Journal of Environmental Radioactivity 134 (2014) 21–26

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

^{40}K in the Black Sea: a proxy to estimate biogenic sedimentation

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A R T I C L E I N F O

Article history:
Received 20 September 2013
Received in revised form
7 February 2014
Accepted 18 February 2014
Available online 14 March 2014

Keywords:
^{40}K
Radiotracers
Biosedimentation
Sevastopol Bay
Black Sea

A B S T R A C T

An approach to estimate the rate of biogenic sedimentation in the Black Sea using the naturally occurring radionuclide ^{40}K has been considered. It allows assessment of the contribution of suspended matter of biological origin to the overall sediment accumulation in the Black Sea coastal, shelf and deep-water areas. Based upon this method, a relationship between the biogenic fraction of the seabed sediments and the water depth has been established with a view to differentiating the contributions of allochthonous and autochthonous suspended matter to the sedimentation rate. Overall, ^{40}K can be considered as an easily applicable proxy to assess sedimentation rate of biogenic fraction of particulate matter in marine environments.

1. Introduction

Sedimentation plays a key role in the transport of suspended matter in the sea, and it governs the self-purification of marine environments against the particle-reactive pollutants, which are buried ultimately in the seabed sediments. Two main sources of sediments can be distinguished, i.e. allochthonous (brought in externally from the land via rivers and wind) and autochthonous (freshly produced in seawater). Allochthonous sediments are terrigenous materials, both lithogenic and biogenic. Autochthonous sediments originate from the complex mixture of biogenic compounds generated in seawater, mostly plankton remains and fecal pellets, but also authigenic (hydrogenous) substances such as ferromanganese or phosphorite nodules which are created *in situ* from the precipitation of dissolved chemicals (e.g., Robert, 2008).

Sedimentation of autochthonous biogenic matter, comprising particulate organic carbon and siliceous or carbonaceous shells of plankton microorganisms, is of particular interest as it may prevail in the sediments accumulated on the seafloor, and is more sensitive to climate change and anthropogenic pressure, in particular eutrophication. Therefore, estimation of the transport and accumulation of biogenic material in the sea is critical for understanding the processes affecting the cycles of a wide range of particle active elements, including carbon, nutrients and trace elements, as well as persistent pollutants (e.g., Brunskill, 2009; Yücel et al., 2012).

There exist several methods to determine the percentage of biogenic component in marine sediments. For example, it may be computed directly as the sum of the organic matter, calcium carbonate ($CaCO_3$) and opal (SiO_2) relative to the total mass of the sediments, or indirectly – as the difference between the total mass and the sum of the lithogenic components (e.g., Gavshin et al., 1988; Brumsack, 2006; Löwemark et al., 2011). In the latter case, the lithogenic fraction can be assessed from the contents of Al, which is abundant, little active biologically and redox insensitive component of the sand, silt and clay, or from the depleted carbon isotopic signature implying that the settling particles are continentally derived (e.g., Hay et al., 1991; Brumsack, 2006; Martinez et al., 2007; Löwemark et al., 2011). Among radioactive isotopes, the naturally occurring long-lived ^{40}K (half-life = 1.248×10^9 yr) is considered as one of the classic radionuclides of lithogenic origin (e.g., Gavshin et al., 1988), and may be applicable as a tool to differentiate between the contribution of lithogenic and biogenic fractions in marine sediments.

Here we examine this assumption regarding the Black Sea, which is an excellent water body to study sedimentation processes because it is a semi-enclosed marine basin having a very large drainage area (~5 times the sea area), a wide continental shelf in its northwestern sector (~25% of the total area of the sea) and a deep-water central basin (max depth = 2212 m) characterized by permanently anoxic water below ~100 m, minimal bioturbation of the seabed sediments and preservation of organic matter under the

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http://dx.doi.org/10.1016/j.jenvrad.2014.02.011
0265-931X/

reducing conditions (e.g., Murray et al., 2005; Panin, 2009; Polikarpov, 2011, 2012; Yücel et al., 2012). Overall, the Black Sea drainage basin is located between European and Asian continents, covering almost 2.5 million km^2 of territory in six Black Sea countries (Bulgaria, Georgia, Romania, Russia, Turkey, and Ukraine) and 16 countries of Central and Eastern Europe. The northwestern part of Black Sea receives the discharge of the Danube River, the largest river in the basin with a mean water discharge of about 200 km^3 yr^{-1}, and the rivers Dnieper, Southern Bug and Dniester contributing about 65 km^3 yr^{-1} (e.g., Izdar et al., 1987; Panin, 2009).

Extensive lithological studies of the Black Sea have revealed a clear zoning of its seafloor in respect of different types of sedimentation (e.g., Gavshin et al., 1988): in the coastal areas, the sediments are mainly terrigenous and their distribution is controlled by lateral dispersal and deposition, rather than direct vertical settling, while in the deep-water basin, the sediments are primarily biogenic and their thickness is laminated (e.g., Gavshin et al., 1988; Hay et al., 1991), reflecting an annual sedimentation cycle wherein the ratio of plankton fossils (mostly coccolithophorid shells) to terrestrial matter is higher in the summer and autumn, coinciding with periods of unicellular algal blooms (Benli, 1987; Gulin, 2000a,b; Gulin et al., 1995; Hay et al., 1991; Izdar et al., 1987).

The goal of this study is to investigate the distribution of ^{40}K in sediments at different Black Sea locations: from the coastal areas adjacent to river mouths and down to the abyssal plain in the central basin with purpose to assess applicability of this natural radionuclide for differentiation of biogenic and lithogenic types of sedimentation processes occurring in marine environments.

2. Material and methods

The sampling was conducted primarily in the NW Black Sea area (Fig. 1), which is influenced by the runoff of the Danube and Dnieper accounting for 75% of the total river discharge to the basin (e.g., Polikarpov et al., 1992; Panin, 2009). Sediment cores were sampled in front of the Danube delta and the Dnieper-Bug estuary, at the NW shelf-edge, slope and in the western deep-sea basin, which is the area of a quasi-permanent cyclonic gyre (Fig. 1, Table 1). Also, the sediment samples were taken within the Sevastopol outer roadstead, across Sevastopol Bay and in the SE Black Sea area adjacent to the mouth of the Coruh river (Fig. 1, Table 1). In

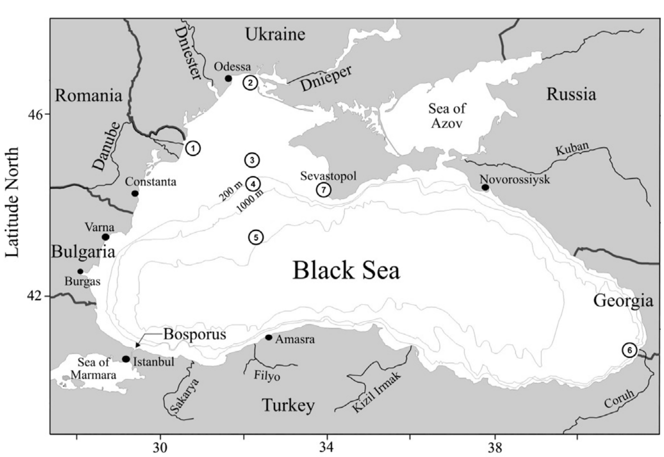

Fig. 1. Location of the sampling sites in the Black Sea. Numbers inside the circles correspond to: 1 – Danube delta front; 2 – Dnieper-Bug estuary front; 3 – NW shelf break; 4 – NW continental slope; 5 – abyssal plain; 6 – Coruh River mouth front; 7 – Sevastopol outer roadstead.

earlier work, these samples were analyzed for the vertical distribution of Chernobyl-derived (^{134,137}Cs, ^{90}Sr, ^{238,239,240}Pu, ^{241}Am) and naturally occurring (^{210}Pb/^{226}Ra, ^{210}Po) radionuclides in order to determine sedimentation rates and for the dating of sediments with the purpose to reconstruct trends of radioactive contamination of the Black Sea (Gulin et al., 1997, 2000a; 2002, 2003; Ketterer et al., 2010; Lazorenko et al., 2009).

Undisturbed sediment cores were recovered with a multiple-corer. The samples were sliced at every 1-cm intervals with an extruder. Wet sediments from each segment were weighed immediately, dried at 40–50 °C and then re-weighed to determine the evaporated water percentage and the porosity. The salinity of the pore water was equated to that measured in the benthic layer at the same station with a portable CTD-instruments Katran-4 (MHI, Ukraine) or SD204 (SAIV, Norway), as described in Schafer et al. (1980). The dried sediments were then ground into a fine powder and compressed into a standard geometry, lids sealed and analyzed for gamma-emitters using the high-purity germanium detectors Canberra-Packard XtRa GX2019 (geometry: coaxial, diameter 53 mm, length 43 mm; resolution: 1.74 keV/1.332 MeV; efficiency: 21.2%) or EG&G ORTEC GMX10P4 (geometry: coaxial, diameter 47.8 mm, length 45.6 mm; resolution: 1.75 keV/1.332 MeV; efficiency: 16.2%). The activity of radionuclides in the sediments was calculated on a salt-free basis. The results of radiometric measurements of ^{40}K concentration in sediments were expressed in the units of mass concentration of the total (radioactive + stable) potassium, gK per kg of the dry sediments, using the value of specific radioactivity of ^{40}K: 1 gK = 30.65 Bq ^{40}K (e.g., Gavshin et al., 1988).

Suspended matter for measurements of particulate ^{40}K was collected on Millipore membrane filters (diameter = 293 mm, nominal pore size = 0.45 μm) from the large-volume (up to 3700 L) water samples taken with an outboard silicone hose and an on-deck high capacity peristaltic pump MasterFlex I/P 7591-5. These samples were collected during the late-spring (end of May 2013) and summer periods in front of the Dnieper-Bug estuary on the NW shelf and in the western deep-water area of the Black Sea. The dried filters were folded to fit the 53 mm diameter counting window and then treated for gamma spectrometry using the abovementioned detectors.

Uncertainties for ^{40}K activity were propagated from the one sigma counting uncertainty, the uncertainty due to background correction and calibration uncertainties. The measurement accuracy was tested in intercomparison runs organized by IAEA (e.g., Sanchez-Cabeza et al., 2008.). The precision of the radiometric measurements was $<$10% at $\pm 1\sigma$. Detection limit was ~0.1 Bq per kg.

3. Results and discussion

Results of our measurements of ^{40}K in the upper 1-cm layer of the Black Sea sediments are given in Table 1. They revealed a gradual decrease in ^{40}K concentration with water depth across the NW continental shelf and down the slope (Fig. 2), beginning from the coastal areas adjacent to the mouths of the Danube and Dnieper rivers. The porosity of surficial sediments at these locations showed, in contrast, a monotonic increase with the water depth (Table 1, Fig. 2) from the lowest value in front of the Danube delta (68%), Dnieper-Bug estuary (67%) and, particularly, Coruh river mouth (47%) to much greater value of porosity (>80%) in the western deep-sea area. Evidently, such trends reflect the decrease in contribution of the coarse-grained ^{40}K-rich lithogenic material to the total mass of the sediments with the increasing distance from the shore, as they become increasingly diluted by the fine-grained, ^{40}K-depleted biogenic matter in the areas remote from the shore, as compared with the coastal sediments. This effect is particularly clear in the deep-water Black Sea basin, where the sediments are