Master's Thesis

Fraction distribution and bioavailability of heavy metals in coastal sediments from industrial bays in the Southeastern Maritime Industrial Region of South Korea

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(Environmental Science and Engineering)

Ulsan National Institute of Science and Technology

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Sung-Deuk Choi

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Abstract

Gwangyang, Jinhae, Busan, and Ulsan Bay were designated as special management sea areas due to active industrial activities, and various pollutants, including heavy metals, were discharged, resulting in higher contamination of sediments than in other areas. Since heavy metals accumulated in sediments are released according to mobility and can have an adverse effect on the ecosystem depending on their mobility, various chemical forms should be considered to accurately evaluate their impact on the environment.

In this study, 67 sediments were collected from four regions and extracted by applying BCR sequential extraction. After that, 11 heavy metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) in sediments were analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES). Based on these results, the concentration and fraction distribution of heavy metals were investigated, characteristics of pollution patterns by region were identified, and ecological risk was evaluated using three indices such as individual contamination factor (ICF), risk assessment code (RAC), and modified potential ecological risk index (MRI).

Cd and Mn had the highest concentration in Jinhae and Gwang bay, respectively, and showed the tendency to increase the F1 fraction as the concentration increased. Cu and Pb had the highest concentration in Busan bay and shows the tendency to increase the F2 fraction as the concentration increased. Zn also had the highest concentration in Busan bay, and as the concentration increased, the non-residual fraction increased. Other heavy metals had a high proportion of F4 fractions. Also, characteristics of pollution patterns were influenced by regional characteristics and industrial complexes, and it could be confirmed in correlation analysis and PCA.

ICF showed that among the four regions, Cd had the highest ecological risk in Jinhae bay, Mn in Gwangyang bay, Cu and Zn in Busan bay, and Pb in Ulsan bay. Other heavy metals showed a low level of ecological risk in all regions. In RAC, among the 11 heavy metals, Cd and Mn showed higher mobility and bioavailability than other heavy metals. Especially in Jinhae bay, the ecological risk of Cd was the highest, and in other bays, Mn showed the highest ecological risk. In MRI, six sites (four sites in Jinhae bay and two sites in Busan bay) were evaluated as a moderate level of ecological risk, and Cd contributed the most to determining the MRI value in almost sites. It means Cd could adversely affect the aquatic environments in all regions. Therefore, it is needed to be careful of the ecological risk caused by Cd.

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I. INTRODUCTION

Heavy metal refers to metallic element which has high density and is toxic in low concentration (Pandey & Madhuri, 2014). Especially, Cd, Cr, Pb, and Hg are classified as toxic heavy metals because they were highly toxic and could have a fatal effect on the human body with only a small amount (Liang et al., 2019). As is classified chemically as a metalloid, however, it is frequently referred to as a metal and is included in toxic heavy metals because of its high toxicity. In addition, heavy metals have characteristics of toxicity, persistence, and bioaccumulation, so heavy metal pollution is a serious problem in the world (Varol, 2011; Zhang et al., 2014).

Figure 1. Type of toxic heavy metals.

In South Korea, industrial complexes are developed along the coast and large cities are distributed. Because of this feature, a large amount of heavy metals emitted by anthropogenic effects such as industrial activities flowed into the coast and accumulated in sediments (Song & Choi, 2017). To manage heavy metal pollution, the Korean government has divided the sea area into “special management sea areas” and “environment preservation sea areas” and established acceptance standards for heavy metal concentrations (Hwang et al., 2016).

However, the pollution level is still high, especially in special management sea areas (Cho et al., 2015; Jeong et al., 2020; Ra et al., 2011; Ra et al., 2014). The mean concentration of heavy metals in special management sea areas and environmental preservation sea areas from 2013 to 2017 are shown in Table 1 (MOF, 2019). TEL means the threshold effects level, which means the concentration that is predicted to have a little negative ecological impact. PEL means the portable effects level, which means the concentration that is very likely to have negative ecological effects. In the case of environment preservation sea areas, the concentration of all heavy metals did not exceed TEL. In the case of special management sea areas, on the other hand, the concentration of several heavy metals exceeded TEL, which means that negative ecological effects might occur. For this reason, attention and management of special management sea areas are continuously needed.

Table 1. Mean concentration of heavy metals in special management sea areas, environment preservation sea areas and sediment quality guideline values in Korea.

	Cu	Pb	Zn	Cd	Cr	Hg	As	Ni
				mg/kg				
Special management sea areas	21.7	44.7	70.9	0.38	70.5	0.09	11.9	28.7
Environment preservation sea areas	7.68	25.3	47.2	0.10	69.1	0.01	8.86	26.3
TEL	20.6	44.0	68.4	0.75	116	0.11	14.5	47.2
PEL	64.4	119	157	2.72	181	0.62	75.5	80.5

However, for a more accurate ecological risk assessment, it is needed to consider not only the total concentration but the mobility and bioavailability of heavy metals (Delshab et al., 2017). When heavy metals are released and deposited, they exist in a variety of chemical forms through physicochemical reactions (Eren et al., 2021) (Figure 2). The mobility and bioavailability of heavy metals are determined by these chemical forms, and if mobility and bioavailability are high, they can adversely affect the aquatic environment (Abdallah & Mohamed, 2019). Therefore, it is important to identify the mobility and bioavailability of heavy metals according to their chemical form.

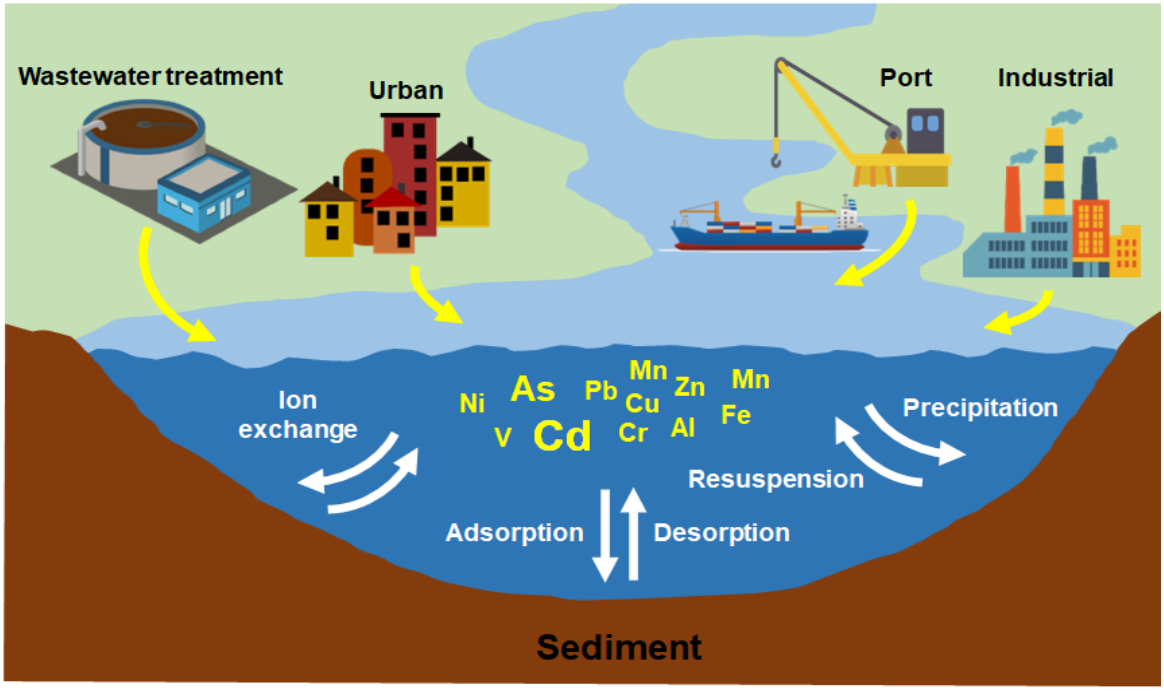

Figure 2. Various mechanisms of heavy metal accumulation.

Generally, the single extraction method is used to analyze the total content of heavy metals, and this information is used to evaluate the level of contamination in sediment. (Chung et al., 2017). However, the single extraction method doesn't consider the chemical forms, so there is a limit to providing important information such as mobility and bioavailability (Moore et al., 2015; Nelson, 2020). In the case of the sequential extraction method, on the other hand, we can get information on the mobility and bioavailability of heavy metals because heavy metals in sediment are extracted by several fractions which are related to chemical forms (Lu & Kang, 2018). In other words, the sequential extraction method is an essential method for accurate ecological risk assessment.

Studies on the sequential extraction of heavy metals in sediment are continuously being conducted around the world (Figure 3). Many studies point out that the information on the total concentration of heavy metals has limitations to understand the mobility and bioavailability of heavy metals and emphasize the sequential extraction method to compensate for this. For example, Nemati et al. (2011) reported the total metal content is not suitable for identifying the mobility and bioavailability of heavy metals, and the use of the sequential extraction method is the proper method for understanding the mobility and bioavailability of heavy metals. Also, most studies evaluate ecological risk by considering the concentration and mobility of heavy metals. Especially, Liu et al. (2018) reported that the ecological risk was evaluated higher when the total content and mobility of heavy metals were considered together. This result shows that the mobility of heavy metals is also an important factor in evaluating accurate ecological risk. In Korea, there have been several studies that analyzed heavy metals in sediments by applying a sequential extraction method. In detail, previous studies were conducted using sediment samples in Kumho River (Kim et al., 2009), Chengyang tungsten mine (Lee et al., 2011), Zn smelters (Kwon et al., 2017) ocean dumping site (Jung et al., 2019), Tawhwa River (Shin et al., 2021), Nakdong River (Son et al., 2021), and Seomjin River (Yang et al., 2021). However, there were no previous studies focusing on special management sea areas.

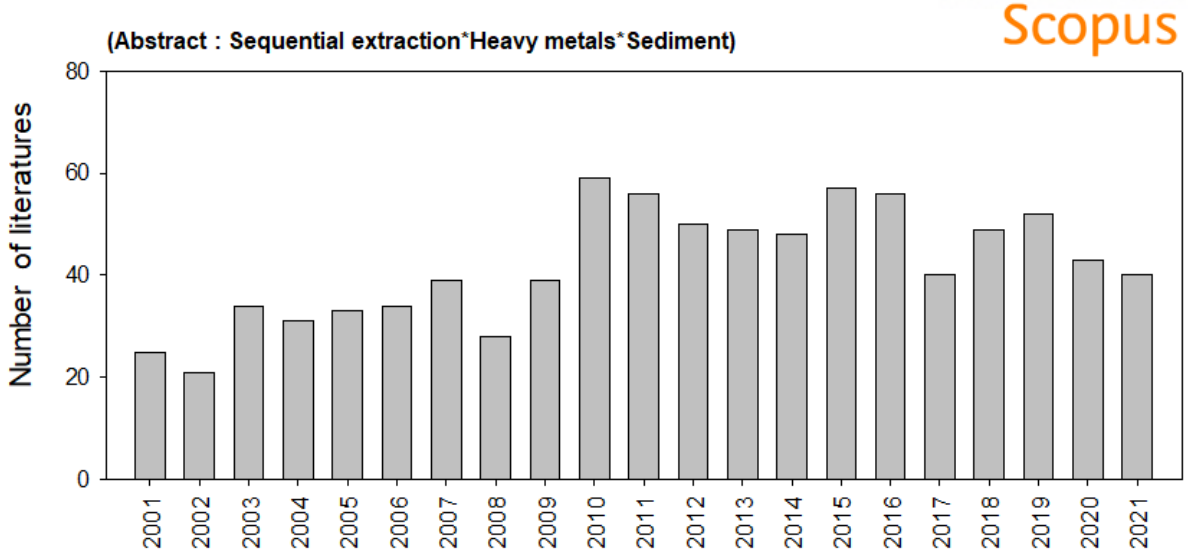

Figure 3. Number of literatures about the sequential extraction of heavy metals in sediment.

Therefore, in this study, we focused on the monitoring of heavy metals in sediment from Gwangyang, Jinhae, Busan, and Ulsan bay among the special management sea areas. The detailed objectives of this study were: (1) to investigate the concentration and fraction distribution of 11 heavy metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn); (2) to identify the characteristic of pollution patterns in four regions; (3) to evaluate ecological risk using three indices (ICF, RAC, and MRI).

II. MATERIALS AND METHODS

2.1 Study area and sampling sites

Gwangyang bay, Jinhae bay, Busan bay, and Ulsan bay are famous for their southeastern coastal industrial areas as various industrial complexes are distributed. First, Gwangyang Bay is famous for having the second-largest steel mill in Korea. Also, there are other industrial complexes, such as petrochemical industrial complexes and fertilizer manufacturing. Second, in Jinhae bay, shipbuilding and machinery manufacturing are mainly distributed, and there are ports for commercial trade. In addition, Masan bay, which has various industrial complexes and wastewater treatment plants, is included in Jinhae bay. Third, Busan bay has the largest port in Korea, which consists of North, South, and Gamcheon ports. Among these, North port is the largest and has frequent port activities. Major industries include machinery manufacturing, electric and electronics, and steel industries. Last, in Ulsan, there are various industrial complexes such as petrochemical, steel, shipbuilding, automobile, and non-ferrous metal industries.

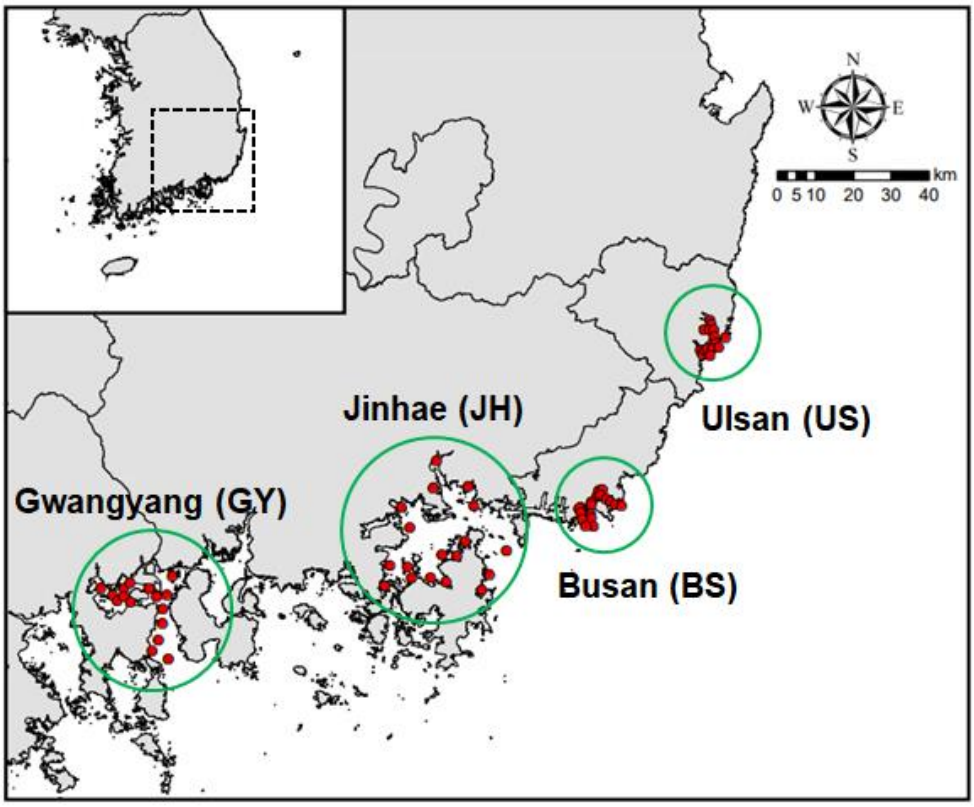

Figure 4. Sampling sites of four bays (Gwangyang, Jinhae, Busan and Ulsan).

Sediment sampling was performed at 16 sites in Gwangyang bay, 18 sites in Jinhae bay, 18 sites in Busan bay, and 15 sites in Ulsan bay. From these four bays, 67 sediment samples were collected using Van Veen grab samplers from March to April 2016. The collected samples were stored in a glass bottle at -20 ℃.

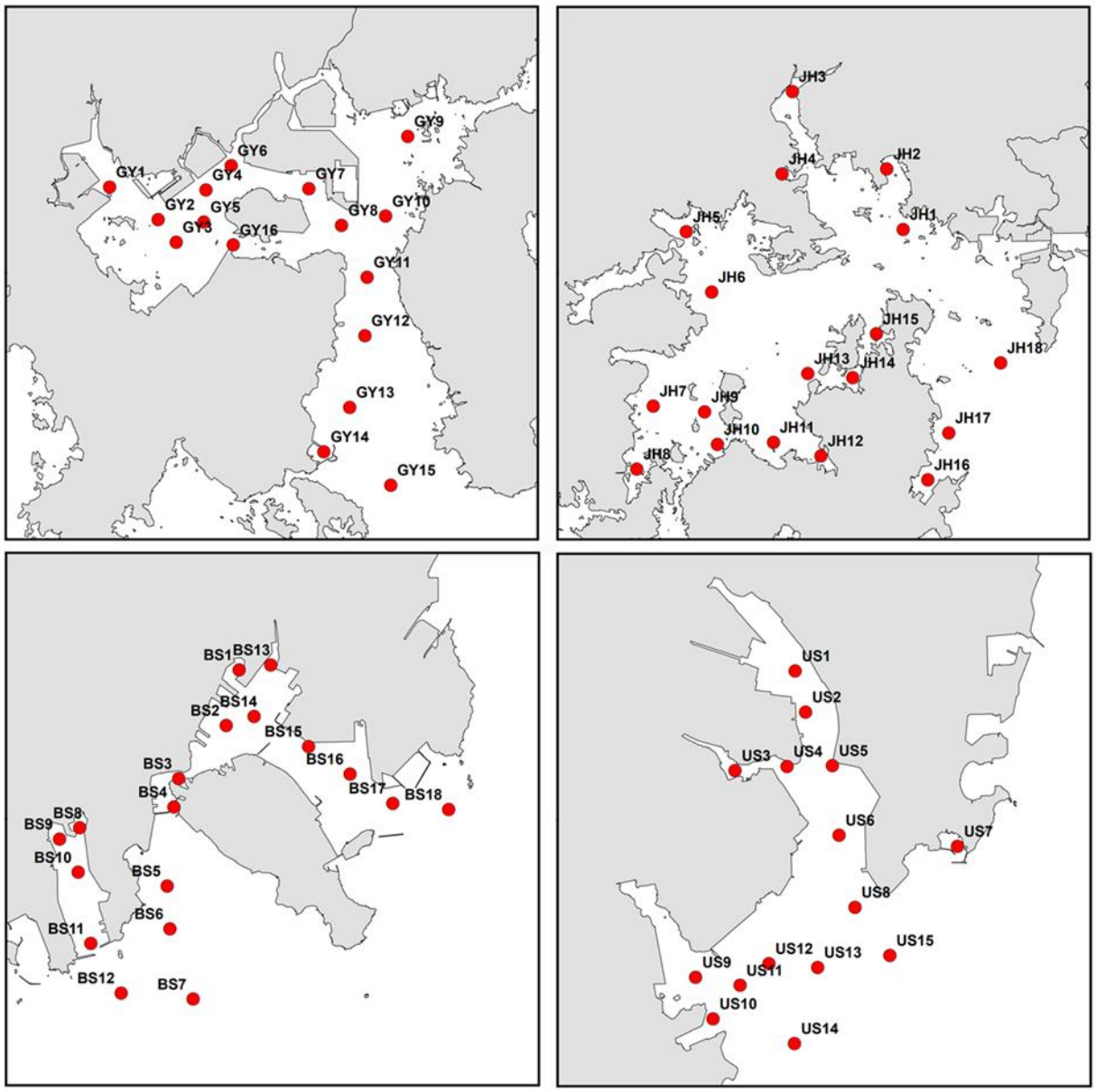

Figure 5. Sampling sites of each bay.

2.2 Sequential extraction

2.2.1 Chemical forms of heavy metals

The chemical forms of heavy metals are divided into four fractions: acid soluble, reducible, oxidizable, and residual fraction according to the binding form (Rauret et al., 1999; Usero et al., 1998) (Table 2). The mobility and bioavailability of heavy metals depend on the degree of binding to the sediment and increase from the residual to the acid soluble fraction (Sungur et al., 2015). Also, heavy metals derived from natural sources are strongly bonded to sediments, but heavy metals derived from anthropogenic sources are weakly bonded (Pempkowiak et al., 1999). For this reason, heavy metals emitted by anthropogenic factors mainly exist in non-residual fraction (acid soluble, reducible, and oxidizable), and heavy metals emitted by natural factors mainly exist in residual fraction (Passos et al., 2010).

Table 2. Chemical forms classification of heavy metals.

Fraction	Binding form	Mobility and bioavailability
F1, Acid soluble	Bound to exchangeable ions and carbonates	F1 > F2 > F3 > F4
F2, Reducible	Bound to iron-manganese oxides	
F3, Oxidizable	Bound to Sulfides/organics	
F4. Residual	Metals bound in lithogenic minerals	

2.2.2 Experimental procedure

The overall experimental procedure is shown in Figure 6. In order to understand the fraction of 11 heavy metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn), BCR sequential extraction devised by the Community Bureau of Reference was applied with some modification (Rauret et al., 1999). The order of the experiment is as follows:

(1) Step 1 (Fraction 1, Acid soluble)

Add 1 g of sediment sample and 40 mL of 0.11 M acetic acid to a 50 mL conical tube and extract by shaking at room temperature for 8 hours. The extract was applied to centrifugation at 3000 rpm for 20 minutes, and then the supernatant was separated. The residue sample was washed using 20 mL of distilled water, shaking it for 15 minutes, and applying centrifugation at 3000 rpm for 20 minutes. After that, discard the supernatant and use the residue sample for the next step.

(2) Step 2 (Fraction 2, Reducible)

Add 40 mL of 0.5 M hydroxylamine hydrochloride (pH 1.5) to the residue from step 1, and extract by shaking at 25 ℃ for 8 hours. The extract was applied to centrifugation at 3000 rpm for 20 minutes, and then the supernatant was separated. The residue sample was washed using 20 mL of distilled water, shaking it for 15 minutes, and applying centrifugation at 3000 rpm for 20 minutes. After that, discard the supernatant and use the residue sample for the next step.

(3) Step 3 (Fraction 3, Oxidizable)

Add 10 mL of 8.8 M hydrogen peroxide to the residue from step 2, and digest at 25 ℃ for 1 hour. After that, it is heated at 85 ℃ for 1 hour, and then further heated to reduce the volume below 3 mL. After adding 8.8 M hydrogen peroxide again, it is heated at 85 ℃ for 1 hour. After cooling, add 50 mL of 1 M ammonium acetate (pH 2.0) and extract by shaking at room temperature for 8 hours. The extract was applied to centrifugation at 3000 rpm for 20 minutes, and then the supernatant was separated. The residue sample was washed using 20 mL of distilled water, shaking it for 15 minutes, and applying centrifugation at 3000 rpm for 20 minutes. After that, discard the supernatant and use the residue sample for the next step.

(4) Step 4 (Fraction 4, Residual)

Add 16 mL of aqua regia to residue from step 3, and digest at room temperature for 8 hours. After that, it was extracted by heated at 130 ℃ for 2 hours and diluted to 30 mL with 1% nitric acid. The extract was applied to centrifugation at 3000 rpm for 20 minutes, and then the supernatant was separated.

Heavy metals in all extraction samples were analyzed by ICP-OES (Figure 7). Instrumental conditions for heavy metal analysis are summarized in Table 3.

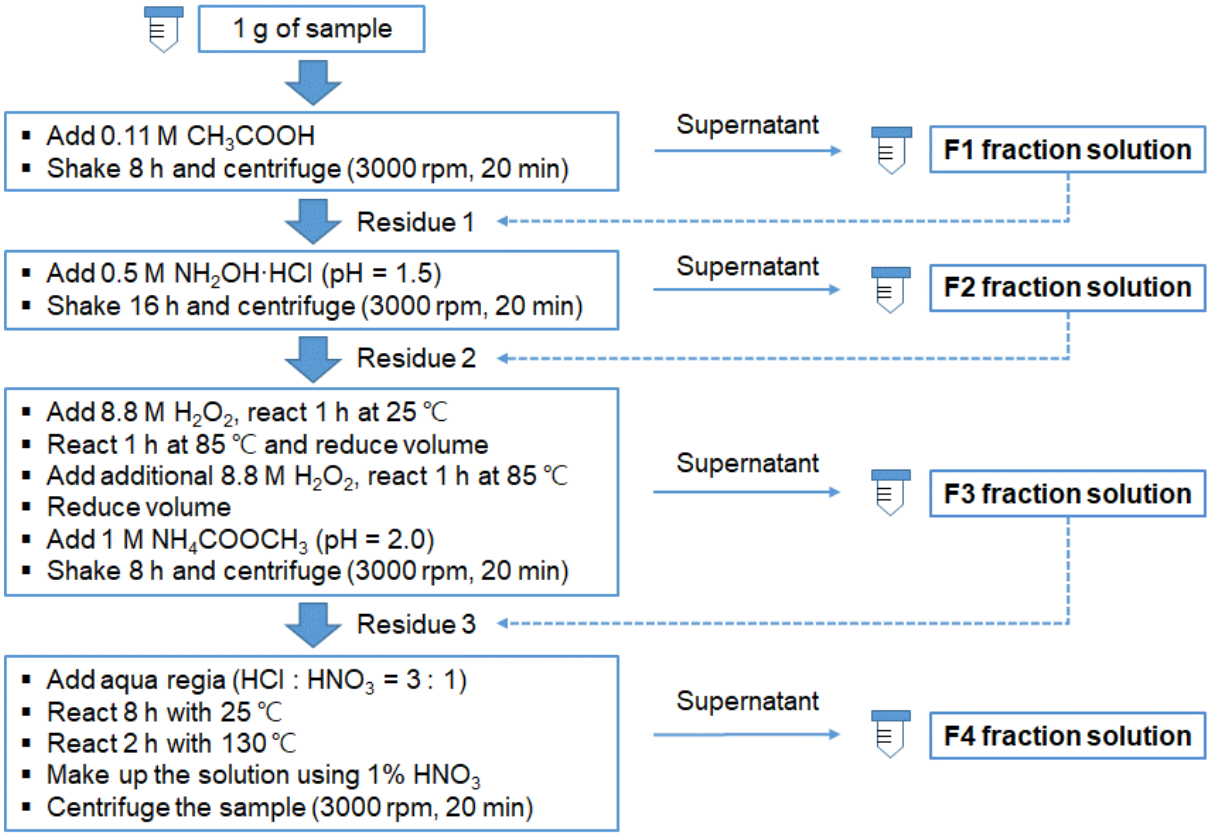

Figure 6. Sequential extraction of heavy metals in sediment.

Table 3. Instrumental conditions for analysis of heavy metals.

Components	Set value
RF power	1200 W
Plasma gas flow rate	15 L/min
Nebulizer gas flow rate	0.7 L/min
Auxiliary gas flow rate	1.5 L/min
Sample uptake delay	20 s
Integration time	0.5 s
Read time	5 s

Figure 7. Analytical instrument (ICP-OES, Varian 720-ES, USA).

2.3 Quality assurance and quality control (QA/QC)

The certified reference material (BCR-701) was analyzed to evaluate the accuracy of sequential extraction at each step. The result of recovery for each step is summarized in Table 4. As a result, compliance results were confirmed as 86 ~ 103% in step 1, 93 ~ 104% in step 2, 94 ~ 103% in step 3, and 81 ~ 133% in step 4.

Table 4. Result of recovery using certified reference material, BCR-701 (n = 7) (mean ± standard deviation in mg/kg)

Fractions	Metals	Certified	Determined	Recovery (%)
Acid soluble (F1)	Cd	7.3 ± 0.4	7.49 ± 0.34	103
	Cr	2.26 ± 0.16	2.12 ± 0.14	94
	Cu	49.3 ± 1.7	49.3 ± 1.69	100
	Ni	15.4 ± 0.9	13.2 ± 0.47	86
	Pb	3.18 ± 0.21	2.75 ± 0.25	86
	Zn	205 ± 6	210 ± 4.20	102
Reducible (F2)	Cd	3.77 ± 0.28	3.91 ± 0.22	104
	Cr	45.7 ± 2.0	44.7 ± 2.12	98
	Cu	124 ± 3	132 ± 7.04	106
	Ni	26.6 ± 1.3	24.9 ± 1.23	93
	Pb	126 ± 3	129 ± 5.13	102
	Zn	114 ± 5	113 ± 1.55	99
Oxidizable (F3)	Cd	0.27 ± 0.06	0.28 ± 0.06	103
	Cr	143 ± 7	142 ± 6.44	100
	Cu	55 ± 4	57.1 ± 2.52	104
	Ni	15.3 ± 0.9	15.2 ± 1.27	99
	Pb	9.3 ± 2.0	8.77 ± 1.64	94
	Zn	46 ± 4	44.5 ± 4.96	97
Residual* (F4)	Cd	0.13 ± 0.08	0.17 ± 0.02	133
	Cr	63 ± 8	56.0 ± 2.18	89
	Cu	39 ± 12	38.6 ± 1.65	99
	Ni	41 ± 4	34.0 ± 1.52	83
	Pb	11 ± 6	8.96 ± 0.35	81
	Zn	95 ± 13	104 ± 4.88	109

*F4 is indicate value.

For internal checks on the sequential extraction, the BCR-701 and the actual sediment sample used in this study were used. The total concentration of heavy metals was analyzed after extraction by applying the same method of extracting step 4. The recovery was calculated by dividing the sum of concentration in four steps (acid soluble + reducible + oxidizable + residual) by the total concentration. In the results using BCR-701, the recovery was 98 to 117% (Table 5). In the results using the actual sediment sample, the recovery rate was 86 to 122% (Table 6). These two results imply that the sum of concentration in four fractions corresponds well to the total concentration of heavy metals.

Table 5. Comparison of result of BCR sequential extraction and total heavy metal extraction using BCR-701 (n = 4).

Metals	F1+F2+F3+F4 (mg/kg)	Total concentration (mg/kg)	Recovery (%)
Cd	11.4	10.1	112
Cr	240	242	99
Cu	267	272	98
Ni	85.1	79.8	107
Pb	146	122	117
Zn	461	470	98

Table 6. Comparison of result of BCR sequential extraction and total heavy metal extraction using actual sediment sample (n = 8).

Metals	F1+F2+F3+F4 (mg/kg)	Total concentration (mg/kg)	Recovery (%)
Al	39062	45360	86
AS	10.6	10.8	98
Cd	0.54	0.49	109
Cr	36.9	35.2	105
Cu	98.1	96.6	102
Fe	36761	41501	89
Mn	538	569	94
Ni	17.9	16.8	107
Pb	40.2	33.1	122
V	45.2	42.8	106
Zn	203	209	97

Method detection limits (MDLs) were calculated by multiplying the standard deviation of seven replicates by 3.14. The MDLs for heavy metals for each fraction are summarized in Table 7. Compared to MDLs, the lower concentration of heavy metals was treated as 0.

Table 7. The value of MDLs of heavy metals for each fraction.

	MDL (mg/kg)										
Fractions	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
F1	0.005	0.021	0.003	0.003	0.004	0.005	0.003	0.006	0.008	0.004	0.003
F2	0.007	0.023	0.004	0.005	0.006	0.006	0.004	0.011	0.020	0.005	0.004
F3	0.025	0.026	0.007	0.005	0.005	0.015	0.004	0.008	0.008	0.005	0.004
F4	0.008	0.027	0.005	0.006	0.008	0.006	0.006	0.009	0.016	0.006	0.005

2.4 Individual contamination factor (ICF)

The individual contamination factor (ICF) is used to assess the degree of risk to the environment by considering the retention time of heavy metal in sediment (Ikem et al., 2003; Saleem et al., 2015). A high ICF value means that the retention time is short, so heavy metal is easily extracted from sediment and has a high potential ecological risk to the environment (Nemati et al., 2011). The ICF is calculated by dividing the sum of concentration in non-residual fraction (F1+F2+F3) by the concentration of residual fraction (F4). The equation of ICF is as follows:

$$ICF = \frac{F1+F2+F3}{F4} \quad (1)$$

The classification of ICF is summarized is summarized in Table 8.

Table 8. Classification of ICF.

ICF	Degree of risk
< 1	Low
1 ~ 3	Moderate
3 ~ 6	Considerable
> 6	High

2.5 Risk assessment code (RAC)

This indice is used to assess ecological risk by considering the mobility and bioavailability of heavy metals (Bastami et al., 2018). The bonding strength between heavy metals and sediments is different for each fraction, and the weaker the bonding strength, the higher the mobility and bioavailability (Jain, 2004). Especially, heavy metals existed in the F1 fraction are most weakly combined with sediments, so they are easily extracted and have high mobility and bioavailability (Sundaray et al., 2011). RAC is an indice that evaluates ecological risk by considering the ratio of the F1 fraction, and the equation is as follows:

$$RAC = \frac{F1}{F1+F2+F3+F4} \times 100 \quad (2)$$

The classification of ICF is summarized is summarized in Table 9.

Table 9. Classification of RAC.

RAC	Ecological risk
< 1	No risk
1 ~ 10	Low risk
11 ~ 30	Medium risk
31 ~ 50	High risk
> 50	Very high risk

2.6 Modified potential ecological risk index (MRI)

The ecological risk of heavy metals is determined by not only the total concentration of heavy metals but also their mobility and bioavailability. (Liu et al., 2018; Zhu et al., 2012). MRI is used to evaluate ecological risk by considering both the concentration and mobility of heavy metals and bioavailability (Jung et al., 2019). The equation is as follows:

$$MRI = \sum_{i=1}^{m} T_r^i \times \frac{\Omega \times C_d^i}{C_r^i} \quad (3)$$

where T_r^i is the toxic-response factor, Ω is the modified index of heavy metal concentration, C_d^i is the total concentration of heavy metals in sediments, and C_r^i is the background concentration of heavy metals in sediments. Ω is calculated by Aδ+B, where A is the percentage of F1 fraction, B is 1-A, and δ is the toxic index according to the RAC. In the case of T_r^i, since only As, Cd, Cr, Cu, Ni, Pb, and Zn have values, MRI was calculated in consideration of only seven heavy metals in this study. The information on its components and the classification of MRI are summarized in Table 10-12.

Table 10. The value of toxic-response factor and background concentration (mg/kg).

Components	Metals							Reference
	As	Cd	Cr	Cu	Ni	Pb	Zn	
Toxic-response factor (T_r^i)	10	30	2	5	5	5	1	(Hakanson, 1980)
Background concentration (C_r^i)	13	0.3	90	45	68	20	95	(Turekian & Wedepohl, 1961)

Table 11. The value of modified index of heavy metal concentration.

Standard	δ
RAC $\leq$ 10	1.0
10 < RAC $\leq$ 30	1.2
30 < RAC $\leq$ 50	1.4
RAC > 50	1.6

Table 12. Classification of MRI.

MRI	Ecological risk
< 150	Low
150 ~ 300	Moderate
300 ~ 600	Considerable
> 600	High

2.7 Statistical analysis

In this study, SigmaPlot 12.0 (Systat Software, USA) was used to conduct the Mann-Whitney rank sum test to confirm the statistical difference. SPSS 20.0 (IBM, USA) was used to understand the relationship between heavy metals using spearman correlation analysis. Also, the principal component analysis (PCA) was carried out to confirm the pollution patterns of heavy metals in sediment from four regions. In detail, it was performed based on the varimax rotational method, and the two principal components with eigenvalues greater than one were used.

III. RESULTS AND DISCUSSION

3.1 Concentration and fraction of heavy metals in sediment

3.1.1 Cadmium (Cd)

Figure 8 and S1 show the concentrations and fractions of Cd in four regions. In this study, the total concentrations of heavy metals are calculated by summing the concentrations in the four fractions. The range of total concentrations was 0.12 to 0.33 mg/kg in Gwangyang bay, 0.18 to 1.30 mg/kg in Jinhae bay, 0.14 to 1.33 mg/kg in Busan bay, and 0.14 to 0.80 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (0.60 mg/kg) > Ulsan bay (0.39 mg/kg) > Busan bay (0.33 mg/kg) > Gwangyang bay (0.19 mg/kg). There were statistical differences between Gwangyang bay and the other three regions (rank sum test: $p < 0.01$), and there were also statistical differences between Jinhae and Busan bay (rank sum test: $p < 0.05$).

Among the four regions, the concentration was highest in BS13 (1.33 mg/kg), followed by JH2 (1.30 mg/kg) and JH3 (1.29 mg/kg). BS13 is the site adjacent to Dong Stream, which is seriously contaminated by the inflow of domestic and industrial wastewater. JH2 is located near a wastewater treatment plant (WWTP), and JH3 is the site close to the river flowing through the industrial complexes. Also, these sites are located near the port, so the contamination of Cd seemed to be high due to activities related to the port and wastewater.

Cd showed a tendency to increase the F1 fraction as the concentration increased. In fact, anthropogenic Cd tends to combine with carbonate minerals because the ionic radius of Cd is similar to Ca forming the carbonate, resulting in co-precipitation (Ji et al., 2019). For this reason, the high F1 fraction of Cd means that there was an influence of anthropogenic sources and that mobility and bioavailability are high, which can affect the aquatic environment.

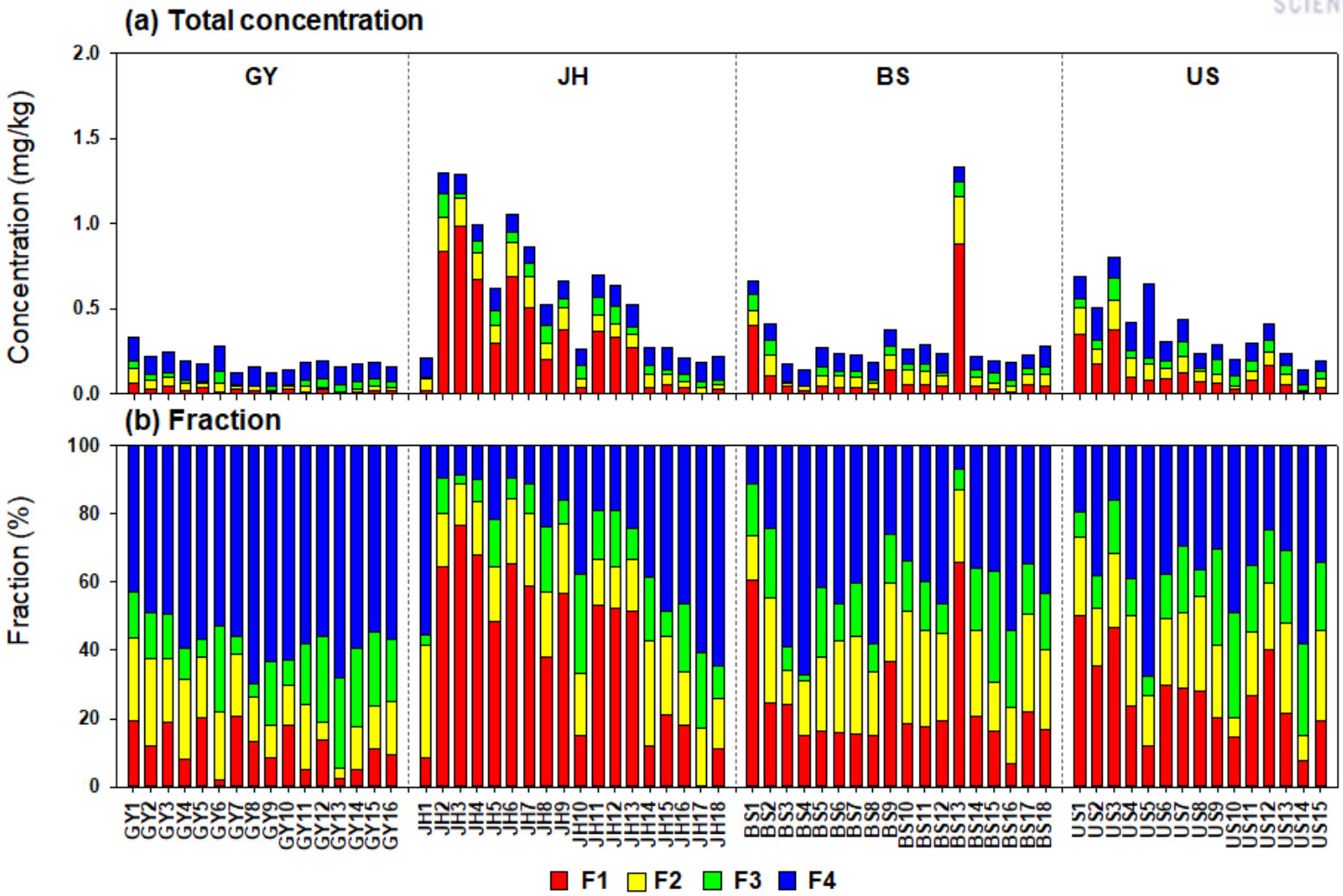

Figure 8. (a) Total concentration and (b) fraction of Cd in four regions.

3.1.2 Manganese (Mn)

Figure 9 and S2 show the concentrations and fractions of Mn in four regions. The range of total concentrations was 419 to 1293 mg/kg in Gwangyang bay, 432 to 921 mg/kg in Jinhae bay, 251 to 654 mg/kg in Busan bay, and 228 to 569 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Gwangyang bay (751 mg/kg) > Jinhae bay (579 mg/kg) > Busan bay (425 mg/kg) > Ulsan bay (389 mg/kg). There were statistical differences in all regions (rank sum test: $p < 0.05$).

Overall, the concentration of Mn was high in Gwangyang bay, and among them, high levels of Mn were observed in GY6 (1234 mg/kg) and GY7 (1293 mg/kg). These two sites had something in common they were located near the steel mill. When iron is smelted in a steel mill to make steel products, Mn is used to increase strength and prevent corrosion (Jeong et al., 2009). For this reason, Mn is widely used in steel mills, so it seemed that the contamination of Mn is high due to this influence.

Mn showed the tendency to increase the F1 fraction as the concentration increased, which is similar to the tendency of Cd. Indeed, anthropogenic Mn exists in a state combined with carbonate because it has a strong affinity with carbonate (Qiao et al., 2013). Therefore, Mn has high mobility and bioavailability, which can be released from sediment, affecting the environment. Among the four regions, Gwangyang bay had the highest proportion of F1 fractions, which means that Gwangyang bay has a large amount of Mn emitted by anthropogenic influence compared to other regions.

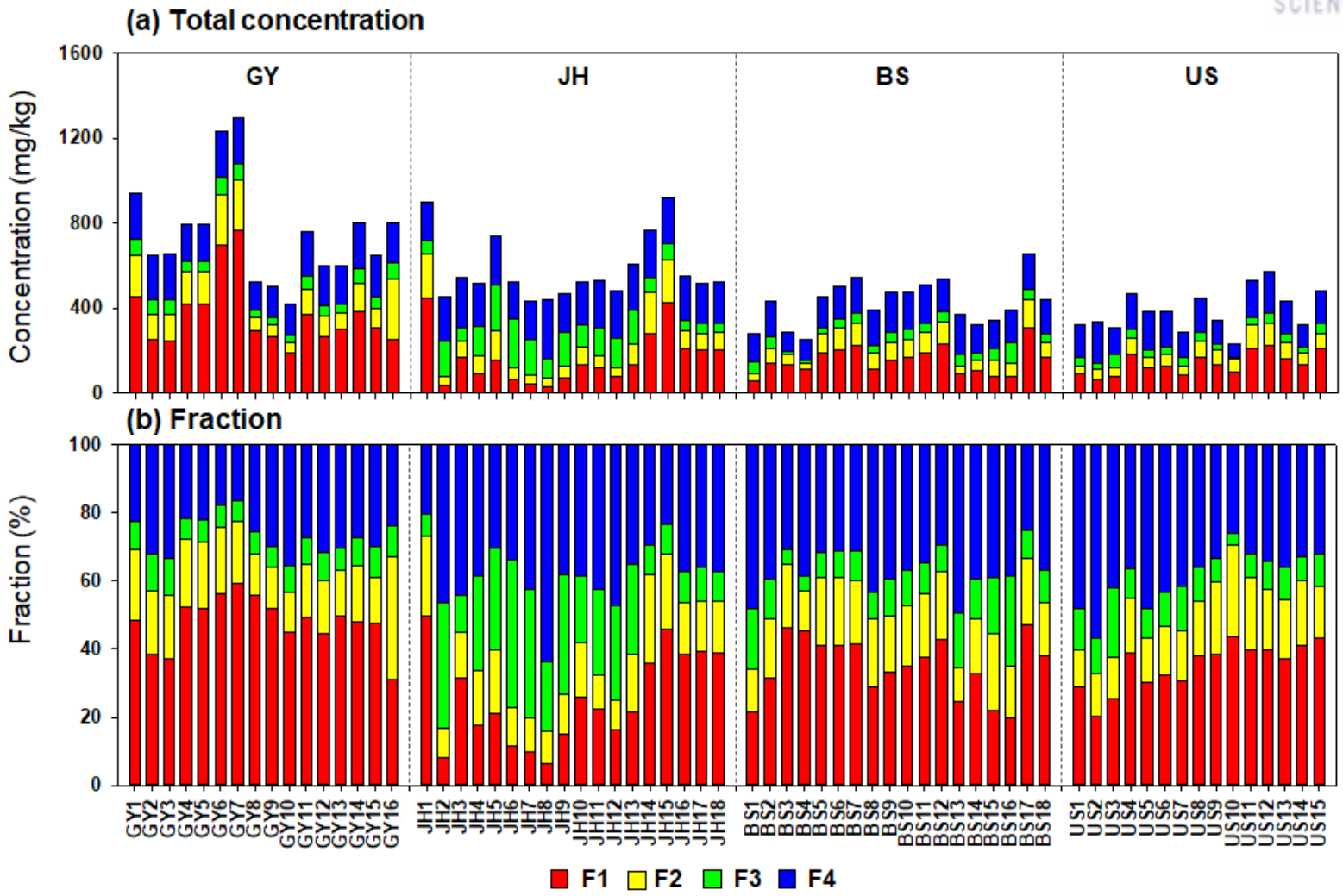

Figure 9. (a) Total concentration and (b) fraction of Mn in four regions.

3.1.3 Zinc (Zn)

Figure 10 and S3 show the concentrations and fractions of Zn in four regions. The range of total concentrations was 52.9 to 136 mg/kg in Gwangyang bay, 103 to 374 mg/kg in Jinhae bay, 62.7 to 533 mg/kg in Busan bay, and 65 to 234 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Busan bay (186 mg/kg) > Jinhae bay (157 mg/kg) > Ulsan bay (155 mg/kg) > Gwangyang bay (95.7 mg/kg). There were no statistical differences in the four regions (rank sum test: $p > 0.05$), except for Gwangyang bay (rank sum test: $p < 0.01$).

The highest concentration of Zn was founded at BS13 (533 mg/kg), which is located near the North port, the largest port in Busan. BS1 (399 mg/kg) and JH3 (374 mg/kg), BS9 (333 mg/kg) also showed high levels of Zn compared to other sites. BS1 is located near the North port like BS13, BS9 is located near Gamcheon port, and JH3 is located near Masan port. In short, these four sites with high concentrations of Zn are commonly adjacent to the port. In general, there are many ships in ports, and the paint used to prevent the corrosion of ships contains Zn (Perumal et al., 2021). Considering this, the paint leaked from the ship during transportation activities might be the main source of contamination for Zn.

Zn showed the tendency to increase non-residual fraction as the concentration increased. Anthropogenic Zn has a strong affinity with non-residual fractions, and this pattern was similar to previous studies (Caplat et al., 2005; Sakan et al., 2016). In particular, in BS1, BS9, BS13, and JH3, which were high concentration sites, the ratio of the F1 fraction was high among non-residual fractions. In the case of B13, which had the highest concentration, the ratio of the F1 fraction was 52%, which was also the highest among all sites. This indicates that the mobility and bioavailability of Zn in these sites were high because Zn is weakly bonded to the sediments than in other sites.

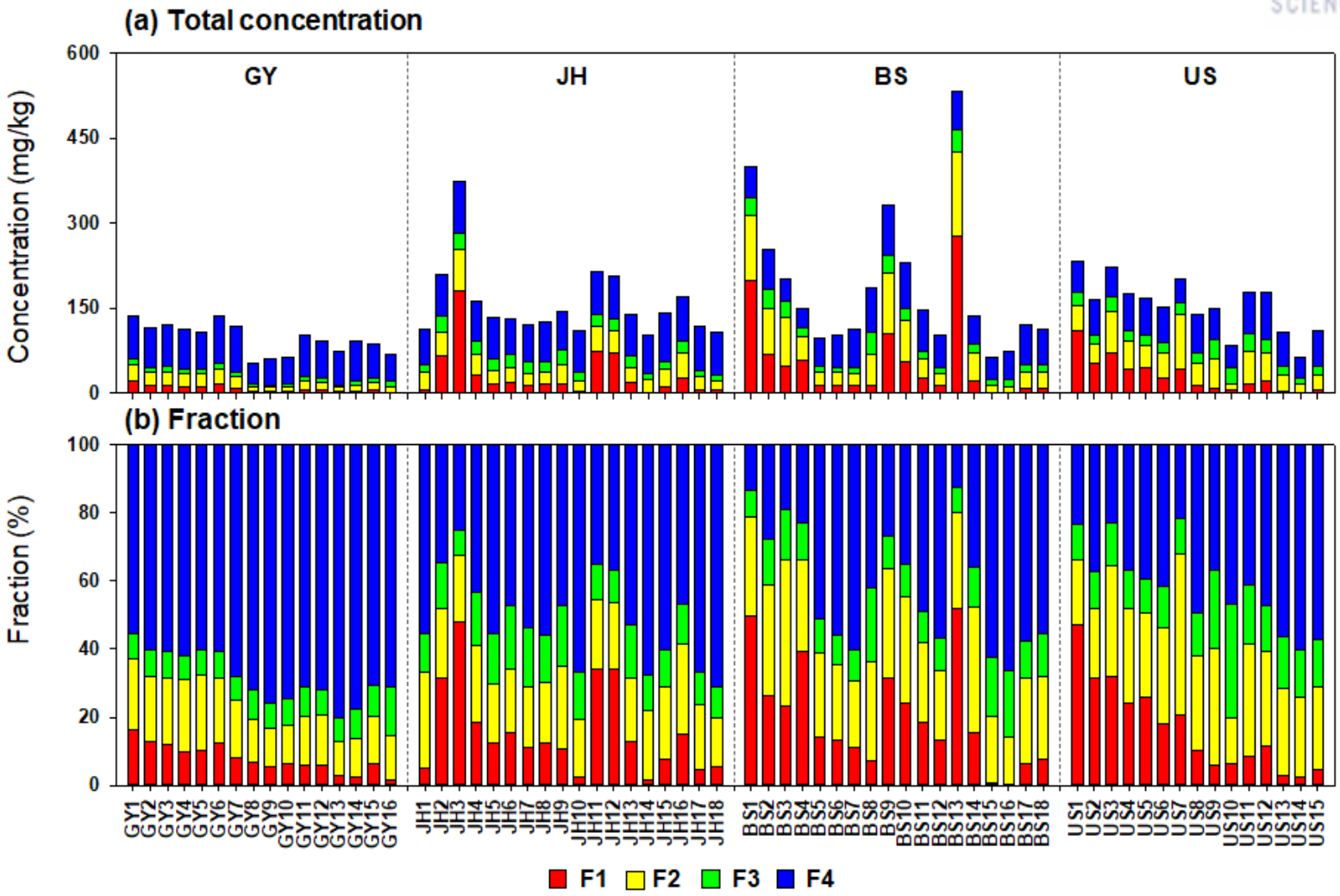

Figure 10. (a) Total concentration and (b) fraction of Zn in four regions.

3.1.4 Copper (Cu)

Figure 11 and S4 show the concentrations and fractions of Cu in four regions. The range of total concentrations was 8.21 to 27.9 mg/kg in Gwangyang bay, 17.5 to 103 mg/kg in Jinhae bay, 12.0 to 416 mg/kg in Busan bay, and 17.0 to 142 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Busan bay (118 mg/kg) > Ulsan bay (60.6 mg/kg) > Jinhae bay (42.9 mg/kg) > Gwangyang bay (15.8 mg/kg). There were no statistical differences in the four regions (rank sum test: $p > 0.05$), except for Gwangyang bay (rank sum test: $p < 0.01$).

Most of the sites with high levels of Cu were found in Busan bay. Among the sampling sites in Busan bay, higher concentrations of Cu were observed in BS1 (320 mg/kg), BS2 (216 mg/kg), BS3 (416 mg/kg), and BS4 (291 mg/kg) compared to other sites, and in particular, BS3 had the highest level among all regions. These sites are located adjacent to the North and South port, where many ships are present. In Ulsan bay, the concentration of Cu was the highest in US7 (142 mg/kg), which is a fishing area with many fishing boats. Antifouling paint is used to prevent organisms from attaching to and growing on the bottom of ships and fishing boats, and this paint contains a lot of Cu (Jeong et al., 2020). For this reason, paint leaked from ships and fishing boats might be the main emission source.

Cu showed the tendency to increase the F2 fraction as the concentration increased. Anthropogenic Cu tends to bond easily to the Fe-Mn oxides which have large adsorption surface areas and form complexes (Yang et al., 2014). Especially BS3, where the highest concentration was observed, the proportion of the F2 fraction accounted for 57%. Unlike other regions, in Jinhae bay, the proportion of the F3 fraction was more dominant than that of the F2 fraction at high concentration levels. This might be explained by the fact that Jinhae bay has a high content of organic matter than other regions (Kang et al., 1993). F2 fraction can be extracted under reducing conditions and F3 under oxidizing conditions, so caution is required.

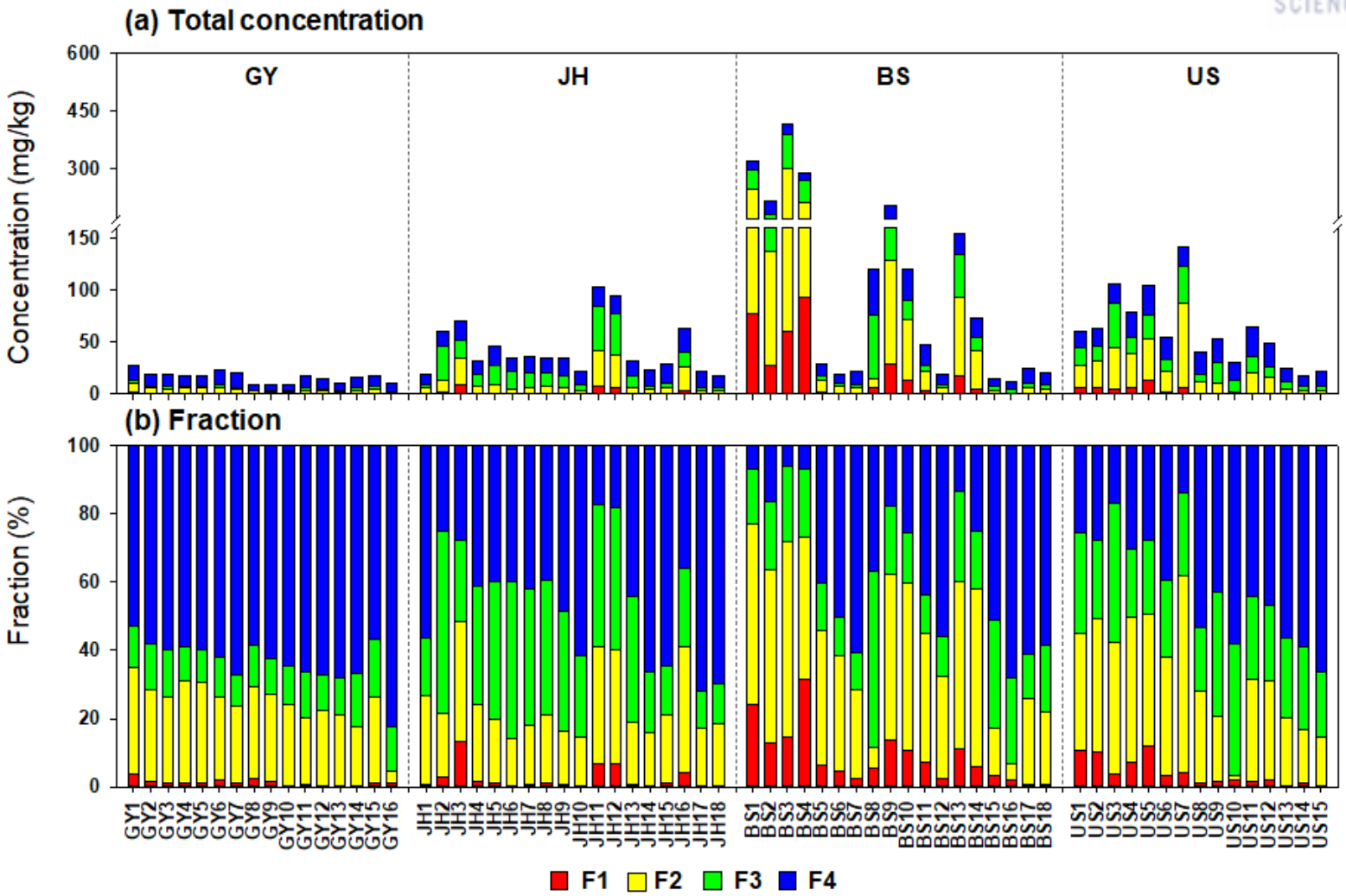

Figure 11. (a) Total concentration and (b) fraction of Cu in four regions.

3.1.5 Lead (Pb)

Figure 12 and S5 show the concentrations and fractions of Pb in four regions. The range of total concentrations was 10.0 to 23.6 mg/kg in Gwangyang bay, 20.2 to 75.0 mg/kg in Jinhae bay, 10.5 to 156 mg/kg in Busan bay, and 16.7 to 57.2 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Busan bay (42.3 mg/kg) > Ulsan bay (39.5 mg/kg) > Jinhae bay (32.3 mg/kg) > Gwangyang bay (18.2 mg/kg). There were statistical differences between Gwangyang bay and the other three regions (rank sum test: $p < 0.01$), and there were also statistical differences between Jinhae and Ulsan bay (rank sum test: $p < 0.05$).

Among all sampling sites, the highest concentration of Pb was confirmed in BS13 (156 mg/kg). In the case of Dong Stream flowing into BS13, the color of the water was black and had a bad smell, and the BMI test result was classified as very bad (IHE, 2016). In fact, as the industrialization of Busan progressed, domestic sewage and industrial wastewater flowed into Dong Stream, accelerating pollution. Considering this point, it seems that the Dong Stream contributed to the Pb contamination of BS13. In addition, JH2, JH3, BS1, BS2, BS3, and BS9 which had relatively high concentrations, including BS13, are commonly close to the port. Therefore, the effect of port activities and wastewater seems to be the main source of pollution in Pb.

Pb showed the tendency to increase the F2 fraction as the concentration increased. Anthropogenic Pb is widely distributed in the F2 fraction because it forms a stable complex by boding with Fe-Mn oxide (Huang et al., 2013). Compared to the ratio of F2 fraction in Cu, the ratio of F2 fraction in Pb was higher because Pb has the highest affinity to Fe-Mn oxide (Han et al., 2015). This tendency was observed in previous studies (Ahdy & Youssef, 2011; Wei et al., 2016). F2 fractions were high at most of the sampling sites, indicating that contamination of Pb mainly originated from anthropogenic sources. Also, the mobility and bioavailability of Pb are high because most of them are easily extracted under the reduction condition in all sites.

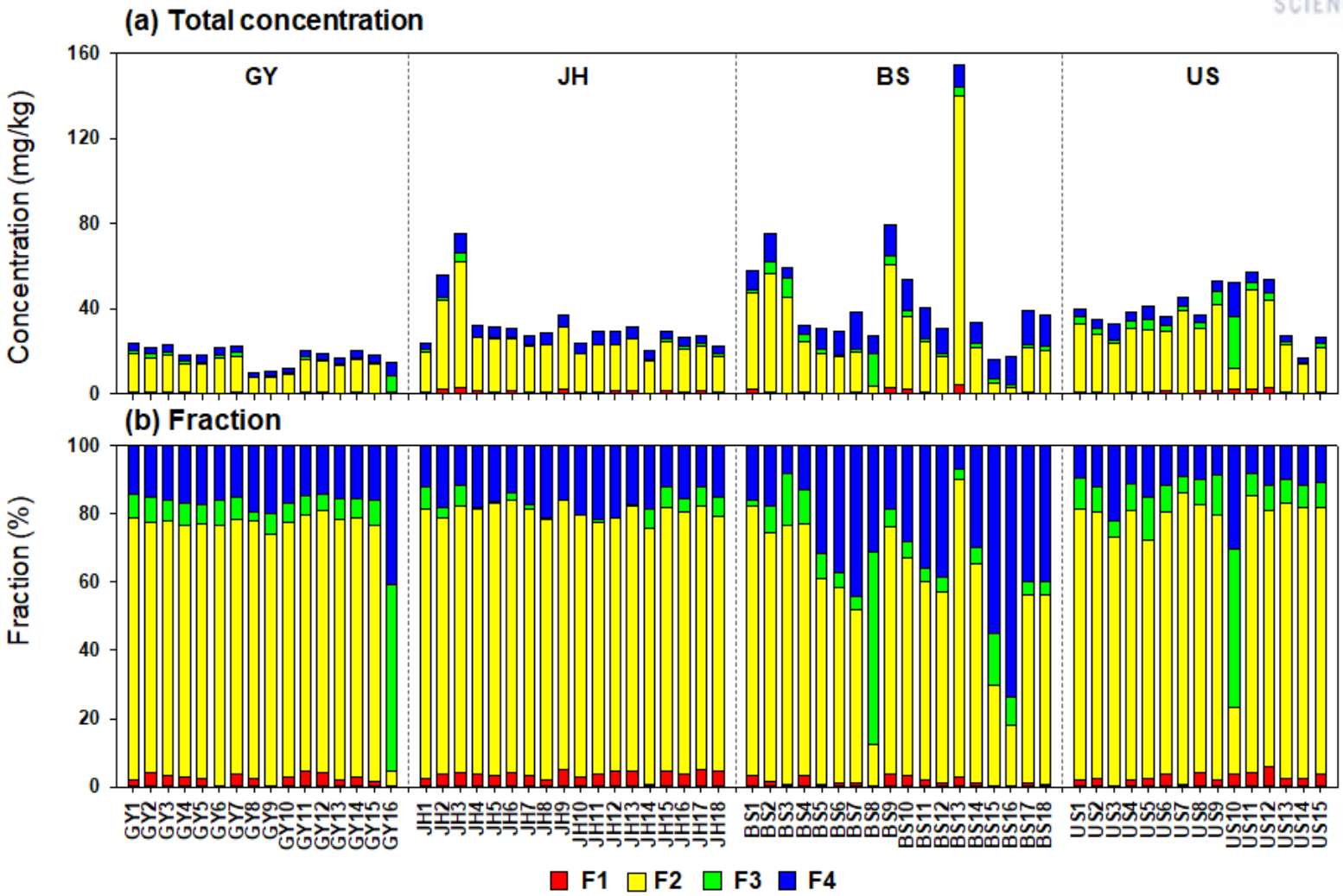

Figure 12. (a) Total concentration and (b) fraction of Pb in four regions.

3.1.6 Chromium (Cr) and nickel (Ni)

Figure 13, 14, and S6 show the concentrations and fractions of Cr and Ni in four regions. In the case of Cr, the range of total concentrations was 20.7 to 43.5 mg/kg in Gwangyang bay, 30.7 to 47.3 mg/kg in Jinhae bay, 16.8 to 73.8 mg/kg in Busan bay, and 7.14 to 40.9 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (38.6 mg/kg) > Busan bay (37.7 mg/kg) > Gwangyang bay (33.9 mg/kg) > Ulsan bay (30.5 mg/kg). There were no statistical differences in the four regions (rank sum test: $p > 0.05$), except for Ulsan bay (rank sum test: $p < 0.01$).

In the case of Ni, the range of total concentrations was 9.58 to 23.7 mg/kg in Gwangyang bay, 13.9 to 25.0 mg/kg in Jinhae bay, 5.36 to 22.8 mg/kg in Busan bay, and 3.00 to 23.5 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (20.7 mg/kg) > Gwangyang bay (17.2 mg/kg) > Ulsan bay (16.8 mg/kg) > Busan bay (16.3 mg/kg). There were no statistical differences in the four regions (rank sum test: $p > 0.05$), except for Jinhae bay (rank sum test: $p < 0.05$).

The highest level of Cr was observed in BS13 (73.8 mg/kg), which was located where the wastewater flowed in. In addition, BS13 was the site with the highest concentration of Cd, Zn, and Pb in Busan bay, and Cr is also presumed to have shown a high level due to similar pollutants. In the case of Ni, the concentrations were similar in most sites except for some sites.

In most sampling sites, the proportion of the F4 fraction was the most dominant. Cr and Ni are similar to the ionic radii of Al and Fe present in the crystal structure of lithogenic minerals, so they tend to exist mainly as a residual fraction as they are substituted (Amini & Qishlaqi, 2020). A high F4 fraction means that the mobility and bioavailability of heavy metals are low, and the probability of extraction from sediment is also low. Exceptionally, in the case of BS13, which had the highest concentration of Cr, the ratio of the non-residual fraction was slightly more dominant than the residual fraction, suggesting that there is some possibility of extraction from the sediment.

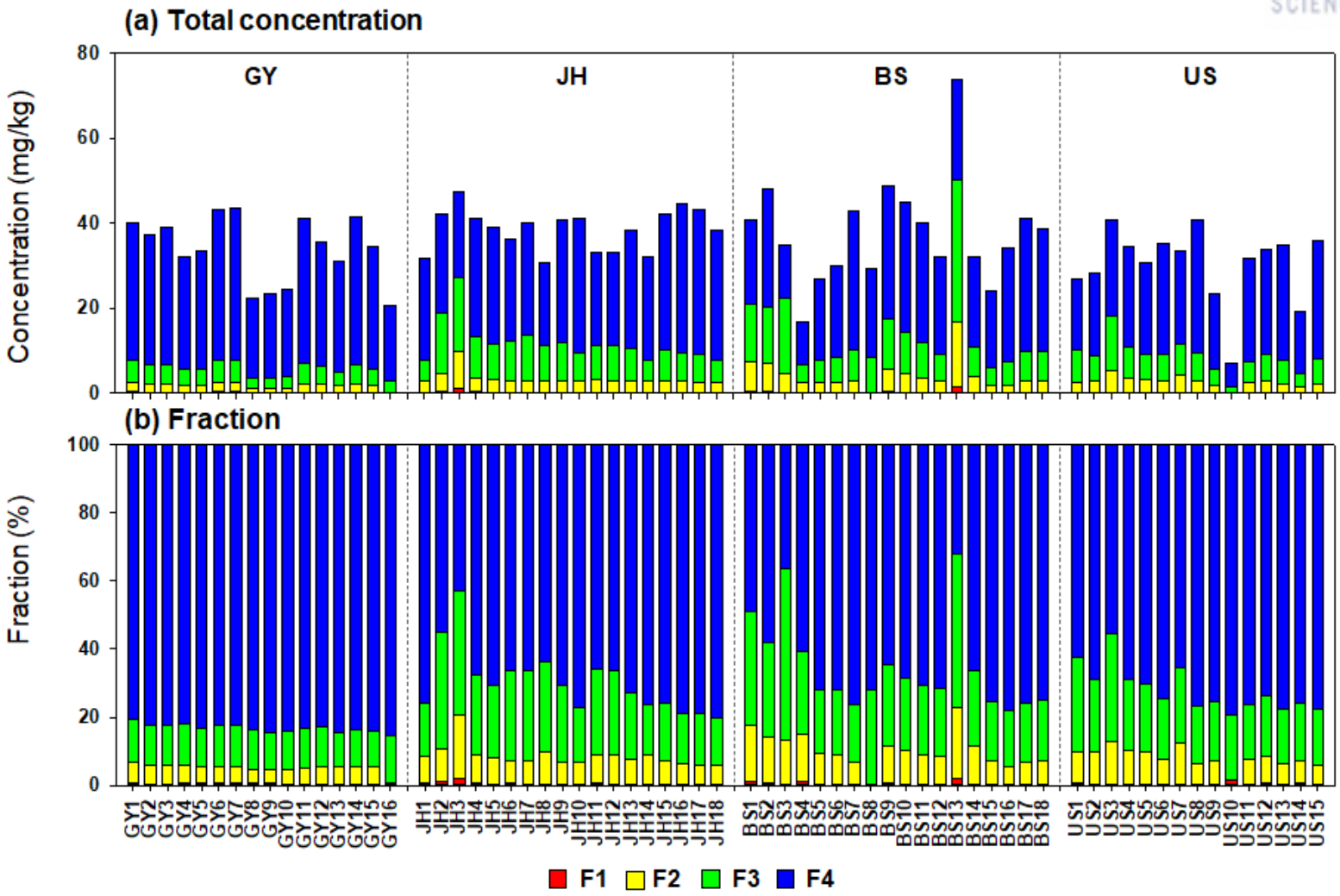

Figure 13. (a) Total concentration and (b) fraction of Cr in four regions.

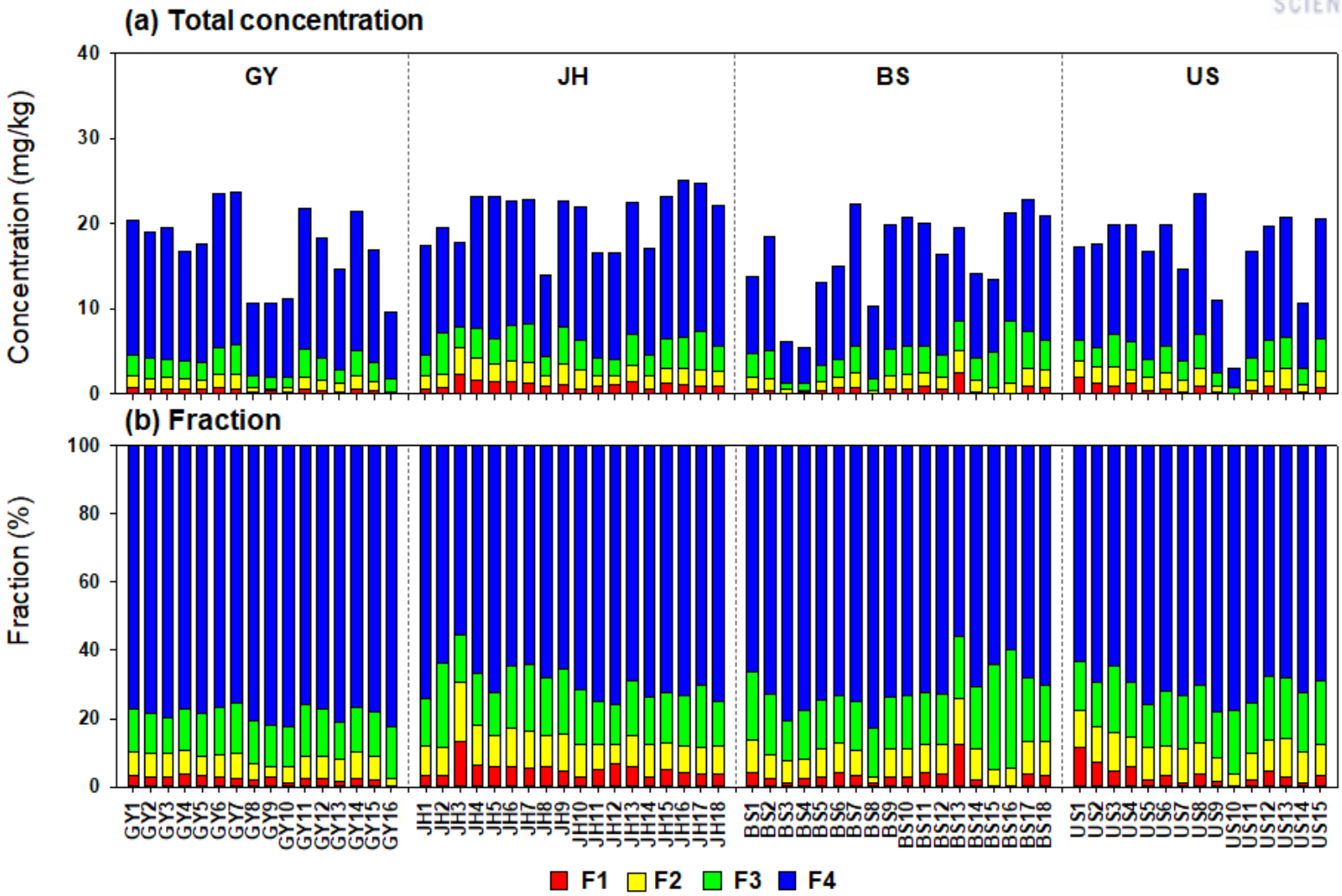

Figure 14. (a) Total concentration and (b) fraction of Ni in four regions.

3.1.7 Aluminium (Al) and iron (Fe)

Figure 15, 16, and S7 show the concentrations and fractions of Al and Fe in four regions. In the case of Al, the range of total concentrations was 22243 to 47450 mg/kg in Gwangyang bay, 38455 to 60184 mg/kg in Jinhae bay, 9509 to 45548 mg/kg in Busan bay, and 4465 to 40140 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (49532 mg/kg) > Gwangyang bay (36512 mg/kg) > Busan bay (30822 mg/kg) > Ulsan bay (28973 mg/kg). There were statistical differences in four regions (rank sum test: $p < 0.05$), except between Busan and Ulsan bay (rank sum test: $p > 0.05$), and between Jinhae and Ulsan bay (rank sum test: $p > 0.05$)

In the case of Fe, the range of total concentrations was 22627 to 42732 mg/kg in Gwangyang bay, 36783 to 46267 mg/kg in Jinhae bay, 15339 to 43641 mg/kg in Busan bay, and 8360 to 41865 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (41532 mg/kg) > Gwangyang bay (34774 mg/kg) > Busan bay (32108 mg/kg) > Ulsan bay (30844 mg/kg). There were statistical differences between Gwangyang and Jinhae bay (rank sum test: $p < 0.01$), between Jinhae and Busan bay (rank sum test: $p < 0.01$), and between Jinhae and Ulsan bay (rank sum test: $p < 0.01$)

For Al and Fe, the F4 fraction was the most dominant at all sampling sites, indicating that it was mainly derived from natural sources. Al and Fe are elements that account for a high proportion of the elements that make up the earth's crust (Fleischer, 1954). Most of them are present in the crystal lattice of minerals and are accumulated due to natural sources such as weathering, so the F4 fraction appears to be the highest in the sediment. Since the proportion of the F4 fraction is the highest, the mobility and bioavailability of heavy metals are likely to be very low.

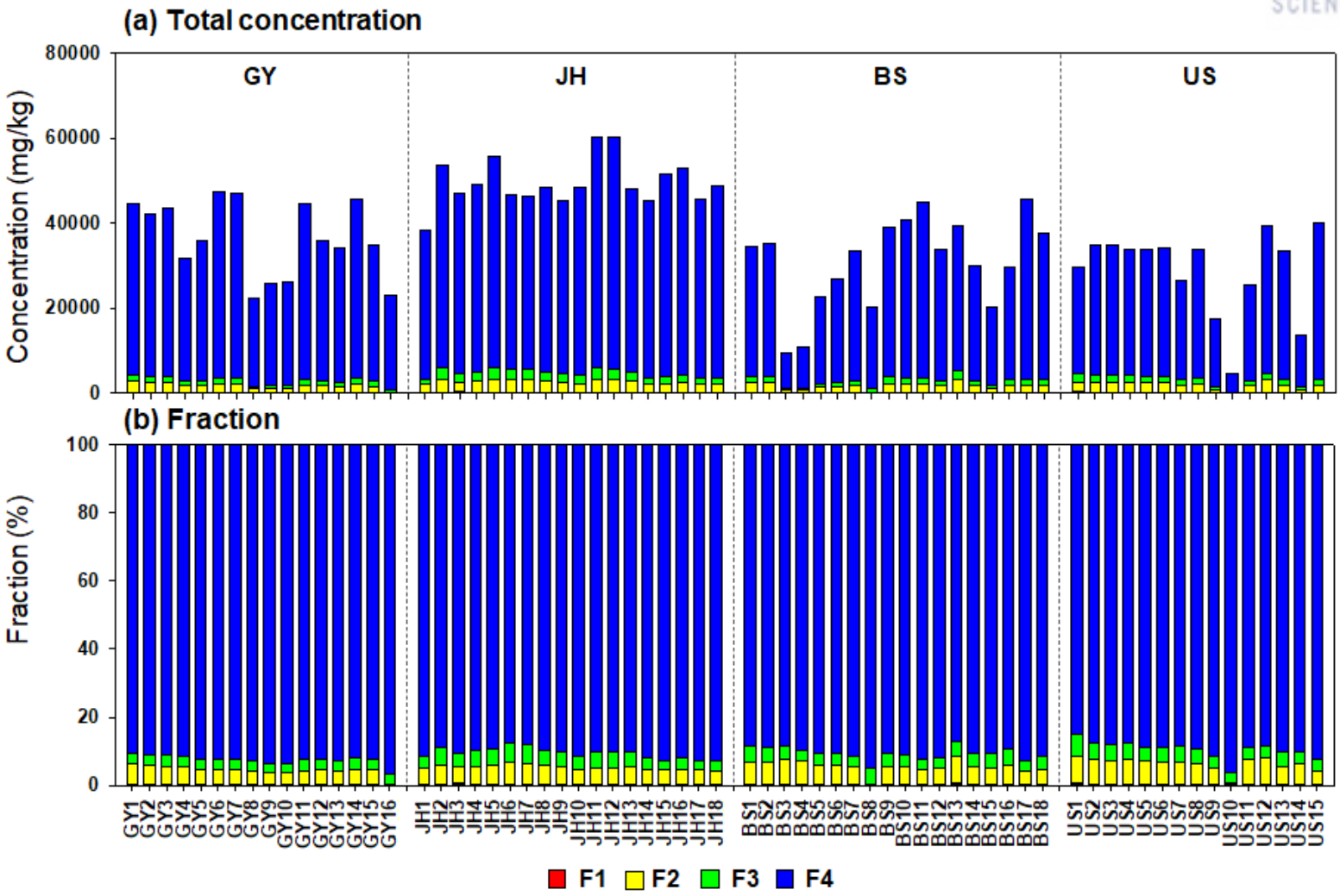

Figure 15. (a) Total concentration and (b) fraction of Al in four regions.

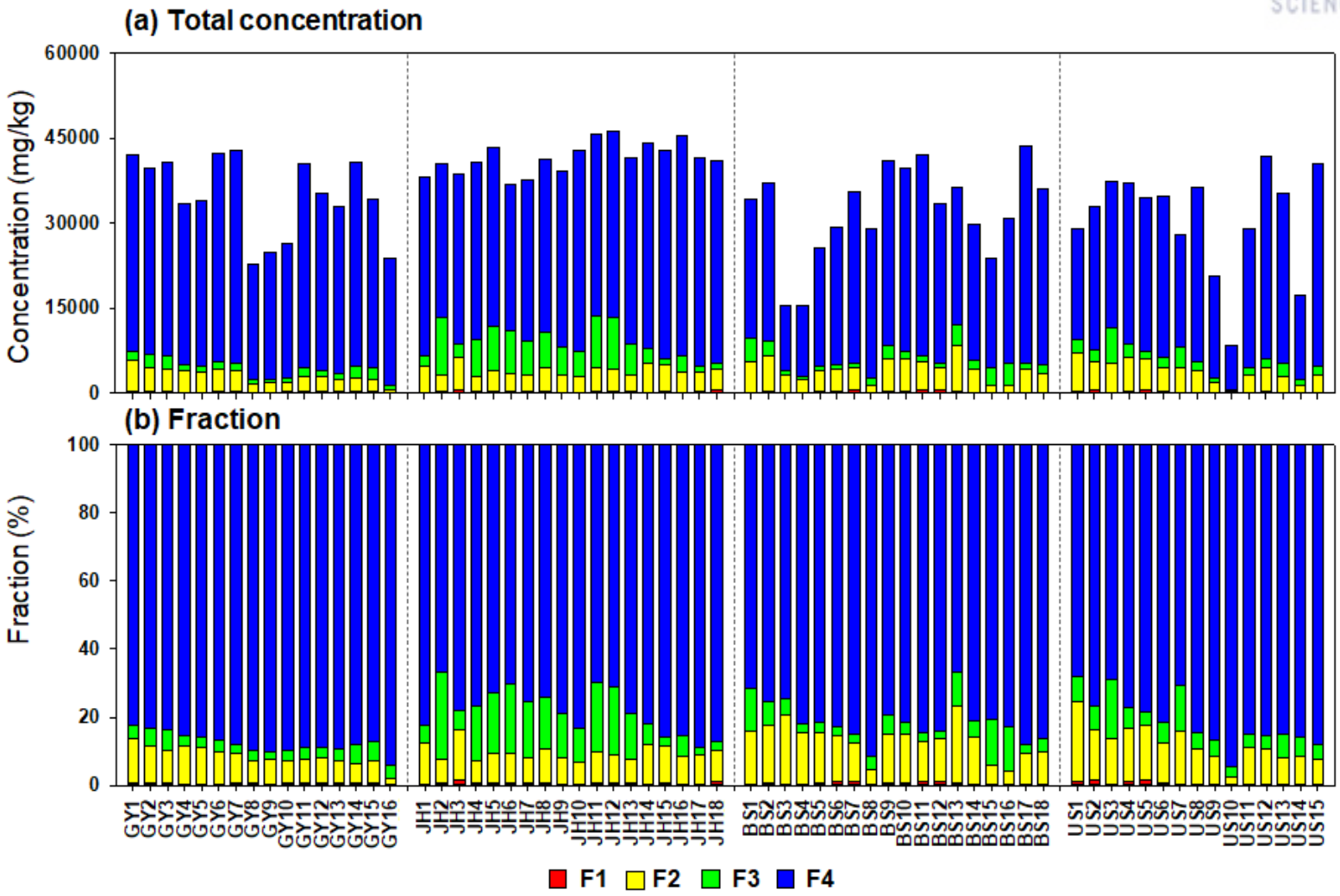

Figure 16. (a) Total concentration and (b) fraction of Fe in four regions.

3.1.8 Arsenic (As) and vanadium (V)

Figure 17, 18, and S8 show the concentrations and fractions of As and V in four regions. In the case of As, the range of total concentrations was 4.36 to 12.2 mg/kg in Gwangyang bay, 7.34 to 14.7 mg/kg in Jinhae bay, 5.08 to 10.4 mg/kg in Busan bay, and 4.78 to 33.1 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Ulsan bay (11.7 mg/kg) > Jinhae bay (9.74 mg/kg) > Gwangyang bay (8.02 mg/kg) > Busan bay (7.49 mg/kg). There were statistical differences between Gwangyang and Jinhae bay (rank sum test: $p < 0.05$), between Jinhae and Busan bay (rank sum test: $p < 0.01$), and between Busan and Ulsan bay (Mann-Whitney rank sum test: $p < 0.05$).

In the case of V, the range of total concentrations was 23.5 to 51.7 mg/kg in Gwangyang bay, 39.8 to 72.2 mg/kg in Jinhae bay, 18.5 to 52.3 mg/kg in Busan bay, and 7.04 to 46.3 mg/kg in Ulsan bay. The order of average concentrations in four regions was: Jinhae bay (58.8 mg/kg) > Gwangyang bay (41.09 mg/kg) > Busan bay (39.4 mg/kg) > Ulsan bay (36.6 mg/kg). There were no statistical differences in the four regions (rank sum test: $p > 0.05$), except for Jinhae bay (rank sum test: $p < 0.01$).

The highest level of As was observed in US5 (33.1 mg/kg), near the petrochemical complex and automobile factories. Therefore, waste or wastewater discharged from the industrial complex seemed to have contributed to the pollution of As. The concentration of V was higher in Jinhae bay than in other regions. This seemed to be related to the regional characteristics of Jinhae bay. In detail, the velocity of sea water in Jinhae bay is slow. Therefore, it might be explained that the dilution effect of V introduced into the ocean was reduced and the concentration was higher than in other regions.

However, when comparing the ratios of the fractions, the F4 fraction was dominant in most sites for both As and V. This means that natural sources affect the concentration of As and V more than anthropogenic sources. In addition, since the F4 fraction is high, As and V are expected to be unlikely to release from sediments.

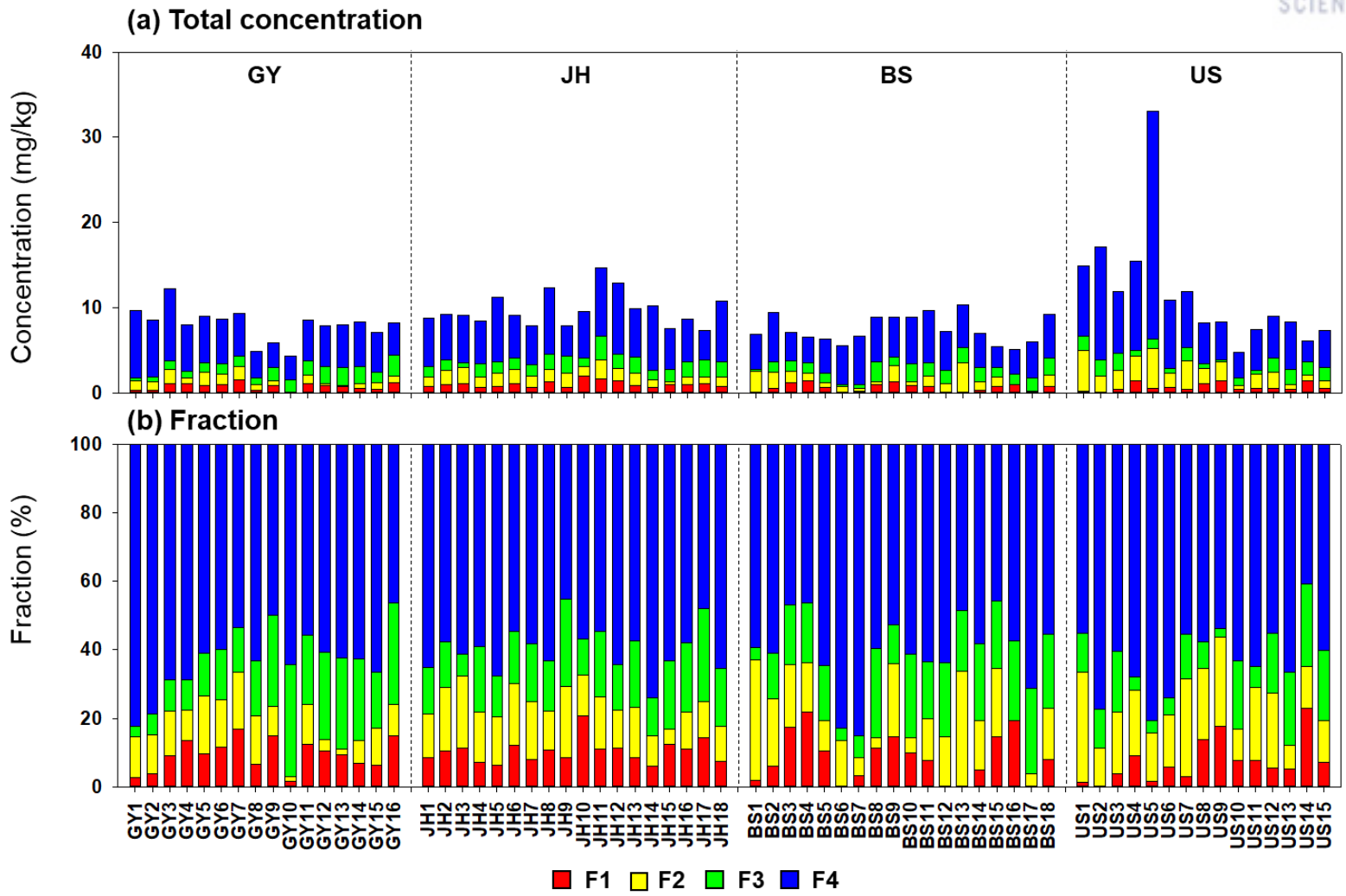

Figure 17. (a) Total concentration and (b) fraction of As in four regions.

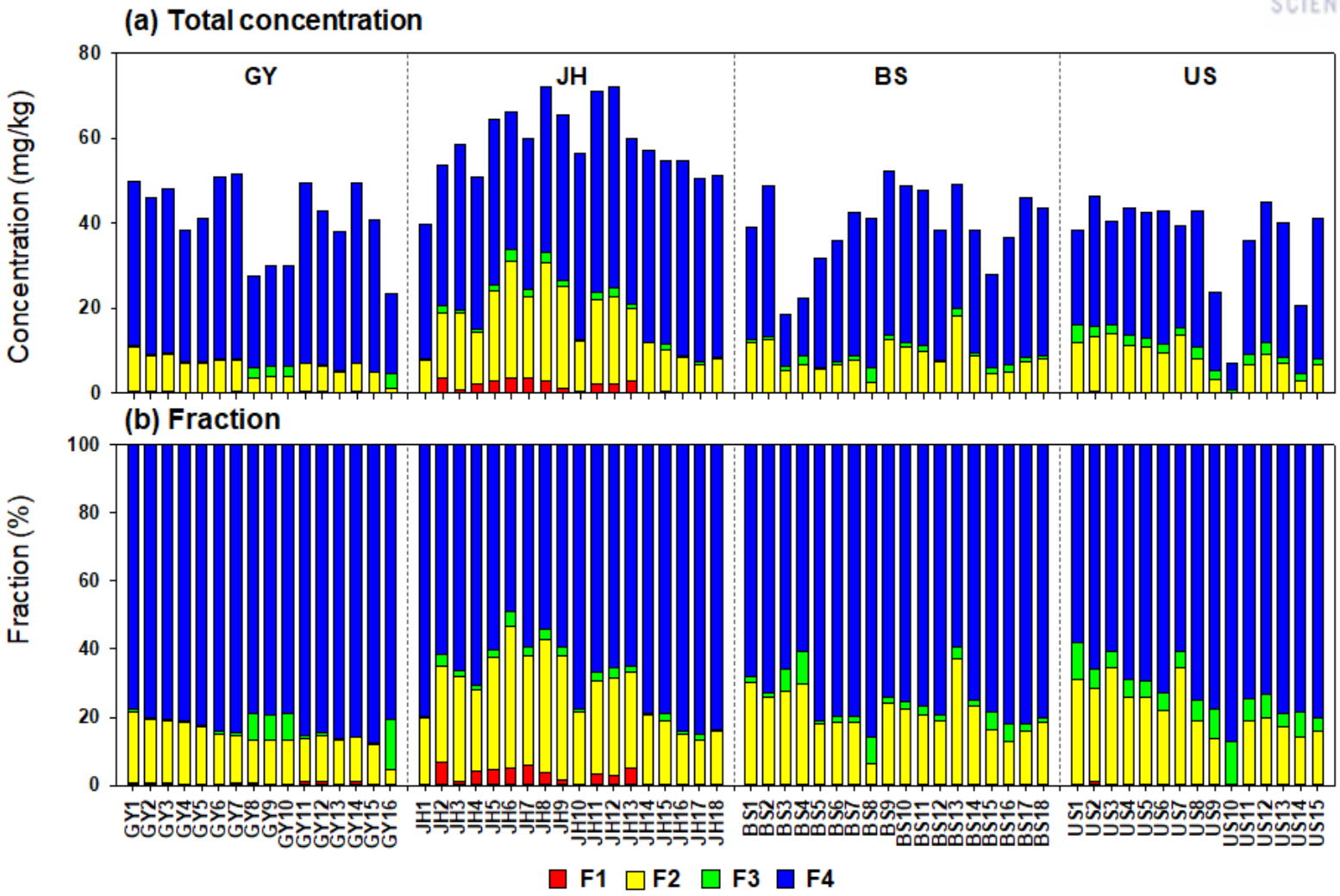

Figure 18. (a) Total concentration and (b) fraction of V in four regions.

3.2 Correlation analysis of heavy metals

Correlation analysis was conducted to identify the relationship between heavy metals. The result of the correlation analysis is summarized in Table 13.

Cd, Cu, Pb, and Zn were highly correlated with each other. In the previous result, the concentration of these heavy has something in common they had high concentrations at sites close to the port. Therefore, a strong positive correlation between these heavy metals might be affected by the effect of port activities. Especially, Cu had a highly positive correlation with Zn. These two metals were contained in the paint used in ships, so this can be a reason for the result of the correlation.

Cr, Ni, and V also showed a high positive correlation. Cr and Ni were usually emitted in the process of shipbuilding, and V was emitted by the combustion of the ship's fuel. Therefore, the common source might be the effect of the shipyard.

In the case of Mn, it showed a negative correlation with Cd, Cu, Pb, and Zn. This seems to be related to the regional characteristics of Gwangyang bay. In Gwangyang bay, landfilling and dredging were carried out to build a steel mill. For this reason, Gwangyang bay showed a high concentration of Mn, but a low concentration of other heavy metals. Therefore, this point seems to have affected the correlation.

Table 13. Spearman correlation analysis between heavy metals.

	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Al	1										
As	0.49**	1									
Cd	0.44**	0.59**	1								
Cr	0.66**	0.25*	0.33**	1							
Cu	0.07	0.43**	0.62**	0.25*	1						
Fe	0.93**	0.49**	0.37**	0.67**	0.11	1					
Mn	0.52**	0.09	-0.19	0.29*	-0.48	0.55**	1				
Ni	0.69**	0.25*	0.26*	0.79**	-0.02	0.72**	0.42**	1			
Pb	0.08	0.38**	0.68**	0.31*	0.89**	0.09	-0.44**	0.072	1		
V	0.93**	0.58**	0.55**	0.66**	0.23	0.88**	0.40**	0.67**	0.22	1	
Zn	0.25*	0.56*	0.70**	0.42**	0.92**	0.28*	-0.29*	0.14	0.87**	0.37**	1

**Correlation is significant at the 0.01 level (2-tailed) and *correlation is significant at the 0.05 level (1-tailed)

3.3 Principal component analysis (PCA)

PCA was conducted to understand the pollution patterns of heavy metals from four regions. Especially, this study focused on identifying pollution patterns of heavy metals by anthropogenic effects by comparing PCA results considering the total concentration and the sum of concentrations in non-residual fraction. In order to perform PCA, the concentration of each heavy metal was normalized by dividing the concentration of each heavy metal by the sum of 11 heavy metal concentrations.

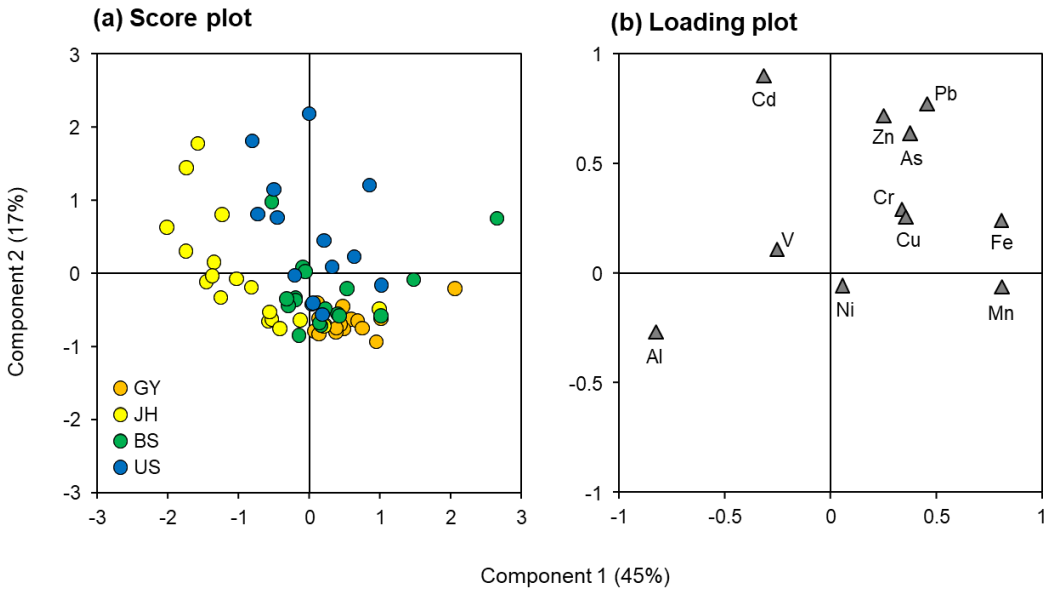

Figure 19. PCA result considering the total concentration of heavy metals.

Figure 19 shows the result of PCA considering the total concentration of heavy metals. The principal component 1 (PC1) and 2 (PC2) explained 45% and 17%, respectively. The PC1 was positively influenced by Fe and Mn and negatively influenced by Al. The PC2 was positively correlated with Cd. In Gwangyang bay, almost samples were correlated with Mn and Ni. In Jinhae bay, most samples had negative PC1 score, which is correlated with Al, Cd, and V. In Busan bay, samples in the score plot had a correlation with Cr, Cu, Ni, and V in the loading plot. In Ulsan bay, the samples were scattered in the score plot. This indicates that Ulsan bay was influenced by diverse heavy metals as there were various industrial complexes.

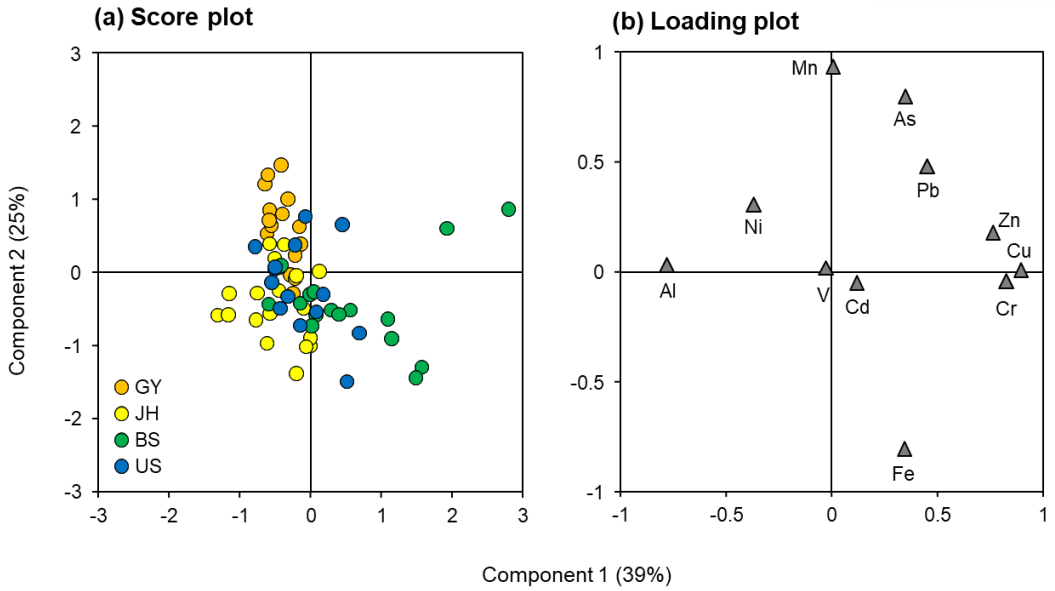

Figure 20. PCA result considering the sum of concentrations in non-residual fraction.

Figure 20 shows the result of PCA considering the sum of concentrations in non-residual fraction. The principal component 1 (PC1) and 2 (PC2) explained 39% and 25%, respectively. The PC1 was positively influenced by Cr, Cu, and Zn and negatively influenced by Al. The PC2 was positively correlated with Mn and negatively correlated with Fe. In Gwangyang bay, most samples were correlated with Mn. That's because Gwangyang bay had a higher sum of concentrations of Mn in non-residual fraction than other regions due to steel manufacturing. In Jinhae bay, samples had a correlation with Al, Cd, Ni, and V. The sum of concentration in non-residual fraction of these heavy metals was higher than in other regions, so it might lead to this result. In Busan bay, several samples were correlated with Cd, Cr, Cu, Fe, and Zn. Especially, Cu and Zn showed the highest concentration in non-residual fraction than in other regions due to the influence of paint used in ships. In the case of Fe, the average concentration was lower than in other regions, but when the normalized concentration of heavy metals was compared, Busan bay showed a higher ratio than the other bays. In Ulsan bay, the samples were scattered in the score plot, which is similar to the result of Figure 19.

Like this, comparing the results of the two PCA, it was confirmed that there were common points but also differences. This indicates that the difference in industrial complexes from each region affected the pollution patterns of heavy metals by anthropogenic influences.

3.4 Ecological risk assessment

3.4.1 Individual contamination factor (ICF)

Figure 21 and 22 show the result of ICF for heavy metals in four regions. The ecological risk of Cd was the highest in Jinhae bay and showed a considerable level of risk on average. This means the retention time of Cd in Jinhae bay is shorter than in other regions, so it is easily released from sediments and the risk to the environment is higher. In fact, the concentration of Cd was the highest in Jinhae bay due to anthropogenic effects, and accordingly, the ratio of the F1 fraction was also the highest. For this reason, it is estimated that Cd showed the highest ecological risk in Jinhae bay due to the high proportion of non-residual fraction. Mn had the highest ecological risk in Gwangyang bay. In Gwangyang bay, the concentration of Mn was high due to the influence of the steel mill, and the ratio of the F1 fraction was also high. Because of this, the ecological risk of Mn seems to be highly evaluated in Gwangyang bay. Cu and Zn showed the highest ecological risk in Busan bay. The concentration of these heavy metals was also highest in Busan bay due to the influence of paint used in ships. Because of these anthropogenic sources, Cu and Zn mainly exist as a non-residual fraction in Busan bay, so the ecological risk seems to be high. For Pb, the F2 fraction was dominant at most sampling sites, resulting in the ecological risk being considerable or high in all regions. In particular, the ecological risk was the highest in Ulsan bay, which is estimated to be affected by various industrial complexes in Ulsan bay. The ecological risk of other heavy metals was evaluated at a low level. Since these heavy metals mainly exist as an F4 fraction and have very low mobility and bioavailability, the ecological risk was also low.

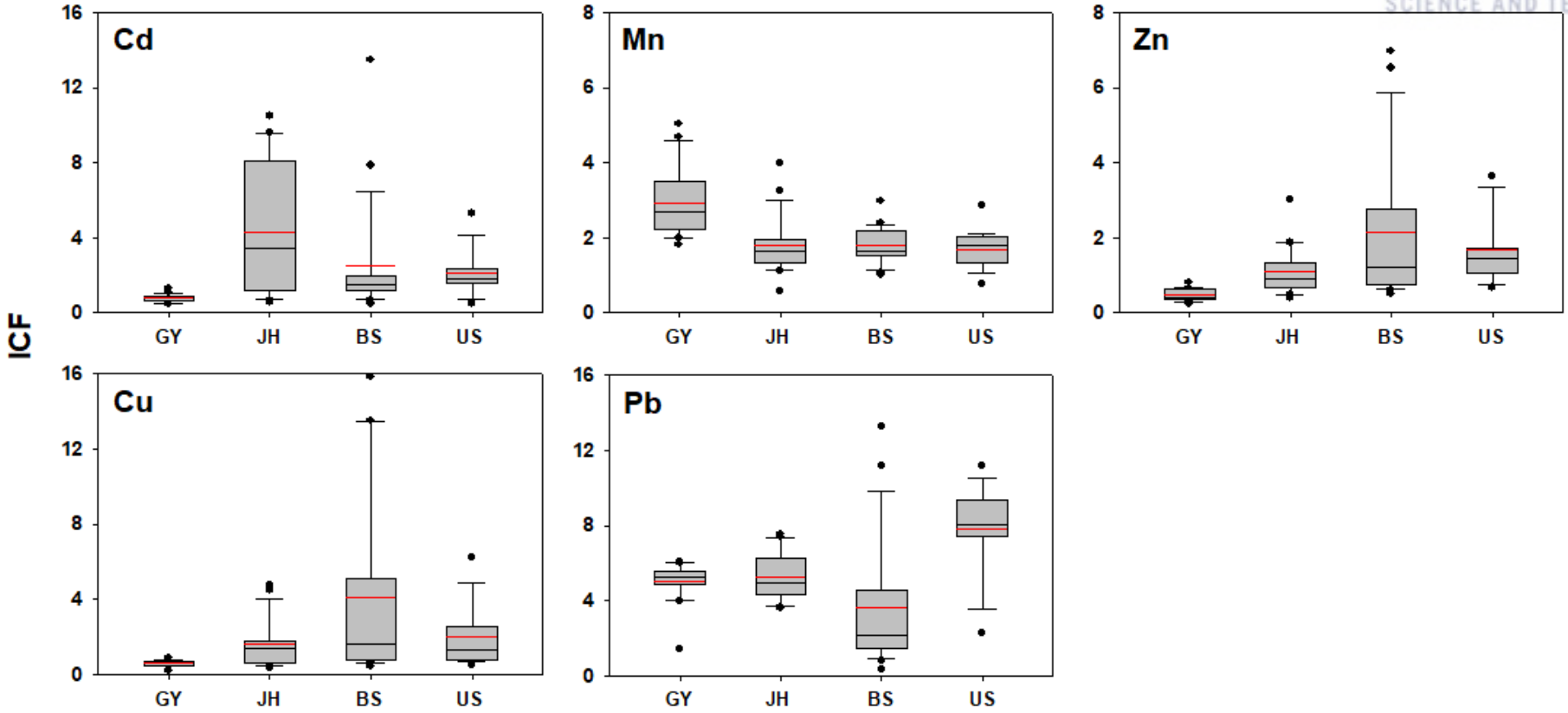

Figure 21. Box plot of ICF for 5 heavy metals (Cd, Mn, Zn, Cu, and Pb) in four regions.

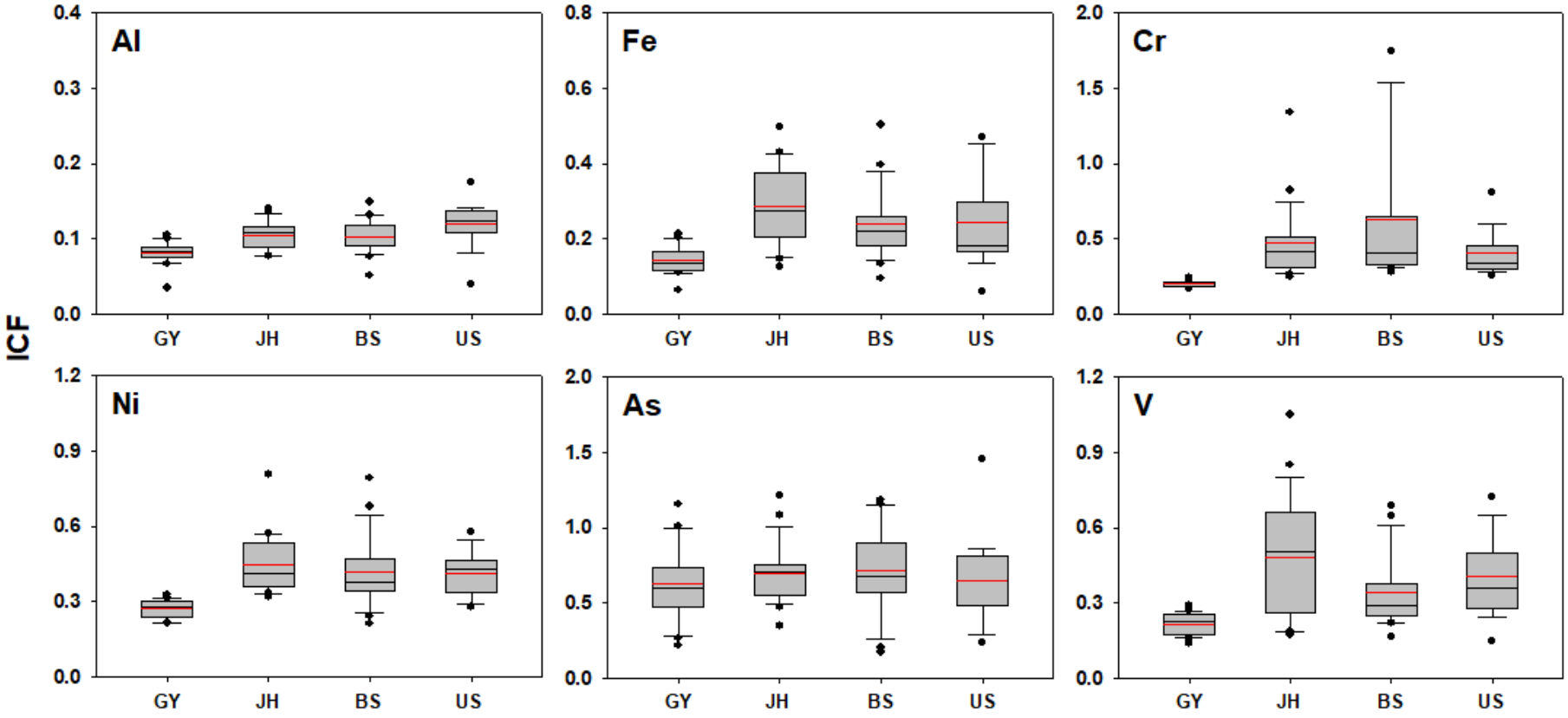

Figure 22. Box plot of ICF for 6 heavy metals (Al, Fe, Cr, Ni, As, and V) in four regions.

3.4.2 Risk assessment code (RAC)

The result of RAC is summarized in Table 14. In Jinhae bay, the ecological risk of Cd was highest among 11 heavy metals and, in other regions, Mn showed the highest ecological risk. The result of RAC in Gwanyang and Jinhae bay were consistent with the result of ICF. It indicates that Mn and Cd are the main heavy metals that affect the aquatic environment of Gwangyang and Jinhae bay, respectively. In Busan and Ulsan bay, the ecological risk of Mn was classified as high, like in Gwangyang bay. This means the F1 fraction of Mn is dominant, so the mobility and bioavailability are high. Therefore, it is necessary to consider the ecological risk of Mn in both regions. On the other hand, the ecological risk of Cu and Pb was classified as low in Busan and Ulsan bay, which was different from the ICF results. In the case of Cu and Pb, the F2 fraction is the most dominant among the four fractions due to the anthropogenic effect in Busan and Ulsan bay. For this reason, the proportion of the F1 fraction is low, so it seems that the ecological risk was evaluated as low in the RAC result. In the case of other heavy metals, it was generally consistent with the ICF results.

Table 14. The RAC value of heavy metals in four regions.

Region	RAC (%)										
	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
GY	0.19	9.43	11.7	0.53	1.22	0.49	47.9	2.37	2.49	0.49	7.75
JH	0.24	10.3	40.0	0.56	2.37	0.64	25.4	5.26	3.73	2.52	15.7
BS	0.20	8.40	23.8	0.54	8.87	0.56	35.0	3.19	1.59	0.04	19.6
US	0.24	23.8	27.0	0.44	4.41	0.53	35.1	3.68	2.86	0.11	16.8

3.4.3 Modified potential ecological risk index (MRI)

Figure 23 shows the result of the MRI. Four sites in Jinhae Bay (JH2, JH3, JH4, and JH6) and two sites in Busan bay (BS1 and BS13) showed moderate ecological risk, and all other sites showed low. The six sites that showed a moderate level of ecological risk had the highest ratio of Cd among the 7 heavy metals in common. This tendency was the same for all sites as well as in 6 sites. Cd has the highest toxic-response factor, mobility, and bioavailability among the 7 heavy metals, so it seems that it occupied a high proportion in all sites. Particularly, the mean concentration of Cd in six sites, where the ecological risk was evaluated as moderate, was more than three times higher than that of other sites, and the F1 fraction ratio was also high.

The order of heavy metals determining MRI values in four regions was Cd > As > Pb > Cu > Ni > Zn > Cr for Gwangyang and Jinhae bay, Cd > Cu > Pb > As > Zn > Ni > Cr for Busan bay, Cd > Pb > As > Cu > Zn > Ni > Cr for Ulsan bay. In common with the four regions, Cd showed the highest rank and Cr showed the lowest rank. This implies that Cd could pose the highest ecological risk to the aquatic environment among 7 heavy metals in four regions. Therefore, it is needed to be careful about the ecological risk of Cd in all regions. Especially in Jinhae bay, the ecological risk of Cd is higher in common as the result of ICF and RAC, so more attention is needed.

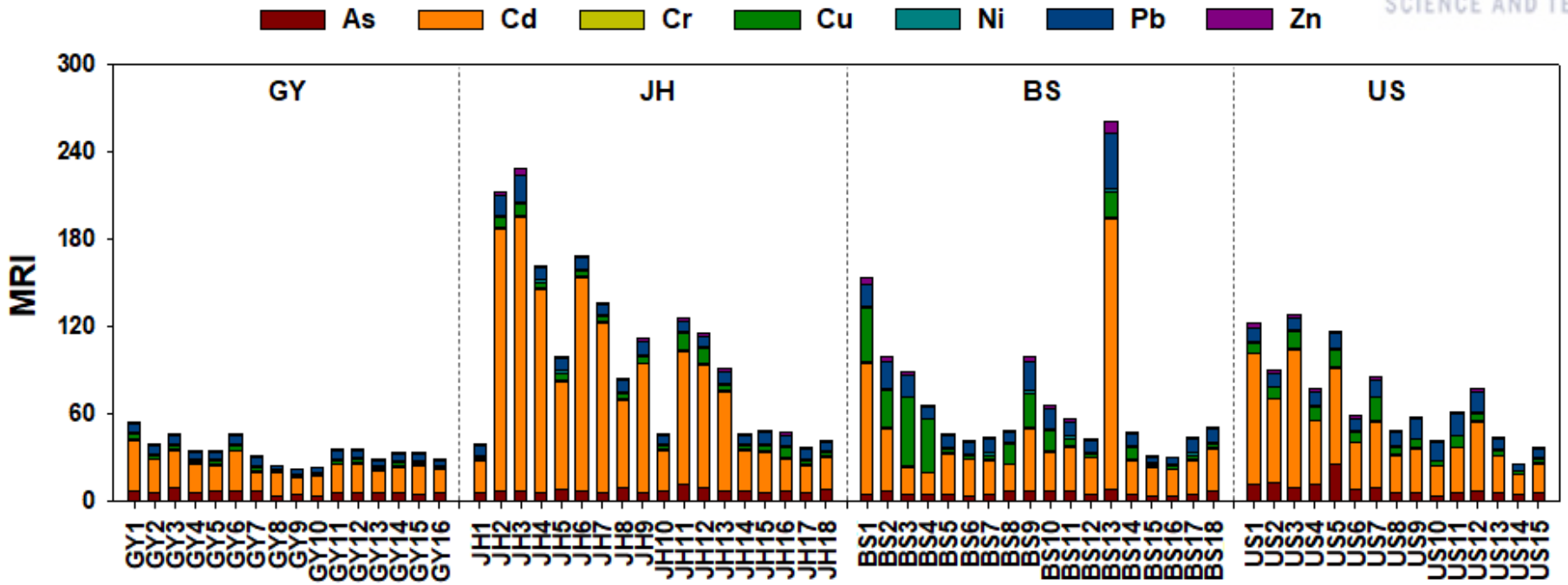

Figure 23. The result of MRI in four regions.

IV. CONCLUSIONS

In this study, the concentration and fraction of 11 heavy metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn) were investigated by applying BCR sequential extraction method to sediments collected from regions (Gwangyang, Jinhae, Busan, and Ulsan bay). Based on this result, the characteristics of pollution patterns by region were identified and ecological risks were evaluated.

In four regions, Cd showed the tendency to increase the F1 fraction as the concentration increased, and the ratio was the highest in Jinhae bay, where the concentration was the highest. Mn also showed the same tendency as Cd, and the ratio was the highest in Gwangyang bay. In the case of Zn, the non-residual fraction tended to increase as the concentration increased. Cu showed the tendency to increase the F2 fraction as the concentration increased, except Jinhae Bay. Especially in Busan bay, where the concentration of Cu is highest, the ratio of F2 fraction was the highest. In the case of Pb, the F2 fraction was dominant in all regions. For other heavy metals, the F4 fraction was the most dominant.

In correlation analysis and PCA results, characteristics of pollution by heavy metals were confirmed by regional features and differences in industrial complexes. Especially in the case of Gwangyang bay, most of the sampling sites are associated with Mn due to the influence of the steel mill. Also, in Busan bay, the effect of Cu and Zn was higher than that of other cities due to port activities.

Three indices (ICF, RAC, and MRI) were used to evaluate the ecological risk. In the ICF results, the ecological risks of Mn in Gwangyang, Cd in Jinhae, Cu and Zn in Busan, and Pb in Ulsan bay were the highest. In the RAC results, Cd in Jinhae bay and Mn in other bays were evaluated as high ecological risk. In the MRI results, four sites in Jinhae and two sites in Busan bay were classified as moderate level of ecological risk. Also, among the 7 heavy metals (As, Cd, Cr, Cu, Ni, Pb, Zn), Cd accounted for a large proportion of MRI value in all regions. Therefore, it is essential to care about the ecological risk of Cd.

This was the first report about the fraction distribution and bioavailability of heavy metals in the special management sea areas (Gwangyang, Jinhae, Busan, and Ulsan bays) in South Korea. Each region showed differences in the concentration and fraction distribution of heavy metals due to regional characteristics and the influence of unique industrial complexes, and accordingly, there was also a difference in the degree of ecological risk. Therefore, appropriate management is needed considering these differences. This study can be useful information for identifying the risk of heavy metals in sediments in southeastern industrial bays of Korea and managing the marine environment.

REFERENCES

Abdallah, M. A. M., & Mohamed, A. A. (2019). Mobility and risk assessment of heavy metals by sequential extraction in coastal sediment south Mediterranean Sea, Egypt. *Marine Systems & Ocean Technology*, *14*(1), 42-50.

Ahdy, H. H. H., & Youssef, D. H. (2011). Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. *Chemistry and Ecology*, *27*(5), 427-443.

Amini, A., & Qishlaqi, A. (2020). Spatial distribution, fractionation and ecological risk assessment of potentially toxic metals in bottom sediments of the Zarivar freshwater Lake (Northwestern Iran). *Limnologica*, *84*.

Bastami, K. D., Neyestani, M. R., Molamohyedin, N., Shafeian, E., Haghparast, S., Shirzadi, I. A., & Baniamam, M. (2018). Bioavailability, mobility, and origination of metals in sediments from Anzali Wetland, Caspian Sea. *Mar Pollut Bull*, *136*, 22-32.

Caplat, C., Texier, H., Barillier, D., & Lelievre, C. (2005). Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. *Mar Pollut Bull*, *50*(5), 504-511.

Cho, J., Hyun, S., Han, J. H., Kim, S., & Shin, D. H. (2015). Historical trend in heavy metal pollution in core sediments from the Masan Bay, Korea. *Mar Pollut Bull*, *95*(1), 427-432.

Chung, C. S., Song, K. H., Choi, K. Y., Kim, Y. I., Kim, H. E., Jung, J. M., & Kim, C. J. (2017). Variations in the concentrations of heavy metals through enforcement of a rest-year system and dredged sediment capping at the Yellow Sea-Byung dumping site, Korea. *Mar Pollut Bull*, *124*(1), 512-520.

Delshab, H., Farshchi, P., & Keshavarzi, B. (2017). Geochemical distribution, fractionation and contamination assessment of heavy metals in marine sediments of the Asaluyeh port, Persian Gulf. *Marine Pollution Bulletin*, *115*(1-2), 401-411.

Eren, S. T., Sungur, A., & Ekinci, H. (2021). Trace metal fractions, sources, and risk assessment in sediments from Umurbey Stream (Canakkale-Turkey). *Environ Monit Assess*, *193*(6), 347.

Fleischer, M. (1954). The abundance and distribution of the chemical elements in the earth's crust. *Journal of Chemical Education*, *31*(9), 446.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, *14*(8), 975-1001.

Han, L., Gao, B., Wei, X., Gao, L., Xu, D., & Sun, K. (2015). The characteristic of Pb isotopic compositions in different chemical fractions in sediments from Three Gorges Reservoir, China. *Environ Pollut*, *206*, 627-635.

Huang, L., Pu, X., Pan, J. F., & Wang, B. (2013). Heavy metal pollution status in surface sediments of Swan Lake lagoon and Rongcheng Bay in the northern Yellow Sea. *Chemosphere*, *93*(9), 1957-1964.

Hwang, D. W., Kim, S. G., Choi, M., Lee, I. S., Kim, S. S., & Choi, H. G. (2016). Monitoring of trace metals in coastal sediments around Korean Peninsula. *Mar Pollut Bull*, *102*(1), 230-239.

Ikem, A., Egiebor, N., & Nyavor, K. (2003). Trace elements in water, fish and sediment from Tuskegee Lake, Southeastern USA. *Water, Air, and Soil Pollution*, *149*(1), 51-75.

The Busan Institute of Health and Environment (IHE), 2016. http://heis.busan.go.kr/data/data 077. aspx. in Korean

Jain, C. K. (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Res*, *38*(3), 569-578.

Jeong, H., Choi, J. Y., Lim, J., Shim, W. J., Kim, Y. O., & Ra, K. (2020). Characterization of the contribution of road deposited sediments to the contamination of the close marine environment with trace metals: Case of the port city of Busan (South Korea). *Mar Pollut Bull*, *161*(Pt A), 111717.

Jeong, Y.-S., Matsubae-Yokoyama, K., Kubo, H., Pak, J.-J., & Nagasaka, T. (2009). Substance flow analysis of phosphorus and manganese correlated with South Korean steel industry. *Resources, Conservation and Recycling*, *53*(9), 479-489.

Ji, Z., Zhang, Y., Zhang, H., Huang, C., & Pei, Y. (2019). Fraction spatial distributions and ecological risk assessment of heavy metals in the sediments of Baiyangdian Lake. *Ecotoxicol Environ Saf*, *174*, 417-428.

Jung, J. M., Choi, K. Y., Chung, C. S., Kim, C. J., & Kim, S. H. (2019). Fractionation and risk assessment of metals in sediments of an ocean dumping site. *Mar Pollut Bull*, *141*, 227-235.

Kang, C.-K., Lee, P.-Y., Park, J.-S., & Kim, P.-J. (1993). On the distribution of organic matter in the nearshore surface sediment of Korea. *Korean journal of fisheries and aquatic sciences*, *26*(6), 557-566.

Kim, Y., Kim, B.-K., & Kim, K. (2009). Distribution and speciation of heavy metals and their sources in Kumho River sediment, Korea. *Environmental Earth Sciences*, *60*(5), 943-952.

Kwon, M. J., Boyanov, M. I., Yang, J. S., Lee, S., Hwang, Y. H., Lee, J. Y., Mishra, B., & Kemner, K. M. (2017). Transformation of zinc-concentrate in surface and subsurface environments: Implications for assessing zinc mobility/toxicity and choosing an optimal remediation strategy. *Environ Pollut*, *226*, 346-355.

Lee, P.-K., Kang, M.-J., Jo, H. Y., & Choi, S.-H. (2011). Sequential extraction and leaching characteristics of heavy metals in abandoned tungsten mine tailings sediments. *Environmental Earth Sciences*, *66*(7), 1909-1923.

Liang, G., Gong, W., Li, B., Zuo, J., Pan, L., & Liu, X. (2019). Analysis of Heavy Metals in Foodstuffs and an Assessment of the Health Risks to the General Public via Consumption in Beijing, China. *Int J Environ Res Public Health*, *16*(6).

Liu, J. J., Ni, Z. X., Diao, Z. H., Hu, Y. X., & Xu, X. R. (2018). Contamination level, chemical fraction and ecological risk of heavy metals in sediments from Daya Bay, South China Sea. *Mar Pollut Bull*, *128*, 132-139.

Lu, Z. B., & Kang, M. (2018). Risk assessment of toxic metals in marine sediments from the Arctic Ocean using a modified BCR sequential extraction procedure. *J Environ Sci Health A Tox Hazard Subst Environ Eng*, *53*(3), 278-293.

Ministry of Maritime Affairs and Fisheries (MOF), 2019. http ://www.mof.go.kr/article/list.do?boardKey=22&menuKey=1009

Moore, F., Nematollahi, M. J., & Keshavarzi, B. (2015). Heavy metals fractionation in surface sediments of Gowatr bay--Iran. *Environ Monit Assess*, *187*(1), 4117.

Nelson, W. (2020). Fractionation of trace metals in coastal sediments from Trinidad and Tobago, West Indies. *Mar Pollut Bull*, *150*, 110774.

Nemati, K., Abu Bakar, N. K., Abas, M. R., & Sobhanzadeh, E. (2011). Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *J Hazard Mater*, *192*(1), 402-410.

Pandey, G., & Madhuri, S. (2014). Heavy metals causing toxicity in animals and fishes. *Research Journal of Animal, Veterinary and Fishery Sciences*, *2*(2), 17-23.

Passos, E. d. A., Alves, J. C., dos Santos, I. S., Alves, J. d. P. H., Garcia, C. A. B., & Spinola Costa, A. C. (2010). Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal*, *96*(1), 50-57.

Pempkowiak, J., Sikora, A., & Biernacka, E. (1999). Speciation of heavy metals in marine sediments vs their bioaccumulation by mussels. *Chemosphere*, *39*(2), 313-321.

Perumal, K., Antony, J., & Muthuramalingam, S. (2021). Heavy metal pollutants and their spatial distribution in surface sediments from Thondi coast, Palk Bay, South India. *Environmental Sciences Europe*, *33*(1).

Qiao, Y., Yang, Y., Gu, J., & Zhao, J. (2013). Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. *Mar Pollut Bull*, *68*(1-2), 140-146.

Ra, K., Bang, J. H., Lee, J. M., Kim, K. T., & Kim, E. S. (2011). The extent and historical trend of metal pollution recorded in core sediments from the artificial Lake Shihwa, Korea. *Mar Pollut Bull*, *62*(8), 1814-1821.

Ra, K., Kim, J.-K., Hong, S. H., Yim, U. H., Shim, W. J., Lee, S.-Y., Kim, Y.-O., Lim, J., Kim, E.-S., & Kim, K.-T. (2014). Assessment of pollution and ecological risk of heavy metals in the surface sediments of Ulsan Bay, Korea. *Ocean Science Journal*, *49*(3), 279-289.

Rauret, G., López-Sánchez, J., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., & Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of environmental monitoring*, *1*(1), 57-61.

Sakan, S., Popovic, A., Andelkovic, I., & Dordevic, D. (2016). Aquatic sediments pollution estimate using the metal fractionation, secondary phase enrichment factor calculation, and used statistical methods. *Environ Geochem Health*, *38*(3), 855-867.

Saleem, M., Iqbal, J., & Shah, M. H. (2015). Geochemical speciation, anthropogenic contamination,

risk assessment and source identification of selected metals in freshwater sediments—A case study from Mangla Lake, Pakistan. *Environmental Nanotechnology, Monitoring & Management*, *4*, 27-36.

Shin, J.-H., Jo, D.-H., & Kim, Y. (2021). Mobility and source apportionment of As and heavy metals in the Taehwa River sediment, South Korea: anthropogenic and seasonal effects. *Environmental Earth Sciences*, *80*(3).

Son, H. W., Shim, S. H., Oh, H., & Choi, J. H. (2021). An Assessment of Heavy Metal Contamination in the Nakdong River Around the Weir. *Water*, *13*(5).

Song, Y., & Choi, M. S. (2017). Assessment of heavy metal contamination in sediments along the coast of South Korea using Cs-normalized background concentrations. *Mar Pollut Bull*, *117*(1-2), 532-537.

Sundaray, S. K., Nayak, B. B., Lin, S., & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments--a case study: Mahanadi basin, India. *J Hazard Mater*, *186*(2-3), 1837-1846.

Sungur, A., Soylak, M., & Ozcan, H. (2015). Investigation of heavy metal mobility and availability by the BCR sequential extraction procedure: relationship between soil properties and heavy metals availability. *Chemical Speciation & Bioavailability*, *26*(4), 219-230.

Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological society of America bulletin*, *72*(2), 175-192.

Usero, J., Gamero, M., Morillo, J., & Gracia, I. (1998). Comparative study of three sequential extraction procedures for metals in marine sediments. *Environment International*, *24*(4), 487-496.

Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of Hazardous Materials*, *195*, 355-364.

Wei, X., Han, L., Gao, B., Zhou, H., Lu, J., & Wan, X. (2016). Distribution, bioavailability, and potential risk assessment of the metals in tributary sediments of Three Gorges Reservoir: The impact of water impoundment. *Ecological Indicators*, *61*, 667-675.

Yang, H. J., Bong, K. M., Kang, T. W., Hwang, S. H., & Na, E. H. (2021). Assessing heavy metals in surface sediments of the Seomjin River Basin, South Korea, by statistical and geochemical analysis. *Chemosphere*, *284*, 131400.

Yang, J., Chen, L., Liu, L. Z., Shi, W. L., & Meng, X. Z. (2014). Comprehensive risk assessment of heavy metals in lake sediment from public parks in Shanghai. *Ecotoxicol Environ Saf*, *102*, 129-135.

Zhang, G., Pan, Z., Hou, X., Wang, X., & Li, X. (2014). Distribution and bioaccumulation of heavy metals in food web of Nansi Lake, China. *Environmental Earth Sciences*, *73*(5), 2429-2439.

Zhu, H.-n., Yuan, X.-z., Zeng, G.-m., Jiang, M., Liang, J., Zhang, C., Yin, J., Huang, H.-j., Liu, Z.-f., & Jiang, H.-w. (2012). Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. *Transactions of Nonferrous Metals Society of China*, *22*(6), 1470-1477.

SUPPLEMENTARY INFORMATION

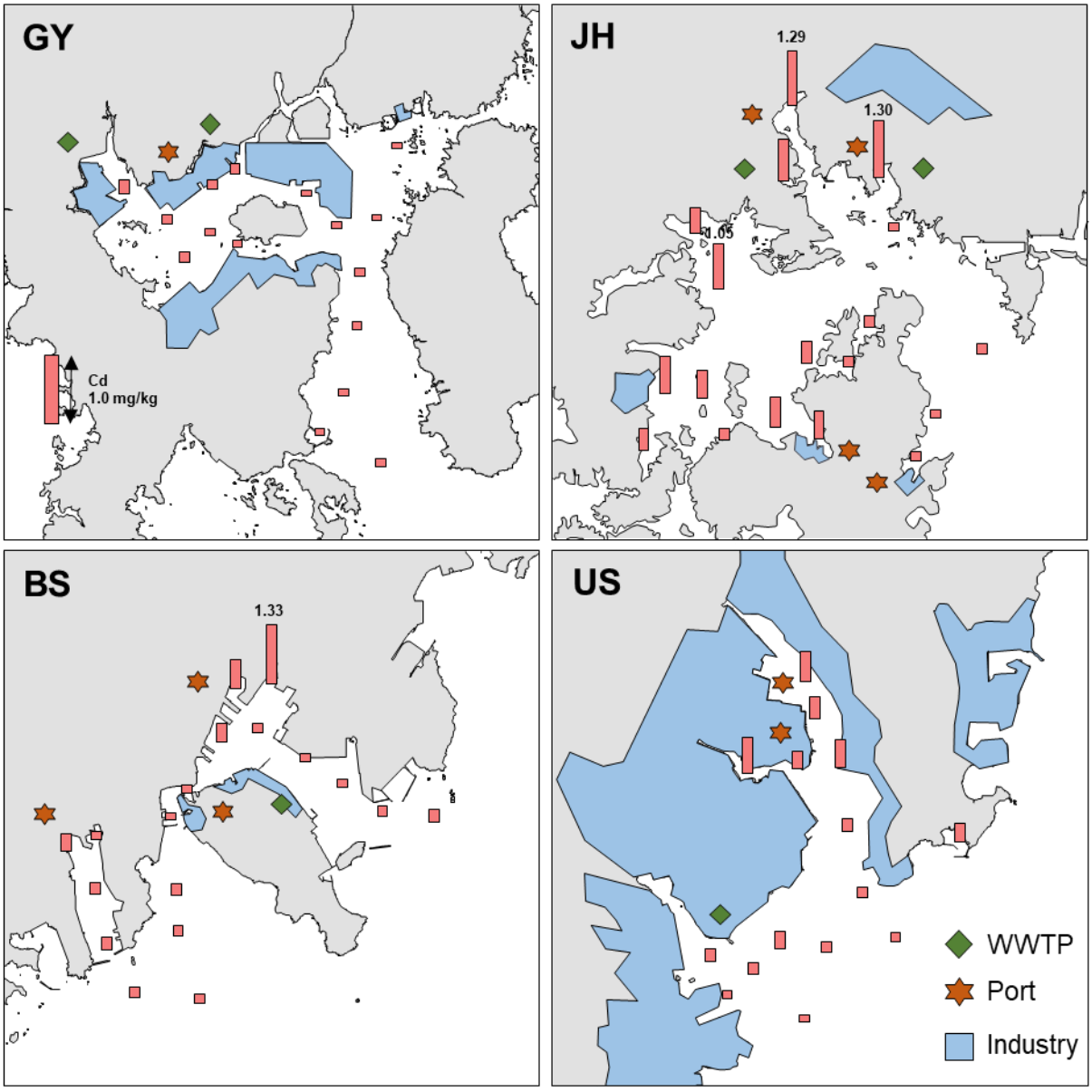

Figure S1. Spatial distribution of Cd in four regions.

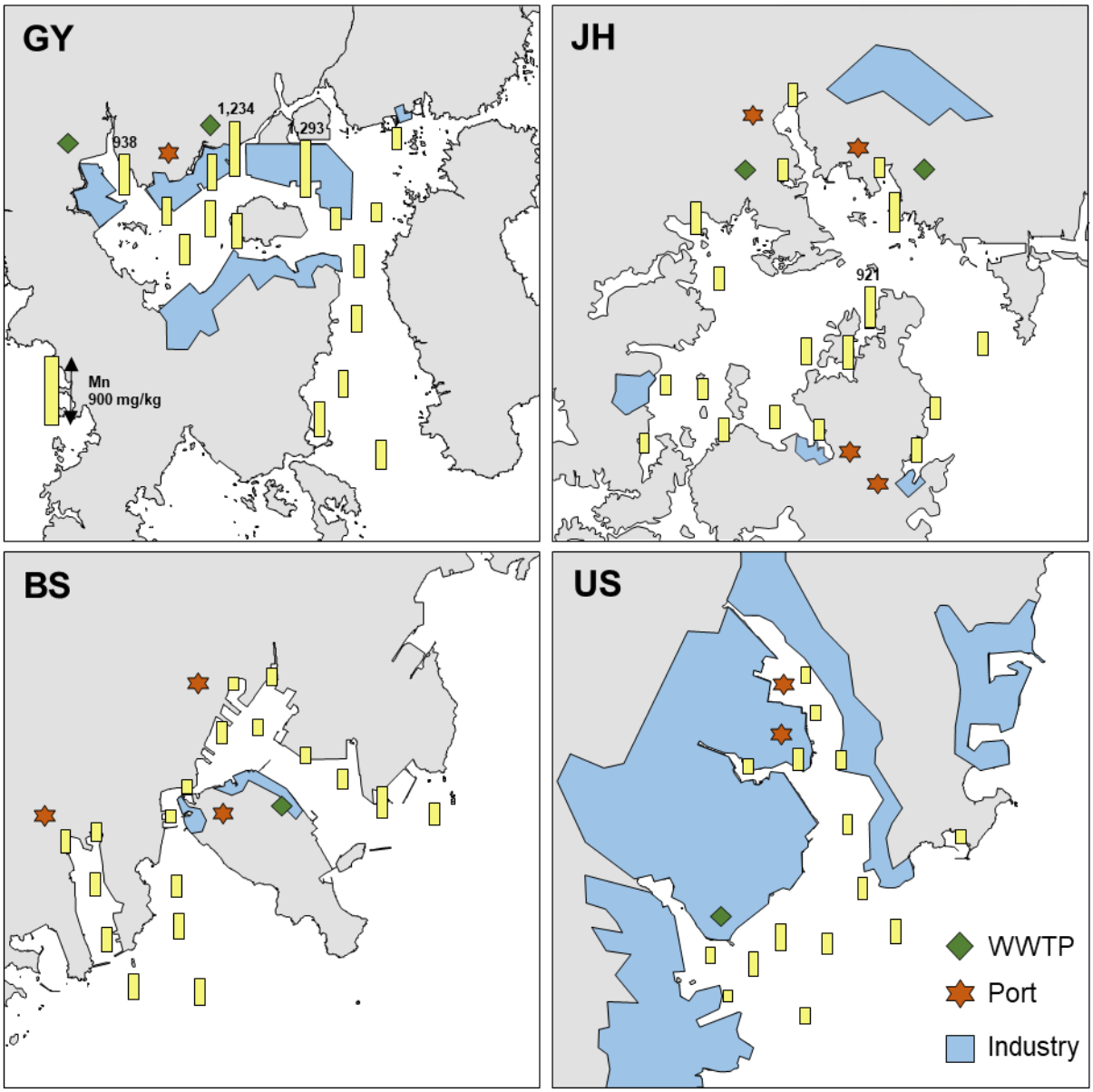

Figure S2. Spatial distribution of Mn in four regions.

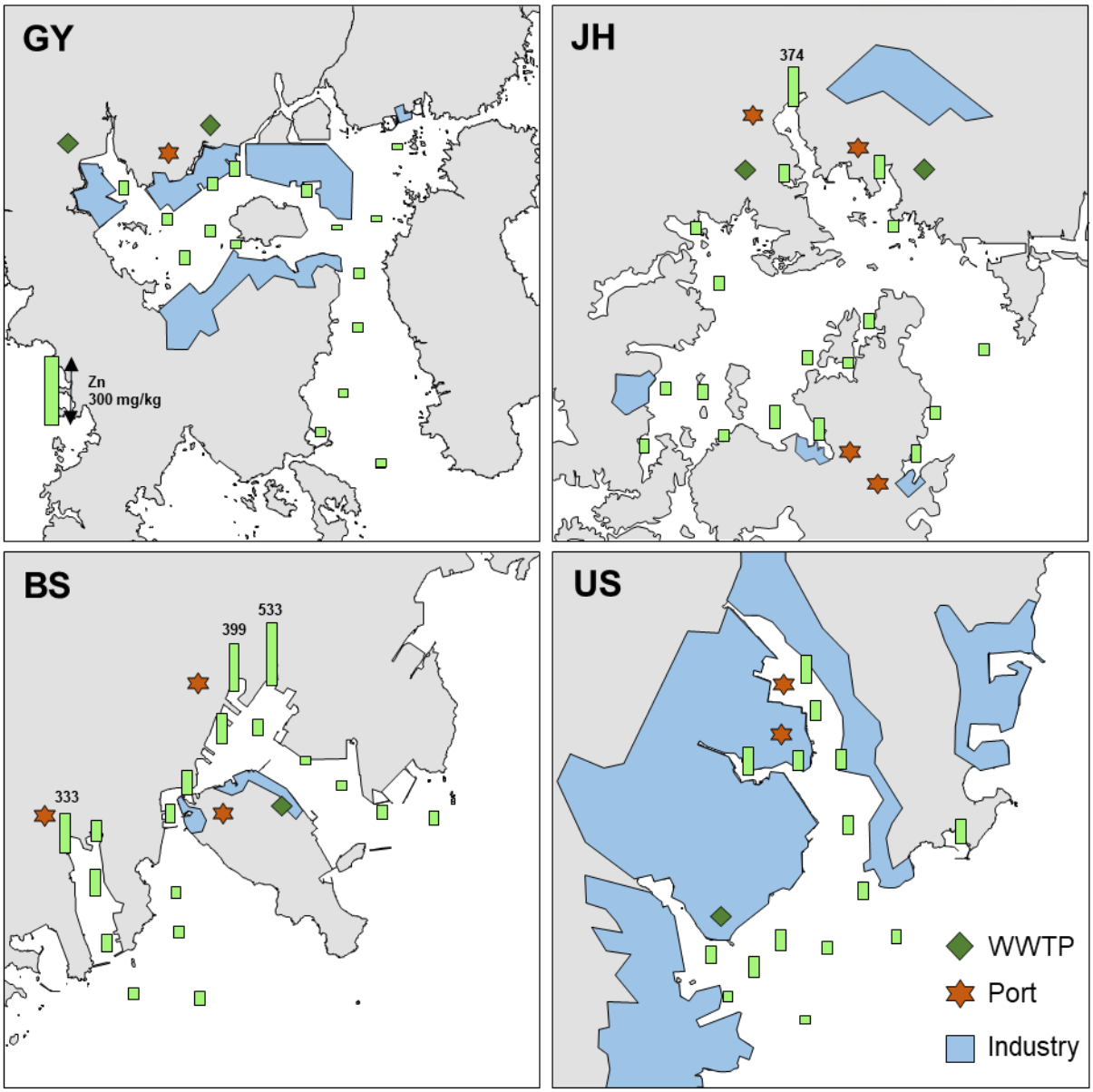

Figure S3. Spatial distribution of Zn in four regions.

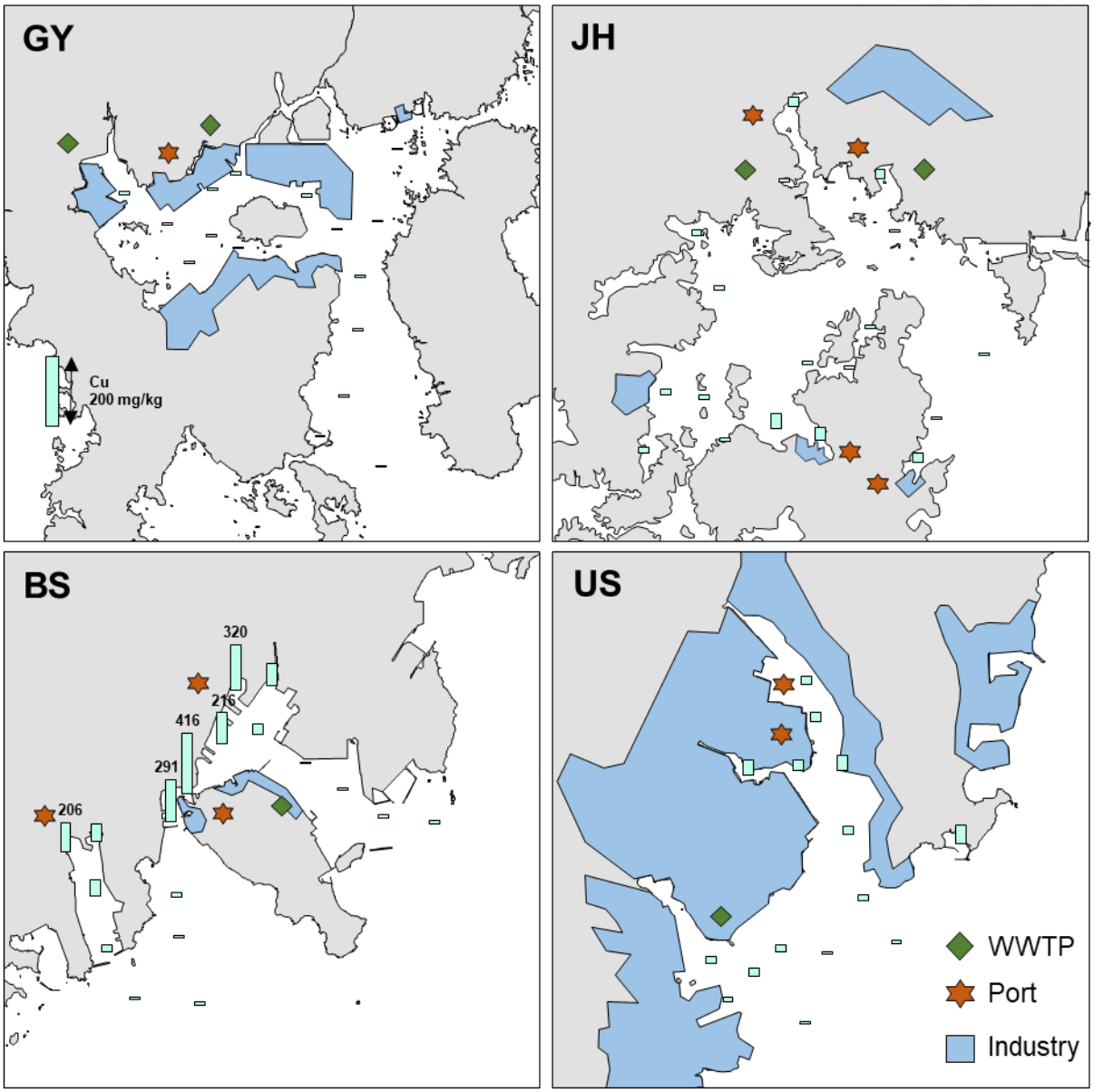

Figure S4. Spatial distribution of Cu in four regions.

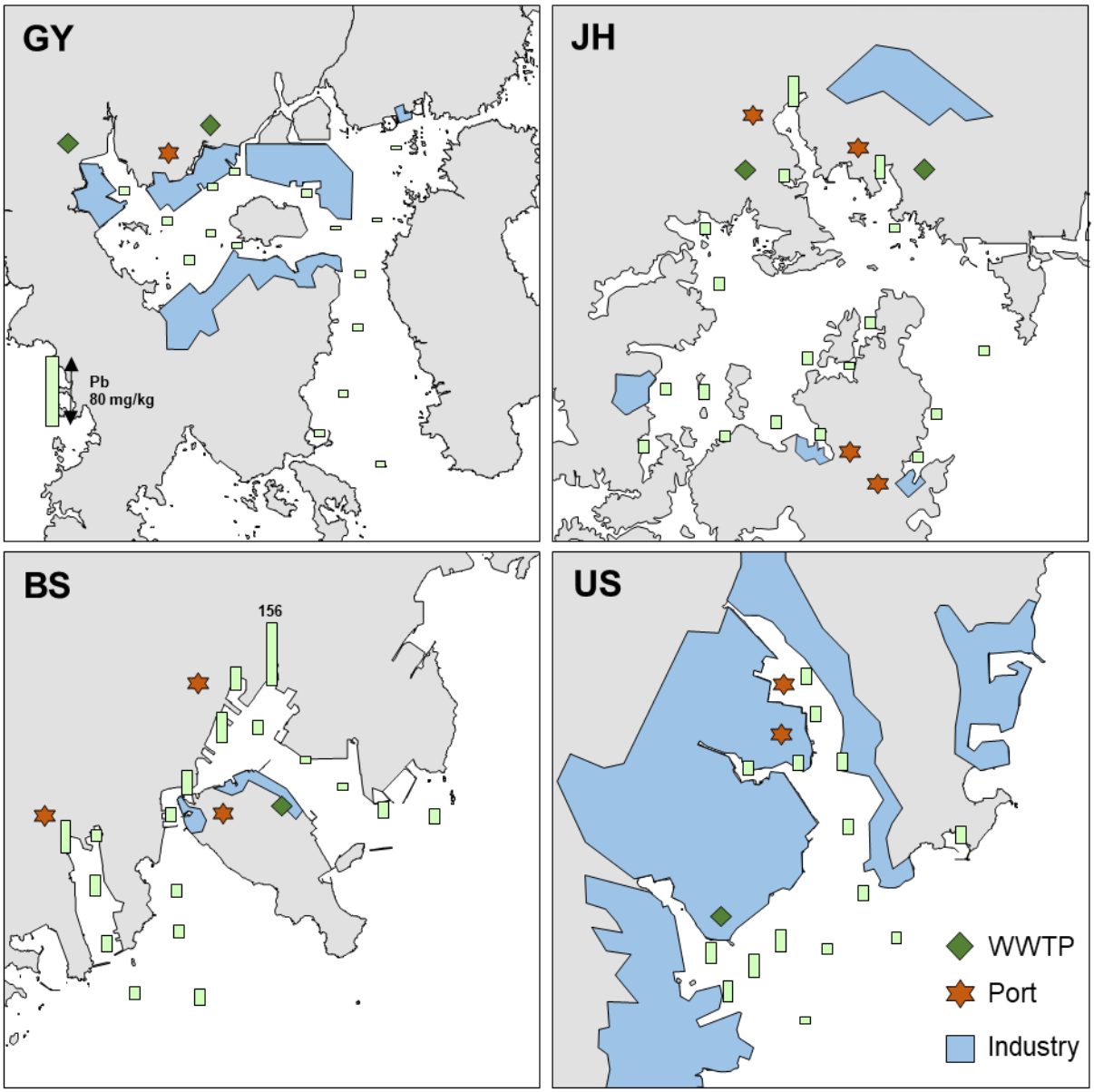

Figure S5. Spatial distribution of Pb in four regions.

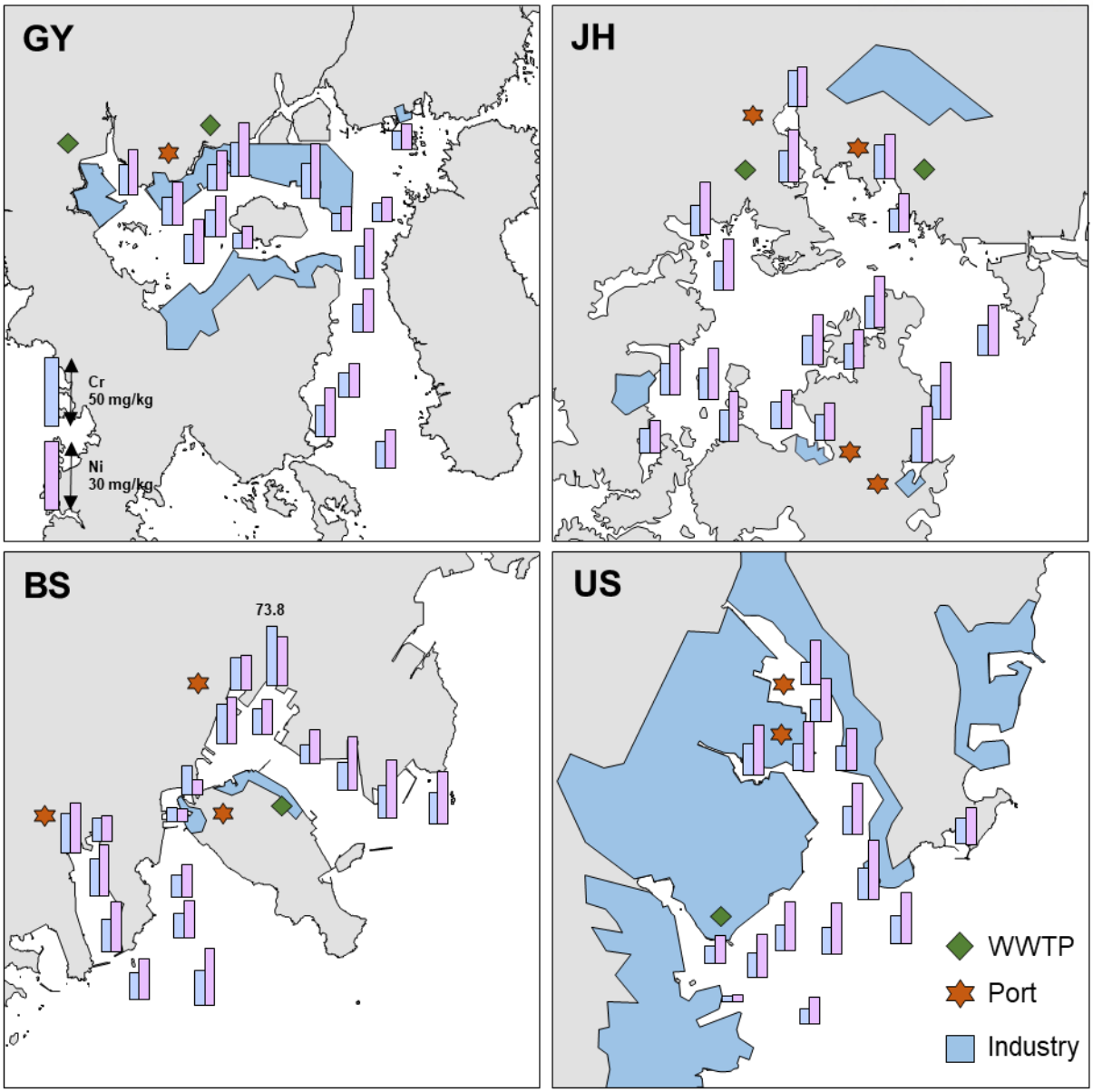

Figure S6. Spatial distribution of Cr and Ni in four regions.

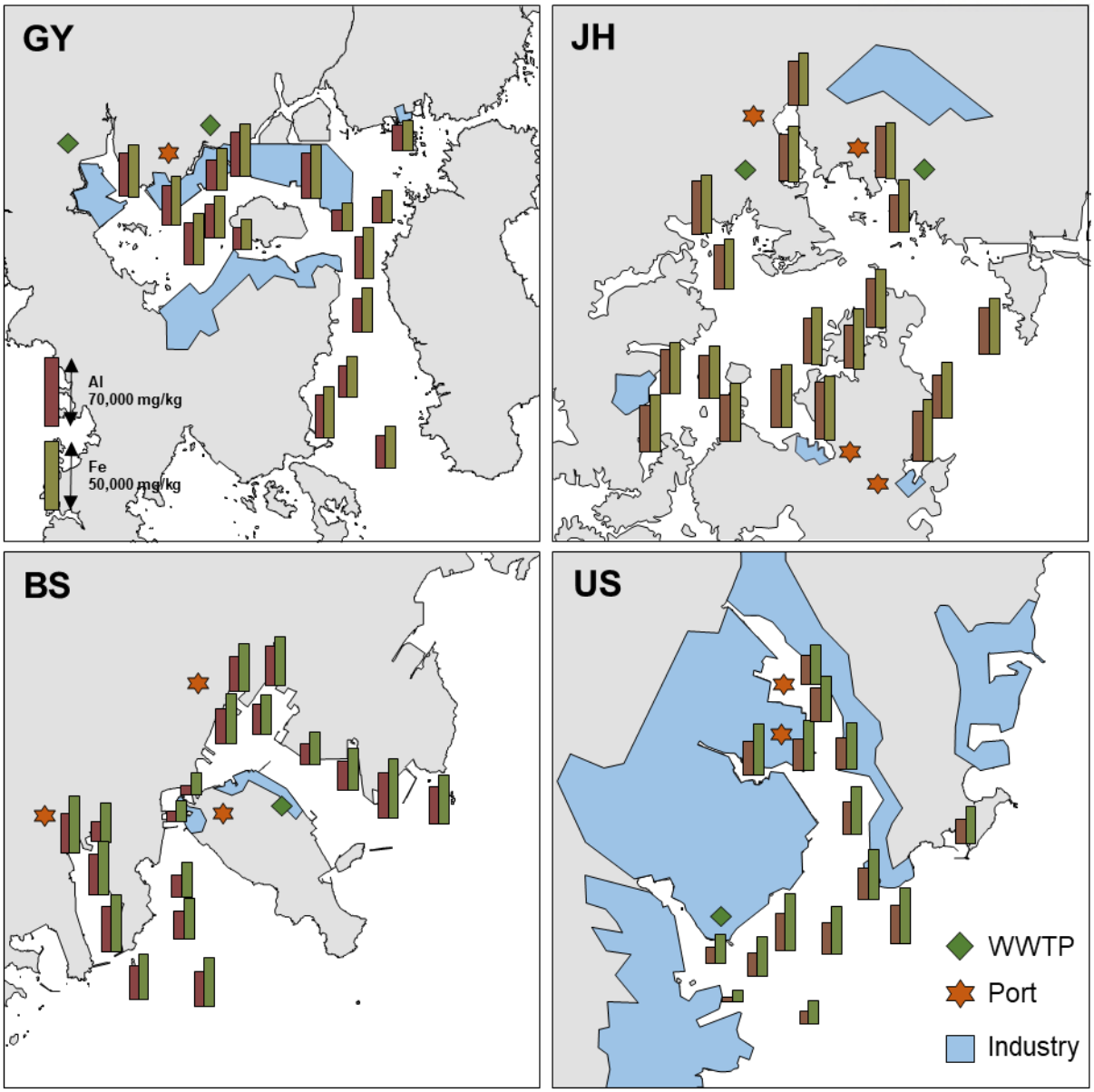

Figure S7. Spatial distribution of Al and Fe in four regions.

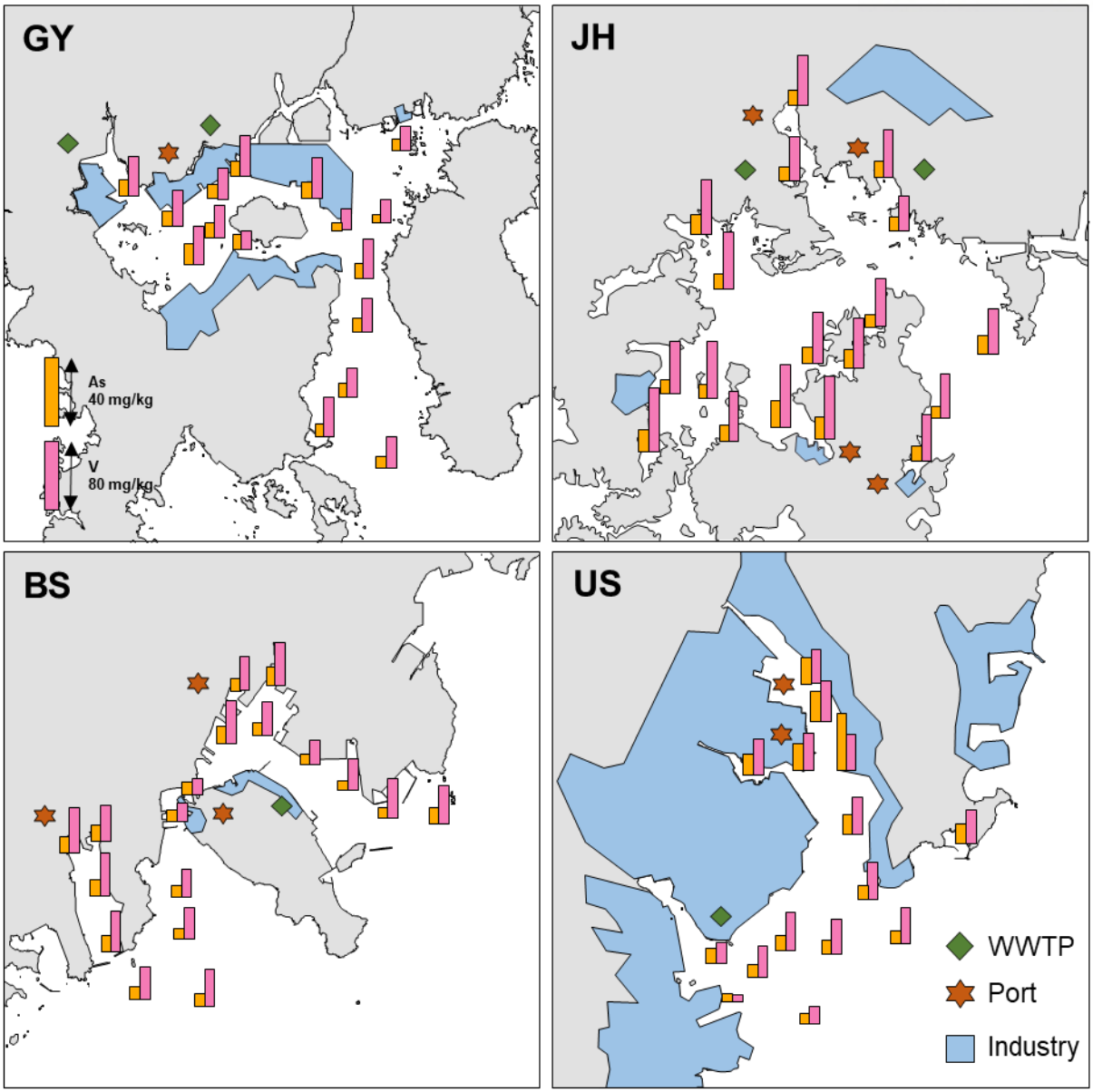

Figure S8. Spatial distribution of As and V in four regions.

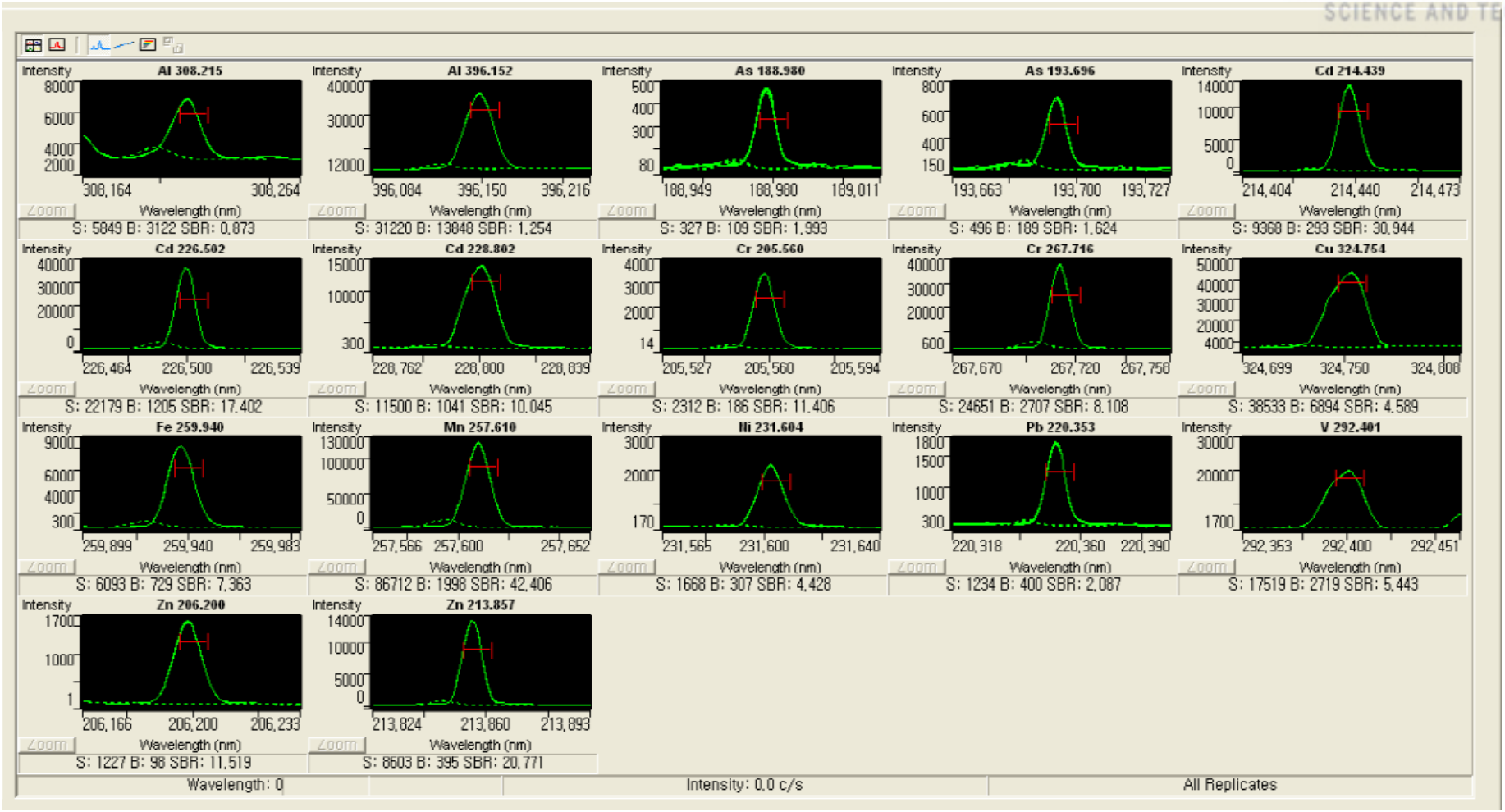

Figure S9. Chromatogram of heavy metal standard.

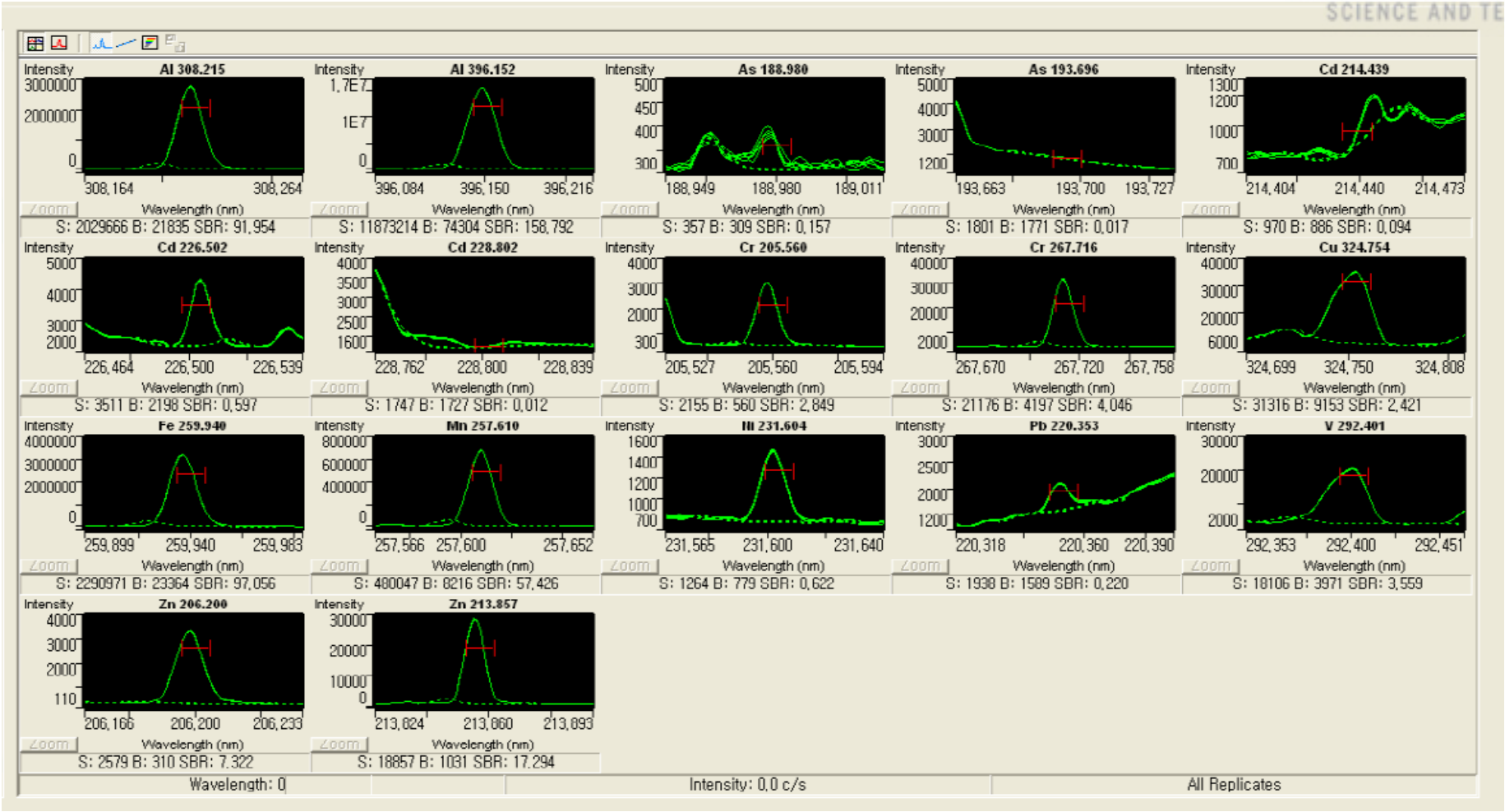

Figure S10. Chromatogram of heavy metals in sediment sample.

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설렘과 두려운 마음을 가지고 EACL 연구실에 처음 방문한 그날, 이 연구실에 잘 적응하여 무사히 졸업할 수 있을지를 고민하던 제가 어느새 2년이라는 시간이 지나 졸업을 하게 되었습니다. 이 분야에서 성장하면서 좋은 결실을 맺을 수 있었던 건 많은 사람들의 도움 덕분입니다.

먼저, EACL 연구실로의 입학을 허락해 주신 최성득 교수님께 감사의 인사를 전하고 싶습니다. 상담 요청이나 질문할 내용이 있어 찾아갈 때마다 아낌없는 조언을 주시며 방향성을 제시해준 교수님의 지도는 연구를 진행할 때 큰 도움이 되었습니다. 학부 전공이 다름에도 환경분석화학 분야에 대한 지식을 거부감 없이 얻을 수 있었던 것은 교수님의 훌륭한 가르침 덕분입니다.

학위논문 심사를 맡아 주신 이창수 교수님과 배효관 교수님께도 감사의 인사를 표합니다. 교수님들께서 주신 소중한 조언 덕분에 학위 논문을 잘 마무리할 수 있었습니다.

2년 동안 석사과정을 하면서 같이 지냈던 EACL 구성원들께 감사의 인사를 드립니다. 연구실 생활에 있어서 기초적인 내용을 알려주셨던 민규 형, 성준이 형, 항상 응원하고 격려해 주시며 여러 가지를 가르쳐 주신 상진이 형, 호영이 형, 처음부터 끝까지 멘토가 되어 아낌없는 조언을 해주었던 인규, 석사과정을 함께하며 서로에게 힘이 되어 주었던 남규, 종현, 질문했을 때 친절하게 답해주었던 Quang, Renato, Tien, Nirmala, Bala, 그리고 언제나 잘 따라주었으며, 본인들이 맡은 일에 책임감 있는 태도로 임하는 상화, 민지, 정태까지 함께 생활하면서 즐거운 추억들을 만들어갈 수 있었습니다. 서로가 바라보는 목표는 다르지만, 언젠가 그 목표를 이루었을 때 서로 웃는 얼굴로 볼 수 있는 날이 오기를 손꼽아 기다리겠습니다.

UCRF 분석센터에 갈 때마다 환한 미소로 반겨 주셨던 선생님들께도 감사를 표합니다. 김철수 선생님, 손희식 선생님, 예 진 선생님, 이윤세 선생님, 그리고 권도규 선생님 덕분에 실험과 기기분석에 대한 지식을 쌓을 수 있었습니다. 항상 좋은 일만 가득하셨으면 좋겠습니다.

마지막으로, 제가 힘들어 할 때마다 든든한 버팀목이자 원동력이 되어주었던 가족들에게 고마운 마음을 전합니다. 언제나 힘이 되어 주는 가족들은 저에게 있어서 가장 큰 자랑이자 축복이었습니다. 항상 행복이 충만하길 빌며 이만 감사의 글을 줄이도록 하겠습니다.

다시한번 도움을 주신 모든 분들께 감사의 인사를 드립니다.