Eurasian Journal of Analytical Chemistry
Volume 3, Number 1, 2008

Comparison of Some Radionuclides in the Marine Coastal Environment of the Black Sea and the Mediterranean

Alexander S. Strezov

Bulgarian Academy of Sciences, Institute for Nuclear Research and Nuclear Energy

Abstract

Ten types of sea algae distributed along the Bulgarian coast have been collected and analyzed for radioactivity content in the period 1996 - 2004. Results have shown that ^{37}Cs concentrations in all analyzed samples were relatively low (less than 10 Bq kg^{-1} dry weight) while the levels of naturally occurring radionuclides, such as ^{226}Ra and ^{210}Pb, were found to be higher in most samples; the highest observed value (896 Bq kg^{-1} dry weight for ^{226}Ra and 68 Bq kg^{-1} for ^{210}Pb was in the green *Bryopsis plumosa* alga.

In addition, most alga species were also found to accumulate ^{210}Pb, which indicates their selectivity to this isotope. On the other hand, brown algae *(Cystoseira barbata & crinita)* have shown a clear selectivity for some nuclides, this selectivity may encourage their use as a biomonitor for pollution by nuclides. Moreover, the red alga species were found to contain the highest levels of Cs.

The coastal areas far from rural settlings were chosen as control sites to evaluate soluble and total metal concentrations and to gain additional information on both the environmental conditions of the area and possible bioaccumulation patterns.

Data from this study were also compared with those previously obtained from neighboring Mediterranean Sea. The results clearly show differences between these two marine ecosystems. Nuclide concentrations recorded along the Bulgarian coast may be used for background levels for intraspecific comparison within the Black Sea area, which information is still very scarce.

Keywords: Radionuclides; Marine algae; Black Sea

ISSN: 1306-3057

1. Introduction

The main objective of this study was to determine the radioactivity baseline and to define the accumulation levels in algae species distributed along the Bulgarian Black Sea coast that can be used as biomonitors. Samples of algae and coastal sediments have been collected from 15 sites and analyzed for artificial (^{137}Cs) isotopes and natural (^{226}Ra, ^{210}Pb) radionuclides during the period 1992 -2004. Results have shown that the highest levels of ^{226}Ra and ^{210}Pb were observed in *Bryopsis plumosa* and *Ceramium rubrum.* The results of these studies were used to investigate and define the algae species that could be used as biomonitors. A very recent study [1] supported by IAEA - Vienna reported the impact of unloading phosphate ore cargoes from ships upon near marine environment leading to elevated content of ^{226}Ra, ^{210}Pb and other natural radionuclides in sediment and surface water.

Since marine algae are well distributed along the coast and can be found in large quantities in addition to the wide range of their applications in cosmetics, paints, shampoo, agriculture (e.g. fertilizers) and pharmaceutical industry, many studies have been performed worldwide to characterize algae species and determine trace elements and radionuclide levels [5-7, 9, 13, 17, 19-22, 24, 25].

The distribution patterns of the radioactive and heavy metal pollutants are studied extensively in the last years to determine the accumulation of radioactive pollutants in marine ecosystems.

The analysis of sediments is widely used for environmental control and evaluation of human impacts, because of their ability to accumulate various pollutants. Marine sediments are able to bind contaminators by sorption, biological uptake of benthic organisms and chemical reactions, thus providing a large reservoir for radionuclides and heavy metals.

Algae are another important factor for heavy metals and nuclides accumulation in marine ecosystems. Some macroalgae species accumulate metal ions (nuclides) from seawater and being in the food chain of marine biota, participate in radionuclide and heavy metal transfer to the biosphere and man.

Radionuclides affect the living organisms in two ways - as heavy metals and by their radiation. In order to provide sufficient data for estimating any radioactivity ecological problem, an environmental monitoring program was performed since 1991 along the Bulgarian Black Sea coast. Studies on radionuclides, trace metals and major elements content in algae distributed along the Bulgarian coast are insufficient even though their classification and distribution are well established.

The aim of this work was to characterize the most common algae species distributed along the Bulgarian coast for radionuclides, trace metals and major elements and to study the possibility of using algae as biomonitors for radionuclides pollution.

The created database for nuclide concentrations in sediments was enlarged with algae species data that will enable the modeling of radionuclide transfers by estimation of concentration variations, accumulation and influence on marine ecosystems.

2. Experimental

The radionuclide and heavy metal content was determined in Black Sea sediments and ten macroalgae species (five green: *Cladophora vagabunda, Ulva rigida, Enteromorpha intestinalis*, *Chaetomorpha gracilis* and *Bryopsis plumosa;* two brown: *Cystoseira crinita* and *Cystoseira barbata;* three red: *Ceramium rubrum, Callithamnion corymbosum* and *Corallina officinalis)* from 35 reference locations. Radionuclides were measured by low level gamma spectroscopy while atomic absorption spectrometry (AAS) was applied for heavy metals (HM) in algae. ETAAS (Perkin – Elmer Zeeman 3030 with graphite furnace) was the method to determine Pb and Cd and flame AAS (Pye Unicam SP 1950 atomic absorption spectrophotometer with air – acetylene flame) was used for Fe, Mn and Cu. The sample treatment, procedures and measurements are described elsewhere [21, 22].

3. Results

The mechanisms of binding contaminants by sediments and algae along the whole Bulgarian Black Sea coast were studied (Fig. 1). The obtained results for three types of sediments – sand, silt and slime (in Bq/kg dry weight), presented on Figs. 2 and 3, show that radionuclide concentrations strongly depend on the sediment nature. All these data confirmed the lack of serious contamination along the Bulgarian Black Sea coast.

The increase in ^{137}Cs concentration in slime sediments and sorption on fine particles leads to cesium scavenging and occurrence at greater depths, which can be explained by physico-chemical interaction processes of the soluble Cs forms with the surrounding media. In sand and sandy sediments the Cs content does not change greatly while a process of ^{137}Cs accumulation is observed in slime and silt sediments. Due to this, sea bottom sediments play a major role in radionuclide redistribution between different components in the ecosystems, which may change the concentration of ^{137}Cs in these parts of the ecosystem.

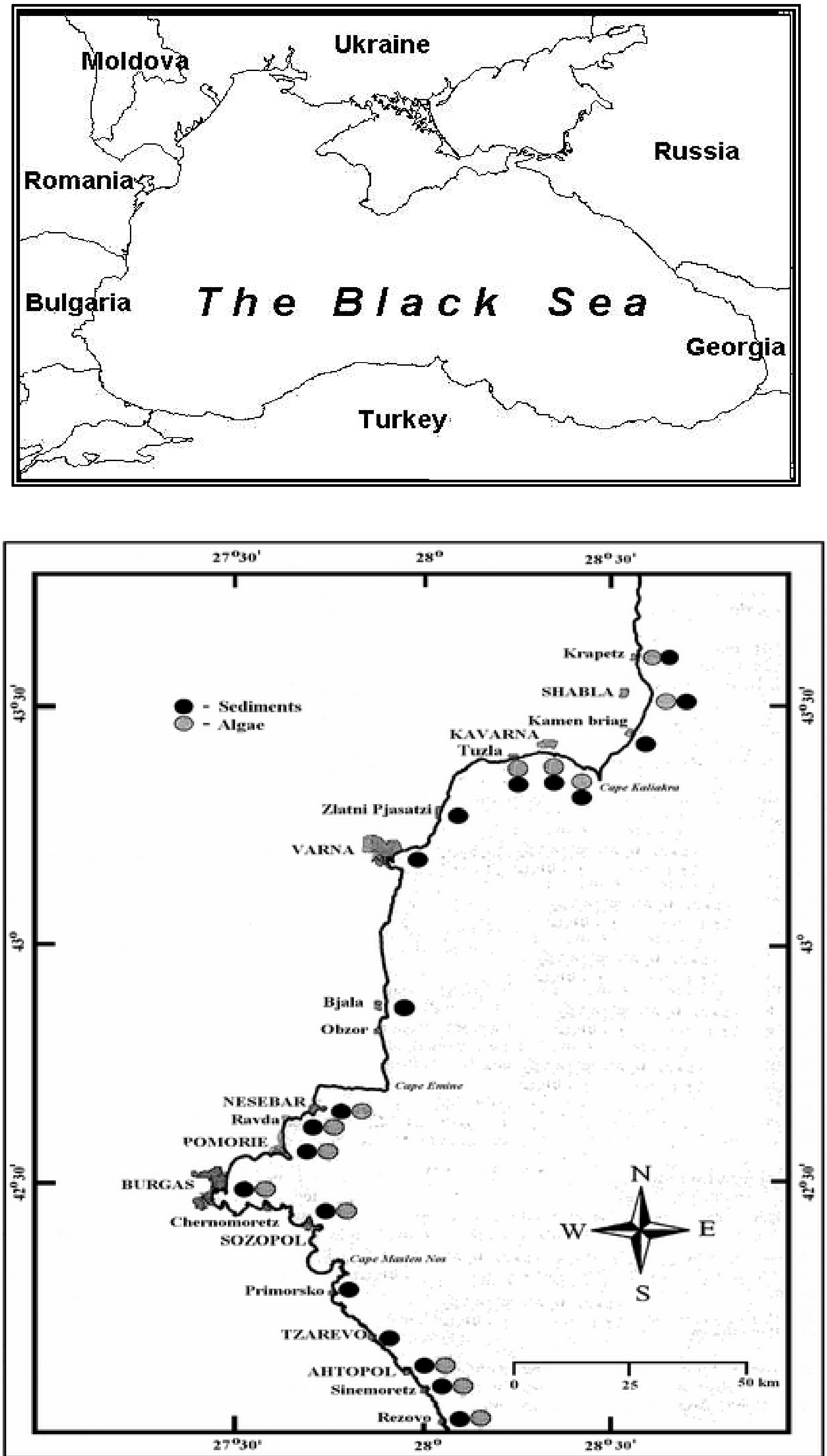

Fig. 1. Diagram of sampling locations at the Bulgarian Black Sea coast.

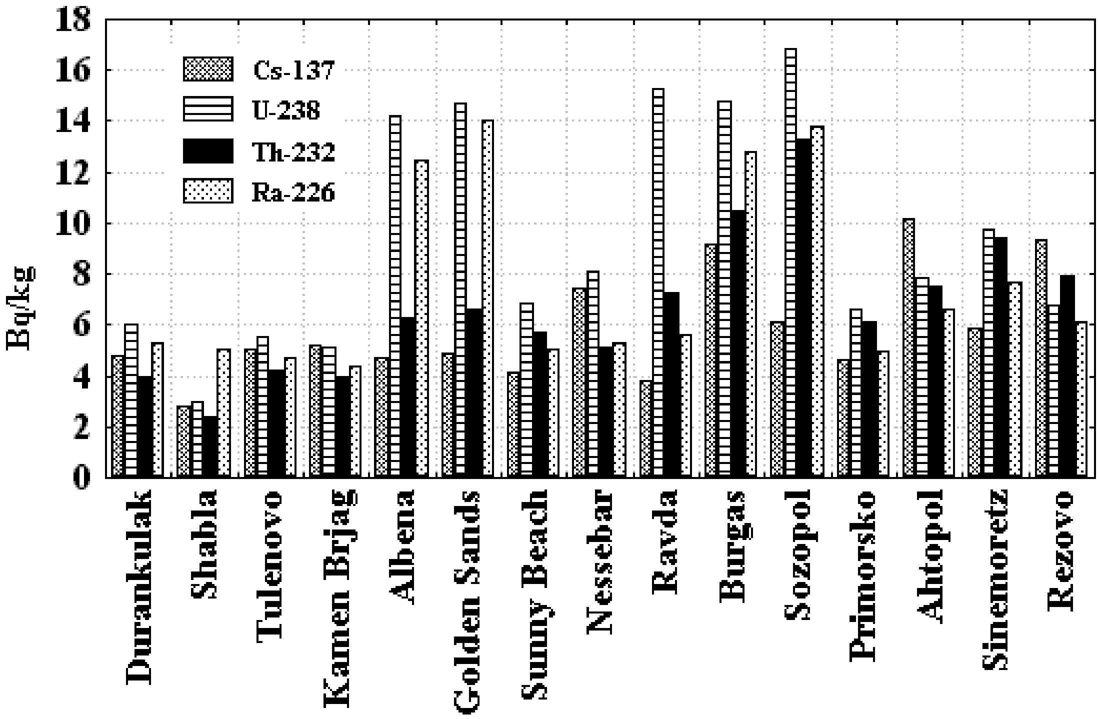

Fig. 2. Nuclide content in sand sediments along the Bulgarian coast

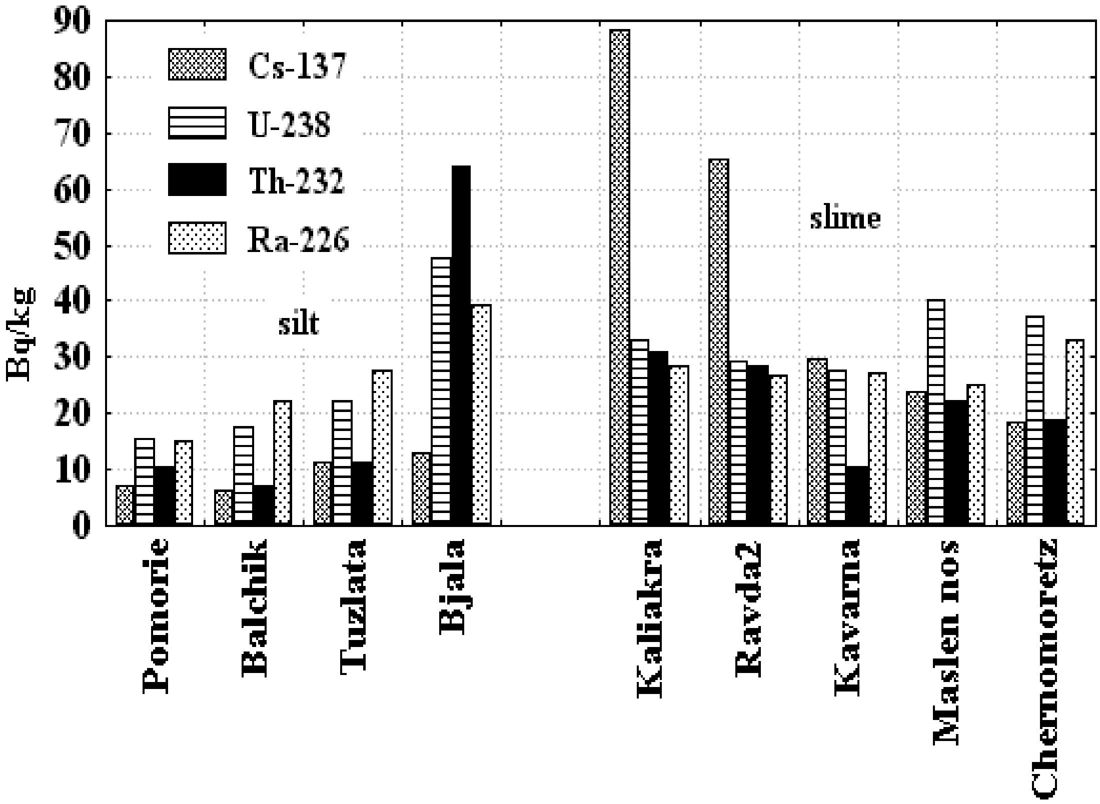

Fig. 3. Mean nuclide content in silt and slime sediments along the Bulgarian coast

The obtained results for natural nuclides show that there is a similarity between the accumulation of ^{238}U and ^{232}Th in Black Sea bed sediments. The measured U and Th values are within the range of those cited in the literature, meaning that there is no serious contamination with U and Th at the Black Sea coast. ^{226}Ra content generally follows the pattern of U and Th with few exceptions.

Table 1. Data for nuclide accumulation in green, brown and red Black Sea macroalgae.

Algae	^{137}Cs		^{226}Ra		^{210}Pb	
	Mean ± SE	Range	Mean ± SE	Range	Mean ± SE	Range
Ulva rigida	4.1 ± 0.7	1.5 – 10.0	8 ± 1	3 – 16	6 ± 1	3 – 15
Ent. intestinalis	3.3 ± 0.8	1.4 – 7.0	8 ± 2	3 – 15	10 ± 2	3 – 15
Clad. vagabunda	4.0 ± 0.8	2.0 – 9.0	12 ± 2	4 – 18	8 ± 1	3 – 14
Chaetom. gracilis	2.3 ± 0.8	1.2 – 5.3	7 ± 2	4 – 11	11 ± 2	5 – 16
Bryopsis plumosa	2.1 ± 0.6	1.4 – 4.1	896 ± 117	650– 1300	63 ± 18	45 – 100
Ceramium rubrum	9.7 ± 0.8	4 – 18	21 ± 2	5 – 39	16 ± 2	4 – 41
Call. corymbosum	4.4 ± 0.7	2.9 – 6.5	6 ± 2	3 – 17	13 ± 4	4 – 30
Cor. officinalis	2.4 ± 0.5	1.2 – 5.4	6 ± 1	2 – 11	12 ± 2	4 – 22
Cyst. barbata	6.1 ± 0.5	3 – 10	12 ± 2	3 – 17	9 ± 1	3 – 18
Cyst. crinita	5.3 ± 0.4	2.6 – 10.0	8 ± 1	2 – 17	12 ± 1	2 – 21

The use of marine organisms as bioindicators for trace metal pollution is very common. Algae and mollusks are among the organisms most often used for this purpose [9]. Macroalgae are able to accumulate trace metals, reaching concentration values that are much higher than the corresponding concentrations in sea water [4, 14]. Algae bind only free metal ions, the concentrations of which depend on the nature of suspended particulate matter [16, 26], which, in turn, is formed by both organic and inorganic complexes. Moreover, algae satisfy all the basic requirements of bioindicators: they are sedentary, their dimensions are suitable, they are easy to identify and to collect, they are widely distributed, and they accumulate metals to a satisfactory degree [8].

The most often used algae in biomonitoring studies are those of the genus *Ulva* because this species is most widespread along the Mediterranean [11, 12] as well as along the Black Sea coast.

The objective of this work was to gather more information on the use of species abundant at the Black area: the green algae *Ulva (rigida + lactuca)*, *Enteromorpha intestinalis, Chaetomorpha gracilic*, *Cladofora vagabunda,* the brown algae *Cystoseira cinita* and *barbata*, the red *Ceramiun rubrum* species, *Calithamnion corumbosum* and *Corallina officinalis.*

For this purpose we evaluated the possible effect of anthropogenic activities on a coastal area of the Bulgarian Black Sea coast. This area, for which the literature is quite scant, is actually not free from industrial activities and therefore is not completely uncontaminated. Moreover, it is affected by the presence of two big towns: Varna and its harbor (~800,000 inhabitants) and Burgas (~500,000 inhabitants). The coastal area of the Black Sea was also sampled as well as the resorts at coast and inflowing rivers close to the shoreline.

Generally, when studying sea pollution, some clearly contaminated stations are chosen and compared with "clean" monitoring sites. In this study similar sites (beaches, river estuaries, ports, etc.) were examined supposedly in order to identify useful "background levels" as a reference for intraspecific comparisons within the Black Sea area, on which information has been very scarce.

As a whole the radionuclide content in all studied algae species is low (except *Bryopsis plumosa*). ^{137}Cs levels were low in all algae samples (Fig 4). The Cs content in *Ulva rigida* species is in the range 1.5 - 8 Bq/kg, in *Ceramium rubrum* – 10 – 17 Bq/kg and in *Cystoseira barbata* - 5 – 9 Bq/kg. Higher Cs concentrations, 26 Bq/kg were found in the alga *Ceramium* from Tuzlata.

Comparing the ability to accumulate ^{137}Cs, the algae species can be arranged as follows:

Clad. vagabunda > *C. rubrum (*over 10 Bq/kg*)* > *Cyst. barbata* > *Cyst. crinita (6.5 – 7 Bq/kg)* > *Ent. intestinalis* > *Callith. corymbosum* (5 Bq/kg).

The natural isotopes concentrations are higher than technogenic ones and the highest concentrations of natural nuclides are registered in the green algae.

^{226}Ra content and measured ^{210}Pb values are in the interval 10 - 30 Bq/kg. Comparatively low are the ^{228}Ac and ^{208}Tl – around 5 Bq/kg. The different levels of nuclide accumulation are presented on Fig. 4.

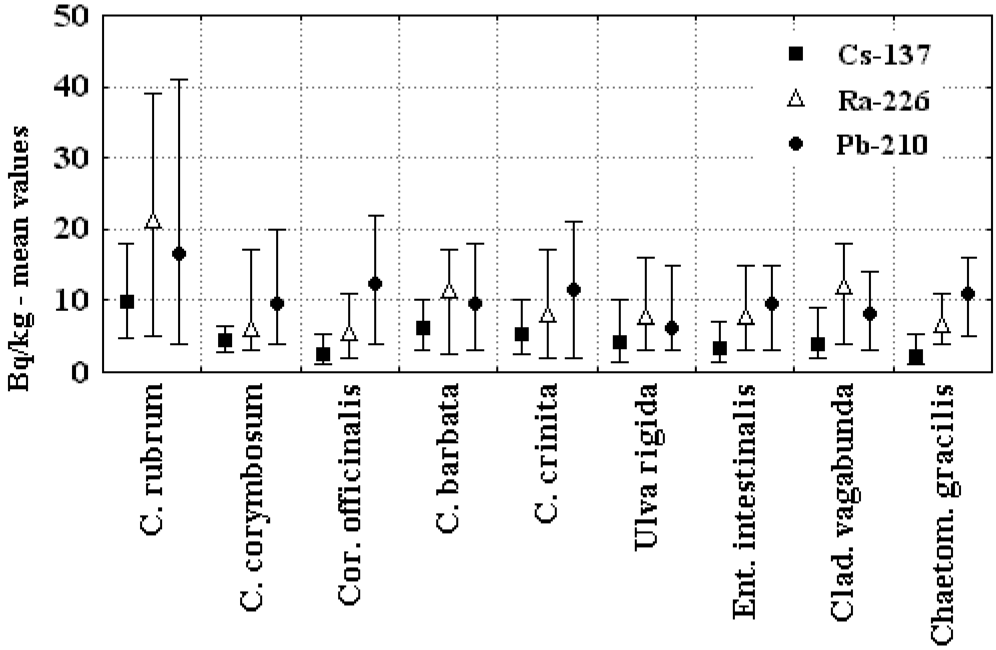

Fig. 4. Radionuclide content in different Black Sea macroalgae species**.**

As it is seen from these data, ^{226}Ra is readily sorbed in *Green Chaetom. gracilis, Ulva rigida, Clad. vagabunda* and *Clad. Coleothrix* while Red *Callith. corymbosum*, *C. rubrum* and the brown species - *Cyst. crinita*, accumulate more ^{210}Pb.

The obtained mean values measured in different seasons are presented on Fig. 5.

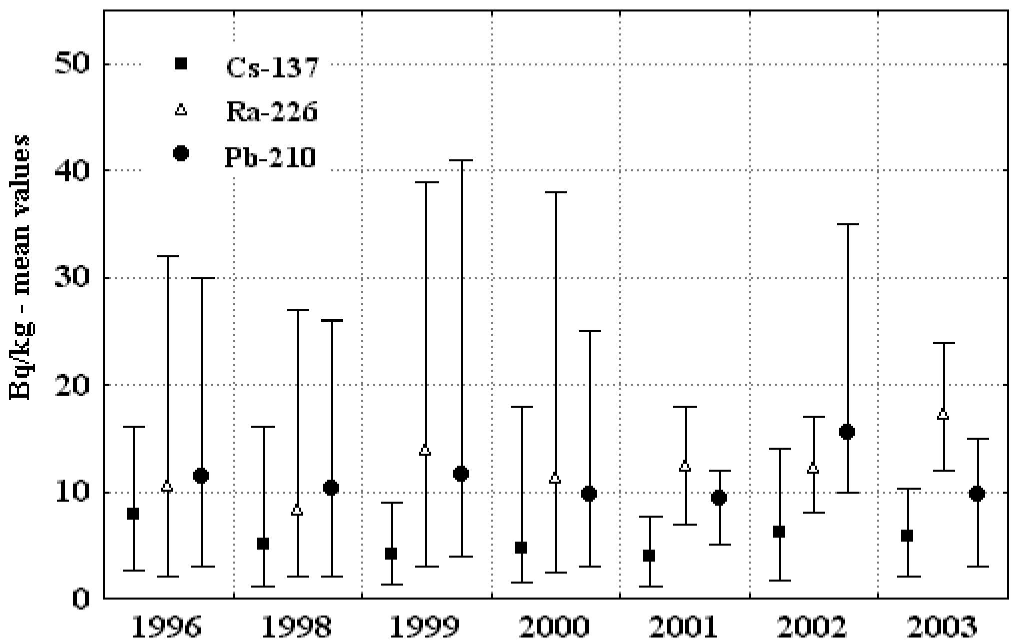

Fig. 5. Mean nuclide content in Black Sea macrophytes depending on sampling

The highest measured natural nuclide concentrations are determined in the green alga *Bryopsis plumosa* (Fig. 6), where the nuclide content differs with three orders of magnitude compared to the other algae species collected from the same site. This fact shows that *Bryopsis plumosa* seems to extract natural nuclides from the U series and Th (^{226}Ra, ^{228}Ac and ^{210}Pb) from the sea water up to the 1000 Bq/kg level. This phenomenon makes *Bryopsis plumiosa* an extremely interesting species to be studied for natural radionuclides at other sites at the Black Sea coast. Similar values for *Bryopsis plumiosa* are reported by [10] at the Romanian Black Sea Coast.

The data for macroalgae obtained by us are compared also with those obtained by Romanian and Turkish authors for radionuclides from the Black Sea region – [3, 15, 24, 25], Mediterranean Sea (Syrian – [2, 18] (Table 2, Fig. 2) and Tyrrhenian Sea (Italian – [8, 29] (Table 3 Fig. 3).

As can be seen from these data, the nuclide content in Bulgarian Black Sea ecosystems is in the range of those obtained for the Black Sea and the neighboring seas.

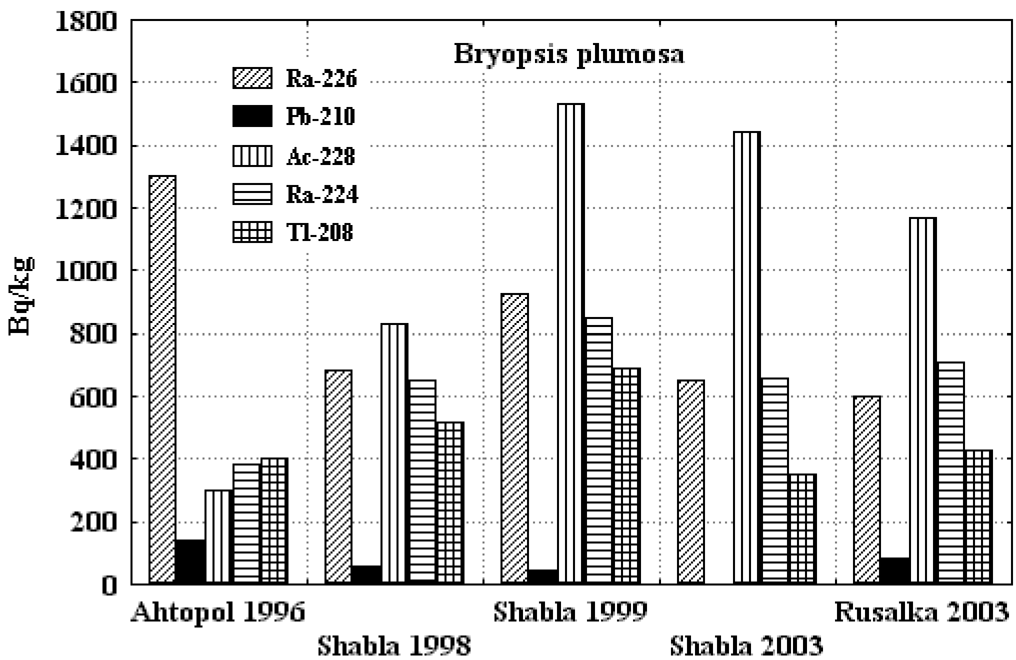

Fig. 6. Nuclide content in green alga *Br. Plumose*

Table 2. Comparison of data for macroalgae from the Black Sea region

Algae	^{137}Cs Bq/kg	^{40}K Bq/kg	^{210}Pb Bq/kg	^{226}Ra Bq/kg
Ceramium rubrum[2]	0.66	-	-	-
Cystoseira sp. [14]	15	900	-	-
Cladophora sp. [14]	n.d.	2170	-	-
Enteromorpha sp. [14]	5	1076	-	-
Chaetomorpha sp. [14]	11	2525	-	-
Ulva sp. [14]	6	930	-	-
Corallina sp. [14]	5	250	-	-
Ceramium rubrum[14]	12	880	-	-
Ulva lactuca [5]	< 3	-	-	-
Cystoseira barbata [5]	5.9	-	-	-
Ulva sp [25]	< 0.66	450	3.49	< 1.7
Cystoseira sp [25]	< 1.1	1600	15.8	<2.4
Ulva lactuca [2]	7.2	-	-	-
*Ulva sp.**	3.4	596	6	9.3
*Ceramium sp**	9.4	1343	13	17
*Cladophora sp. **	12	1300	8	12
*Enteromorpha sp. **	4.5	690	7	10
*Cystoseira sp.**	5.4	1400	12	11
*Chaetomorpha sp.**	2.3	1860	10	7
*Corallina sp. **	2.1	140	12	10
*Callithamnion sp **	4.4	1580	10	7

* this work

Table 3. Comparison between nuclide contents in algae from Black and Mediterranean Seas

Nuclide	Ulva rigida		***Cystoseira barbata***	
Bq/kg	**Mediterranean**[2]	**Black Sea**	**Mediterranean**[2]	**Black Sea**
^{137}**Cs**	< 0.66	3.4 ± 0.6	< 0.47	5.4 ± 0.5
^{210}**Pb**	13.93 ± 0.95	6 ± 1	4.89 ± 0.42	10 ± 2
^{226}**Ra**	< 1.7	9.3 ± 1.2	1.2 ± 0.2	13 ± 2

4. Conclusions

Radionuclide (^{137}Cs, ^{226}Ra and ^{210}Pb content) accumulation was studied in macroalgae from several geographic zones along the Bulgarian Black Sea coast during the period 1996 – 2003 and accumulation capacity of different algae species was determined. Analysis results confirm that macrophytes can be used as reliable indicators for marine environmental assessment.

The obtained results compare the radionuclide content in the three algae phyla – green, red and brown and the status of the marine environment in all studied areas is evaluated.

This paper fills the gap of radionuclide macroalgae data from almost the whole Bulgarian Black Sea coast and the data can be used as an important stage in realization of monitoring and control of marine ecosystem status.

The natural isotope concentrations are higher than the technogenic ones. The highest concentrations of natural nuclides are measured in the red alga *Ceramium rubrum*.

As a whole, the radionuclide content in all studied algae species is low except the green *Bryopsis plumosa,* where natural nuclides are with several orders of magnitude higher than in other algae at the same locations.

Comparison of the obtained data with those of neighboring countries – Romania, Turkey, Greece and obtained by other Mediterranean authors (e.g. Syrian) show that the results are in the range of those obtained for the Black Sea and the neighboring seas.

References

1. Al-Masri, M.S., Mamish, S., Budeir, Y., 2002. The impact of phosphate loading activities on near marine environment: the Syrian coast. Journal of Environmental Radioactivity 58, 35-44.
2. Al-Masri M S, Mamish S., Budier Y., 2003. Radionuclides and trace metals in eastern Mediterranean Sea algae, Journal of Environmental Radioactivity. 67: 157-168
3. Bologa A., Apa M., Cociasu A., Cuingoglu E. Patrascu V., Pecheanu I., Piescu V. Popa L., 1996. Present level of contaminants in the Romanian Black Sea sector, IAEA TecDoc 1094, 469- 475
4. Bryan, G.W., Langston, W.J., 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environ. Pollution 76, 89-131.

5. Calmet, S., Charmasson, G., Gontier, A., Meinesz, C.F., 1991. Chernobyl radionuclides in the Mediterranean seagrass *Posidonia oceanica.* Journal of Environmental Radioactivity 13, 157-173.

6. Carlson, L., Holm, E., 1992. Radioactivity in *Fucus vesiculosus* L from the Baltic Sea following the Chernobyl accident. Journal of Environmental Radioactivity 15, 231-248.

7. Christensen, G.C., Selnaes, T.D., 1999. Study of marine activity along the Norwegian coast, 1980-1984. In: International Atomic Energy Agency (Ed.), Marine Pollution, 49 (IAEA-TECDOC-1094, IAEA-SM-339).

8. Conti, M.E., 2002. SEAM Ed., Rome, II monitoraggio biologico della qualita ambientale. Rome, 181pp

9. Dahlgaard, H., Boelskifte, S., 1992. A model describing the accumulation and time-integration of radioactive discharges in the bioindicator *Fucus Vesiculosus.* Journal of Environmental Radioactivity 16, 49-63.

10. Dovlete C. and Osvath I. (1992) Radium and Its Daughters in Bryopsis plumosa *Radiation Protection Dosimetry*, **45** 301-302

11. Haritonidis, S., Malea, P., 1995. Seasonal and local variation of Cr, Ni and Co concentrations in *Ulva rigida C.* Agardh and *Enteromorpha linza* (Linnaeus) from Thermaikos Gulf, Greece. Environ. Pollut. 89, 319-327

12. Haritonidis, S., Malea, P., 1999. Bioaccumulation of metals by the green alga in *Ulva rigida* from Thermaikos Gulf, Greece. Environ. Pollut. 104, 365-372.

13. Horn, X., Yan, X., 1998. Study on the concentration and seasonal variation of inorganic elements in 35 species of marine algae. Science of Total Environment 222, 141-156.

14. Foster, P., 1976. Concentrations and concentration factors of heavy metals in brown algae. Environ. Pollut. 10, 45-53

15. Guven K.C., Topcuoglu S., Gungor N., 1993. Chernobyl radioactivity in Algae Collected from the Marmara and Black Sea. *Turkish J. Nucl. Sciences* 20: 21-30

16. Luoma, S.N., 1983. Bioavailability of trace metals to aquatic organisms a review. Sci. Total Environ. 28, 1-22

17. Nicholas, S.F., Kathryn, A., Burns, R.D., Cherry, M., 1983. Accumulation and cellular distribution of ^{214}Am, ^{2,0}Po, and ^{210}Pb in two marine algae. Marine Ecology 11, 233-237.

18. Othman, I., Yassine, T., Bhat, I., 1994. Measurements of some radionuclides in the marine coastal environment of Syria. The Science of Total Environment 53, 57-60.

19. Rainbow P., 1995. Biomonitoring of Heavy Metals Availability in the Marine Environment, Marine Pollution Bulletin, 31, 183 – 192.

20. Rissanen, K., Ikaheimonen, T.K., Matishov, D.G., Matishov, G.G., 1999. Radioactive cesium, cobalt, and plutonium in biota, algae, and sediment in the unrestricted areas of the Russian Arctic sea. In: International Atomic Energy Agency (Ed.), Marine Pollution, 12 (IAEA-TECDOC-1094, IAEA-SM-354).

21. Sartoni, G., De Biasi, A.M., Cryptogami, E., 1999. A survey of the marine algae of Milos Hand Greece. Algol 20, 271-383.

22. Strezov, A., Stoilova, T., Petkov, P., Hristoskova M., 1999. Technologic and natural radionuclides in Black Sea sediment and algae. In: International Atomic Energy Agency (Ed.), Marine Pollution, 29 (IAEA-TECDOC-1094, IAEA-SM-354).

23. Strezov, A., T. Nonova, 2005. Radionuclide Uptake in Red Macroalgae from the Bulgarian Black Sea Coast, J Rad. Nucl. Chem. 266: 411-417.

24. Topcuoglu S, Guven K., Kucukcezzar R., Kut D., Esen N. 1996. J Rad. Nucl. Chem. 214, 319 – 325.

25. Topcuoglu S, Kut D, Esen N, Gungor N. Olmez E. Kirbasoglu C., 2001. ^{137}Cs in biota and samples from Turkish coast of the Black Sea, 1997-1998 J Rad. Nucl. Chem. 250**:** 381-384

26. Volterra, L., Conti, M.E., 2000. Algae as biomarkers, bioaccumulators and toxin producers. In: Conti, M.E., Botre, F. (Eds.), The Control of Marine Pollution: Current Status and Future Trends; Int. J. Environ. Pollut. 13 (1-6), 92-125, Inderscience Enterprises Ltd., Milton Keynes, UK

Corresponding author: Alexander S. Strezov

Address: Bulgarian Academy of Sciences, Institute for Nuclear Research and Nuclear Energy, Sofia 1784, blvd. Tzarigradsko shosse № 72

Phone: (3592) 79795000395

Fax: (3592) 9753619

E-mail: strezov@inrne.bas.bg