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Metals in Coastal Sediments Adjacent to the Youngkwang Nuclear Power Plant, West Coast of Korea

YEONG-GIL CHO[1], SUNG RYULL YANG[2] AND KYUNG-YANG PARK[1]
[1]*Dept. of Marine Resources, Mokpo National University, Chonnam 534-729, Korea*
[2]*Dept. of Environmental Engineering, Kwangju University, Kwangju 502-703, Korea*

Coastal sediments collected near the Youngkwang Nuclear Power Plant were analysed for major (Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, MnO), trace (Ba, Sr, V, Co, Cr, Cu, Ni, Zn, Pb) metal, and P_2O_5 contents. The composition of bulk metals from most stations fits within the range as those in the average crustal and sedimentary rocks, suggesting that the anthropogenic perturbation of these components is insignificant. The abundance and distribution of total contents for the majority of metals in the surface sediment could be explained by the grain size and were associated with mud (<63 μm) contents. However, distributions of Ca, K, Sr and Ba did not have any significant association with the sediment grain size. This may be due to the geochemical coherence among these metals in certain minerals abundant in coarse grained fractions. The distribution of Pb appears to be partly affected by the contribution from aerosol fallout. Using the R-mode factor analysis, we show that the variance of the metal contents could be explained by four factors which account for 93.7% of the total variance. It appears that texturally controlled and/or sorting factors influenced by fine fraction are the most dominant factors which determine the relative abundance and distribution of metals in the study area.

INTRODUCTION

There has been a growing interest in the environmental problems near the Youngkwang coastal region since the Korea Electric Power Corporation (KEPCO) began operation of the nuclear power plants. In particular, major concern has been focused on the discharge of cooling water effluents as well as radioactive wastes to the coastal ecosystem.

In spite of the concerns, insufficient effort has been concentrated to the environmental investigation of the area. In 1992, a joint KEPCO-KORDI oceanographic survey was undertaken to investigate the environmental impact in the coastal region adjacent to the Youngkwang Nuclear Power Plant (KEPCO, 1992). Recently, a study on the variation of basic ecosystem characteristics due to environmental pollution was carried out (Cho, 1995). Considering the number of oceanographic articles published, the information is relatively abundant for the western and southern coastal areas, but quite limited for the southwest coast of Korea. Especially, articles about the coastal region bordering the Youngkwang Nuclear Plant are still scarce.

This paper reports the distribution of major and trace metals and factors controlling them in coastal sediments near Youngkwang. The results herein represent a portion of a more comprehensive study of the coastal marine sediments around Korea, which deals with the distribution and occurrence of heavy metals and geochemistry of the sediments. This result could provide a baseline for determining the magnitude of heavy metal contributions from future industrial developments and/or from other activities which may cause changes in heavy metal inputs to the coastal region.

MATERIALS AND METHODS

Surface sediment samples were obtained with a van Veen grab at 35 coastal stations adjacent to the Youngkwang Nuclear Plant between October 22~23, 1995 (Fig. 1). Immediately after collection, sediment samples were placed in polyethylene bags, carried to the laboratory, and subjected to granulometric and geochemical analyses.

Sediment grain size analyses were performed using the sieve and pipet procedure (Carver, 1971). Organic matter contents were determined by combusting dried samples in a muffle furnace for 24 hours at 450°C. Metal contents of sediment were determined by ICP-AES (Inductively Coupled Pla-

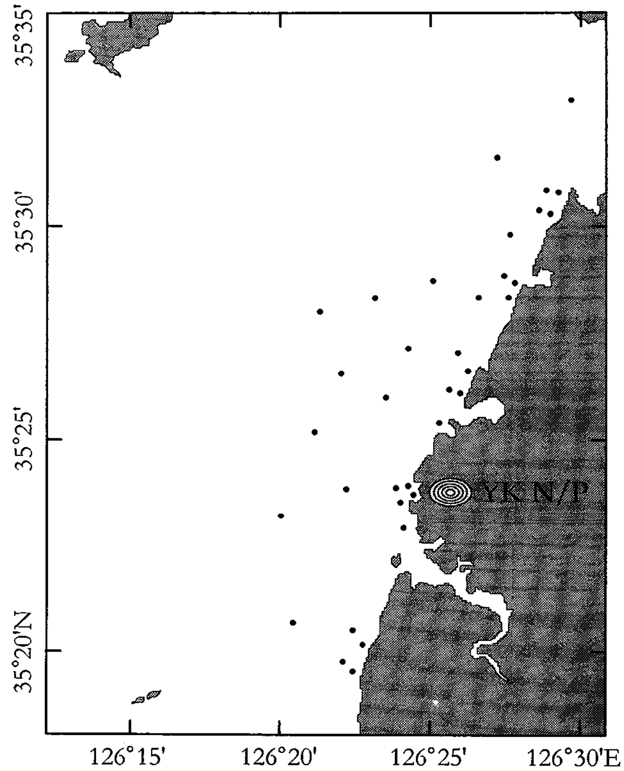

Fig. 1. A map showing the study area and sampling sites. YK N/P is the Youngkwang Nuclear Plant.

sma Atomic Emission Spectrometer) after digesting the samples in a mixture of $HF/HClO_4$. The accuracy for metal determination was estimated by standard reference materials (NBS1646 of NIST and PACS-1 of NRC). The relative deviations of these standards from certified values were less than 5% for Al_2O_3, Na_2O, K_2O, MgO, CaO, P_2O_5, MnO, V, Co, Ni, Cu, Zn and Pb, and less than 10% for Fe_2O_3, TiO_2 and Cr. The estimated precision based on replicate analyses was 5% for TiO_2, Cr and Zn, and 3% for the rest of the components.

RESULTS AND DISCUSSION

Grain size and organic matter distribution

The analytical results of grain size and organic matter content (LOI; loss on ignition) in sediment samples are given in Table 1. The grain size distribution of surface sediments consisted of a wide range of size classes. The sediments close to the coastline were primarily comprised of sand with low percentages of mud (<63 μm), usually less than 5%. This is due to the differences in hydrodynamic regime, as tidal currents and waves scour the area adjacent to the coastline (KEPCO, 1992). Progressing from the coastline towards the deep waters, the silt and clay portion increased. In open water stations, the fraction of mud was higher than 90%.

Table 1. Grain size compositions and contents of organic matters (LOI)

STN	Sand (%)	Silt (%)	Clay (%)	Mz (ϕ)	LOI (%)
1	1.2	52.1	46.7	8.0	4.71
2	4.7	62.7	32.6	7.1	4.01
3	3.8	81.8	14.4	6.1	2.48
4	8.8	59.4	31.8	7.0	3.65
5	15.3	59.1	25.6	6.4	3.52
6	6.0	64.0	30.0	7.1	2.64
7	5.2	56.0	38.8	7.6	4.55
8	28.2	45.4	26.4	6.1	2.93
9	27.8	44.6	27.6	6.3	2.80
10	0.6	79.3	20.1	6.6	2.31
11	8.9	51.4	39.7	7.4	5.30
12	40.4	50.3	9.3	4.9	3.16
13	27.0	54.0	19.0	5.8	3.50
14	11.2	44.0	44.8	7.7	5.34
15	90.8	5.9	3.3	3.2	1.18
16	84.0	15.4	0.6	3.3	1.14
17	90.7	6.5	2.8	3.1	1.37
18	96.0	2.3	1.7	2.8	1.55
19	96.2	2.1	1.7	2.9	1.29
20	97.9	1.3	0.8	2.7	1.24
21	96.6	1.1	2.3	2.7	1.22
22	98.8	1.0	0.3	2.6	1.41
23	97.0	1.6	1.4	2.8	1.62
24	100.0	0.0	0.0	2.6	1.36
25	100.0	0.0	0.0	2.8	1.29
26	97.8	1.4	0.8	2.8	1.28
27	97.9	1.5	0.5	3.2	1.19
28	97.1	2.1	0.8	2.9	1.12
29	97.9	1.4	0.7	3.0	1.15
30	96.1	3.0	0.9	3.1	1.46
31	97.1	2.0	0.9	3.1	1.17
32	61.0	34.6	4.4	3.8	1.25
33	95.4	3.4	1.1	3.1	1.27
34	13.1	77.7	9.2	5.3	1.76
35	3.4	52.1	44.5	7.9	4.32
Min	0.6	0.0	0.0	2.6	1.12
Max	100.0	81.8	46.7	8.0	5.34
Avg	57.0	29.2	13.9	4.7	2.33
Std	42.3	29.0	16.1	2.0	1.35

The LOI of the samples fell in the range between 1.1% and 5.3% (mean=2.3%). The fractions of LOI in sediments appear to be controlled primarily by the sediment texture (Fig. 2) as is often the case in coastal marine sediments around Korea (Lee *et al.*, 1989; Cho *et al.*, 1993, 1994). There is an increase in LOI values with the distance from the coastline, which is similar to the distribution of fine grained sediments. The fact that the percentage of mud shows a positive linear correlation with LOI (r=0.84; see Table 3) supports such trends. The inverse relationship between the LOI and sand fractions

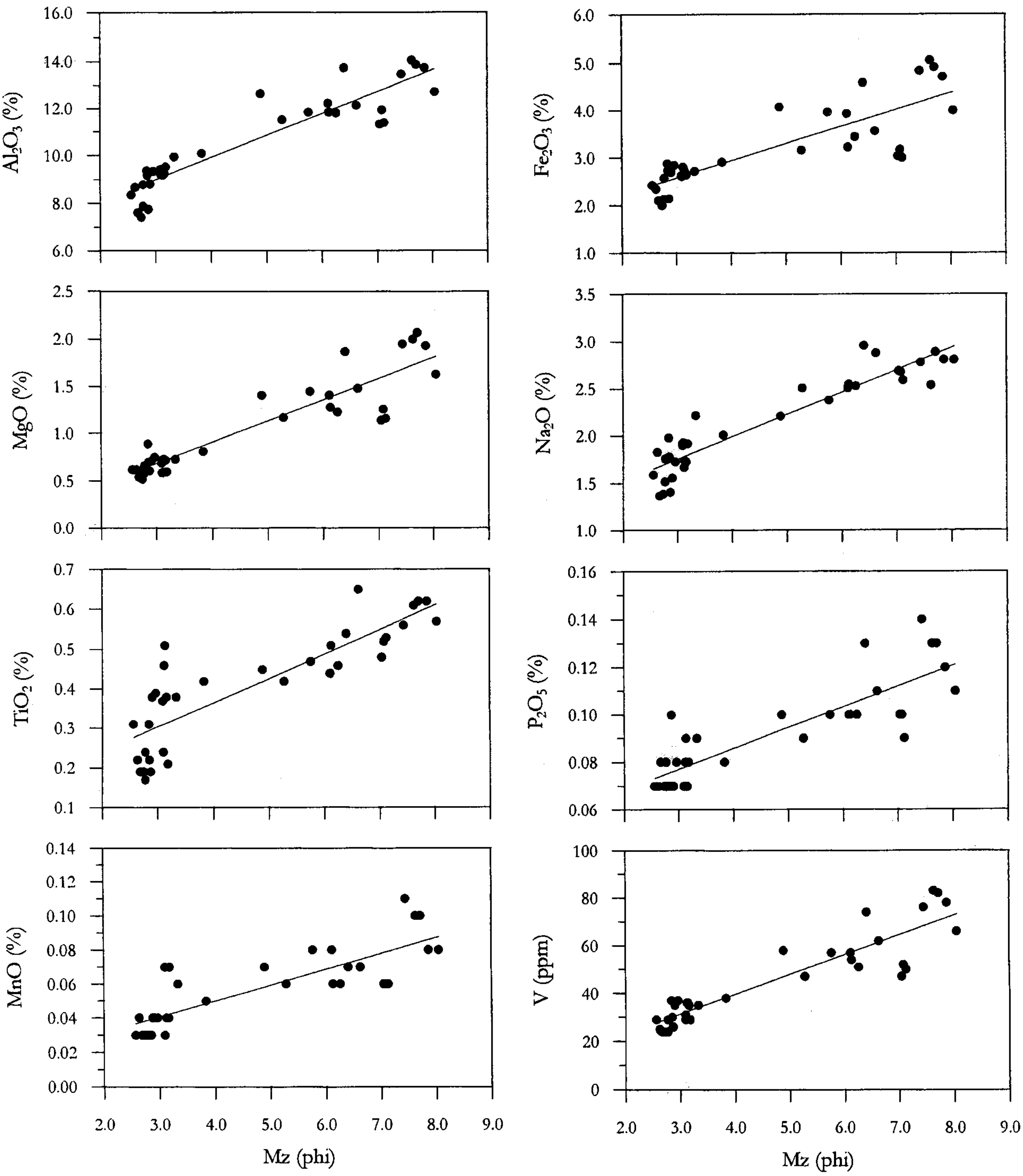

Fig. 2. Pair diagrams relating the content of metals and LOI (loss on ignition) with the mean grain-size (Mz) of sediments.

suggests that sand grains in sediments could act as diluents for organic matter.

The distribution of metals in surface sediments

The content of metals in surface sediments showed a wide range of values (Table 2). In general, these variations in metal contents of sediment primarily reflect the variations in sediment grain size. Compared with coarse grained sediment samples, it is apparent that contents of Al_2O_3, Fe_2O_3, MgO, Na_2O, TiO_2, MnO, V, Cr, Co, Ni, Cu, Zn and P_2O_5, in fine grained sediments can largely be accounted for by silt and clay proportions (Table 2). A strong positive correlation of metals with mud percentages (Table 3) and mean grain-size (Fig. 2)

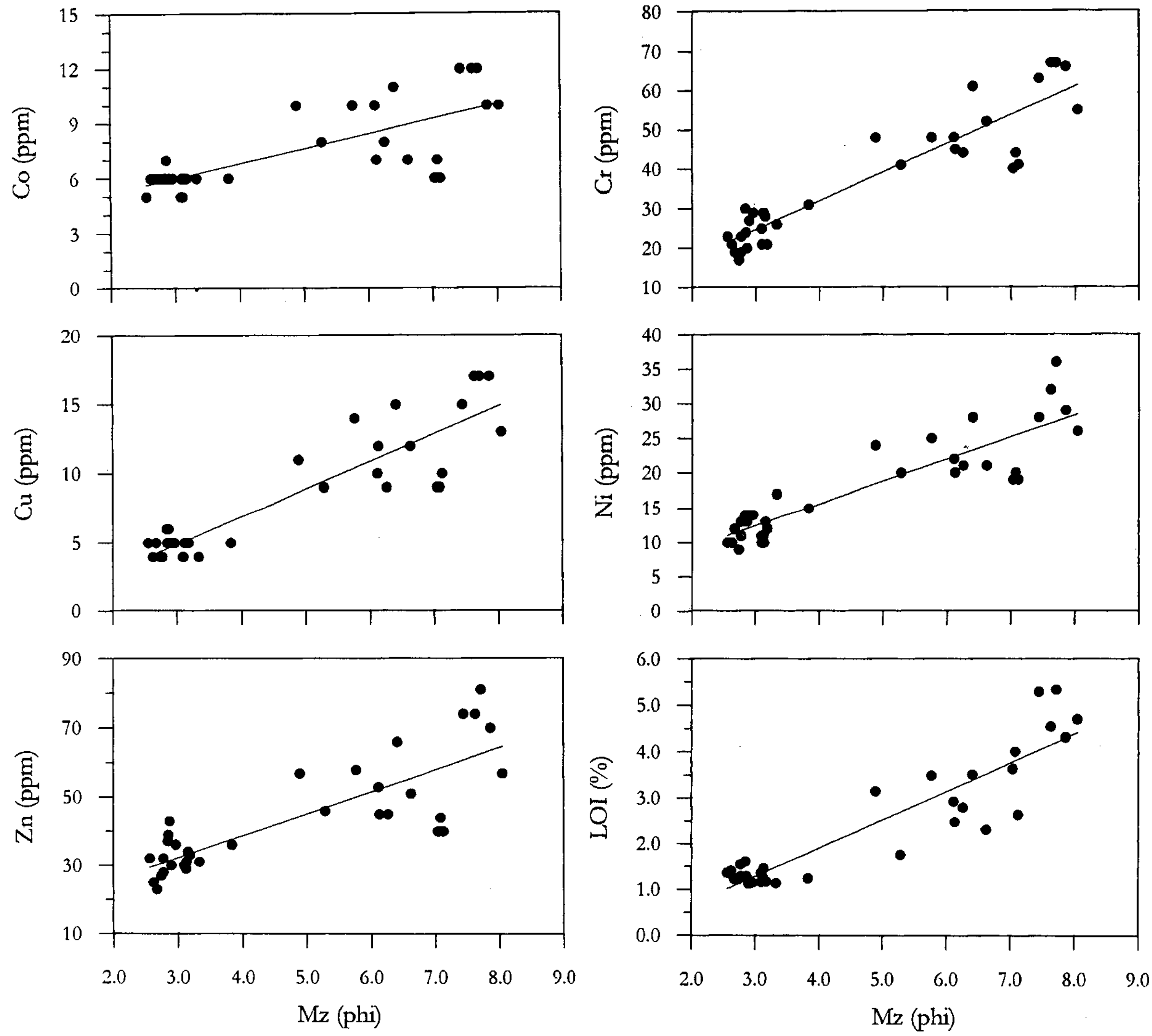

Fig. 2. Continued

Table 2. The mean, standard deviation (std) and coefficient variation ($\sigma_x/\bar{x}$) of metals in bulk sediments as compared with that in the muddy and sandy sediments (unit in %, *ppm)

	Bulk Samples (n=35)			Muddy samples (n=16)			Sandy samples (n=19)		
	Mean	Std	$\sigma_x/\bar{x}$	Mean	Std	$\sigma_x/\bar{x}$	Mean	Std	$\sigma_x/\bar{x}$
Al_2O_3	10.56	2.02	0.19	12.53	0.96	0.08	8.91	0.77	0.09
Fe_2O_3	3.19	0.86	0.27	3.92	0.73	0.19	2.57	0.28	0.11
MgO	1.06	0.49	0.46	1.53	0.33	0.22	0.67	0.09	0.14
CaO	1.32	0.78	0.59	1.29	0.11	0.08	1.34	1.07	0.80
Na_2O	2.15	0.51	0.23	2.65	0.20	0.08	1.74	0.23	0.13
K_2O	2.85	0.19	0.07	2.74	0.16	0.06	2.95	0.14	0.05
TiO_2	0.41	0.14	0.36	0.53	0.07	0.14	0.30	0.10	0.34
P_2O_5	0.09	0.02	0.22	0.11	0.02	0.14	0.08	0.01	0.12
MnO	0.06	0.02	0.40	0.08	0.02	0.22	0.04	0.01	0.32
Ba*	611.1	80.5	0.13	542.9	42.0	0.08	668.5	56.3	0.08
Sr*	182.0	19.2	0.11	181.7	11.6	0.06	182.3	24.2	0.13
V*	45.2	18.2	0.40	62.1	12.6	0.20	31.0	5.0	0.16
Co*	7.4	2.2	0.30	9.1	2.1	0.23	5.9	0.5	0.08
Cr*	36.9	15.7	0.43	51.9	9.9	0.19	24.3	4.3	0.18
Cu*	8.3	4.4	0.53	12.4	3.1	0.25	4.7	0.7	0.14
Ni*	17.8	7.2	0.40	24.4	5.1	0.21	12.3	2.1	0.17
Zn*	43.1	15.5	0.36	56.3	13.2	0.23	31.9	4.9	0.15
Pb*	24.4	5.2	0.21	24.1	6.6	0.27	24.7	3.8	0.16

Table 3. Correlation coefficients among the textural and chemical parameters

	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Ba	Sr	V	Co	Cr	Cu	Ni	Zn	Pb	Sand	Mud	LOI
Al_2O_3	1.00	0.95	0.97	-0.18	0.94	-0.40	0.87	0.87	0.88	-0.73	-0.20	0.97	0.84	0.97	0.93	0.94	0.90	0.09	-0.91	0.91	0.88
Fe_2O_3		1.00	0.97	-0.14	0.82	-0.28	0.81	0.88	0.88	-0.72	-0.30	0.98	0.92	0.97	0.94	0.95	0.96	0.22	-0.78	0.78	0.88
MgO			1.00	-0.06	0.89	-0.45	0.84	0.92	0.86	-0.83	-0.21	0.99	0.91	0.99	0.98	0.97	0.96	0.11	-0.88	0.88	0.93
CaO				1.00	-0.20	-0.27	-0.22	0.22	-0.04	-0.16	0.80	-0.10	0.10	-0.09	0.04	-0.01	0.08	-0.17	0.04	-0.04	0.00
Na_2O					1.00	-0.49	0.84	0.80	0.80	-0.69	-0.12	0.88	0.69	0.89	0.84	0.85	0.78	-0.06	-0.94	0.94	0.82
K_2O						1.00	-0.60	-0.48	-0.26	0.78	-0.16	-0.46	-0.25	-0.48	-0.49	-0.44	-0.35	0.31	0.65	-0.65	-0.43
TiO_2							1.00	0.76	0.70	-0.76	-0.22	0.88	0.61	0.89	0.81	0.78	0.74	-0.03	-0.82	0.82	0.74
P_2O_5								1.00	0.85	-0.76	0.06	0.91	0.88	0.91	0.91	0.91	0.92	0.07	-0.82	0.82	0.88
MnO									1.00	-0.56	-0.10	0.87	0.86	0.85	0.84	0.86	0.86	0.16	-0.78	0.78	0.84
Ba										1.00	0.09	-0.82	-0.69	-0.83	-0.84	-0.78	-0.76	0.05	0.80	-0.80	-0.78
Sr											1.00	-0.24	-0.14	-0.23	-0.16	-0.16	-0.12	-0.29	0.02	-0.02	-0.16
V												1.00	0.89	0.99	0.97	0.96	0.95	0.12	-0.87	0.87	0.91
Co													1.00	0.88	0.90	0.92	0.94	0.26	-0.70	0.70	0.86
Cr														1.00	0.97	0.96	0.95	0.10	-0.89	0.89	0.91
Cu															1.00	0.96	0.95	0.07	-0.88	0.88	0.91
Ni																1.00	0.96	0.13	-0.85	0.85	0.91
Zn																	1.00	0.15	-0.78	0.78	0.90
Pb																		1.00	0.10	-0.10	0.09
Sand																			1.00	-1.00	-0.84
Mud																				1.00	0.84
LOI																					1.00

also confirms that carriers for these metals are predominantly fine grained fractions. Meanwhile, the inverse correlation between the metal and sand fractions shows that most of the metals investigated are diluted by the presence of high sand contents. This may be due to the lack of clay minerals, oxyhydroxides and fine organic materials in this fraction.

Unlike most of the metals studied, CaO, K_2O, Sr, Ba and Pb showed little difference between coarse- and fine-grained sediment samples (Table 2). Positive and significant correlations were observed between CaO and Sr (r=0.80), K_2O and Ba (r=0.78), sand and K_2O (r=0.65), as well as sand and Ba (r=0.80), which suggests common sources and/or similar enrichment mechanisms for these metals. There were weak or even negative correlations between Pb and other metals studied. The effect of grain size on the distribution of Pb was also insignificant. These facts suggest that Pb in surface sediments has been derived from different sources than other metals.

To compare the levels of bulk metal contents in surface sediments of this area with those from a variety of sources and regions, the content of metals were normalized to that of aluminum. A strong posi-

Table 4. Metal/Al ratio and enrichment factor in sediment samples higher than 90% of mud (<63 μm)

		YKC[1]	YS[2]	YSE[3]	KE[4]	BIF[5]
Mud (%)		95.3(±2.9)	94.6(±3.9)	98.8(±1.3)	92.4(±1.8)	95.6(±2.8)
Metal/Al ratio (ppm/%)	Mn	86.8(±15.4)	44.9(±1.4)	81.1(±17.1)	98.8(±31.4)	72.6(±16.6)
	Co	1.27(±0.27)	1.75(±0.06)	1.57(±0.11)	1.38(±0.12)	1.48(±0.11)
	Cr	7.8(±1.0)	10.4(±0.2)	9.2(±0.4)	9.2(±0.7)	17.2(±3.9)
	Cu	1.9(±0.3)	3.2(±0.1)	2.7(±0.5)	3.5(±0.6)	20.4(±8.6)
	Ni	3.6(±0.4)	5.5(±0.3)	4.4(±0.3)	4.7(±0.3)	5.1(±0.9)
	Zn	8.2(±1.5)	11.8(±0.3)	11.5(±2.1)	11.5(±0.7)	22.0(±5.3)
	Pb	3.2(±0.8)	2.8(±0.4)	3.3(±0.5)		
Enrichment factor[6]	Mn	0.87(±0.15)	0.45(±0.01)	0.81(±0.17)	0.99(±0.31)	0.73(±0.17)
	Co	0.68(±0.14)	0.93(±0.03)	0.84(±0.06)	0.73(±0.06)	0.79(±0.06)
	Cr	0.77(±0.10)	1.01(±0.02)	0.90(±0.04)	0.90(±0.06)	1.68(±0.38)
	Cu	0.41(±0.07)	0.69(±0.02)	0.59(±0.11)	0.76(±0.13)	4.42(±1.86)
	Ni	0.50(±0.06)	0.77(±0.04)	0.62(±0.04)	0.66(±0.05)	0.72(±0.13)
	Zn	0.45(±0.08)	0.64(±0.02)	0.63(±0.11)	0.63(±0.04)	1.20(±0.29)
	Pb	1.41(±0.35)	1.23(±0.16)	1.44(±0.22)		

[1]This study (n=9); [2]Yellow Sea (Cho *et al.*, 1993. n=4); [3]Youngsan estuary (unpublished data, n=39); [4]Keum estuary (Cho *et al.*, 1993. n =4); [5]Banweol intertidal flat (Cho, 1994. n=15); [6]$Ei=[(C_i/C_{Al})sample]/[(C_i/C_{Al})standard]$, Data of standard (average crust) from Martin and Whitfield (1983).

tive covariance of Al_2O_3 with most metals (Table 3) reflects that aluminium is effective in normalizing for most of the granular and mineralogical variability of metals in surface sediments. In Table 4, the metal/Al ratios for some trace metals in selective sediment samples which contain >90% of material finer than 63 μm are compared with results from other coastal locations in Korea. The metal/Al ratios from this study are generally lower than those from other areas, although the percentages of mud fraction are similar. Especially, the ratios for Cr, Cu and Zn are much lower compared to the values found in sediments from polluted areas, such as the Banweol intertidal flat (Jung *et al.*, 1996). Therefore, it is reasonable to conclude that the modest level of metals in Youngkwang coastal region indicates a low metal input of anthropogenic origin. Low values of enrichment factors, which was proposed by Li (1981), in all of the selective samples support the above conclusion (Table 4).

Factors affecting the distribution of metals in sediments

Since the factors controlling the distribution of individual metals in marine sediments are complex, it is useful to apply the factor analysis to extract simple and meaningful relationships and patterns from the large data set (Harman, 1967; Calvert, 1976). In this study, the R-mode factor analysis was used to determine the factors controlling the distribution of metals in sediments. The factors, which are statistically most dominant features of the data variation, were derived from a correlation matrix. The eigenvalues of the correlation matrix, the percentage variance, and the cumulative variance explained by the factors are shown in Table 5. These indicate that 93.7% of the variance of the data is explainable by four factors. The Varimax rotated R-mode factor pattern for four factors is given in Table 6. The identity of individual factors could be deduced from examining the factor pattern.

Factor 1 is the most important factor which explains 72.2% of the variance. It contains significant high loadings on most metals (Al_2O_3, Fe_2O_3, MgO, Na_2O, TiO_2, P_2O_5, MnO, V, Co, Cr, Cu, Ni and Zn) as well as on LOI and mud. This association is considered to reflect the aluminosilicate control, most probably by the clay fraction. The antipathy of this association with sand fraction (Table 3) and the lack of any regional differentiation among mud samples (Table 2) suggest that this is a texturally controlled factor and/or a sorting factor influenced by fine fractions.

The high loadings of K_2O (0.92) and Ba (0.71) in factor 2 is explained in terms of the geochemical coherence of these elements with feldspar which is abundant in sand-sized detrital grains. Indeed, potassium and barium are generally known to be associated with potassium feldspar (Rankama and Saha-

Table 5. Eigenvalues of the correlation matrix

Eigenvalues	Cumulative % of total variance explained	Proportion
15.1694	72.24	72.24
2.2841	83.11	10.88
1.4766	90.14	7.03
0.7416	93.68	3.53
0.5060		
0.2531		
0.1636		
0.1117		
0.0794		
0.0587		
0.0522		
0.0382		
0.0233		
0.0141		
0.0127		
0.0084		
0.0033		
0.0021		
0.0009		
0.0005		
0.0000		
Sum 21.0000		

Table 6. The Varimax-rotated R-mode factor pattern

	Factor1	Factor2	Factor3	Factor4	Communality
Al_2O_3	**0.91**	-0.22	-0.16	0.00	0.99
Fe_2O_3	**0.96**	-0.13	-0.18	0.10	0.98
MgO	**0.95**	-0.29	-0.10	0.03	0.99
CaO	0.02	-0.13	**0.94**	-0.03	0.99
Na_2O	**0.79**	-0.30	-0.14	-0.12	0.96
K_2O	-0.23	**0.92**	-0.18	0.17	0.97
TiO_2	**0.70**	-0.49	-0.24	-0.07	0.87
P_2O_5	**0.91**	-0.26	0.20	0.03	0.94
MnO	**0.91**	0.00	0.01	0.06	0.90
Ba	-0.66	**0.71**	-0.02	0.03	0.96
Sr	-0.14	0.00	**0.93**	-0.14	0.97
V	**0.93**	-0.30	-0.14	0.03	0.99
Co	**0.96**	-0.05	0.05	0.16	0.96
Cr	**0.92**	-0.33	-0.13	0.03	0.99
Cu	**0.93**	-0.32	-0.03	0.00	0.97
Ni	**0.94**	-0.24	-0.04	0.05	0.96
Zn	**0.97**	-0.16	0.03	0.05	0.98
Pb	0.13	0.16	-0.14	**0.97**	1.00
Sand	-0.76	0.46	0.01	0.12	0.97
Mud	**0.76**	-0.46	-0.01	-0.12	0.97
LOI	**0.90**	-0.25	-0.03	0.01	0.88

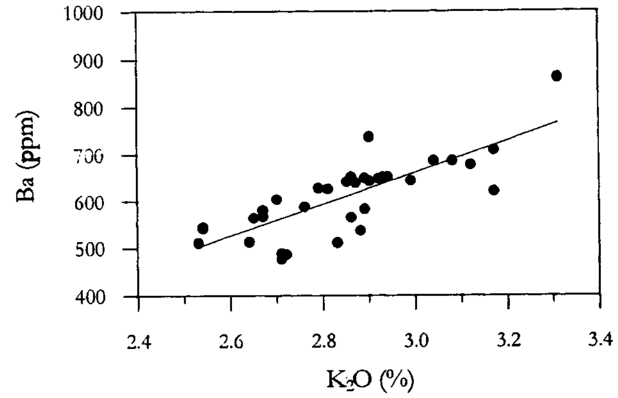

Fig. 3. The relationship between K_2O and Ba.

ma, 1950; Bowen, 1979). When the content of Ba was plotted against that of K_2O, a tendency of covariance between these two elements could be deciphered (Fig. 3). This suggests that the variance of these elements is dominated by the co-occurrence of feldspar.

Factor 3 clearly involves the carbonate. The association of CaO (0.94) and Sr (0.93) with factor 3 is accounted for by the influence of locally abundant carbonate debris. Furthermore, the variance of these materials is dominated by the occurrence of calcium carbonate shells. The dependence of this factor on the absolute CaO content, hence the carbonate content, is illustrated in Fig. 4. The positively scored samples are mainly sandy sediments and shells which are present as sand-sized grains.

Factor 4, significantly loaded with only Pb, could not be elucidated from our data set. There was no evidence of anthropogenic input by examining the other trace metal data. However, a major portion of Pb released into the environment by human activity eventually reaches the sea via aeolian transport (Bru-

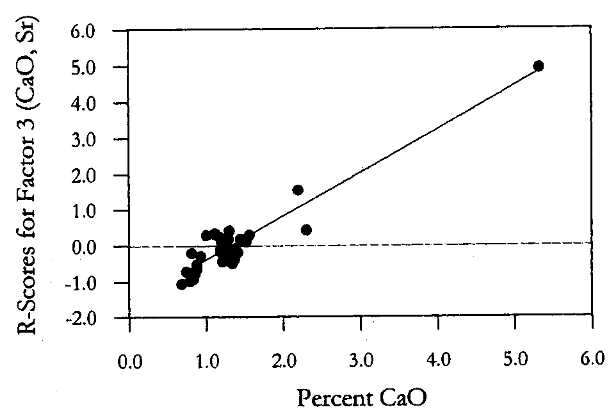

Fig. 4. The interdependence of R-scores for factor 3 (CaO, Sr) and the abundance of CaO.

land *et al.*, 1974; Ng and Patterson, 1982). It is plausible that the Pb factor is due to the additional atmospheric input of aerosol fallout with high Pb content.

CONCLUSIONS

Metal contents in surface sediments from the coastal region near Youngkwang Nuclear Power Plant were examined and compared with those from other coastal areas. Also, the dominant factors which control the composition of metals are explored by the R-mode factor analysis to elucidate the major factors controlling the abundance and distribution of metals.

The aluminium normalized metal concentrations indicate that they are at or near the background level and that variations in their concentrations are the results of granular variability in the sediments. However, high levels of Pb, exceeding the background level, were observed in the sediments. This enrichment could be accounted for by the deposition of Pb-rich aerosol, although the contribution from natural sources cannot be ruled out entirely.

The factor analysis shows that the variance of the metal distribution from surface sediments of the Youngkwang coast can be explained by a few parameters; which are natural granular variation, and the degree of geochemical coherence among some elements. The most dominant factor is the association of Al_2O_3, Fe_2O_3, MgO, Na_2O, TiO_2, MnO, V, Co, Cr, Cu, Ni, Zn and P_2O_5. The distribution of these elements with high positive loadings on this factor is dominated by the inclusion in structural positions of clay minerals. Feldspars in sand-sized population give rise to factor containing K_2O and Ba. The carbonate debris account for the factor containing Ca and Sr.

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