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Assessments of Tritium Concentration in the Some Water Samples around Rize

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ABSTRACT The aim of this study is to determine tritium levels in the seawater of Fırtına and Hemşin in Rize region, and along the coastline where these two rivers flow into. Sampling process was examined by applying ASTM D4107-08 method. Experimental studies were conducted by using scintillation device. Sampling coordinates were recorded by Magellan Explorist 510-GPS. After having collected 26 samples from Fırtına River, 23 samples from Hemşin River, and 28 samples from the seawater along the coastline, tritium concentration were calculated for 77 samples in total. Minimum detectable activity concentration (MDC) was determined as 1.36 Bq/L. The average tritium activity concentrations for Fırtına, Hemşin Rivers water samples and seawater samples for average tritium activity concentrations which were determined by liquid scintillation counting system were calculated as 2.666±1.136 Bq / L, 2.298±1.111 Bq / L and 1.874±1.161 Bq / L respectively. 2 water samples from Fırtına River, 6 water samples from Hemşin River, and 8 water samples taken from the seawater along the coastline were lower than MDC.

Keywords: Radioactivity, Tritium, LSC.

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1. INTRODUCTION

Tritium (^{3}H) is a radiogenic form of hydrogen, used in research, nuclear power plants (NPP). Tritium has a half-life of 12.3 years and decays to ^{3}He with emission of a low-energy beta particle with maximum energy of 18.6 keV [1]. Tritium is produced naturally by cosmic ray interactions with hydrogen in the upper atmosphere and transfers to the troposphere. The environmental levels of this radionuclide were raised during nuclear weapon tests [2-6].

Once released to the atmosphere, inorganic tritium is rapidly oxidised to tritiated water (HTO). HTO can enter the human body by inhalation, absorption through the skin or ingestion of food and drinking water [7–9]. In the body, HTO is mixed rapidly with extracellular and intracellular tissue water, with a fraction replacing the hydrogen bound in organic molecules. Therefore, monitoring the internal exposure to HTO is important. HTO is one of the tritium forms that are harmful for humans, and it causes the most harm after internal exposure [10, 11].

Currently, there is no NPP in Turkey; however, agreements have been signed for the installation of an NPP. This NPP will be a pressurized water reactor type, scheduled to be in operation in 2019 [12].

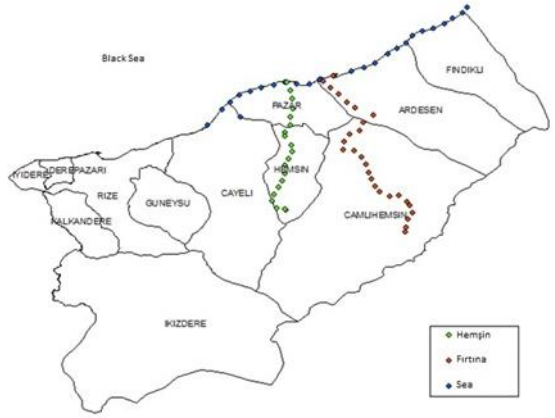

Figure 1. *Location of sampling regions.*

The aim of this study is to determine tritium levels in the water of Fırtına and Hemşin in Rize region, and along the coastline where these two rivers flow into. These results of this study will be used as baseline data for dose assessment of the regions when an unexpected tritium release occurs.

2. EXPERIMENTAL

Rize, which was selected as the pilot region, is a province of northeast Turkey, on the eastern Black Sea coast. Rize lies between latitudes of 40° 20' and 41° 20' N and longitudes of 40° 22' and 41° 28' E. Rize has a catchment area of 3920 km^2. It is on the north side of the range of mountains that runs along the Black Sea coast. Summers are cool (average 22°C), winters are warm (average 7°C), and it is wet all year. The population of Rize is 331,041 people [13].

Two large rivers (Fırtına and Hemşin) of Rize province water samples and seawater tritium values of samples (Fig. 1) were investigated by using LSC (Liquid Sintillation Counter) with ASTM D4107-08 method. About 500 mL of water sample was collected in a polyethylene bottle. The samples were treated rapidly to avoid unexpected contamination. Interferences during the counting such as quenching reduce the efficiency of detection. Therefore, a distillation process is usually applied to the sample to prevent quenching.

The background tritium concentration in the samples is relatively low [7, 14, 15] and hence sample preparation is needed. About 25 mL of water sample was added to 1.25 mg active charcoal, shaked vigorously for about 30 sec, and then filtered to obtain a clear filtrate. Then the filtrate was distilled. Distillation removes color but not all chemical impurities. These impurities react with scintillation liquid and cause luminescence. To remove luminescence, the samples had to be stored in a scintillation vial for 2–5 days in an opaque place or container before the measurement [4]. 10 ml of distilled sample was given into a measuring plastic vial (Zinsser Analytics, 20 ml), and scintillation cocktail (Ultima Gold LLT, Perkin Elmer Inc.) was added up to total volume of 20 ml. The plastic vials do not include ^{40}K, so they are more suitable for lower background levels and higher counting efficiency as compared with glass vials. Also, the vials were shaken for about one minute in order to make homogeneous solutions. Besides, the vials were cleaned outside with ethanol before placing them into the counter to prevent contamination.

A background sample was prepared by using twice-distilled groundwater with a low tritium concentration. The measurements were performed with a low-level liquid scintillation counter (Perkin Elmer Tricarb 2910 TR). The measurement time was set to 75 min × 10 times to evaluate the detection uncertainty and minimum detectable concentration (MDC). The measurement uncertainty was evaluated at the 95 % confidence level. The MDC for this method was calculated using Equation (1) [16].

$$\mathrm{MDC} = \frac{16.7x3.29\sqrt{cpm_b.t_s.\left(1+\frac{t_s}{t_b}\right)+3}}{\epsilon.t_s.V} \quad (1)$$

where cpm_b is the count rate of the background (cpm), t_s is the counting time of the sample (minute), t_b is the counting time of the background (minute), ε is the efficiency and V is the sample volume (liter).

Table 1. *Measurement results for samples spiked with different concentrations of a certified standard tritium source.*

Sample name	Spiked Activity (Bq L^{-1})	U[a] (%)	Measured activity (Bq L^{-1})	U[a] (%)	Relative bias (%)
HAS[b]	4.84E + 06	3.2	4.75E + 06	5.7	1.9
MAS[c]	4.02E + 03	3.2	3.77E + 03	5.9	6.2
LAS[d]	1.55E + 01	3.2	1.45E + 01	6.3	6.5

[a]Relative expanded standard uncertainty (k = 2).
[b]High-activity tritium sample.
[c]Medium-activity tritium sample.
[d]Low-activity tritium sample.

To verify this analysis method, three samples spiked with different levels of a certified standard tritium source (Eckert & Ziegler, P.O. No.: P700723, Source No.: 1676–44) were prepared and measured. The spiked and the measured activities are given in Table 1. Measurements were made at a 10:10 mixing ratio of the samples and the scintillation cocktail.

Table 2. *Tritium concentration and altitude information in Fırtına river water samples.*

Sample Code	Altitude of Sampling Point (m)	Tritium Concentration (Bq / l)
N1	2268	2.740±1.28
N2	2200	<MDC
N3	1945	2.409±0.921
N4	1754	2.075±1.241
N5	1585	1.941±1.381
N6	1492	1.874±1.162
N7	1379	<MDC
N8	1173	1.740±1.271
N9	1032	2.141±1.111
N10	1043	2.744±1.112
N11	782	3.145±1.112
N12	696	3.413±1.112
N13	590	2.744±1.112
N14	551	3.011±1.112
N15	518	2.610±1.112
N16	289	3.078±1.112
N17	282	3.346±1.112
N18	222	3.413±1.112
N19	181	2.543±1.112
N20	148	2.677±1.112
N21	124	3.279±1.112
N22	109	2.744±1.112
N23	70	3.011±1.112
N24	47	1.874±1.111
N25	24	2.476±1.112
N26	0	2.944±1.288
Maximum		3.413±1.112
Minimum		1.740±1.271
Average		2.666±1.136

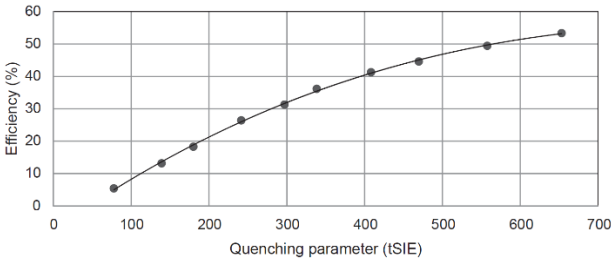

Figure 2. *Quench curve for tritium.*

A quenching calibration curve method was applied to determine the detection efficiency. Ten standard tritium samples with different quenching levels were prepared. The same tritium concentration was used in all the samples. To obtain different quenching effects, various volumes of the quenching agent (carbon tetrachloride) were added into vials. Then, vials were counted in the tritium (0–18.6 keV) counting windows, and the quench curve (Figure 1) of tritium was obtained by using the quenching parameter (tSIE).

Table 3. *Tritium concentration and altitude information in Hemşin river water samples.*

Sample Code	Altitude of Sampling Point (m)	Tritium Concentration (Bq / l)
P1	1165	<MDC
P2	1130	2.476±1.257
P3	967	<MDC
P4	818	4.417±1.242
P5	809	2.677±1.381
P6	688	3.346±1.163
P7	701	2.610±1.305
P8	580	1.606±1.271
P9	432	2.409±1.111
P10	356	<MDC
P11	318	2.476±1.112
P12	259	<MDC
P13	438	2.075±1.111
P14	164	2.543±1.112
P15	140	2.075±1.111
P16	135	2.141±1.111
P17	124	2.409±1.111
P18	109	<MDC
P19	70	2.476±1.112
P20	67	<MDC
P21	39	2.275±1.111
P22	11	2.543±1.112
P23	0	2.075±1.111
Maximum		4.417±1.242
Minimum		1.606±1.271
Average		2.298±1.111

Table 4. *Tritium concentration in seawater samples.*

Sample Code	Tritium Concentration (Bq / l)
D1	2.409±1.288
D2	1.740±1.257
D3	<MDC
D4	<MDC
D5	2.275±1.381
D6	2.141±1.162
D7	1.874±1.305
D8	3.681±1.272
D9	2.008±1.111
D10	<MDC
D11	<MDC
D12	<MDC
D13	<MDC
D14	<MDC
D15	2.128±1.111
D16	2.744±1.112
D17	2.075±1.111
D18	2.128±1.111
D19	1.941±1.111
D20	1.606±1.111
D21	2.208±1.111
D22	1.472±1.111
D23	1.807±1.111
D24	1.740±1.111
D25	<MDC
D26	2.008±1.111
D27	1.807±1.111
D28	1.807±1.111
Maximum	3.681±1.272
Minimum	1.472±1.111
Average	1.874±1.161

3. RESULTS

Table 2-4 shows the results of tritium concentration for the water samples taken along the Fırtına and Hemşin River waters and the coastline where these rivers emanate.

The average tritium concentration for 26 samples taken from Fırtına river was calculated as 2.666 ± 1.136 Bq / L (22.593 ± 9.627 TU). The maximum tritium concentration was found to be of 3.413 ± 1.112 Bq / L (28.924 ± 9.424 TU) with sample code N-12 and N-18. The lowest tritium concentration was found to be 1.74 ± 1.271 Bq / L (14.746 ± 10.771 TU), with sample code N-8 with 1173 m peak at 45.35807K - 06.76575D coordinates. Two samples were under the MDC.

The mean tritium concentration for 23 samples taken from Hemşin river was calculated as 2.298 ± 1.111 Bq / L (19.475 ± 9.415 TU). The highest tritium concentration was found to be 4.417 ± 1.242 Bq / L (37.432 ± 10.525 TU), with sample code P-4 with 818 m at 45.34244K-06.56770D coordinates. The lowest tritium concentration was found to be 1.606 ± 1.271 Bq / L (13.610 ± 10.771 TU), with sample code P-8 with a peak at 45.40544K -

06.58703D at 580 m. Six samples were under the MDC. The average tritium concentration for 28 samples taken from sea water samples was calculated as 1.874 ± 1.161 Bq / L (15.881 ± 9.839 TU). The highest concentration of tritium was found to be 3.681 ± 1.272 Bq / L (31.195 ± 10.780 TU) at 45.58654K-06.52483D, with sample code D-8. The lowest tritium concentration was found to be 1.472 ± 1.111Bq / L (12.475 ± 9.415 TU) at 45.68705K - 06.77067D, with sample code D-22. 8 samples were under the MDC.

Table 5. *The concentrations of tritium in water samples from Turkey and other study areas.*

Country	Tritium Concentration (Bq / l)	Sample Type	Reference
Japan (North Island)	2.42 ± 0.81 Bq/L (20.48±6.85 TU)	River water	[18]
Japan (South Island)	1.00 ± 0.36 Bq/L (8.46±3.05 TU) (20.31-134.56 TU)	River water	[18]
Spain	3.6±0.6 Bq/L (30.47±5.08 TU) (18.7 TU)	River water	[17]
India	0.51±0.04Bq/L (4.34±0.34 TU)	River water (Varahi)	[20]
India	0.66±0.09 Bq/L (5.61±0.84 TU)	River water (Markandeya)	[20]
Finland	0.92 Bq/L (7.8 TU)	Sea water	[19]
Finland	0.60 Bq/L (5.08 TU)	River water	[19]
Ireland	0.9-2.4 Bq/L (7.62-22.17 TU)	Sea Water	[21]
Turkey	1.64±0.94 Bq/L (13.88±7.95 TU)	River water (Büyükdere)	[25]
Turkey	1.72±0.94 Bq/l (14.56±7.95 TU)	River water (İkizdere)	[25]
Turkey	2.66±1.13Bq/l (22.59±9.62 TU)	River water (Fırtına)	Present Study
Turkey	2.29±1.11Bq/L (19.48±9.42 TU)	River water (Hemşin)	Present Study
Turkey	2.29±1.11Bq/L (19.48±9.42 TU)	Sea Water	Present Study

Totally 16 of 77 water samples were found to be below the MDC as a result of tritium concentration analysis. The concentration of tritium in Fırtına river water was higher than in Hemşin river water.

There are many studies of tritium activity levels in river and sea waters of different parts of the world. In order to be able to compare the present work, the average or variation values of the tritium concentration of some of these studies are given in Table 5. The results obtained in the present study are much lower than the results obtained from the river water samples of Spain [17] while the Japan (North Island) river water samples [18] were in close range with the obtained results. As can also be seen from Table 4. Fırtına and Hemşin river water samples have higher concentrations of tritium than Japan (South Island), Finland, Indian, Ireland, French river water samples [18-24].

4. CONCLUSION

Tritiated water concentrations were measured in 2 rivers and Sea water located in the northeast part of Turkey, Rize that were not directly influenced by the releases from any nuclear facilities. The average and the maximum tritium concentration in the water samples of 77 in the study area region was 2.279±1.136 Bq L^{-1}, 4.417± 1.242 Bq L^{-1}, respectively. About 21 % of the results are below the MDC (1.36 Bq L^{-1}). The measured values are lower than those in Japan (North Island) and Spain, but higher than those in Japan (South Island), India, Ireland, Finland. This indicates that environmental regions are important factors. Tritium continues to be a useful tracer in a post nuclear leak. Considering low concentrations in precipitation, the absence of the tritium transient allows for direct assessment of dwelling times by comparing precipitation and river water tritium concentrations. Briefly, the results of this study will be used as baseline data for dose assessment of the regions when an unexpected tritium release occurs.

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