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Determination of radioactivity levels and heavy metal concentrations in seawater, sediment and anchovy (*Engraulis encrasicolus*) from the Black Sea in Rize, Turkey

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ABSTRACT

Seawater, sediment and fish (anchovy) samples consumed in the Rize province of the Eastern Black Sea region of Turkey were collected from five different stations. The radioactivity levels (^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs) were determined in all the samples using a high-purity germanium detector. While ^{226}Ra, ^{232}Th and ^{40}K radionuclides were detected in all samples, the radionuclide concentration of ^{137}Cs, except for the sediment samples (mean activity is 9 ± 1.4 Bq kg^{-1}), was not detected for the seawater and fish samples. The total annual effective dose rates from the ingestion of these radionuclides for fish were calculated using the measured activity concentrations in radionuclides and their ingested dose conversion factor. Also, the concentrations of some heavy metals in all the samples were determined. The activity and heavy metal concentration values that were determined for the seawater, sediment and fish samples were compared among the locations themselves and with literature values.

Fish is one of the most important parts of the human diet. *Engraulis encrasicolus* (Linneaus, 1758) is known as the Black Sea anchovy in Turkey. This small marine pelagic species always dominates the fishery landings of Turkey. In 2009 it was the most commonly caught fish species with a total of 204.699 tons; 80.78% of the total catch was landed from the Eastern Black Sea region (TUIK, 2010). Per capita consumption of seafood in Turkey is about 8 kg. Larger cities and especially the Black Sea region increase the mean of fresh fish consumption. In the Eastern Black Sea, the anchovy is known as the "national meal," and its per capita consumption is about 25 kg (Knudsen, 2009); this amount is more than the EU average (FAO, 2007).

Radionuclide (natural and artificial) and heavy metal pollutants in the marine environment have been recognised as a serious environmental concern (Pappa et al., 2016). Radioactive contamination, also called radiological contamination, constitutes radioactive substances on surfaces or within solids, liquids or gases (including the human body), where their presence is unintended or undesirable, or the process giving rise to their presence in such places (IAEA, 2007). Pathways that could supply significant amounts of natural radionuclides in the marine environment are: river runoff (effluent discharge to rivers and from coastal locations), direct groundwater discharge, and windblown particles (Cochran, 1992; Dunk et al., 2002; Linsley et al., 2004). Radioactive substances have been introduced to the Black Sea in small quantities from nuclear power plants, and in more significant amounts after the nuclear power plant disaster in Chernobyl in 1986. Marine ecosystems were seriously affected by the deposited material from the accident; one of the nearest seas to the reactor is the Black Sea (Baltas et al., 2016). The physical processes of water movement and mixing, marine chemistry, marine sediments, accumulation and redistribution of radionuclides by marine organisms, all affect the fate of radionuclide transport (Al-Qaradawi et al., 2015).

There has been recent worldwide concern about the detection of radionuclides and heavy metals in sediment, water and fish, and in concentrations that exceed limits set by some health authorities for human consumption. Heavy metals are discharged into the marine environment through urban discharge, agriculture, mining, combustion and industrial discharge, and can remain in solution or in suspension and precipitate to the bottom, or be taken up by organisms, thus creating a potential source of heavy metal pollution in the aquatic environment (Bilandzic et al., 2011). A large amount of heavy metal has always been present in seawater and sediment, from which it may have been concentrated during its passage through the marine food chain; the high concentrations noted in some fish may have resulted from the discharge of industrial waste containing heavy metals to the marine environment in particular areas. It is known that fish may accumulate heavy metals through direct absorption, or via their food chain, and pass them to human beings, by consumption, causing chronic or acute diseases (Calza et al., 2004).

Other studies have focused on radioactivity levels and heavy metal concentrations in fish species (Korkmaz Görür et al., 2012), heavy metal concentrations in marine organisms and sediments (Topcuoğlu et al., 2002) and radioactivity levels in sea water, sediment and mussel samples (Baltas et al., 2016) at the Turkish Black Sea coast. The need for further studies is made all the more important given the levels of radioactivity and heavy metals in the marine environment. The aim of this

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study is to determine the radioactivity levels and heavy metal concentrations in seawater, sediment and fish samples collected from the Black Sea in Rize.

A location map (Iyidere 41°00′N 40°23′E, Derepazari 41°00′N 40°25′E, Rize Center 41°01′N 40°31′E, Rize Harbor 41°01′N 40°31′E and Cayeli 41°05′N 40°43′E) showing where the seawater, sediment and fish samples were collected in 2009 is shown in Fig. 1. The seawater samples were taken from the same stations as the sediment. All the samples were collected in 12 L capacity linear polypropylene bottles. The bottles were cleaned using a modified procedure (Laxen and Harrison, 1981). The temperatures and pH values of the seawater samples collected from this area were measured as 17–19.5 °C and 7.5–8.2, respectively. Some information related to the seawater sample is compared to literature values in Table 1.

The sea sediment samples (5 cm depth), 0.5–1 kg each, were collected from the sea shore in the locations and were packed in a nylon made of non-radioactive material, sealed and labelled to avoid mix up and contaminations.

The fish samples were captured from these locations. A total of 15 samples was collected in all from each of the five sample locations equally along the Rize shore.

Detailed sample preparation procedures for seawater and sediment samples have been presented elsewhere for gamma activity measurements (Baltas et al., 2016). Also, the collected fish samples were homogenised and ashed in a temperature-controlled furnace at 470 °C for 24 h to remove moisture, and sieved through a 2 mm mesh. The ashed samples were sealed in cylindrical polyethylene plastic containers of 100 mL volume.

Before the gamma measurements, all the containers were kept sealed for four weeks in order to reach the equilibrium of ^{226}Ra and its short-lived progeny. Gamma spectrometry measurements were conducted with a high-resolution HPGe gamma-ray spectrometry system. A detailed description of the detector characteristics, system operation and calibration has been presented elsewhere (Baltas et al., 2014).

The gamma-ray transitions of energies 351.9 keV (^{214}Pb) and 609.3 keV (^{214}Bi) were used to determine the activity concentration of the ^{226}Ra series. The gamma-ray lines at 911.1 keV (^{228}Ac) and 583.1 keV (^{208}Tl) were used to determine the activity concentration of the ^{232}Th series. The activity concentrations of ^{40}K and ^{137}Cs were measured directly through gamma line emission at 1460.8 and 661.6 keV, respectively. The activity values were given as Bq kg^{-1} in dry weight for sediment and fish, and Bq L^{-1} for the seawater samples.

Table 1
Comparison of seawater quality parameters with published results.

Parameter	Literature	Present study
pH	6.0–9.0[a]	7.50–8.21
Suspended solids (mg L^{-1})	30[a]	0.199
Temperature (°C)	8–24[b]	17–19.5
Salinity (‰)	13–19.5[b]	18

[a] Ordinance (2004).
[b] Çevik et al. (2008).

The activity concentrations for ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in the measured samples were computed using the following equation:

$$C = \frac{N}{\varepsilon \cdot P_\gamma \cdot T \cdot m} \quad \left(\text{Bq kg}^{-1}\right) \tag{1}$$

where N is the net counting rate of the gamma ray, ε is the photo peak efficiency of the used detector, Pγ is the absolute transition of gamma decay, t is the counting time in seconds, and m is the mass of the sample in kg or the volume of the sample in litres.

The minimum detectable activity (MDA) of the present measurement system was calculated as follows (Currie, 1968):

$$\text{MDA} = \frac{\sigma\sqrt{B}}{\varepsilon \cdot P_\gamma \cdot T \cdot m} \tag{2}$$

where MDA is in Bq kg^{-1}, σ is the statistical coverage factor, which is equal to 1.645 (confidence level 95%), and B is the background for the region of interest of a certain radionuclide. The MDA for the radionuclides of interest was calculated as 0.16 Bq kg^{-1} for ^{226}Ra, 0.24 Bq kg^{-1} for ^{232}Th, 0.02 Bq kg^{-1} for ^{137}Cs, and 1.69 Bq kg^{-1} for ^{40}K. The activity concentration of ^{226}Ra, ^{232}Th, ^{137}Cs and ^{40}K is given as the certified value for certified reference material (IAEA-447) and is equal to 25.04, 37.3, 371.11 and 550 Bq kg^{-1}, respectively. The activity concentrations of ^{226}Ra, ^{232}Th, ^{137}Cs and ^{40}K for the counting system were calculated to be 23.96, 35.7, 362.55 and 521 Bq kg^{-1}, respectively.

The human body is exposed to various types of radiation that are emitted from sources in the environment at any moment. Because of the harmful biological effects of radiation, dose estimation is required. The annual effective dose to humans from fish samples was estimated. The annual fish (anchovy) consumption value of a person is 5.67 kg in Turkey (TUIK, 2006). A dose conversion factor (Sv Bq^{-1}) can then be

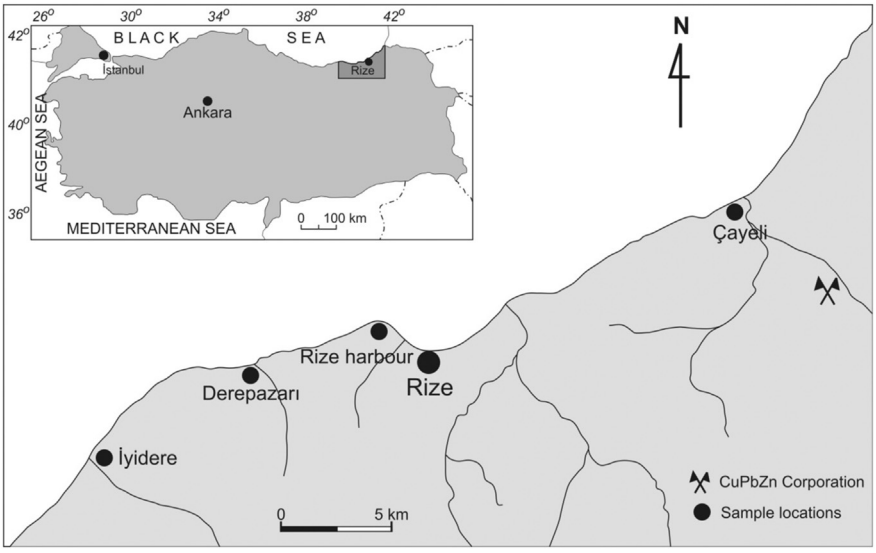

Fig. 1. Location of sampling sites indicating the Eastern Black Sea region of Turkey.

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