted water.

In this study, Instrumental neutron activation analysis (INAA) using Tajoura reactor will be utilized for determination of trace elements in four different species of algae materials as an indicative sample of environmental pollution and for monitoring any possible pollution level. These species are selected because they are abundant along the Libyan coastline. Four coastal sites of Libya have been selected, namely, Janzour, Tajoura, Al Khums and Misurata. The precision and the accuracy of the results were evaluated by analyzing the refer-

ence materials.

2. Experimental

The study focuses on elemental content of algae as a bio-indicator using Tajoura nuclear research reactor based on instrumental neutron activation analysis (INAA). Four algae species, namely, *Ulva*, *Jania*, *Systosira* and *Caulerba* were manually collected from four sites along the Libyan coast. The algae were collected from about seven meters from the shore and about half meter deep. Samples were then placed in plastic mesh and washed several times with sea water. Following the washing, the samples were kept in special containers. The samples were carefully screened and classified according to their types. Samples were thoroughly washed several times with distilled water and placed in plastic dishes. After that, all samples were dried inside the oven at 60 °C for about 24 hours in order to remove any moisture. The algae samples then were crashed to a powder form using agate and pestle. About (115-160) mg of each sample was sealed in pre-cleaned cylindrical polyethylene vials for irradiation. Few hundred mgs of two SRM, IAEA 140TM Sea Weeds and NIST 15480 Typical Diet were also prepared. In addition to that, three Al-Au wires for flux correction were also prepared. Samples, reference material were placed inside a newly designed Al-irradiation container. Au monitors were positioned along the vertical axis of the Al irradiation container to account for any flux variation within the container. The container was irradiated for 8 hours in total neutron spectrum in channel 6-1 of Tajoura reactor at neutron flux 2×10^{13} n/cm² s in a vertical channel 6-1 of (TRC-10) water cooled, water moderated research reactor of the TNRC (Figure 2.1).

After irradiation and appropriate radioactive decay of the sample and standards (The samples were cooled for 4 days to 1week); irradiated samples were mounted on perspex plates and the radioactive assay was carried out using a 30 % relative efficiency HPGe detector coupled to MCA with 8k conversion gain. The irradiated samples and SRM were counted in identical geometry with respect to the detector. The distance of the sample from the detector was set at 3 cm. The dead time didn't exceed 10 %. Two modes of measurements were chosen, 2 and 17 hour. The Au

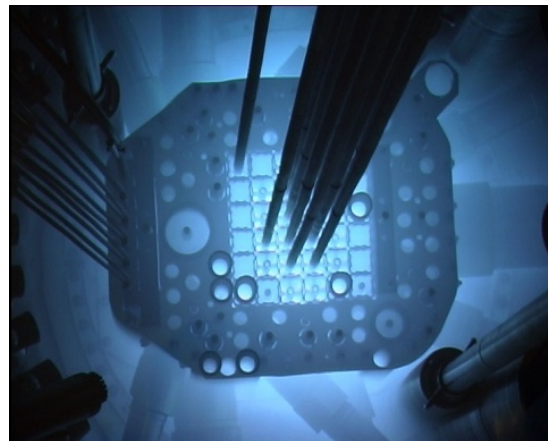


Figure 2.1: Depicts the vertical channels of the Tajoura reactor and the tubes used for short irradiation are also seen in the far left of the photo.

monitors were measured for 15 min. at reference distance (19 cm from the detector). Using a computer software, the peaks were fitted, their peak areas (and hence the relative intensities of various γ -transitions) are determined to calculate the abundance of various elements present in the sample. The specific activities of Au wires were calculated and found no variations along the container. Finally, all these information were converted into a list of elements and their concentrations. All spectra were collected using Emcaplus card and the elemental concentrations were calculated using simple software based on Microsoft Office Excel.

3. Results and Discussion

In this study, multielement analysis of four types of algae was performed by instrumental neutron activation analysis (INAA) following established quality assurance procedures. The relevant nuclear data for 22 nuclides used for analysis in this work is given in Table 3.1. Two standard reference materials, IAEA Seaweeds 140 and NIST 15480 Typical Diet, were used for quality assurance of the analytical procedure and the results are presented in Table 3.1.

The obtained results have been compared with the reported values and found to agree very well within the limits of the experimental errors. Table 3.2 reveal that the following list of elements

Table 3.1: Elemental concentrations in NIST 15480 Typical Diet (mg/kg, unless stated otherwise).

No.	Element	Certified values	This work
1	Br*	9.64	12.5 ± 0.8
2	Ce* µg/kg	-	2.27
3	Co	0.028 ± 0.0025	0.026 ± 0.0028
4	Cr	-	0.13 ± 0.014
5	Cs* µg/kg	9.8	15.6 ± 6
6	Fe	35.3 ± 3.77	34.02 ± 2.38
7	Hg*	0.005	0.025
8	Rb	-	3.7 ± 0.86
9	Sb µg/kg	9 ± 2	7.7 ± 0.42
10	Sc* µg/kg	0.8	0.94 ± 0.1
11	Se	0.245 ± 0.028	0.25
12	Zn	24.6 ± 1.79	25.85 ± 0.6

As, Ba, Ca, Ce, Co, Cr, Hf, Sc, Sr, Th and Zn has been determined in marine algae jania samples collected from the four sites. The elemental concentrations turned out to be higher in the samples collected from Al Khums. This is could be attributed to the sample collection has been carried out near the harbour or may be due to the inflow of drainage along the sampling site. In contrast, the concentration levels for the following elements Au, Br, Hg, Sb and Se, as elucidated in Table 5. were substantially higher in jania samples collected from Tajoura beach. This probably due to the sampling site was in the vicinity of the diffuse inputs from marine biology research center activities. Concentrations of Fe and Sm are relatively higher in jania samples collected from Misurata beach and that is might be due to the industrial activities output of the steel factory. Janzour beach on the other hand, has higher concentrations of La, Rb and U as illustrated in Figure 5.7. This may possibly be attributed to a sewage outfall located in the area.

Table 3.3 present a list of elements (As, Au, Ba, Ca, Ce, Co, Cr, Fe, Hf, Hg, La, Sc, Se, Sm and Th) that has been obtained in marine algae *Sytosira* collected from the three locations, Tajoura, Al Khums and Misurata. The concentrations of the elements turned to be higher in the samples collected from Tajoura. It's evident that the concentration of these elements is relatively higher in Tajoura beach than the others, as a result of chemicals that might be discharged through the

drain system of Marine Biology Research Center. But Br, Cs, Rb and Zn show higher concentration in Al khums beach and that could be attributed to sampling collection site was very close by the harbor area. Misurata beach showed relatively higher concentrations in Sb, Sr and U. Again, this could be due to human activities in the area.

Table 3.4 characterizes the elemental concentration in *Ulva* type collected from Tajoura and Janzour. Higher concentration of Au, Ba, Br, Ca, Ce, Co, Cr, Cs, Fe, Hf, Hg, La, Sb, Sm, Sr, U and Zn found in the samples collected from Tajoura. But As, Rb, Sc, Se, Th are comparatively higher in Janzour. This may possibly be attributed to a sewage outfall located in the area. The present results showed wide range of variation in the concentrations of the twenty two elements analyzed in the four algae species. Also, the present results revealed that the concentrations of trace elements in marine algae of the Libyan coast are on the lowest side as compared with other published studies on other beaches around the world. For example concentration of some elements in the marine algae type *Ulva* from Sri Lanka [5], for example, As = 8 mg/kg, Co = 5 mg/kg, Rb = 3.0 mg/kg, Se = 0.8 mg/kg and Sm = 6 mg/kg are relatively higher than the obtained results for the same specie sampled from Libyan coast such as, As = 0.13 mg/kg, Co = 0.2 mg/kg, Rb = 1.5 mg/kg, Se = 0.53 mg/kg, Sm = 0.0034 mg/kg. Therefore, the data obtained for *Ulva* specie sampled from the Libyan coast doesn't indicate any source of pollution when compared with other published data.

Conclusion

To support the use of nuclear analytical techniques for environmental studies and to prove the potential of INAA as a routine monitoring tool to determine environmental pollution levels, analytical procedures were established using standard reference materials. Toxic and trace elements in a set of four algae materials were analyzed quantitatively. INAA using Tajoura reactor and high resolution γ -ray spectrometry has been exploited for the determination of 22 elements in the algae materials. The method was justified by analyzing standard reference materials and the results agree very well with the certified values.

Table 3.2: Elemental concentrations in algae Jania (mg/kg, unless stated otherwise).

No.	Element	Location			
		Zanzour	Tajoura	Khoms	Misurata
1	As	6.5	0.154	23.5	1.45
2	Au	0.008	0.0549	0.0047	0.00431
3	Ba	22.5±5	27.16±5	45±5.7	35.33 ± 7
4	Br	74.5±6.3	163.5±2	91.5±4	110 ± 3.5
5	Ca %	15.6±1.7	14.5±0.77	17.3±0.25	16.3 ±0.4
6	Ce	0.81±0.81	1.338±0.44	1.41±0.08	1.012±0.067
7	Co	0.105±0.0057	0.2725±0.02	0.6±0.02	0.385 ±0.05
8	Cr	0.71±0.085	1.5±0.2	1.7±0.16	1.2±0.077
9	Cs µg/kg	17±2.2	15±1.2	2.65±0. 02	48 ±6
10	Fe	388.25±29	447.75±28	361.5±28	654 ±25
11	Hf µg/kg	27±9	675±180	780±28	46±9
12	Hg	nd	0.01425	nd	nd
13	La	17.83±4	6.7±0.42	0.195±0.035	0.106±0.017
14	Rb	1.5±0.019	0.94±0.084	0.54±0.02	0.745±0.16
15	Sb µg/kg	14.5±4	28±2.5	9.5±0. 07	20±1
16	Sc µg/kg	95±8.6	124±6	140±10	125±5
17	Se µg/kg	64.5±7	466±70	280±10	79±16
18	Sm	0.114±0.005	0.34±0.02	0.135±0.007	0.79±0.028
19	Sr	1655±166	1575±45	1864±170	1732±22.5
20	Th µg/kg	43±4.5	95±7	185±20	95±7
21	U	0.3575	0.2665	0.265	0.2
22	Zn	57.5±6	75±7	145±5.5	90±10

Table 3.3: Elemental concentrations in algae *Systosira* (mg/kg, unless stated otherwise).

No.	Element	Locations		
		Tajoura	Khoms	Misurata
1	As	37.5	18.18	3.48
2	Au	0.0731	0.0113	0.0137
3	Ba	69.83±10.6	51.66±9.6	46.16±11
4	Br	— — —	238.33±17.9	146.66±8
5	Ca %	1.7±0.36	1.45±0.14	0.29±0.01
6	Ce	1.85±0.2	0.28±0.1	0.395±0.035
7	Co	0.68±0.16	0.2675±0.043	0.4975±0.017
8	Cr	1.985±0.13	0.36±0.02	0.46±0.04
9	Cs µg/kg	11.3±4.5	21±5	14.5±2
10	Fe	445.75±32	183.5±9	225.75±11
11	Hf	1.245±0.2	0.027±0.001	0.0245±0.008
12	Hg	0.1661	— — nd —	— nd — —
13	La	2.15±0.2	0.45±0.13	0.2±0.06
14	Rb	2.2±0.17	2.41±0.6	1.515±0.007
15	Sb µg/kg	16.5±0.7	13.25±3	36.5±2
16	Sc µg/kg	80.5±0.7	23±3	30±1.6
17	Se µg/kg	111±14	8.7±0.06	120±59
18	Sm	0.92±0.003	0.145±0.05	0.071±0.002
19	Sr	338±15.5	229±39	2027±152
20	Th	0.61±0.0064	0.17±0.007	0.0155±0.0035
21	U	0.0291	0.284	0.81
22	Zn	175.5±16	209±10	73.75±1.7

Table 3.4: Elemental concentrations in algae Ulva (mg/kg, unless stated otherwise).

No.	Element	Locations	
		Janzour	Tajoura
1	As	0.132	0.116
2	Au	nd	0.01
3	Ba	6.5±2	22±2.98
4	Br	9.41±0.5	240.66±5.6
5	Ca %	0.7±0.1	1.2±0.07
6	Ce	0.42±16	0.57±0.05
7	Co	0.2±0.026	0.21±0.034
8	Cr	0.72±0.14	2.2±0.07
9	Cs µg/kg	2±0. 3	3±0. 5
10	Fe	188.75±13	855.66±46.5
11	Hf	0.049±0.007	0.127±0.007
12	Hg	nd_	0.0657
13	La µg/kg	5±0. 4	180± 90
14	Rb	1.485±0.16	0.605±0.007
15	Sb µg/kg	16.8±2	17.6±11
16	Sc µg/kg	35±7	28±9
17	Se	0.053±0.02	0.0256±0.09
18	Sm µg/kg	3.4±0. 03	25.5±2
19	Sr	102±2.82	273.5±36
20	Th µg/kg	84.5±6	80±9
21	U	nd	0.242±0.01
22	Zn	69±5	216±5.6

In order to account for any neutron flux variation in the irradiation container in channel 6-1 (used for irradiation in the present study) of Tajoura reactor, several Au wires were irradiated with the samples and their specific activities were calculated and found almost identical; therefore no correction has been applied. The results obtained in all algae species are found to be varying from one location to another. In conclusion, concentration levels of a wide range of trace elements in algae originated from four different locations have been established. The concentrations of most elements determined in the algae collected from the Libyan coastline samples were lower than those found in the other part of the world. The variation on elemental concentration indicates that certain type of algae preferentially bioaccumulate certain elements. For a majority of elements, there were only marginal concentration differences between the four species, probably reflecting the regional background levels at an anthropogenic effect in studied locations. Since no

work has previously been done on algae species in these sites, these results may represent baseline data for metal concentrations within and between algae species, sampling sites and time of collection. Based on the levels of metal concentrations quantified in the species, and the fact that the algae species studied were abundant at the sampling sites throughout the year period, it is concluded that most of the species studied can be used as bio-indicators for studying marine pollution for the elements analyzed. Algae can be outstanding indicators of natural and/or artificial changes in biodiversity (both in terms of abundance and composition) due to changes in biotic and anthropogenic factors, and hence are excellent monitors of environmental changes. On the other hand, more experimental and field studies with longer sample period of algae are obviously needed if they are to be used as bio-accumulated and to determine the long term trends.

References

- [1] G.W. Bryan, L. G. Hummerstone, 1973, Brown seaweeds as indicators of heavy metals in estuaries in south west England. *J Mar Biol Assoc UK* 53:705-720.
- [2] A. Melhus, K. L. Seip, H. M. Seip, S. Myk-
lested, 1978, A preliminary study of the use of benthic algae as biological indicators of heavy metal pollution in Sorfjorden, Norway. *Environ Pollut* 15: 101-107.
- [3] J. Brodie and G.C. Zuccarello, 2007, Systematics of the species-rich algae: red algal classification, phylogeny and speciation. In *The taxonomy and systematics of large and species-rich taxa: building and using the Tree of Life* (eds. T.R. Hodkinson and J.Parnell), Systematics Association Series, CRC Press, pp. 317-330.
- [4] Abugassa & M. Ramadan, 2002. Private communication.
- [5] J. Ranjith and R. Matthias, 1996. Department of Botany, University of Kelaniya, Sri Lanka Institute of Applied Physical Chemistry, Research Centre Juefich, D-52425 Juelich, Germany Environmental Geochemistry and Health 18, 63-68.