■ 論 文 ■

Deposition Properties of ^{137}Cs in Marine Sediments

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Abstract - The concentration of ^{137}Cs, the particle size, and the contents of TOC, H, N and S were measured for sediments collected in the adjacent sea to Yangnam, Korea. The concentrations of ^{137}Cs in sediments are in the range of <MDA-7.19 Bq/kg-dry and linearly correlated with particle size and TOC, H and N contents in sediment. The distribution coefficients of ^{137}Cs for sediments strongly depend on particle size and TOC content of sediments. The results of multiple regression analysis suggest that humic substances may have great influence on the deposition of ^{137}Cs in sediment.
Key words : sediment, cesium, particle size, humic substance, distribution coefficient

Introduction

The ^{137}Cs was spread into the environment globally by the atmospheric nuclear weapon tests between 1950s and 1960s. The concentration of ^{137}Cs, which was deposited on soil by fallout, depends on the physical and chemical properties of soil.[1] In the sea, ^{137}Cs was deposited on the surface of marine sediment by adsorption on floating matters or direct precipitation of colloidal forms.[2] It is also strongly adsorbed on clay particles and is virtually non-exchangeable.[3] Therefore, the concentration of ^{137}Cs in marine sediment may be influenced by particle size, mineral composition and organic matter contents of marine sediments. The relationships among particle size and organic matter content and ^{137}Cs concentration have been studied widely to find the distribution properties and the behavior of ^{137}Cs in soil. However, there are not enough reports on the relationships in marine sediments.

In this work, ^{137}Cs concentration, particle size and total organic carbon, hydrogen, nitrogen and sulfur contents of marine sediments were measured. The distribution of ^{137}Cs and the relationship among ^{137}Cs concentration, particle size and organic matter contents of marine sediments were investigated to study the deposition properties of ^{137}Cs in marine sediments collected in the East Sea near Yangnam, Korea. Also ^{137}Cs concentrations in seawater were measured to assess the distribution coefficient of ^{137}Cs.

Materials and Methods

Sediment and seawater samples were collected in the adjacent sea to Yangnam from 24 June to 24 July 2000, shown in Fig. 1. The

deepest seawater depth in the sampling region was 92 m. The temperature of the sampled sediments was in the range of 4.7-20.8 ℃. The salinity of seawater was in the range of 33.6-35.4 ‰, nearly same level as recent values reported in the East Sea.[4]

Marine sediment samples were collected by a grab sampler from 382 locations as shown in Fig. 1. The samples were dried at 90 ℃, powdered and then sieved to a particle size smaller than 2 mm to guarantee the homogeneity of the samples. The sieved sediment samples were put in the 1 L Marinelli beaker and the gamma-ray spectra were measured by HPGe detector system. The spectra were analyzed and then the activities of gamma-ray emitting nuclides including ^{137}Cs were determined.

The particle size of the sediment was analyzed for 90 wet sediment samples. The sediments coarser than 63 μm were sieved through a nest of sieves and separated on the basis of particle size using the Wentworth grade classification. The particle size distribution of the coarse fraction was determined from the weight of the separated sediment after drying and the sediments less than 63 μm were analyzed using a Micromeritics SediGraph 5100D Particle Size Analyzer. In this work, the average particle sizes of sediments were expressed in median phi notation, where $M_d\varphi = -\log_2$ of the median value of the particle diameters in millimeter, at which cumulative weight percent is 50 %. [5]

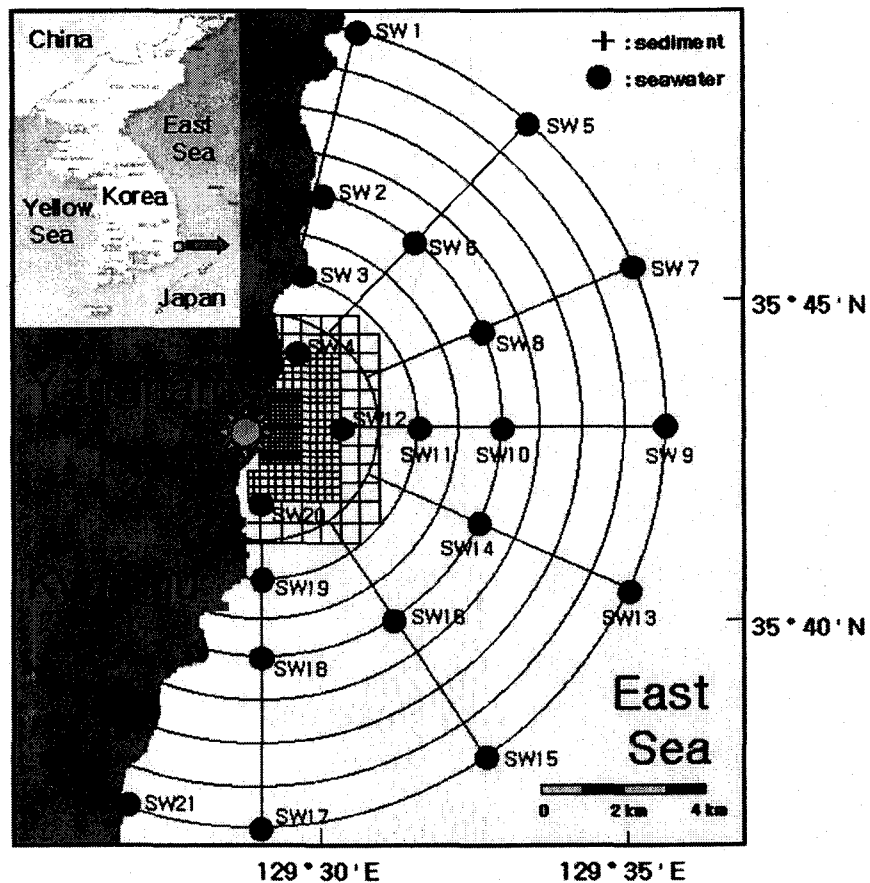The contents of total carbon (TC), H, N and S for 90 sediment samples were measured

Fig. 1. Sampling locations in the adjacent sea to Yangnam, Korea.

using an Elementar Vario EL elemental analyzer after removing the salt in the sediment by enough dilution with DI water. The content of TOC was measured using a Shimadzu SSM5000A Total Organic Carbon Analyzer.

Seawater samples were collected at 21 stations, shown in Fig. 1. At each sampling station, surface and subsurface seawater samples were collected by a submersible pump. The samples were acidified by conc. HCl immediately after sampling. The concentration of ^{137}Cs in seawater was measured using gamma-ray spectrometers after ammonium molybdate phosphate (AMP) precipitation.

Results and Discussion

Distribution of ^{137}Cs in marine sediments

The horizontal distribution of ^{137}Cs of sediments in the adjacent sea to Yangnam is shown in Fig. 2. The concentrations of ^{137}Cs are in the range of <MDA-7.19 Bq/kg-dry. Those values are smaller than or close to the level reported by others: in the range of <MDA-10.4 Bq/kg in surface sediments from the Pechora Sea [6] and in the range of 8.3-25.4 Bq/kg-dry in the surface sediments of the East Sea located among South Korea, Japan and Russia.[7] Thus the level of ^{137}Cs concentrations in sediment of this work is close to the level caused by atmospheric nuclear weapon tests and the Chernobyl accident.

Effect of particle size

The particle size distribution of marine sediments is closely related to that of ^{137}Cs in marine sediments. The quantitative relationship between ^{137}Cs concentration and particle size in sediments is shown in Fig. 3. The concentrations of ^{137}Cs in marine sediments increase linearly with the increase of $M_d\varphi$ (decrease in particle size). This means that fine
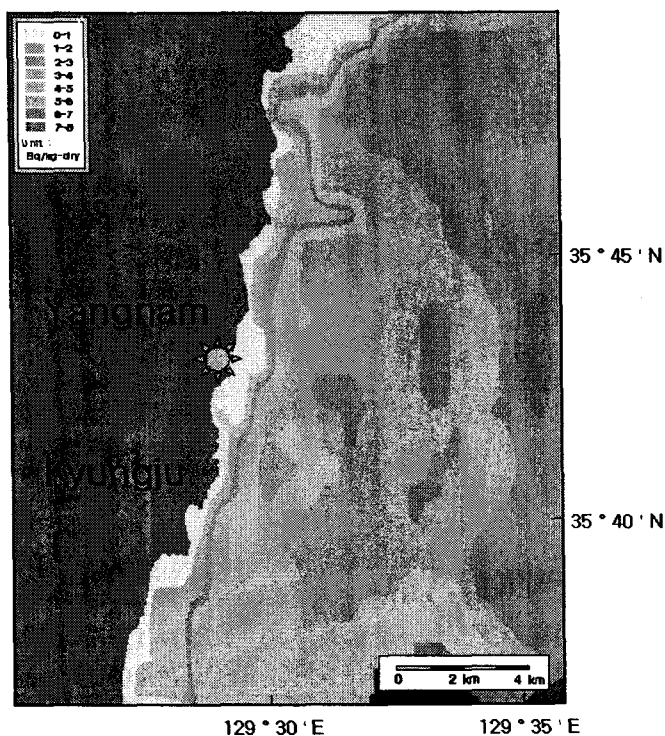

Fig. 2. Contour map showing horizontal distribution of ^{137}Cs concentrations of marine sediments in the adjacent sea to Yangnam, Korea.
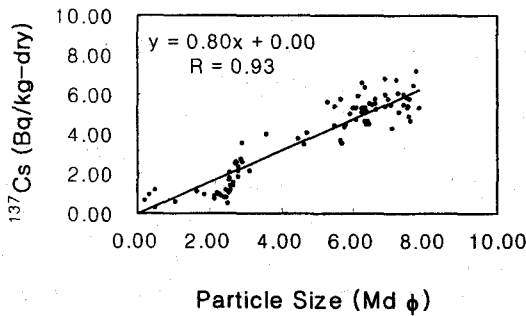
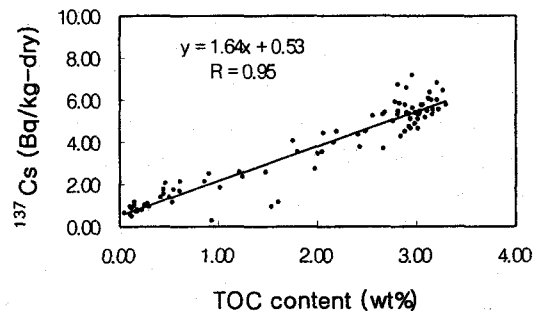Fig. 3. Relationship between the concentration of ^{137}Cs and particle size of marine sediments.

Fig.4. Relationship between the concentration of ^{137}Cs and TOC content in marine sediments

particles play important roles in the distribution of ^{137}Cs and total surface area of the sediment.[1,3] The increased surface areas of sediments and the large cation exchange capacity (CEC) of clays increase the adsorption capability of [137]Cs.

Effect of organic matter content

The adsorption of Cs may occur at cation exchangeable sites in soil particles. A number of analytical data have supported that most of the CEC has arisen from soil organic matter.[8] This may be the same in sediments in the marine environment. Marine sediments contain complex mixtures of organic compounds, which are mostly composed of humic substances. Primary humic substances are mainly insoluble humin and secondary humic substances are humic and fulvic acids formed by oxidation of humin. Humic substances in marine sediments can be derived from organic material produced either in terrestrial or marine environments[9]. The elementary composition of them is mostly within the following ranges: C, 45-55 %; O, 30-45 %; H, 3-6 %; N, 1-5 %; and S, 0-1 %.[10] Thus the contents of humic substances which play important roles in complexing agent in nature[11] should be related to the contents of C, O, H, N and S in sediment and the contents of those elements may represent the amounts of humic substances.

The relationship between the concentration of ^{137}Cs and TOC content in sediments is shown in Fig. 4. Correlation analysis indicates that there is a strong linear relationship[12] between the concentration of ^{137}Cs and the content of TOC, H and N with correlation coefficient R > 0.95. The concentration of ^{137}Cs and the content of S have a linear correlation with R = 0.78.

The relationships between content of TOC and H and N are linear with R > 0.96. TOC content and S content have a linear relationship with R = 0.79 though this value is lower than that of H and N contents. Also, H content apparently increased with N and S contents (R = 0.98 for N, R = 0.80 for S).

The contents of TOC, H, N and S, which come from humic substances, also linearly increase with the decrease of particle size. The results of a linear correlation analysis between particle size (x) in $M_d\varphi$ and the contents of TOC, H, N and S (y) in wt% were y = 0.44 x - 0.12 (R=0.90) for TOC, y = 0.16 x (R=0.93) for H, y = 0.04 x 0.02 (R=0.93) for N, and y = 0.05 x (R=0.79) for S, respectively.

Multiple regression analysis

Multiple regression analysis was used to investigate the relationship between the concentration of ^{137}Cs and the measured sedimentological parameters (particle size and TOC content). The results of the analysis show that all the measured variables have linear relationships, as expressed in Fig. 5. The multiple regression technique using the SAS system provides a linear function of experimental variables:
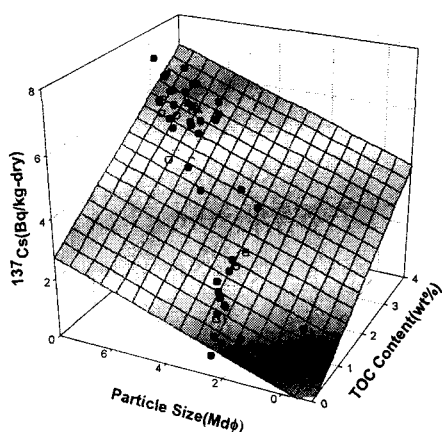
Fig. 5. Relationship among ^{137}Cs concentration, particle size and TOC content in marine sediments.

$$Y = 0.17+1.06V_1+0.32V_2 \qquad (1)$$

where Y is the concentration of ^{137}Cs in Bq/kg-dry, V_1 is the content of TOC in wt% and V_2 is particle size in $M_d\varphi$. The correlation coefficient, R is 0.97 and the standardized regression coefficients, which show the relative consequence of each variable, are 0.62 for TOC and 0.37 for particle size. We are unable to estimate the influence of each variable using the standardized regression coefficients because there is a problem in collinear data between TOC and particle size with a high regression relation as previously observed in Section 3.3. Thus the stepwise estimation method gives a regression equation of principal components:

$$Y = 0.53+1.64V_1 \qquad (2)$$

where V_1 is TOC content in wt%. Therefore TOC content affects the deposition of ^{137}Cs greater than particle size of sediment.

Concentrations of ^{137}Cs in seawater

The measured concentrations of ^{137}Cs in surface and subsurface seawater samples are given in Table 1. The ^{137}Cs concentrations in surface and subsurface waters are in the range of 2.4-4.5 and 2.3-4.3 mBq/L with an average

of 3.2±0.6 and 3.4±0.5 mBq/L, respectively. These values are in good agreement with those reported by other authors [4, 13, 14 and 15] for the East Sea.

The vertical profiles of ^{137}Cs in three stations SW9, SW10 and SW12 are plotted in Fig. 6, showing very little variation with increasing depth, a pattern similar to that observed at shallow seawater over 200 m in depth in the East Sea[4, 14] and in the western North Pacific.[16] In the coastal seawater of the East Sea, thermocline is about 200 m in depth. The seawater is mixed well in a layer above thermocline. [137]Cs may be mixed easily in shallow seawater, for most ^{137}Cs are in ion form.[17]

Distribution coefficient of [137]Cs

The distribution coefficient K_d for a radionuclide is an important parameter describing the distribution of the radionuclide between solid matter and solution. K_d is a measurement of the intensity of the radionuclide adsorption by soil particulate matter and is associated with the chemical and physical properties of soil such as mineralogy, pH and CEC and initial radionuclide concentration.[1, 18] K_d was considered for adsorption of ^{137}Cs and is defined as.[19]

$$K_d = \frac{\text{concentration of } [137]\text{Cs in sediment}}{\text{concentration of } [137]\text{Cs in water}} \qquad (3)$$

In this study, K_d was calculated by the ratio of ^{137}Cs concentration in the sediments to that of the seawater. The distribution coefficients of ^{137}Cs increase with decreasing particle size and increasing TOC content of sediment. The distribution coefficient for ^{137}Cs in our samples is in the range of 226-2200. This value is in the range of 1×10^2-2×10^4, which is the recommended distribution coefficient of cesium for coastal areas from IAEA.[19]
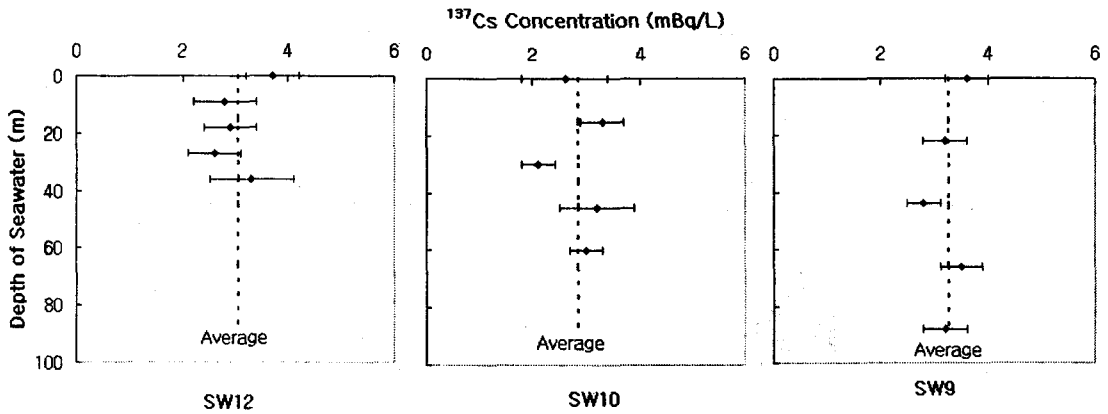
Fig. 6. Vertical profiles of ^{137}Cs in three stations SW9, SW10 and SW12 in the adjacent sea to Yangnam, Korea.

Table 1. Concentrations of ^{137}Cs in seawater in the adjacent sea to Yangnam, Korea.

Location	Seawater depth (m)	Concentration of ^{137}Cs in seawater		
		Surface (mBq/L)	Subsurface (mBq/L)	Surface / Subsurface
SW1	27	2.7 ± 0.3	2.3 ± 0.5	1.17
SW2	30	2.8 ± 0.4	2.6 ± 0.5	1.08
SW3	17	3.2 ± 0.4	3.7 ± 0.5	0.86
SW4	17	3.3 ± 0.4	3.5 ± 0.4	0.94
SW5	48	2.8 ± 0.3	3.7 ± 0.6	0.76
SW6	39	2.8 ± 0.4	3.6 ± 0.5	0.78
SW7	78	3.3 ± 0.4	4.3 ± 0.7	0.77
SW8	54	2.6 ± 0.4	3.7 ± 0.6	0.70
SW9	92	3.6 ± 0.4	3.2 ± 0.4	1.13
SW10	62	2.6 ± 0.8	3.0 ± 0.3	0.87
SW11	47	2.9 ± 0.4	2.9 ± 0.4	1.00
SW12	36	3.7 ± 0.5	3.3 ± 0.8	1.12
SW13	90	3.1 ± 0.6	3.8 ± 0.4	0.82
SW14	59	4.5 ± 1.3	3.8 ± 0.4	1.18
SW15	66	2.4 ± 0.7	4.2 ± 0.9	0.57
SW16	42	4.0 ± 0.7	3.4 ± 0.4	1.18
SW17	25	3.8 ± 0.5	3.2 ± 0.4	1.19
SW18	29	3.2 ± 0.4	3.2 ± 0.4	1.00
SW19	26	4.0 ± 0.4	3.2 ± 0.6	1.25
SW20	16	3.9 ± 0.7	3.1 ± 0.4	1.26
SW21	15	2.9 ± 0.6	3.6 ± 0.6	0.81
Average		3.2 ± 0.6	3.4 ± 0.5	0.97 ± 0.20

Conclusions

The concentrations of ^{137}Cs in sediment and seawater and some physical and chemical properties of sediments were measured in the adjacent sea to Yangnam, Korea to study the deposition properties of ^{137}Cs in marine sediments.

The concentrations of ^{137}Cs in marine sediments are in the range of <MDA-7.19 Bq/kg-dry in the adjacent sea to Yangnam and turn out to be the same level as that caused by the nuclear weapon tests fallout. The concentrations of ^{137}Cs in marine sediments linearly increase with decreasing particle size and increasing the contents of TOC, H, N and S of sediments. The adsorption possibility of ^{137}Cs becomes higher with decreasing particle size that means increasing total surface areas of particles in sediments. The relationships between TOC, H, N and S contents and particle size of sediment are also linear. The humic substance composed of C, H, N, O and S, is the most important class of complexing agent that occurs naturally. Thus it can be concluded that particle size and contents of the humic substances play very important roles in the deposition of ^{137}Cs in marine sediments. The multiple regression result shows that TOC content affects the deposition of ^{137}Cs greater than particle size of sediment.

The ^{137}Cs concentrations of seawater in the adjacent sea to Yangnam are in the range of 2.3-4.5 mBq/L. The distribution coefficients of ^{137}Cs depend on particle size and TOC content of sediments and are in the range of 226 -2200.

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