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The Distribution of ^{228}Ra in, and the Eddy Diffusivity of, Surface Waters of the Coastal Southwestern East Sea

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Radium isotopes were measured in 11 surface water samples collected during April 26-29, 1994 in the coastal southwestern East Sea. Manganese fiber extraction techniques were used to concentrate Ra isotopes from large volume seawater samples. The activities of ^{228}Ra in the coastal southwestern East Sea were in the range of 5.74 to 7.68 dpm/100L in eleven samples. The ^{228}Ra activities generally decrease seaward with increasing distance from the coast. In order to estimate the horizontal eddy diffusion coefficients, we applied a simple one-dimensional diffusion model to their distribution. The horizontal eddy diffusivity in the coastal southwestern East Sea were estimated to be in the order of 10^6 cm^2/sec.

INTRODUCTION

Radium is an alkaline earth element and exists mostly in dissolved phase in sea water as Ra^{2+}. Radium is classified as biointermediate element. Radium isotopes are continuously produced from the decay of thorium isotopes.

Most of ^{226}Ra in the ocean water is produced by the decay of ^{230}Th in bottom sediments. ^{226}Ra is released to sediment pore water and subsequently diffuses upward into the bottom water (Cochran and Krishinaswami, 1980). Since Koczy (1957) suggested that ^{226}Ra was a useful time tracer with its half-life of 1,622 years in studying oceanic mixing processes occurring on a time scale of a few thousand years, geochemical behaviour of Ra isotopes and its potential as time tracer were intensively studied during GEOSECS program of 1970's.

^{228}Ra with a half-life of 5.75 years could be a useful tracer in studying mixing processes in the coastal sea or near-bottom waters (Yamada *et al.*, 1986; Somayajulu *et al.*, 1987; Kasemsupaya *et al.*, 1993). ^{228}Ra is supplied to coastal sea water from the decays of its parent nuclide ^{232}Th in shelf sediments and dispersed to the open sea by advection and diffusion of surface water. Thus the concentration of ^{228}Ra decreases seaward with increasing distance from the coast. Kaufman *et al.* (1973), Knauss *et al.* (1978) and Moore *et al.* (1980) have studied horizontal movements within the surface water from the distribution of ^{228}Ra by estimating horizontal eddy diffusion coefficients. The vertical distribution of ^{228}Ra has been determined to estimate vertical eddy diffusion coefficients across and/or within the thermocline and near-bottom region (Trier *et al.*, 1972; Moore, 1972; Okubo, 1980; and Somayajulu *et al.*, 1987).

In this study, we have attempted to measure ^{226}Ra and ^{228}Ra in coastal waters of the East Sea (Sea of Japan). We determined the distribution of ^{228}Ra activities in the coastal southwestern East Sea to estimate horizontal eddy diffusion coefficient of the surface waters.

MATERIALS AND METHODS

Study area

The East Sea is a marginal sea (area: 1,007,600 km^2, mean depth: 1,684 m, maximum depth: 4,049 m) surrounded by the Korean peninsula and Japanese islands and connected to neighbouring seas through four straits: Korea, Tsugaru, Soya and Tartarskiy Straits (Woo *et al.*, 1995). The East Sea water below 200 m is occupied by a remarkably uniform water mass which is characterized by relatively low salinities and temperatures (0.1-0.3°C,

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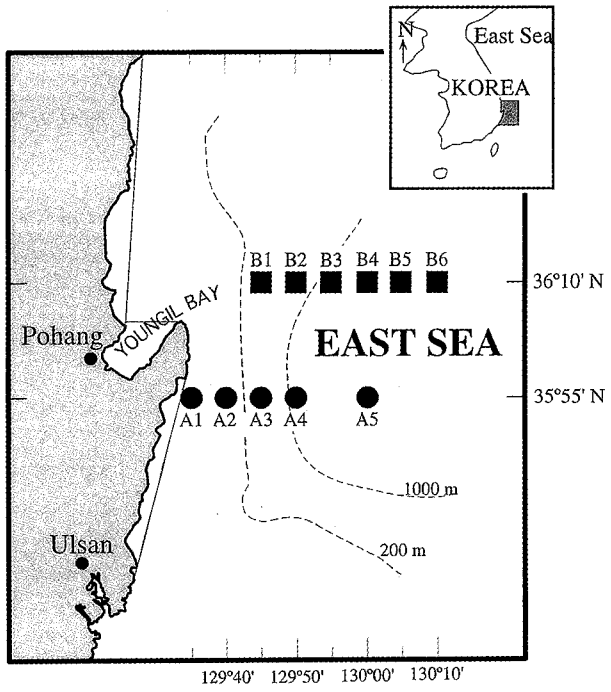

Fig. 1. A map showing the sampling stations. Circles represent the locations of surface water sampling on the line of 35° 55' N and squares on 35° 55' N.

34.0-34.1‰) and it is called the East Sea Proper Water. The East Korea Warm Current branched from Tsushima Currents flows northward along the Korean coast (Lee, 1992).

Surface water sampling

Surface water samples were collected during *R/V Tamyang* cruise on April 26-29, 1994 at the coastal southwestern part of the East Sea from the 5 stations on the line of 35° 55' N and 6 stations on that of 36° 10' N (Fig. 1). The surface water samples were collected by utilizing ship's pre-installed pump system designed for obtaining clean sea water samples. The samples were divided into two parts: one part (about 240 liter) was transferred to three 80-liter plastic containers, and the other part (about 60 liter) was stored in polyethylene carboys for the $Ba(Ra)SO_4$ coprecipitation. Locations of each station were exactly recorded by a global positioning system (Furuno GP-500). Temperature and salinity were measured by a CTD (Sea-Bird Electronics 911 plus).

Radium isotopes analysis

We prepared Mn-fiber following the procedures described by Moore *et al.* (1976). Briefly, the 0.4 M $KMnO_4$ solution was heated to 80-85°C in 2-liter beakers. A batch of fluffed fiber was soaked in the hot $KMnO_4$ solution for an hour until the fiber turned black. Then, the fiber was drew from the beaker and stand for 1 day. It was washed with distilled deionized water (DDW) and stored in a vinyl bag.

The surface water samples were immediately passed through two Mn-fiber cartridges (30 cm length × 7 cm inner diameter) connected in a series with flow rates of 5-7 liter/min (registered with a flow meter). Then, the Mn-fiber was removed from the cartridge and stored in vinyl bags.

Mn-fiber method is very effective for extracting radium isotopes from sea water (Reid *et al.*, 1979; Moore *et al.*, 1985). Moore and Reid (1973) reported radium uptake efficiency of 95%±5% for Mn-fiber. It is not necessary to know extraction efficiency of Mn-fiber for the determination of the activity ratios between ^{228}Ra and ^{226}Ra. If the extraction efficiency is precisely known, Mn-fiber can be used for determination of the specific activities of ^{226}Ra and ^{228}Ra in seawater (Reid *et al.*, 1979).

If we assume no isotopic fractionation between ^{228}Ra and ^{226}Ra during the extraction onto the Mn-fiber, and the extraction efficiencies of the first and the second column of Mn-fiber are same, then the extraction efficiency (E) and the specific activity may also be calculated directly from the following equations (Lee, 1991).

$$E = 1 - (A_2/A_1) \quad (1)$$

where A_1 and A_2 are measured radium activities of the first and the second columns, respectively.

Radium activity (A_0) of the sea water is:

$$A_0 = A_1/E \quad (2)$$

Figure 2 shows a leaching processes of Mn-fiber following the procedures described by Moore *et al.* (1985). The Mn-fiber was leached with hot (50°C) 1 M hydroxylamine hydrochloride solution, 30% H_2O_2 and concentrated HCl. The solution was filtered through Whatman NO. 2 filter paper and the fiber was rinsed with 1 M HCl. This washing procedure was repeated 3 times and the washing solution was filtered.

About 50 ml of concentrated sulfuric acid was added to the leached solution and stirred. About 2 g of $BaCl_2$ was dissolved in 200-300 ml of DDW. About 70 ml aliquot of $BaCl_2$ solution was added to the sample and stirred. Radium isotopes in solution

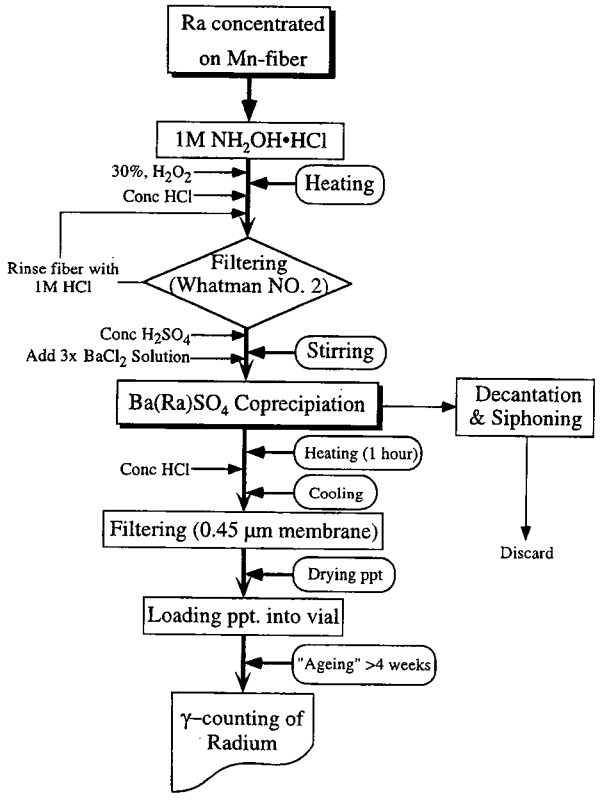

Fig. 2. A flow diagram showing the radium extraction procedures utilized in this study.

were associate with $BaSO_4$ and co-precipitated as $Ba(Ra)SO_4$.

Waiting for the settling of $Ba(Ra)SO_4$ precipitates, the precipitate was filtered with membrane filter (MPS, pore size: 0.45 μm). The $Ba(Ra)SO_4$ precipitates was dried at 60°C in a dry oven for 3 days and cooled in a desiccator. The precipitate was transferred into a pre-weighed plastic counting vial. The vial was weighed again to determine the net weight of $Ba(Ra)SO_4$ precipitates. Using this weight, the chemical yield was calculated by the following equation:

$$\text{Chemical Yield (\%)} = \frac{\text{weight of } Ba(Ra)SO_4 \text{ in vial (g)}}{\text{weight of dissolved } BaCl_2 \times 1.1209} \times 100 \quad (3)$$

where, 1.1209 is the weight conversion factor from $BaCl_2$ to $BaSO_4$.

The yield of radium recovery by $BaSO_4$ coprecipitation was estimated to be 100% within analytical error (Kim, 1992).

The vials containing the $Ba(Ra)SO_4$ precipitates were tightly sealed with caps and epoxy glue to keep the gaseous ^{222}Rn from escaping. In order to secure the equilibrium between Ra and Rn, the samples were aged for 21 days. The activities of ^{228}Ra and ^{226}Ra were measured by non-destructive gamma-ray spectrometry using a well-type intrinsic germanium detector (Canberra Model GCW 2021) following the modified procedure of Kim and Burnett (1983). The activities of ^{228}Ra were counted via ^{228}Ac peaks at 338.4 keV, 911.1 keV and 969 keV. ^{226}Ra activities were determined via ^{214}Pb photopeaks at 295.2 keV, 351.9 keV and ^{214}Bi at 609.3 keV.

RESULTS AND DISCUSSION

A seasonal thermocline was located at about 30~130 m depth (B1: 30-60 m, B2: 40-80 m, B4: 60-130 m) (Fig. 3.) and the permanent thermocline at about 60-180 m depth (B1: 60-80 m, B2: 80-100 m, B4: 130-160 m, B6: 130-180 m) (Shin, 1994). The depth of the thermocline became gradually deeper with the distance from the coast. The halocline was located at the same depth of thermocline (80-200 m). The vertical profiles of temperature and salinity are shown in Fig. 3. The surface water temperatures in the study area were between 15.11 and 15.64°C, decreasing seaward from the coast. The salinities of the surface waters above the permanent thermocline were in a ranged of 34.61 to 34.67‰. The vertical pattern of salinity distribution in the surface layer was more complicated than that of temperature.

The horizontal distribution of ^{226}Ra and ^{228}Ra

The results of our determination of radium isotopes in the surface waters of the East Sea are presented in Table 1. The activities of ^{226}Ra were in the range of 6.91-10.74 dpm/100L, increasing seaward with increasing distance from the coast. These ^{226}Ra activities are generally in good agreement with the previously measure values (Okubo, 1980; Harada *et al.*, 1986; Yang *et al.*, 1992).

The activities of ^{228}Ra were in the range of 5.74 to 7.68 dpm/100L in eleven samples and the mean value was 6.642 ± 0.059 dpm/100L. The lowest ^{228}Ra activity was found at B5 and the highest activity at A1. The activities of ^{228}Ra at station A1 and A2 on continental shelf, was significantly higher than those of the other stations and decreased seaward with increasing distance from the coast (Table 1). This suggests that ^{228}Ra is supplied to by shelf waters from shelf sediments, and disperse seaward

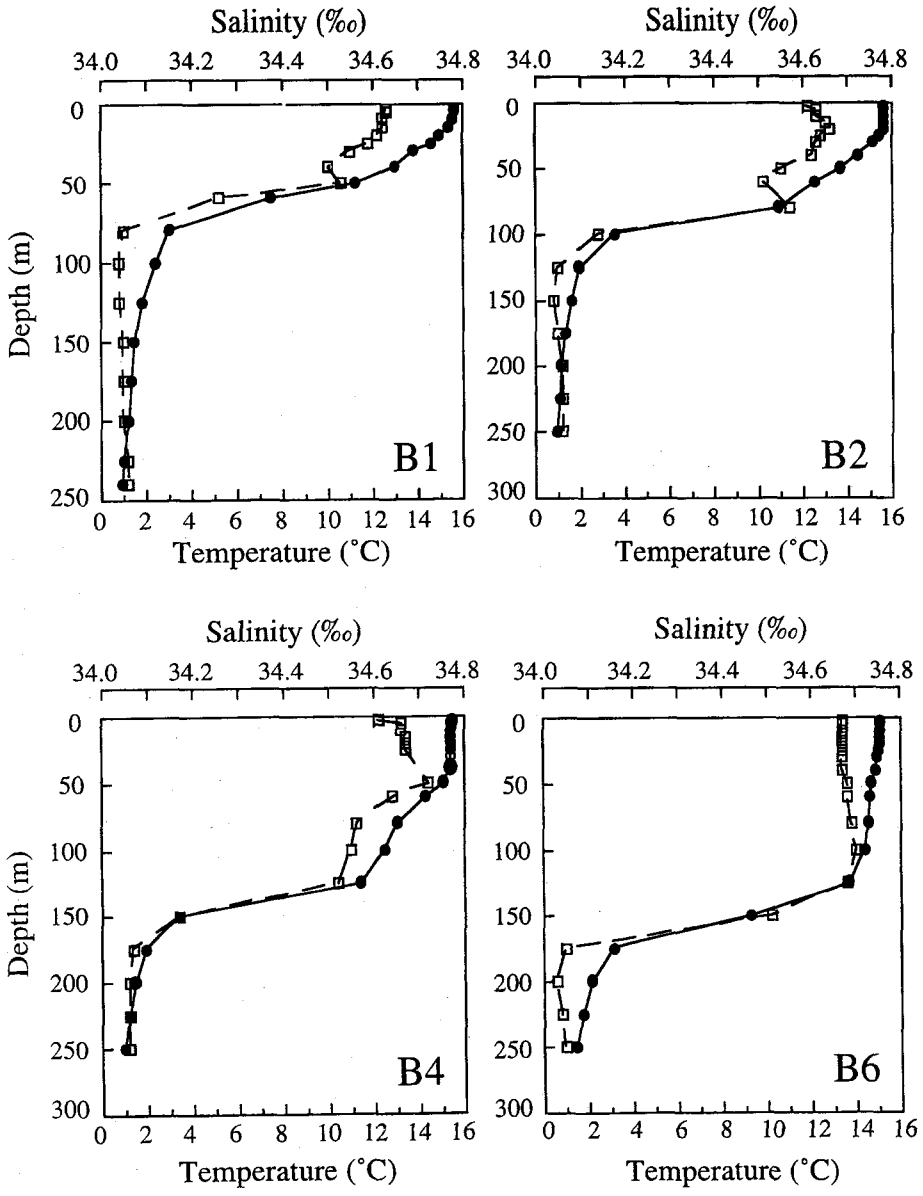

Fig. 3. Vertical profiles of salinity and temperature of St. B1, B2, B4 and B6 as recorded by a CTD in April 1994. Solid circles represent temperature and open squares salinity.

through surface waters by diffusive mixing processes (Fig. 4a.). The plot of ^{228}Ra activity versus distance from the coastline is shown in Fig. 4b.

One-dimensional diffusion model

In this study one-dimensional, diffusion model is used for the estimation of horizontal eddy diffusion coefficients. This model has been used in previous studies of water mass mixing by ^{228}Ra (Moore *et al.*, 1972, 1980; Kaufman *et al.*, 1973; Knauss *et al.*, 1978; Yamada and Nozaki, 1986; Kasemsupaya *et al.*, 1993). We applied the model equation to the horizontal distribution of ^{228}Ra activities in the surface waters of the East Sea.

If we assume that eddy diffusion plays a key role in dispersion of ^{228}Ra in the surface layer and the system is in a steady state, then:

$$\frac{dC}{dt} = K_h \frac{\partial^2 C}{\partial x^2} - \lambda C = 0 \qquad (4)$$

where, x is the distance in east-west direction from the coastline (cm), K_h the horizontal eddy diffusion coefficient (cm^2/sec), λ decay constant (sec^{-1}), and C the activity of ^{228}Ra (dpm/100L).

Table 1. Activities of radium isotopes, Ra-226 Ra-228, in surface waters of the coastal East Sea in April 1994 determined by manganese fiber extraction and gamma-ray spectroscopic techniques. Errors for the radium activities are based on 1-sigma counting statistics

Station No.	Location		Distance* from the coast (km)	Activities (dpm/100L)		Activity ratio
	Latitude	Longitude		Ra-226	Ra-228	
A1	35°55' N	129° 35' E	2.3	6.91±0.16	7.68±0.13	1.111±0.031
A2		129° 40' E	11.5	6.93±0.15	7.41±0.13	1.069±0.030
A3		129° 45' E	20.8	7.92±0.14	7.07±0.19	0.893±0.028
A4		129° 50' E	30.0	8.22±0.19	6.95±0.25	0.846±0.035
A5		130° 00' E	48.6	9.58±0.24	5.99±0.14	0.625±0.022
B1	36° 10' N	129° 45' E	33.0	7.63±0.16	6.76±0.16	0.886±0.028
B2		129° 50' E	42.3	7.79±0.18	6.74±0.32	0.866±0.046
B3		129° 55' E	51.6	8.00±0.16	6.19±0.22	0.774±0.032
B4		130° 00' E	60.8	8.51±0.19	5.89±0.20	0.692±0.028
B5		130° 05' E	70.1	9.45±0.23	5.67±0.18	0.601±0.024
B6		129° 10' E	79.3	10.74±0.25	5.74±0.15	0.534±0.019
Mean				8.223±0.057	6.642±0.059	0.8296±0.009

*Distance measured along the east-west direction.

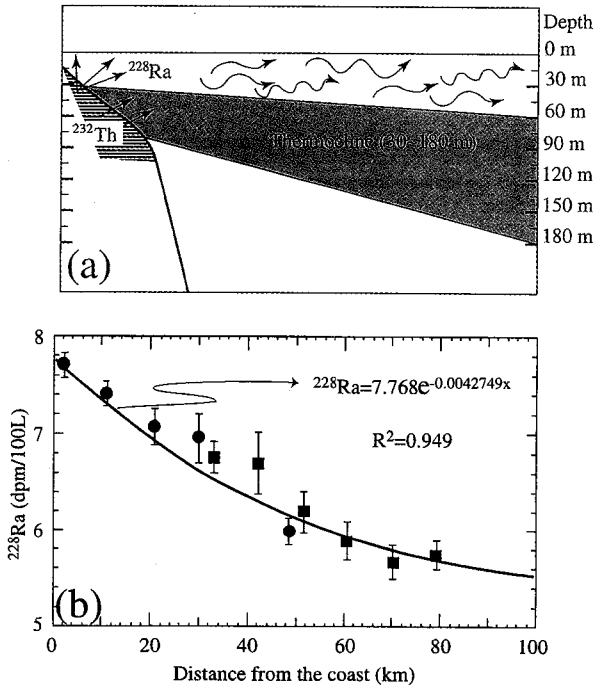

Fig. 4. (a) A conceptual sketch showing the diffusive pathway of ^{228}Ra in the ocean. Short arrows denote diffusion of ^{228}Ra across the sediment-water interface, (b) Plots of ^{228}Ra activity as a function of distance from the coastline in the southwestern East sea. Circles indicate stations on the line of 35° 55' N and squares on 36° 10' N.

The boundary conditions are,

1) $C = C_0$ at $x = 0$
2) $C \rightarrow 0$ at $x \rightarrow \infty$.

A general solution to the equation (4) is as follows:

$$C = C_0 \exp[-(\lambda/K_h)^{1/2} \cdot x] \quad (5)$$

We estimated the value of K_h by fitting equation (5) to the plot of ^{228}Ra activity versus distance from the coastline (Fig. 4b), yielding the following equation:

$$^{228}Ra = (7.768 \pm 0.110) \exp[-(0.004275 \pm 0.000330) \cdot x] \quad (R^2 = 0.949)$$

Thus the K_h was estimated to be $(1.79 \pm 0.28) \times 10^6$ cm^2/sec ($=10^{(6.25 \pm 0.07)}$).

Our estimate is in the same order as the value from the Seto Inland Sea (Kasemsupaya *et al.*, 1993: 1.1-1.4 $\times 10^6$ cm^2/sec) and Long Island Sound (Kaufman *et al.*, 1973: 0.5-5 $\pm 10^6$ cm^2/sec). On the other hand, Kaufman *et al.* (1973) and Moore (1980) reported the K_h values ranging from 10^7 to 10^8 cm^2/sec in the surface waters of the Australian Pacific and the North Atlantic Ocean.

CONCLUSIONS

In order to estimate the horizontal eddy diffusion coefficients in the coastal surface waters of the East Sea, we measured the ^{228}Ra and ^{226}Ra activities and applied a simple "one-dimensional" diffusion model to their distribution. The activities of ^{228}Ra were in the range of 5.74 to 7.68 dpm/100L and the mean activity was 6.642±0.059 dpm/100L. From the surface water distribution of ^{228}Ra activities, the horizontal eddy diffusion coefficients in the coastal waters of the southwestern East Sea were estimated to be in the order of 10^6 cm^2/sec. This result may provide useful information concerning the diffusion of coastal waters and dissolved pollutants to the East Sea.

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