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Measurements of ^{224}Ra and ^{223}Ra in the Nakdong River estuary and the South Sea of Korea

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The horizontal distributions of ^{224}Ra (half life=3.4 days) and ^{223}Ra (half life=11.3 days) were measured in surface seawaters of the Nakdong River estuary and the South Sea of Korea in April and October 2002. In order to determine these short-lived Ra isotopes, we used a delayed coincidence counter which is much more rapid and accurate than traditional methods. In an estuarine mixing zone (salinity, ~16 ppt), the activities of ^{224}Ra and ^{223}Ra were much greater than what would be expected from a mixture of freshwater and seawater in the Nakdong River estuary. This excess Ra may be a result of Ra desorption from fresh sediments originating from the river upstream. However, in the more open areas of the Nakdong River estuary (salinity>30 ppt) and the South Sea of Korea, ^{224}Ra and ^{223}Ra activities decreased exponentially as a function of distance offshore. Using the decrease of ^{223}Ra with distance offshore in the South Sea of Korea, we estimated the apparent horizontal eddy diffusivities. The apparent eddy diffusion coefficients in South Sea of Korea are calculated to be approximately 3500-8000 m^2/sec.

Key words: ^{223}Ra, ^{224}Ra, Apparent Eddy Diffusion Coefficient, Coastal Waters

INTRODUCTION

Radium isotopes have been used extensively to determine the mixing and transport rates of different water masses (Moore, 1969; Reid, 1984; Moore *et al.*, 1986; Nozaki *et al.*, 1991), to determine the residence times of water masses (Nozaki *et al.*, 1989), and to trace groundwater signals in the coastal waters (Moore, 1996; Krest *et al.*, 1999; Charette *et al.*, 2001; Scott and Moran, 2001). In general, long-lived ^{228}Ra (half life=5.8 yrs) and ^{226}Ra (half life=1622 yrs) are useful for open-ocean studies, while short-lived ^{224}Ra (half life=3.4 days) and ^{223}Ra (half life=11.3 days) are useful for tracing coastal processes, such as in estuaries, salt marshes, and the coastal oceans, which occur over a time scale of a few days (Bollinger and Moore, 1984; Levy and Moore, 1985; Webster *et al.*, 1994; Moore *et al.*, 1995; Hancock and Murray, 1996; Torgersen *et al.*, 1996).

The transport of material through the coastal ocean plays an important role in global biogeochemical cycles. However, physical mixing fluxes are difficult to quantify because coastal-water systems are very complex and variable in space and time. In order to overcome such complexity and variability, one needs to determine the time-integrated dispersion coefficients of coastal waters on a coastal time scale. For this purpose, ^{224}Ra and ^{223}Ra are very suitable.

However, the use of short-lived ^{224}Ra and ^{223}Ra tracers has been hampered by difficulties in measurement with traditional methods (Rama *et al.*, 1987; Hamilton *et al.*, 1994; Alvarado *et al.*, 1995). Thus, in this study, we utilized new techniques recently developed by Moore and Arnold (1996) and Kim *et al.* (2001). Moore and Arnold (1996) used a delayed coincidence counter designed originally by Griffin *et al.* (1963) for the detection of radon isotopes produced from ^{224}Ra and ^{223}Ra. Similarly, Kim *et al.* (2001) measured radon daughters using an alpha counter, which is commercially available for radon-in-air monitoring. These methods are very simple, rapid, and accurate compared to traditional methods.

Using these new methods, we measured ^{224}Ra and ^{223}Ra in the Nakdong River estuary and the South

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Sea of Korea for the first time. The major objectives were to determine the horizontal gradient of ^{224}Ra and ^{223}Ra for calculating the time-integrated coastal eddy diffusivity in this region, and to determine the behavior of radium in the estuarine mixing zone located downstream of an artificial river-dam.

MATERIALS AND METHODS

Study site

The South Sea of Korea is shallower than 100 m and is connected to the Yellow Sea, East Sea, and East China Sea (Fig. 1). Major water masses such as the Tsushima water and the Yellow Sea Warm water are moving northeastward and are mixed with Korean coastal waters on route (Gong, 1971, Kim and Lee, 1982; Byun and Chang, 1988; Jin, 2000). High primary production and biomass are often observed in the water-mass frontal zone. In addition, the South Sea of Korea is a reservoir of material originating from many rivers such as the Changjiang River (China), Seomjin River (Korea), and Nakdong River (Korea). Due to such oceanographic importance, a number of physical and biogeochemical studies have been conducted in the South Sea of Korea

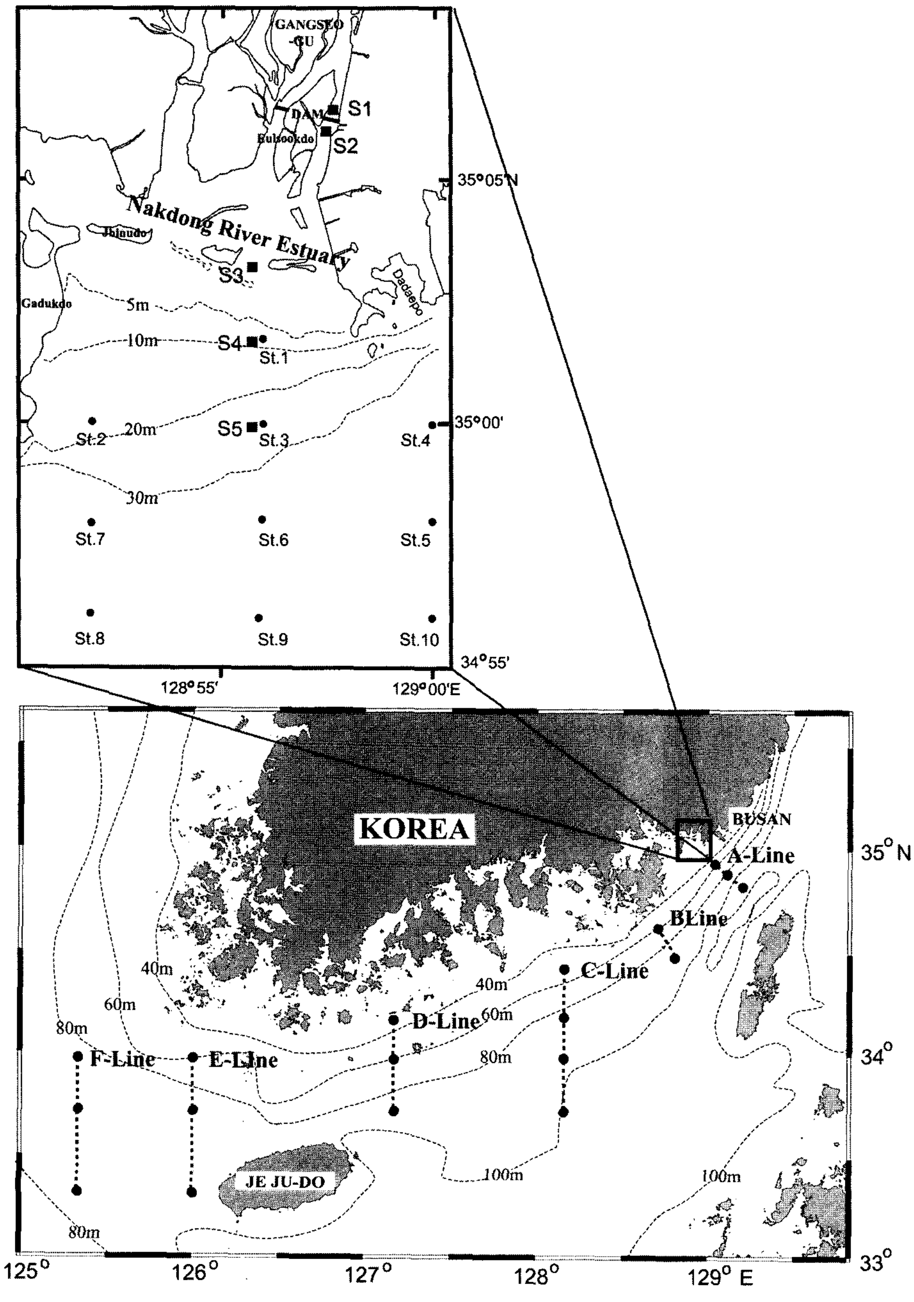

Fig. 1. A map showing the study areas and the sampling locations. The filled squares represent sampling sites occupied in April 2002, and filled circles in October 2002.

(Pang et al, 1992; Cho and Kim, 1994; Suk *et al.*, 1996; Kim and Rho, 1997; Chung *et al.*, 2000). However, the information on eddy diffusivity of coastal waters is very limited. Thus, we attempted to determine the time-integrated eddy diffusivity using Ra tracers.

The Nakdong River estuary is located in the southeastern region of Korea (Fig. 1). The Nakdong River is the longest river in Korea extending approximately 525 km in length from south to north. Although it has an extensive catchment area, runoff is limited due to the construction of the Nakdong River Dam at the downstream end. The average discharge rate of river water is about 423 m^3/s (http://www.kowaco.or.kr). The surface sediment in the Nakdong River estuary is comprised mostly of sand, and partially of silt and clay. The sea-level difference between high and low tide is 0.4–1.5 m in the estuary (http://www.kowaco.or.kr). The Nakdong River Dam controls the river-water discharge, and prevents the intrusion of saltwater upstream. In this peculiar estuarine environment, we measured ^{224}Ra and ^{223}Ra in order to determine the geochemical sources for Ra.

Determination of ^{224}Ra and ^{223}Ra

For the measurement of Ra isotopes, we collected more than 200-L seawater samples on-board R/V Tamyang from the Nakdong River estuary and the South Sea of Korea in October 2002. In addition, we collected Ra samples from the Nakdong River estuary near the dam in April 2002 using a small vessel. The Ra samples were gravity fed through a plastic column (4.5 cm diameter, 20 cm length) filled with Mn fiber (~60 g-wet) at a flow rate of lower than 1 L/min. This procedure quantitatively extracts Ra in seawater onto the Mn-fiber (Kim *et al.*, 2001). The Mn-fiber is prepared by impregnating acrylic fiber with MnO$_2$ as described by Yamada and Nozaki (1986).

The Mn-fiber samples were hand-squeezed to remove excess water and placed in a plastic column (2.5 cm diameter, 20 cm length). The column was connected to a radon-in-air counting system. The Ra daughters (Rn) are circulated through an air-loop connected to a desiccant column to remove any moisture that immobilizes the charged Po species; an air filter to keep out particles and attached radon daughters; and a radon-in-air monitor (RAD7) where Rn daughter isotopes (^{218}Po and ^{216}Po) are electrostatically precipitated onto a semiconductor detector which produces alpha spectra thus allowing isotopic separation by energy discrimination (Kim *et al.*, 2001).

Then, the samples were used to determine both ^{224}Ra and ^{223}Ra using a delayed coincidence counter (DCC) developed by Moore and Arnold (1996) in the laboratory. Although this method determines Rn isotopes for Ra determination, the Rn measurement principle is different from the RAD7 method. With this DCC approach, signals from a detector are sent to a delayed coincidence circuit which discriminates decays of the ^{224}Ra daughters, ^{220}Rn and ^{216}Po, from decays of the ^{223}Ra daughters, ^{219}Rn and ^{215}Po. The detection efficiency (two alpha decays per Ra decay) is much higher than the method developed by Kim *et al.* (2001). However, one disadvantage is increased likelihood of chance coincidence between ^{224}Ra and ^{223}Ra when the activity of one radium isotope is much higher than the other.

RESULTS AND DISCUSSION

Horizontal distributions of Ra isotopes in seawater

The activities of ^{224}Ra ranged from 5 to 50 dpm/100 L downstream of the Nakdong River Dam in April 2002. This large variation is shown against salinity in Fig. 2. The activities of ^{224}Ra were much higher in the freshwater-seawater mixing zone (salinity between 10–30 ppt) than expected from a mixture of freshwater and seawater endmembers. This may be due to effective desorption of Ra from fresh sediments originating from the river upstream. A similar pattern was reported in other estuaries, such as Winyah Bay and Savannah River coastal estuaries in the eastern U.S. and Bega River estuary in Australia (Elsinger and Moore, 1983, Rama *et al.*, 1987; Hancock

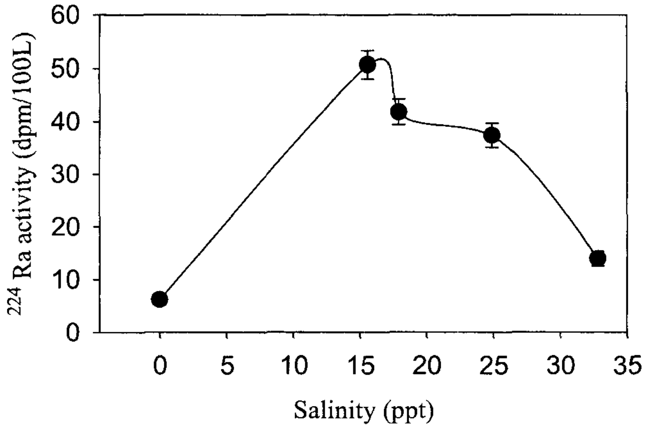

Fig. 2. A plot of ^{224}Ra activity versus salinity in surface waters of the Nakdong River estuary in April 2002.

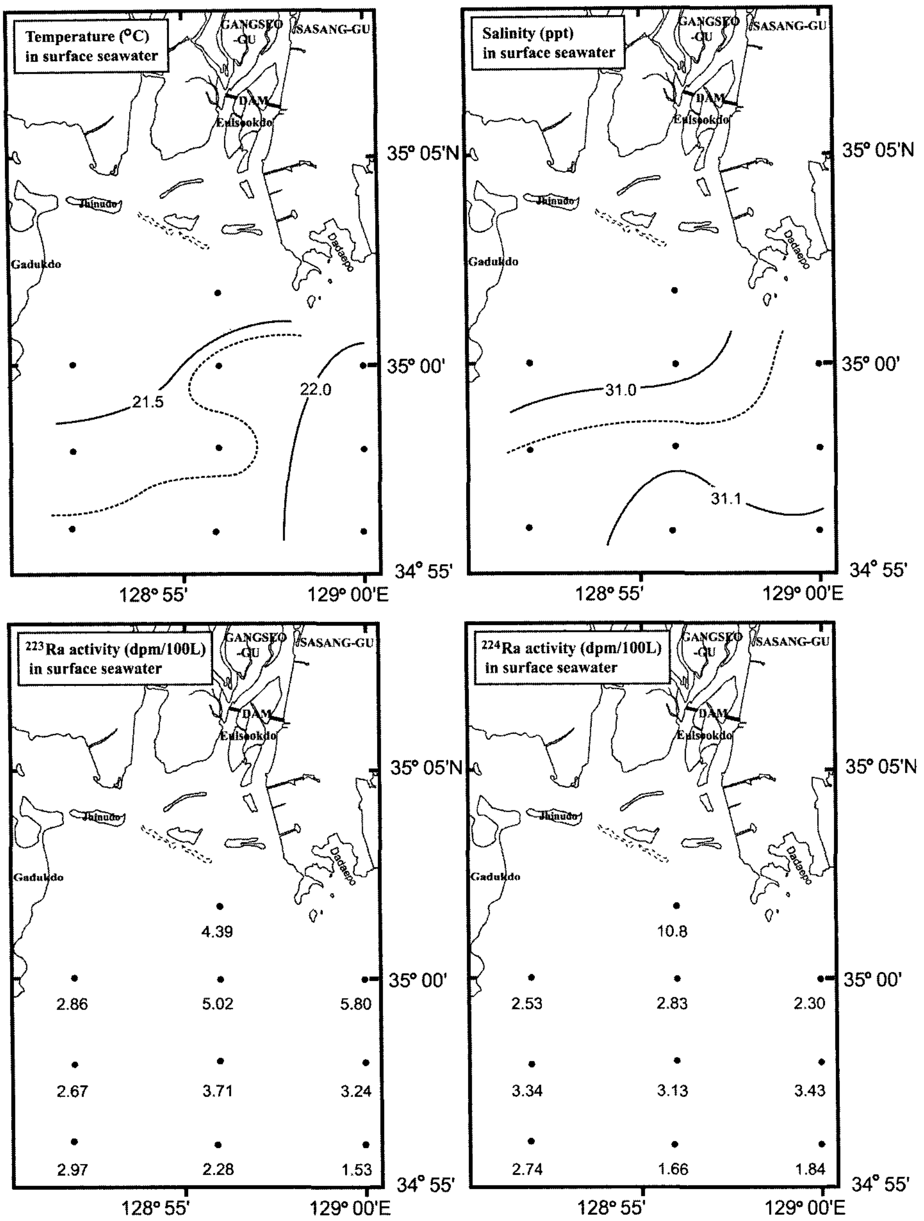

Fig. 3. The horizontal distributions of temperature, salinity, ^{223}Ra and ^{224}Ra in surface seawaters of the Nakdong River estuary in October 2002.

et al., 2000).

On the other hand, Yang *et al.* (2002) suggested possible contributions to the excess Ra supply from submarine groundwater discharge when the hydraulic gradient is larger. However, the source of excess Ra in April 2002 is likely to be due to the desorption of Ra in fresh sediments since the water level of the dam was low (< 0.3 m), with a large discharge of water from the dam. As such, the highest Ra activity was found at Stn.# 2, the nearest site to the dam.

In October 2002, we occupied more open areas of the Nakdong River estuary. Salinity fell into a narrow range (30–32 ppt), decreasing with distance offshore (Fig. 3). The activities of ^{224}Ra and ^{223}Ra showed a similar pattern, except for Stn. 4. In this station, the highest ^{223}Ra activity was observed, although ^{224}Ra activity and salinity were relatively lower. Thus, this water mass may be associated with different water origins in terms of geochemical characteristics.

In the South Sea of Korea, the north-south gradient of temperature and ^{223}Ra was significant, with a similar trend for salinity and ^{224}Ra (Fig. 4). The range of salinity shown in this season is significantly lower than that of the pristine Kuroshio water (salinity, 34.6–34.9 ppt). Such a lowered salinity has been attributed to the influence of Changjiang diluted water, occurring during summer and fall in this region. Thus, the gradient of Ra isotopes can be used to cal-

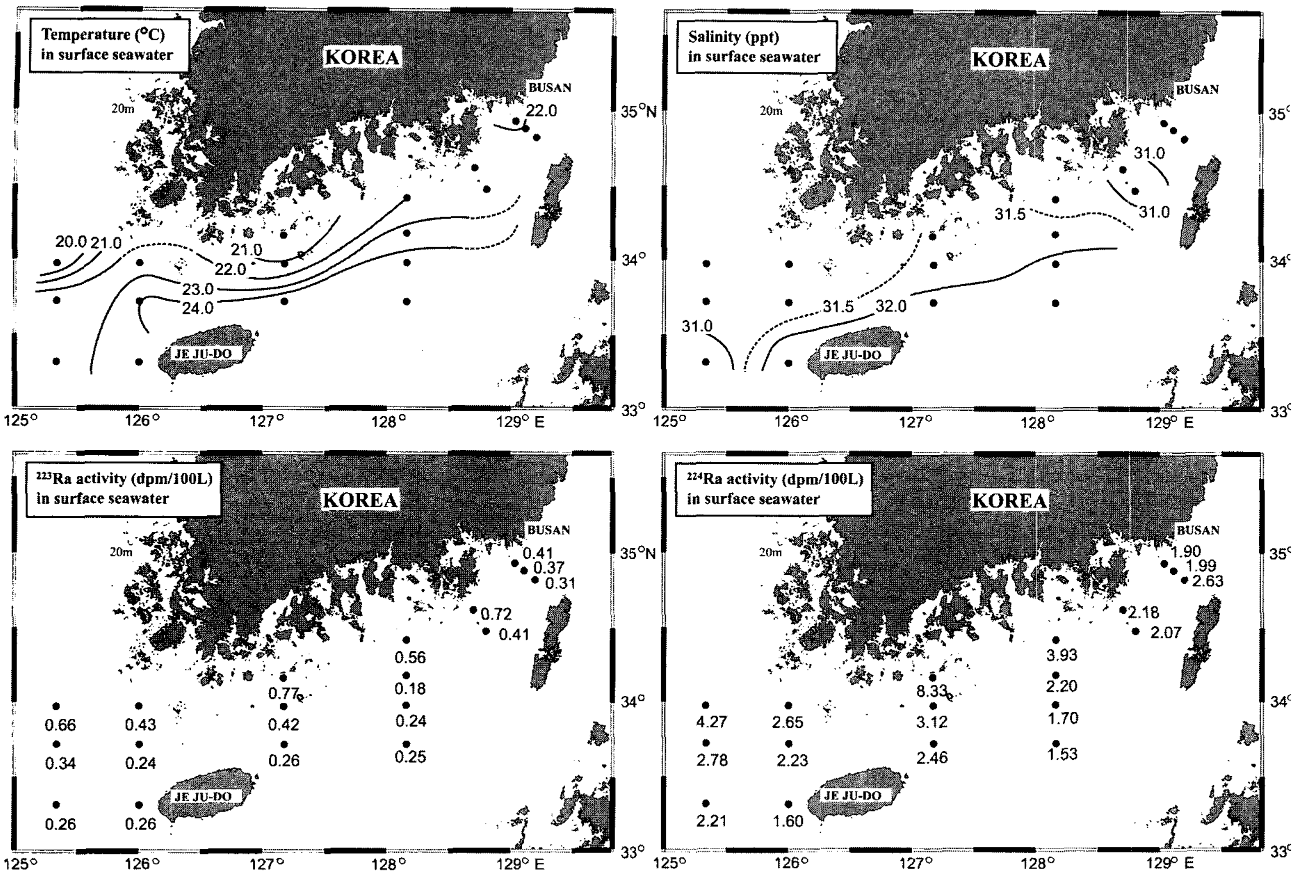

Fig. 4. The horizontal distributions of temperature, salinity, ^{223}Ra and ^{224}Ra in surface seawaters of the South Sea of Korea in October 2002.

culate the eddy diffusivity of coastal waters (Moore, 2000).

Horizontal eddy diffusivity of coastal waters

The change in concentration of a conservative tracer as a function of distance offshore may be expressed as a balance of advection and diffusion. If the offshore distribution is dominated by diffusion with constant K_h, the other term may be neglected (Moore, 2000). In order to calculate the apparent eddy diffusion coefficient (K_h) using ^{223}Ra tracer, we assume that there is no additional input of Ra except from nearshore. The formation of the pycnocline in this season may isolate the surface water from the inputs from below. Under this assumption (Moore, 2000), the apparent eddy diffusion coefficients can be calculated using the following equation.

$$A_x = A_0 \exp\left[-x\sqrt{\frac{\lambda}{K_h}}\right] \qquad (1)$$

where A_x is the ^{223}Ra activity at distance x from the coast, A_0 is the ^{223}Ra activity at distance 0 from the coast and λ is the decay constant (0.0613 day^{-1}). Here, if the exchange is dominated by eddy diffusion rather than advection at steady state, a plot of ^{223}Ra as a function of distance from the coast can be used to estimate K_h.

The decrease in activity as a function of distance offshore is shown in Fig. 5. The lines C and D have a slope of –0.0137 dpm 100 L^{-1} km^{-1} (r^2=0.50), and lines E and F have a slope of –0.0094 dpm 100L^{-1} km^{-1} (r^2=0.63) in the regressions between ^{223}Ra and distance offshore. Using equation (1) above, the values of the apparent eddy diffusion coefficient derived from ^{223}Ra are K_h=3748 m^2/sec for lines C and D and K_h=7962 m^2/sec for lines E and F. Although there are large uncertainties, these values are slightly higher than those in other regions such as Baja California (100–5000 m^2/sec) in the North Pacific determined using ^{228}Ra (Huh and Ku, 1998), South Atlantic Bight (360–420 m^2/sec) in the Atlantic Ocean using ^{223}Ra (Moore, 2000), and Kuroshio system (40–4000 m^2/sec) in the western North Pacific

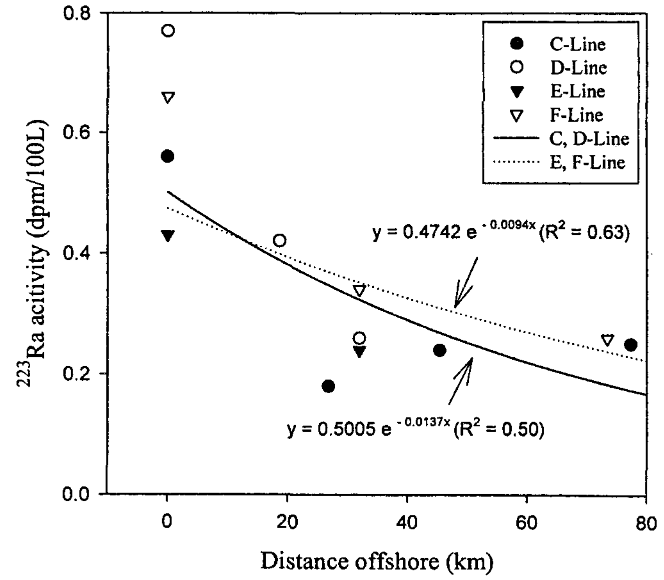

Fig. 5. A plot of ^{223}Ra activity versus distance offshore. The data for lines A and B were not included since the decrease with the distance offshore was not distinct.

using ^{228}Ra (Yamada and Nozaki, 1986). In general, the apparent eddy diffusion coefficients in the western part of Jeju Island (7500–8000 m^2/sec) were much greater than those in the eastern part (3500–4000 m^2/sec). This implies that more effective horizontal mixing of coastal material takes place in the western part of Jeju Island relative to the eastern part.

CONCLUSIONS

The activities of ^{224}Ra increased significantly during freshwater-seawater mixing processes owing to efficient desorption from fresh sediments. However, ^{224}Ra and ^{223}Ra decreased gradually from the coast as a function of distance offshore, mainly due to decay during mixing processes, in the open ocean (salinity >30 ppt). Based on this observed decrease of ^{223}Ra with distance offshore, we estimated the time-integrated eddy diffusivity in the South Sea of Korea. The eddy diffusivity was higher in the western part of Jeju Island, relative to the eastern part. This suggests efficient diffusion of coastal material into the open ocean in the western part during the sampling season. However, further extensive studies in the future are necessary to estimate coastal material fluxes with more detailed spatial and temporal resolution using these Ra isotopes.

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