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Determination and evaluation of natural radioactivity and heavy metal levels in the aquatic environment of trans-boundary rivers: Maritza, Tundja and Arda

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Abstract The main problem in the trans-boundary river system is that heavy metal and radioactive pollution can cause long-term effects on ecosystems. Therefore the natural radioactivity and heavy metal levels in the Maritza, Tundja and Arda Rivers, common for Bulgaria and Turkey, were determined for 3 years period (2007–2010). Gross alpha, gross beta and total radium isotopes activities, uranium and heavy metal concentrations of the surface water of the rivers were investigated and also terrestrial gamma and gamma dose rate were measured. The results were compared with reported data from other countries of the world and the recommended international standards. The results gathered in this study may provide background data on the natural radioactive and heavy metal levels of these trans-boundary rivers.

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Introduction

Radioactivity present in surface continental waters is mainly due to the presence of the primordial radioactive elements incorporated into the Earth's crust during its formation, and the radioactive decay products of these primordial elements and radionuclides are formed in the atmosphere by cosmic ray interactions. Nevertheless, other artificial radionuclides have also appeared due to human activities such as nuclear power plants, nuclear weapons tests, manufacturing and the usage of radioactive sources. The other human activities (mining, milling and processing of uranium ores and mineral sands, manufacturing of fertilizers, burning of fossils fuels, metal refining, etc.) have raised the activity concentrations of natural radionuclides in the environment [1, 2].

Radioactive materials can reach to surface continental waters by various pathways. River water could be contaminated by groundwater or surface runoff of rainwater transporting leached radionuclides from cities, mine waste, deposits, soil weathering, agricultural areas, etc. [3, 4]. Correspondingly, the radioactive elements may enter to the body via food, water or air. Given the special conditions of water as a universal solvent, it is a potentially important carrier of dissolved radionuclides, which could be absorbed by the population through the food chain [5].

Considering inadequate water sources, high population growth rate and irrational use of water sources, water will be the most important issue in the near future. This issue constitutes a major problem for Turkey because of its limited water resources. Furthermore, since the country has the trans-boundary watercourses, water issues attain an international dimension [6]. Taking into account the geological location and neighbours of Turkey, this dimension becomes the most important issue. The sustainable use of natural resources in the long term, prevention of pollution, protection of the environment and the natural areas are the main social and political objectives. Present day environmental problems are affecting every country in the region, and they require international cooperation for solutions. Due to its location between the Mediterranean and Black Sea, Turkey has been affected by river pollution flowing into these two seas. This affects many national endeavours from tourism to fishing, from biodiversity to human health and in many other fields.

Geographically, Turkey's territory is divided into several river basins, which show a large variation in average annual precipitation, evaporation and surface run-off parameters. Trans-boundary, also partly boundary-forming, watercourses are located in the north-western, north-eastern and the south-eastern regions of Turkey [7]. The Maritsa basin, one of the major river systems of the Eastern Balkans, is shared by Bulgaria, Greece and Turkey. Water for irrigation as well as flood control is the main disputed issues in the basin, particularly between Turkey and Bulgaria [8].

The main problem in the trans-boundary river system is that heavy metal and radioactive pollution can cause long-term effects on ecosystems even through their impact has no visible influence in comparison to other pollutants. Therefore a number of studies have been conducted for the determination of heavy metals and radioactivity concentration both in non cross-border and trans-boundary river systems [9–12]. On the other hand determination and correlation of natural radioactivity and heavy metal concentrations in Maritza basin (Turkey site) is rather absent. Within this context, radioactivity and heavy metal concentrations in the most substantial trans-boundary rivers (Maritza, Tundja and Arda) between Turkey, Bulgaria and Greece were determined in order to establish database for water resources management and scientific collaboration within region. In this way, background information for future radiological studies was provided, and the relationships between basic radiological parameters in rivers and potential sources were studied along with seasonal variations. Moreover, variability of the studied elements along the river basins and the existence of significant statistical correlation between them were assessed.

Materials and methods

Study area

The trans-boundary basin of the river Maritza is shared between three European countries; Bulgaria, Greece and Turkey (Fig. 1). Bulgaria is upstream, Turkey and Greece are downstream. The Maritza River is one of the longest rivers of the Balkan Peninsula, stretching for approximately 530 km, originating from the Rila Mountains in Western Bulgaria. Its total watershed area is 53,000 km^2 and it discharges into the Aegean Sea at the border of Greece and Turkey. About 66 % of the total surface area of the river is in Bulgarian territory, 28 % in Turkish territory and 6 % in Greek territory [13]. Considering the delta area alone, 90 % belongs to Greece and the remaining 10 % to Turkey. The river basin hosts a total population of approximately 2 million people. The Greek part of the river basin is a rural area of about 3,300 km^2 with 85,000 inhabitants. The Maritza flows through many settlement areas including Pazardzhik, Plovdiv, Dimitrovgrad and Svilengrad in Bulgaria, Edirne in Turkey and Kastanies, Pythio, Didymoteicho and Lavara in Greece [14]. At the point where the Maritza is close to the three-way border between Bulgaria, Greece and Turkey, it first forms a natural boundary between Bulgaria and Greece for about 15 km, then, for about 187 km, it forms the border between Turkey and Greece in the Thrace Region before finally reaching to the Aegean Sea. The Maritza River enters the Aegean Sea near the Gulf of Saroz and forms a delta of about 188 km^2 of which 150 km^2 lie in Greek territory. The delta is a typical Mediterranean delta formed by the alluvial deposits and shaped by interaction with the sea [8].

The Maritza basin is fed by four main tributaries: the Arda (*Ardas*) (Bulgaria and Greece), the Tundja (*Tundzha*) (Bulgaria and Turkey), the Erythropotamos (mostly in Greece) and the Ergene (in Turkey). After the three-way border, close to Edirne, the Maritza is joined by two important tributaries, the Arda River from the south and the Tundja River from the north.

The *Tundja* River is originated from the Stara Planina Mountains (Balkan Mountains) in the centre of Bulgaria. It then flows eastwards along the Balkan Mountains towards the Turkish border. For about 15 km the Tundja forms the border between Turkey and Bulgaria, and it flows about 30 km through Turkey before merging with the Maritza.

The *Arda* River springs from the Eastern Rhodope Mountains in Southern Bulgaria from where it flows eastwards. After 240 km on Bulgarian territory, it flows for 30 km in Greece before joining to the Maritza River at the Turkish border.

The Ergene River originates from the southern part of Strandzha Mountain, and flows for 281 km before joining to the Maritza near the Turkish city of İpsala.

To evaluate the results for natural radioactivity and heavy metal concentrations, rainfall information of the studied area is quite important. Therefore, the available rainfall information for the Marmara Region was provided from the Turkish State Meteorological Service for the

Fig. 1 Studied rivers and the sampling points of surface water

period of 1990–2010, and presented monthly between 2007 and 2009 (Fig. 2a). The total amount of rainfall between 1990 and 2010 is also shown in Fig. 2b. The mean annual precipitation for Edirne City varies as 575 mm (2007), 385 mm (2008), 791 mm (2009) and 768 mm (2010), according to data from Turkish State Meteorological Service (2010) [15].

Flow patterns of the Maritza and Tundja have shown great seasonal and annual variations. During summer, particularly in dry periods, the flow rate of Tundja reduces drastically, which is partly caused by the operation of dams upstream in Bulgaria. Table 1 shows the mean values of monthly discharge ($m^3 s^{-1}$) for the Maritza, Tundja and Arda Rivers. Based on the data gathered at flow monitoring stations in western Edirne, the medium discharge rate of the Maritza is 182 $m^3 s^{-1}$, having a range from 1.7 to 10.4 $m^3 s^{-1}$. Annual water discharge rate of the Maritsa basin is 8 Billion Cubic Meter (BCM). In the Turkish territory, the Ergene contributes 1.2 BCM, the Tundja 0.4 BCM and the Maritza East Bank 0.2 BCM to the drainage per year. Water originating from Bulgaria contributes 0.6 BCM to the Tundja; the Maritza and the Arda add 5.1 BCM per year. The basin of Maritsa river tributaries in Greece contribute about 0.5 BCM per year [8].

The Maritza River/basin is exposed to industrial waste, urban sewage and agricultural discharge from three countries, namely Turkey, Bulgaria and Greece, and these discharges increase the load of organic and inorganic pollutants in the delta area. The agricultural activity in the three countries is also intense and the use of fertilizers and pesticides is widespread. The main land in the Bulgarian section of the basin is used for farming, mining (gold, uranium) and pastures. Coal fired power plants and uranium mining activities in Bulgaria, particularly in southeast Bulgaria and in the Central Rhodopes, can give rise to enhance the radionuclide concentrations of the Maritza and Tundja Rivers.

Sample collection

Samples of river water (104) were collected during wet and dry seasons in August 2007, October 2008, May and September 2009 and April 2010 from 34 different stations in Maritza, Tundja and Arda Rivers. Sampling points of Arda River were limited to only 4 samples due to the swampy ground of the riverbank in which it was difficult to reach to the sampling area during the study period. Sampling sites for each river are indicated in Fig. 1 and Table 2

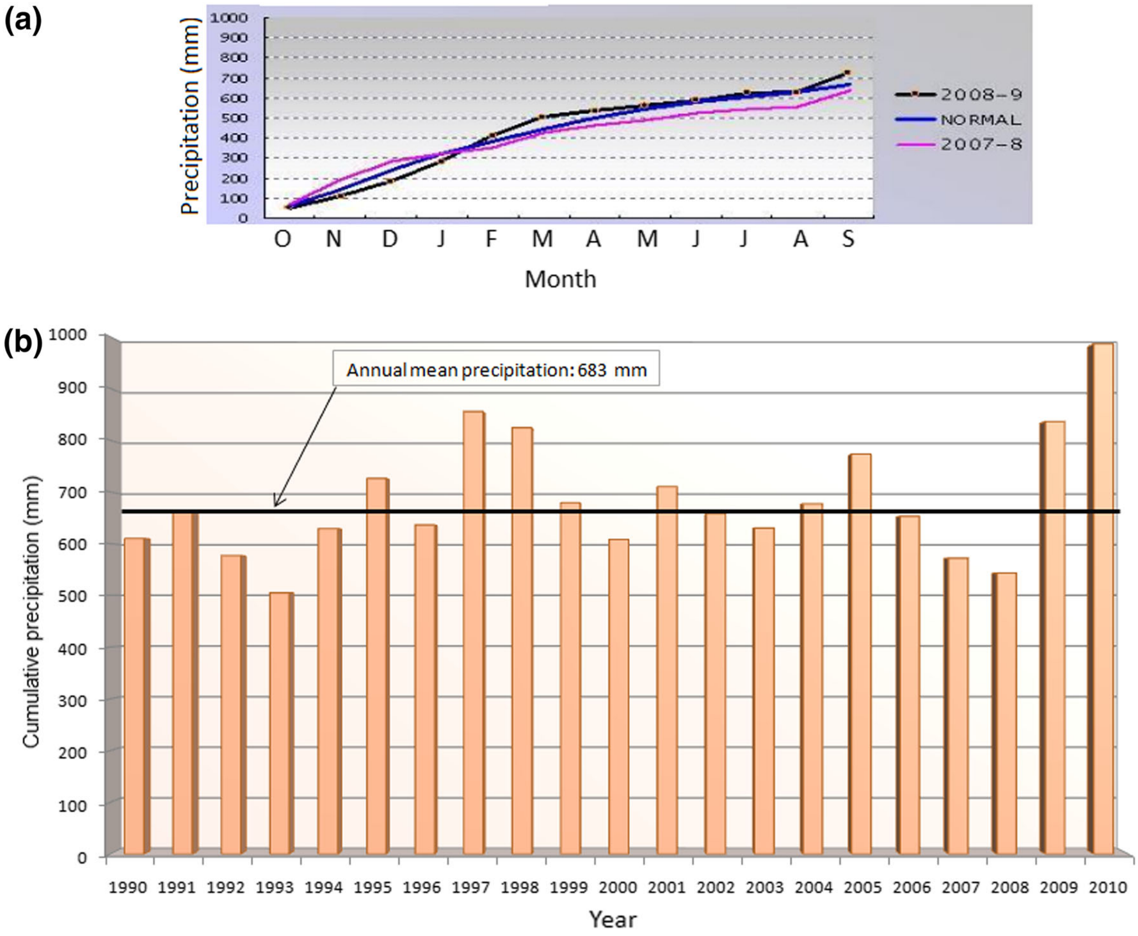

Fig. 2 The cumulative rainfall in Edirne from 2007 to 2009 (**a**), the amount of rainfall in Marmara region from 1990 to 2010 (**b**)

Table 1 Mean monthly values of discharge (m^3 s^{-1}) for the Maritza, Tundja and Arda Rivers

Maritza–Tundja–Arda River		
October: 54.84–12.93–23.03	November: 69.01–21.89–60.34	December: 96.61–32.82–129.21
January: 99.76–38.40–114.72	February: 140.66–57.87–154.94	March: 163.11–61.70–126.03
April: 186.99–53.23–100.41	May: 184.89–46.85–71.91	June: 127.38–28.09–47.37
July: 74.17–12.94–22.51	August: 54.73–10.29–11.50	September: 46.72–9.94–10.95

using geographical coordinates obtained by Geographical Positioning System (Garmin Etrex Venture Cx, GPS).

Surface water samples were taken from riverbanks using 2 L plastic bottles, previously rinsed by distilled water, and their physicochemical properties such as temperature, pH, conductivity, and dissolved oxygen were measured on site at the time of sampling after transferring the samples to the laboratory, their alkalinity was determined titrimetrically. In addition gross alpha, gross beta, total radium activities, uranium and heavy metal concentrations were later determined in the laboratory.

Sample preparation

Surface water might carry large amounts of suspended solids, which should be removed during water treatment processes since they could severely affect the measurement. Therefore samples were immediately acidified with (0.2 v/v) ultra-pure nitric acid to pH < 2 as acidification minimizes the adsorption of metals onto wall of the containers, prevents growth of microorganisms, precipitations, polymerizations and colloid formations. Then, they were transported to the laboratory for the analysis. Each water

Table 2 Collected water samples with sampling coordinates (UTM) from the Maritza, Tundja and Arda Rivers between August 2007 and April 2010

Sample code	Sampling date	Sampling coordinate (UTM)	Sample code	Sampling date	Sampling coordinate (UTM)
M-1	August, 2007	35T0464365/4608970	M-30	October, 2008	35T0421958/4508930
M-2	August, 2007	35T0464154/4611097	M-31	October, 2008	35T0423014/4509757
M-3	August, 2007	35T0464036/4611487	M-32	October, 2008	35T0424650/4510066
M-4	August, 2007	35T0462778/4612563	M-33	October, 2008	35T0426318/4511395
M-5	August, 2007	35T0426143/4510684	M-34	October, 2008	35T0430816/4518239
M-6	August, 2007	35T0426437/4511883	M-35	October, 2008	35T0429716/4517849
M-7	August, 2007	35T0426613/4512712	M-36	May, 2009	35T0458445/4612718
M-8	August, 2007	35T0430899/4518421	M-37	May, 2009	35T0465067/4608514
M-9	August, 2007	35T0438507/4521766	M-38	May, 2009	35T0466274/4612571
M-10	August, 2007	35T0437518/4520017	M-39	May, 2009	35T0430898/4518416
M-11	August, 2007	35T0436545/4518117	M-40	May, 2009	35T0426630/4512652
M-12	August, 2007	35T0435800/4516420	M-41	May, 2009	35T0425896/4510641
M-13	August, 2007	35T0434442/4515537	M-42	May, 2009	35T0426167/4510358
M-14	August, 2007	35T0432603/4515970	M-43	May, 2009	35T0419801/4509324
M-15	August, 2007	35T0431234/4514515	M-44	May, 2009	35T0421289/4508972
M-16	August, 2007	35T0429412/4514045	M-45	May, 2009	35T0419573/4509176
M-17	August, 2007	35T0425061/4510320	M-46	September, 2009	35T0465183/4608656
M-18	August, 2007	35T0423883/4510001	M-47	September, 2009	35T0458845/4612720
M-19	August, 2007	35T0423053/4509891	M-48	September, 2009	35T0465067/4608514
M-20	August, 2007	35T0422003/4509110	M-49	September, 2009	35T0462754/4612568
M-21	August, 2007	35T0420506/4509246	M-50	September, 2009	35T0426143/4510682
M-22	October, 2008	35T0465624/4608311	M-51	September, 2009	35T0426399/4511572
M-23	October, 2008	35T0465033/4608314	M-52	September, 2009	35T0426648/4512631
M-24	October, 2008	35T0464311/4608794	M-53	September, 2009	35T0422004/4509074
M-25	October, 2008	35T0462678/4612386	M-54	September, 2009	35T0421981/4509324
M-26	October, 2008	35T0460641/4612881	M-55	April, 2010	35T0465181/4608675
M-27	October, 2008	35T0458763/4612583	M-56	April, 2010	35T0462742/4612542
M-28	October, 2008	35T0419542/4509179	M-57	April, 2010	35T0430869/4518118
M-29	October, 2008	35T0421035/4509050	M-58	April, 2010	35T0426576/4512490
M-59	April, 2010	35T0426151/4510667	T-23	May, 2009	35T0462234/4626148
M-60	April, 2010	35T0422087/4509096	T-24	May, 2009	35T0465607/4632442
T-1	August, 2007	35T0461850/4614292	T-25	September, 2009	35T0463133/4615689
T-2	August, 2007	35T0462138/4615062	T-26	September, 2009	35T0463340/4615741
T-3	August, 2007	35T0463220/4615230	T-27	September, 2009	35T0462779/4616501
T-4	August, 2007	35T0463112/4615677	T-28	September, 2009	35T0463426/4622188
T-5	August, 2007	35T0463341/4616087	T-29	September, 2009	35T0463424/4623332
T-6	August, 2007	35T0463894/4616456	T-30	September, 2009	35T0462158/4623730
T-7	October, 2008	35T0463291/4615554	T-31	September, 2009	35T0462240/4626144
T-8	October, 2008	35T0463074/4615498	T-32	September, 2009	35T0463206/4627955
T-9	October, 2008	35T0462729/4616320	T-33	September, 2009	35T0463738/4628938
T-10	October, 2008	35T0463840/4622153	T-34	September, 2009	35T0464071/4630487
T-11	October, 2008	35T0462960/4623293	T-35	April, 2010	35T0463129/4615692
T-12	October, 2008	35T0462201/4625197	T-36	April, 2010	35T0463357/4615741
T-13	October, 2008	35T0462715/4626955	T-37	April, 2010	35T0462775/4616493
T-14	October, 2008	35T0465397/4631900	T-38	April, 2010	35T0463052/4621862
T-15	May, 2009	35T0463304/4615669	T-39	April, 2010	35T0463400/4623352
T-16	May, 2009	35T0463156/4616531	T-40	April, 2010	35T0462080/4624592

Table 2 continued

Sample code	Sampling date	Sampling coordinate (UTM)	Sample code	Sampling date	Sampling coordinate (UTM)
T-17	May, 2009	35T0463327/4615745	T-41	April, 2010	35T0462986/4627571
T-18	May, 2009	35T0462780/4616509	A-1	August, 2007	35T0464991/4608528
T-19	May, 2009	35T0462611/4620718	A-2	August, 2007	35T0465595/4608209
T-20	May, 2009	35T0463274/4621892	A-3	September, 2009	35T0464991/4608528
T-21	May, 2009	35T0463757/4622696	A-4	April, 2010	35T0464991/4608528
T-22	May, 2009	35T0462157/4623727			

sample was filtered through a Whatman No 42 filter paper, and the solid matter was discarded. Alkalinity of the river water samples was titrimetrically determined.

In situ measurements

Gamma survey measurements were conducted by Scintex gamma survey meter and the outdoor terrestrial gamma radiation (TGR) dose rates were measured 1 m above the ground of the riverbank using a portable radiation dosimeter (Thermo Eberline) that are calibrated by Turkish Atomic Energy Autority, Çekmece Nuclear Research and Education Center (SSDL, Accredited Laboratory), and dose rates were recorded in μR h^{-1} and then converted to nGy h^{-1}. Temperature, pH, conductivity and dissolved O_2 in water samples were measured in the river at the time of sampling with thermometer, HANNA 8521 pH meter, WTW LF 318/SET conductivity meter and WTW Oxi 315i & Cell Ox 325 electrode system, respectively. Conductivity values were normalized to 25 °C using a temperature coefficient of 2.3 % per °C [16, 17].

Analytical procedure

Gross alpha and beta measurements

To determine the total alpha and beta radioactivity of surface water samples, one liter of sample was evaporated to dryness on a hot plate, and the residue was fixed onto an aluminum planchette, then measured for 50 min by ZnS(Ag) scintillation alpha counter (Eberline, SAC-4 Model) with 40 % counting efficiency [18]. Gross beta counting was performed using an alpha–beta radiation counter (HandECount, Eberline) with 22 % counting efficiency. The detection efficiencies of the counting systems are determined by counting KCl (Merck) for alpha–beta counter and U_3O_8 reference material (IAEA-S13) for alpha counter.

The results were given as arithmetic means calculated from the results of each sample. The total alpha and total beta activities were calculated using the net counts by the following equations:

$$A_\alpha = \frac{0.0167 \times N}{E \times V} \tag{1}$$

$$A_\beta = \frac{0.0167 \times N}{ECF_\beta \times V} \tag{2}$$

where A_α and A_β are the alpha and beta activities in Bq, respectively; N is the sample net counts per minute for alpha and beta activity; E is the alpha detector efficiency and ECF_β is the efficiency correction factor, which is calculated from the calibration curve (correlation coefficient: 0.99) obtained using a KCl source, and finally V represents the volume of water sample (1 L).

Total radium isotopes analysis

Radium concentrations of 1 L surface water collected from the rivers were determined by counting their total alpha activities. Briefly, the water sample was transferred to a beaker, and 20 mL 12 N HCl and 1 mL 0.1 M $BaCl_2 \cdot 2H_2O$ carrier were added to the sample. The solution was heated up to boiling point and then 20 mL 18 N H_2SO_4 was added to the solution slowly while stirring. The solution was continuously stirred for 30 min while heating. Radium isotopes were co-precipitated as $Ba(Ra)SO_4$. The sample was allowed to settle at room temperature for 1 h and then filtered quantitatively through a 0.45 μm Whatman membrane filter. The filter was dried under an infrared lamp, and the precipitate was counted using a ZnS(Ag) alpha scintillation counter (Eberline SAC-4 Model) [19]. The detection efficiency of the ZnS(Ag) detector was determined by counting barium sulfate from the standard samples to which standard solutions of ^{226}Ra, containing activity concentrations ranging from 0.037 to 0.925 Bq L^{-1}, had been added. A standard solution of 370 Bq mL^{-1} ^{226}Ra was obtained from the Turkish Atomic Energy Authority Çekmece Nuclear Research and Training Centre (CNAEM). The minimum detectable activity determined by this method was 0.08 Bq g^{-1}.

Uranium and heavy metal determination

A UA-3 uranium analyzer (Scintrex) was used to measure the uranium concentration of the water samples. The method is based on the fluorescence of a uranium complex by addition of a buffered inorganic complexing reagent, Fluran, to the sample during analysis. The UA-3 analyzer was calibrated by measuring the response of the instrument to uranyl standards with known concentrations, namely 2 and 20 ppb in the range of the interest. The signal of the sample of unknown uranium content is compared with that of the standard. An analysis with sensitivity higher than 0.05 mg L^{-1} of uranium can be achieved without pre-concentration or treatment of the sample even in the presence of many potentially interfering species.

Heavy metal concentrations in river water samples were determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 2000 DV). The operating conditions employed for ICP-OES analysis were 1300 W RF power, 15 L min^{-1} plasma flow, 0.2 L min^{-1}auxiliary flow, 0.8 L min^{-1} nebulizer flow, 1.5 mL min^{-1} sample uptake rate. ICP Multi Element Standard Solution IV CertiPUR reference material in 1,000 ± 10 mg/L (Merck) was used for calibration of ICP-OES. Standard solutions for the calibration were prepared by diluting the stock reference solution.

Results and discussion

Terrestrial gamma and gamma dose rate measurements

The outdoor terrestrial gamma dose rates are given in Fig. 3 for the Maritza, Tundja and Arda Rivers. The values of terrestrial gamma count rates ranged from 40 to 95 cps with a mean value of 63 ± 12 cps for the Maritza Riverbank, from 30 to 60 cps with a mean value of 45 ± 7 cps for the Tundja Riverbank and from 40 to 70 cps with a mean value of 58 ± 12 cps for the Arda Riverbank. Likewise the values of gamma radiation dose rates ranged from 35 to 132 nGy h^{-1} with a mean value of 66 ± 26 nGy $h^{-1}$for the Maritza Riverbank, from 35 to 88 nGy h^{-1} with a mean value of 58 ± 16 nGy h^{-1} for the Tundja Riverbank and from 44 to 105 nGy h^{-1} with a mean value of 79 ± 26 nGy h^{-1} for the Arda Riverbank. As a result, the mean value of the dose rates was calculated as 68 ± 23 nGy h^{-1} and ranged from 35 to 132 nGy h^{-1} for all riverbanks during the project period.

Using the UNSCEAR [20] recommended dose conversion coefficient 0.7 Sv Gy^{-1}, an outdoor occupancy factor of 26 %, the annual effective dose (HE) is calculated in mSv using Eq. (3) [21];

$$\mathrm{HE}\left(\mathrm{mSv\ year}^{-1}\right) = \mathrm{Dose\ rate}\left(\mathrm{nGy\ h}^{-1}\right) \times 24\,\mathrm{h} \times 365\,\mathrm{days} \times \mathrm{OF} \times 0.7 \times 10^{-6} \qquad (3)$$

The average annual effective dose equivalent received outside in the Edirne Region from the riverbanks of the Maritza, Tundja and Arda Rivers ranged from 0.04 to 0.13 mSv $year^{-1}$ with a mean value of 0.08 ± 0.02 mSv $year^{-1}$. The average value of world annual effective dose equivalent is 0.41 mSv indoor and 0.07 mSv for outdoor [20].

Physicochemical parameters

The minimum, maximum, mean and standard deviation of the physicochemical parameters pH, conductivity, dissolved oxygen and alkalinity for the Maritza, Tundja and Arda Rivers water during 2007–2010 are given in Table 3.

The conductivities of the water samples are generally low at the sampling points where the discharge is formed by the melted ice coming from the snow-capped peaks in Edirne and also from the discharge of Bulgarian dams in the dry season. A more pronounced difference occurs in the waters of the Maritza River, in which the typical conductivity ranges from 0.36 to 1.82 mS cm^{-1} but where a local maximum of 29.52 mS cm^{-1} occurs due to water intrusion from the Aegean Sea affecting water quality and wetland life near the Gulf of Saroz.

Gross alpha, gross beta and total radium isotopes activity

The levels of gross alpha, gross beta and total radium isotopes activity in Bq L^{-1} during 2007–2010 are shown for the Maritza (Fig. 4) and the Tundja and Arda Rivers (Fig. 5), respectively. In addition, Table 4 reports the minimum, maximum and mean values (SD) of those values.

Gross alpha activities of the Maritza, Tundja and Arda River waters ranged from 0.010 to 1.090, 0.010 to 0.070, 0.020 to 0.070 Bq L^{-1}, respectively. The highest gross alpha concentration (1.090 Bq L^{-1}) was observed in the Maritza (M-3). High levels of gross alpha activity were observed only during the dry season (August 2007). This could be explained by (i) the presence of lignite coal mining around Edirne and (ii) the impact from the phosphate fertilizers used in agricultural areas. In addition, it may have resulted from the low river flow, which is caused by low influx of fresh water, dewatering from irrigation, evaporation etc. during dry months compared to other months in the rest of the year [9].

Gross alpha activity in natural water is mainly caused by uranium isotopes (^{234}U, ^{235}U and ^{238}U) and ^{226}Ra because thorium solubility is low. Principally ^{226}Ra and, occasionally, ^{232}Th, ^{210}Po or ^{224}Ra are the main contributors to the alpha particle activity [22].

Gross beta activities of the Maritza, Tundja and Arda River waters varied from 0.001 to 0.060 Bq L^{-1}, from 0.001 to 0.080 Bq L^{-1} and from 0.001 to 0.005 Bq L^{-1}, respectively. For the beta activity, it can be said that ^{40}K and ^{228}Ra radioisotopes are the main source of its origin [22]. The

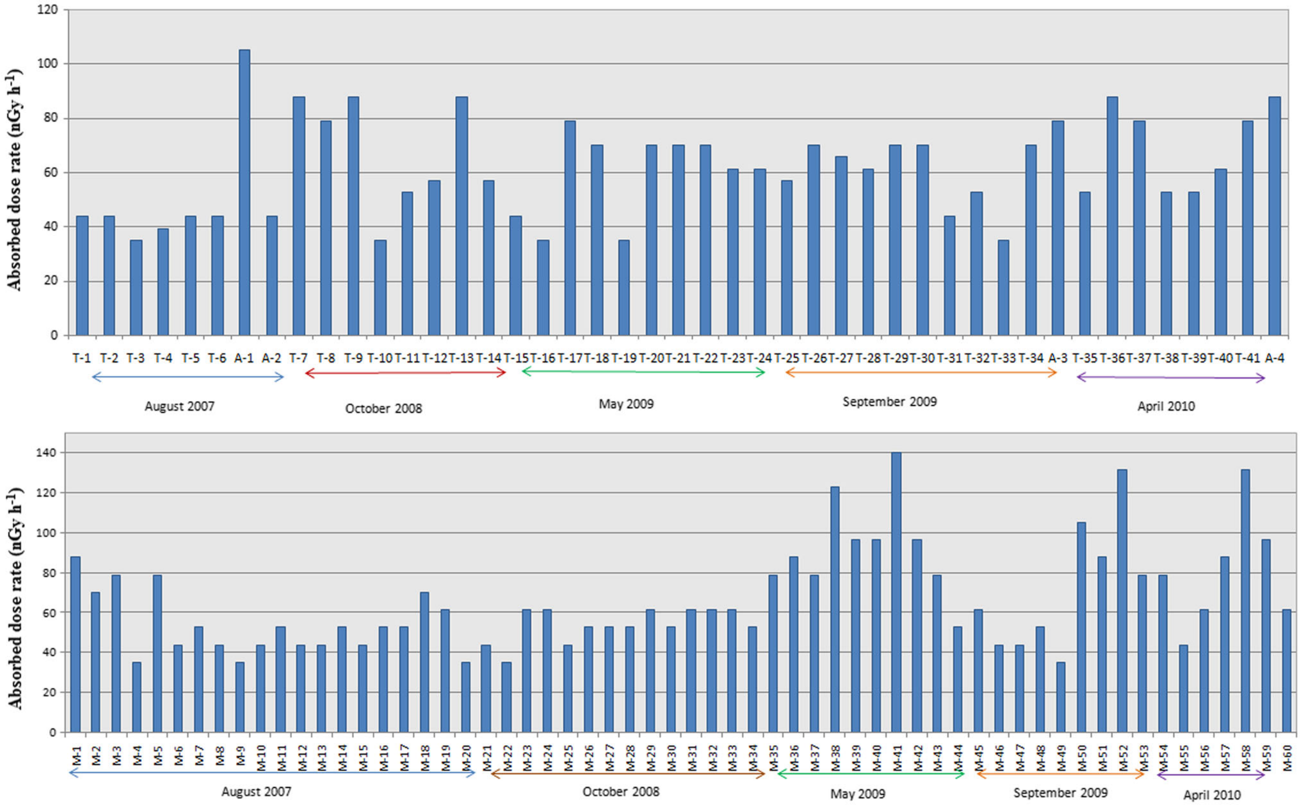

Fig. 3 Distribution curve of average dose rate of the seasonal terrestrial gamma radiation in the Maritza, Tundja and Arda riverbanks

highest gross beta activity concentration was observed in April for the Maritza, Tundja and Arda Rivers. The reason of this result could be attributed to high flow rate of the rivers in April. High discharge causes flooding and high water flow, so agricultural lands along the river submerse, leading to dissolution of K, the beta emitter. Therefore it can be suggested that gross beta values are higher in the water samples of the trans-boundary rivers during the periods of flooding.

Total radium isotopes activity concentrations were between 0.008 and 0.385 Bq L^{-1}, 0.010 and 0.120 Bq L^{-1} and 0.020 and 0.040 Bq L^{-1} for the Maritza, Tundja and Arda River waters, respectively. Gross alpha and total radium activity concentration in the rivers reached the highest values due to the decreasing flow rate of rivers in dry season.

The results of the radioactivity measurements are very important because river waters are utilized for irrigation purposes in the Maritza Basin. The data obtained from the present study have been compared with reported data from other countries of the world. The mean gross α and β activities in the Maritza, Tundja and Arda River waters are lower than those observed for the Firtina River (0.033 ± 0.004 Bq L^{-1}) [23], Batman (0.047 ± 0.009 Bq L^{-1}) and Tigris River (0.047 ± 0.009 Bq L^{-1}) [22]. While our results of gross alpha activities are high in any case, the gross beta activities are lower than those reported for the river waters of Epirus (from 0.022 ± 0.009 to 0.086 ± 0.094 Bq L^{-1}), Macedonia (0.084 ± 0.026 Bq L^{-1}) and Thessalia (0.078 ± 0.046 Bq L^{-1}) (Greece) [9], Seyhan River (0.2453 Bq L^{-1}) (Adana) [24], Ebro river (0.213 ± 0.012 Bq L^{-1}) (Northeast Spain) [1], Bendimahi river (from 0.02 ± 0.01to 3.12 ± 1.16 Bq L^{-1}) (Van) [10]. In addition, the mean gross alpha, gross beta and total radium isotopes activities in the river waters were lower than the values reported by WHO (gross α: 0.1 Bq L^{-1}, gross beta: 1 Bq L^{-1}) and EPA (gross α: 0.56 Bq L^{-1}, gross radium: 0. Bq L^{-1}) [25, 26].

Determination of uranium and heavy metal concentrations in the river waters

Table 4 presents the variation of uranium concentration within the range of 0.020–1.500, 0.020–1.000, 0.300–0.500 μg L^{-1} for the Maritza, Tundja and Arda River waters, respectively. The mean, minimum and maximum dissolved Cu, Zn, Fe, Al and Mn concentrations are also presented in Table 4. The content of the U for three river was lower than those reported by WHO (0.015 mg L^{-1}) [25], EPA (0.03 mg L^{-1}) [26] and ICRP-30 (0.002 mg L^{-1}) [27]. The mean concentrations of Cu and Zn were lower than the TSE-266 (Cu:2 mg L^{-1}, Zn: 5 mg L^{-1}) [28], WHO (Cu:

Table 3 Mean, minimum and maximum values of the pH, conductivity, alkalinity and dissolved oxygen in river waters of the Maritza, Tundja and Arda

Parameters	Maritza			Tundja			Arda		
	Min	Max	Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean (SD)
pH	7.00	8.50	7.70 (0.30)	7.20	8.47	7.80 (0.30)	7.30	7.46	7.38 (0.06)
Conductivity (mS cm^{-1})	0.36	29.52	3.78 (7.00)	0.08	1.35	0.81 (0.32)	0.45	0.85	0.63 (0.20)
Alkalinity $NaHCO_3$ (g L^{-1})	0.17	0.76	0.39 (0.10)	0.35	0.77	0.47 (0.10)	0.17	0.41	0.28 (0.12)
Dissolved O_2 (mg L^{-1})	3.15	12.15	7.94 (2.30)	4.80	10.6	7.70 (1.85)	8.2	8.85	8.53 (0.46)

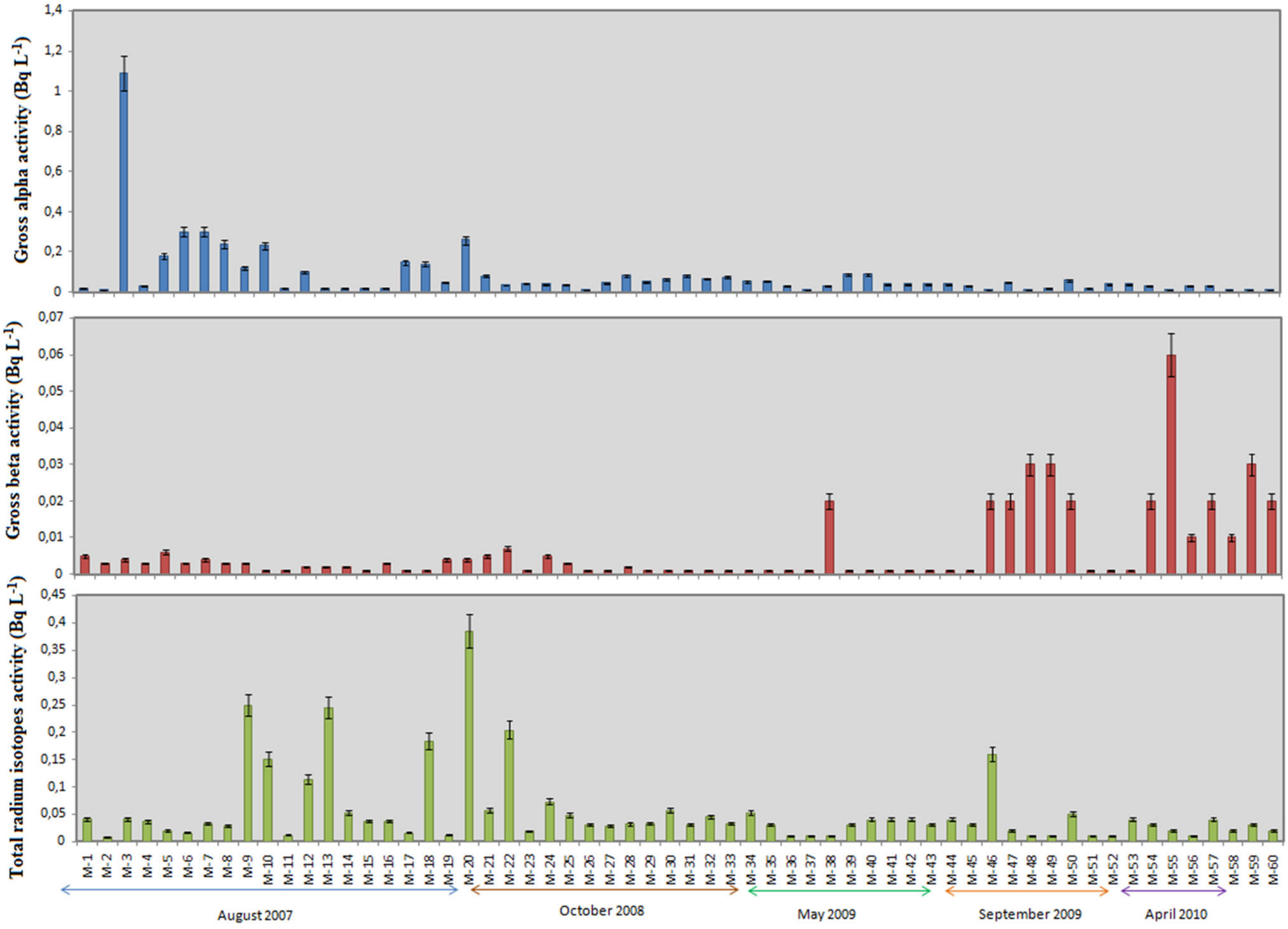

Fig. 4 Distribution of the gross alpha, gross beta and total radium isotopes activities in the Maritza surface water samples

2 mg L^{-1}) [29], EPA (Cu: 1 mg L^{-1}, Zn: 5 mg L^{-1}) [26] and EU (Cu: 2 mg L^{-1}) [30] standards while Fe and Al were relatively higher than these standards TSE-266 (Fe: 0.2 mg L^{-1}, Al: 0.2 mg L^{-1}), WHO (Al: 0.05 mg L^{-1}), EPA (Fe: 0.3 mg L^{-1}, Al: 0.2 mg L^{-1}) and EU (Fe: 0.2 mg L^{-1}, Al: 0.2 mg L^{-1}). The moreover concentrations of Mn for the river waters were lower than guidelines given by WHO (0.4 mg L^{-1}) but higher than those given by TSE-266 (0.05 mg L^{-1}), EPA (0.05 mg L^{-1}) and EU (0.05 mg L^{-1}).

The maximum concentrations for Cu, Al, Fe and Zn were observed during summer. The seasonal variation for these metals could be due to the low river flow, which is caused by the low influx of fresh water, de-watering from irrigation, evaporation etc. during these months compared to the rest period of the year.

Comparing the heavy metal concentration of the water samples and recommended international standards such as WHO [29], it could be stated that the rivers studied in the

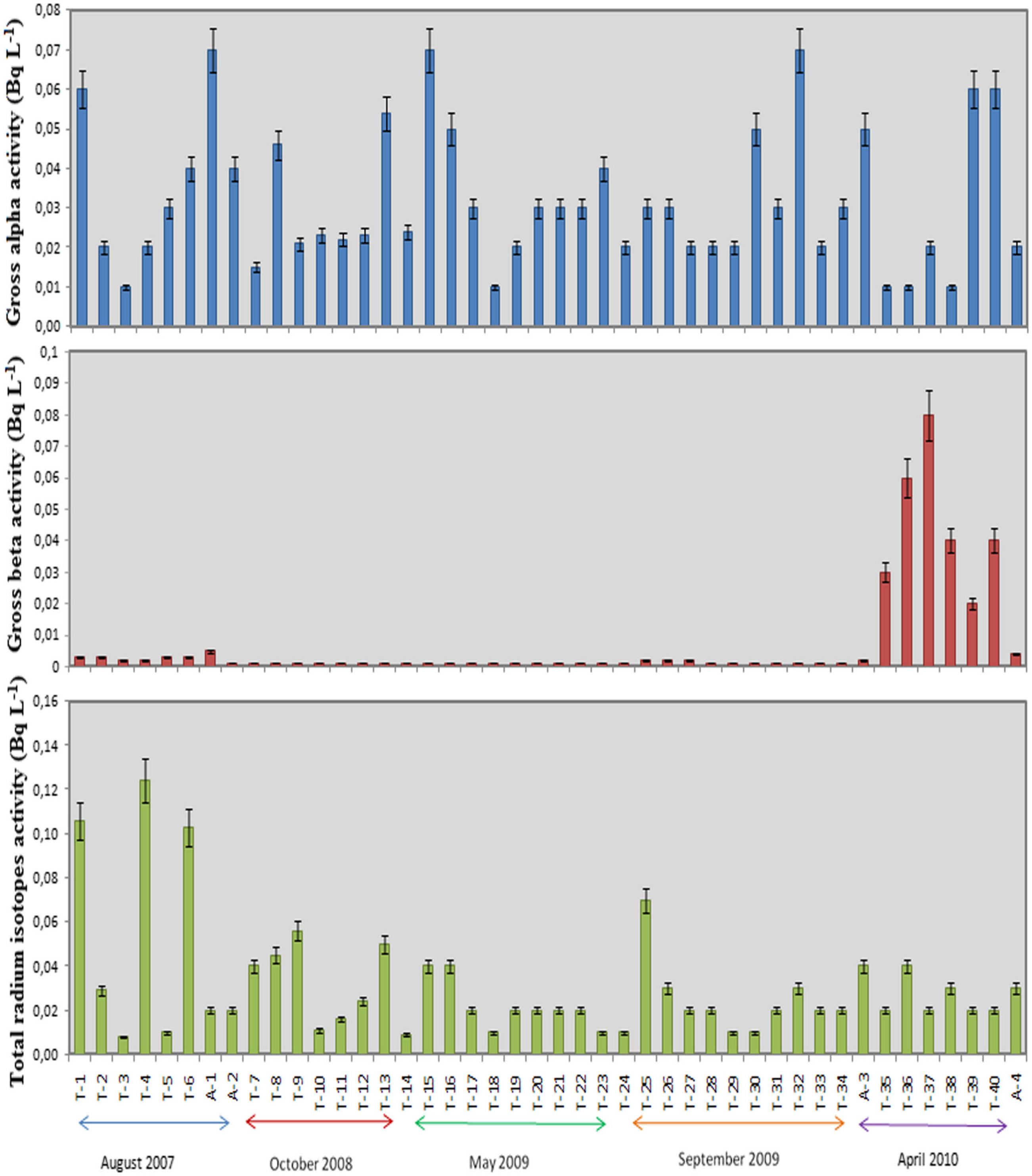

Fig. 5 Distribution of the gross alpha, gross beta and total radium isotopes activities in the Tundja and Arda surface water samples

current research were not significantly contaminated, only Fe and Al concentrations were found slightly higher than the international standards. This phenomenon can be explained by the contribution of the metal pollutants from industrial plants located Edirne Region, Ergene River-Turkey and also in Bulgaria and Greece. As mentioned in literature by Vasilikiotis et al. [12], main industrial wastewaters contaminating the rivers come from heavy industries such as metallurgy, chemical production, power production, paintings and textiles, etc. in Bulgaria [12, 31]. There are

Table 4 Mean, minimum and maximum values of gross alpha, gross beta, total radium isotopes, uranium and heavy metals in river waters of the Maritza, Tundja and Arda (with 95 % confidence level)

	Maritza			Tundja			Arda		
	Min	Max	Mean (SD)	Min	Max	Mean (SD)	Min	Max	Mean (SD)
Radioactivity									
Gross α (Bq L^{-1})	0.010	1.090	0.083 ± 0.010	0.010	0.070	0.031 ± 0.002	0.020	0.070	0.045 ± 0.020
Gross β (Bq L^{-1})	0.001	0.060	0.007 ± 0.001	0.001	0.080	0.008 ± 0.002	0.001	0.005	0.003 ± 0.002
Total radium isotopes (Bq L^{-1})	0.008	0.385	0.054 ± 0.005	0.010	0.120	0.031 ± 0.003	0.020	0.040	0.028 ± 0.009
Uranium (μg L^{-1})	0.020	1.500	0.464 ± 0.048	0.020	1.000	0.310 ± 0.074	0.300	0.500	0.400 ± 0.277
Heavy metal									
Cu (mg L^{-1})	0.007	0.160	0.026 ± 0.004	0.002	0.024	0.010 ± 0.001	0.012	0.140	0.014 ± 0.003
Zn (mg L^{-1})	0.016	0.093	0.043 ± 0.002	0.007	0.336	0.067 ± 0.020	0.042	0.095	0.066 ± 0.021
Fe (mg L^{-1})	0.312	4.054	0.995 ± 0.080	0.211	2.468	0.734 ± 0.111	0.110	0.635	0.484 ± 0.247
Al (mg L^{-1})	0.180	4.948	0.985 ± 0.107	0.100	2.237	0.542 ± 0.101	0.063	0.449	0.333 ± 0.179
Mn (mg L^{-1})	0.056	0.586	0.211 ± 0.011	0.070	0.521	0.205 ± 0.032	0.074	0.309	0.196 ± 0.123

also mining activities in the mountainous Bulgarian part of the basin. In fact, they have only local impacts, coming pollution by heavy metals. There are 11 tailing ponds for mining waste in the Bulgaria. The basin also accommodates the region which has the largest open cast mining of coal in Bulgaria. Moreover several industries in the Thracian region of Turkey flush their effluents, some of them without treatment, directly into the Ergene River and its branches [32]. On the other hand, intensive agriculture in those regions requires the usage of considerable amounts of pesticides and artificial fertilizers [12]. Consequently the general source of the pollution in Maritza basin can be summarized under the light of these literature results.

Correlation analysis

The statistical processing of the data was performed using the Minitab 16 Statistical software package. The correlations between the heavy metal contents and radioactivity concentrations in river waters were determined. Due to the observed data of Maritza and Tundja–Arda rivers generally are not normally distributed and also have outliers, the Spearman's rho correlation analysis was selected and results were illustrated as Table 5. As shown in Table 5 for the Maritza River, there are strong positive correlations between U and Al, Cu Fe, Mn and Zn, and also between each metal. However there is a weak negative correlation between total radium isotopes, gross α and Al, Cu Fe, Mn and Zn and, there is a positive correlation between total radium isotopes and gross α activity. While correlation between gross β and heavy metals is positive, correlation between gross β and grossα, total radium isotopes and uranium is negative.

A strong negative correlation is observed between uranium and heavy metals for Tundja–Arda river waters. The total radium isotopes have strong positive correlation with heavy metals and strong negative correlation with uranium. The gross α showed positive correlation with heavy metals and total radium isotopes, while negative correlation with uranium. There is a positive correlation between gross β and heavy metals, total radium isotopes and gross α while negative correlation is observed between gross β and uranium.

Conclusion

The main objective of the current study was to analyze and assess the status of the Turkish Trans-boundary Rivers. In particular, the study provides an informative source for the countries in order to identify the potential research areas for enhanced cooperation between the riparian states. In the EU-Turkey accession partnership, the trans-boundary waters have already been identified as a priority issue, which demands short-term considerations and progress.

The present work supplies quantitative information about the radioactivity and heavy metal levels in the Maritza, Tundja and Arda Rivers in 3 year period (2007–2010). Significant differences in radium isotopes concentrations at the sites along the Maritza River were attributed to the run-off of phosphate fertilizers and operation of the coal mines in the region, whereas seasonal variations were mainly due to the flow changes. The average annual effective dose equivalent in riverbank of Maritza, Tundja and Arda in Edirne region ranged from 0.04 to 0.13 mSv $year^{-1}$ with mean value of 0.08 ± 0.02 mSv $year^{-1}$ for outdoor, which is in agreement with 0.07 mSv $year^{-1}$ world average (UNSCEAR 2000). Terrestrial gamma dose rate and annual effective dose equivalent is influenced significantly by the geological structure of the area.

Table 5 Spearman's rho correlation matrix among the variables for Maritza and Tundja–Arda River combined water samples

		Al (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	U (μg/L)	Ra (Bq/L)	Total α (Bq/L)	Total β (Bq/L)
Maritza	Al (mg/L)	1								
	Cu (mg/L)	0.995**	1							
	Fe (mg/L)	0.999**	0.995**	1						
	Mn (mg/L)	0.999**	0.993**	0.999**	1					
	Zn (mg/L)	0.996**	0.993**	0.996**	0.995**	1				
	U (μg/L)	0.994**	0.988**	0.994**	0.992**	0.992**	1			
	Ra (Bq/L)	−0.202	−0.197	−0.194	−0.189	−0.221	−0.19	1		
	Total α (Bq/L)	−0.352*	−0.344*	−0.351**	−0.363*	−0.334*	−0.243	0.323*	1	
	Total β (Bq/L)	0.086	0.077	0.085	0.086	0.075	−0.206	−0.064	−0.268*	1
Tundja–Arda	Al (mg/L)	1								
	Cu (mg/L)	0.814**	1							
	Fe (mg/L)	0.998**	0.818**	1						
	Mn (mg/L	0.757**	0.673**	0.765**	1					
	Zn (mg/L	0.787**	0.957**	0.799**	0.749**	1				
	U (μg/L)	−0.861**	−0.824**	−0.843**	−0.671**	−0.724**	1			
	Ra (Bq/L)	0.821**	0.926**	0.822**	0.707**	0.887**	−0.832**	1		
	Total α (Bq/L)	0.570**	0.799**	0.583**	0.853**	0.836**	−0.656**	0.849**	1	
	Total β (Bq/L)	0.489*	0.769**	0.488**	0.479*	0.725**	−0.366	0.868**	0.778**	1

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed)

The highest heavy metal concentrations (Cu, Fe, Al, Zn and Mn) in the studied rivers were observed during summer. This result may be attributed to the absence of rainfall and the enrichment of the river mainly by groundwater, and the anthropogenic influence of urban and industrial wastewater in the Maritza, Tundja and Arda Rivers located near the town of Edirne. The heavy metal content of waters in Maritza, Tundja and Arda River is generally acceptable for some metals. For three rivers, U, Zn and Cu concentrations were lower than the guidelines given by ICRP-30, TSE-266, WHO, EPA and EC while Fe and Al concentrations were relatively higher than those reported in these guidelines. Spearman's rho Correlation matrix analysis showed the interactions between radioactivity and heavy metals. The highest correlations in river water samples were found between U and the other metals, namely.

It is known that the monitoring and assessment of the effects of individual discharges at field sites are often quite difficult. Stricter control of effluent discharges will be of higher importance in the future. Cooperation mechanism in the Maritza River basin in terms of pollution control, beyond the existing bilateral frameworks and involving all three riparian countries, should be established.

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