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Distribution and environmental impacts of heavy metals and radioactivity in sediment and seawater samples of the Marmara Sea

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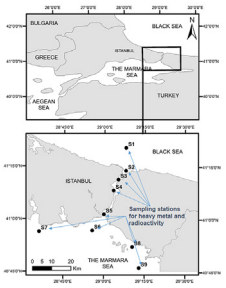
HIGHLIGHTS

- The natural radionuclides and heavy metals in the sea sediments were analyzed.
- The radiological hazard in the sea sediments was reported.
- The total alpha and beta activity concentrations in the sea waters were determined.
- The heavy metal concentrations in some sediments of the Marmara Sea were over the acceptable limits.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the natural and anthropogenic radioactivity levels in the sediment samples collected from the Marmara Sea in Turkey were determined. The average activity concentrations (range) of ^{226}Ra, ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs were found to be 23.8 (13.8–34.2) Bq kg^{-1}, 18.8 (6.4–25.9) Bq kg^{-1}, 23.02 (6.3–31.1) Bq kg^{-1}, 558.6 (378.8–693.6) Bq kg^{-1} and 9.14 (4.8–16.3) Bq kg^{-1}, respectively. Our results showed that the average activity concentrations of ^{226}Ra, ^{238}U and ^{232}Th in the sediment samples were within the acceptable limits; whereas the average activity concentration of ^{40}K in the sediment samples was higher than the worldwide average concentration. The average radium equivalent activity, the average absorbed dose rate and the average external hazard index were calculated as 100.01 Bq kg^{-1}, 48.32 nGy h^{-1} and 0.27, respectively. The average gross alpha and beta activity in the seawater samples were found to be 0.042 Bq L^{-1} and 13.402 Bq L^{-1}, respectively. The gross alpha and beta activity concentrations increased with water depth in the same stations. The average heavy metal concentrations (range) in the sediment samples were 114.6 (21.6–201.7) μg g^{-1} for Cr, 568.2 (190.8–1625.1) μg g^{-1} for Mn, 39.3 (4.9–83.4) μg g^{-1} for Cu, 85.5 (11.0–171.8) μg g^{-1} for Zn, 32.9 (9.1–73.1) μg g^{-1} for Pb and 49.1 (6.8–103.0) μg g^{-1} for Ni. S5 station was heavily polluted by Cr, Cu, Ni and Pb. The results showed that heavy metal enrichment in sediments of the Marmara Sea was widespread.

1. Introduction

Natural radionuclides such as ^{238}U series, ^{232}Th series and ^{40}K are present in various degrees in soil, sediment, water, plants and air (Dugalic et al., 2010; Saç et al., 2012). Distributions of natural

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radionuclides depend on the geological and geographical conditions of each region in the world (Bozkurt et al., 2007; Aközcan, 2012). Man-made or anthropogenic radionuclides; accidents in nuclear reactors and fission products from nuclear testing or industrial activities are pollution sources that could have serious impacts on the marine environment (Papaefthymiou et al., 2013). Natural and anthropogenic radionuclides can be transported by different media over short or long distances and finally deposited in sea sediments (Ergül et al., 2013; El-Taher and Madkour, 2011). The Marmara and Black sea region in Turkey were highly contaminated after the Chernobyl nuclear power plant accident. After the accident, ^{137}Cs concentrations increased greatly in the Marmara Sea due to large inputs from the Black Sea water. Therefore, determining the distribution of natural and anthropogenic radionuclides is necessary for environmental monitoring, nuclear safeguards and nuclear forensic studies.

Natural waters contain both α (e.g., ^{238}U) and β (e.g., ^{40}K) emitters in a wide range of concentrations (Değerlier and Karahan, 2010; Akyıl et al., 2009). Levels of natural radionuclides in seawater may be increased as a result of human activities (Ehmann and Vance, 1991). Measurements of gross alpha and beta activities in seawater provide essential information about radioactivity that could present a risk to human health. (Al-Amir et al., 2012; Turhan et al., 2013).

Toxic pollutants, such as heavy metals have been dramatically increased as a result of urbanization, industrial and agricultural activities (Mansour et al., 2013) although these metals are natural constituents of the Earth's crust and are present in all ecosystems (Uluturhan et al., 2011). Finally, heavy metals can be deposited in sea sediments. Therefore, it is necessary to determine the distribution and pollution degree of heavy metal in sediments.

The scope of the present study is (1) to determine the levels of natural and anthropogenic radionuclides (^{226}Ra, ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs) in sea sediments; (2) to investigate six heavy metals (Cr, Mn, Cu, Zn, Pb and Ni) in sea sediments; (3) to assess total alpha and beta activity concentrations in seawater; (4) to compare the present results with previous studies.

2. Materials and methods

2.1. Study area

Istanbul located along the coasts of the Marmara Sea and the Istanbul Strait (Bosphorus) hosts 15% of the population and 30% of industrial activities of Turkey. At the same time, the Istanbul is the largest contributor of pollution in the Marmara region (Okuş et al., 2008). The Marmara Sea is important in terms of affecting the human health, ecosystems and the fishing potentials. The Sea has 280 km long, 80 km wide and a maximum depth reaching 1.370 m. The sea covers a surface area of approximately 11.350 km^2 dividing Turkey's Asian and European parts. The Sea of Marmara together with Bosphorus and Dardanelle straits is an inner sea between the Black Sea and the Mediterranean Sea (Fig. 1). The Sea is subjected to pollution due to industrial waste, municipal waste disposal and high volume of ships. 25% of the wastewater of the total city population is discharged via creeks into the Marmara Sea and Bosphorus coastal waters. (Okuş et al., 2008). Furthermore, the contaminants discharge into the Marmara Sea by a surface current from the Black Sea and a deep current from the Mediterranean Sea (Topcuoğlu et al., 2004). The Black Sea and the Marmara Sea were highly contaminated after the Chernobyl nuclear power plant accident. As a result of these factors, the pollution levels in the Marmara Sea have increased in the recent years.

2.2. Analyses of ^{238}U, ^{232}Th, ^{40}K and ^{137}Cs in the sediment samples

The sediment samples were taken from different depths at nine stations from the Marmara Sea. The all samples were collected using a Van Veen Grab sampler on board the R/V Arar of Istanbul University in January 2010 and were taken at water depths ranging between 50 and 92 m from sea level. The coordinates were determined by using GPS (Geographical Position System). The locations of sampling are given in Fig. 1. After collection, the samples were placed in labeled plastic bags and kept frozen until analyses. In the laboratory, the collected sediment samples were oven dried for 24 h at 105 °C. Then, the samples were sieved through a 0.2 mm porous sieve. The dried and sieved samples were transferred to 1000 ml airtight containers and stored for a period of 1 month to reach secular equilibrium between ^{238}U and ^{232}Th and their progeny. Each sample as well as the background, was counted using p-type a coaxial HPGe detector with 50% relative efficiency and an energy resolution of 1.8 keV at 1332.5 keV of ^{60}Co. The absolute efficiency calibration of system was carried out using a solid nuclide mixture of gamma reference materials sealed in standard Marinelli beakers with an active volume of 1000 ml and IAEA reference materials RGU-1(U-ore), RGTh-1(Th-ore) and RGK-1 (K_2SO_4). The counting time for each sample was 50.000 s. Background measurements were subtracted in order to get net counts for the sample. The activity concentrations of ^{238}U and ^{232}Th were calculated by assuming secular equilibrium with their decay products. The peaks at the 186.0 keV (^{226}Ra), the 351.9 keV (^{214}Pb) and the 609.3 keV (^{214}Bi) were used to determine the activity concentration of ^{238}U. The peaks at the 911.2 keV (^{228}Ac) and the 583.2 keV (^{208}Tl) were used to determine the activity concentration of ^{232}Th. The activity concentration of ^{40}K was directly measured from gamma-ray line at 1460.8 keV. The 661.7 keV gamma transition was used to determine the ^{137}Cs activity.

In this study, the results were evaluated in terms of the radiation hazard by means of the Ra- equivalent activity (Ra_{eq}) and external hazard index (H_{ex}).

Radium equivalent activity (Ra_{eq}) is an index defined according to the estimation that 1 Bq kg^{-1} of ^{226}Ra, 0.7 Bq kg^{-1} of ^{232}Th and 13 Bq kg^{-1} of ^{40}K produce the same γ-ray dose. The Ra_{eq} can be calculated through the following relation (Agbalagba and Onoja, 2011):

$$Ra_{eq} = C_{Ra} + 1.43\ C_{Th} + 0.077\ C_K \quad (1)$$

The external terrestrial gamma dose rate (D) at 1 m above the ground (in nGy h^{-1} by Bq kg^{-1}) is given as;

$$D\ (nGy\ h^{-1}) = 0.462\ C_{Ra} + 0.604\ C_{Th} + 0.0417\ C_K \quad (2)$$

The external hazard index (H_{ex}) is obtained by;

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \leq 1 \quad (3)$$

The maximum value of H_{ex} equal to unity corresponds to the upper limit of Ra_{eq} (370 Bq kg^{-1}) (Beretka and Mathew, 1985).

In equations (1)–(3), C_{Ra}, C_{Th} and C_K are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively.

2.3. The gross alpha and beta analyses in the seawater samples

A total of 18 seawater samples were collected from the Marmara Sea in January 2010. The seawater samples were taken from two layers, namely surface and bottom layer. The samples were collected from nine stations on board the R/V Arar of Istanbul University. Sampling was carried out with a Rosette sampler