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Research Paper

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The State of Marine Pollution in the Waters adjacent to Shipyards in Korea - 2. Assessment of the Pollution of Heavy Metals in Seawater around Major Shipyards in Summer 2010

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국내 조선소 주변해역의 해양오염 현황 - 2. 2010년 하계 대형조선소 주변 해수의 중금속오염 평가

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Abstract : *In order to elucidate the current state of marine pollution of heavy metals around major shipyards in Korea, seawater samples were collected at eleven sampling stations and four control stations around 4 major shipyards located in the southeastern coast of Korea in summer 2010, and 6 kinds of metals such as copper(Cu), zinc(Zn), iron(Fe), cadmium(Cd), lead(Pb) and mercury(Hg) in seawater samples were analyzed. The analyses of heavy metals in seawater showed that the mean Cu concentrations in seawater around 4 major shipyards were in the range of 0.817∼1.638 ㎍/L which were lower than Korean environmental standards of 20 ㎍/L for the protection of human health(PHH) and of 3 ㎍/L for short-term protection of marine ecosystem(SPME) but higher than Cu concentration at control station by a factor of up to 2.75. The mean Zn concentrations were in the range of 0.228∼0.567 ㎍/L which were lower than Korean environmental standards of 100㎍/L for PHH and 34 ㎍/L for SPME but higher than Zn concentration at control station by a factor of up to 5.91. The mean Fe concentrations were in the range of 3.332∼7.410 ㎍/L which were higher than Fe concentration at control station by a factor of up to 6.75. The mean Cd concentrations were in the range of 0.013∼0.028 ㎍/L which were lower than Korean environmental standards of 10 ㎍/L for PHH and 19 ㎍/L for SPME but higher than Cd concentration at control station by a factor of up to 2.33. The mean Pb concentrations were in the range of 0.007∼0.126 ㎍/L which were lower than Korean environmental standards of 50 ㎍/L for PHH and 7.6 ㎍/L for SPME. The mean Hg concentrations were in the range of 0.002∼0.004 ㎍/L which were lower than Korean environmental standards of 0.5 ㎍/L for PHH and 1.8 ㎍/L for SPME. Although the concentrations of metals such as Cu, Zn and Fe which were used in shipbuilding works were lower than Korean environmental standards for PHH and SPME, the fact that the concentrations of Cu, Zn and Fe at sampling stations around major shipyards were higher than those at control stations implies that the works in shipyards had some effects on marine water quality around shipyards. Therefore, marine environment management such as the prevention and control of the discharge of various pollutants from shipyards is required on national level.*

Key Words : *Marine pollution, Heavy metals, Major shipyards, Environmental standards, Shipbuilding works, Marine environment management*

요 약 : 국내 대형 조선소 주변해역의 중금속오염 현황을 밝히기 위하여 2010년 여름에 4개의 대형 조선소 주변 11개의 채수정점과 4개의 대조정점에서 해수 시료를 채취하여 6종의 금속(Cu, Zn, Fe, Cd, Pb, Hg)을 분석하였다. 조선소별 주변해역 수중의 금속을 분석한 결과, (1) 구리(Cu)의 평균 농도는 0.817∼1.638 ㎍/L로 해역환경기준(사람의 건강보호기준 20 ㎍/L, 해양생태계 보호 단기기준 3 ㎍/L)보다 낮았지만, 대조정점에 비하여 1.64∼2.75배의 높은 값을 나타냈다. (2) 아연(Zn)의 평균 농도는 0.228∼0.567 ㎍/L로 해역환경기준(사람의 건강보호기준 100 ㎍/L, 해양생태계 보호 단기기준 34 ㎍/L)보다 낮았지만, 대조정점에 비하여 1.62∼5.91배의 높은 값을 나타냈다. (3) 철(Fe)의 평균 농도는 3.332∼7.410 ㎍/L로 대조정점에 비하여 1.30∼6.75배의 높은 값을 나타냈다. (4) 카드뮴(Cd)의 평균 농도는 0.013∼0.028 ㎍/L로 해역환경기준(사람의 건강보호기준 10 ㎍/L, 해양생태계 보호 단기기준 19 ㎍/L)보다 낮았지만, 대조정점에 비해 1.18∼2.33배의 높은 값을 나타냈다. (5) 납(Pb)의 평균 농도는 0.007∼0.126 ㎍/L로 해역환경기준(사람의 건강보호기준 50 ㎍/L, 해양생태계 보호 단기기준 7.6 ㎍/L)보다 낮았다. (6) 수은(Hg)의 평균 농도는 0.002∼0.004 ㎍/L로 해역환경기준(사람의 건강보호기준 0.5 ㎍/L, 해양생태계 보호 단기기준 1.8 ㎍/L)보다 낮았다. 비록 모든 중금속의 수중 농도가 해역환경기준보다 낮다고 할지라도, 선박건조작업에 사용되는 구리, 아연, 철과 같은 중금속의 농도가 대조해역에 비해 조선소 주변해역에서 높다는 것은 조선소의 영향에 기인하는 것을 암시한다. 따라서 조선소로부터 각종 오염물질이 해양에 유입되지 않도록 통제하고 해양오염을 방지하는 국가적 차원의 해양환경관리가 필요하다.

핵심용어 : 해양오염, 중금속, 대형조선소, 환경기준, 선박건조작업, 해양환경관리

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1. Introduction

The owner of marine facility shall make a report on such facility to the Minister of Oceans and Fisheries under the provisions of Article 33 of Marine Environment Management Act of Korea. The shipyard means a workplace or facility where ships are built, repaired or broken up, and is designated as a marine facility of item Da of subsection 1 by the table 1 attached to the Enforcement Ordinance of the Marine Environment Management Act.

Total 178 shipyards were reported to be distributed across the country and to account for 26.5 % of all marine facilities, and 45 % of total shipyards were concentrated around southeastern area of Korea, as of the end of the year 2009(Kim, 2010a; Kim, 2010b). Marine environment is, therefore, likely to be deteriorated in this area(Kim and Han, 2014).

Major shipyards took passive attitudes and evaded reporting their facilities to the Minister of Oceans and Fisheries by reason that shipbuilding facility or shipbuilding yard is clearly stipulated in the type of marine facilities but not expressly stated in the scope of marine facilities of item Da of subsection 1 by the table 1 attached to the Enforcement Ordinance of Marine Environment Management Act(MLTM, 2010).

In process of shipbuilding, the potential for the discharge of various metals such as copper(Cu), zinc(Zn) and iron(Fe) from shipbuilding yards to their surrounding waters always exists. It is, therefore, necessary to investigate the current state of pollution of heavy metals in seawater around major shipyards of Korea(Kim and Han, 2014).

In Korea, most of studies and researches for heavy metals in coastal area focused on sediments(Kim et al., 2008a; Kim et al., 2008b; Kim et al., 2012a; Kim et al., 2012b; Kim and Um, 2013; Kim and Jang, 2014) and the concentrations of trace metals in the organs of minke whale were measured by Jeon et al.(2012). Some studies on the vertical distribution and behavior of trace metals in the Pacific, Atlantic and Indian Oceans were conducted by Bruland(1980), Yeats and Campell(1983) and Saager et al.(1992), and a few researches for heavy metals in seawater around Korea were performed by Lee et al.(1984), Kim et al.(2007) and Kim et al.(2008b). It is, however, difficult to find any research for heavy metals in seawater around major shipyards in Korea.

In this study, for the purpose of elucidating the current state of marine pollution of heavy metals around major shipyards in Korea, seawater samples were collected at eleven sampling stations and four control stations around 4 major shipyards which are located in southeastern area of Korea, and six kinds of metals in seawater were analyzed.

The outcomes of this study are expected to be used as a basic reference to establish local or national plans for the prevention of marine pollution around nationwide shipyards of Korea.

2. Reviews of metal-related literatures

2.1 Groups of metals

Metals are natural constituents of seawater. Metals of biological concern may be divided into three groups, namely, light, transitional and heavy metals. Light metals such as sodium, potassium, calcium, etc. are normally transported as mobile cations in aqueous solutions. Transitional metals, for example, iron, copper, cobalt and manganese are essential in low concentrations but may be toxic in high concentrations. Heavy metals such as mercury, lead, tin, selenium and arsenic are generally not required for metabolic activity and are toxic to the cell at quite low concentrations(Clark, 1986).

2.2 Characteristics of metals

Absorption of heavy metals from solutions is dependent on active transport systems in some microorganisms and sea urchin larvae, but generally in plants and animals it is by passive diffusion across gradients created by adsorption at the surface, and by binding by constituents of the surface cells, body fluids, etc.. An alternative and important pathway for animals is when metals are adsorbed onto or are present in food, and by the collection of particulate or colloidal metal by a food-collecting mechanism such as the bivalve gill. There are considerable variation in the extent of which plants and animals can regulate the concentrations of metals in the body. Plants and bivalve mollusca are poor regulators of heavy metals. Decapod crustaceans and fish are generally able to regulate essential metals such as zinc and copper, but nonessentials such as mercury and cadmium are less well regulated(Clark, 1986).

Usually, trace metals exist infinitesimally in natural water such as seawater and fresh water(Bruland et al., 1991), and many are essential for living organisms. Trace metals may, however, be classified as persistent pollutants, because they are hardly degraded in the environment. They have a tendency to accumulate in organisms and to magnify accumulation concentrations higher and higher in organs or tissues of organisms through food chains in ecosystem(Kim et al., 2008b). Heavy metals which flowed into the sea can turn into particulate through biogeochemical cycle, deposit and accumulate on the sediments after all, and may cause biological effect on marine organisms such as benthos which inhabits the sediments(Salomons and Forstner, 1984).

3. Sampling and analysis

3.1 Collection of seawater samples

Seawater samples were collected at three sampling stations(A1, A2 and A3) and one control station(AC) around A-shipyard in Ulsan, at two sampling stations(B1 and B2) and one control station(BC) around B-shipyard in Busan, at three sampling stations(C1, C2 and C3) and one control station(CC) around C-shipyard, and at three sampling stations(D1, D2 and D3) and one control station(DC) around D-shipyard in Geojedo for 5 days from August 2 to August 6, 2010, using specialized online pump with filter for collection of metals on board the ship(Fig. 1).

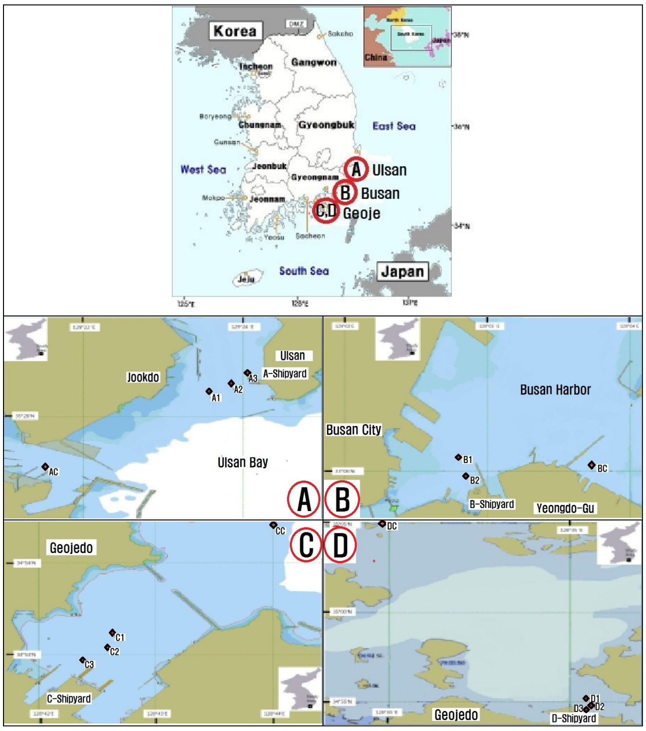

Fig. 1. Sampling stations around 4 major shipyards in Korea.

3.2 Method of analysis

Seawater samples were added by undiluted solution of nitric acid(HNO_3) and pre-treated, and analyzed for copper(Cu), zinc(Zn), iron(Fe), cadmium(Cd) and lead(Pb) by Inductively Coupled Plasma Mass Spectrometer(ICP-MS, Perkin Elmer: Elan 6000). Mercury(Hg) was analyzed by Automatic Mercury Analyzer (AMA-254, Milestone). Analytical results of metal concentration in the SRM(CASS-4, MESS-2) showed the recovery rates to be 97 % (Cu), 98 %(Zn), 99 %(Cd), 95 %(Pb) and 99 %(Hg), respectively.

4. Results and discussion

The results of seawater analyses were shown in Table 1 and the average concentrations of six kinds of metals around four major shipyards were illustrated in Table 2.

Table 1. Analysis results of seawater samples collected around 4 major shipyards in Korea (Unit: μg/L)

Ship-yard	St.	Position		Cu	Zn	Fe	Cd	Pb	Hg
		Lat.(N)	Long.(E)						
A	A1	35°28'25"	129°23'33"	0.814	0.045	2.592	0.025	0.008	0.002
	A2	35°28'38"	129°23'51"	1.636	1.040	5.757	0.031	0.004	0.002
	A3	35°28'46"	129°24'07"	1.297	0.564	13.880	0.029	0.008	0.008
Control	AC	35°27'02"	129°21'29"	0.455	0.105	1.098	0.012	0.026	0.002
B	B1	35°06'06"	129°02'47"	1.253	0.588	5.380	0.019	0.010	0.002
	B2	35°05'58"	129°02'51"	2.022	0.545	6.387	0.021	0.021	0.002
Control	BC	35°06'03"	129°03'44"	0.600	0.349	4.100	0.017	0.072	0.001
C	C1	34°53'14"	128°42'36"	1.317	0.379	6.011	0.019	0.020	0.002
	C2	34°53'04"	128°42'34"	0.551	0.136	2.869	0.012	0.010	0.002
	C3	34°52'56"	128°42'22"	0.584	0.170	1.116	0.007	0.070	0.002
Control	CC	34°54'34"	128°44'00"	0.297	0.041	16.235	0.010	0.052	0.002
D	D1	34°55'03"	128°35'56"	0.871	0.413	4.781	0.015	0.036	0.002
	D2	34°54'57"	128°35'53"	0.926	0.179	3.655	0.013	0.334	0.002
	D3	34°54'50"	128°35'50"	1.506	0.561	7.918	0.019	0.008	0.002
Control	DC	35°05'10"	128°29'06"	0.673	0.065	4.201	0.012	0.012	0.002

4.1 Copper(Cu)

The concentrations of copper at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 2.

The average Cu concentration at three sampling stations A1, A2 and A3 around A-shipyard in Ulsan was 1.249 μg/L and was 2.75 times higher than 0.455 μg/L at control station AC. The average Cu concentration at two sampling stations B1 and B2 around B-shipyard in Busan was 1.638 μg/L and was 2.73 times higher than 0.600 μg/L at control station BC. The average Cu concentration at three sampling stations C1, C2 and C3 around C-shipyard in Geojedo was 0.817 μg/L and was 2.75 times higher than 0.297 μg/L at control station CC. The average Cu concentration at three sampling stations D1, D2 and D3 around D-shipyard in Geojedo was 1.101 μg/L and was 1.64 times higher than 0.673 μg/L at control station DC.

With regard to average Cu concentrations at sampling stations around shipyards, B-shipyard ranked the first by 1.638 μg/L, A-shipyard the second by 1.249 μg/L, D-shipyard the third by 1.101 μg/L, and C-shipyard the fourth by 0.817 μg/L.

The average Cu concentrations at sampling stations around A-shipyard, B-shipyard and C-shipyard were 2.73～2.75 times higher than those at control stations and were very similar to one another, while the average Cu concentration at sampling stations around D-shipyard was 1.64 times higher than that at control station. This implies that lots of copper was used in anti-fouling paint for ships' hulls and this use inevitably resulted in copper being transferred to the marine environment from shipyards.

Despite the existence of a number of detoxifying and storage systems for copper, it is the most toxic metal, after mercury and silver, to a wide spectrum of marine life, hence its value in anti-fouling preparations(Clark, 1986). There is no danger to humans of copper poisoning from seafood. Copper in the sea is not regarded as a health hazard(Clark, 1986).

Around four major shipyards, the Cu concentrations at all sampling stations were 0.551～2.022 μg/L and those at all control stations were 0.297～0.673 μg/L as shown in Table 1. The Cu concentrations at all sampling and control stations were higher than 0.060～0.319 μg-Cu/L in the seawater of the East Sea(Kim et al., 2007), 0.220～0.590 μg-Cu/L in the seawater of Gaduk Channel, Korea(Kim et al., 2008b) and 0.034～0.334 μg-Cu/L in the North Pacific Ocean(Bruland, 1980), and were lower than Korean environmental standards of 20 μg-Cu/L for the protection of human health and of 3.0 μg-Cu/L for short-term protection of marine ecosystem as provided in the table attached to Article 2 of the Enforcement Decree of the Framework Act on Environmental Policy, as shown in Table 2.

Table 2. Comparison of heavy metals between Korean environmental standards of marine environment and mean values observed at sampling stations in seawater around shipyards

Heavy metals	Environmental standards(μg/L)			Ship-yard	Mean values observed (μg/L)	Control (μg/L)
	PHH	SPME	LPME			
Cu	20.0	3.0	1.2	A	1.249	0.455
				B	1.638	0.600
				C	0.817	0.297
				D	1.101	0.673
Zn	100.0	34.0	11.0	A	0.550	0.105
				B	0.567	0.349
				C	0.228	0.041
				D	0.384	0.065
Fe	-	-	-	A	7.410	1.098
				B	5.884	4.100
				C	3.332	16.235
				D	5.451	4.201
Cd	10.0	19.0	2.2	A	0.028	0.012
				B	0.020	0.017
				C	0.013	0.010
				D	0.016	0.012
Pb	50.0	7.6	1.6	A	0.007	0.026
				B	0.016	0.072
				C	0.033	0.052
				D	0.126	0.012
Hg	0.5	1.8	1.0	A	0.004	0.002
				B	0.002	0.001
				C	0.002	0.002
				D	0.002	0.002

PHH: standard for Protection of Human Health
SPME: Short-term standard for Protection of Marine Ecosystem
LPME: Long-term standard for Protection of Marine Ecosystem

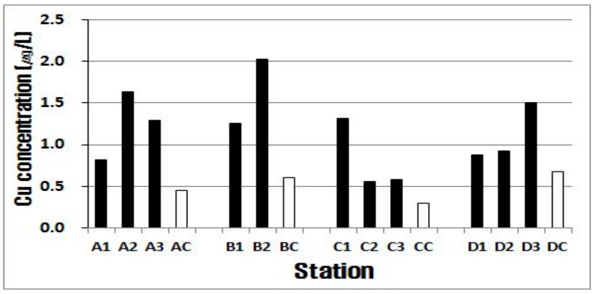

Fig. 2. Comparison of Cu concentrations in seawater between sampling stations and control station.

4.2 Zinc(Zn)

The concentrations of zinc at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 3.

The average Zn concentration at three sampling stations A1, A2 and A3 was 0.550 μg/L and was 5.24 times higher than 0.105 μg/L at control station AC. The average Zn concentration at two sampling stations B1 and B2 was 0.567 μg/L and was 1.62 times higher than 0.349 μg/L at control station BC. The average Zn concentration at three sampling stations C1, C2 and C3 was 0.228 μg/L and was 5.56 times higher than 0.041 μg/L at control station CC. The average Zn concentration at three sampling stations D1, D2 and D3 was 0.384μg/L and was 5.91 times higher than 0.065 μg/L at control station DC.

With regard to average Zn concentrations at sampling stations around shipyards, B-shipyard ranked the first by 0.567 μg/L, A-shipyard the second by 0.550 ㎍/L, D-shipyard the third by 0.384 ㎍/L, and C-shipyard the fourth by 0.224 ㎍/L.

The average Zn concentrations at sampling stations around A-shipyard, C-shipyard and D-shipyard were 5.24～5.91 times higher than those at control stations and were very similar to one another, while the average Zn concentration at sampling stations around B-shipyard was 1.62 times higher than that at control station. This implies that lots of zinc was used in galvanized coatings of metals for ships' hulls(Clark, 1986) and zinc wastes were likely to be discharged to sea from shipyards.

Around four major shipyards, the Zn concentrations at all sampling stations were 0.136～1.040 ㎍/L and those at all control stations were 0.041～0.349 ㎍/L as shown in Table 1. The Zn concentrations at all sampling and control stations were similar to 0.016～1.563 ㎍-Zn/L in the seawater of the East Sea(Kim et al., 2007), 0.16～1.29 ㎍-Zn/L in the seawater of Gaduk Channel, Korea(Kim et al., 2008b) and 0.006～0.602 ㎍-Zn/L in the North Pacific Ocean(Bruland, 1980), and were lower than Korean environmental standards of 100 ㎍-Zn/L for the protection of human health and of 34 ㎍-Zn/L for short-term protection of marine ecosystem as shown in Table 2.

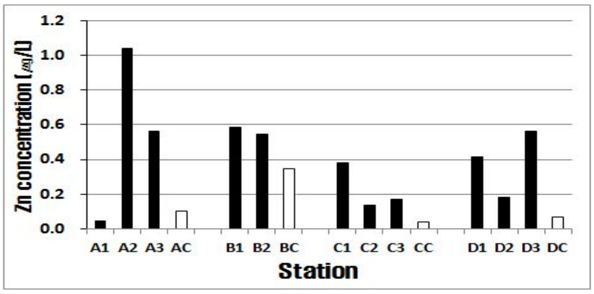

Fig. 3. Comparison of Zn concentrations in seawater between sampling stations and control station.

4.3 Iron(Fe)

The concentrations of iron at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 4.

The average Fe concentration at three sampling stations A1, A2 and A3 was 7.410 ㎍/L and was 6.75 times higher than 1.098 ㎍/L at control station AC. The average Fe concentration at two sampling stations B1 and B2 was 5.884 ㎍/L and was 1.44 times higher than 4.100 ㎍/L at control station BC. The average Fe concentration at three sampling stations C1, C2 and C3 was 3.332 ㎍/L and was much lower than 16.235 ㎍/L at control station CC. It was unusual that the Fe concentration at control station CC was 16.235 ㎍/L and was much higher than those at the other control stations AC, BC and DC. The average Fe concentration at three sampling stations D1, D2 and D3 was 5.451 ㎍/L and was 1.30 times higher than 4.201 ㎍/L at control station DC.

With regard to average Fe concentrations at sampling stations around shipyards, A-shipyard ranked the first by 7.410 ㎍/L, B-shipyard the second by 5.884 ㎍/L, D-shipyard the third by 5.451 ㎍/L, and C-shipyard the fourth by 3.332 ㎍/L.

The average Fe concentration at sampling stations around A-shipyard was 6.75 times higher than that at control station and ranked the first, and the average Fe concentrations at sampling stations around B-shipyard and D-shipyard were 1.30～1.44 times higher than those at control stations and were very similar to each other. This implies that plenty of iron was used in iron plates of ships' hulls, and lots of iron dust and welding slag were likely to be transferred to the marine environment from shipyards. It was, however, unusual that the average Fe concentration at sampling stations around C-shipyard was much lower than that at control station.

Around four major shipyards, the Fe concentrations at all sampling stations were 1.116～13.880 ㎍/L and those at all control stations were 1.098～16.235 ㎍/L as shown in Table 1.

Iron is not usually a significant contaminant of the sea, but it has come to prominence over sea dumping of ‘red mud’ from the extraction of alumina from bauxite, and ‘acid iron waste’ from the production of titanium dioxide. Both wastes contain a large amount of iron(Clark, 1986).

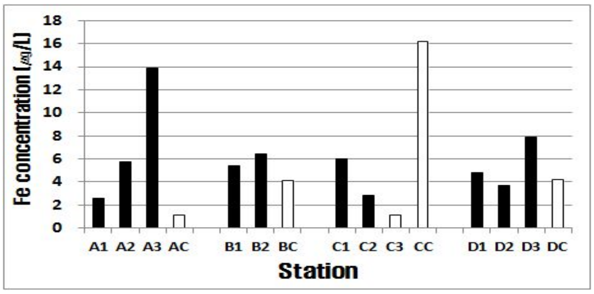

Fig. 4. Comparison of Fe concentrations in seawater between sampling stations and control station.

4.4 Cadmium(Cd)

The concentrations of cadmium at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 5.

The average Cd concentration at three sampling stations A1, A2 and A3 was 0.028 ㎍/L and was 2.33 times higher than 0.012 ㎍/L at control station AC. The average Cd concentration at two sampling stations B1 and B2 was 0.020 ㎍/L which was 1.18 times higher than 0.017 ㎍/L at control station BC. The average Cd concentration at three sampling stations C1, C2 and C3 was 0.013 ㎍/L and was 1.30 times higher than 0.010 ㎍/L at control station CC. The average Cd concentration at three sampling stations D1, D2 and D3 was 0.016 ㎍/L and was 1.33 times higher than 0.012 ㎍/L at control station DC.

With regard to average Cd concentrations at sampling stations around shipyards, A-shipyard ranked the first by 0.028 ㎍/L, B-shipyard the second by 0.020 ㎍/L, D-shipyard the third by 0.016 ㎍/L, and C-shipyard the fourth by 0.013 ㎍/L.

While the average Cd concentration at sampling stations around A-shipyard was 2.33 times higher than those at control stations and ranked the first, the average Cd concentrations at sampling stations around B-shipyard, C-shipyard and D-shipyard were 1.18～1.33 times higher than those at control stations and were very similar to one another. This implies that some cadmium was likely to be released to the marine environment from shipyards.

Around four major shipyards, the Cd concentrations at all sampling stations were 0.007～0.031 ㎍/L and those at all control stations were 0.010～0.017 ㎍/L as shown in Table 1. The Cd concentrations at all sampling and control stations were similar to 0.011～0.058 ㎍-Cd/L in the seawater of the East Sea(Kim et al., 2007), 0.011～0.029 ㎍-Cd/L in the seawater of Gaduk Channel, Korea(Kim et al., 2008b) and 0.0003～0.127 ㎍-Cd/L in the North Pacific Ocean(Bruland, 1980), and were lower than Korean environmental standards of 10 ㎍-Cd/L for the protection of human health and of 19 ㎍-Cd/L for short-term protection of marine ecosystem as shown in Table 2.

Cadmium is widely distributed in the Earth's crust, but is particularly associated with zinc and it is produced commercially only as a by-product of zinc smelting. The iron, steel, and non-ferrous metal industries produce dust, fumes, waste water, and sludge containing cadmium. Zinc used in galvanized coatings of metals contains about 0.2 % cadmium as an impurity. It is estimated that all this cadmium is lost to the environment through corrosion within four to twelve years. Cadmium was suspected of being responsible for an outbreak of itai-itai disease in a Japanese village on the Jintsu river. It was attributed to contamination of rice by cadmium from the effluent from a zinc smelter(Clark, 1986).

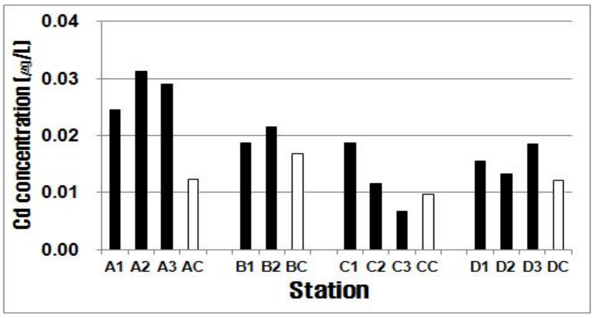

Fig. 5. Comparison of Cd concentrations in seawater between sampling stations and control station.

4.5 Lead(Pb)

The concentrations of lead at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 6.

The average Pb concentration at three sampling stations A1, A2 and A3 was 0.007 ㎍/L and was much lower than 0.026 ㎍/L at control station AC. The average Pb concentration at two sampling stations B1 and B2 was 0.016 ㎍/L and was much lower than 0.072 ㎍/L at control station BC. The average Pb concentration at three sampling stations C1, C2 and C3 was 0.033 ㎍/L and was lower than 0.052 ㎍/L at control station CC. The average Pb concentration at three sampling stations D1, D2 and D3 was 0.126 ㎍/L and was 10.50 times higher than 0.012 ㎍/L at control station DC.

With regard to average Pb concentrations at sampling stations around shipyards, D-shipyard ranked the first by 0.126 ㎍/L, C-shipyard the second by 0.033 ㎍/L, B-shipyard the third by 0.016 ㎍/L, and A-shipyard the fourth by 0.007 ㎍/L.

While the average Pb concentration at sampling stations around D-shipyard was 10.50 times higher than that at control station, the average Pb concentrations at sampling stations around A-shipyard, B-shipyard and C-shipyard were 0.007～0.033 ㎍/L, were lower than those at control stations, and were similar to one another.

Around four major shipyards, the Pb concentrations at all sampling stations were 0.004～0.334 ㎍/L and those at all control stations were 0.012～0.072 ㎍/L as shown in Table 1. The Pb concentrations at all sampling and control stations were higher than 0.002～0.160 ㎍-Pb/L in the seawater of the East Sea(Kim et al., 2007) and 0.004～0.332 ㎍-Pb/L in the seawater of Gaduk Channel, Korea(Kim et al., 2008b), and were lower than Korean environmental standards of 50 ㎍-Pb/L for the protection of human health and of 7.6 ㎍-Pb/L for short-term protection of marine ecosystem as shown in Table 2.

Much lead in metallic form, in battery casings and plates, in sheet and pipes, etc. is recovered and recycled, but most lead used in compound form is lost to the environment. Lead aerosols are carried to Earth in rain and snow and are widely scattered. Local high concentrations of lead may be caused by special circumstances. Compared with other metals, lead in the sea is not particularly toxic and at concentrations up to 0.8 ppm, lead nitrate even enhances the growth of the diatom *Phaeodactylum* presumably through the nutrient effect of the nitrate. High concentrations of lead can be accumulated by some animals without apparent harm. Although lead is held responsible for serious damage to health on land, such contamination of the sea and marine products as occurs does not appear to be a matter for concern(Clark, 1986).

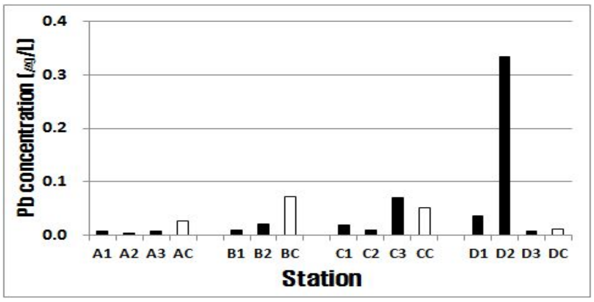

Fig. 6. Comparison of Pb concentrations in seawater between sampling stations and control station.

4.6 Mercury(Hg)

The concentrations of mercury at eleven sampling stations and four control stations around 4 major shipyards were compared one another, as shown in Fig. 7.

The average Hg concentration at three sampling stations A1, A2 and A3 was 0.004 μg/L and was a little higher than or nearly equal to 0.002 μg/L at control station AC. The average Hg concentration at two sampling stations B1 and B2 was 0.002 μg/L and was a little higher or nearly equal to 0.001 μg/L at control station BC. The average Hg concentration at three sampling stations C1, C2 and C3 was 0.002 μg/L and was equal to 0.002 μg/L at control station CC. The average Hg concentration at three sampling stations D1, D2 and D3 was 0.002 μg/L and was equal to 0.002 μg/L at control station DC.

With regard to average Hg concentrations at sampling stations around shipyards, A-shipyard ranked the first by 0.004 μg/L, and B-shipyard, C-shipyard and D-shipyard ranked the second by 0.002 μg/L. However, the average Hg concentrations at all sampling stations around four major shipyards were 0.002～0.004 μg/L, were similar to one another, and were a little higher than or nearly equal to 0.001～0.002 μg/L at all control stations.

Around four major shipyards, the Hg concentrations at all sampling stations were 0.002～0.008 μg/L and those at all control stations were 0.001～0.002 μg/L as shown in Table 1. The Hg concentrations at all sampling and control stations were similar to 0.0017～0.0183 μg-Hg/L in Gaduk Channel of Korea(Kim et al., 2008b) and 0.001～0.050 μg-Hg/L in the open oceans(Clark, 1986), and were lower than Korean environmental standards of 0.5 μg-Hg/L for the protection of human health and of 1.8 μg-Hg/L for short-term protection of marine ecosystem as shown in Table 2.

Mercury is lost to the atmosphere and in waste waters from the chlor-alkali industry, and mercurial compounds are inevitably dispersed into the environment by the uses such as ‘slimicides’ used in the lumber and paper pulp industries to prevent fungal growth, anti-fouling paints for ship hulls, pesticides and seed dressings in agriculture, and in pharmaceuticals. Following the discovery in the early 1960s of the dangers to human health of mercury in the sea, there has been a marked reduction in inputs from some major sources in some areas. Major sources of mercury in coastal waters are rivers, marine outfalls, and wastes dumped directly into the sea. The fact that mercury is toxic to humans has been known for centuries. In the 20th century, mercury has been the only contaminant introduced by man into the sea that has certainly been responsible for human death. Mercury poisoning resulting from pollution of the sea occurred at the small Japanese coastal town of Minamata in 1953. This mercury poisoning was called as Minamata disease(Clark, 1986).

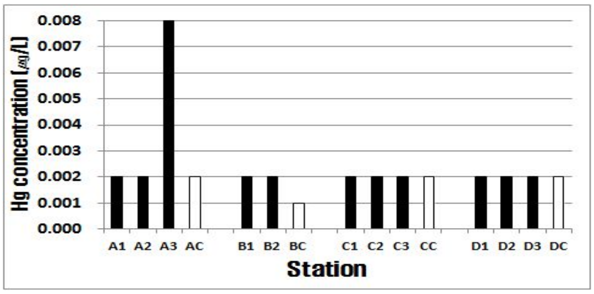

Fig. 7. Comparison of Hg concentrations in seawater between sampling stations and control station.

5. Conclusion

Seawater samples were collected at eleven sampling stations and four control stations around 4 major shipyards located in the southeastern coast of Korea in summer 2010, and 6 kinds of heavy metals in seawater samples were analyzed. The concentrations of heavy metals in seawater around major shipyards in Korea was summarized as follows.

1. The mean concentrations of copper(Cu) in seawater around 4 major shipyards were in the range of 0.817～1.638 μg/L, and were lower than Korean environmental standards of 20 μg/L for the protection of human health and of 3.0 μg/L for short-term protection of marine ecosystem but higher than Cu concentrations at control stations by a factor of 1.64～2.75.

2. The mean concentrations of zinc(Zn) were in the range of 0.228～0.567 μg/L, and were lower than Korean environmental standards of 100 μg/L for the protection of human health and of 34 μg/L for short-term protection of marine ecosystem but higher than Zn concentrations at control stations by a factor of 1.62～5.91.

3. The mean concentrations of iron(Fe) were in the range of 3.332～7.410 μg/L, and were higher than Fe concentrations at control stations by a factor of 1.30～6.75.

4. The mean concentrations of cadmium(Cd) were in the range of 0.013～0.028 μg/L, and were lower than Korean environmental standards of 10 μg/L for the protection of human health and of 19 μg/L for short-term protection of marine ecosystem but higher than Cd concentrations at control stations by a factor of 1.18～2.33.

5. The mean concentrations of lead(Pb) were in the range of 0.007～0.126 μg/L, and were lower than Korean environmental standards of 50 μg/L for the protection of human health and of 7.6 μg/L for short-term protection of marine ecosystem.

6. The mean concentrations of mercury(Hg) were in the range of 0.002～0.004 μg/L, and were lower than Korean environmental standards of 0.5 μg/L for the protection of human health and of 1.8 μg/L for short-term protection of marine ecosystem.

7. Although the concentrations of metals such as copper(Cu), zinc(Zn) and iron(Fe) which were used in shipbuilding works were lower than Korean environmental standards of marine water quality as provided in the table attached to Article 2 of the Enforcement Decree of the Framework Act on Environmental Policy, the fact that the concentrations of Cu, Zn and Fe at sampling stations around major shipyards were higher than those at control stations implies that the works in shipyards had some effects on marine water quality around shipyards. Therefore, marine environment management such as the prevention and control of the discharge of various pollutants from shipyards is required on national level.

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