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Cesium and strontium in Black Sea macroalgae

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ABSTRACT

The trace level of metals and particularly radioactive ones should be monitored to evaluate the transfer along the trophic chain, assess the risk for biota and can be used for global changes assessment. Plants respond rapidly to all changes in the ecosystem conditions and are widely used as indicators and predictors for changes in hydrology and geology. In this work we represent our successful development and applications of a methodology for monitoring of stable and radioactive strontium and cesium in marine biota (Black Sea algae's). In case of radioactive release they are of high interest. We use ED-XRF, gamma spectrometers and LSC instrumentation and only 0.25 g sample. Obtained results are compared with those of other authors in same regions. The novelty is the connection between the radioactive isotopes and their stable elements in algae in time and space scale. All our samples were collected from Bulgarian Black Sea coast.

1. Introduction

Black Sea is a semi-enclosed basin, were water exchange with Mediterranean Sea through the Bosphorus straits via two-layer exchange asymmetric transport (Staneva et al., 1999). Black Sea coastal zone is influenced by riverine outflow, in particular at the northwest part, from the water discharge of Danube, Dnieper, Dniester Rivers. The coastal zone agricultural and industrial activities and treatment stations (Dineva, 2011) also influence the ecosystem. Industrial wastes, organic fertilizers, domestic solid wastes, anthropogenic radionuclides, chemicals used in the treatments plants etc. are the main components of the pollution.

The increase in concentrations of anthropogenic radionuclides in marine ecosystems can have an impact on growth and development of marine biota. It is a prerequisite for the occurrence of serious damages and changes in the structure of ecological communities. The reason is their double toxicity, radioactive and chemical.

Radionuclides rapidly redistributed and accumulate in various components such as bottom sediments, benthic and other organisms in such polluted waters and can be consumed by plankton, accumulated by algae and transferred to higher developed organisms via the food chain. This provides different modifications/mutations on cellular and molecular level that affect the vital processes and functions in organisms, like formation of tumors and different chromosome alterations (Bolognesi et al., 2004). Of particular interest is the behavior of certain long-lived nuclides such as ^{137}Cs and ^{90}Sr due to their high toxicity to living organisms. The change in the radiation situation of the Black Sea after the Chernobyl accident resulted in multiple studies of radionuclide accumulation processes in biota (Egorov et al., 1999, 2001; Topchuoglu, 2001; Gulin et al., 2002). The Black Sea received a great amount of radionuclide impact due to its geographical position as the closest marine basing to the accident site.

The ^{137}Cs and ^{90}Sr content in the Black Sea environment significantly increased after the Chernobyl accident (Kulebakina et al., 1988; Bologa et al., 1998; Eremeev et al., 1995). In 1991 Portakal et al. found 30 times higher levels of ^{137}Cs in comparison with the quantity (0.7–16.6 mBq l^{-1}) according to Vaculovskiy et al. (1977) before the Chernobyl accident.

Most of the investigations of chemical pollutants and radioactive contaminant in Black Sea are related to the evaluation their distribution in the water, accumulation capacity of bottom sediments and estimation of accumulation factors of some widely spread in the Black Sea macroalgae species (Bologa et al., 1998; Popa, 1999; Egorov et al., 2001; Gulin et al., 2002; Topcuoglu et al., 2004).

Marine macrophytes, being one of the primary stages in the trophic chain, play a major role in marine ecosystems (Kilgore et al.,

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1993). They have the ability to accumulate in their tissues high concentrations of potential pollutant in the water column. Algae interact with the environment through processes that include chemical bio-concentration, excretion, organic matter production and decomposition (Carpenter and Lodge, 1986). This ability is affected by contact time, contaminant concentration, pH, salinity, regeneration capabilities, algal biomass etc. They are particularly suitable for assessment of marine contamination as indicators for the living status of marine ecosystems and predictors for changes in hydrology and geology (Försberg et al., 1988; Phillips, 1990). The establishment of the metal species (radionuclide and stable isotopes) content in macroalgae tissues allows the assessment of the quantity of bio-available pollutants and gives information about their effect on different algae species. This eliminates the need for complex studies of the chemical form of some contaminants in the environment.

The most commonly studied Black Sea algae species are red algae – *Ceramium rubrum*, green algae – *Ulva lactuca*, *Ulva rigida*, *Enteromorpha intestinalis* and brown algae – *Cystoseira barbata* and *Cystoseira crinita* (Güven et al., 2007; Topcuoğlu, 2005, 2010).

The uptake, accumulation and toxicity of elements that we study are strongly dependent on the exposure conditions and vary within and among species. The effects of physical, chemical and biological factors affecting the uptake, accumulation and toxicity of the metals can explain these differences (Tessier and Turner, 1995; Newman et al., 2001).

The long term observation of Black Sea macroalgae indicates a decreasing trend of macroalgae species in general and of oligosaprobic species in particular in response to increased level of eutrophication (Dimitrova et al., 1998). The total loss of macrophytes accounted for more than half as compared to the first half of the last century, whereas green *Chlorophyta* species increased by 50% during the same period. The mass development of *Chlorophyta* and red *Rhodophyta* species is an indication of increased organic content and nutrients (BSC, 2008). During last decades there is the massive disappearance of the perennial brown alga *Cyst. barbata* on the Black Sea shelf (Bologa and Sava, 2012). A direct relation exists among the nutrient loading, increasing phytoplankton grown, restricted light penetration and reduction of macroalgae biomass (Hough et al., 1989). Another important factor that leads to a reduction of macroalgae in the Black Sea is anthropogenic impacts on coastal ecosystems.

The aim of this study is to present a methodology for radiochemical separation of trace concentrations of radioactive strontium and cesium in small biota samples, to give information about accumulation capacity of six widely distributed Black Sea macroalgae species and to obtain data about the Sr and Cs content in ecosystems along the Bulgarian coastal zone.

2. Experimental

2.1. Sampling

The collected macroalgae species are three green (*Chlorophyta*) – *U. rigida*, *Ent. intestinalis*, *Cladophora vagabunda*, two brown (*Phaeophyta*) – *Cyst. barbata*, *Cyst. crinita* and one red (*Rhodophyta*) – *Cer. rubrum*.

All these species belong to the group of attached macroalgae, having the annual development maximum in spring and summer. In this regard, sampling was conducted in spring-summer period when all studied species were at its maximum stage of development.

All the plants were collected in the period 2000–2010. Sampling sites were selected to cover the whole Bulgarian coastal line – northern regions Shabla and Tuzlata, central regions Ravda and Burgas and southern regions Ahtopol and Rezovo (Fig. 1).

2.2. Preliminary sample preparation

Macroalgae were collected by hand at depths of 0–2 m. Samples were washed with sea water to remove adherent sand and attached marine benthic organisms. After careful separation and species packing in pre-cleaned plastic bags, macroalgae were frozen and transported to the laboratory where all samples were washed with double distilled water, dried (80 °C) and homogenized. About 0.25 g biota samples were mineralized (HNO_3, $HClO_4$), filtrated and evaporated to dryness. Then samples were dissolved in distilled water. After that Ra isotopes were separated by self-deposition on manganese disks (pH = 7, 24 h deposition) and calcium phosphate precipitation techniques were applied to prepare samples for radiochemical determination of ^{90}Sr.

Another part of dried algae samples was also packed for ^{137}Cs determination by gamma spectrometry.

2.3. Calcium phosphate precipitation technique

After acidification to pH 2 (with HNO_3) in each sample were added yield tracers (for U and Th and stable lead) as well as carrier $Sr(NO_3)_2$ for chemical recovery assessment. After that to each sample were added 1.25 mol l^{-1} $Ca(NO_3)_2$, beakers were covered with watch glasses and placed on a hot plate. Once the samples boiled, the watch glasses were taken off and in each samples were added 2–3 drops phenolphthalein indicator, 3.2 mol l^{-1} $(NH_4)_2HPO_4$ solution and enough concentrated NH_4OH to reach the phenolphthalein end point and form $Ca_3(PO_4)_2$ precipitate. Samples were heated about 30 min. The formed precipitates were allowed to settle until solution, centrifuged and separated. Precipitates were dissolved with concentrated HNO_3, evaporated to dryness, redissolved in 3 mol l^{-1} HNO_3 and U and Th were separated by UTEVA – Resin® (Eichrom Industries, USA).

2.4. Radiochemical separation of ^{90}Sr

The radioactive strontium was separated with Sr – Resin® (Eichrom Industries, USA), (Fig. 2). This technique was applied to combine the Sr separation to the existing in our laboratory follow-up extraction of the Po, U, Th, Pb and Ra isotopes (Tosheva et al., 2006).

The precipitates were allowed to settle, centrifuged, dissolved in 3 M HNO_3 and pass via UTEVA resin (Eichrom Industries, USA) to remove Th and U isotopes. The first solution fraction containing lead and strontium isotopes was loaded into the Sr – Resin® (Eichrom Industries, USA) column to determine ^{90}Sr.

A set with "blank" and "standards" samples were prepared and analyzed to assess the precisions of radiochemical procedure for Sr separation each time prior algae sample preparation. The results for blanks varied between 0.010 and 0.049 Bq sample^{-1}. The standards give also stable values with uncertainties lower than 10%. The standards are 0.08, 0.5 and 0.9 Bq (progressive increasing standards). The obtained values during the all period of investigations vary between 0.073 and 0.090 Bq for the standard 0.08 Bq, between 0.474 and 0.526 Bq for standard 0.5 Bq and between 0.872 and 0.921 Bq. for standard 0.090 Bq.

Strontium isotope was stripped with 0.05 mol l^{-1} HNO_3 and ^{90}Sr activity was measured by LSC (Guardian, Perkin–Elmer Inc. analyzer). Chemical yield for this adapted procedure was estimate gravimetrically via $Sr(NO_3)_2$.