Heavy Metal Contamination and Spatial Differences in Redox Condition of the Artificial Shihwa Lake, Korea

Sangmin Hyun, Eun-Soo Kim[*] and Woo-Hyun Paeng

Southern Coastal Environmental Research Division of South Sea Institute,
Korea Ocean Research and Development Institute (KORDI), Geoje 656-830, Korea
*Marine Environment and Climate Laboratory, Korea Ocean Research and
Development Institute (KORDI), Seoul 425-600, Korea

Five sediment cores from the tidal flat of artificial Lake Shihwa are analyzed in terms of sedimentology and geochemistry to evaluate the heavy metal contamination and redox condition of surficial sediment following the Shihwa seawall construction. The variability of concentrations of various elements depends on the depositional environment, and reflects the various redox conditions and sediment provenances. The amounts of Ti and Al and their ratio of Ti/Al with respect to Li clearly indicate that there is an anthropogenic contribution to the surficial sediment. The high concentrations of heavy metals suggest an anthropogenic contribution at ST. 34 and ST. 22. Concentrations of most elements (Cr, Cu, Zn and Pb) are higher near the Shihwa-Banwol industrial complex than in the central part of Lake Shihwa. Concentrations of heavy metal in surficial sediment near the Shihwa-Banwol industrial complex are two to eight times higher than in the center of Lake Shihwa. Enrichment factors (EF), which are normalized by the unpolluted shale, suggests a significant metallic contamination near the Shihwa-Banwol industrial complex (SBIC).

The redox condition is divided into two anoxic and mixed oxic/suboxic zones based on the carbon:sulfur (C/S) ratios of organic matter and elemental relationships. Correlations among geochemical elements Mn, U and Mo are significantly different from site to site, and may therefore be an indicator of the spatial redox condition. Controlling factors for switching anoxic/oxic conditions are thought to be water depth and the differences in industrial effluent supply. The variations of the Cu/Mn ratio in the sediments confirms above mentioned spatial differences of a redox condition in part, and therefore shows a location-dependence redox condition in sediments at four other sites. The redox condition of the surficial sediment characteristics of the Shihwa Lake are controlled by its geographic location and water depth.

Key Words : Lake Shihwa, Sediments, Metallic pollution, Redox condition

1. Introduction

The Shihwa Lake, located along the western coast of Korea, was formed by constructing an artificial dike in 1994 (Fig. 1). Prior to 1994, Shihwa Lake was a typical tidal flat, named Banwol tidal flat. The environmental changes in the ecosystem and an

Corresponding Author : Sangmin Hyun, Southern Coastal Environmental Research Division of South Sea Institute, Korea Ocean Research and Development Institute (KORDI), Geoje 656-830, Korea
Phone : +82-55-639-8590
E-mail : smhyun@kordi.re.kr

anthropogenic contamination caused by a seawall construction has been of interest to scientific investigation[1~4]. It is well known that large amounts of industrial effluents supplied from the surrounding Shihwa-Banwol industrial complex (SBIC) cause significant and rapid environmental changes. Therefore, Shihwa Lake has been the subjected of investigation for a number of environmental researchers since the plan to protect Shihwa Lake against environmental degradation was developed. However, it was difficult to improve the already deteriorated environment. A current focus is on environment improvement by
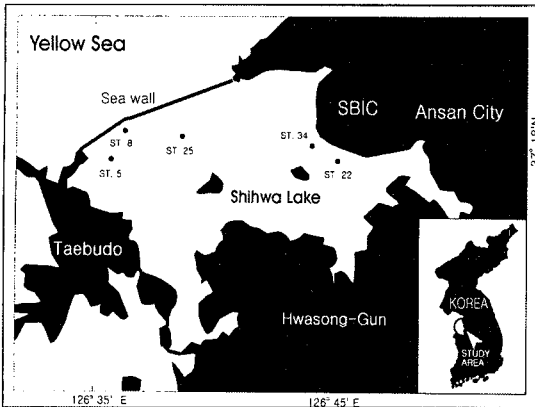
Fig. 1. Location map of the studied area and five
cores site are illustrated.

exchange with natural seawater.

According to the survey results in the summer of
1996, Shihwa Lake displayed clear density strati-
fication at a water depth of 6-8 m, and maintained
an anoxic bottom environment throughout the year[3].
This strong stratification is interpreted as the result of
freshwater input from the drainage of the surrounding
area. However, the stratification became shallow, and
switched from a depth of 6-8 m in 1997 to 3-3.5 m
in 1998[3], due to the commencement of seawater
input since July 1997. Previous works[5,6] suggest that
the anoxic of the bottom conditions and a strong
stratification of the water mass caused the grossly
polluted area to become an azoic area. These
previous works indicate that .environments in Shihwa
Lake were changeable, depending on several con-
ditions related to seawater input or/and the shutout of
seawater and occasional input of seawater. If Shihwa
Lake had been experienced repeated spatiotemporal
environmental changes within a short period, the
resultants would be reflected in the surficial sediments.

Most previous studies on Shihwa Lake were con-
ducted to determine changes in biological diversity
and the physico-chemical water mass character[1,3]. In
contrast, few studies were conducted on heavy me-
tallic pollution and the redox condition of surficial
sediment. Environmental research using geochemical
tools provided valuable data because any environ-
mental changes would inevitably be recorded in the
sediment column. The purpose of this study is to
understand the cause of variation in subsurface redox
conditions as well as to evaluate heavy metallic pol-
lution for the unique artificially made Lake environment.

2. Geography and Sedimentary facies

Shihwa Lake is 25 km long and 4 km wide,
covering an area of 61 Km^2 (Fig. 1). Shihwa Lake
can be divided into two bathymetric regions, namely,
a channel and a flat area. Sediment samples collected
close to the seawall contains shell fragments, and are
composed of alternated sandy to silty sediment. On
the other hand, sediments near the Banwol industrial
complex consisted primarily of clay and silt and do
not contains shell fragments.

Core sediment samples suggest that the sediment
facies are strongly related to a sediment source and a
water mass system, reflecting rather complicated sedi-
mentary environments. Visual core description, grain
size analysis and soft X-ray radiography examinations
show that the core sediment face can be divided into
three types; laminated mud or sandy mud, homo-
genous mud or sandy mud and shelly sandy mud[3].

The water depth of Lake Shihwa ranges from
about 4 to 18 m, and its variation in part depends on
the opening of a seawall. Therefore, seawater input
from the open sea through the floodgate influence the
water mass characteristic. It is believed that the
intermediate and deep water of Shihwa Lake is
almost stagnant during the seawater shutdown. Fresh-
water input from four main drainages plays an im-
portant role in the circulation of water mass[3].
However, bottom conditions are primarily anoxic,
even though sluggish ventilation occurs by repeated
freshwater input. This changeable stratification affects
the redox condition as well as the biological activity
and heavy metal accumulation in the Lake.

3. Materials and Methods

Five cores (ST. 5, ST. 8, ST. 22, ST. 25 and ST.
34) were collected by a portable gravity core in
March and June in 1997 (Table 1). The bathymetry
measurements were also conducted by using a pre-
cision depth recorder (PDR-101) during sample col-
lection. Gravity cores were dissected and half of the
core sediments were analyzed for elemental concen-
tration after drying at 105℃ for more than 24 hours.
The remaining half of the sediment sample was used
for X-ray radiography to interpret the sedimentary
structure. Geochemical analysis is conducted in terms
of organic matter (total organic carbon (TOC), C/N

Table 1. Core location and collected water depth

Station	Latitude	Longtitude	Water depth (m)	Core length (cm)
ST. 5	37°17.572'N	126°36.142'E	7	30
ST. 8	37°18.349'N	126°36.723'E	17	57
ST. 22	37°17.390'N	126°45.888'E	4	78
ST. 25	37°18.166'N	126°39.335'E	9	73
ST. 34	37°17.792'N	126°44.382'E	4	65

ratio and C/S ratio), carbonate content, and major and minor elements.

TOC, total nitrogen (TN) and total sulfur (TS) were analyzed using a CHNS analyzer (Carloerbar Na-1500) at the Korea Ocean Research and Development Institute (KORDI). Total carbon (TC) concentration was determined using untreated powdered samples. TOC were measured after being treated with 1N hydrochloric acid. Carbonate contents were calculated using the weight difference between TC and TOC as follows:

Carbonate content (%)
= (total carbon (%) − total organic matter (%))×8.33

TS contents were used directly from the CHNS results. The C/N ratio was defined as the ratio of TOC to TN and C/S ratio was defined as the ratio of TOC to TS.

Total concentrations of element in bulk sediments were conducted by using inductively coupled plasma atomic emission spectrophotometry (ICP/AES) at the Korean Basic Science Institute (KBSI). Samples were digested with a mixture of hydrofluoric acid (HF), perchloric acid (HClO₄) and nitric acid (HNO₃) after drying at 105℃ for 24 hr and grinding. The analytical results were checked with a standard (MAG-1). All analytical errors for $CaCO_3$, TOC, and TS were less than 10 %, and for major and minor elements were below 5 %.

4. Results and Discussion
4.1. Sedimentary depositional environments and geochemistry

It is well known that the sedimentation of this area is primarily influenced by the microtidal regime[7]. Most of the core sediments contain very coarse sand to clay size particles. The vertical characteristics of the short core sediment show a distinctive boundary between the upper and lower

layer with sharp color contrast, which is clearly reflected in the X-radiograph observation. The sedimentary interval presented between 5 and 10 cm in core ST. 8 has a very strange characteristic in terms of its color. Detailed core description by visual and X-radiograph observations suggest that the sediments of this interval were derived by artificially sprinkled terrigenous sediments i.e., *Whangtou (Loess-soil)*, used as a preventive measure for red tide occurrence[3]. Also, a distinctive boundary between tidal and lake sediment at the lower part of the core is recognized by the X-radiograph[3]. This indicates that the upper sediment deposited more rapidly on pre-existing sediments, causing the development of a different sedimentary. Surface sediments exhibit a dark color with a distinct color boundary, suggesting that the bottom environment probably remain anoxic or hypoxic in some restricted areas.

Sediment containing shell fragments with sandy mud occurs near the seawall floodgate i.e., ST. 5. Laminated mud sediments are presented inside of Shihwa Lake (ST. 22 and ST. 34). The sediments of Shihwa Lake can be classified into three facies; laminated mud or sandy mud, homogeneous mud or sandy mud and shelly sandy mud facies based on grain size, sedimentary structure and sedimentological characteristics[3].

The Al and Ti, typical conservative terrigenous elements[8,9], are used to evaluate sediment characteristic, and therefore their relationship provides insight into the source of terrigenous materials. When both conservative elements have an identical trend with proportionally, the sediment can be considered to have a common source or a uniform composition. In Fig. 2(A), the Ti/Al variations are illustrated and its variation is expressed with respect to Li normalization[10]. The trend of Ti/Al shows a relatively narrow range of variation except a sample from ST. 8, which corresponds to a depth about 5-6 cm, showing a Ti/Al ratio of about 0.14. This value is much higher than those of other samples (about 0.07). This sediment interval is interpreted as *Whangtou* which is used in the lake to prevent the rising of the red tide. This compositional change is probably the result of artificially sprinkled soils. It is thought that a relatively small area of Shihwa Lake can be imprinted by exogenous sediment supply. The C/N ratio variation in this interval of ST. 8 showing
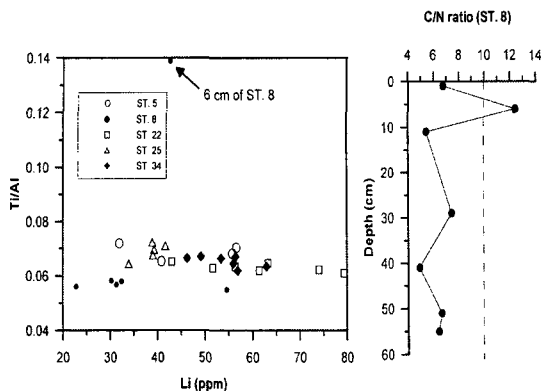
Fig. 2. Ti/Al ratio with respect to Li (ppm) (A) and C/N ratio (B) variation. Note a point comes from the allochothonous material (Loess-soil) at ST. 8.

a value over 10 in this interval confirms these artificially sprinkled soils (B in Fig. 2).

4.2. Organic matter, carbonate content, C/N and C/S ratio

A maximum value of TOC (1.15 %) occurs in the surface sediment sample of ST. 22, and a minimum value (0.08 %) is observed in the samples layer of 11 cm depth at ST. 8. Carbonate content shows a maximum value (3.5 %) in the surface sediment at ST. 5, and a minimum value (about 0.3 %) at ST. 8 and ST. 25. The C/N and C/S ratios are highly variable, both spatially and vertically. The highest values of C/N and C/S ratios occur at 6 cm depth at ST. 8 and at 5 cm in ST. 22, respectively (Table 2). As the C/N ratio and C/S ratio in the sediment reflect sediment characteristics and the sedimentary environment, the large variation observed among these factors indicates a rather complicated depositional environment in Shihwa Lake[3].

The mechanisms of organic carbon preservation in sediments are controlled by surface biogenic productivity, an increase in organic carbon preservation, and input from terrigenous organic matters[11]. The C/N ratio, which indicates characteristic of organic matter, is used to interpret a diverse source of organic matters[11~13]. Organic matter in sediment originating from in situ marine organisms exhibit C/N ratio of less than 10, compared to greater than 10 for terrigenous sources. The analytical results of organic matter are shown in Table 2. Among five core

samples, the highest C/N ratio (12.4) value occurred at about 6 cm of ST. 8, which clearly indicates a terrigenous source. All other samples exhibit ratios of less than 10 (usually 5 to 8.5 in this study), which suggest prevalence of marine organic matter. However, organic matter in sediments from 5 cm in ST. 8 are clearly of terrigenous origin. These sediments correspond to Whangtou, which is sprinkled to prevent red tide occurrence.

The C/S ratio also indicates a sedimentary environment[14,15]. Different sedimentary environments exhibit different C/S ratios[16]. The C/S ratio of most marine environments is about 2.8, with a positive correlation between TOC and TS[17]. As shown in Fig. 3, the C/S ratio varies between 5.61 at ST. 22 and 0.89 at ST. 25. C/S ratios were highly variable and greater than in typical marine shale. This variability of the C/S ratio is probably due to a rapid accumulation of non-marine sediments prior to early diagenetic process[3]. Also, the possibility of mixing from diverse sources of sediment could be another possible explanation. Considerable changes in the sedimentary environment for the Shihwa Lake sediments are detectable from the down core C/S ratios.

It is noteworthy that the carbonate content is usually high in most shallow sea or coastal environments. However, the carbonate content in the sediment of the Shihwa Lake exhibits relatively low, but large differences between upper and lower section of the sediment cores. In the open ocean sediment, carbonate contents are usually controlled by the carbonate compensation depth, bottom water condition and in situ calcareous productivity. The carbonate content at sediment of the Shihwa Lake is relatively small, ranging between 0.29 to 3.47 %. However, Shihwa Lake had exposed as a tidal flat and thus low content of carbonate can be attributed to low carbonate production or carbonate dissolution due to significant anoxic bottom conditions. The presence of a low carbonate content in relatively shallow and rapidly accumulating sediments has already been reported previously[18,19]. The evolution in dissolved carbon dioxide from the oxidation of organic matters increases in situ dissolution of $CaCO_3$. Therefore, a relatively low carbonate content in the sediment of the study area is probably responsible for the prevalent anoxic or hypoxic bottom water condition.

Table 2. Analytical results of the organic matters for the five cores

Depth (cm)	Total Carbon(%)	TOC(%)	Sulfur(%)	CaCO₃(%)	C/N	C/S ratio
ST. 5						
0	0.62	0.20	0.10	3.47	5.22	2.03
10	0.45	0.15	0.07	2.51	5.26	2.09
20	0.23	0.19	0.05	0.39	6.03	3.63
29	0.27	0.21	0.05	0.55	6.41	4.25
ST. 8						
1	0.71	0.53	0.20	1.52	6.76	2.70
6	0.42	0.38	0.11	0.33	12.4	3.64
11	0.15	0.08	0.06	0.55	5.47	1.35
29	0.15	0.11	0.05	0.29	7.45	2.29
41	0.21	0.10	0.07	0.87	4.94	1.59
51	0.29	0.25	0.07	0.32	6.67	3.70
55	0.28	0.25	0.06	0.25	6.44	4.31
ST. 22						
0	1.25	1.15	0.22	0.85	8.14	5.10
5	1.08	0.92	0.16	1.36	7.11	5.61
12	0.41	0.30	0.09	0.96	5.84	3.18
20	0.45	0.30	0.21	1.20	5.65	1.46
29	0.72	0.63	0.32	0.73	7.31	2.00
50	0.47	0.35	0.26	0.98	6.02	1.36
70	1.03	0.81	0.38	1.83	6.39	2.16
ST. 25						
0	0.43	0.23	0.15	1.60	6.77	1.53
10	0.26	0.19	0.21	0.61	6.83	0.88
29	0.24	0.21	0.22	0.29	7.68	0.98
50	0.27	0.23	0.24	0.40	7.33	0.92
70	0.28	0.17	0.20	0.92	6.63	0.89
ST. 34						
1	0.57	0.50	0.15	0.58	6.45	3.42
11	0.97	0.87	0.42	0.86	7.45	2.09
21	0.57	0.50	0.22	z0.65	7.76	2.27
30	0.57	0.45	0.20	0.99	6.81	2.23
34	0.26	0.19	0.08	0.58	5.90	2.20
41	0.82	0.71	0.26	0.92	7.34	2.73
51	0.56	0.44	0.30	1.00	6.83	1.47
61	0.46	0.36	0.25	0.83	7.34	1.44
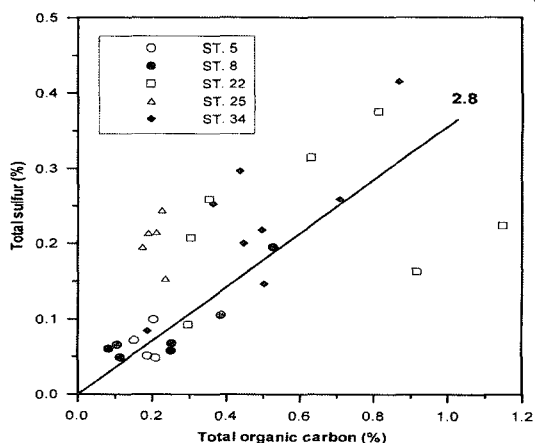
Fig. 3. Total sulfur content (%) vs. Total organic carbon (%). A line assuming relation of the normal oxic marine environments.

4.3. Heavy metal contamination and uncouplings with redox condition

The analytical results of the sediment from five stations are illustrated in Table 3. The inter-station metallic concentration is characterized by an increasing tendency toward the Shihwa-Banwol industrial complex (SBIC). Especially, surface sediments at ST. 22 and ST. 34 are clearly enhanced in heavy metals with high amplitude (Table 3). However, the sediment in the central area of Shihwa Lake (ST. 5 and ST. 8) do not show any significant variation in heavy metal concentration, which shows close values to average shale concentrations. Anthropogenic discharge from the Shihwa-Banwol complex is likely to be responsible for the increase in trace metals in some stations.

Table 3. Analytical results of the major and minor elemental concentration

Statoin	Depth**	Na*	Mg	Al	Fe	K	Ca	Ti	Li	V	Cr	Co	Ni	Cu	Zn	Zr	Mn	Sr	Ba	Mo	Cd	Pb
ST. 5	0	1.89	1.05	7.48	3.25	2.58	0.54	0.51	55.8	73	61	15	32	19	66	137	312	151	442	0.9	0.12	16.2
	10	1.66	0.84	6.58	2.70	2.56	0.93	0.43	40.9	56	50	11	22	11	50	140	314	182	513	0.4	0.16	14.6
	20	1.73	1.06	7.53	3.23	2.53	0.55	0.53	56.6	73	64	15	32	17	64	154	296	150	468	0.5	0.24	15.5
	29	1.67	0.74	6.26	2.47	2.55	0.96	0.45	31.9	50	48	10	21	14	50	165	337	193	542	0.6	0.21	18.2
ST. 8	0	1.85	1.05	8.39	4.14	2.60	0.52	0.46	54.6	86	73	16	40	39	108	115	434	139	510	1.5	0.19	23.9
	5	1.41	0.84	10.95	5.50	2.48	0.33	1.52	42.6	113	81	15	47	153	100	86	1076	105	558	1.0	0.34	54.1
	11	1.75	0.68	6.36	2.36	2.62	0.71	0.37	30.3	47	41	14	36	95	44	121	325	191	596	1.0	0.23	44.0
	29	1.81	0.70	5.99	2.33	2.71	0.74	0.34	31.3	43	38	13	34	54	43	81	311	197	578	1.5	0.28	39.4
	41	1.83	0.70	6.38	2.38	2.79	0.72	0.37	32.4	46	41	16	35	39	45	127	315	197	565	0.7	0.31	52.5
	45	1.50	0.55	5.18	1.91	2.28	0.58	0.29	22.8	36	33	16	48	85	34	91	261	157	453	1.7	0.21	38.8
ST. 22	0	1.77	1.08	7.57	3.41	2.67	0.56	0.48	56.4	74	108	14	40	102	150	151	297	150	466	2.3	0.26	33.9
	5	1.50	1.42	9.34	4.88	2.78	0.43	0.57	79.4	99	145	11	23	12	228	122	389	122	520	1.2	0.14	19.4
	12	1.78	0.85	6.75	2.72	2.61	0.67	0.44	43.0	58	58	10	19	10	78	118	328	171	509	0.2	0.14	15.6
	20	1.83	1.04	7.15	3.34	2.93	0.76	0.45	51.6	69	89	11	22	12	124	128	448	169	481	0.3	0.15	19.4
	29	1.97	1.21	7.58	3.82	2.72	0.58	0.49	63.3	79	107	12	22	13	175	114	508	150	479	0.5	0.16	17.1
	50	1.91	1.17	7.58	3.71	2.43	0.58	0.47	61.4	76	119	34	74	45	215	108	423	151	457	1.3	0.13	28.5
	70	1.66	1.19	8.19	4.55	2.67	0.47	0.51	74.1	92	176	22	66	179	268	128	499	128	474	1.4	0.53	76.6
ST. 25	0	1.79	0.86	6.51	2.77	2.54	1.30	0.45	39.3	56	46	12	26	15	52	138	350	191	511	0.7	0.16	23.6
	10	1.84	0.94	6.75	2.97	2.58	0.73	0.48	41.7	61	57	14	28	16	55	180	368	177	510	0.7	0.31	19.0
	29	1.85	0.88	6.59	2.76	2.74	0.70	0.45	39.1	56	50	13	26	14	51	137	332	177	498	0.6	0.20	19.0
	50	1.87	0.89	6.56	2.84	2.73	0.80	0.47	38.9	57	53	13	26	15	51	211	354	188	519	0.7	0.32	15.9
	70	1.64	0.75	6.34	2.60	2.76	0.69	0.41	34.0	51	46	13	25	14	47	158	335	182	552	0.6	0.24	16.1
ST. 34	0	1.74	1.12	7.52	3.65	2.56	0.60	0.50	56.5	75	138	21	91	398	415	176	446	154	453	3.4	1.06	34.1
	10	1.78	1.09	7.37	3.45	2.67	0.65	0.49	53.4	68	163	17	75	242	279	140	486	168	476	2.3	0.50	38.7
	20	1.70	1.22	8.07	3.91	2.75	0.61	0.51	63.0	84	84	20	45	46	98	149	557	153	453	0.7	0.30	49.9
	29	1.97	1.14	7.51	3.43	3.07	0.63	0.49	56.0	74	94	18	45	81	129	159	457	159	468	0.9	0.19	51.2
	40	1.83	1.09	7.91	3.61	2.62	0.59	0.49	56.9	75	99	18	48	105	157	142	417	154	511	1.2	0.43	41.4
	50	1.91	1.02	7.14	3.23	2.70	0.70	0.48	49.2	66	106	16	40	154	110	149	396	170	492	1.0	0.20	31.1
	60	1.87	0.99	6.98	3.03	2.70	0.68	0.46	46.3	63	78	15	35	66	99	159	453	177	498	0.6	0.13	23.3

*Elemental concentrations are expressed as % from Na to Ti, and other are ppm
** is expressed as cm

In this study, eight elements (V, Cr, Co, Ni, Cu, Zn, Zr and Pb) are subject to interpretation to evaluate the degree of lake sediment contamination. The concentration of these eight elements in each station clearly shows that heavy metals concentrations in sediment are generally higher near the surface than the deeper parts of sediment. When every value is compared to the average shale concentration as a reference[20], eight elemental concentrations display large fluctuations with respect to average shale values. The remarkable fluctuations are present for Cu, Zn and Mn in ST. 22 and ST. 34 (Table 3). On the whole, the metallic concentration is as much as one and a half to ten times greater than the average shale concentration.

The degree of metallic pollution, which may be used as a proxy for assessing the overall environmental deterioration is evaluated by using an enrichment factor (EF). Enrichment factors of these elements are calculated and drown using following formular.

$$\text{Enrichment Factor (EF)} = \frac{(\text{Metal/Al})_{\text{sediment}}}{(\text{Metal/Al})_{\text{background}}}[21]$$

High values of EF in Cu, Zn and Pb are recognized at ST. 34 and ST. 22, which are located near the SBIC. Especially, for Cu and Zn, the surface sediment of ST. 34 shows about nine and five times higher than average shale values, respectively. Therefore, it is believed that a relatively large amount of industrial effluent has probably been bought to these sites. These kind of vertical and inter-station variations in several heavy metal concentrations are important in evaluating the change in pollution.

It is well known that heavy metal pollution has a significant effect on benthic communities. A lack of biodiversity of benthic biota may reflect the effects of trace metal concentration because their occurrence is limited to a very restricted area or directly linked to the pollutant input[22,23]. Foraminiferal research at the same location clearly indicates that the number of

total benthic foraminifera/10 g (dry weight) sharply decreases at the two stations (ST. 22 and ST. 34), suggesting a possible anthroporogenic heavy metal contamination[24]. In addition, the results of the annual examination of the benthic community variation by Ahn et al.[1] support the possible influence of industrial effluent.

4.4. Spatiotemporal variations in redox condition

In the previous section, it was discussed briefly that the subsurficial sediment condition is very changeable based on the C/S ratio of organic matter.

Similarly, the redox condition is evaluated by the elemental concentration. Concentrations of Mn, Mo, and U, and their relationship are known to be indicators of the redox condition in the sediment column. Especially Mo can easily accumulate under anoxic conditions due to the sluggish ventilation of deep water[25,26]. Accordingly, the relationship and contents among these three elements can provide information on bottom sediment condition. At ST. 25, the correlation coefficients of Mo *vs.* Mn, U *vs.* Mn and U *vs.* Mo are 0.89, 0.76 and 0.65, respectively, suggesting a typical anoxic bottom environment (Table 4). However, ST. 34 and ST. 22, which are located

Table 4. Correlation coefficients of major and minor elements at station ST. 25 and ST. 34

ST. 25	Mg	Al	Fe	K	Ca	Ti	Li	V	Cr	Co	Ni	Cu	Zn	Zr	Mn	Sr	Ba	Mo	Cd	Pb	U
Na (%)	0.92	0.82	0.79	(0.24)	0.05	0.90	0.86	0.81	0.67	0.19	0.59	0.47	0.74	0.33	0.45	(0.05)	(0.87)	0.52	0.28	0.17	0.85
Mg (%)		0.97	0.96	(0.49)	0.05	0.98	0.98	0.98	0.82	0.40	0.86	0.74	0.94	0.32	0.70	(0.19)	(0.83)	0.64	0.36	0.26	0.91
Al (%)			0.96	(0.47)	(0.10)	0.92	0.95	0.98	0.87	0.57	0.94	0.75	0.95	0.26	0.70	(0.40)	(0.77)	0.52	0.40	0.21	0.88
Fe (%)				(0.54)	0.01	0.97	0.94	0.99	0.89	0.53	0.94	0.88	0.95	0.46	0.86	(0.18)	(0.65)	0.73	0.52	0.18	0.94
K (%)					(0.72)	(0.47)	(0.64)	(0.58)	(0.15)	0.14	(0.60)	(0.73)	(0.73)	0.18	(0.67)	(0.27)	0.40	(0.72)	0.21	(0.82)	(0.25)
Ca (%)						0.07	0.21	0.04	(0.44)	(0.78)	(0.07)	0.21	0.21	(0.34)	0.18	0.78	(0.22)	0.53	(0.59)	0.83	(0.18)
Ti (%)							0.94	0.96	0.84	0.40	0.83	0.80	0.90	0.49	0.79	0.06	(0.72)	0.75	0.49	0.17	0.96
Li (%)								0.97	0.72	0.30	0.87	0.76	0.98	0.17	0.71	(0.13)	(0.85)	0.67	0.21	0.45	0.83
V (ppm)									0.86	0.50	0.95	0.86	0.98	0.35	0.82	(0.22)	(0.72)	0.69	0.43	0.26	0.90
Cr (ppm)										0.82	0.85	0.72	0.73	0.64	0.73	(0.45)	(0.42)	0.46	0.79	(0.26)	0.94
Co (ppm)											0.65	0.42	0.37	0.48	0.43	(0.78)	(0.02)	0.00	0.76	(0.52)	0.58
Ni (ppm)												0.87	0.94	0.27	0.83	(0.39)	(0.56)	0.58	0.44	0.23	0.80
Cu (ppm)													0.86	0.48	0.99	0.05	(0.32)	0.87	0.50	0.25	0.75
Zn (ppm)														0.17	0.80	(0.16)	(0.75)	0.70	0.25	0.46	0.79
Zr (ppm)															0.58	0.12	0.17	0.51	0.93	(0.63)	0.67
Mn (ppm)																0.09	(0.24)	0.89	0.58	0.15	0.76
Sr (ppm)																	0.16	0.50	(0.24)	0.30	(0.18)
Ba (ppm)																		(0.31)	0.16	(0.52)	(0.57)
Mo (ppm)																			0.34	0.34	0.65
Cd (ppm)																				(0.71)	0.70
Pb (ppm)																					(0.11)

ST. 34	Mg	Al	Fe	K	Ca	Ti	Li	V	Cr	Co	Ni	Cu	Zn	Zr	Mn	Sr	Ba	Mo	Cd	Pb	U
Na (%)	(0.50)	(0.53)	(0.69)	0.63	0.50	(0.61)	(0.56)	(0.54)	(0.32)	(0.63)	(0.53)	(0.36)	(0.46)	(0.02)	(0.62)	0.44	0.47	(0.45)	(0.59)	(0.09)	0.32
Mg (%)		0.85	0.92	0.26	(0.72)	0.92	0.97	0.95	0.01	0.82	0.25	(0.03)	0.12	0.02	0.72	(0.83)	(0.73)	0.11	0.25	0.87	0.69
Al (%)			0.93	0.00	(0.85)	0.84	0.95	0.94	(0.11)	0.73	0.11	(0.15)	0.01	(0.22)	0.50	(0.90)	(0.31)	(0.00)	0.22	0.78	0.63
Fe (%)				(0.10)	(0.82)	0.96	0.98	0.95	0.13	0.89	0.38	0.14	0.27	(0.04)	0.58	(0.91)	(0.58)	0.27	0.46	0.72	0.65
K (%)					0.11	(0.10)	0.10	0.11	(0.38)	(0.13)	(0.45)	(0.53)	(0.49)	(0.00)	0.17	(0.00)	(0.19)	(0.51)	(0.57)	0.57	(0.18)
Ca (%)						(0.72)	(0.83)	(0.80)	(0.08)	(0.82)	(0.43)	(0.19)	(0.39)	(0.14)	(0.31)	0.91	0.33	(0.35)	(0.56)	(0.59)	0.27
Ti (%)							0.94	0.90	0.26	0.89	0.46	0.25	0.34	0.01	0.54	(0.88)	(0.70)	0.35	0.49	0.75	0.65
Li (%)								0.98	0.01	0.85	0.26	(0.01)	0.14	(0.05)	0.62	(0.92)	(0.59)	0.13	0.32	0.84	0.67
V (ppm)									(0.15)	0.85	0.16	(0.08)	0.06	0.04	0.60	(0.92)	(0.58)	0.04	0.27	0.80	0.77
Cr (ppm)										0.21	0.85	0.81	0.81	(0.04)	(0.06)	(0.03)	(0.25)	0.84	0.66	(0.07)	0.44
Co (ppm)											0.60	0.44	0.54	0.41	0.41	(0.90)	(0.74)	0.53	0.71	0.55	(0.53)
Ni (ppm)												0.93	0.98	0.37	0.07	(0.35)	(0.51)	0.98	0.93	(0.00)	0.24
Cu (ppm)													0.96	0.48	0.07	(0.22)	(0.16)	0.98	0.91	(0.27)	0.30
Zn (ppm)														0.47	(0.07)	(0.29)	(0.43)	0.99	0.95	(0.13)	0.32
Zr (ppm)															(0.10)	(0.14)	(0.48)	0.43	0.50	(0.22)	(0.03)
Mn (ppm)																0.29	(0.65)	(0.10)	(0.20)	0.51	(0.48)
Sr (ppm)																	0.46	(0.28)	(0.50)	(0.72)	0.57
Ba (ppm)																		(0.41)	(0.45)	(0.45)	0.49
Mo (ppm)																			0.95	(0.14)	0.30
Cd (ppm)																				0.05	0.10
Pb (ppm)																					(0.55)

( ) indicates minus value

near the Shihwa-Banwol industrial complex, do not show any strong correlation among these elements even though relatively high amounts of industrial effluents are expected to have been input at these sites. Instead, about four or five times of accumulation in Mo is recognized, and no clear relationship among the three elements (Table 4). Relatively shallow depths (4 meter water depth) at these sites are (ST. 22 and ST. 34) favorable to benthic mixing (e.g., bioturbation and/or circulation), therefore are probably maintaining suboxic bottom conditions. The correlation coefficients of Mn, Mo and U at ST. 22 and ST. 34 vary between 0.007 and 0.64, indicating partially oxic/suboxic conditions.

In the previous section, the enrichment factor of each station are discussed. Especially, ST. 34 and ST. 22 show a more strong contamination than ST. 25 in most elemental concentration. However, ST. 25 indicates a typical anoxic bottom condition. This implies that the redox condition is not related to the accumulation of heavy metals. Even though ST. 34 and ST. 22 have a relatively high concentration in heavy metal, they maintain stable bottom condition even though a partial anoxic signal is recognized. Probably this is caused by water circulation. The water depth of the two sites (ST. 22 and ST. 34) is shallower than other sites. More active water circulation at the two sites may prevent anoxic bottom conditions even though the two sites can be easily contaminated by effluent from SBIC. The relationships among these three elements coincide roughly with a sedimentary environment based on the C/S ratio with large fluctuation at the station. Sluggish ventilation due to the strong density stratification caused by repeated seawater and freshwater input is also one of the important reasons. Relatively shallow depth at these sites is favorable of surface circulation, probably maintaining oxic bottom condition.

The Cu/Mn ratio of the sediment is an indicator of the bottom condition. High accumulation and depletion of Cu and Mn in anoxic sedimentary environments of Shihwa Late has been reported previously[2]. In Fig. 4, the Cu/Mn ratios of the five cores are illustrated. ST. 34 and ST. 22 show large fluctuation in the Cu/Mn ratio compared to ST. 25 where there is almost no variation. If we accept the assumption of Jung et al.[2] large fluctuations in the Cu/Mn ratios at ST. 34 and ST. 22 demonstrate
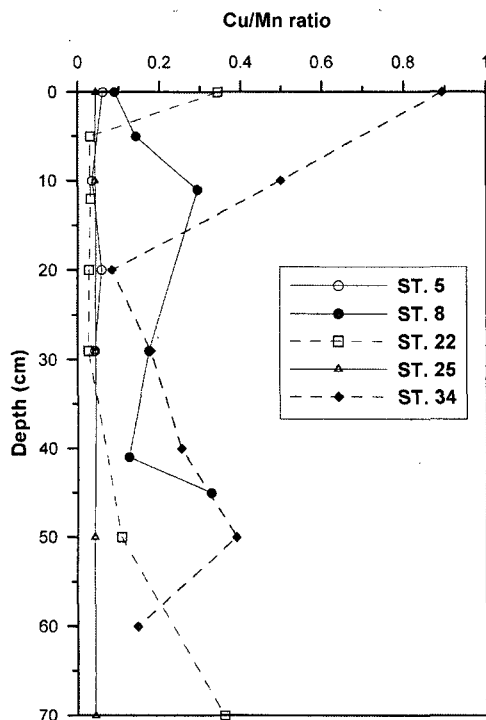

Fig. 4. Vertical variations of the Cu/Mn ratio. High Cu/Mn ratio at ST. 22, ST. 34, and some part of ST. 8 is thought to potential partial anoxic bottom conditions.

dramatic sedimentary environmental change due to the sediment supply or a change in the water column system. This also implies changeable redox conditions, and seems to indicate a switching of partial sub-anoxic condition. These two sites are characterized by an increase in the Mo concentration, probably as a consequence of the anoxic condition. Scarcity of benthic foraminifera and benthic organisms confirms an anoxic bottom environment in part. Oxygen depleted conditions results in the establishment of some azoic zone[6].

5. Conclusions

The concentrations of elements are dependent on the sediment characteristics, reflecting sedimentary environments. Especially, the amounts of the Ti/Al ratio with respect to Li concentration clearly indicates that some parts of the sediments were supplied artificially i.e, an allochothonous origin. The depositional environments clearly show a source-dependent variation. The concentrations of eight elements (V,

Cr, Co, Ni, Cu, Zn, Zr and Pb) are higher near the Shihwa-Banwol industrial complex (SBIC) than in the central part of Shihwa Lake. The concentrations of these elements in surficial sediment near the Shihwa-Banwol industrial complex are two to eight times higher than in the central part of Shihwa Lake. High values of the enrichment factor (EF) in Cu, Zn and Pb are recognized at ST. 34 and ST. 22, indicating a substantial anthropogenic enrichment of heavy metals. Especially, for Cu and Zn, the surface sediment of ST. 34 shows about nine and five times higher than average shale values. The bottom redox condition is divided into two categories; anoxic, and mixed oxic/suboxic based on the C/S ratio of organic matter and an elemental relationship. The concentration of Mn, Mo and U, and their correlation coefficients show a distinctive difference, and thus can be used as an indices of a redox condition. The relationship of these elements clearly suggests that an anoxic bottom condition is present at ST. 25. Controlling factors for bottom redox condition are thought to not be due to the elemental accumulation (degree of industrial effluent supply), but likely to be due to water depth, and circulation of surface water.

Acknowledgements

References

1) Ahn, I. Y., Y. C. Kang and J. W. Choi, 1995, The influence of industrial sffluents on intertidal benthic communities in Panwol, Kyeonggi Bay (Yellow Sea) on the west coast of Korea, Mar. Pollut. Bull., 30(3), 200-206.

2) Jung, H. S., C. B. Lee, Y. G. Cho and J. K. Kang, 1996, A mechanism for the enrichment of Cu and depletion of Mn in anoxic marine sediments, Banwol intertidal flat, Korea, Mar. Pollu. Bull., 32, 782-787.

3) KORDI, 1998, A study on environmental changes in Shihwa Lake, 230pp.

4) Choi, J. H., J. W. Kang, D. B. Hong and Y. A. Park, 2000, Distribution of organic carbon, organic nitrogen and heavy metals in Lake Shihwa sedi-

ments, J. Kor. Soc. Oceanog., 5, 276-284 (in Korean).

5) Hong, J. S., R. H. Jung, I. S. Seo, K. T. Yoon, B. M. Choi and J. W. Yoo, 1997, How are the spatio-temporal distribution patterns of benthic macrofaunal communities affected by the construction of Shihwa Dike in the west coast of Korea, J. Kor. Fish. Soc., 30, 882-895 (in Korean).

6) Lee, J. H. and C. H. Koh, 1999, Abundance of Polychaetes in Lake Shihwa, Korea, J. Kor. Soc. Oceanog., 34, 122-131.

7) Lee, C. B., Y. A. Park and C. H. Koh, 1985, Sedimentology and geochemical properties of intertidal surface sediments of the Panweol area in the southern part of Kyeonggi Bay, Korea, J. Ocean. Soc. Korea, 20, 20-29.

8) Goldberg, E. D. and G. O. S. Arrhenius, 1958, Chemistry of pelagic sediments, Geochim. Cosmochim. Acta, 13, 153-212.

9) Moorby, S. A., 1983, The geochemistry of transitional sediments recovered from the Galapagos hydrothemal mounds field during DSDP Leg 70-implication for mound formation, Earth. Planet. Sci. Lett., 62, 367-376.

10) Aloupi, M. and M. O. Angelidis, 2001, Normalization to lithium for the assessment of metal contamination in coastal sediment cores from the Aegean Sea, Greece. Mar. Environ. Res., 52, 1-12.

11) Stein, R., 1990, Organic carbon content/sedimentation rate relationship and its paleoenvironmental significance for marine sediments, Geo-Mar. Lett., 10, 37-44.

12) Stein, R., 1991, Accumulation of Organic Carbon in Marine Sediments, In: Lecture Notes in Earth Science, Springer, Berlin, 217pp.

13) Muller, P. J., 1997, C/N ratio in Pacific deep-sea sdiments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays, Geochim. Cosmochim. Acta, 41, 765-776.

14) Leventhal, J. S., 1983, An interpretation of carbon and sulfur relationship in Black Sea sediments as indicator of environments of deposition, Geochim. Cosmochim. Acta, 47, 133-137.

15) Berner, R. A., 1984, Sedimentary pyrite formation: An update, Geochim. Cosmochim. Acta, 48, 605-615.

16) Berner, R. A. and R, Raiswell, 1983, Burial of

organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory, Geochim. Cosmochim. Acta., 47, 855-862.

17) Raiswall, R. and R. Benner, 1986, Pyrite and organic matter in Phanerozoic normal marine shales, Geochim. Cosmochim. Acta, 50, 1967-1976.

18) Emerson, S. and M. Bender, 1982, Carbon fluxes at the sediment-water interface of the deep-sea: Calcium carbonate preservation, J. Mar. Res., 39, 139-162.

19) Berelson, W. M., D. E. Hammond and G. A. Cutter, 1990, In situ measurements of calcium carbonate dissolution rates in deep-sea sediments, Geochim. Cosmochim. Acta, 54, 3013-3020.

20) Forstner, U. and G. T. W. Wittman, 1981, *Metal pollution in the Aquatic Environment*, Springer Verlag, Berlin, 486pp.

21) Rubio, B., M. A. Nombela and F. Vilas, 2000, Geochemistry of major and tracer elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution, Mar. Pollut. Bull., 40, 968-980.

22) Reish, D. J., 1972, The use of marine inverte

brates as indicators of varying degrees of marine pollution, In M. Ruivo ed., Marine pollution and sea life, Fishing News Books, London, UK, 203-207pp.

23) Swartz, R. C., D. W. Schults, G. R. Ditsworth, W. A. DeBen and F. A. Cole, 1985, Sediment toxicity, contamination and macrobenthic communities near a large sewage outfall, In T. P. Boyle ed., Validation and predictability of laboratory methods for assessing the fate and effects of contaminants in aquatic ecosystems. ASTMSTP 865, American Society for testing and materials, Philadelphia, USA, 152-175pp.

24) Shin, I. C. and H. I. Yi, 1998, Spatial and temporal variations of foraminiferas as an indicator of marine pollution, Kor. J. Geoph. Res., 26, 59-73.

25) Bertine, K. K., 1972, The deposition of molybdenum in anoxic waters, Mar. Chem., 1, 43-53.

26) Calvert, S. E. and T. F. Pedersen, 1993, Geochemistry of recent oxic and anoxic marine sediments: implications for the geological record, Mar. Geol., 113, 67-88.