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Radioactivity Levels in Ceramium rubrum collected from Eastern Black Sea Coast of Turkey

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Abstract

The Black Sea is a unique sea with its natural properties. In last decades, the Black Sea has suffered from the pollution that creates detrimental effects in its ecosystem. The some of the main pollutants in the Black Sea are the artificial radionuclides formed after the Chernobyl Nuclear Power Plant disaster (137Cs, 90Sr) and the radionuclides formed due to the human and natural activities (238U, 232Th, 40K). In many surveys, biomonitor organisms such as macroalgaes were used for the determination of radioactivity levels in The Black Sea. The aim of this study is to determine the activity levels of natural and artificial radionuclides in Ceramium rubrum (a species of red macroalgae) collected from five provinces and eighteen stations in Eastern Black Sea Coast of Turkey. The activity analyzes of samples were carried by using a HPGe gamma spectroscopic detector system and a Genie 2000 software programme. The maximum radioactivity levels of 238U, 232Th, 137Cs and 40K were measured as 23.8 Bq.kg-1, 36.1 Bq.kg-1, 4.8 Bq.kg-1 and 882 Bq.kg-1, respectively.

Keywords: radioactivity, macroalgae, *Ceramium*, radionuclide, gamma.

1. INTRODUCTION

The Black Sea is one of the most threatened inland sea of the world. It lies between Asia and Europe continents. It has 4869 km coastline. The Black Sea is bordered by six countries coast line lenght with 1700 km of Turkey, 414 km of Bulgaria, 322 km of Georgia, 256 km of Romania, 421 km of Russia and 1756 km of Ukraine (Stanchev et al., 2011).

There are rich natural beauties, high mountains, developed cities, towns, harbors and shores around the Black Sea but its marine environment is getting poorer each day because of increasing pollution (Begun et al., 2012). The Black Sea is not only polluted by the six bordered countries but also by seventeen countries in its catchment area. The big rivers that pass through these countries transport uncontrolled domestic, industrial and agricultural wastes to the Black Sea (Bat et al., 2018). Furthermore, It is well known that the Black Sea ecosystem has been seriously exposed to the radioactive pollution due to the Chernobyl nuclear power plant accident which occured on 26 April 1986 (Fabry et al., 1993).

After the CNPP accident a large amount of radionuclides (134Cs, 137Cs, 131I, 90Sr) released to the atmosphere and some of them reached the seas through rainfall, winds and streams (IAEA 2006; Yao et al., 2014). 137Cs is one of the most dangerous anthropogenic radionuclides due to its long physical and biological half-life, 30 years, (IAEA, 2005). In addition to the artificial radionuclides, natural radioactive nuclides which take place by the formation of the earth such as 238U, 232Th and 40K are found in the marine environments. Natural radioactivity levels in the seas may vary from region to region, earthquake activities and erosion of rocks (Malain et al., 2012; Amin et al., 2013).

Natural and artificial radionuclides may cause to exposure radiation to living organisms and human. According to the United Nations Scientific Committee on the Effects of Atomic Radiation, the average annual dose of people exposed to natural and artificial sources is approximately 3 mSv (UNSCEAR, 2008).

Macroalgae are resistant organisms that can store radionuclides in their bodies. They are used to determine the radioactive pollution level in the seas and to evaluate the radiation dose that people may be exposed to.

Ceramium rubrum is a red macroalgae allows to detect radioactive contamination in marine environments (Varlam and Patrascu, 2002). Besides, Ceramium rubrum is an important macroalgae where the agar is extracted which is utilised for the medicine, pharmaceutical and food industries (Serkedjieva, 2004; Sava et al., 2009).

The aim of this study is to determine the activity levels of natural and artificial radionuclides (238U, 232Th, 137Cs and 40K) in Ceramium rubrum (a species of red macroalgae) collected from five provinces and eighteen stations in Eastern Black Sea Coast of Turkey.

2. METHODS

In this study, *Ceramium rubrum* samples were collected from 18 stations in 5 provinces (Artvin, Rize, Trabzon, Giresun, Ordu) of Eastern Black Sea Region of Turkey. The samples were thoroughly washed in the sea water and removed from sand, gravel and other foreign materials. 100-300 g of each sample of *Ceramium rubrum* were weighed and dried in an oven at 80 °C for 12 hours. The dried samples were milled, passed through an 1mm sieve, placed in 100 ml plastic containers, and stored for one month for radioactive equilibrium. The samples were counted as 50.000 s for gamma spectrometric analysis. Gamma spectroscopic analysis of the samples were carried out with Genie2000 programme and HPGe detector (Ortec) system has a 55% counting efficiency and energy resolution of 1.9 keV at 1332 keV (Akçay, 2013).

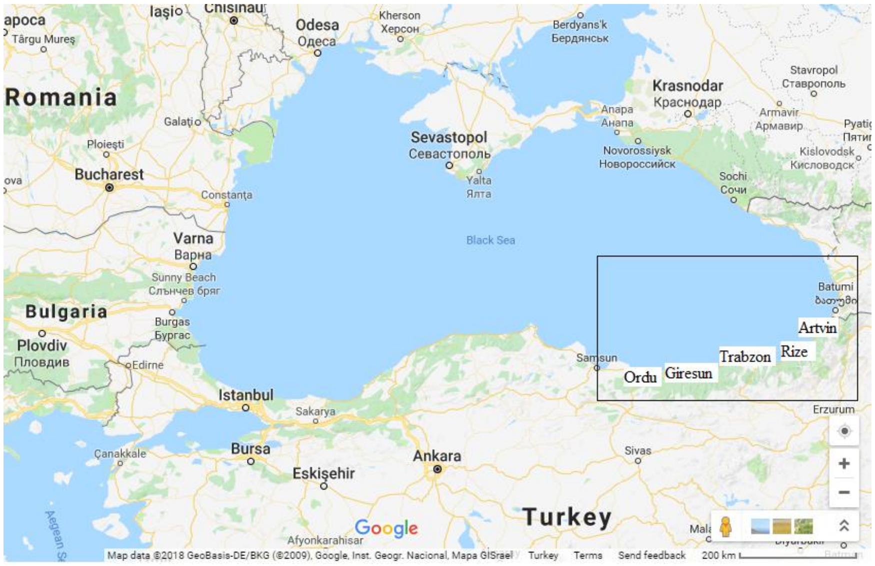

FIG. 1. Sampling area

To determine the activity of the ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radionuclides, the corresponding net area for each peak in the spectrum was taken into consideration. For the ^{238}U series the peaks at 295.2 keV (^{214}Pb), 352 keV (^{214}Pb) and 609.4 keV (^{214}Bi) and for the ^{232}Th series the peaks at 238.6 keV (^{212}Pb), 583.1 keV (^{208}Tl) and 911,1 (^{228}Ac) were used. ^{137}Cs and ^{40}K radionuclides were obtained by their main gamma line energies of 661.6 keV and 1460.7 keV (Akçay, 2013).

The radioactivity concentrations of ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K were calculated by Equation 1 where the net area under each peak: N, sample mass: m, counting time: t, efficiency of detector ε and gamma irradiation branching rate: % (Akçay, 2013).

$$A(\mathrm{Bq/kg}) = \frac{N}{m.t.\,\varepsilon.\%} \tag{1}$$

The minimum detection limit (mdl) of the detector measurement system for each radionuclide was obtained using Equation 2 (IAEA, 1989). Here, t: counting time, Y: abundance, m: mass and η: photopical output. The minimum detection limit (mdl) for ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K are calculated as follows: 2.9 Bq.kg^{-1}, 1.2 Bq.kg^{-1}, 0 Bq.kg^{-1} and 8.4 Bq.kg^{-1}, respectively.

$$\mathrm{mdl} = 4.66\sqrt{\mathrm{Background}}\,/t.Y.m.\eta \tag{2}$$

In order to compare the internal effective radiation dose of *Ceramium rubrum* samples with the limit values allowed by international organizations for foodstuffs, Equation 3 was used (ICRP, 1996). Here, i refers to a algae group, the coefficients U_i and C_r refer to the consumption rate (kg.y^{-1}) and activity concentration of the radionuclide r of interest (Bq.kg^{-1}), respectively, and $g_{T,r}$ is the dose conversion coefficient for the ingestion of radionuclide r (Sv.Bq^{-1}) in tissue T.

$$H_{T,r} = \sum (U_i C^r) g_{T,r} \tag{3}$$

3. RESULTS AND DISCUSSIONS

The sampling stations and ^{238}U, ^{232}Th, ^{137}Cs, ^{40}K radioactivity concentrations of *Ceramium rubrum* samples collected from five provinces and eighteen stations in Eastern Black Sea Coast of Turkey are given in Table I. According to the results, uranium and potassium activity were observed in all stations. The radioactivity of cesium and thorium was detected below the detection limit in some stations.

TABLE I. ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radioactivity concentrations of *Ceramium rubrum* samples (Bq.kg^{-1} dry weight) and their internal effective radiation dose (µSv.y^{-1})

Sample no	*Station*	^{238}U	^{232}Th	^{137}Cs	^{40}K	$H_{T,r}$
S1	Artvin (Arhavi)	12.5±2.1	36.1±6.5	3.55±0.9	320±17	8.15
S2	Rize (Fındıklı)	17.8±2.3	16.2±2.8	3.29±0.8	258±15	7.81
S3	Rize (Ardeşen)	<mdl	3.3±0.7	3.30±0.6	496±18	3.40
S4	Rize (Pazar)	14.1±1.9	13.9±2.4	4.09±0.9	664±29	9.17
S5	Rize (Çayeli)	23.8±4.3	13.5±2.8	3.87±0.7	882±24	13.23
S6	Rize (Merkez)	20.0±2.7	23.8±4.1	<mdl	110±10	8.00
S7	Rize (Çiftekavak)	12.9±1.4	9.4±1.6	2.62±0.6	348±17	6.51
S8	Rize (İyidere)	7.3±0.8	21.5±4.1	3.52±0.9	283±17	5.41
S9	Trabzon (Merkez)	12.8±2.4	26.1±4.9	4.01±1.1	200±18	6.77

S10	Trabzon (Akçaabat)	19.7±1.8	20.3±3.2	3.17±0.6	264±14	8.67
S11	Trabzon (Salacık)	5.8±0.7	15.7±2.9	3.84±0.7	290±15	4.62
S12	Trabzon (Mersin)	3.7±0.6	12.5±2.1	4.12±0.6	356±13	4.22
S13	Trabzon (Gülbahçe)	3.3±0.2	9.6±1.8	2.64±0.7	149±9	2.58
S14	Trabzon (Çarşıbaşı)	19.5±2.8	13.5±2.5	3.30±0.9	182±14	7.62
S15	Giresun (Eynesil)	22.5±2.7	23.1±4.1	<mdl	229±18	9.40
S16	Giresun (Çavuşlu)	11.1±1.2	12.4±1.9	4.80±0.9	235±12	5.54
S17	Ordu (Perşembe)	5.7±1.1	<mdl	<mdl	30±3	1.78
S18	Ordu (Fatsa)	7.8±1.2	5.0±0,9	3.01±0,7	252±13	4.16

mdl is the minimum detection limit.

Table II summarizes that minimum, maximum and mean values of the ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radioactivity concentrations of *Ceramium rubrum* samples. Taking into account Table I and Table II, ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K was detected between <mdl-23,8 Bq.kg^{-1}, <mdl-36,1 Bq.kg^{-1}, <mdl-4,8 Bq.kg^{-1} and 30-882 Bq.kg^{-1} respectively. The highest ^{238}U and ^{40}K radioactivity were found at the Rize (Çayeli) station. The highest ^{232}Th and ^{137}Cs radioactivity were observed in Artvin (Arhavi) and Giresun (Çavuşlu) station, respectively.

TABLE II. The minimum, maximum and mean values of the ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radioactivity concentrations of *Ceramium rubrum* samples (Bq.kg^{-1} dry weight)

Province	*Sample Size*		*^{238}U*	*^{232}Th*	*^{137}Cs*	*^{40}K*
		min	-	-	-	-
Artvin	1	max	-	-	-	-
		average	12.5	36.1	3.5	320
		min	<mdl	3.3	<mdl	110
Rize	7	max	23.8	23.8	4.0	882
		average	13.7	14.5	2.9	434
		min	3.3	9.6	2.6	148
Trabzon	6	max	19.7	26.0	4.1	356
		average	10.8	16.3	3.5	240
		min	11.1	12.4	<mdl	229
Giresun	2	max	22.5	23.1	4.8	235
		average	16.8	17.8	2.4	232
		min	5.7	<mdl	<mdl	30
Ordu	2	max	7.8	5.0	3.0	252
		average	6.7	2.5	1.5	141
		min	<mdl	<mdl	<mdl	30
Total	18	max	23.8	36.1	4.8	882
		average	13.0	16.2	3.5	300

mdl is the minimum detection limit.

Table III shows the comparison of the levels of ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radioactivity values detected in *Ceramium rubrum* samples in this study and other studies. According to datas the ^{238}U radioactivity obtained in this study is lower than that Varinlioğlu et al. (1997) found in and the ^{232}Th value is higher than Varinlioğlu et al. (1997) reported. The value of ^{137}Cs radioactivity obtained in this study was found to be higher in the studies of Varinlioğlu et al. (1997), Goddard and Jupp (2002) and Zalewska and Saniewski (2011) as compared to the values found lower in the studies of Nonova and Strezov (2005), Sawidis et al. (2003), Snoeijs and Notter (1993) and Güven et al. (1993). This level is below the permissible limit of 1000 Bq.kg^{-1} (ICRP, 2004) for foodstuffs. ^{40}K radioactivity was found to be higher than Varinlioğlu et al. (1997) reported and lower than observed in the other studies.

TABLE III. Comparison of ^{238}U, ^{232}Th, ^{137}Cs and ^{40}K radioactivity in *Ceramium rubrum* samples with various studies (Bq.kg^{-1})

Province	^{238}U	^{232}Th	^{137}Cs	^{40}K
Nonova and Strezov, 2005 (Bulgaria)	39	-	14,6	2100
Sawidis et al., 2003 (Greece)	-	-	300.3	-
Zalewska and Saniewski, 2011 (Poland)	-	-	<mdl	-
Snoeijs and Notter, 1993 (Sweden)	-	-	115	1739
Goddard and Jupp, 2002 (United Arab Emirates)	-	-	<0.6	1700
Güven et al., 1993 (Turkey, Sinop)	-	-	12	906
Varinlioğlu et al., 1997 (Turkey, İskenderun)	13	10	<mdl	550
Present study	23.8	36.1	4.8	882
ICRP, 2004	-	-	1000	-

mdl is the minimum detection limit.

4. CONCLUSIONS

In this study, the levels of 238U, 232Th, 137Cs and 40K radioactivity were determined in the Ceramium rubrum samples collected from 18 stations and five provinces in Eastern Black Sea Coast of Turkey. The highest 238U, 232Th, 137Cs and 40K radioactivity levels were found 23.8 Bq.kg-1, 361 Bq.kg-1, 4.8 Bq.kg-1 and 882 Bq.kg-1, respectively. This study indicates that Ceramium rubrum is a good bioindicator for the determination of natural and artificial radionuclide levels in the seas and these values are comparable with the values obtained by other studies. The mean 137Cs radioactivity level in present study is below the permissible limit of ICRP (1000 Bqkg) for foodstuffs. At the same time, as the highest calculated internal effective radiation dose value (13.23 µSv.y-1) was found to be significantly lower than the average annual dose of people exposed to natural and artificial sources, 3 mSv.y-1, (UNSCEAR, 2008). For this reasons, it can be said that the radioactivity levels of Ceramium rubrum samples in this study is no risk for the human.

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REFERENCES

[1] Akçay, N., Determination of radioactivity levels for sea water, sediment and some macroalgae in Black Sea coast, Doctorate Thesis, Karadeniz Technical University, Graduate School of Sciences, Trabzon, 2013.

[2] Amin, Y.M., Mahat, R.H., Nor, R.M., Khandaker, M.U., Takleef, G.H., Bradley, D.A., “The presence of natural radioactivity and ^{137}Cs in the South China Sea bordering peninsular Malaysia”, Radiation Protection Dosimetry, 156, 4, 475-480 (2013).

[3] Bat, L., Öztekin, A., Şahin, F., Arıcı, E., Özsandıkçı, U., “An overview of the Black Sea pollution in Turkey”, MedFAR, 1, 2, 67-86 (2018).

[4] Begun T., Muresan M., Zaharia T., Dencheva K., Sezgin M., Bat L., Velikova V., 2012. Conservation and Protection of the Black Sea Biodiversity. Review of the existing and planned protected areas in the Black Sea (Bulgaria, Romania, Turkey) with a special focus on possible deficiencies regarding law enforcement and implementation of management plans. EC DG Env. MISIS Project Deliverables.

[5] Fabry, V., Osvath, I., & Froehlich, K., "Environmental pollution of the Black Sea: A search for answers". IAEA Bulletin, 35, 2, 20-24 (1993).

[6] Goddard, C.C & Jupp, B., “The radionuclide content of seaweeds and seagrasses around the Coast of Oman and the United Arab Emirates”, Marine Pollution Bulletin, 42, 1411-1416 (2002).

[7] Guven, K.C., Topcuoglu, S., & Gungor, N., “Chernobyl radioactivity in algae collected from the Marmara and Black Sea”. Turkish Journal of Nuclear Sciences, 21-31 (1993).

[8] International Commission of Radiation Protection (2004), Protecting people against radiation exposure in the aftermath of a radiological attack. Final TG draft. ICRP, Ottawa.

[9] International Commission on Radiological Protection (1996), Age-depended doses to members of the public from intake of radionuclides: Part 5 Compilations of ingestion and Inhalation dose coefficient. Publication 72, ICRP, Ottawa.

[10] IAEA, 1989, Measurement of Radionuclides in Food and Environment, TRS, No. 295.

[11] IAEA, 2005, Worldwide marine radioactivity studies (WOMARS). Radionuclide levels in oceans and seas. International Atomic Energy Agency, Vienna.

[12] International Atomic Energy Agency (IAEA), 2006. Environmental Consequences of the Chernobyl Accident and their Remediation: Twenty Years of Experience.

[13] Malain, D., Regan, P. H., Bradley, D. A., Matthews,M., Al-Sulaiti, H. A. and Santawamaitre, T., “An evaluation of the natural radioactivity in Andaman beachsand samples of Thailand after the 2004 tsunami”, Appl. Radiat. Isot. 70, 1467-1474 (2012).

[14] Nonova, T & Strezov, A., “Radionuclide uptake in red macroalgae from Bulgarian Black Sea Coast”, Journal of Radioanalytical and Nuclear Chemistry, 266, 3 411-417 (2005).

[15] Sava, D., Rotaru-Stăncic, M., Doroftei, E., Arcuş, M., “Pharmaceutical importance of some multicellular red algae species from the Romanian Black Sea Shore”, Annals of RSCB, 14, 2, 297-300 (2009).

[16] Sawidis, T., Heinrich, G., Brown, M.T., “Cesium-137 concentrations in marine macroalgae from different biotopes in the Aegean Sea (Greece)”, Ecotoxicology and Environmental Safety, 54, 249-254 (2003).

[17] Serkedjieva, J., “Antiviral activity of the red marine alga *Ceramium rubrum*” Phytotherapy Research, 18, 6, 480-483 (2004).

[18] Snoeijs, P., & Notter, M. (1993). Radiocaesium from Chernobyl in benthic algae along the Swedish Baltic Sea coast (SLU-REK-R--72).

[19] Stanchev, H., Palazov, A., Stancheva, M., Apostolov, A., “Determination of the Black Sea area and coastline length using GIS methods and Landsat 7 satellite images”, Geo-Eco-Marina, 17, 27-31 (2011).

[20] UNSCEAR, United Nations Scientific Committee on the Effects of Atomic Radiation, Sources and Effects of Ionizing Radiation, Volume I (Sources) Report to the General Assembly, Scientific Annexes A and B, 2008.

[21] Varinlioğlu, A., Küçükcezzar, R., Köse, A.,“Radioecological measurements in the algae from İskenderun Bay”, Toxicological & Environmental Chemistry, 64, 1-4, 75-79 (1997).

[22] Varlam, C., Patrascu, V., “^{3}H and ^{137}Cs in marine components from the coastal Black Sea area”, Journal of Environmental Protection and Ecology, 3, 2, 474-482 (2002).

[23] Yao, Y., Volchek, K., Lambert, P., Brown, Carl., Semmler, J., Guindon, A., Dumouchel, T., Mahilrajan, T., McCall, M. (2014). Environmental impacts of the Fukushima and Chernobyl accidents and their remediation: A review. Proceedings of the 37th AMOP Technical Seminar on Environmental Contamination and Response. 145-174.

[24] Zalewska,T., Saniewski,M.,“Bioaccumulation of ^{137}Cs by benthic plants and macroinvertebrates”, Oceanological and Hydrobiological Studies, 40, 3, 1-8 (2011).