■ 논 문 ■

Tritium Concentrations in Surface Seawater around Korean Peninsula

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Abstract – An electrolytic enrichment technique was used to measure low levels of tritium in seawater around the Korean peninsula. Tritium concentrations were determined for surface seawater samples collected from the East Sea, the South Sea, and the Yellow Sea. The tritium concentrations in surface seawater samples from the study area ranged from 0.12 Bq L^{-1} to 1.50 Bq L^{-1} with a mean value of 0.60±0.35 Bq L^{-1}. The means of the tritium concentration were 0.54 ±0.30 Bq L^{-1} for the East Sea, 0.48±0.35 Bq L^{-1} for the South Sea, and 0.77±0.32 Bq L^{-1} for the Yellow Sea. The tritium concentrations in the sea areas did not show much difference no matter where the samples were taken. Due to the limited number and distribution of sampling points, no systematic change in tritium levels with latitude was observed. Measured tritium levels were similar to those observed in other data collected near Japan, but higher than mid-Pacific Ocean measurements.

요약 – 전해농축법을 이용하여 한국 주변 해역 해수중 저준위 삼중수소를 측정하였다. 동·서·남해안에서 채취된 표층해수중 삼중수소를 측정한 결과, 삼중수소 농도는 0.12 Bq L^{-1}에서 1.50 BqL^{-1} 범위내의 값을 나타내었으며 그 평균값은 0.60±0.35Bq L^{-1}였다. 해역별 평균 삼중수소 농도는 동해안에서 0.54±0.30 Bq L^{-1} 남해안에서 0.48±0.35 Bq L^{-1}, 서해안에서 0.77±0.32 Bq L^{-1}의 농도분포를 각각 나타내었으며, 해역별로 큰 차이를 나타내지 않았다. 또한, 시료채취지점이 매우 좁은 위도범위내에 한정되어 있어 위도에 따른 삼중수소 농도의 체계적인 변화는 관찰되지 않았다. 본 연구에서 얻어진 표층해수중 삼중수소 농도 준위는 일본 근해에서 조사된 결과와 매우 유사하였으며, 태평양지역에서의 삼중수소 농도에 비해서는 약간 높은 값을 나타내었다.

INTRODUCTION

Tritium is one of the natural radionuclides produced in the atmosphere by the interaction of cosmic rays with the atmospheric gases. The tritium content of the atmosphere increased greatly by a series of atmospheric nuclear weapon tests which yielded 1.7×10^8 TBq of tritium, particularly during the period 1954-1962[1, 2]. The tritium level has decreased gradually since the partial test ban treaty(PTBT) became effective in 1963. As a source of tritium in the environment, tritium released from the nuclear facilities has become more significant than that from weapons tests at present. Most of tritium injected into the environment is present as tritiated water(HTO) and is ultimately transferred into the ocean by precipitation, molecular exchange, and river runoff. The dynamics of tritium in the ocean is especially important because the ocean is one of the largest sinks of tritium. Furthermore, public interest has focused on the radioactive pollution of the marine environment since 1993 when the White Book [3] revealed the former USSR and the Russia have dumped large quantity of liquid and solid radioactive waste into the Far Eastern Sea areas since late 1950's. However, enough baseline data to estimate marine environmental impact by various tritium sources such as nuclear power plants, radioactive wastes and unexpected nuclear accidents have not been accumulated in Korea yet. For this reason, it is necessary to obtain baseline data which would enable the assessment of public exposure and environmental impact by the accidentally released tritium.

Recent enhancement of the detecting ability of liquid scintillation counting systems has made it possible to detect tritium directly as low as 1 Bq L^{-1}[4, 5]. However, most tritium level in the seawater is lower than 1 Bq L-1. Accordingly, the electrolytic enrichment technique was applied to measure tri-

tium in seawater samples. The reproducibility of the electrolytic enrichment system was also investigated. This work was carried out to obtain background tritium level in the marine environment using surface seawater samples around Korea.

MATERIALS AND METHODS

During the period of October 1994 to May 1995, surface seawater samples around Korea were taken three times from 21 sampling stations by the National Fisheries Research and Development Agency of Korea. Surface seawater samples were collected by immersing a pump below sea level. The sampling locations are shown in Fig. 1.

The electrolytic cell was designed as such that 1000 grams(g) of samples could be enriched to 60 g in a single step by electrolysis. The cell was plugged by a silicon cap. Through a polyethylene tube, the evolved gas was transferred to a bubbler filled with silicon oil which kept the cell at a slightly positive pressure to avoid possible contamination from the laboratory atmosphere.
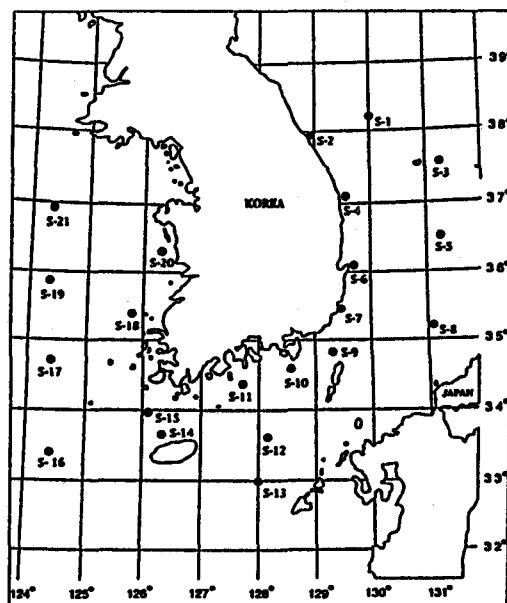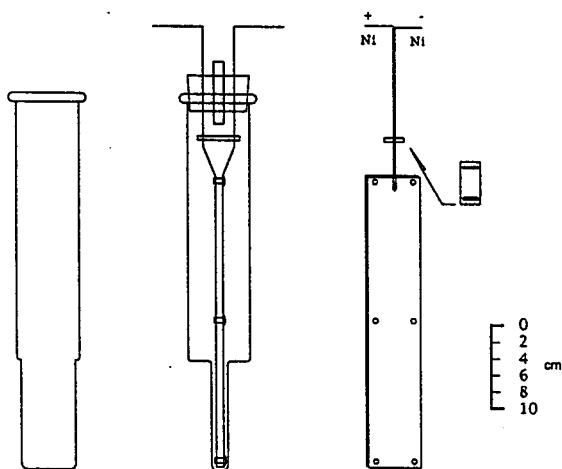

Fig. 1. Sampling Locations.

Fig. 2. An electrolysis cell unit.

The anode and the cathode were fabricated from high purity nickel(99.999 %) sheet 1 mm thick, and were 350 mm long and 63 mm wide(Fig. 2). The electrodes were spot-welded to nickel rods which pass through the cell cap. The electrode spacing was maintained accurately at 5 mm by six Teflon spacers. Prior to every run the electrodes were washed by concentrated hydrochloric acid solution. The reproducibility of the electrodes in an electrolysis run was then checked before assaying samples. After distilling all the samples, the samples were made alkaline by adding 0.8 % w/w sodium peroxide which prevented corrosion of the electrodes during the electrolytic enrichment.

The cell unit, which consisted of two spiked cells, a tritium-free water sample (blank) and thirteen sample cells, were connected in series and immersed in 10% ethyleneglycol aqueous solution controlled at 1-2 ℃ . For the preparation of the spiked cell, 997 g of tritium-free water was transferred into the cell and was made alkaline by adding 0.8 % w/w sodium peroxide. A portion of tritiated standard solution (Amersham Co.) of known specific activity was spiked to the electrolyte.

The initial current was 10 A, which pro-duced a current density around 45 mA cm^{-2} when the electrolyte weight was 1000 g. As the electrolysis proceeded, the level of the electrolyte in the cell decreased. While the level of the electrolyte in the cell was in the "wide zone", the current was set to 10 A. Once the electrolyte level reached to the "narrow zone", however, the current was reduced to 3 A manually so that the current density did not exceed 100 mA cm^{-2} .

Generally, the constant current density and fixed cumulative current were effective in minimizing evaporation loss and obtaining reliable data on the enrichment factor. Therefore, an ampere-hour meter was incorporated in the circuit. The electrolysis was automatically switched off when the current reached a preset cumulative current. On completion of electrolysis, each cell was weighed to determine the final volume of water. The electrolyte was transferred into a distillation flask, and then neutralized with anhydrous lead chloride. After distilling the electrolyte, an aliquot 8 mL of the distilled water was transferred to a Teflon vial and was mixed with 12 mL of Insta-gel XF(Packard) cocktail. After cooling in the counter at 13 ℃ under dark condition for one day, tritium concentrations in the samples were measured by the liquid scintillation counter (LKB, QUANTULUS 1220) for 500 min. The concentration was measured ten times for each sample. Statistical error analysis based on the chi-square test was applied to a series of data obtained by counting a sample repeatedly. All data for each sample were checked for Poisson and Gaussian distribution, and corrected for the decay that had occurred between date of sampling and analysis. The liquid scintillation counter was calibrated with a tritiated standard solution supplied by Amersham International. The quenching was corrected by the external standard channel ratio method using [226]Ra internal source. The chemiluminescence contribution, if any, was automatically subtracted from the total

counting rate to obtain a net counting rate ascribable to tritium only. The background counting rate was determined with a background sample prepared from tritium-free ground water collected from deep well. The counting efficiency for tritium was 27–28 %. The counting system showed a background of 0.75 0.10 cpm within the optimum window. The detection limit for tritium in the present system using the electrolytic enrichment method was about 0.1 Bq L^{-1} which was calculated using standard deviation of background counting rate.

RESULTS AND DISCUSSION

Evaluation of variations in enrichment factors

Generally, the enrichment of tritium by electrolysis is given by the following equation [6]:

$$V_f/V_i = (T_f V_f/T_i V_i)^\beta \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where V_i is the initial volume or weight

of the sample,

V_f is the final volume or weight of the sample,

T_i is the initial tritium activity,

T_f is the final tritium activity,

and b is the chemical separation factor.

When volume reduction factor (V_i/V_f), tritium concentration factor (T_f/T_i), and tritium retention $(T_f V_f/T_i V_i)$ factor are denoted as N, Z, and R, respectively, equation (1) can be reduced to $1/N = R^\beta$. When the samples in a set of cells, connected in a series and containing equal weight of water and electrolyte, are electrolyzed at a constant temperature, the enrichment factors such as b, N, and R may be different from cell to cell in a single run and also different from run to run in a single cell. Accordingly, the variation of enrichment factors was checked ten times. The means of the enrichment factors and their variations obtained from ten runs are summarized in Table 1. When the overall mean of N was 16.4, those of Z, R, and b were 12.2,

Table 1. Electrolytic enrichment factors on the cell units

Cell	A	B	A	B	A	B	A	B	A	B	Overall
Electrode	1	2	3	4	5	6	7	8	9	10	mean
Number of run(n)	10	9	10	10	9	10	8	10	10	10	x, $(\sigma/X,\%)$
Volume reduction											
N^*	16.7	16.9	16.6	16.3	16.4	17.1	16.4	15.3	16.4	16.0	16.4(28.9)
σN^{**}	2.17	1.05	1.18	1.04	0.95	2.29	1.00	0.66	1.04	1.07	1.25(40.7)
Concentration factor											
Z^*	12.1	12.5	11.7	11.9	12.8	12.0	11.8	12.0	12.1	11.9	12.2(3.4)
σZ^{**}	1.94	0.93	0.85	0.86	1.04	2.04	0.89	0.75	0.87	0.84	1.1(40.9)
$\sigma Z/Z(\%)$	8.48	8.68	7.34	3.98	5.44	7.69	5.81	4.64	3.22	6.77	
Retention factor											
R^*	0.76	0.74	0.74	0.75	0.73	0.77	0.72	0.75	0.73	0.77	0.75(21.7)
σR^{**}	0.046	0.057	0.045	0.028	0.043	0.053	0.031	0.027	0.020	0.046	0.04(29.1)
$\sigma R/R(\%)$	6.05	7.70	6.08	3.73	5.89	6.88	4.31	3.60	2.74	5.97	
Separation factor											
σ^*	10.9	9.50	8.85	9.25	8.53	11.2	8.40	8.97	8.01	11.0	9.46(11.7)
$\sigma\beta^{**}$	3.30	2.35	1.50	1.12	2.45	3.04	1.98	1.93	1.55	1.87	2.11(30.8)
$\sigma\beta/\beta(\%)$	17.3	24.8	17.9	11.7	15.1	26.5	14.9	11.6	6.85	19.9	

Conc. HCl, as a detergent, was used to clean and to refresh the surface of electrodes in the series of experiments

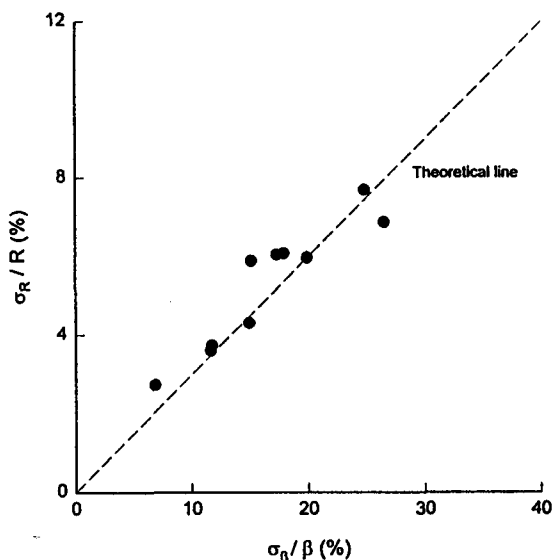 * : Mean value of each factor

  ** : Variation of each factor

Fig. 3. Relationship between $(\sigma_R)/R)$ and (σ_β/β) on the large-volume electrolytic cell
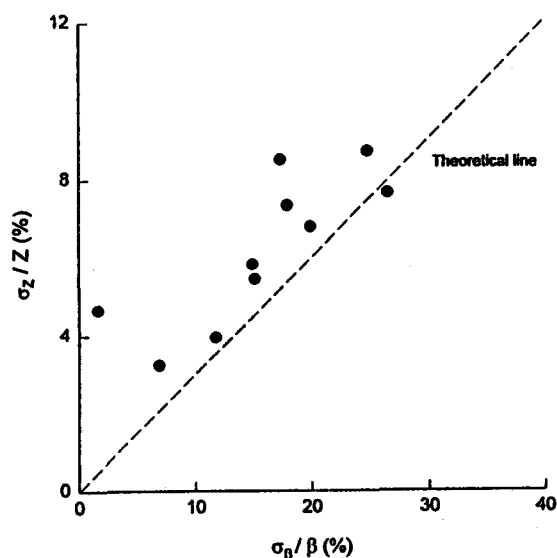

Fig. 4. Relationship between $(\sigma_Z)/Z)$ and (σ_β/β) on the large-volume electrolytic cell

0.75, and 9.46, respectively. The variation of R was relatively smaller than those of Z and b as other authors [7, 8] reported previously. The relationship between the variation of b and those of Z or R can be expressed as the

following equations [8]:

$$(\sigma_R/R)/(\sigma_\beta/\beta) \cong (\ln N)/\beta \cdots\cdots\cdots\cdots\cdots\cdots(2)$$
$$(\sigma_Z/Z)/(\sigma_\beta/\beta) \cong (\ln N)/\beta \cdots\cdots\cdots\cdots\cdots(3)$$

In equations (2) and (3), the correlations between σ_R/R and σ_β/β and σ_Z/Z and σ_β/β can be approximated to straight lines through the origin with the slope $\ln N/\beta$ if the means of N and b are constant. Figures 3 and 4 are the correlation curves for the equations (2) and (3) in the large-volume electrolytic cell. The relationship between σ_R/R and σ_β/β was in good accordance with the straight line with a slope of 0.30 which was calculated by inserting the overall means of N and b into $(\ln N)/\beta$. On the other hand, the slope of the curve between σ_Z/Z and σ_β/β showed more deviation from the theoretical value. This phenomenon implied that for a given separation factor b, change of the retention

factor R was smaller than that of the concentration factor Z, which suggested that using retention factors rather than concentration factors give better results for the determination of tritium by electrolytic enrichment.

During the electrolysis process, the volume reduction factor N may also be different from cell to cell or from run to run due to non-uniform evaporation and spray losses of the samples, even if the same cumulative current is applied to all the cells. Accordingly, change of N would cause change in the factors R and Z. The relationships between the variation of N and those of R and Z can be expressed as

the following equations [8]:
$$(\sigma_R/R)/(\sigma_N/N)=1/\beta \cdots\cdots\cdots\cdots\cdots(4)$$
$$(\sigma_Z/Z)/(\sigma_N/N)=1 - (1/\beta)\cdots\cdots\cdots\cdots\cdots(5)$$

The variation of R in equation (4) is not so sensitive as that of N because (1/b) is very small, whereas Z in equation (5) varies almost to the same degree as N. In other words, the variation of N or that of the final volume V_f strongly affects the variation of Z, not that of R. Figures 5 and 6 were drawn by plotting s_R / R and s_Z/Z

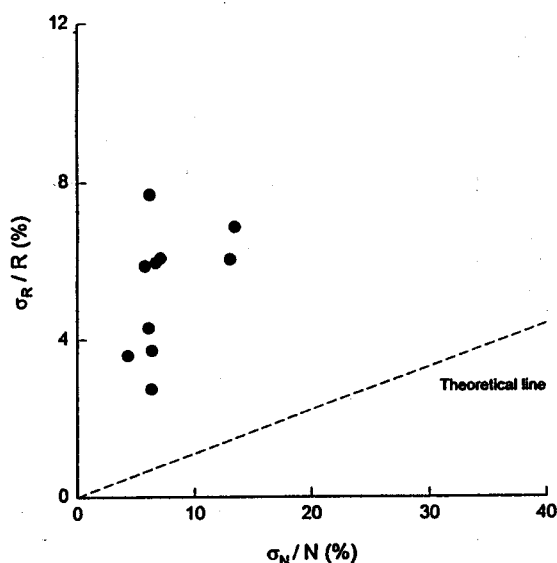Fig. 5. Relationship between(σ_R/R) and (σ_N/N)on the large-volume electrolytic cell.

Fig. 6. Relationship between(σ_Z/Z)and (σ_N/N)on the large-volume electrolytic cell.

against σN/N to clarify the equations (4) and (5). The relationship between σ_Z/Z and σN/N was in good accordance with the theoretical one derived from the overall mean of b, while the values of σ_R/R were almost independent of σ_N/N, as expected from the equation (4). The result suggested that the estimation of enrichment process using retention factor R was more precise than using concentration factor Z for the determination of tritium in water samples. Therefore, tritium concentrations in water samples could be calculated by the following equation:

$$T=\{(A-B)\pm(\sigma_A{}^2+\sigma_B{}^2)^{1/2}\}/N \times R \times V \times E \cdots \cdots (6)$$

where T is the tritium concentration (Bq L^{-1}),

A and σ_A are the total count rate and counting error for the sample,

B and σ_B are the count rate and counting error for the background sample,

N is the volume reduction factor,

R is the mean value of retention factors obtained from two standard tritium spiked cells,
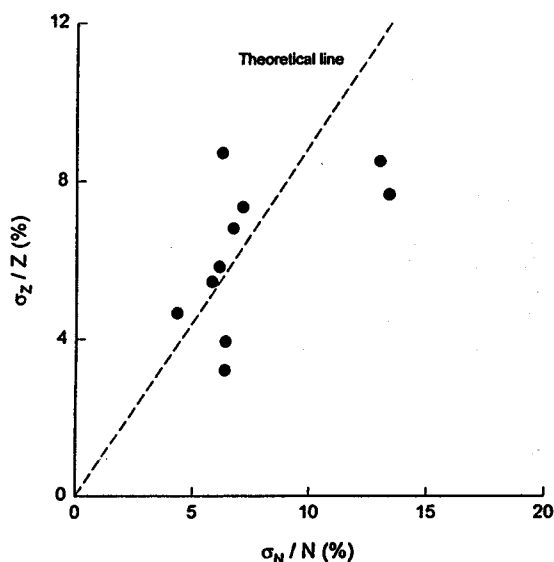
V is the sample volume,

and E is the counting efficiency.

Distribution of tritium in surface seawater

Table 2 shows the tritium concentration in the surface seawater samples around Korea. The ranges of the tritium concentration were 0.39 -1.50 Bq L^{-1} for the first expedition, 0.12 -1.42 Bq L^{-1} for the second expedition, and 0.15 -0.95 Bq L^{-1} for the third expedition. The means of the tritium concentration were 0.77±0.31 Bq L^{-1}, 0.60± 0.38 Bq L^{-1}, and 0.42±0.24 Bq L^{-1} for the first, the second, and the third expedition, respectively. Considering the standard deviation, the mean values of tritium concentration from each expedition were not significantly different from each other. Figure 7 shows the distribution of tritium concentrations in seawater. The ranges of the tritium concentration in the surface seawater samples were 0.14 - 1.28 Bq L^{-1} for the East Sea, 0.12 - 1.50 Bq L^{-1} for the South Sea, and 0.27 - 1.29 Bq L^{-1} for the Yellow Sea. The means of the tritium concentration were 0.54±0.30 Bq L^{-1}, 0.48±0.35 Bq L^{-1}, and 0.77±0.32 Bq L^{-1} for the East Sea, the South Sea, and the Yellow Sea, respective-

ly. Considering the standard deviation, the tritium concentrations in the samples did not show much variation within the area sampled, although the mean of the tritium concentration in the Yellow Sea was a little higher than those in other seas. The tritium concentrations were similar to 0.71 ± 0.21 Bq L^{-1} which was observed in the surface seawater samples around Japan[9]. Generally, tritium concentrations in the surface seawater around Korea were relatively higher than the mean tritium concentration, 0.4 Bq L^{-1}, in the surface seawater samples from the Pacific Ocean[10]. The tritium concentrations in the seawater samples neighboring to the land were higher than those in the samples from the open seas such as the Pacific Ocean, which presumably resulted from the inflow of the high-tritium groundwater from the land. Analyzing 12 water samples from major reservoirs in Korea, Kim et al.[11] reported

Table 2. Tritium concentrations in surface seawaters

Station No	Location	Tritium concentration(Bq/L)		
		1st Oct.-Nov.94	2nd Dec.94	3rd Feb.-Mar.95
S-1	38° 12.6′ N 130° 00.0′ E	0.65±0.03*	0.29±0.03*	0.39±0.04
S-2	37° 53.7′ N 128° 52.5′ E	--	0.65±0.02	0.43±0.04
S-3	37° 33.2′ N 131° 14.6′ E	0.74±0.08	0.14±0.02	0.33±0.04
S-4	37° 03.4′ N 129° 28.8′ E	--	0.27±0.03	--
S-5	36° 30.3′ N 131° 14.0′ E	0.86±0.10	0.78±0.12	--
S-6	36° 04.6′ N 129° 36.9′ E	0.57±0.06	1.28±0.12	--
S-7	35° 28.5′ N 129° 27.3′ E	--	0.90±0.10	--
S-8	35° 11.4′ N 131° 06.6′ E	--	0.18±0.02	--
S-9	34° 50.2′ N 129° 19.5′ E	1.50±0.14	0.12±0.01	0.18±0.02
S-10	34° 35.5′ N 128° 34.5′ E	--	0.73±0.07	0.40±0.05
S-11	34° 20.8′ N 127° 43.9′ E	0.39±0.04	0.24±0.03	0.55±0.06
S-12	33° 37.3′ N 128° 09.2′ E	1.06±0.11	0.42±0.05	0.12±0.01
S-13	33° 00.0′ N 128° 00.0′ E	0.39±0.04	0.12±0.01	0.24±0.03
S-14	33° 38.3′ N 126° 21.3′ E	0.44±0.05	0.42±0.05	N.D [#]
S-15	33° 58.5′ N 126° 06.0′ E	--	0.67±0.06	0.15±0.02
S-16	33° 24.4′ N 124° 24.0′ E	0.98±0.09	0.95±0.11	0.27±0.03
S-17	34° 43.0′ N 124° 23.4′ E	--	1.42±0.08	0.37±0.04
S-18	35° 20.0′ N 125° 49.3′ E	0.84±0.08	0.73±0.05	0.31±0.03
S-19	35° 51.3′ N 124° 22.8′ E	--	0.52±0.06	0.78±0.09
S-20	36° 19.8′ N 126° 14.4′ E	0.77±0.07	1.29±0.12	0.95±0.10
S-21	36° 55.5′ N 124° 22.3′ E	--	0.54±0.06	0.83±0.08
Average		0.77±0.31**	0.60±0.38	0.42±0.24**

* : Counting error

** : Standard deviation

- : The sample was not analyzed.

\# : lower than the detection limit(0.1 BqL^{-1})

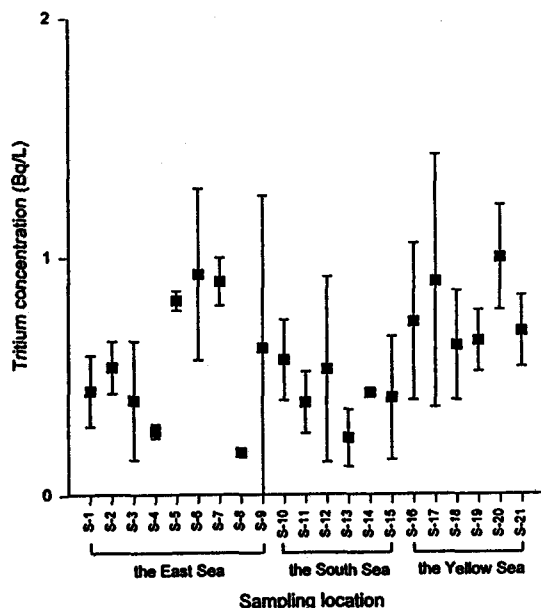Fig. 7. The means of tritium concentrations in surface seawaters from the East, the South and the Yellow Seas.

Fig. 8. Correlation between tritium concentrations in surface seawaters and latitudes of sampling locations

that tritium concentrations were in the range of 0.88 - 6.74 Bq L^{-1}. The magnitude of the increase of tritium concentration in seawater samples would be dependent upon the geographical factors such as mixing ratios of the groundwater to the seawater, the tritium concentrations of the groundwater, and turnover rates of the surface seawater. Figure 8 shows the distribution of tritium concentrations with latitude. Kaji [12] reported that tritium concentration in the seawater samples from the Pacific Ocean increased with increasing latitude from 10 °N to 50 °N. In this work, however, tritium concentration did not show much difference with increasing latitude. This tendency is presumably due to the narrow range of latitudes sampled in this study.

CONCLUSION

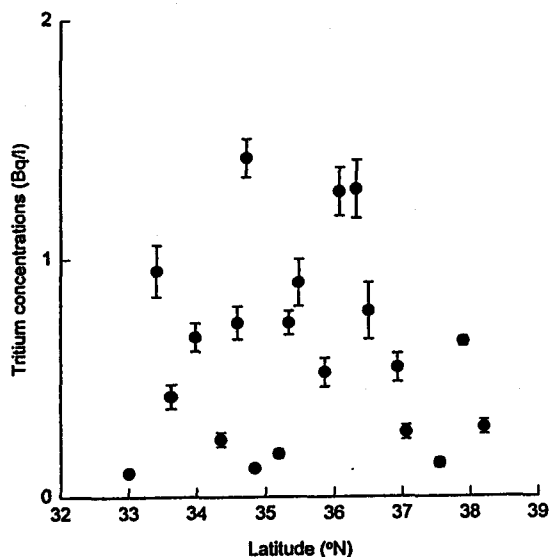An electrolytic enrichment technique was used to measure low levels of tritium in seawater around the Korean peninsula. The variation of R (tritium retention factor) was relatively smaller than those of Z (tritium concentration factor) and b (chemical separation factor). The retention factor R was almost independent from the volume reduction factor N, while the concentration factor Z varied in proportion to the volume reduction factor N. Accordingly, in the electrolysis process the retention factor R will lead to better precision for the determination of tritium in water samples.

The tritium concentrations in surface seawaters from all sampling locations ranged from 0.12 Bq L^{-1} to 1.50 Bq L^{-1} with a mean value of 0.60±0.35 Bq L^{-1}. The means of the tritium concentration were 0.54±0.30 Bq L^{-1} for the East Sea, 0.48±0.35 Bq L^{-1} for the South Sea, and 0.77±0.32 Bq L^{-1} for the Yellow Sea.

Tritium levels measured in waters adjacent to the Korean peninsula were similar to those measured in the vicinity of Japan, but higher than others reported for the mid-Pacific Ocean. Contributions from high-tri-

tium groundwaters nearer to land may account for this difference. No correlation of tritium level with sampling latitude was observed in this study.

Although ten nuclear power plants are in operation and six nuclear power plants are under construction in Korea, we have not accumulated much environmental radioactivity data, especially for the marine environment. Therefore, the results obtained from this work can be used as valuable baseline data for tritium concentrations in the surface seawater around Korea.

ACKNOWLEDGMENT

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