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Determination of radioactivity and heavy metals of Bakirçay river in Western Turkey

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HIGHLIGHTS

- Radioactive and heavy metal contaminations of Bakırçay River were determined in sediments and water samples.
- Pollution potentials of these contaminations and their distributions throughout the river were investigated.
- Radium concentrations levels in the river water varied under 0.36 Bq/L.
- Obtained data were evaluated statistically.

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ABSTRACT

In this study, radioactive and heavy metal contaminations in sediments and waters of Bakırçay River in Western Turkey were investigated to determine their pollution potential. The radium concentrations in the water samples were measured using the collector-chamber method. The radioactivities of ^{40}K, ^{226}Ra and ^{232}Th in sediments and soils were found to be 45.30 to 839.19 Bq kg^{-1}, 35.26 to 160.57 Bq kg^{-1} and 1.86 to 131.49 Bq kg^{-1}, respectively. The activity of ^{226}Ra in the water samples ranged from 0.09 to 0.36 Bq/L. To determine the radiological hazard of natural radioactivity in the samples, the external terrestrial gamma dose rate in air (n Gyh^{-1}), annual effective dose rate (mSv y^{-1}), radium equivalent activity (Bq kg^{-1}) were calculated and compared with internationally recommended values.

1. Introduction

Natural radionuclides such as the uranium-238 series and thorium-232 series and potassium-40 are present everywhere in the world (Bolca et al., 2007). ^{226}Ra, ^{228}Ra and ^{40}K are of most concern due to their high solubility and mobility. The knowledge of the activities and distributions of these radionuclides are of interest since it provides useful information in the monitoring of environmental contaminations (Yii et al., 2009).

Radium radionuclides are of radiological importance to human; water and aquatic lives and plants containing radium radioisotopes taken up from river soil and sediment. Rivers transport particulate materials and dissolved species from land to sea. Qualitative and quantitative knowledge of the natural radioactivity in river and coastal ecosystems is important in itself since it concerns with the most abundant radionuclide (^{40}K) and other radionuclides liable to cause radiation protection problems under extreme conditions (Chowdhury et al., 1999).

Trace contaminants in coastal marine environments and especially in estuarine systems are important since these areas are biologically productive and receive considerable pollutant inputs from land-based sources via river runoff and sewage outfalls (Maskaoui et al., 2002).

The interactions between rivers and seawaters, which take place in estuaries, are very complex. Thus, the trace element inputs from rivers to the sea affect salinity produced in the mixing area of the estuary (Martinez-Aguirre and García-León, 1994).

The length of Bakırçay River, which is the study region, is about 129 km and there are three important branch of this river. Its first branch originates from mountains in the northeast part of Kırkağaç town and it is connected to Bakırçay River from the north of Soma town. Its second branch, which is born from mountains in Savaştepe region, is Yarcılı River. Its third branch is born from Madra Mountain. These three branches are connected together in the middle of the catchment (Ortabuk, 2007). In this study, the areas between Soma and Çandarlı along the river were sampled.

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This work seeks to determine the levels of radioactivity and heavy metal elements in the Bakırçay River, which arises in Balıkesir and flows through Manisa–Soma–Kınık and joins to Aegean Sea in Çandarlı.

2. Materials and methods

2.1. Sample collection

Samples were collected from 25 sites on the Bakırçay River during the dry season, from May 2007 to August 2007. River sediments were taken from 1 to 10 m distance from the river side. Three samples from each site were taken, each one is about 1 kg of wet weight, placed in plastic bags and transported to the laboratory. Sediment samples were dried in an oven at about 105 °C for 3 days, pulverized, weighed and packed into cylindrical screw-cap plastic containers and sealed. Water samples were collected in 500 mL polyethylene bottles. Chemical parameters such as Cd, Cr, Cu, Fe, Ni, Mn and Zn of river water were measured by using ICP-OES in laboratory.

2.2. ^{226}Ra analyses in waters

The levels of radium in the water were analyzed using the collector-chamber method in the laboratory (Kumru, 1992; Erees et al., 2006, 2007). Samples of 100 mL water were collected from study fields. All samples were transferred to radon bubblers, purged and sealed, flooded with pressurized aged air for 20 min and stored for 7 days (Fig. 1). The radium content was calculated from the radon that was generated during the storage time. Alpha disintegrations were then directly measured by an alpha scintillation counter system (Eberline model SAC-4). The counting time was 50 min for each sample. The collector chamber was calibrated with reference radium standards (Sac, 1994).

2.3. Analyses of ^{226}Ra, ^{232}Th and ^{40}K in sediment and soil samples

Homogenized samples (100 g for sediment) were sealed in polyethylene beakers. All samples were stored for 40 days to attain secular equilibrium between ^{226}Ra and its short-lived decay products. The activity concentrations of the natural radionuclides; ^{226}Ra, ^{232}Th and ^{40}K of the sediment samples were determined using a NaI(Tl) gamma-ray spectrometer system (Tennelec 3 × 3" well-type). The ^{226}Ra activity determination was based on 1.76 MeV gamma rays from ^{214}Bi. The activity of ^{232}Th was determined by the 2.62 MeV gamma rays from ^{208}Tl. The activity of ^{40}K was determined through its 1.46 MeV gamma rays (Bolca et al., 2007). Each measurement is performed with a counting time of 10,000 s.

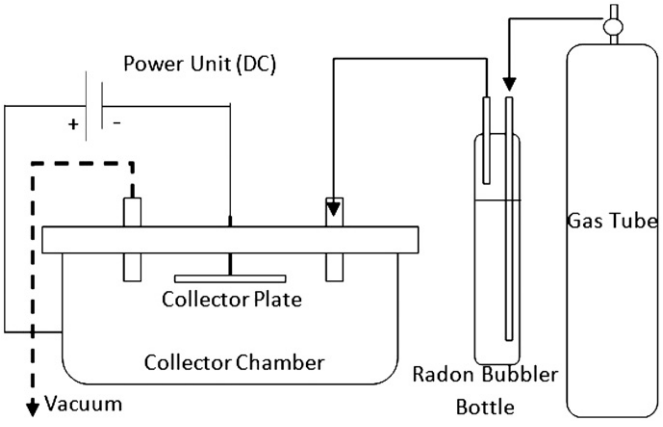

Fig. 1. Collector method to measure radium content in the waters.

2.4. Gamma radiation dose calculations

The external terrestrial gamma dose rate in air at a height of about 1 m above the ground was calculated using the following formula (UNSCEAR, 2000; Wang and Lu, 2007; Camgöz and Yaprak, 2009):

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

where C_{Ra}, C_{Th}, and C_{K} are the concentrations of radium, thorium, and potassium, respectively. The annual effective dose rate given by UNSCEAR was calculated from the equation:

$$\text{Effective dose rate (m Svy}^{-1}) = D\ (\mathrm{nGy\ h^{-1}}) \times 8760(\mathrm{hy^{-1}}) \times 0.2 \times 0.7(\mathrm{Sv\ Gy^{-1}}) \times 10^{-6} \quad (2)$$

$\mathrm{Ra_{eq}}$ is 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 and it is calculated through the following relation:

$$\mathrm{Ra_{eq}} = C_{\mathrm{Ra}} + 1.43C_{\mathrm{Th}} + 0.07C_{\mathrm{K}} \quad (3)$$

In this equation the C_{Ra}, C_{Th} and C_{K} are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in Bq kg^{-1}, respectively.

2.5. Heavy metal analyses in sediment and water samples

A PerkinElmer Optima 2000 DV ICP-OES instrument was used to determine the total element concentrations in sediment and water samples. For calibration, multi-element standard solution (Merck) containing all the metals between 20 μg mL^{-1} to 100 μg mL^{-1} of concentrations were prepared and measured. Each element was measured based on the wavelengths: Cd (214.438 and 226.502 nm), Cr (276.654 and 283.563 nm), Cu (324.754 and 327.396 nm), Fe (238.207 and 259.940 nm), Mn (257.610 and 259.370 nm), Ni (217.467 and 231.604 nm), Pb (220.353 and 261.418 nm) and Zn (231.856 and 334.502 nm).

3. Results and discussion

3.1. Radioactivity and heavy metal levels of Bakırçay River

The natural radioactivity of soil and sediment samples was measured using NaI(Tl) gamma-ray spectrometry. The environmental gamma background at the laboratory site determined with an empty PVC beaker was subtracted from the measured gamma-ray spectrum of each sample. Fig. 2 presents activities obtained from gamma spectrometric measurements for soil samples for ^{226}Ra activities ranged from 19.50 to 250.49 Bq/kg with average value of

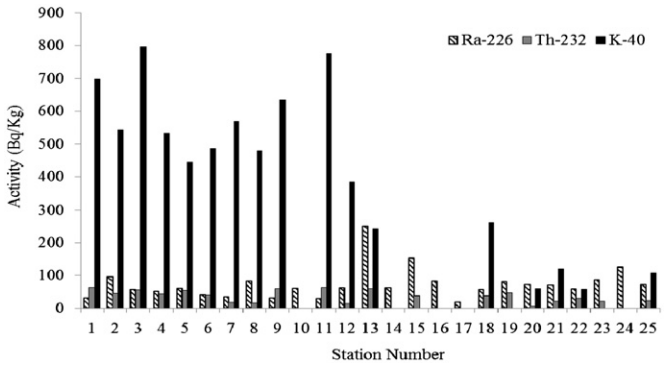

Fig. 2. ^{226}Ra, ^{232}Th and ^{40}K activity concentrations of soil samples.

74.39 Bq/kg and for ^{232}Th and ^{40}K, concentrations ranged from ND (Non-detectable) to 64.67 Bq/kg and ND to 796.56 Bq/kg with average of 30.67 Bq/kg and 287.98 Bq/kg, respectively.

The ^{226}Ra, ^{232}Th and ^{40}K activity concentrations of Bakırçay River sediments were found between ND and 160.57 Bq kg^{-1}, ND and 131.49 Bq kg^{-1}, ND and 839.19 Bq kg^{-1}, respectively (Fig. 3). The worldwide levels of ^{226}Ra, ^{232}Th and ^{40}K in soil are given by UNSCEAR as 35 Bq kg^{-1}, 30 Bq kg^{-1} and 400 Bq kg^{-1}, respectively (UNSCEAR, 2000). According to UNSCEAR, 1993 report, the natural radionuclide concentrations in ash and slag from coal-fired power stations are significantly higher than the corresponding concentrations in the earth's crust. Arithmetic averages of reported concentrations in escaping fly ash are 265 Bq kg^{-1} for ^{40}K, 240 Bq kg^{-1} for ^{226}Ra, and 70 Bq kg^{-1} for ^{232}Th.

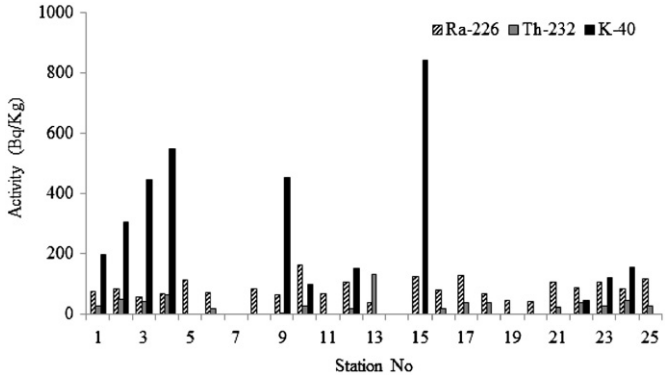

Fig. 3. Natural radioactivity concentrations of sediment samples.

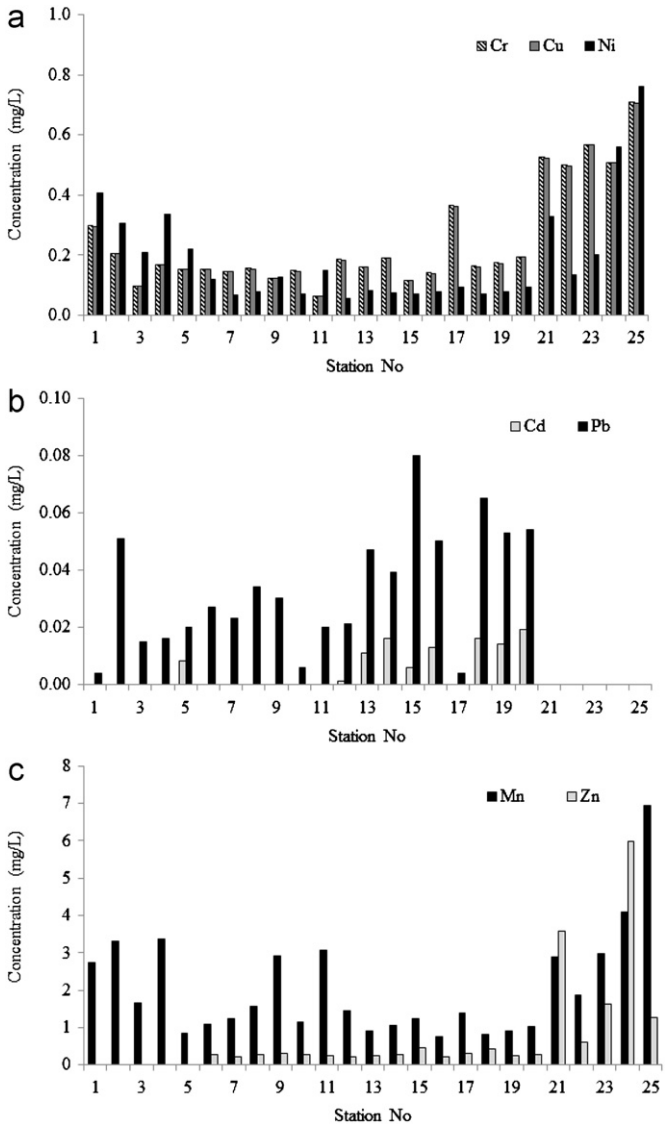

Fig. 4. (a) Cr, Cu and Ni, (b) Cd and Pb, and (c) Mn and Zn concentrations of sediment samples.

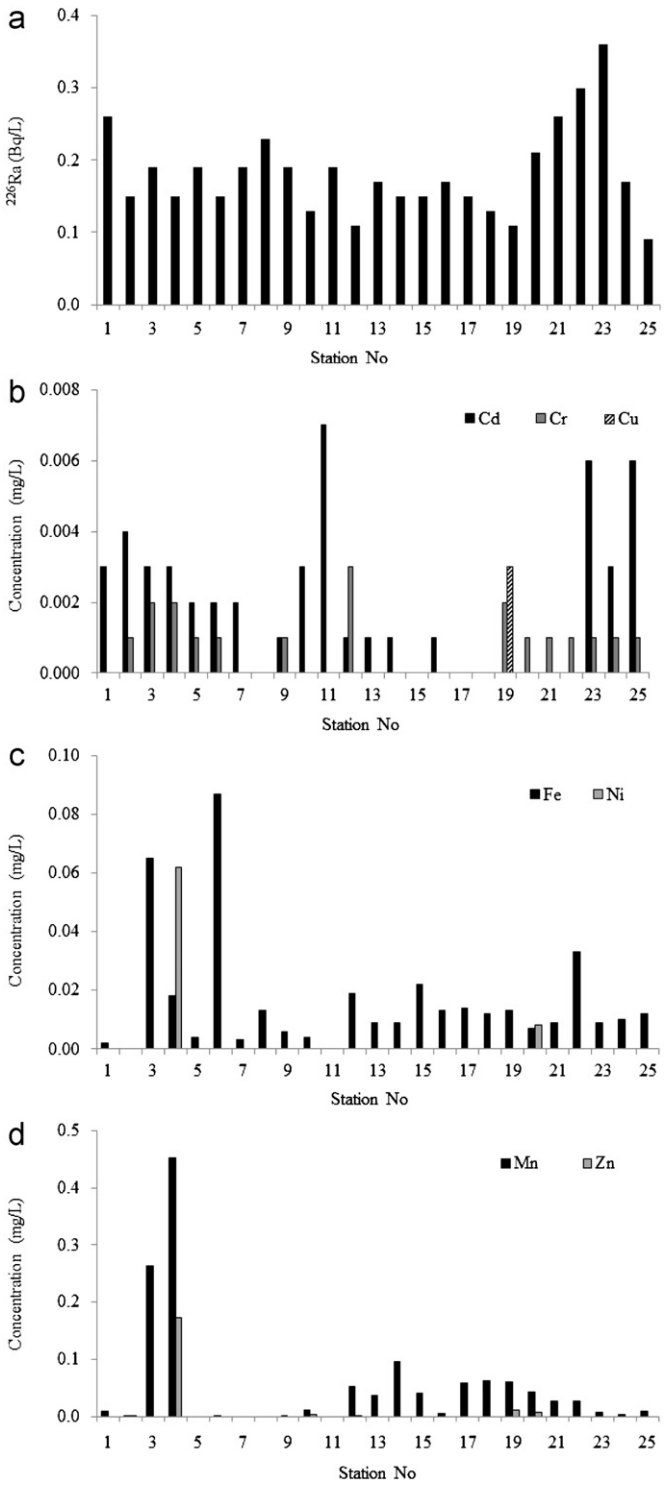

Fig. 5. (a) ^{226}Ra activity concentrations, (b) Cd, Cr and Cu, (c) Fe and Ni, and (d) Mn and Zn concentrations of water samples.

Table 1
A literature comparisons of ^{226}Ra, ^{232}Th and ^{40}K concentrations of sediment and soil samples.

Studies	Region	Sample	^{226}Ra	^{232}Th	^{40}K
Shenber (1997)	Tripoli/Libya	Soil	10.5	9.5	270
Bakac and Kumru (2001)	Gediz River/Turkey	Sediment	17.00–257.00	1.22–69.58	2.96–1038.96
Gunkal, 2001	Bakırçay River/Turkey	Sediment	41	554	–
Hanslik et al. (2005)	Czech Rep.	Sediment	49	–	–
Kurnaz et al. (2007)	Fırtına Valley/Turkey	Soil	50	42	643
Kurnaz et al. (2007)	Fırtına Valley/Turkey	Sediment	39	38	573
Narayana et al. (2007)	Some major rivers on the southwest coast of India	Soil	38.0–73.3	5.8–80.0	369.3–891.5
Narayana et al. (2007)	Some major rivers on the southwest coast of India	Sediment	34.1–196.7	ND-142.0	289.8–997.8
Santawamaitre et al. (2011)	Chao Phraya River/Thailand	Soil	–	60.7–69.1	393–478
Suresh et al. (2011)	Ponnaiyar River, India	Sediment	–	ND-106.11	201.23–467.71
Montes et al. (2012)	Buenos Aires/Argentina	Soil	27–69	3–41	531–873
In this study	Bakırçay River/Turkey	Soil	19.50–250.49	ND-64.67	ND-796.57
In this study	Bakırçay River/Turkey	Sediment	ND-160.57	ND-131.49	ND-839.19

Table 2
pH, Eh, ^{226}Ra and heavy metal levels of the river water samples.

No.	pH	^{226}Ra (Bq/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Zn (mg/L)
1	8.47	0.26	0.003	0.000	0.000	0.002	0.009	0.000	0.000
2	8.45	0.15	0.004	0.001	0.000	0.000	0.001	0.000	0.001
3	8.20	0.19	0.003	0.002	0.000	0.065	0.263	0.000	0.000
4	8.39	0.15	0.003	0.002	0.000	0.018	0.453	0.062	0.173
5	8.51	0.19	0.002	0.001	0.000	0.004	0.000	0.000	0.000
6	8.39	0.15	0.002	0.001	0.000	0.087	0.002	0.000	0.000
7	8.62	0.19	0.002	0.000	0.000	0.003	0.000	0.000	0.000
8	8.32	0.23	0.000	0.000	0.000	0.013	0.000	0.000	0.000
9	8.52	0.19	0.001	0.001	0.000	0.006	0.002	0.000	0.000
10	8.44	0.13	0.003	0.000	0.000	0.004	0.011	0.000	0.004
11	8.52	0.19	0.007	0.000	0.000	0.000	0.000	0.000	0.000
12	8.44	0.11	0.001	0.003	0.000	0.019	0.052	0.000	0.001
13	8.26	0.17	0.001	0.000	0.000	0.009	0.037	0.000	0.000
14	8.41	0.15	0.001	0.000	0.000	0.009	0.096	0.000	0.000
15	8.42	0.15	0.000	0.000	0.000	0.022	0.041	0.000	0.000
16	8.17	0.17	0.001	0.000	0.000	0.013	0.005	0.000	0.000
17	7.66	0.15	0.000	0.000	0.000	0.014	0.058	0.000	0.000
18	7.73	0.13	0.000	0.000	0.000	0.012	0.063	0.000	0.000
19	7.59	0.11	0.000	0.002	0.003	0.013	0.061	0.000	0.011
20	8.42	0.21	0.000	0.001	0.000	0.007	0.043	0.008	0.008
21	7.72	0.26	0.000	0.001	0.000	0.009	0.027	0.000	0.000
22	8.05	0.30	0.000	0.001	0.000	0.033	0.026	0.000	0.000
23	8.38	0.36	0.006	0.001	0.000	0.009	0.007	0.000	0.000
24	7.95	0.17	0.003	0.001	0.000	0.010	0.003	0.000	0.000
25	8.11	0.09	0.006	0.001	0.000	0.012	0.009	0.000	0.000

The results of the heavy metals in the sediment samples for Cr, Cu, Ni, Cd, Pb, Fe, Mn, and Zn varied from 0.071 to 0.637 mg/L, 0.630 to 0.706 mg/L, 0.058 to 0.763 mg/L, 0.000 to 0.019 mg/L, 0.000 to 0.08 mg/L, 54.550 to 534.600 mg/L, 0.765 to 6.950 mg/L and 0.000 to 5.970 mg/L, respectively. As seen from the Figs. 4 and 5, it has been observed that the heavy metals in sediment and water samples collected from the upper region of the river are slightly higher than those in others. This is because these sample areas are close to the thermal power plant and industrial areas of Soma city. A detailed literature comparison of natural radioactivity levels of sediment and soil samples were given in Table 1.

It was observed that Cd, Cr, Fe and Mn concentrations in the sediments and river waters were higher in the first and last stations than the others (Table 2). These heavy metals accumulate at the river delta. We can say that an upper part of the river is affected from the coal mines. A similar trend is observed with some heavy metals in water samples (Fig. 5).

As shown in Table 2, there were small changes in pH measurements throughout the river. In the summer, the confluence of the river and the sea is closed so that the river water can be used for irrigation; however, the seawater mixes with the river water because there is no difference in the water levels of this area and the sea.

The radium concentration in the river waters was found to vary between 0.09 and 0.36 Bq/L. The maximum allowed value for radium concentration of drinking water and house hold usage is 0.185 Bq/L (USEPA, 1976). Taking into consideration of this limit sharp increases were observed at some points, as shown in Fig. 5. The middle and upper sampling regions were very noticeable.

3.2. Gamma radiation dose from radionuclides in soil and sediment

The external terrestrial gamma dose rates, annual effective dose rate and radium equivalent activities were calculated (Figs. 6 and 7). External terrestrial gamma dose rates are found between 0.0 and 95.7 nGy h^{-1}. The mean gamma dose rate was estimated to be 56.8 nGy h^{-1}. These levels are in the range between 28 and 120 (56) nGy/h given by UNSCEAR (1993). The annual effective dose rates were determined from 0.0 to 0.12 mSv y^{-1} and the average is 0.69 mSv y^{-1}. The annual effective dose is marginally below the International Commission on Radiological Protection (ICRP) recommended annual effective dose of 1 mSv y^{-1} for the general public (Kant and Chakarvarti, 2003). The radium equivalent activity (Ra_{eq}) was generally used to estimate the γ-ray radiation hazards to humans. The radium equivalent activity varies considerably in different soil samples.

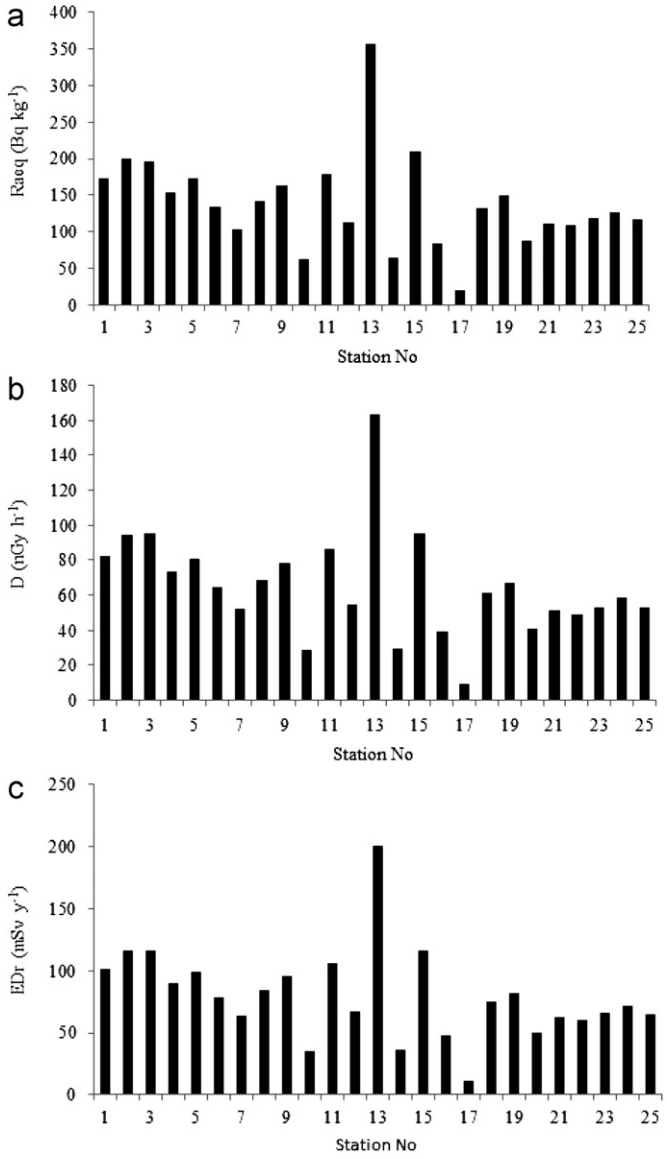

Fig. 6. (a) Ra equivalent activities, (b) external terrestrial gamma dose rates and (c) annual effective dose rates in soils.

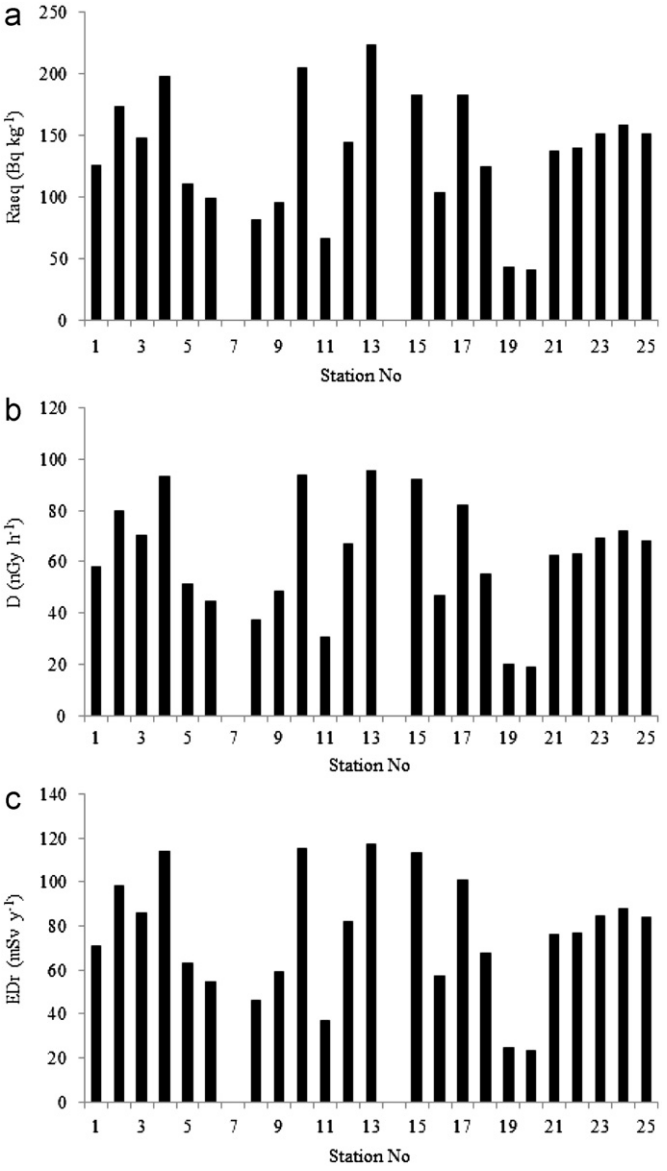

Fig. 7. (a) Ra equivalent activities, (b) external terrestrial gamma dose rates and (c) annual effective dose rates in sediments.

The average radium equivalent activity was calculated as 123.3 Bq kg^{-1}, which is within the range of 0.0 and 204.3 Bq kg^{-1}. All calculated values are lower than the suggested maximal admissible value of 370 Bq kg^{-1} recommended by the Organization for Economic Cooperation and Development (OECD, 1979). Ra-equivalent activities, external terrestrial gamma dose rates and annual effective dose rates in soils and sediments are given in Figs. 6 and 7. According to these results, it has been observed that radioactivity values in soil and sediment samples in the middle of the river are high. In addition, it has been found that the gamma dose rates are also high in these parts.

4. Conclusions

The cause of the pollution of the river was investigated and observed that pollution was accumulated in most of the upper region. As a result of our study some parts of the river were found to be heavily contaminated. A considerable increase in radioactivity and heavy metal levels was observed in our study. The reason for this may be the intensity of agricultural practices and industrialization in these areas. The results show that levels of radium increase in the upper parts of the river. Soma thermic power plant and coal mines located in these regions may increase Ra-226 concentrations.

As shown in the Fig. 3, it has been observed that ^{40}K concentrations were higher in some sample points than the others. The excess of ^{40}K radioactive elements in these areas of the river may have resulted from over-fertilization. The high levels of heavy metals such as Cr, Cu, Ni, Mn, Fe, Zn and Pb in the upper part of the river was because of the nearby coal power plants in Soma located at the northwest of Turkey and some small industrial waste around the town of Bergama.

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