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Assessment of Heavy Metals Eluted from Materials Utilized in Artificial Reefs Implemented in South Korea

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Abstract: In this study, we aimed to investigate the effect of artificial reefs (ARs) made from concrete, steel, and steel slag on the concentrations of As, Cd, Cr^{6+}, Cu, Hg, Ni, Pb, and Zn in marine ecosystems. We conducted a field investigation of the concentration of heavy metals (HMs) in seawater and marine organisms in the East Sea, South Korea and complemented it with an indoor elution experiment. The concentrations of the eight HMs in the field investigation and elution experiment satisfied the environmental standards. In the elution experiment, elution of Cr^{6+} from the concrete models was confirmed; however, it may be insignificant in marine ecosystems. These results revealed that the effect of ARs made from concrete, steel, and steel slag on the concentration of HMs in the marine environment was insignificant.

Keywords: seawater; marine organism; concrete; steel; steel slag

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1. Introduction

The macro-algae forests in the ocean are major components of the ocean material cycle as a primary producer, and they also provide habitat and spawning grounds for fish [1]. Antoine de Ramon et al. [2] reported that macro-algae forests can remove 53 billion tons of CO_2 per year if they cover 9% of the ocean. Macro-algae forests contribute to a healthy ocean ecosystem as well as an increase in blue carbon; however, they are vanishing due to an increase in seawater temperature caused by global warming [3,4]. Ocean afforestation projects with artificial reefs (ARs) are being widely adopted worldwide as a countermeasure against the dilemma of the vanishing of macro-algae forests. Many studies on afforestation or reforestation using AR have shown successful results by acting as artificial substrata for macro-algae [5–7].

AR is defined as a human-created underwater structure. They are typically formed to promote the renewal of marine organisms (e.g., fish, shellfish, and seagrass). Over 40 countries have implemented ARs to continuously use and protect fishery resources [8–10]. AR projects in South Korea started in 1971, and as of 2019, a total of 229,733 ha of ARs had been installed [11]. Various ARs are being developed to improve their capabilities and cost-effectiveness, and 87 types of AR have been developed and installed in the coastal seas of South Korea [12,13]. Concrete is primarily used as an AR material because it is cost-effective and easy to mold [14]. Other opportunity materials are also being used to reduce material costs and to recycle by-products [15]. In the U.S., most steel reefs are built from abandoned structures, such as decommissioned vessels, petroleum platforms, and bridges [16]. Triton ARs, which were developed with steel slag by POSCO and RIST corporations, are installed on Ulleung Island in South Korea to foster macro-algae forests [17,18]. Along with the diversification of materials utilized in ARs, the adverse effects of ARs on marine ecosystems are an emerging problem. While there are many studies on the effect of ARs on marine ecosystems [15,19–21], quantitative evaluation of heavy metal (HM) elution from ARs is limited.

The HM contamination of the ocean is a concern at a local as well as a global scale because of their permanence and toxicity [22,23]. HMs can cause biological accumulation and a reduction in species diversity and abundance in marine ecosystems [24]. HMs not only degrade marine ecosystems but also affect humans. Critically high concentrations of HMs in seawater and marine organisms may cause concerns for humans who rely on marine resources for space, recreation, and food [25]. Most HMs in the coastal sea were introduced from rivers and non-point sources in an anthropogenic manner [26]. Fowler [27] reported that coastal seas located near densely populated areas typically have the highest HM concentrations. To cope with HM contamination, it is necessary to monitor and account for the factors that likely lead to high HM concentrations.

In this study, we investigated the effect of ARs, which were made from concrete, steel, and steel slag, on the concentrations of eight HMs (As, Cd, Cr^{6+}, Cu, Hg, Ni, Pb, and Zn) in seawater and in marine organisms. An indoor elution experiment was also conducted to quantitatively evaluate the HM elution from the materials employed in ARs. Our results provide researchers and professionals with knowledge of the environmental safety of AR.

2. Materials and Methods

2.1. Concentrations of Heavy Metals in Seawater and Marine Organisms

The study area was the east coast of South Korea with a depth of 5–24 m. In this region, afforestation projects with artificial reefs were conducted every year to restore coastal environments damaged by coral bleaching [28]. In 2019, 62,513 ha of artificial reefs were installed, however, there are no studies on the relationship between ARs and HMs [12]. We selected six AR sites for the field experiment, consisting of three materials and two installation years. The materials used were concrete, steel, and steel slag, and the installation years were 2016 and 2020. Natural rock 1 km from the AR site was considered as a control site. The locations and depths of the sites are listed in Table 1 and shown in Figure 1. The cases were identified as follows: concrete AR-control (CC), concrete AR-built in 2016 (C16), concrete AR-built in 2020 (C20), steel AR-control (SC), steel AR-built in 2016 (S16), steel AR-built in 2020 (S20), triton AR-control (TC), triton AR-built in 2016 (T16), triton AR-built in 2020 (T20). Triton AR represents the AR made with steel slag. We compared the concentrations of HMs in the AR sites with those in the control sites. The results of S16 were compared with those of CC, considering location. We also checked whether the concentration of HMs at the AR sites satisfied the environmental standard values. The marine ecosystem protection standards (MEPS) of South Korea [29] were adopted as criteria for HMs in seawater, and the standards of eight countries for the allowed concentration of HMs in shellfish and mollusks (SACHM) were considered for HMs in marine organisms [30]. The standard values of the MEPS and SACHM are listed in Table 2.

Table 1. Location and depth of sites for control and experiment.

Cases		Latitude (N)	Longitude (E)	Depth (m)
Concrete AR	CC	36°09.168′	129°24.097′	5
	C16	36°09.126′	129°24.155′	10
	C20	36°08.974′	129°24.035′	10
Steel AR	SC	35°35.026′	129°27.930′	10
	S16	36°09.485′	129°24.572′	19
	S20	35°34.611′	129°28.068′	24
Triton AR	TC	36°09.824′	129°24.234′	11
	T16	36°09.826′	129°24.214′	9
	T20	36°09.682′	129°24.278′	13

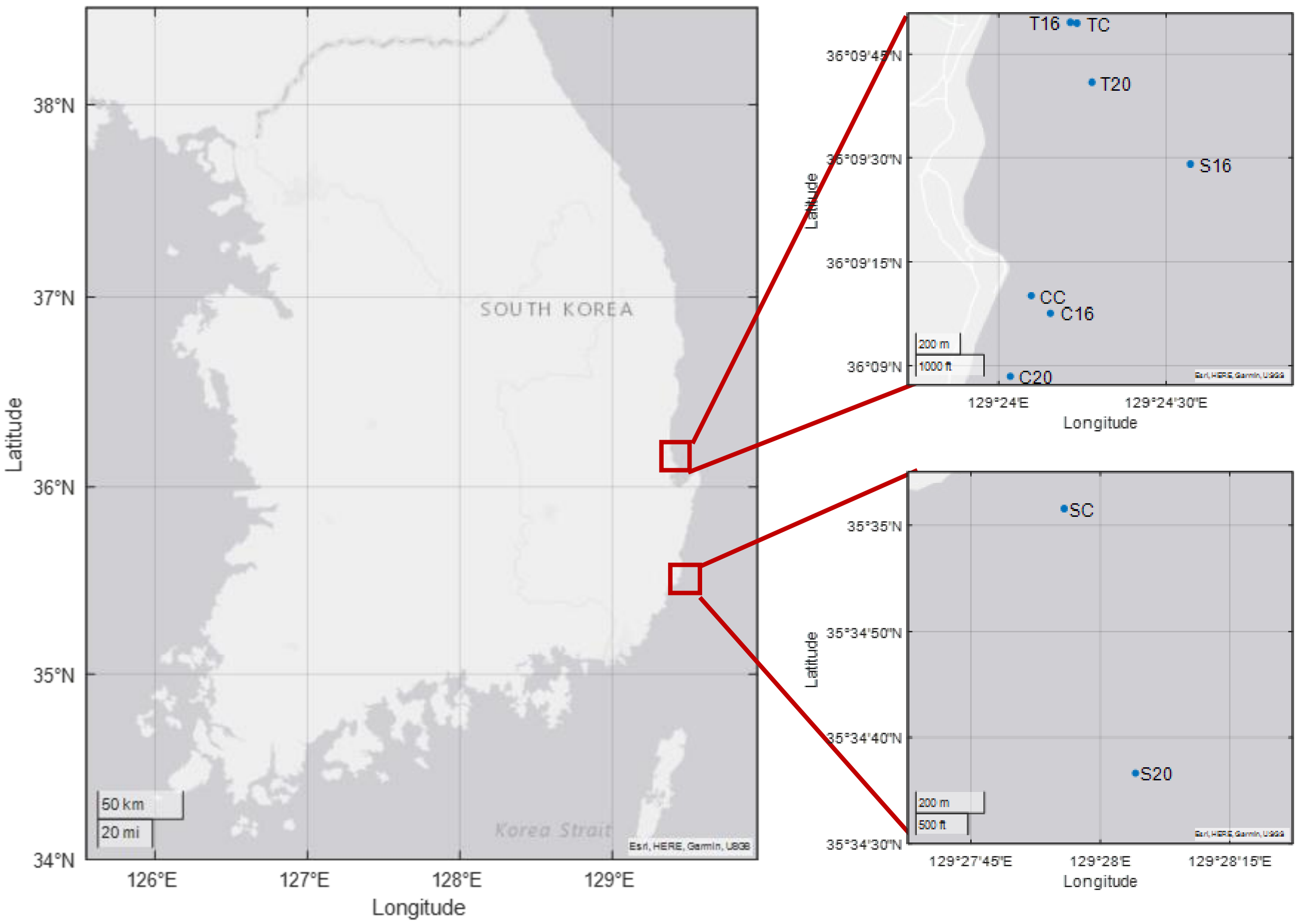

Figure 1. Location of the AR and control sites.

Table 2. Standards for concentration of HMs in seawater and marine organisms.

Standards for Concentration of HMs		As	Cd	Cr^{6+}	Cu	Hg	Ni	Pb	Zn
MEPS for HMs in seawater ($\mu g\ L^{-1}$)	Short-term [1]	9.4	19	200	3.0	1.8	11	7.6	34
	Long-term [2]	3.4	2.2	2.8	1.2	1.0	1.8	1.6	11
SACHM for HMs in marine organisms ($mg\ kg^{-1}$)		-	1.0–5.5	-	30–100	0.5–1.0	-	2–10	1000
HPS for in-door elution experiment ($\mu g\ L^{-1}$)		50	10	50	20	0.5	-	50	100

[1] Short-term standards for one-time observation, [2] Long-term standards for annual average. Abbreviations: HMs, heavy metals; MEPS, marine ecosystem protection standards; SACHM, standards for allowed concentrations of heavy metals; HPS, health protection standards of South Korea.

Field sampling of seawater and marine organisms was conducted at the AR and control sites by divers in June 2021, September 2021, November 2021, and Janurary 2022. The water samples were immediately sent to the laboratory (Marine Eco-Technology Institute, MEI, Busan, Korea) in high-density polyethylene (HDPE) bottles, filtered through a glass microfiber filter (GF/C-47, Whatman, London, UK), and analyzed for the concentration of HMs except for Hg in seawater using an auto-meter (SeaFAST SP3 System, ESI, Omaha, NE, USA). The Hg concentration was determined using a Hg analyzer (PSA 10.025 Millennium Merlin, PS Analytical, Deerfield Beach, FL, USA). Marine organisms, which were weak-mobility species attached to the AR and natural rock, were collected by a diver and immediately sent to the laboratory (Eco Technology, Busan, Korea). The concentrations of HMs, except Hg, in marine organisms were analyzed using ICP-MS (iCAP Q, Thermo Scientific, Waltham, MA, USA) after the destruction process, and Hg was determined using a Hg analyzer (DMA-80, Milestone, Sorisole, Italy). We conducted ANOVA and *t*-test to determine whether there was a significant difference between the results (e.g., between the AR and control sites).

2.2. In-Door Elution Experiment

In the field, it is challenging to quantitatively evaluate the effect of AR on the marine environment because of the advection process generated by the current. Therefore, we conducted an indoor elution experiment for HM elution from the materials utilized in the ARs. The AR models for the experiment were made of concrete (KS L 5201), steel (SUS304), and steel slag [17] with a size of $20 \times 20 \times 6$ cm^3. The experiment was conducted to represent the natural environment and was thus conducted in consideration of natural seawater and a 100% water exchange rate per day for 30 days. The natural seawater used in the experiment was collected from the southern sea of South Korea (35.0988° N, 129.1228° E) and filtered through a glass microfiber filter (GF/C-47, Whatman) before the experiment. The experiment was conducted using 20 L water tanks, and the water temperature was fixed at 20 ± 2 °C. The pH and oxidation-reduction potential (ORP) were measured using an auto-meter (YSI-ProDSS), and the concentrations of the eight HMs were analyzed using the same method used for field sampling. We compared the results of the experiment with their control case, which was only seawater without AR models, and tested whether the concentration of HMs satisfied the health protection standards (HPS) of South Korea [29] (Table 2).

3. Results

3.1. Concentrations of Heavy Metals in Seawater

A heat map of the HM concentrations in seawater collected at the AR and control sites is shown in Figure 2. All concentrations of HMs in seawater showed no significant difference between the AR sites (*p*-values of ANOVA analysis > 0.05). The As concentration of S16 in June 2021 was 1.639 μg L^{-1}; which was 0.427 μg L^{-1} higher than that of the CC. The Cd concentration at the AR sites ranged from 0.011–0.034 μg L^{-1}. The Cr^{6+} concentrations of S20 and T20 in June 2021 were 0.425 μg L^{-1}, which were higher than those of SC and TC. The Cu concentrations of C16 in 2021.09, T20 in November 2021, and S16 in Janurary 2022 were higher than those in the control sites. The Hg concentrations in all periods and sites were less than 0.002 μg L^{-1}, except for June 2021. The Hg concentration at AR sites in June 2021 was 0.005–0.010 μg L^{-1}. The Ni concentration at T20 in June 2021 was 1.117 μg L^{-1}, which was higher than those of TC and T16. The Ni concentrations at S20 in all periods were higher than those in SC. The Pb concentration of C16 in June 2021 was 0.931 μg L^{-1} which was higher (by 0.380 μg L^{-1}) than that of CC. The Zn concentration in C16 in June 2021 was 7.048 μg L^{-1}. This was higher than other observations.

All HM concentrations in seawater collected at the AR sites satisfied the MEPS and showed no significant difference from their control case (*p*-values of *t*-test > 0.05). In the seasonal comparison, the concentrations of Cd, Cr^{6+}, and Hg observed in June 2021 were higher than in other periods. The concentrations of HMs in seawater collected at the AR sites built in 2016 and 2020 showed no significant difference (*p*-values of *t*-test > 0.05).

3.2. Concentrations of Heavy Metals in Marine Organisms

A heat map of the HM concentrations in marine organisms attached to AR sites and natural rocks is shown in Figure 3. The species of *Hypsogastropoda*, *Mytilus coruscus*, *Halocynthia roretzi*, and *Styela clava* were collected. Marine organisms were not detected at C16 and S20 in June 2021. The HM concentration in marine organisms was defined as the HM weight per wet weight of the marine organism.

(a) Concentration of HMs in seawater ($\mu g\ L^{-1}$)

Date	Site	As	Cd	Cr^{6+}	Cu	Hg	Ni	Pb	Zn
2021.06	CC	1.212	0.024	0.316	0.44	0.007	0.443	0.551	7.685
	C16	1.181	0.024	0.294	0.509	0.01	0.397	0.931	7.048
	C20	1.321	0.022	0.276	0.324	0.005	0.248	0.05	1.13
	SC	1.315	0.021	0.304	0.244	0.007	0.281	0.052	0.689
	S16	1.639	0.029	0.418	0.335	0.007	0.311	0.1	2.668
	S20	1.263	0.034	0.425	0.504	0.008	0.578	0.076	2.869
	TC	1.535	0.024	0.344	0.331	0.008	0.268	0.077	1.57
	T16	1.41	0.024	0.266	0.376	0.006	0.327	0.281	3.708
	T20	1.528	0.026	0.425	0.453	0.009	1.117	0.403	3.781
2021.09	CC	1.345	0.012	0.105	0.354	0.001	0.263	0.163	0.872
	C16	1.516	0.021	0.233	0.735	0.001	0.389	0.295	5.2
	C20	1.245	0.012	0.139	0.406	0.001	0.349	0.088	1.969
	SC	1.172	0.017	0.132	0.419	0.001	0.352	0.131	1.828
	S16	1.539	0.018	0.16	0.332	0.001	0.323	0.298	1.81
	S20	1.161	0.019	0.125	0.691	0.001	0.598	0.081	3.723
	TC	1.336	0.017	0.161	0.619	0.001	0.314	0.299	2.583
	T16	1.234	0.012	0.213	0.364	0.001	0.292	0.128	1.718
	T20	1.205	0.011	0.147	0.41	0.001	0.306	0.202	1.705
2021.11	CC	1.069	0.032	0.135	0.689	0.001	0.937	0.618	4.484
	C16	1.06	0.028	0.132	0.49	0.001	0.751	0.194	4.102
	C20	1.097	0.028	0.122	0.477	0.001	0.766	0.131	3.236
	SC	1.267	0.021	0.128	0.492	0.001	0.462	0.444	2.91
	S16	1.147	0.021	0.148	0.8	0.002	0.506	0.258	3.06
	S20	1.184	0.026	0.152	0.506	0.001	0.893	0.045	4.769
	TC	1.131	0.027	0.17	0.661	0.001	1.007	0.128	3.534
	T16	1.123	0.025	0.123	0.474	0.001	0.65	0.064	2.662
	T20	1.158	0.026	0.141	0.85	0.001	0.63	0.1	3.239
2022.01	CC	1.413	0.017	0.135	0.689	0	0.257	0.047	2.546
	C16	1.463	0.017	0.132	0.49	0.001	0.232	0.031	0.872
	C20	1.58	0.019	0.122	0.477	0	0.351	0.193	4.049
	SC	1.511	0.021	0.128	0.492	0.001	0.238	0.02	0.658
	S16	1.481	0.017	0.148	0.8	0	0.512	0.137	4.154
	S20	1.449	0.022	0.152	0.506	0	0.805	0.191	1.808
	TC	1.277	0.015	0.194	0.373	0.001	0.325	0.14	1.991
	T16	1.255	0.015	0.146	0.234	0.001	0.24	0.192	1.99
	T20	1.232	0.017	0.17	0.305	0	0.428	0.103	1.994

(b) Concentration of HMs averaged for a year in seawater ($\mu g\ L^{-1}$)

Site	As	Cd	Cr^{6+}	Cu	Hg	Ni	Pb	Zn
CC	1.26	0.021	0.173	0.543	0.002	0.475	0.345	3.897
C16	1.305	0.022	0.198	0.556	0.003	0.442	0.363	4.305
C20	1.311	0.02	0.165	0.421	0.002	0.428	0.116	2.596
SC	1.316	0.02	0.173	0.412	0.002	0.333	0.162	1.521
S16	1.451	0.022	0.219	0.567	0.002	0.413	0.199	2.923
S20	1.264	0.025	0.213	0.552	0.003	0.719	0.098	3.292
TC	1.32	0.021	0.217	0.496	0.003	0.478	0.161	2.419
T16	1.255	0.019	0.187	0.362	0.002	0.377	0.166	2.519
T20	1.281	0.02	0.221	0.505	0.003	0.62	0.202	2.68

Figure 2. (**a**) Heat map of heavy metal concentrations in seawater collected at control and artificial reef sites in June 2021, September 2021, November 2021, and Janurary 2022 and (**b**) averaged for a year.

Concentration of HMs in marine organisms (mg (kg wet wt.)$^{-1}$)

		Species	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
2021.06	CC	Hypsogastropoda	7.259	0.049	0.11	10.28	0.012	0.11	0.134	34.59
	C16	Not detected								
	C20	Mytilus coruscus	2.57	0.227	0.098	1.017	0.002	0.217	0.251	17.48
	SC	Hypsogastropoda	12.87	0.077	0.195	10.89	0.006	0.181	0.202	40.8
	S16	Mytilus coruscus	2.724	0.393	0.097	1.015	0.002	0.223	0.305	19.69
	S20	Not detected								
	TC	Hypsogastropoda	9.145	0.05	0.359	14.22	0.001	0.154	0.201	47.07
	T16	Hypsogastropoda	24.3	0.577	0.12	7.53	0.018	0.079	0.271	42.21
	T20	Hypsogastropoda	9.666	0.084	0.299	11.22	0.001	0.155	0.353	48.36
2021.09	CC	Halocynthia roretzi	6.477	0.124	0.217	1.754	0.034	0.326	0.274	71.96
	C16	Halocynthia roretzi	2.916	0.099	0.066	3.549	0	0.267	0.086	96.74
	C20	Mytilus coruscus	3.954	0.424	0.249	0.992	0.001	0.311	0.242	41.11
	SC	Hypsogastropoda	14.91	0.097	0.511	14.34	0.014	0.216	0.21	30.37
	S16	Mytilus coruscus	4.099	0.55	0.189	1.207	0	0.257	0.333	27.07
	S20	Mytilus coruscus	3.781	0.287	0.712	2.103	0.002	0.81	1.113	20.79
	TC	Halocynthia roretzi	4.71	0.101	0.14	2.121	0.025	0.263	0.18	71.05
	T16	Halocynthia roretzi	2.604	0.089	0.075	3.143	0.002	0.246	0.074	75.56
	T20	Styela clava	1.23	0.021	0.251	1.963	0.001	0.513	0.506	11.96
2021.11	CC	Halocynthia roretzi	1.2	0.081	0.1	1.827	0	0.253	0.251	68.72
	C16	Halocynthia roretzi	1.399	0.144	0.104	1.198	0.001	0.232	0.251	100.8
	C20	Mytilus coruscus	1.714	0.448	0.39	1.259	0.001	0.662	1.78	42
	SC	Halocynthia roretzi	1.4	0.107	0.768	9.709	0	0.714	0.935	105.1
	S16	Mytilus coruscus	2.352	0.534	0.252	1.485	0	0.484	0.697	48.42
	S20	Mytilus coruscus	1.414	0.239	0.705	1.719	0	0.699	0.938	28.12
	TC	Halocynthia roretzi	2.067	0.166	0.098	5.056	0.001	0.3	0.208	117.7
	T16	Halocynthia roretzi	1.715	0.17	0.133	4.914	0.001	0.296	0.207	92.95
	T20	Styela clava	2.854	0.05	0.331	2.555	0	1.232	0.67	17.89
2022.01	CC	Halocynthia roretzi	1.156	0.067	0.061	2.133	0.006	0.183	0.124	56.59
	C16	Halocynthia roretzi	0.233	0.017	0.009	0.517	0.001	0.036	0.034	11.33
	C20	Mytilus coruscus	0.799	0.168	0.108	0.604	0.006	0.1	0.226	14.58
	SC	Halocynthia roretzi	1.693	0.086	1.928	10.5	0.011	1.316	1.841	70.76
	S16	Mytilus coruscus	1.214	0.285	0.131	0.721	0.01	0.122	0.401	24.34
	S20	Mytilus coruscus	1.546	0.212	0.792	1.531	0.006	0.664	0.669	21.12
	TC	Halocynthia roretzi	1.474	0.087	0.232	2.993	0.007	0.292	0.296	60.01
	T16	Hypsogastropoda	1.024	0.072	0.691	8.705	0.008	0.312	0.43	28.46
	T20	Halocynthia roretzi	1.625	0.108	0.413	4.978	0.006	0.422	0.705	87.78

Figure 3. Heat map of the concentrations of heavy metals in marine organisms attached to the natural rock (control case) and artificial reefs.

The As concentration in *Hypsogastropoda* collected at T16 in June 2021 was 24.3 mg kg^{-1}; which was higher than 9.145 mg kg^{-1} of TC, but this was a temporary result. During other periods, the As concentrations of T16 were lower than those of TC.

Mytilus coruscus was collected at S16 in all periods, and the Cd concentration in *Mytilus coruscus* was higher than that in CC. This could be due to differences in species between S16 and CC. Unlike S16, *Hypsogastropoda* and *Halocynthia roretzi* were detected in CC. The Cd content of *Mytilus coruscus* was 0.011%, which was higher than the 0.002% of *Hypsogastropoda* and 0.001% of *Halocynthia roretzi* (Figure 4).

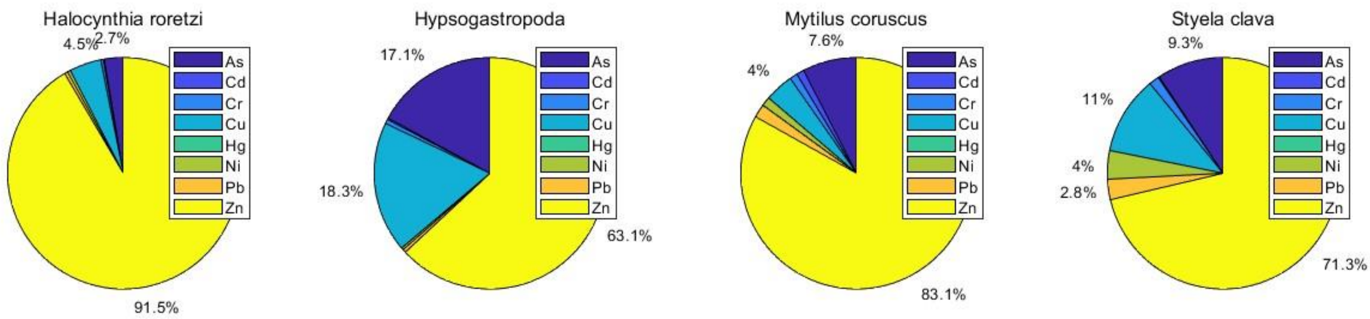

Figure 4. Composition of eight heavy metals of *Halocynthia roretzi*, *Hypsogastropoda*, *Mytilus coruscus*, and *Styela clava*.

The mean value of Cu concentration at the triton AR sites was 5.626 mg kg^{-1}, while those at the concrete and steel AR sites were 1.305 and 1.398 mg kg^{-1}, respectively. The Cu concentration of T16 in Janurary 2022 was 8.705 mg kg^{-1}, which was higher than that at TC (2.993 mg kg^{-1}).

The Hg concentrations at the AR sites were 0.000–0.034 mg kg^{-1}. The Hg concentration of T16 in June 2021 was 0.018 mg kg^{-1}, which was higher than that at TC (0.001 mg kg^{-1}).

The concentrations of Ni in marine organisms collected at S20 and T20 in September 2021 and at C20 and T20 in November 2021 were higher than those in the control case. This could be due to differences in species between the control and AR sites. In the AR sites, *Mytilus coruscus* and *Styela clava* were detected, whereas in the control sites, *Hypsogastropoda* and *Halocynthia roretzi* were detected. The composition of Ni in *Mytilus coruscus* and *Styela clava* was 1.3 and 4.0%, respectively, whereas it was 0.3 and 0.4% for *Hypsogastropoda* and *Halocynthia roretzi*, respectively. The concentrations of Pb in marine organisms collected at S20 and T20 in September 2021, at C20 and T20 in November 2021, and at T20 in Janurary 2022 were higher than in the control case.

The Zn concentration in *Halocynthia roretzi* collected at C16 in November 2021 was 100.8 mg kg^{-1}, which was higher than 68.7 mg kg^{-1} at CC.

All HM concentrations in marine organisms showed no significant difference between AR sites except Cu (p-values of ANOVA analysis > 0.05, except Cu), and all observations satisfied SACHM. At several AR sites, the concentration of HMs in marine organisms was higher than that in their control case, but this could be due to the difference in species between AR and control sites. The HM composition of marine organisms differed depending on the species (Figure 4). The Cd content of *Mytilus coruscus* was higher than that of *Hypsogastropoda* and *Halocynthia roretzi*, and the composition of Ni in *Mytilus coruscus* and *Styela clava* was higher than that of *Hypsogastropoda* and *Halocynthia roretzi*. The composition of Cd, Cr, Hg, Ni, and Pb in all species was less than 4.0%, and Zn showed the highest composition of 63.1–91.5%.

We calculated the correlation between the concentration of HMs in seawater and marine organisms to determine whether the concentration of HMs in seawater affected the concentration of HMs in marine organisms (Figure 5). The concentrations of Cr, Cu, Hg, and Pb in marine organisms were negatively correlated with the concentrations in seawater, and the correlations of As, Cd, Ni, and Zn concentrations between marine organisms and seawater were 0.13, 0.16, 0.18, and 0.10, respectively. The effect of HMs in seawater on the concentration of HMs in marine organisms was insignificant in the study area.

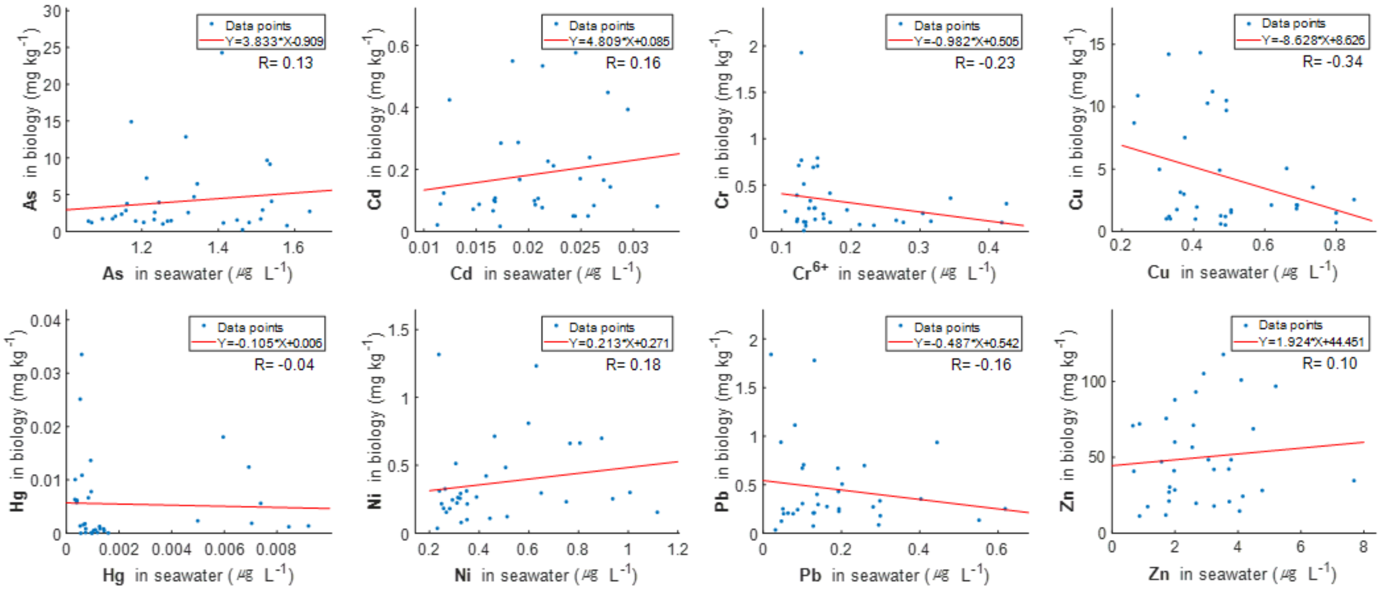

Figure 5. Scatter plots (1:1) and correlation between concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the seawater and marine organisms.

3.3. Indoor Elution Experiment

The changes in pH, ORP, and concentration of HMs in the indoor elution experiment are shown in Figure 6. The pH of seawater in the water tanks for the control and steel AR was 7.86–8.22 and 7.78–8.22, respectively, showing no considerable change during the experiment. Contrarily, the pH of the concrete and triton ARs increased up to 8.94 and 9.40 after four days from initial values of 7.98 and 7.95, respectively. This was caused by the chemical reaction of the calcium oxide (CaO) contained in the cement and steel slag. CaO reacts with H_2O and binds calcium hydroxide ($Ca(OH)_2$). $Ca(OH)_2$ is decomposed into calcium ions (Ca^{2+}) and hydroxide ions (OH^-), resulting in an increase in pH. Cement and steel slag contain 50–60% and 30–60% CaO, respectively [31–33]. The ORP of concrete and triton AR showed no significant difference from the control case, with values of 151.5–207.1 mV and 158.1–232.8 mV, respectively, and the ORP of the control case was 141.6–206.5 mV. The ORP of steel AR showed a repetition of decrease and recovery, which could be due to the corrosion reaction of the iron contained in steel and water exchange, respectively. DO and ORP were reduced on the metal surface during the corrosion reaction [34].

The concentration of eight HMs in the AR cases showed no significant difference from the control case, except for the Cr^{6+} concentration of concrete ARs and Hg concentration of steel AR. The Cr^{6+} concentration of concrete AR after five days was 8.689 μg L^{-1}, which was higher than the 1.096 μg L^{-1} concentration in the control case. The Hg concentration of steel AR after two days was 0.006 μg L^{-1}, which was higher than the 0.002 μg L^{-1} concentration in the control case. However, these results were temporary. The concentrations of the two HMs decreased over time; after nine days, they showed no significant difference from the control case. The Ni concentrations of concrete and triton AR after four days were 4.217 μg L^{-1} and 3.429 μg L^{-1}, respectively, which were lower than the 7.975 μg L^{-1} of the control case, which could be due to the relatively high pH of the AR cases. An increase in pH results in a reduction in Ni concentration [35]. All concentrations of HMs used during the experiment satisfied the HPS.

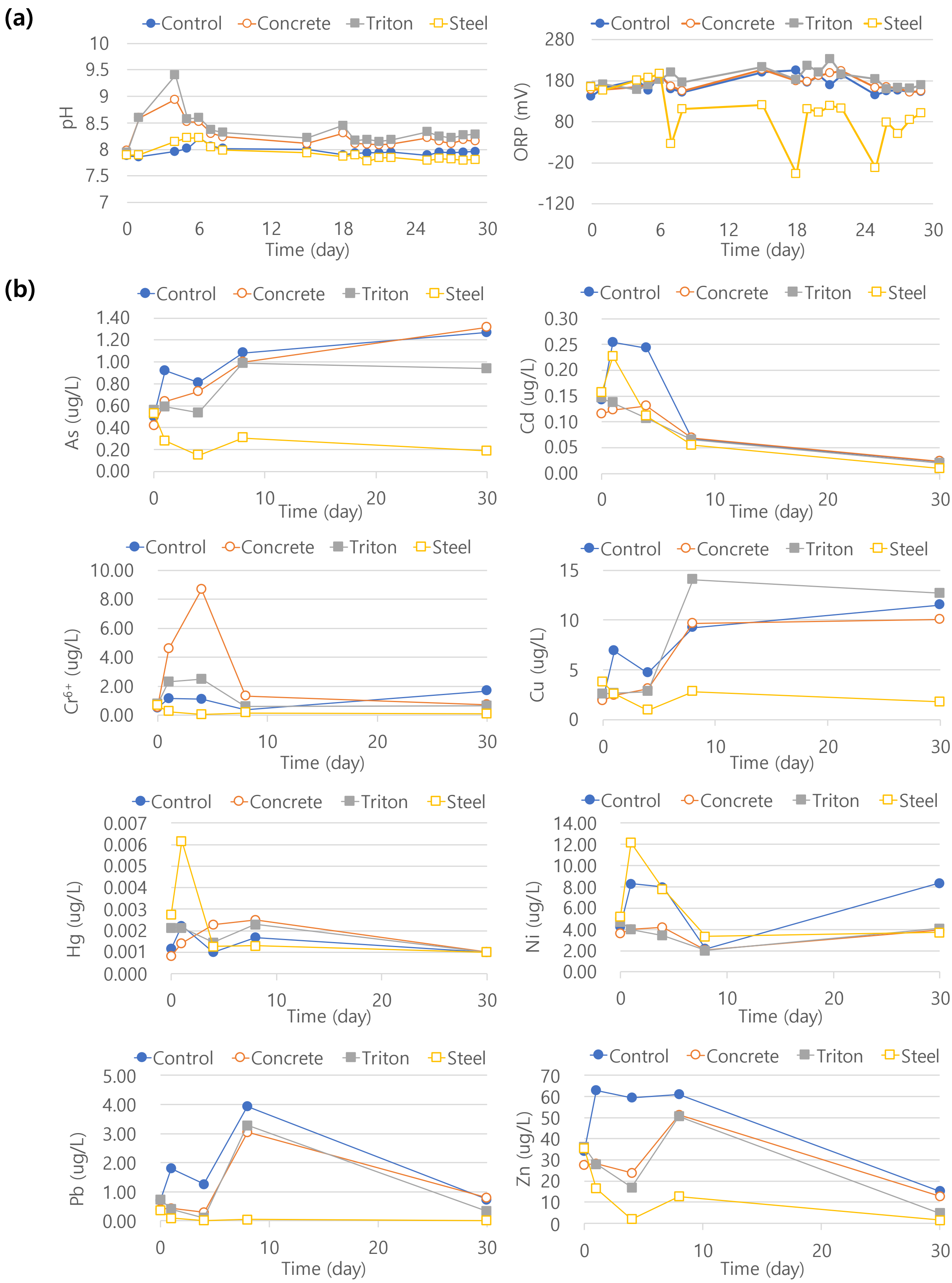

Figure 6. Results of the indoor elution experiment with natural seawater exchange. (**a**) Changes in the pH and ORP and (**b**) the concentrations of heavy metals for the control (without artificial reef model) and artificial reef cases.

4. Discussion

HMs elusion problem of ARs is important because of their permanence and toxicity. Monitoring for HM concentrations is needed to ensure the stability of ARs. Unfortunately, studies on the effects of AR on the HM concentrations in seawater and marine organisms have been neglected. To the best of our knowledge, there are no studies regarding the comparison of HM elution between materials utilized in ARs as well as installation years of ARs.

In this study, there were no significant differences of HM concentrations between the materials as well as the installation years ($p > 0.05$), and all HM concentrations satisfied the environmental standards. These results may ensure the stability of ARs in HM elution. Further, we envisage that the development of eco-friendly material improves the stability of ARs. Eco-friendly concrete with electric arc furnace oxidizing slag is safe in term of leaching of HMs because of chemical bonding in the curing process [36], and environmentally-friendly materials with steel slag developed by JFE Steel Corporation showed a high stability in seawater due to the $CaCO_3$ contained in the materials [37].

The several HM concentrations in marine organisms collected at the AR sites were higher than those in the control site; however, this was stemmed from the difference of species. For instance, the Cd concentration in *Mytilus coruscus* collected at S16 was higher than that in *Hypsogastropoda* and *Halocynthia roretzi* collected at control site, and the Ni concentrations in *Mytilus coruscus* collected at AR sites was higher than those in *Hypsogastropoda* and *Halocynthia roretzi* collected at control site. We showed the HM concentrations and contents (%) in the marine organisms in Section 3.2. Likewise, the mean Cd concentration in *Mytilus coruscus* collected in the coast of South Korea during 2003–2004 was 0.725 mg kg^{-1}; which was higher than that in the *Hypsogastropoda* (0.041–0.721 mg kg^{-1}) and *Halocynthia roretzi* (0.187 mg kg^{-1}), and the Ni concentration in *Mytilus coruscus* was higher than that in the *Hypsogastropoda* and *Halocynthia roretzi* [38].

5. Conclusions

We investigated the effect of ARs composed of concrete, steel, and steel slag on the concentrations of As, Cd, Cr^{6+}, Cu, Hg, Ni, Pb, and Zn in seawater and marine organisms over a period of a year. The concentrations of HMs in ARs were not only compared with those in the control case, but we also evaluated whether the values satisfied various environmental standards. The concentrations of eight HMs in seawater and marine organisms at the AR sites showed no significant difference from those in the control case and satisfied the environmental standards. Several HMs in marine organisms attached to the ARs showed higher concentrations than their control counterparts; however, this was caused by different species detected in the ARs and control cases. From the indoor elution experiment to quantitatively evaluate the HM elution from materials employed in ARs, it was confirmed that the concentrations of eight HMs in the experiment satisfied the environmental standards under conservative experimental conditions. These results reveal that the effect of ARs made of concrete, steel, and steel slag on the concentration of HMs in the marine environment was insignificant, showing no significant difference from those in the control case and satisfying the various environmental standards. In further investigation, the several limitations in this study such as the difference of species (discussed in Section 3.2) and location of sites (S20) will improved.

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