

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.

For more information visit [www.intechopen.com](http://www.intechopen.com)



# Sustainable Environment – Monitoring of Radionuclide and Heavy Metal Accumulation in Sediments, Algae and Biota in Black Sea Marine Ecosystems

Alexander Strezov  
*Institute for Nuclear Research & Nuclear Energy  
Bulgaria*

## 1. Introduction

The implementation of advanced methods and technology in the field of marine ecosystems studies is important to assess the impact of pollutants on marine ecosystems and biodiversity and biota interactions, including reliable study of radionuclide and heavy metal content in soils, sediments and algae. Creation of data bases for long term environmental management of pollution; evaluation of ecological impact of human activities and management of sustainable environment – coastal zone and continental shelf, including assessment and forecasting techniques, is needed to understand the impacts of various activities on ecosystems, to contribute to protect the ecosystems from pollution and to develop long-term models for management of the coastal zone.

Improved knowledge of marine processes, ecosystems and interactions will facilitate the basis of new ecological status, the sustainable use of the marine environment and resources, while fully respecting ecosystem integrity and functioning, and to promote the development of new, integrated management concepts.

That is why the determining of variations of ecosystem functioning; concepts for a safe and environmentally responsible use of the seafloor and sub-seafloor resources; management models of transport pathways and impacts of pollutants, key elements and nutrients in marine environments is the main task of modern marine radioecology.

Another target is to develop a predictive capability for variations in ecosystem functioning and structure for better assessment of naturally occurring mechanisms of ecosystem behaviour. Research activities will address the effects of environmental factors and interactions at sea boundaries and interfaces in relation to ecosystem functioning and alteration, distinguish natural from anthropogenic variability, assess the role of extreme environments and their communities. The obtained results will facilitate the assessment of sedimentary systems for the sustainable management and use of the sea shelf.

Transport pathways and impacts of pollutants, key elements and nutrients in the marine environment will support the implementation and further development promote the

advancement of relevant conventions for the reduction of nutrient and pollutant loads of the sea. Research activities should address the transport, cycling, coupling and accumulation of nuclide and heavy metal pollutants. The impact of pollutants should be addressed, their uptake by organisms, their ecotoxicological effects and the synergistic effects of multiple pollutants upon the marine ecosystems.

Another important task is the reducing the anthropogenic impact on biodiversity and the sustainable functioning of marine ecosystems, facilitating the development of safe, economic and sustainable exploitation technologies requiring safe and economic (yet sustainable) exploitation of marine resources by improving the scientific basis of sustainability.

Complex monitoring of Global changes and marine ecosystems for modelling and adequate management for sustainable environment have to include the foremost requirement to better characterise, observe and monitor the marine environment.

The objective is to stimulate "clean" technological developments for oceanic environments, to develop integrated coastal management concepts, including cost-benefit assessments, to alleviate pollution, flooding and erosion, in particular of fragile coastlines, and to ensure sustainable resource utilisation. Anticipated deliverables are integrated management tools and concepts for the coastal zone ecosystem; long-term predictions of coastal zone changes; reliable, economic and environmentally compatible coastal protection measures against flooding and erosion; effective monitoring in coastal, shelf and slope areas.

Emphasis should be put on efficiency, speed, reliability, environmental friendliness and safety. In parallel, attention will be given to the improvement of sample collection and handling (including samples from sea drilling), the exploitation of distributed sample collections, and inter-calibration exercises, networking and joint experiments. Special attention will be given to the problems of coastal inlets (tidal basins, estuaries, lagoons, arias, brachial zones).

## 2. Radionuclides in the marine environment

Since 1945 there has been a continuous release of technogenic radionuclides to the environment, leading to their accumulation in the seas and oceans, the main source of contamination being nuclear weapons tests in the atmosphere, on land and in water. The Danube was the main contributor for nuclides in the Black Sea region before 1986 (mainly  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ ) (Polikarpov 1966; Kulebakina et al., 1984; Sokolova et al., 1971), while the Dnyepyr took second place.

After the Chernobyl accident a considerable increase occurred in nuclides quantity in the environment (Buessler K., 1987; Kulebakina et al, 1988, 1989; Baumann, et al, 1989; Broberg 1989; Hadderingh et al, 1989). The Black Sea being near to the reactor accepted great quantity direct atmospheric radionuclide fallout. Additionally Chernobyl nuclides entered and continued to enter the environment carried by the big rivers - Dnyepyr, Dnester, Danube.

A major part of the distribution and migration of long lived nuclide contaminants (mainly  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ) are not only the hydrophysical processes but also the biosedimentation and sorption on bottom sediments and concentration by biota. It is known that  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  fallout before 1986 are found in sea water mainly in soluble forms (Shvedov et al., 1962), and are weakly affected by biological migration (contrary to other nuclides as  $^{141}\text{Ce}$ ,  $^{144}\text{Ce}$ ,  $^{103}\text{Ru}$ ,

$^{95}\text{Zr}$  etc.). Chernobyl radionuclides are characterized by a higher content of nonsoluble forms (even “hot” particles) which are part of the reactor fuel. These peculiarities affect the behavior of the Chernobyl nuclides in sediments and their accumulation in biota. The contamination of sea bed sediments by  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  had a “spot” character which was due to the way Cs entered the environment at the beginning - mainly airborne on different particles.

Cesium penetrated rather quickly the water depths - in 1987 Cs was measured up to 120 m, while in 1988 it reached 200 - 250 m. The observed phenomenon of “self decontamination” of Black Sea waters was due to the radioactivity spots dilution and secondly to interaction of dissolved Cs with the bottom sediments (Polikarpov 1987, 1988, Kulebakina 1988, 1989).

The natural nuclides members of uranium 238 and thorium 232 also enter the environment by several pathways and are also accumulated in biota.

So it is necessary to assess scientifically the impacts of discharges on humans and to identify the most important critical 'pathways' or 'groups' and the risks involved also attempt to consider multiple exposure routes. It can indeed be argued that radioactive pollution control is more successful in producing a mature methodology which is unifying in respect of all radioactive substances and there are only a few cases where conventional pollutants are successfully ranked against each other - such as in considering their relative importance as 'greenhouse' gases or the relative toxicity of certain similar organic compounds. However, in conventional pollution control, one further step is taken after risk assessment, one which is absent from radioactive pollution control - namely, the information generated in the earlier stages is used to produce 'environmental quality standards' against which absolute concentrations, trends and the effectiveness of pollution control at source can be clearly measured. Thus, if instead of considering, e.g. plutonium or technetium in units of 'concentration', we consider them as contributors to the overall 'dose', we cease to treat them as 'substances' in their own right and simultaneously regard the world as a 'brown-field site' already 'contaminated'. However, ecological toxicology (ecotoxicology) is required for predicting real world effects and for site-specific assessments. Ecotoxicology and ecology have shown similar developmental patterns over time; closer cooperation between ecologists and toxicologists would benefit both disciplines. Ecology can be incorporated into toxicology either extrinsically (separately, e.g., providing information on pre-selected test species) or intrinsically (e.g., as part of test species selection) - the latter is preferable. General guidelines for acute and chronic testing and criteria for species selection differ for ecotoxicology and environmental toxicology, and are outlined. An overall framework is proposed based on ecological risk assessment, for combining ecology and toxicology (environmental and ecological) for decision-making.

### **3. The Black Sea marine ecosystem**

The pollution of marine ecosystems by nuclides and heavy metals has been a world-wide problem in the last decades. The Black Sea ecosystem and ecological status has been damaged mainly as a result of chemical pollution. Much of the pollutants come from major rivers and from smaller sources in all Black Sea coastal countries. The Black Sea water column is heavily impacted by a great number of pollutants originating from different sources of direct and indirect discharge of land based sources - sewage, fallout etc. from economies of coastal states.

The Black sea is a half-enclosed sea, with 40°27'N-46°32'N latitude and 27°27'E- 41°42'E longitude. Together with Azov Sea, it covers an area of 462000 km<sup>2</sup>. Its east to west dimension is 1150 km and from north to south is 610 km. In the Black sea main basin, the depth of water approaches 2200 m, and the western shelf zone is comparatively shallow. The Black sea is surrounded by six countries and is linked with the Mediterranean sea through the Bosphorus, and the Azov Sea to the north.

The Black Sea has experienced the worst environmental degradation of all of the world's oceans. The situation has become so severe that it has affected the health, well being, and standard of living of the people in the immediate area. Most of the six coastal countries - Bulgaria, Georgia, Romania, Russia, Turkey, and Ukraine - have unstable or collapsed economies. The Black Sea's area is 431,200 km<sup>2</sup>. About 160 million people live in the Black Sea catchment basin, including 80 million only in the Danube River basin. Although international agreements, strategic plans, and national environmental programs are in place, the severe economical problems have significantly slowed environmental monitoring, remediation, and restoration efforts. The environmental crisis and subsequent dramatic changes in the Black Sea's ecosystem and resources are a direct effect of both natural and anthropogenic causes: an enormous increase in the nutrient and pollutant load from three major rivers, the Danube, Dnyestr, and Dnyep; from industrial and municipal wastewater pollution sources along the coast; and from dumping on the open sea. The coastal industries discharge wastes directly into the sea with little or no treatment. The countries of the Black sea basin do their efforts to protect the nature of the sea by formulating international rules for the cleaning of water areas from oil and wastes. Nuclides and heavy metals in the marine environment constitute a potential risk to the flora and fauna species, including humans through food chains. Furthermore, there is increasing evidence that presence of nuclides and heavy metals is linked to the exacerbation of some microbial diseases in aquatic organisms. At sufficiently high concentrations, heavy metals are toxic to the organism, and so, it is important their concentrations to be monitored especially when increased above the normal levels in the environment before the effects on marine organisms. Nuclides and heavy metals are the most harmful elemental pollutants and are of particular concern because of their toxicities to humans. They include both essential elements like iron and toxic metals like cadmium and mercury. Most of them show significant affinity to sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. Cadmium, copper, lead and mercury ions bind to the cell membranes hindering the transport processes through the cell wall. Some of the metalloids, elements on the borderline between metals and nonmetals, are significant water pollutants (Manahan, 1999).

The concentrations of rivers pollutants (domestic and industrial discharges) provide useful information about the sources that have the potential to lead to local pollution problems along the Black sea coast. The shallow, biologically productive layer of the Black sea receives water from a waste drainage basin of about 17 countries. Pollutants, transported by the rivers, constitute the main source of pollution in the Black sea.

According to Zaitzev, (1992), the estimation of land based sources, the sea annually receives big amounts of mineral nitrogen, mineral and organic phosphorus, as well oil and oil products, detergents, zinc, lead, mercury, copper, arsenic, chromium.

Aquatic organisms, especially macroalgae, are widely used as bioindicators for the study of marine contamination by radionuclides and heavy metals. Some species tolerate high



levels of pollutants and can successfully be used to obtain reliable information of marine ecological status.

#### 4. Radionuclides in Black Sea marine ecosystems

Radionuclides are a part of anthropogenic pollutants in the Black sea marine ecosystems. Massive amounts of industrial effluents are transported by the big rivers that enter the Black sea (Danube, Dnyeper, Dnester etc). The change in the radiation situation in the Black Sea after the Chernobyl accident stimulated multiple studies of radionuclide accumulation processes in biota as the Black sea received a great amount of radionuclides, due to its geographical position. The complex analysis of pollutants is a major task for modern ecology in obtaining reliable information about the type and quantities of substances entering the marine environment. The analysis of environmental matrixes, such as water/sediments/algae, provides a picture of the total contaminant load in a given ecosystem.

The contamination of Black sea littoral zone is a powerful factor affecting the phytobentos dynamics. The technogenic and natural nuclide releases due to human activities in the marine ecosystems lead to a change in contaminant content and may affect the composition of species in the marine environment (Bologa et al 1996, Guven et al. 1993). The complex analysis of pollutant concentrations in the marine environment gives reliable information for the types and quantities of contaminants that enter the hydrosphere. The change in the radiation situation of the Black sea after the Chernobyl accident was the reason for multiple studies on radionuclide accumulation processes in biota. The Black sea received a great amount of radionuclide impact due to its geographical position as the closest marine basin to the accident site. The technogenic radionuclides got into the marine ecosystems through atmospheric fallout and through the big rivers Danube, Dnieper and Dnester that enter the northwest Black sea corner. For this reason, the level of anthropogenic nuclides should be monitored to evaluate the radioactivity transfer along the trophic chain and assess the radiation risk for biota in the marine ecosystem.

Since 1945 there has been a continuous release of technogenic radionuclides to the environment started, leading to their accumulation in the seas and oceans, the main source of contamination being nuclear weapons tests in the atmosphere, on land and in water. The Bulgarian Black Sea coast received a great amount of radionuclide impact during nuclear tests in 1960ies and after 1986 being close to Chernobyl NPP, a considerable direct atmospheric radionuclide fallout occurred in the environment. Additionally, Chernobyl nuclides entered the marine environment mostly in the northwest corner of the Black Sea carried by the big rivers - Dnyepyr, Dnester, Danube (Keondjan et al., 1990) plus pollutant emissions carried by the local rivers (Tuncer, *et al.*, 1998).

Marine sediments are widely used for environmental control because of their ability to accumulate various pollutants. Macroalgae are another important medium for nuclide accumulation in marine ecosystems. Radionuclides affect the living organisms both as heavy metals and by their radiation. They participate in radionuclide and heavy metal transfer to the biosphere and man as elements of the food chain of marine biota. Many authors have investigated migration of radionuclides as well as biological effects of ionizing radiation in the Black sea environment.

A monitoring program for measuring technogenic and natural radionuclides in marine environmental samples from the Bulgarian Black sea coast has been utilized since 1991.

The radionuclide content dependency of on the season, location, type of sediment and type of algae and the comparison of radionuclide content in bottom sediments and algae from one and the same sampling location gives information for the mechanisms of radionuclide transfer from the sediments to biota as well as the trend of the potential hazard for the marine ecosystems.

## 5. Radionuclides in the Black Sea sediments

A major part of the distribution and migration of long lived nuclide contaminants (mainly  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ) are not only the hydrophysical processes but also the biosedimentation and sorption on bottom sediments and concentration by biota. It is known that  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  fallout are found in sea water mainly in soluble forms and are weakly affected by biological migration (contrary to other nuclides as  $^{141}\text{Ce}$ ,  $^{144}\text{Ce}$ ,  $^{103}\text{Ru}$ ,  $^{95}\text{Zr}$  etc.). Chernobyl radionuclides are characterised by a higher content of nonsoluble forms (even "hot" particles) which are part of the reactor fuel. These peculiarities affect the behaviour of the Chernobyl nuclides in sediments and in their accumulation in biota. The contamination of sea bed sediments by  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  had a "spot" character which was due to the way Cs entered the environment at the beginning - mainly airborne on different particles.

Caesium penetrated rather quickly the water depths - in 1987 Cs was measured up to 120 m, while in 1988 it reached 200 - 250 m. The observed phenomenon of "self decontamination" of Black Sea waters was due to the radioactivity spots dilution and secondly to interaction of dissolved Cs with the bottom sediments (Polikarpov et al 1987, Kulebakina et al 1988, 1989).

The association of radionuclides with sediments in coastal and estuary areas makes the sediments a large reservoir for radionuclides affecting significantly specific marine ecosystems. As the sea water is constantly in contact with organic and inorganic matter from sea bed sediments, the first necessary step in the estimation of radionuclide migration is the measurement of radionuclide content in sea bed sediments (as a first stage in food chain towards man) and set up a data base for radioisotope content in the Black Sea.

The measurement of technogenic and natural radionuclides in sea bed sediments was carried out in each season of every year after 1991 - spring, summer and autumn, because in this way the estimation of concentration variations of the contaminants, their accumulation and influence on marine ecosystems can be followed. The intercomparison between the data for the technogenic and natural radionuclides gives the whole picture of isotope impact at a chosen reference point.

Many authors - Russian and Ukrainian scientists, (Polikarpov, Kulebakina et al., 1988, 1989), Turkish - Topcuoglu 2001, Guven 2002, Bulgarian (Strezov 1996, 1998; Romanian - Bologa, Patrascu 1996) have performed measurements in the Black Sea.

The impact of Chernobyl on marine ecosystems was intensively studied and much data were published in recent years. Many authors investigated the distribution of Chernobyl radionuclides and their accumulation in lake sediments as well as in sea bed sediments.

The coast of Bulgaria, extending 270 km is mainly soft sedimentary limestone or sandstone, overlaid in many areas with beach or wind-blown sand. In the north, suspended material from the Danube delta has settled, carrying a lot of intertidal mud. The association of

radionuclides with sediments in coastal and estuary areas makes sediments a large reservoir for radionuclides affecting significantly specific marine ecosystems. As the seawater is constantly in contact with organic and inorganic matter from sea shelf, the first necessary step in the estimation of radionuclide migration is the measurement of radionuclide content in sea bed sediments and setting up a radioecological data base. Receiving relevant information for radionuclide concentrations in coastal waters and sediments is an important stage in realization of monitoring and control of marine ecosystems at the coast (Fig 1).

The main method for measuring the nuclei content in sediments and algae was the high resolution gamma spectroscopy performed on large high purity Ge semiconductor detectors with nuclear electronic tracts using sophisticated software.

The upper layer of sediments was collected from approximately 1 m<sup>2</sup> of the bottom acquiring about 2-3 kg of solid phase plus several litres of aqueous phase. The depth of the sample layer was maximal 3 cm to evaluate radionuclide content on the surface of the sea bed. In this way the potential seasonal variations could be estimated. The sample collection was performed by experienced scuba divers who carefully selected the sample site to avoid or minimize the differences of samples in particle size, depth and distance from shore, so that the comparison of the sea bed samples of different seasons could be done with greater level of confidence, reliability and accuracy.

Samples were also collected and data obtained for the main Black Sea resorts - Albena, Golden sands, Sunny Beach etc. as well as for some of the main cities along the Bulgarian Black Sea coast. These data were compared with samples taken from definitely clean areas. The contribution of the inflowing rivers for radioisotope content in the Black Sea was also studied sampling river's estuaries and comparing them with the inland sections of the same rivers. So the influence of the river on the adjacent area was compared with that of the sea.

The obtained results (Fig. 2) for Black Sea sediment samples show that radionuclide concentrations strongly depend on the nature of the sea bed sediments, because the data obtained for sand sediments are within a close range while those for silt and slime ones are higher and vary to a much greater extent.

The beach matrix from the near shore sediments at these locations is mainly sand and <sup>137</sup>Cs data are within a close range: Sunny Beach - 3.2 - 5.6 Bq/kg, Golden Sands - 1.8 - 6.9 Bq/kg, Albena - 3.4 - 7.3 Bq/kg, Tulenovo 4.0-7.1 Bq/kg, Kamen Briag - 4.4-6.6 Bq/kg, Balchik - 4.6 - 7.8 Bq/kg, Primorsko 4.0 - 5.6 Bq/kg, Sinemoretz - 3.6 - 7.8 Bq/kg. It should be noted that all sand sediment data fall within 8 Bq/kg level except Albena, Golden sands, Ravda, Burgas and Sozopol where nuclide content is higher.

The highest measured cesium content (Fig. 3) on the Bulgarian Black Sea coast is at the north locations with slime sediments - Kaliakra (mean 89 Bq/kg), Kavarna (mean 30 Bq/kg) and central Ravda2 (mean 65 Bq/kg). This fact can be attributed to the influence of the big rivers Danube, Dnyepr, Dnester, entering the northwest part of the Black Sea.

The increase in <sup>137</sup>Cs concentration in slime sediments and sorption on fine particles leads to caesium scavenging and occurrence at greater depths, which is due to physico-chemical interaction processes of the soluble Cs forms with the surrounding media. In sand and sandy sediments Cs content does not change greatly while the process of <sup>137</sup>Cs accumulation



is observed in slime and silt sediments. Due to such a process, sea bottom sediments play a major role in radionuclide redistribution between different components in the ecosystems, which change the concentration of  $^{137}\text{Cs}$  in the water as it is accumulated more in the sediments.

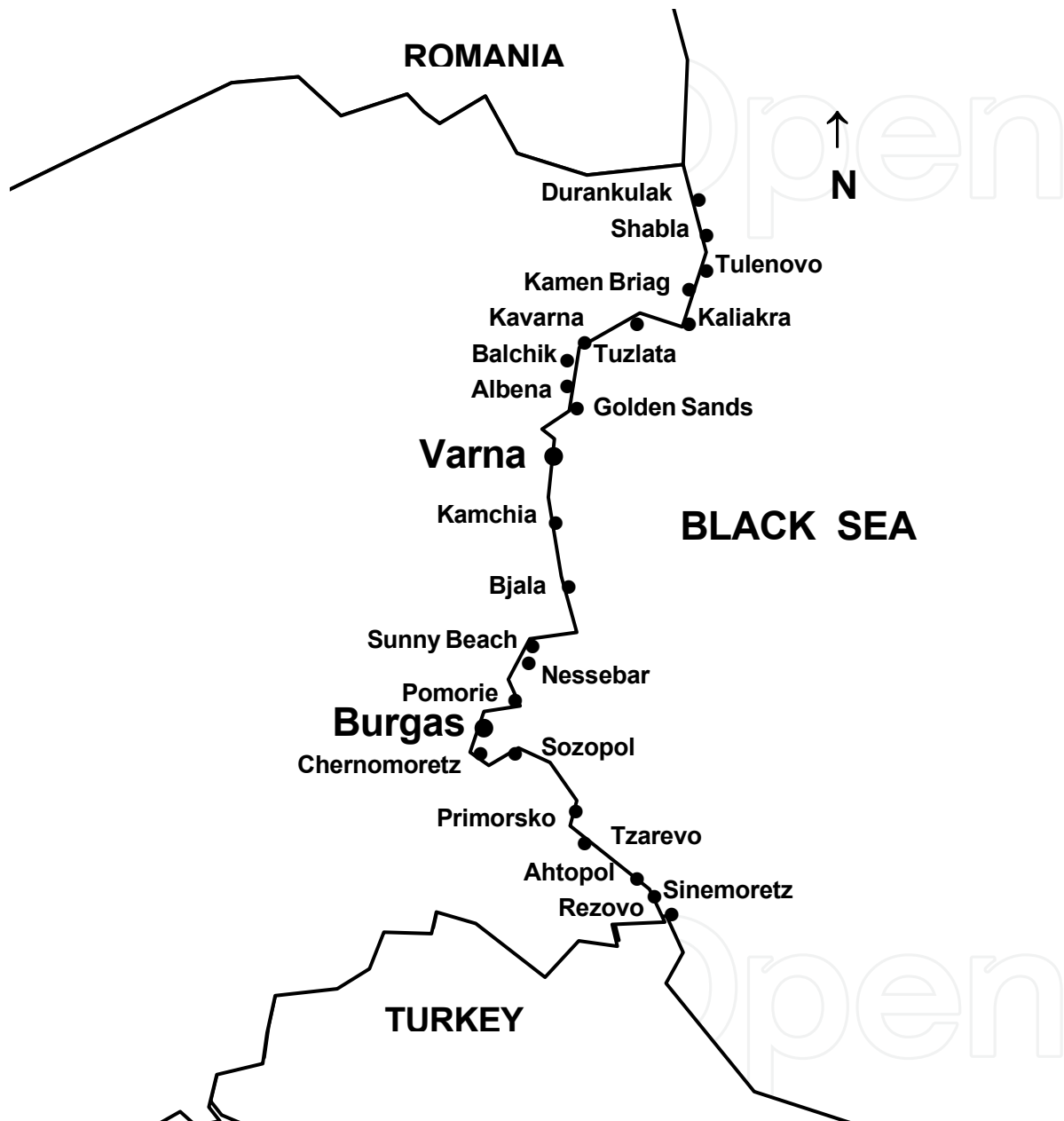
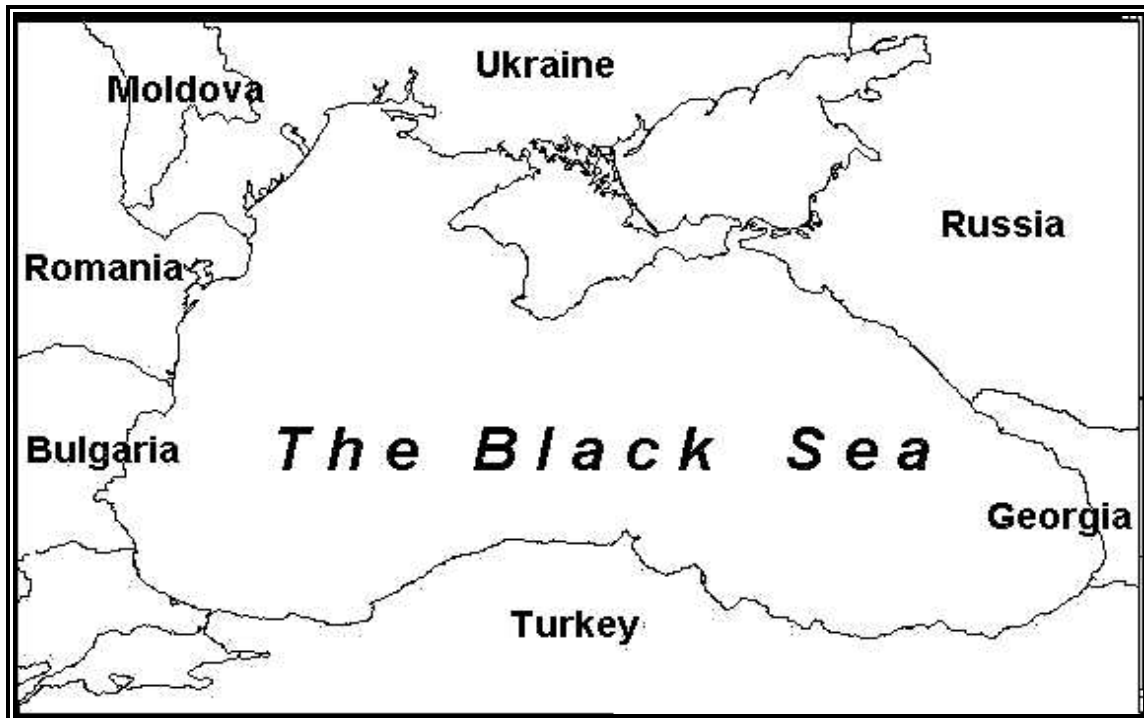


Fig. 1. Scheme of sampling locations along the Bulgarian Black Sea coast

The observed dependence of radionuclide content on sediment type is valid also for the natural nuclides in sediments. The lowest concentrations of natural nuclides is in the sand sediments from the north locations - Duran Kulak, Shabla, Tulenovo, Kamen briag and the measured natural nuclide concentrations are:  $^{238}\text{U}$  (4.0 - 10) Bq/kg,  $^{232}\text{Th}$  (3.4 - 10) Bq/kg,  $^{226}\text{Ra}$  (3.6 - 9) Bq/kg. Low content was obtained at Sunny beach, Nessebar and Primorsko:  $^{238}\text{U}$  (3 - 8) Bq/kg,  $^{232}\text{Th}$  (4.4 - 8) Bq/kg,  $^{226}\text{Ra}$  (3.5 - 6.2) Bq/kg (Fig 2).



Radionuclide content in Black Sea sediments  
*Gamma Spectroscopy*

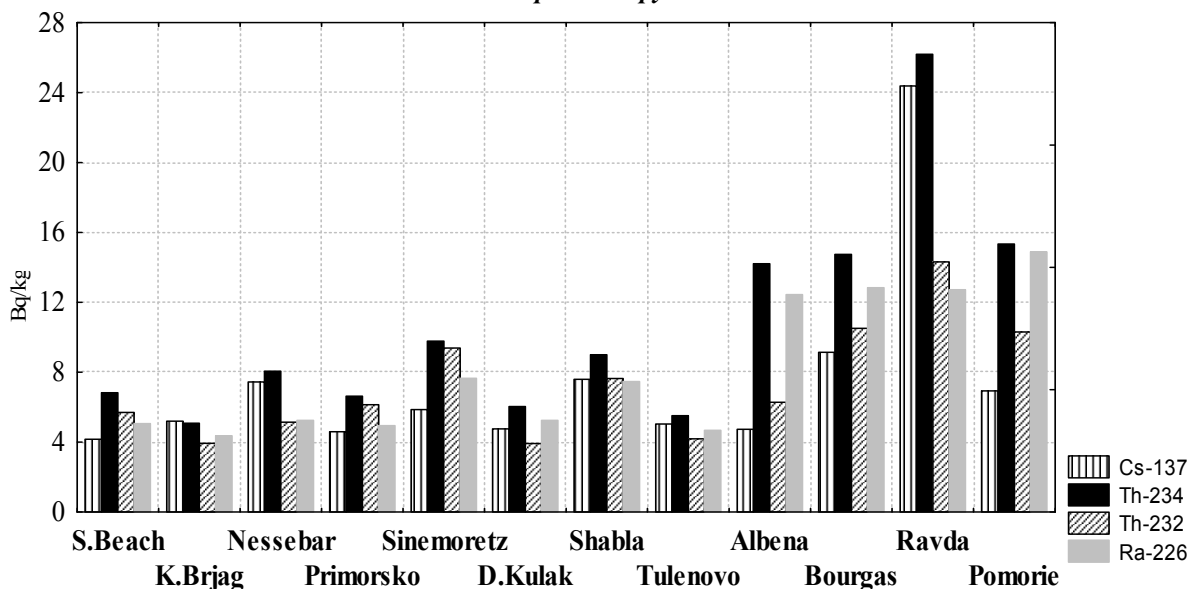


Fig. 2. Nuclide content in sand sediments along the Bulgarian coast

The obtained mean values for silt sediments are between sand and slime ones with exception of Bjala, whose values for  $^{238}\text{U}$  are in the range 14 - 77 Bq/kg;  $^{232}\text{Th}$  12- 110 Bq/kg;  $^{226}\text{Ra}$  10 - 77 Bq/kg and are the highest measured at the silt and slime locations (Fig.4, 5). The data on Fig. 3 show that all natural nuclide content in slime sediments varies around 30 Bq/kg, (except  $^{232}\text{Th}$  at Kavarna,  $^{238}\text{U}$  at Maslen nos and Chernomoretz), showing some uniformity of natural nuclide concentrations along the whole coast.

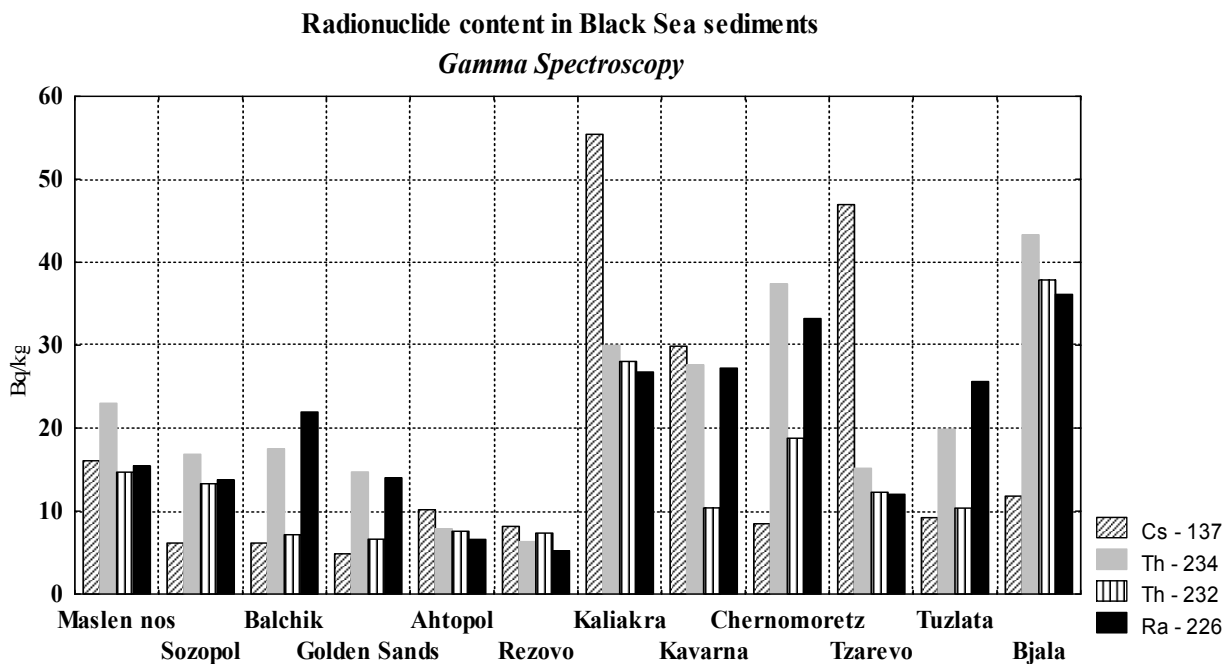


Fig. 3. Mean nuclide content in silt and slime sediments along the Bulgarian coast

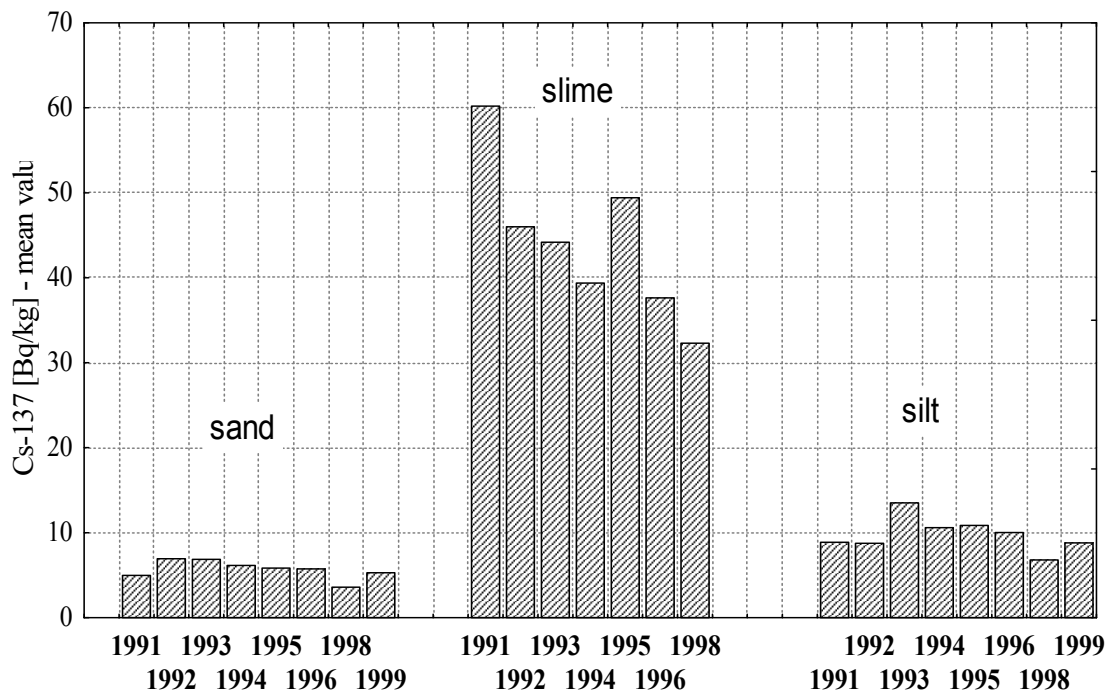


Fig. 4. Mean <sup>137</sup>Cs content in sediments during the period 1991 - 1999

The highest values for natural nuclides content (similarly to Cs) are obtained for the slime sediments - the obtained results for <sup>238</sup>U vary in the different years in the range 5 - 50 Bq/kg, <sup>232</sup>Th - 4.0 - 35 Bq/kg and <sup>226</sup>Ra - 9 - 50 Bq/kg. The mean values of <sup>238</sup>U, <sup>232</sup>Th and <sup>226</sup>Ra specific activities for slime sampling locations are presented on Fig. 3 and these values show the maximum natural nuclide content at the Bulgarian Black Sea coast. The obtained

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

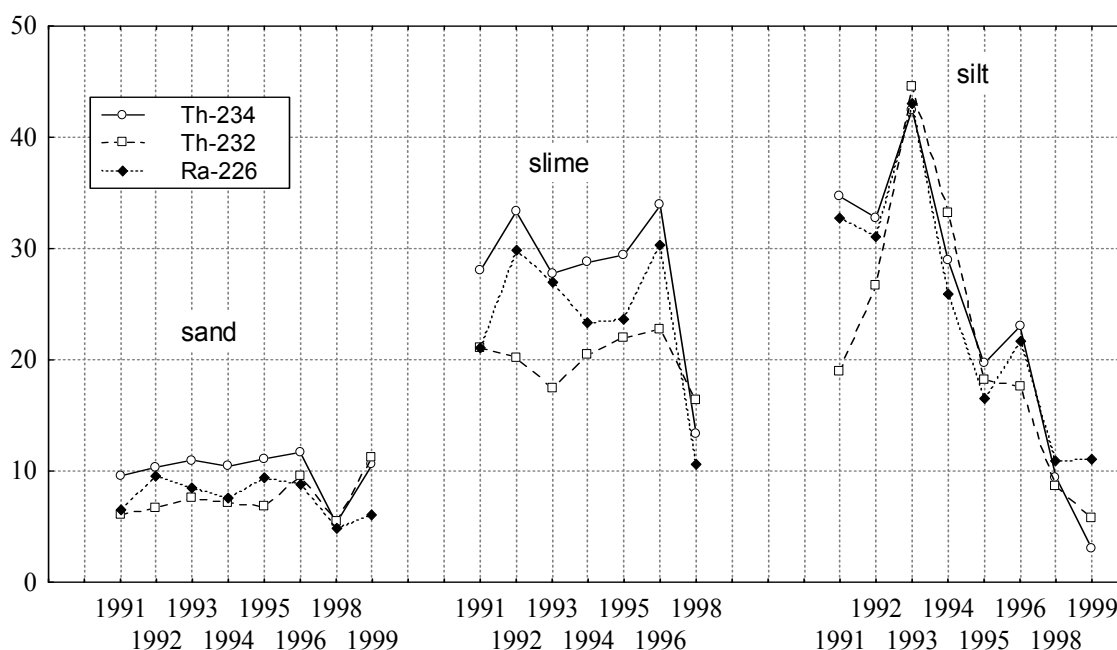


Fig. 5. Natural nuclide content (Bq/kg) in Black sea sediments in the 1991 – 1999 period

Samples were taken from deep sediments (56 – 155 m) from the Bulgarian territorial waters plus two samples at maximal depth 2040 m and also were measured for radionuclide content.

The obtained results (Fig. 6) show that Cs content is rather low (compared to the shelf), while natural nuclide concentrations increase with the depth.  $^{226}\text{Ra}$  nuclide concentration is higher in the middle depths (55 – 90 Bq/kg) than other natural nuclides while at the bottom 2000 m U content is the highest (90 – 135 Bq/kg). The character of deep sediment samples is slime except at 2000 m where the matrix is very hard in structure and black in color.

The multivariable (cluster) analysis of all measured sediment samples (145) for eight consecutive years depending on all measured nuclides shows that the type of sediment is a basic factor for nuclide accumulation in sediments (Fig. 6). The nuclide values for all sand sediments are combined in one cluster (from Albena to Shabla max Euclidian distance is 2.5). The second cluster includes locations close in geographical position and sediment type (slime) - Tuzla, Kavarna and Tzarevo, while Bjala, Chernomoretz and Kaliakra are completely separate from the rest.

The performed correlation analysis for tree consecutive season, for each type of sediment at all locations shows, that there is no clear season dependence of isotope concentrations - the calculated correlation coefficients between different seasons are close to 1. The statistical analysis of all nuclide data for all sampling sites (Fig 7) groups together sites with similar sediment matrix (sand, silt or slime) which supports the assumption of nuclide sorption dependence on the type of sediment matrix.

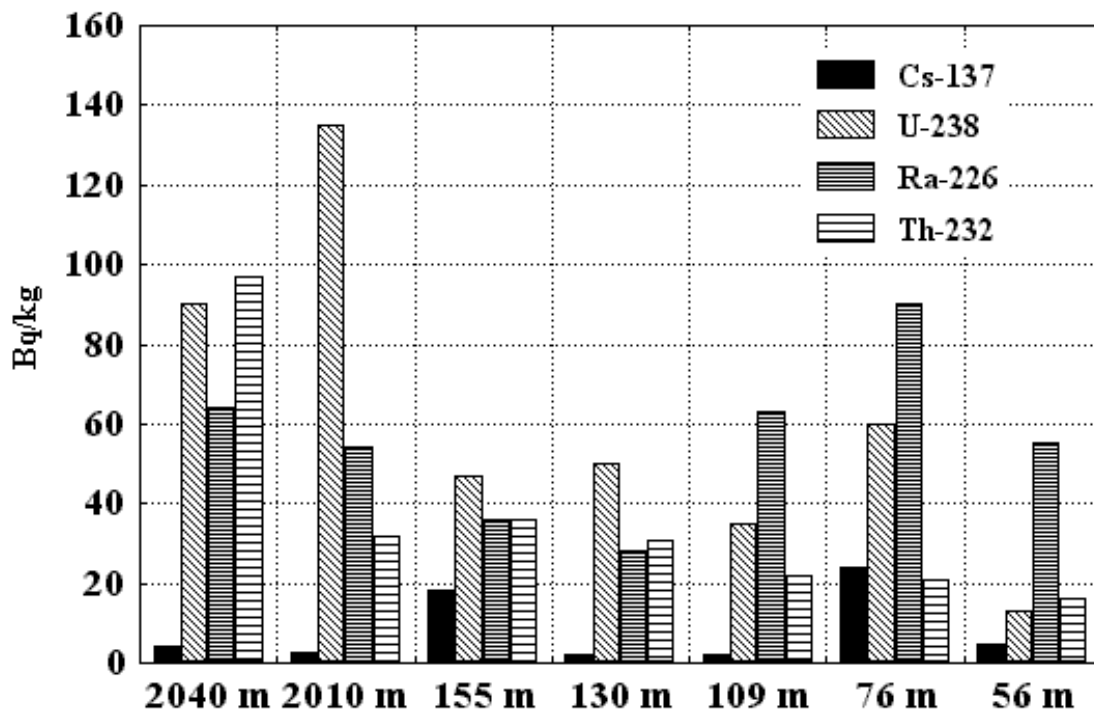


Fig. 6. Mean nuclide content in deep-sea sediment samples

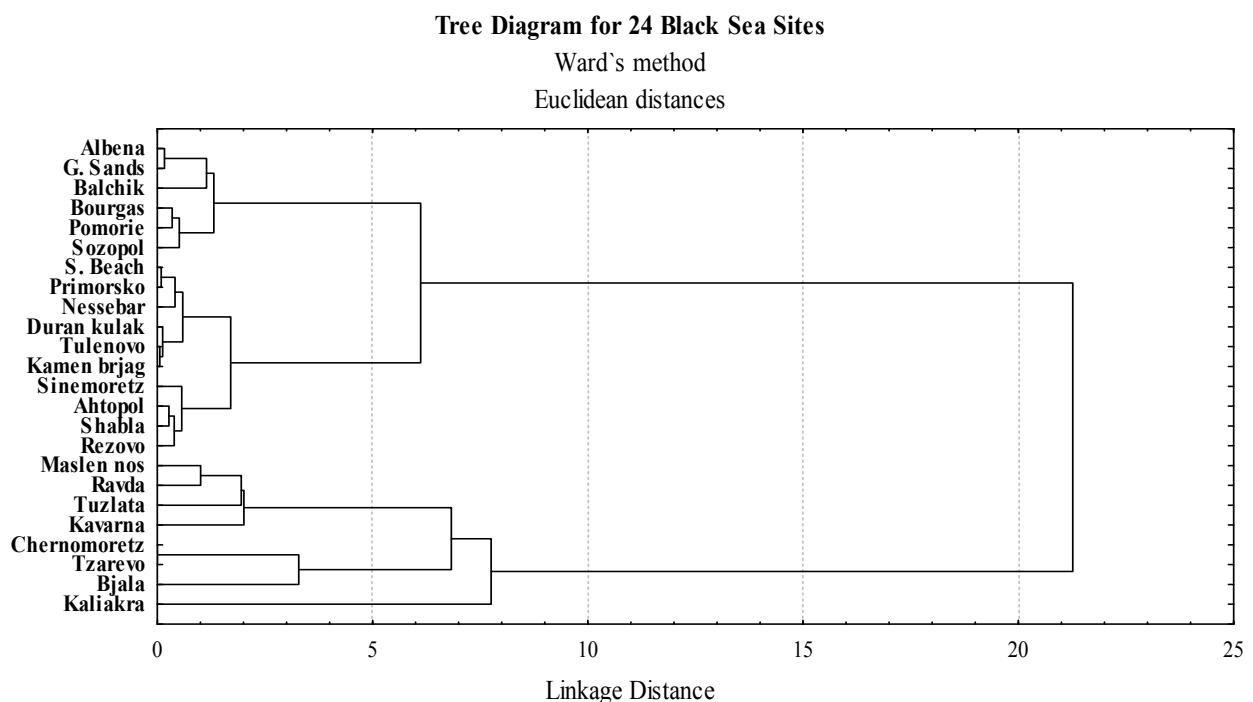


Fig. 7. Tree diagram of Black Sea sediments depending on radionuclide content.

## 6. Nuclide content in macroalgae

The data on the radionuclide content in different algae species are presented in Table 1 and in Figs. 5 and 6. The  $^{137}\text{Cs}$  content in different algae species vary on average between 3 and 20 Bq/kg. The content of natural nuclides is close to the lowest limits of detection (LLD).



The most interesting species is *Bryopsis plumosa* whose  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  nuclide contents are with some orders of magnitude higher than the same nuclides in other species.

The  $^{226}\text{Ra}$  contents in Black sea macrophytes vary in the range 2-25 Bq/kg for brown and 3-18 Bq/kg for green species. The accumulation intervals for  $^{226}\text{Ra}$  are close to each other for the two brown species and for *Ulva*, *Cladophora* and *Enteromorpha*, respectively.

The mean values of Ra vary for different species in the range 6.8-11.7 Bq/kg and can be arranged as follows:

$$\text{Ceranium rubrum} > \text{Clad. vagabunda} = \text{Cyst. barbata} > \text{Cyst. crinita} > \\ \text{Calith. corumbosum} = \text{Ulva rigida} = \text{Ent. intestinalis} > \text{Chaetom. Gracilis.}$$

It is evident that the mean values are close to each other and if they are combined, the total mean for all brown and green algae is the following:  $10 \pm 1$  Bq/kg ( $N = 40$ , range 2-25 Bq/kg) for brown species and  $8.6 \pm 0.7$  Bq/kg ( $N = 40$ , range 3-28 Bq/kg) for the green ones. Mean Ra content in red algae is 15 Bq/kg, range 2-39 Bq/kg, which shows similar pattern of natural nuclide accumulation by the algae species along the Black sea coast.  $^{210}\text{Pb}$  content in all algae species is in the range 3 - 40 Bq/kg, which is close to the values of neighbouring Mediterranean Sea and shows the level of this nuclide from recently deposited particles.

Nuclide	No of samples	Mean value $\pm$ SD	Minimum value	Maximum value
<i>Chlorophyta</i>				
$^{40}\text{K}$	40	$1009 \pm 90$	300	2500
$^{137}\text{Cs}$	40	$4.2 \pm 0.5$	1.2	13.0
$^{226}\text{Ra}$	40	$10 \pm 1$	3	28
$^{210}\text{Pb}$	40	$8.8 \pm 0.9$	3	22
<i>Phaeophyta</i>				
$^{40}\text{K}$	40	$1492 \pm 53$	1025	2250
$^{137}\text{Cs}$	40	$6.1 \pm 0.4$	2.6	12.0
$^{226}\text{Ra}$	40	$10 \pm 1$	2	25
$^{210}\text{Pb}$	40	$12 \pm 1$	2	30
<i>Rhodophyta</i>				
$^{40}\text{K}$	36	$1146 \pm 110$	90	2100
$^{137}\text{Cs}$	36	$7.4 \pm 0.8$	1.2	18.0
$^{226}\text{Ra}$	36	$15 \pm 2$	3	39
$^{210}\text{Pb}$	36	$15.8 \pm 1.5$	4	40

Table 1. Nuclide content (Bg/kg) in Black sea algae

The radionuclide content in marine ecosystems and especially in algae is in the limits of published data for the Black Sea and the Mediterranean.

The  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  content of the radionuclides has been measured in sediments and macroalgae located in several geographic zones along the Bulgarian Black sea coast, during the period from 1991 to 1999. The accumulation capacity and radionuclide content for different algae species also was determined for three algae phyla in the marine environment. No great difference was found in nuclide accumulation in algae, but the red species seem to accumulate nuclides to a higher degree than the brown and green species.

The data show that macrophytes can be used as reliable indicators for marine environmental assessment. With this paper we intend to fill the lack of data concerning radionuclides in sediments and macroalgae along the whole Bulgarian Black Sea coast. The data can be used as reference levels for further monitoring and control of the marine ecosystem status.

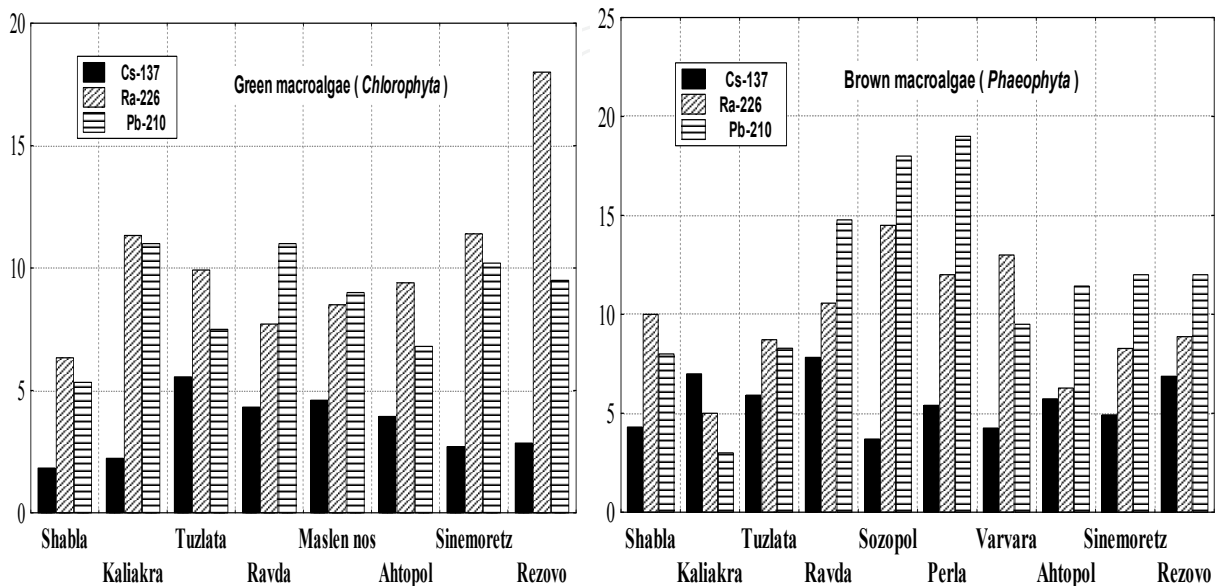


Fig. 8. Nuclide contents (Bq/kg) in green and brown algae

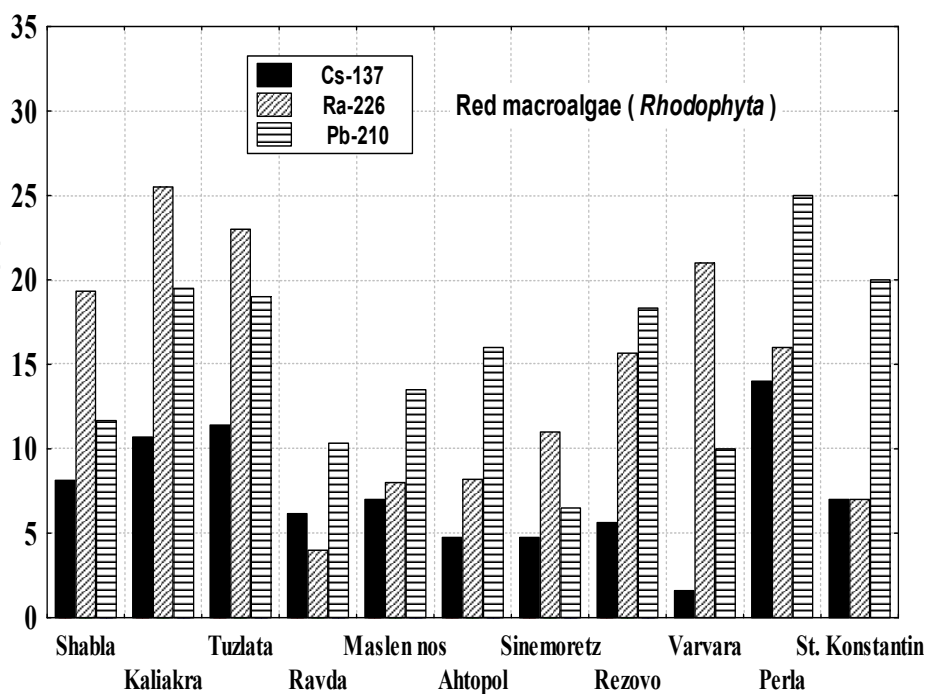


Fig. 9. Nuclide contents (Bq/kg) in Black Sea macrophytes - *Rhodophyta*

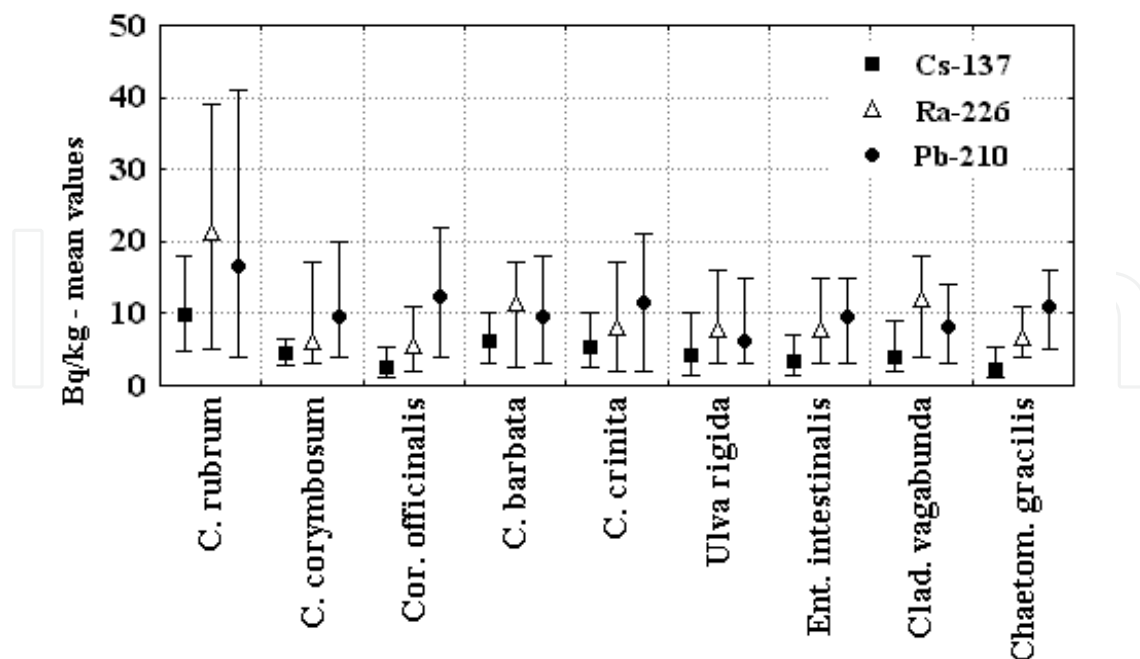


Fig. 10. Comparison of nuclide contents (Bq/kg) in Black Sea algae in different algae species

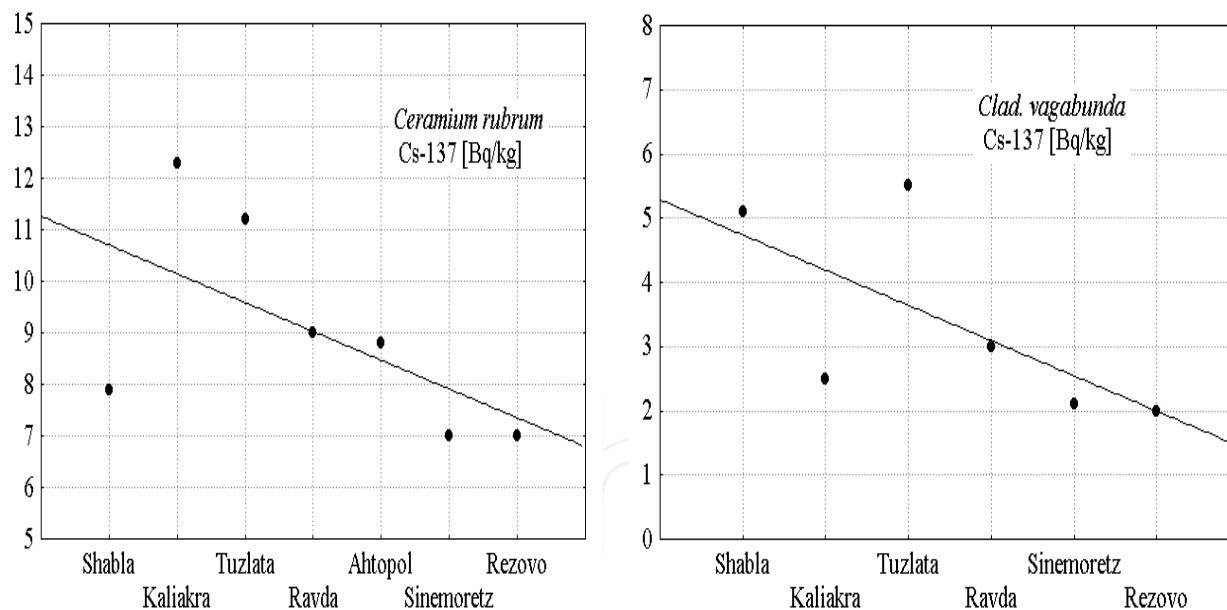


Fig. 11. <sup>137</sup>Cs content in macroalgae – local variations

The analysis of all alga samples for natural radionuclides content from <sup>238</sup>U series - <sup>226</sup>Ra and <sup>210</sup>Pb. Showed <sup>226</sup>Ra concentration values in the range 2 - 28 Bq/kg for red (mean 15 ± 2); for brown 2 - 17 Bq/kg (mean 9.8 ± 0.8) and for green 3 - 18 Bq/kg (mean 9 ± 1). Accumulation intervals for <sup>226</sup>Ra are close for the two brown and for green *Ulva rigida*, *Clad. vagabunda* and *Ent. intestinalis*. The <sup>226</sup>Ra mean values in different species can be arranged as follows:

*Cer. rubrum* > *Clad. vagabunda* = *Cyst. barbata* > *Cyst. crinita* = *Ulva rigida* = *Ent. intestinalis* > *Chaetom. gracilis* > *Callith. corymbosum* = *Cor. officinalis*.

The obtained  $^{210}\text{Pb}$  average values content in studied algae vary between 4 and 35 Bq/kg (mean  $15 \pm 1$ ) for red, 2 and 21 Bq/kg (mean  $11 \pm 1$ ) for brown and from 3 to 16 Bq/kg (mean  $8 \pm 1$ ) for green algae. If  $^{210}\text{Pb}$  mean values are arranged depending on algae species, the following order is obtained:

*Cer. rubrum* > *Callith. corymbosum* > *Cor. officinalis* = *Cyst. crinita* > *Chaetom. gracilis* > *Ent. intestinalis* > *Cyst. barbata* > *Clad. vagabunda* > *Ulva rigida*

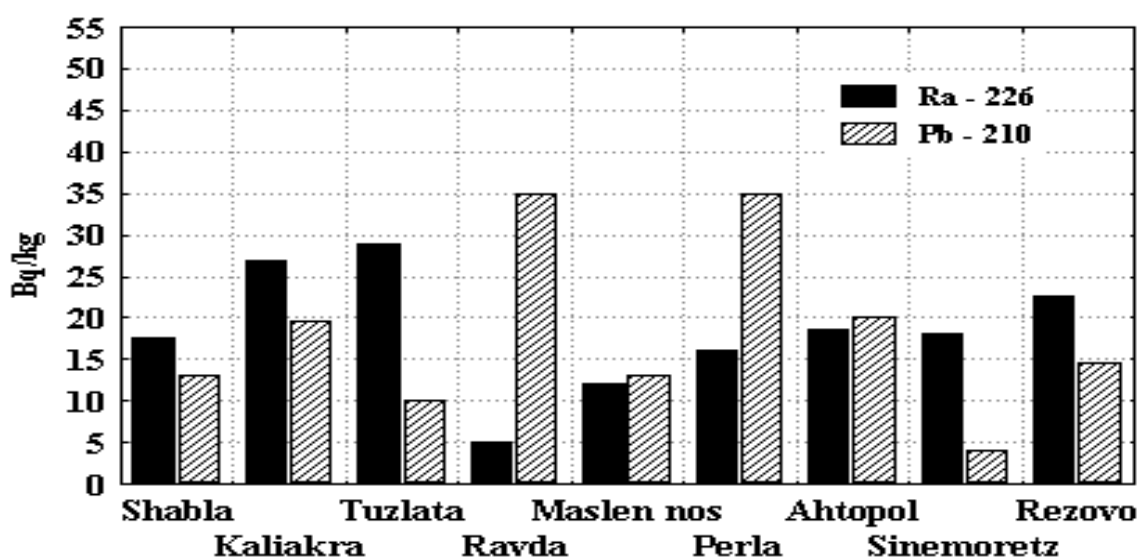


Fig. 12. Mean  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  content (Bq/kg) in *Ceramium rubrum*

## 7. Heavy metal levels in Black Sea sediments

The distribution of the recent bottom sediments in the Black sea shows a variable pattern. The sediment composition and origin depend on the provenance areas, hydrodynamic and lithodynamic activity in the contact zone of the sea, and on the morphology of the bottom topography. Sediment formation is also influenced by the solid riverine runoff and coastal abrasion, slope-derived supply, and biogenic and chemogenic matter (Ignatov, 2008).

Heavy metal concentrations in surface sediments can provide historical information on heavy metal inputs at that location. Such surface sediment samples are also used as environmental indicators to reflect the current quality of marine systems for many pollutants. (Förstner et al., 1980). Nijenhuis et al., (1999) reported that the enrichment of trace elements in marine sediments may, in general, originate from the following sources; super and subjacent sediments, through diagenesis; suboxic shelf and slope sediments, hydrothermal input; aeolian input; fluvial runoff; sea water. Heavy metal levels in sediment from the Black Sea were investigated by many researchers (Ergul et al., 2008; Topcuoglu et al., 2002; and 2004, Strezov et al., 2003) that measured heavy metal concentrations in sediment samples and found dependence upon seasonal changes within the water column

as well as anthropogenic and geological inputs such as weathering and run-off from land-based sources. Furthermore, metal concentrations in both surface sediments and sinking particles also suggest that heavy metal concentration is generally enhanced in the eastern region along the Black sea coast of Turkey.

Bulk heavy metal (Fe, Mn, Co, Cr, Ni, Cu, Zn and Pb) distributions and their chemical partitioning together with total organic carbon and carbonate data were studied in 0-2 cm oxic to anoxic surface sediments, obtained at 18 stations throughout the Black sea by Kiratli et al., (1996). Chemical partitioning of the heavy metals revealed that Cu, Cr and Fe seem to be significantly bound to the detrital phases whereas carbonate phases tend to hold considerable amounts of Mn and Pb.

Coban et al., (2009) found heavy metals in sediment at significant levels of 0.47 µg/g for Cd, 67.95 µg/g for Cr, 30.21 µg/g for Cu, 274.4 µg/g for Mn, 37.03 µg/g for Ni, 39.14 µg/g for Pb and 84.6 µg/g for Zn, that were comparable with those found in the estuarine areas of other countries in the region.

Topcuoglu et al., (2003b) determined the radionuclides  $^{137}\text{Cs}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  and Cd, Pb, Cu, Zn and Mn in sediment samples collected from two stations at the eastern Turkish coast of the Black sea. The result from this study showed that radionuclide concentrations in the sediment fraction were significantly higher because of the influence of collection sites. In general, the heavy metal concentrations in that study were not higher than those previously observed. However, Pb and Cu levels increased in sediment in the Turkish area of the Black Sea during the investigated years.

In conclusion, heavy metal pollution in the Black sea has attracted considerable research attention since last 20 years. Sources of heavy metals in the Black sea ecosystem can be mainly attributed to terrestrially derived waste water discharges, agricultural and industrial run-off, river run-off atmospheric deposition of combustion residues, and shipping activities. It is clear from many studies conducted that the heavy metal pollution in the Black sea should be taken into account. In the last 20 years, in some areas of Black sea, metal concentrations in sea water exceeded the accepted levels. Especially, lead and cadmium levels were found higher in fish species than the legal limit for human consumption. High levels of heavy metals have been reported by the authors, suggesting that heavy metal pollution in algae and sediments from certain regions of Black Sea is rather high.

The Black Sea is a unique ecosystem because it is an inner sea with low salinity, half-isolated from the Mediterranean with hydrology and phytobentos different from the other seas in the same biogeographic region.

The antropogenic contamination of marine ecosystems is a very important stress factor and defines the necessity for systematic monitoring and control of contaminants (heavy metals – HM, radionuclides, etc.) that affect marine biota. The main sources of Black Sea pollution are atmospheric fallout, the big rivers run-off as well as local pollutant emissions (Tuncer et al., 1998).

Macrophytic algae, being one of the primary stages in the trophic chain, play a major role in marine ecosystems (Kilgore et al., 1993). Algae interact with the environment through processes that include chemical bioconcentration, excretion, organic matter production and decomposition (Carpenter and Lodge, 1986). They have been used as a signal for the living



status of marine ecosystems and considered as valuable indicators for HM assessment in the major components of the water ecosystems because of their accumulation capacity (Forsberg *et al.*, 1988). Some algae possess ecological mutability so they can survive in contaminated habitat (Kalugina-Gutnik, 1975). Closely related species may exhibit different accumulation capabilities for trace elements, so there is a need to identify indicators that are biologically dominant and widespread in the ecosystems. This will allow intraspecific comparison of accumulated metal concentrations over large geographical areas (Rainbow, 1995; Rainbow and Phillips, 1993).

HM are among the most studied contaminants in marine ecosystems. Their effect is through direct poisoning as well as by accumulation and transfer along the trophic chain, by which they influence the functioning of biosphere (Babich *et al.*, 1985).

Metal levels in algae reflect local geology or local anthropogenic activities and the contamination is generally similar to background levels of the sites. Today's HM concentrations in marine environment are generally more than 10 times higher than it was in prehistoric times. The levels are consistently higher in surface waters than in deeper layers. The macrophytic species from phylum Chlorophyta (green) are widely distributed in the coastal Black Sea ecosystems and some of them (*Ulva rigida*, *Enteromorpha intestinalis*, *Cladophora vagabunda*) can be found in almost all areas and environmental pollution was studied by means of green algae. These species have been extensively used to monitor marine pollution for Mn, Cu, Pb and Cd in various geographical areas (Favero *et al.*, 1996; Muse *et al.*, 1999).

Many authors have investigated biogeochemical migration of anthropogenic contaminants (HM, radionuclides) in the Black Sea environment (Polikarpov *et al.*, 1991; Roeva, 1996; Guven *et al.*, 1992; Topcuoglu *et al.*, 1998, 1999, 2001) while information about heavy and toxic metals at the Bulgarian coastal zone is scarce and insufficient.

Data were obtained by Atomic Absorption (AAS) and X-Ray fluorescence analysis for the accumulation and seasonal distribution of Fe, Mn, Cu, Pb and Cd in six green macrophytes, collected from eight locations along the Bulgarian Black Sea coast during the period spring 1996 to summer 2002. Fe has a great binding capability for alga lipids and is accumulated to the highest degree in the Black Sea green macrophytes.

The measured Fe concentrations are with one or two orders of magnitude higher than the other HM (with mean value 650  $\mu\text{g/g}$ ). Maximum Fe values are obtained for *C. vagabunda*, *C. coleothrix* and *C. gracilis*, while in the other three species Fe content is three times lower (Figure 2). A higher value of Fe is observed in *E. intestinalis* from Sinemoretz and Rezovo (autumn 1996 and summer 2000, respectively). The lowest Fe concentration was measured in *U. rigida* species from Ravda (spring 1998) and at Ahtopol (autumn 1996).

If mean Fe values are compared in all green algae depending on the location, a tendency is obtained of increasing Fe content from north to south. If Fe values are plotted for each green species vs. location, it is clear that the observed north-south tendency is mainly due to *Enteromorpha* species whose values increase southwards. Fe concentration for the other green species is more constant with geographical location (e.g., mean Fe values vs. location for *U. rigida* are in the range  $300 \pm 170 \mu\text{g/g}$  for the whole Black Sea coast).

The results for Mn vary in more narrow interval than Fe (mean value 84  $\mu\text{g/g}$ ). Low Mn content is measured for *U. rigida*, *E. intestinalis* and *B. plumosa*, while the highest is obtained for *C. coleothrix*. Mn concentrations in different regions change in the following order:

Ahtopol < Kaliakra < Shabla < Tuzlata  $\approx$  Ravda < Sinemoretz < Rezovo.

The mean Mn values for Tuzlata, Ravda and Sinemoretz are close and it is evident that there is no geographic dependence for Mn content. Our data show that green algae from Kaliakra (north) and Ahtopol (south) sites accumulate Fe and Mn to the lowest extent while the highest content is measured at Rezovo (south).

The high Fe and Mn biosorption, compared to the other HM, is connected with their function and major role in the metabolic processes in marine organisms.

The trace element Cu (like Fe) belongs to the group of biologically important metal ions. Trace metals should be monitored because they play an important role in metabolism and their high or low concentrations can be equally harmful to the living organisms. Cu, Pb and Cd content in green algae are presented in Figure 3.

The Cu data interval is wider compared to Pb and Cd but if mean values ( $\mu\text{g/g}$ ) for all algae are compared, we get for Cu  $5.6 \pm 0.5$ , Pb  $3.3 \pm 0.3$  and Cd  $1.1 \pm 0.2$ . The accumulation patterns sequence is the same for all green algae except *C. coleothrix* where Pb prevails.

Cu mean values are relatively constant along the whole Bulgarian coast (unlike Fe and Mn), and the low Cu content in the environment means that there is no contamination in the marine ecosystems with Cu. The same is true for Pb and Cd whose mean value variations are also small. These results can be explained with the lack of industrial pollution along the coast, except close to the big cities (ports) of Burgas and Varna. The studied locations in this paper are outside the dwellingplaces and this is done in order to obtain the characteristic background values for the measured HM concentrations along the whole coast.

The highest Cu content is measured in *E. intestinalis* from Rossenetz -  $148 \mu\text{g/g}$ , which is due to the known anthropogenic contamination of the copper mine in the vicinity. The synergism between Cu and Fe is clearly demonstrated in Rossenetz as Fe value is also high ( $4890 \mu\text{g/g}$ ) while the Pb and Cd values are normal.

The behavior of Pb in water ecosystems is complex and its concentration in a great number of natural waters is not higher than  $1 \mu\text{g/g}$ . Pb is found in seawaters mainly in the form of different organic compounds. Pb content in the studied Black Sea alga species varies in a more narrow interval than Cu. *C. gracilis*, *C. vagabunda*, *E. intestinalis* and *B. plumosa* species accumulate Pb in a rather similar way. Pb content variations along the coast are small (like Cu) which also means lack of contamination with Pb.

The determination of Cd content is an important task for the monitoring of HM in marine ecosystems. Cd is poisonous for living organisms even in low concentrations, so it is a hazardous anthropogenic contaminant that should be controlled. It can be concluded from the data in Figure 3 that Cd is present in green algae in comparatively low concentrations - from  $0.2$  to  $3.2 \mu\text{g/g}$  dry weight. The lowest Cd content is in the southern region Sinemoretz, but as a whole the concentration range is narrow in all sites with no geographic dependence. Judging from the alga type, the highest degree of Cd accumulation is found in *C. coleothrix*, while the lowest in *Bryopsis* and *U. rigida*.

Data were measured for Zn and Cr content in some of the studied green algae and the obtained mean values for Zn in *Ulva*, *E. intestinalis* and *B. plumosa* is 15  $\mu\text{g/g}$  (*C. vagabunda* - 23  $\mu\text{g/g}$ ) while for Cr in *Ulva*, *C. vagabunda* and *C. gracilis* - 1.3  $\mu\text{g/g}$  is obtained (*E. intestinalis* - 3.1  $\mu\text{g/g}$ ). The Zn and Cr results for Black Sea macroalgae confirm the lack of HM pollution (like Cu, Pb and Cd) along the Bulgarian coast.

The correlation between accumulation levels of HM concentrations is an important factor for evaluation HM behavior in biota and the determining of these correlations. The coefficient data for *Enteromorpha* and *Ulva* macroalgae show negative correlations between Cd and all measured metals in the two algae species. Pb also correlates negatively with all metal ions in *Enteromorpha* and only with Cu in *Ulva*.

Significant positive correlation coefficient (synergistic interaction between HM) was obtained only for the pair Fe-Mn in *Enteromorpha* while negative correlation (antagonistic) was obtained for Cu-Cd in *Ulva*. These correlation coefficients differ from unit and therefore the correlation dependence is not clearly expressed, meaning that the variables are connected but with weak functional dependence.

All Black Sea green algae data are subjected to cluster analysis for all toxic metal accumulation. The obtained tree diagram for all HM (Figure 9) shows that the algae are combined in two main groups plus *C. coleothrix*. The first main group consist of *Ulva* and *Bryopsis* linked by *Chaetomorpha*. The second group is *Enteromorpha* and *C. vagabunda*.

If the cluster analysis is performed for the toxic elements Cu, Pb and Cd, again two main groups are obtained - first group containing *C. coleothrix* and *Chaetomorpha*. The second group is divided in two - *Enteromorpha*, *Bryopsis*, *C. vagabunda* linked with *Ulva*. The main influence on these clusters is due to the presence of Cu because if we exclude Cu from the cluster process the obtained tree diagrams are less affected.

If we assess the obtained algae data depending on the chemical nature of the HM, the obtained tree diagram clearly separates Fe and Cu while Pb and Cd are strongly linked which is clear as these two elements belong to one and the same group of the Periodic table.

Data were obtained for Fe, Mn, Cu, Pb and Cd content in the most widespread Black Sea green macroalgae for the period 1996–2003 (Figs. 9-13) HM environmental behavior in the marine environment of eight locations (Shabla, Tuzlata, Kaliakra, Ravda, Rossenetz, Ahtopol, Sinemoretz, Rezovo), distributed along the whole Bulgarian coast, has been studied. All obtained results prove the dependence of toxic metal accumulation on green algae species as well as on the location.

It can be concluded that Fe, Mn, Cu, Pb and Cd concentration in Black Sea green macroalgae decrease during the studied period. *U. rigida* species accumulate the lowest concentrations of the studied metals. The highest Fe, Mn, Pb and Cd content has been measured in macrophytes from Tuzlata and Rezovo. High Cu concentration is observed in the southern coastal area - Ahtopol and Sinemoretz (the highest at Rossenetz).

All Black Sea green algae data are subjected to cluster analysis for all toxic metal accumulation. The obtained tree diagram for all HM (Figure 15) shows that the algae are combined in two main groups plus *C. coleothrix*. The first main group consist of *Ulva* and *Bryopsis* linked by *Chaetomorpha*. The second group is *Enteromorpha* and *C. vagabunda*.

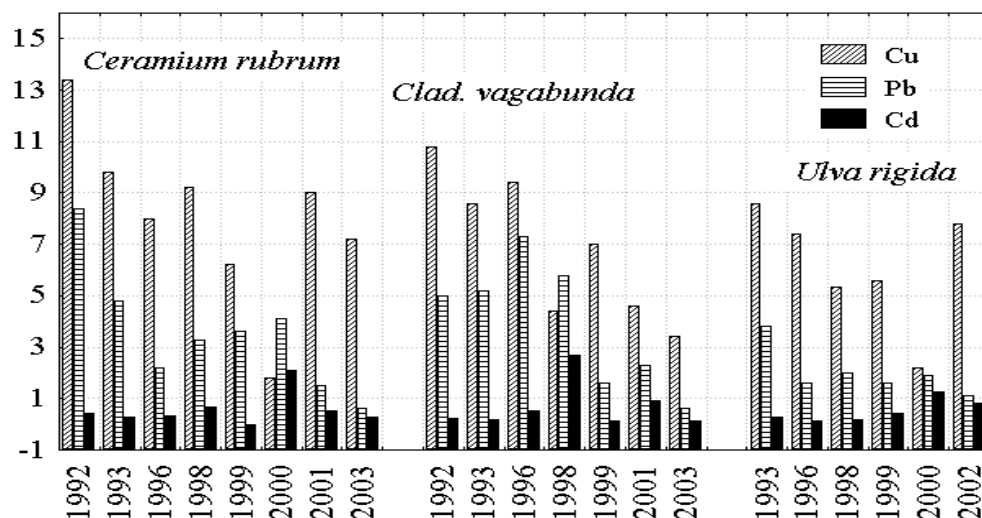


Fig. 13. Seasonal variations of HM concentrations (mg/g) in three alga species

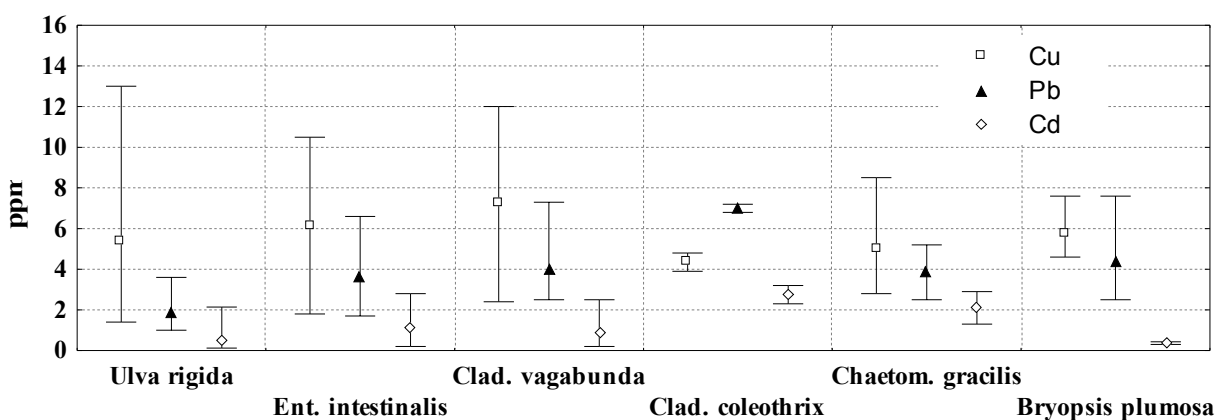


Fig. 14. Mean Cu, Pb and Cd content ( $\mu\text{g/g}$ ) in different algae species

If the cluster analysis is performed for the toxic elements Cu, Pb and Cd, again two main groups are obtained – first group containing *C. coleothrix* and *Chaetomorpha*. The second group is divided in two – *Enteromorpha*, *Bryopsis*, *C. vagabunda* linked with *Ulva*. The main influence on these clusters is due to the presence of Cu because if we exclude Cu from the cluster process the obtained tree diagrams are less affected.

If the obtained algae data are assessed depending on the chemical nature of the HM, the obtained tree diagram clearly separates Fe and Cu while Pb and Cd are strongly linked which is understandable as these two elements belong to one and the same group of the Periodic table.

In conclusion it can be pointed out that Chlorophyta and Rhodophyta algae phyla can be used as bioindicators for monitoring of the ecological state of the Black Sea environment. A comparative analysis of contaminants in different Bulgarian coastline regions leads to the conclusions that the data obtained for red and green macroalgae illustrate the level of contamination by HM and nuclides at seven locations of the Black Sea Coast.

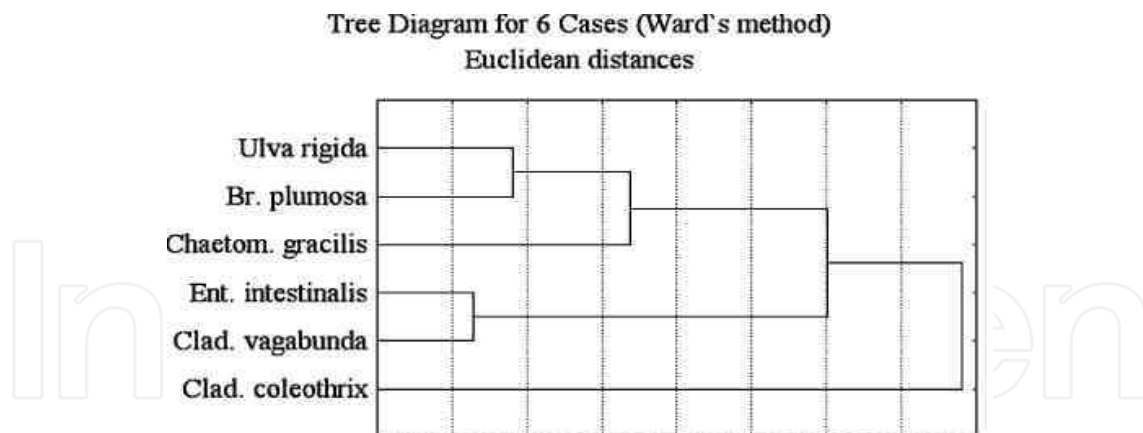


Fig. 15. Tree diagram for heavy metal content in green algae species

The studies of Black Sea macroalgae for marine environmental showed that there is no strict seasonal or local dependence of hazardous element content. All results seem to depend on the biological specificity of the algae and all data show a lack of serious pollution in areas without direct human impact along the Bulgarian Black Sea coast.

All obtained results show that use of macroalgae in marine environmental monitoring reduces the need for complex studies on chemical speciation of aquatic contaminants.

## 8. Heavy metal levels in Black Sea organisms

Topcuoglu et al. (2003a) investigated the metal content in macroalgae samples collected from the Black sea Turkish coast in the period 1998 to 2000. According to the findings of this study, the heavy metal pollution decreased in Turkish coast of the Black sea in the investigated years (Table 2). In another study it was determined that the Turkish Black sea coast was subjected to heavy metal pollution and the metal concentrations in macroalgae, sea snails and mussels were very high. (Topcuoglu et al., 2002). Romeo et al., (2005) studied the accumulation of trace metal concentrations by measuring them in the mussel collected in the Black sea. The authors found that Cd, Cu, Zn, Hg, Fe, Mn concentration changed between 0.96-1.74  $\mu\text{g/g}$ , 6.64-8.05  $\mu\text{g/g}$ , 108-190  $\mu\text{g/g}$ , 26-33  $\text{ng/g}$ , 95-106  $\mu\text{g/g}$  and 14.5-24.5  $\mu\text{g/g}$  mussels, respectively.

Tuzen et al., (2009) measured the trace element concentration in different marine algae (*Antithamnion cruciatum* and *Phyllophora nervosa*) collected from middle and east Black Sea. They found that the highest trace element concentration was determined for iron and the lowest for cadmium (Table 2). The authors suggested that the marine algae samples should be analyzed more often in Turkey with respect to toxic elements. Edible marine algae samples could be used as a food supplement to help meet the recommended daily intakes of some mineral and trace elements.

Zinc, copper, cadmium, lead and cobalt concentrations in Mediterranean mussel *Mytilus galloprovincialis* and sea snail *Rapana venosa* from the Sinop coasts of the Black sea have been measured (Turk-Culha et al., 2007). Significant differences were found in metal concentrations between the species. Similar significant differences observed with regard to different metals. The concentrations of Pb, Cd and Co were determined under detection



limit for the species. The other metal levels in the Mediterranean mussel and the sea snail were significantly higher than those in fishes.

From 1996 to 2002, Fe, Mn, Cu, Pb and Cd distribution in six green macroalgae species from the Bulgarian Black Sea coast were determined by Strezov et al, (2005a). For all algae, average heavy metal concentrations were 650 µg/g for Fe, 184 µg/g for Mn, 5.6 µg/g for Cu, 3.3 µg/g for Pb and 1.1 µg/g for Cd. These data show that heavy metal contents in different species demonstrate various degree of metal accumulation. The obtained higher values in the northern part of the studied zone can be attributed to the discharge influence of the big rivers entering the Black sea, such as Danube, Dnyeper, Dnyester, and local pollutant emissions, as well. The obtained data also show that there is no strong contamination in green macroalgae with heavy and toxic metals along the whole Bulgarian Black sea coast.

Metal contamination in the Black sea alga species (green and red) was studied from 1992 to 2003, using radionuclide approach (Strezov et al, 2005b). They found that radionuclide and metal concentrations depend on the macrophyte nature and all data show the lack of strong pollution along the Bulgarian Black sea coast.

## 9. Data comparison between neighboring seas

The comparison of the data (Tables 6 – 8) for radioecological status of the Black sea marine ecosystems and the Mediterranean marine ecosystems concerning the radionuclide and trace metal content indicated no strong anthropogenic pollution along the Bulgarian shore as the Mediterranean data are higher. When comparing the accumulation of HM in one and the same algae the corresponding data for Black sea algae are lower than those from the Marmare Sea or the Mediterranean.

Species	Metals						Reference
	Cd	Co	Zn	Mn	Pb	Cu	
Mussels	<0.02-	<0.05-5.36	78.12-	5.66-22.8	<0.05-2.60	7.21	Topçuoğlu <i>et al.</i> (2002)
Sea snail (soft)	2.01-	<0.05-0.7	73.3-	3.90-	<0.5	36.19	
* <i>Ulva lactuca</i>	<0.02/	<0.05/	21.2/	45.1/	<0.1/	13.8	Topçuoğlu <i>et al.</i> (2003)
1998/1999	<0.02	<0.05	9.6	21.8	<0.1	3.87	
* <i>Cystoseira</i>	<0.02/	<0.05/	35.1/	32.1/	<0.1/	5.7	
1998/1999	<0.02	<0.05	13.9	6.7	<0.1	2.2	
* <i>Pterocladia</i>	1.53/	<0.05/	119.8/	91.1/	<0.1/	10.3	
<i>capillacea</i>	1.36	<0.05	86.2	52.1	<0.1	5.3	
** <i>Ulva lactuca</i>	<0.2/	<0.05/	13.5/	41.1/	<0.1/	11.3	
1998/1999	<0.2	<0.05	394.4	12.5	<0.1	7.7	
** <i>Cystoseira</i>	<0.02/	<0.05/	43.9/	27.3-	<0.1/	593	
1998/1999	<0.02	<0.05	191.5	22.7	<0.1	590	
** <i>Pterocladia</i>	<0.02	<0.05	176.8	10.8	<0.1	<0.03	
<i>capillacea</i> 1999							
<i>Cystoseira c.</i>	0.22-1.87	-	-	9-60	0.4-6.3	0.3-6.0	Strezov-Nonova (2003)
<i>Cystoseira b.</i>	0.10-1.25	-	-	9-54	0.7-2.4	0.6-9.0	
Mussels	<0.02	-	312-396.5	46.9-73.05	<0.05-108	11.75-23.25	Bakan & Böke-Özkoç (2008)

\*West Black Sea: \*\* East Black Sea: ^ µg/kg

Table 6. Heavy metal levels (µg/g dry wt) in some living organism from the Black Sea

Algae	Cd	Cr	Cu	Mn	Zn	Pb	Reference
<i>Ulva lactuca</i>	1.35	< 1	7.5	-	34.2	6.5	Guven, 1998
<i>Cystoseira barbata</i>	1.3	< 1	4.2	-	33	5.3	Guven, 1998
<i>Ulva lactuca</i>	0.5	0.5	24	50	24.1	23.5	Topcuoglu, 2001a
<i>Cystoseira barbata</i>	0.75	0.95	6.85	25	97	14	Topcuoglu, 2001b
<i>Ceramium rubrum</i>	0.8	1.5	16	59	62	11	Topcuoglu 2001
<i>Ulva sp</i>	0.24	4.78	4.7	194	26.1	-	Malea, 2000
<i>Ulva sp</i>	0.6	1.56	5.5	-	5.2	3.68	Muse, 1999
<i>Enteromorpha sp.</i>	0.07	0.54	11.4	21	14	1.06	Favero, 2002
<i>Ulva sp</i>	0.18	1.63	5.8	-	45	1.94	Conti, 2003
<i>Padina pavonica</i>	1.56	3,6	13.3	-	84	11.4	Campanella 2001
<i>Ulva sp</i>	0.8	1.8	5.6	40	24	1.7	Strezov, 2005a
<i>Ceramium s</i>	0.9	6	7.6	120	22	2.2	Strezov, 2005a
<i>Cladophora sp.</i>	1	7	6	170	19	3.5	Strezov, 2005a
<i>Enteromorpha sp.</i>	0.8	5.3	7	47	14	2.4	Strezov, 2005a
<i>Cystoseira sp.</i>	0.3	2.3	4	42	1.6	18	Strezov, 2005b
<i>Chaetomorpha sp</i>	1.3	7	5	180	12	2.7	Strezov, 2005b
<i>Corallina sp.</i>	0.7	4.8	15	55	13	1.4	Strezov, 2005b
<i>Callithamnion sp</i>	0.5	3.7	5.4	87	18	2.3	Strezov, 2005b

Table 7. Trace metal content (mg/kg) in marine algae from the Black and Mediterranean seas

Algae	<sup>137</sup> Cs	<sup>40</sup> K	<sup>210</sup> Pb	<sup>226</sup> Ra	Reference
<i>Ceramium rubrum</i>	0.8	-	-	-	Bologna (1996)
<i>Cystoseira sp.</i>	15	900	-	-	Guven (1993)
<i>Cladophora sp.</i>	n.d.	2170	-	-	Guven (1993)
<i>Enteromorpha sp.</i>	5	1076	-	-	Guven (1993)
<i>Chaetomorpha sp.</i>	11	2525	-	-	Guven (1993)
<i>Ulva sp.</i>	6	930	-	-	Guven (1993)
<i>Corallina sp.</i>	5	250	-	-	Guven (1993)
<i>Ceramium rubrum</i>	12	880	-	-	Guven (1993)
<i>Ulva lactuca</i>	< 3	-	-	-	Topcuoglu (2001a)
<i>Cystoseira barbata</i>	5.9	-	-	-	Topcuoglu (2001b)
<i>Ulva sp</i>	< 1.2	900	3.49	< 1.7	Al-Masri (2003)
<i>Cystoseira sp</i>	< 1.1	1800	8	1.2	Al-Masri (2003)
<i>Ulva lactuca</i>	7.2	-	-	-	Othman (1994)
<i>Ulva sp.</i>	3.4	596	6	9.3	Strezov, (2005a)
<i>Ceramium sp</i>	9.4	1343	13	17	Strezov, (2005b)
<i>Cladophora sp.</i>	12	1300	8	12	Strezov, (2005a)
<i>Enteromorpha sp.</i>	4.5	690	7	10	Strezov, (2005a)
<i>Cystoseira sp.</i>	5.4	1400	12	11	Strezov, (2005b)
<i>Chaetomorpha sp.</i>	2.3	1860	10	7	Strezov, (2005a)
<i>Corallina sp.</i>	2.1	140	12	10	Strezov, (2005b)
<i>Callithamnion sp</i>	4.4	1580	10	7	Strezov, (2005b)

Table 8. Radionuclides mean content in Black sea algae (Bq/kg)

Aquatic organisms, especially macroalgae, are widely used as bioindicators for the study of marine contamination by radionuclides and heavy metals. Some species tolerate high levels of pollutants and can successfully be used to obtain reliable information of marine ecological status. In order to evaluate the ecological status of coastal habitat and provide valuable data for estimation of contamination with radionuclides in Bulgarian Black sea, a monitoring program was started and performed along the coast. Eleven macroalgae species were monitored by collecting samples from 20 reference locations during the 1996-2005 period.

In this way the accumulation of hazardous contaminants was traced over a long period of time and tendencies for the behaviour of those elements were evaluated. The same comparison was made for radionuclides (Table 8) in the studied algae species and Black Sea Cs content was found to be similar to the other basins while natural nuclides were slightly higher in the Black sea.

## 10. Conclusion

Radionuclide and HM accumulation capacity has been studied in Black sea sediments three algae phylum along the Bulgarian Black Sea coast during the period 1996 – 2004. The natural isotope concentrations are higher than technogenic ones and red alga *Ceramium rubrum* shows the highest level of nuclide concentrations. The status of the marine environment in all studied areas was evaluated by cluster analysis of macroalgae data from all geographic zones. Analysis results show logical geographic dependence of contaminant content and locations of higher content are distinctly separated from those of clean areas.

The full scale monitoring done on the whole Bulgarian Black Sea coast resulted in collecting information for the different equilibrium processes, taking place in the coastal regions which govern the radioactive pollution of rivers, adjacent salt lakes, sea sediments and water and other harmful effects of human activities but also their behaviour in the marine ecosystems (algae, sea mussels, fish and other marine organisms the rates of exchange and the pathways towards man). It can be pointed out that Chlorophyta and Rhodophyta algae phyla can be used as bioindicators for monitoring of eco-toxicological state of the Black Sea environment. A comparative analysis of contaminants in different Bulgarian coastline regions leads to following conclusions:

- A data base for isotope accumulation, sorption and migration of nuclides and HM is created to help the future assessment and biosphere in whole Bulgarian coastal zone.
- The data obtained for red and green macroalgae illustrate the level of contamination at the locations of the Black Sea Coast
- There is no strict seasonal or local dependence of hazardous element content. All results seem to depend on biological specificity of the algae
- All data show the lack of serious pollution along the Bulgarian Black Sea coast.
- All obtained results for sediments and macroalgae in marine environmental monitoring reduces the need of complex studies on chemical speciation of aquatic contaminants and makes algae valuable indicators for the seawater quality assessment.
- Modelling the transfer processes of radionuclides in environment and the different pathways of isotope migration in the marine environment to predict the potential hazard for the population

## 11. References

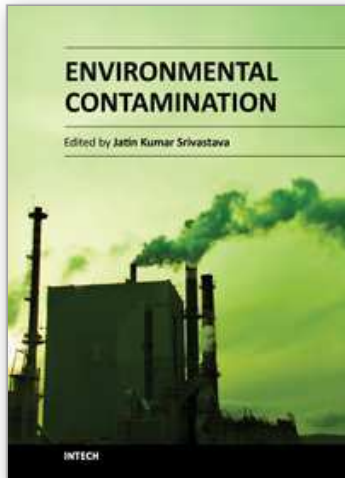
- Al-Masri M, S. Mamish, Y. Budier. 2003. Radionuclides and trace metals in eastern Mediterranean Sea algae, *J. Env. Radioact.* 67, 157-168
- Babich, H., Devaris, M., Stotzki, G.: 1985, 'The mediation of mutagenicity and clastogenicity of heavy metals by physiochemical factors', *Environ. Res.* 37, 325-331.
- Bakan, G. and Böke-Özkoç, H. 2008. An ecological risk assessment of the impact of heavy metals in surface sediments on biota from mid-Black sea coast of Turkey. *Int. Journal of Environmental Studies*, 64: 45-57.
- Baumann, M., Segl, M., Wefer, G., von Bodungen, B., 1989. Chernobyl Derived Radiocaesium in the Norwegian Sea: Flux between Water Column and Sediment. In *The Radioecology of Natural and Artificial Radionuclides XV Regional Congress of IRPA*, Gotland Sweden, 318-323.
- Bologa A., M. Apa, A. Cociasu, E. Cuingoglu, V. Patrascu, V. Piescu, L. Popa, 1996. Present level of contaminants in the Romanian Black Sea sector, *IAEA TechDoc 1094*, 469-475
- Broberg, A., 1989. Distribution of Cs-137 in Lake Sediments. In *Radioecology of Natural & Artificial Radionuclides XV Regional IRPA Congress*, Gotland, Sweden, 301-305
- Buesseler, K.O., Livingston, H.D., Hohjo, S., Hay, B.J., Manganini, S.J., Degens, E., Ittekkot, V., Izdar, E., Konuk, T., 1987. Chernobyl Radionuclides in a Black Sea Sediment Trap. *Nature* 329, 825-828.
- Coban, B., N Balkis, A. Aksu. 2009. Heavy metal levels in sea water and sediment of Zonguldak, Turkey. *Journal of Black Sea/Mediterranean Environment*, 15, 23-32.
- Conti M. E., G. Cecchetti. 2003. A biomonitoring study: trace metals in algae and molluscs from Tyrrhenian coastal areas, *Environ. Res.* 93, 99-112
- Ergul, H.A., S. Topcuoglu, E. Olmez, C. Kirbasoglu. 2008. Heavy metals in sinking particles and bottom sediments from the eastern Turkish coast of the Black Sea. *Estuarine, Coastal and Shelf Science*, 78, 396-402
- Favero N., M. Frigo. 2002. Biomonitoring of metal availability in the southern basin of the lagoon of Venica (Italy) by means of macroalgae, *Wat. Air Soil Poll.* 140, 231-246
- Förstner, U., W. Salomons. 1980. Trace metal analysis on polluted sediments, I: assessment of sources and intensities. *Environmental Technology Letters* 1, 494-505.
- Güven, K.C., Topcuoglu, S., Kut, D., Esen, N., Erentürk, N., Saygi, N., Cevher, E., Güvener, B., Öztürk, B. (1992). Metal uptake by Black Sea Algae. *Bot. Marina*, 35, 337-340.
- Güven K., Topcuoglu S., Gungor. N. 1993. Chernobyl radioactivity in Algae Collected from the Marmara and Black Sea. *Turkish J. Nucl. Sciences* 20, 21-30
- Güven K., Okus E., Topcuoglu S., Esen N., Kucukcezzar R., Seddingh E., Kut. D. 1998. Heavy Metal Accumulation in Algae and Sediments of Black Sea coast of Turkey *Tox. Env. Chem.*, 67, 435-440
- Hadderingh, R. H., Kema, N.V. (1989). Distribution of Cs-137 in the Aquatic Food-chain of IJsselmeer after the Chernobyl Accident. In *The Radioecology of Natural and Artificial Radionuclides. XV Regional Congress of IRPA*, Gotland Sweden, 325-330
- Ignatov, E. 2008. Coastal and Bottom Topography, the Black Sea Environment, Springer Verlag Berlin Heidelberg, 62 pp.
- Kalugina - Gutnik A.A. (1975). Phytobentos of the Black Sea. *Naukova dumka Kiev*, p. 16.
- Kilgore, J., Dibble, E., Hoover, J. 1993. Relationships between fish and aquatic plants: A plan of study, *Miscellaneous paper A-93-1*, U.S. Army Corps of Engineers WES, Vicksburg, MS.



- Kulebakina, L.G., Zesenko, A.J. (1984). Dynamics of contamination levels of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in water and hydrobionts in the Danube River delta and surrounding part of the Black Sea. *Radiochemical Ecology & Problems of Contamination Kiev, Naukova Dumka*, 16-40.
- Kulebakina, L., Egorov, V., Polikarpov, G. 1988. Redistribution and of  $^{137}\text{Cs}$  in Black Sea water in 1986 - 1988 (in Russian), *Gidrobiologicheski Journal* 24, 69.
- Kulebakina, L. and Polikarpov, G., 1989. Radiological Investigation of Black Sea Ecosystems after the Chernobyl Accident. *Proc. Conference on Radioecology High Tatras, Chechoslovakia*, 131-155.
- Keondjan V.P, Kudin A.M., Terehin Yu., Kiev, 1990. Practical Ecology of Sea Regions. The Black Sea, *Naukova Dumka*, 46 - 56
- Kiratli N., M. Ergin. 1996. Partitioning of heavy metals in surface Black Sea sediments, *Applied Geochemistry*, 11, 775-788.
- Malea P, S.Haritonidis. 2000. Use of green alga *Ulva rigida* as an indicator species to reassess metal pollution in Thermaikos Gulf, Greece, after 13 years *J. Appl. Phicology*, 12, 169-176
- Manahan, S. 1999. Environmental Chemistry, Seventh edition, Lewis Publishers, New York, London, Washington, pp 783.
- Muse J., J.Stripeikis, F.Fernandez, L.Huicqui, M.Tudino, C.Carducci, O.Troccoli. 1999. – Seaweeds in the assessment of heavy metal pollution in the Gulf San Jorge, Argentina *Env. Poll.*, 104, 315-322.
- Nijenhuis I., H. Bosch, J. Sinninghe, H. Burmsack, G.De Lange. 1999. Organic matter and trace element rich sapropels and black shales: a geochemical comparson. *Earth and Planetary Science Letters*, 169, 277-290.
- Othman I., J.Yassine, I.Bhat. 1994. Measurements of some radionuclides in the marine coastal environments of Syria. *Sci Tot. Env.* 53, 57-60
- Polikarpov, G. 1966. Radioecology of Aquatic Organisms, N. Holland Publ. Company, Amsterdam.
- Polikarpov G.G., Kulebakina L.G., Timoshchuk V.I. and Stokozov N.A. (1991).  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in surface waters of the Dniepr River, the Black Sea and the Aegean Sea in 1987 and 1988. *J. Environ. Radioactivity*, 13, 25-34.
- Rainbow, P. 1995. Biomonitoring of heavy metal availability in the marine environment. *Mar. Poll. Bull.* 31, 183-192
- Rainbow, P. S. Phillips, D. 1993. Cosmopolitian biomonitors of trace metals, *Mar. Pollut. Bull.* 26, 593-601.
- Roeva, N. N., Rovinski, F. and Kononov, E.: 1996, 'Specific features of heavy metal behavior in different nature media', *Zhurnal Analytichnoy Khimii* 51, 384-391.
- Romeo M., C. Frasila, M. Gnassia-Barelli, G. Damiens, D. Micu, G. Mustata. 2005. Biomonitoring of trace metals in the Black Sea (Romania) using mussels *Mytilus galloprovincialis*. *Water Research*, 39, 596-604.
- Sokolova, I. 1971. Calcium,  $^{90}\text{Sr}$  and Strontium in Marine Organisms (in Russian), Kiev, *Naukova Dumka*, 239-246
- Strezov, A., M. Milanov, P. Mishev, T. Stoilova. 1998. Radionuclide accumulation in near-shore sediments along Bulgarian Black Sea coast. *Appl. Radiat Isotopes* 49 (12), 1721-1728
- Strezov, A., T.Stoilova, A. Jordanova, N. Petkov. 1999. Determination of Cs and Natural Radionuclide Concentrations in Sediments, Algae & Water. *Water Sci. Tech.* 39, 21-26.



- Strezov A., T. Nonova. 2003. Monitoring of Fe, Mn, Cu, Pb and Cd levels in two brown macroalgae from the Bulgarian Black sea coast. *Int. J. Env. Analyt Chemistry*, 83, 1045-1054
- Strezov A., T. Nonova. 2005a. Environmental Monitoring of Heavy Metals in Bulgarian Black Sea Green Algae. *Environmental Monitoring and Assessment*, 105, 99-110.
- Strezov A., T. Nonova. 2005b. Comparative analysis of heavy metal and radionuclide contaminants in Black Sea green and red macroalgae, *Water Science & Technology*, 51 1-8.
- Shvedov V., Ivanova, L., Maximova, A., Stepanov, A. (1962). Radioactive Substances Content and Distribution in Sea Water. In *Radioactive Contamination of the Environment*, ed. Shvedov V. and Shirokov S., Moscow, 236-242
- Topcuoglu, S., Esen, N., Egilli, E., Gungor, N, Kut, D., 1998. Trace Elements and <sup>137</sup>Cs in Macroalgae and Mussels from the Kilyos in Black Sea, *Proc. Int. Symposium on Marine Pollution Monaco 1998*, IAEA SM-354 pp. 283-284.
- Topcuoglu, S., N. Gungor. 1999. Radionuclide Concentrations in Macroalgae and Sediment Samples from the Bosphorus, *Turk. J. Mar. Sci.* 5, 19-29.
- Topcuoglu S, D. Kut, N. Esen, N.Gungor, E.Olmez, C Kirbasoglu. 2001. <sup>137</sup>Cs in biota and samples from Turkish coast of the Black Sea, 1997-1998. *J Rad. Nucl Chem* 250, 381-384
- Topcuoglu S., K. Guven, C.Kirbasoglu, N.Gungor, S.Unlu, Z.Yilmaz. 2001. Heavy Metals in marine algae from Sile in the Black Sea *Bull. Env. Contam. Toxicol.*, 67, 288-294
- Topcuoglu S., C.Kirbasoglulu, N.Gungor. 2002. Heavy metals in organisms and sediments from Turkish coast of the Black Sea, 1997-1998. *Environmental International*, 27, 521-526.
- Topcuoglu S., K. Guven, N.Balkis, C.Kirbasoglu, 2003a. Heavy metal monitoring of marine algae from the Turkish coast of the Black Sea, 1998-2000. *Chemosphere*, 52, 1683-1688.
- Topcuoglu S., H.Ergul, A.Baysal, E.Olmez, D.Kut. 2003b. Determination of radionuclide and heavy metal concentrations in biota and sediment samples from Pazar & Rize stations in eastern Black Sea. *Fresenius Environmental Bulletin*, 12, 695-699.
- Topcuoglu S., E. Olmez, C. Kirbasoglu, Y. Yilmaz, N. Saygin. 2004. Heavy metal and radioactivity in biota and sediment samples collected from Unye in the eastern Black Sea. *Proceedings 37<sup>th</sup> CIESM Congress*. Barcelona, Spain, 250 pp.
- Tuncer G, T.Karakas, T.Balkas, C.Gokcay, S.Aygnn, C.Yeteri, G.Tuncel. 1998. Land based sources of pollution along the Black Sea Coast of Turkey: Concentrations and Annual Loads to the Black Sea. *Marine Pollution Bulletin*, 36, 409-423.
- Turk-Culha S., L. Bat, M. Culha, A. Efendioglu, M. Andac, B. Bati. 2007. Heavy metals levels in some fishes and molluscs from Sinop., Peninsula of the Southern Black Sea, Turkey, . Rapport , *38th CIESM Congress Proceedings* , 323 pp.
- Tuzen, M. 2009. Toxic and essential trace elemental content in fish species from the Black Sea, Turkey. *Food and Chemical Toxicology*, 47, 1785-1790.
- Zaitzev Y. 1992. Ecological state of the Black Sea shelf zone, Ukrainian coast. Review, *Hydrobiol, Journal*, 28 (4), 36.



## **Environmental Contamination**

Edited by Dr. Jatin Srivastava

ISBN 978-953-51-0120-8

Hard cover, 220 pages

**Publisher** InTech

**Published online** 29, February, 2012

**Published in print edition** February, 2012

Nature minimizes the hazards, while man maximizes them. This is not an assumption, but a basic idea of the findings of scientists from all over the world. The last two centuries have witnessed the indiscriminate development and overexploitation of natural resources by man causing alterations and impairment of our own environment. Environmental contamination is the result of the irrational use of resources at the wrong place and at the wrong time. Environmental contamination has changed the lifestyle of people virtually all over the world, and has reduced the extent of life on earth. Today, we are bound to compromises with such environmental conditions, which was not anticipated for the sustenance of humanity and other life forms. Let us find out the problem and its management within this book.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Alexander Strezov (2012). Sustainable Environment – Monitoring of Radionuclide and Heavy Metal Accumulation in Sediments, Algae and Biota in Black Sea Marine Ecosystems, Environmental Contamination, Dr. Jatin Srivastava (Ed.), ISBN: 978-953-51-0120-8, InTech, Available from:  
<http://www.intechopen.com/books/environmental-contamination/sustainable-environment-monitoring-of-radionuclide-and-heavy-metal-accumulation-in-sediments-algae-a>

**INTECH**  
open science | open minds

#### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

#### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen