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Monitoring Heavy Metal Contamination Using Rocky Oyster (*Saccostrea glomerata*) in Haiphong-Halong Coastal Area, North Vietnam

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ABSTRACT: To understand the present status of metal contamination along the Haiphong-Halong coast, the concentrations of As, Cd, Cr, Cu, Pb, and Zn were seasonally determined in rock oysters from four sites during 2013. The results indicated that a high concentration of heavy metals was found in oysters. The average concentrations of Zn and Cu were extremely high, ranging from 823.6–3201.6 and 238.1–1597.8 mg/kg dry wt., respectively, followed by As, Cd, Pb and Cr with concentrations of 10.10–19.33, 3.53–12.74, 0.79–6.20, and 0.81–4.47 mg/kg dry wt., respectively. The highest concentrations of heavy metals, Cd, Cr, Pb and Zn, found in Dinh Vu could be influenced by anthropogenic inputs. In addition, the runoff in the rainy season greatly influences the accumulation of heavy metals in oysters from Dinh Vu and Do Son. The maximum levels of Cd, Cu, Zn and As could potentially create toxicological concerns from a human health point of view and rocky oysters from the polluted sites should not be consumed.

Key words: Coast, Health risk, Heavy metals, Oyster, Seasons

INTRODUCTION

Marine pollutions have threated the aquatic ecosystems in Vietnam since the rapid economic growth recently (Ho and Egashira 2000; Phuong et al. 2010). Among anthropogenic pollutants, heavy metal contaminations are of particular concern as a result of industrial activities and application of a large quantity of agricultural chemicals in coastal areas, especially the Haiphong- Halong coast (Cao and Nguyen 2009). Furthermore, National Marine Environmental Monitoring Network of Vietnam reported that the high levels of Cu and As were found in water and sediment along the north coast and other metals, Pb and Zn, tend to increase annually (VEPA 2012). However, to assess marine water quality merely based upon the metal contaminants in the water and sediment is not sufficient, because they only provide information on what kind of pollutant to be found, where they were found, and at what concentrations, while concentrations of contaminants in biota can reveal adverse biological effects and provide information on the ecological health of marine waters. However, in this area this kind of information is scarce. Rock oysters, *Saccostrea spp.*, are well-established biomonitors of availability of heavy metals because they, are hardy and sessile, does not self-regulate or naturally chelate contaminants. (Scanes and Roach 1999; Robinson et al. 2005). In Vietnam, *Saccostrea glomerata* that widely distributes in littoral areas along the coast are found commonly attached on rocks, boulders, and underwater structures. The rock oyster is also consumed as seafood by local people, but there is a lack of information related to heavy metals in the oysters in northern Vietnam. Knowledge about heavy metal concentrations in native species is very important for understanding the water quality, public health, and risk from human consumption. Therefore, the objective of the study is to investigate heavy metal contamination in the rock oyster at different sampling sites and seasonal variation along Haiphong-Quangning coastal waters.

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MATERIALS & METHODS

Haiphong–Halong area is located in a subtropical climate zone and has two distinct seasons, the dry season and the rainy season. During the rainy season (May–September), heavy rains and typhoons frequently occur and last for a few days or a week. The annual precipitation for this region of Northern Vietnam is 1,800 mm. Conversely, during the dryer, cooler season (October–April), rainfall is low and the rivers dry up. Water temperatures during the rainy season range from 25–29°C, while water temperatures during the dry season range from 15–23°C.

Rock oysters, *S. glomerata*, were collected during low tide in the rocky intertidal zone at the four sites (M1, M2, M3 and M4) in 2013 (Fig. 1). The sampling was conducted in the dry (March) and in rainy seasons (July). Three of these four sites, M1, M2, and M3, are situated in the coastal area of the Bach Dang estuary, which is one of the main tributaries of the Red River Delta in North Vietnam. Site M2 is located near the Dinh Vu industrial zone and river port (Haiphong port) of Haiphong urban area. M1 and M2 are strongly affected by river-flows from the Bach Dang River as well as tides and tidal cycles from the sea; therefore, the salinity of these sites varies greatly and depends upon seasonal changes. M3 is located in the west of Cat Ba Island, where seawater is dominant. The last site, M4, is located at the inlet of Cua Luc bay (Ha Long city), where the sources of pollutants derived from human activities, such as coal mining, Cai Lan port activities, tourism and municipal wastes. These activities may greatly contribute to total heavy metal concentrations in the area. While sites M1 and M2 are mainly affected by river water, the salinity ranged from 10 to 25%o. Sampling sites M3 and M4 are influenced mainly by seawater and salinity ranged from 25 to 32%o.

Approximately 35 diploid oysters of similar size (2.5-3 cm) were collected from each site. A stainless steel hammer and rod were used to separate oysters from the surface to which they were attached. The collected oysters were washed with local seawater and transported in polyethylene z-lock bags to the lab in an icebox. All of the samples were then stored at -20°C until the next steps.Rock oysters were defrosted at room temperature before dissecting. Each oyster was then carefully opened by slicing the adductor muscle. The oyster was removed from the shell using plastic forceps, placed in an acid-washed glass tray to determine the wet weight and then dried in an oven. Due to their small size, three oysters were pooled into one sample, and 8-10 replicates from each site were analysed for heavy metals concentrations.The microwave method was carried out to digest the samples, as described in a previous study by Le et al. (2009). The concentrations of six elements, As, Cr, Cu, Zn, Cd, and Pb, were measured with an inductively coupled plasma mass spectrometer (ICP-MS) (ELAN 9000 Perkin Elmer, USA). Matrix effects and instrumental drift in ICP-MS were corrected by Scandium (Sc), Indium (In), and Bismuth (Bi) as internal standards. The accuracy of the method was assessed with a standard reference material, DORM 3 (National Research Council, Ottawa, Canada). The recoveries of As, Cd, Cu, Pb and Zn were 96.4, 92.5, 106.4, 86.4, and 91.4%, respectively. The results are expressed as the mean ± SD (mg/kg). Differences between data were analysed using the Mann Whitney U-test. Differences among data were examined by an analysis of variance (Kruskal-Wallis ANOVA and median test)

RESULTS & DISCUSSION

The mean levels of heavy metals in the oysters collected from the selected sites at the two seasons are presented in Table 1. The average concentrations of Zn an Cu were extremely high, ranging from 823.6–3201.6 and 238.1–1597.8 mg/kg dry wt., respectively, followed by As, Cd, Pb and Cr with concentrations of 10.10–19.33, 3.53–12.74, 0.79–6.20, and 0.81 –4.47 mg/kg dry wt., respectively.

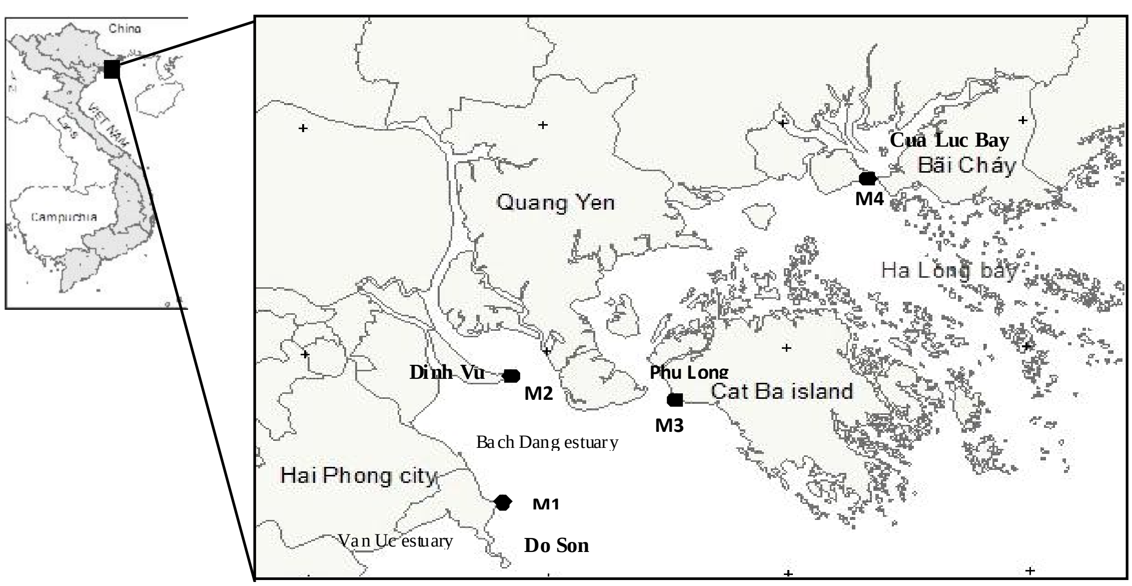

Fig.1. Sampling locations along the Haiphong-along coast

Table 1. Spatial and temporal variation of metal levels (mg/kg) in oysters along the Haiphong-Halong coast.

Heavy metals	Dry season				Comparison
	M1 (n=8)	M2 (n=7)	M3 (n=7)	M4 (n=9)	
As	10.26±1.00	11.29±0.64	10.10±0.71	16.03±1.10	M4>M1, M3
Cd	8.07±0.57	8.68±0.60	4.58±0.99	3.53±0.51	M1, M2>M4
Cr	1.35±0.12	4.47±1.62	0.81±0.32	1.80±0.13	M2>M1, M3
Cu	583.7±87.1	532.8±16.7	478.3±247.4	238.1±56.9	M1, M2, M3>M4
Pb	0.91±0.10	2.23±0.43	1.33±0.11	0.79±0.20	M2, M3>M1, M4
Zn	1194.7±128.3	1529.2±67.2	885.3±152.6	823.6±169.1	M1, M2>M3, M4
	Wet season				
	M1 (n=8)	M2 (n=7)	M3 (n=7)	M4 (n=9)	
As	10.15±0.90	11.97±0.71	10.72±0.90	19.33±1.23	M4>M1, M2, M3
Cd	11.19±1.92	12.74±1.69	7.55±0.91	6.47±1.02	M1, M2>M3, M4
Cr	1.17±0.15	1.69±0.34	1.55±0.24	1.35±0.26	M2>M1
Cu	790.7±75.0	1597.8±76.7	793.8±371.5	578.0±29.7	M2>M4
Pb	1.86±0.15	6.20±1.43	2.27±0.42	1.78±0.52	M2>M1, M3, M4
Zn	1227.2±249.1	3201.6±560.8	1432.2±539.5	2358.7±577.2	M2>M1, M3; M4>M1

Comparing the present data with those of oysters from New South Wales (Scanes and Roach 1999) and around the world (Cantillo 1997), a similar ranking of metal concentrations in oyster tissue was found, Zn > Cu > As> Cd > Cr > Pb, which reflected the typical metal richness of the Saccostrea species (Cantillo 1997). It is not surprising to find extremely high levels of Cu and Zn in oysters because oyster blood amebocytes are known to sequester these metals (Robinson et al. 2005). In this study, the concentrations of all heavy metals in the oysters at the low-level sites were comparable to the world background level (Cantillo 1997), but they were lower than those in New South Wales (Scanes and Roach 1999). In contrast, the concentrations of Zn, Cu, Cr, Pb and Cd in the oysters from the high-concentration site exceeded the world and New South Wales (NSW) levels, the concentrations of As were lower than those at 85% of the concentrations of the New South Wales background level (NSWBG), but these concentrations exceeded the world and NSWBG media levels. Hence, the metal concentrations of the oysters at the high-concentration sites in this study revealed heavy metal contamination derived from anthropogenic inputs.

In the dry season, almost all metals in oyster from the sites (M1 and M2) in the Bach Dang estuary were present at greater levels than those in Phu Long (M3) and Cua Luc Bay (M4). Indeed, Cd, Cr, Cu and Zn were found at higher levels in samples from both sites M1 and M2 than in samples from sites M3 and M4. Among the metals, the levels of Cd at M1 and M2 were significantly higher than those at M4 ($p<0.05$).

Meanwhile, Cr, Zn and Pb were found at the highest levels at site M2, significantly higher than at M1 and M3 for Cr. The highest levels of Zn were found at M1 and M2, and the highest levels of Pb were found at M2 and M3 ($p<0.05$). Concentrations of Cu in oysters were found to be the lowest at site M4, compared to all other sites ($p<0.05$), but there was also a significant difference between the Cu concentrations in oyster samples from M1 and M4. Unlike other metals, the concentration of As was highest in oysters from site M4, but this concentration was only signiûcantly higher than in samples from sites M3 and M1 ($p<0.05$).The metal concentrations in oysters measured during the rainy season showed similar results to those found during the dry season among the sampled sites. The concentrations of Cd, Cr, Cu, Zn and Pb were highest in oyster samples from site M2, whereas the As concentration was highest in samples from site M4. However, there was a difference in the level of metal concentrations among sites between the seasons. The concentration of Cr was only significantly different between M1 and M2, and a significant difference in the concentration of Cu was found between M2 and M4 ($p<0.05$). In the case of Zn, the concentration in oyster samples from M2 was significantly higher than in oysters from M1 and M3. The concentration of Zn in samples from M4 was also significantly higher than in samples from M1. Samples from M2 showed the highest level of Pb compared to all other sites ($p<0.05$).The differences in the metal concentrations in oyster tissues between sampling sites might be influenced significantly by anthropogenic inputs. The M2 site, for example, received a high metal contamination load from industrial zones in the Haiphong urban areas, such as from harbour and shipyard activities and the coal-fired power plant located in the major branch of the Bach Dang River. Coal-fired power plants can cause environmental pollution in surrounding aquatic systems because the smallest particles of fly ash are often enriched with heavy metals (Fulekar and Dave 1986). Additionally, Alam et al. (2012) showed that high level of heavy metals, specifically Cd, Cr, Pb, Cu and Zn, in sediment and aquatic organisms can be related to the discharge of power plant wastes.

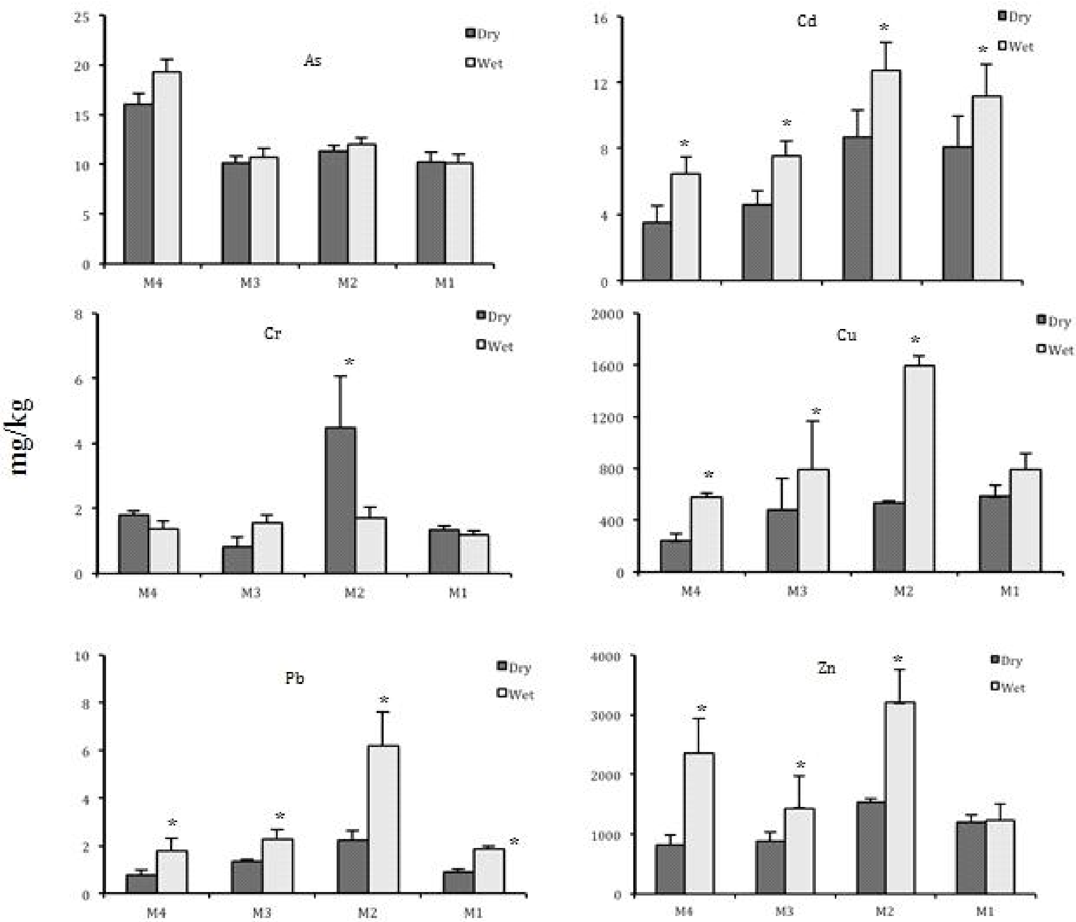

Fig. 2. Difference of heavy metal levels in oyster from sampling sites and seasons

Table 2. Domestic and international standards for metal concentrations (mg/kg) in oysters and other seafood.

Locations	WB	Cu	Pb	Zn	Cd	As (inorg.)	Cr	Ref.
Vietnam	W	30	1.5	100	1.0	1.0	-	MoH, 2007
Singapore	W	-	2.0	-	1.0	1.0	-	AVA, 2006
Thailand	D	133	6.67	667	-	-	-	MPHT, 1986
Malaysia	W	30	2.0	100	1.0	-	-	MFR, 1985
Present data	W	50-336	0.2-1.3	173-672	0.7-2.7	2.1-4.1*	0.2-0.9	
	D	238 – 1598	0.8 - 6.2	823 – 3202	3.5 - 12.7	10.1 - 19.3*	0.8-4.5	

The Cua Luc bay area is also suffering from increasing pollution due to industry, tourism and urban development, especially coal mining activities, which are the major source of contamination in the area (Khristoforova et al 2007). However, the lower levels of heavy metals, except As, in oysters at the M4 site compared to the M2 site might be caused by the difference in flocculation processes occurring between the sites. During estuarine mixing, dissolved metals are thought to absorb onto the suspended material and settle in riverbeds with seaward salinity gradients (Biati and Karbassi 2010; Biati et al. 2010). This absorption of free metal ions onto suspended material could reduce the potential environmental risk of metals as well as metal accumulation within an organism's tissues (Dojlido and Best 1993). Additionally, the seawater that was predominant in Cua Luc bay invaded in further upstream-ward of the rivers because of weak water flow. Therefore, flocculation often occurred from riverward in the river mouths inside Cua Luc bay. In contrast, flocculation in the Bach Dang estuary expands seaward with a main depositional area several kilometres downstream and offshore from the river mouth (van Maren 2007). In the case of As, the highest level of As found in oysters at site M4 indicated that the pollution source derived from coal mining activities; the coal exploitation excavates a large quantity of soil, rock and coal from underground. The dirt and waste from coal mining, which contains a high level of As, might affect the area (Garelick et al. 2008). Furthermore, Ho et al. (2010) found that only As was of concern as the concentration of As exceeded the international sediment quality guidelines affected by coal mining activities from Ha Long Bay. While the source of contamination of Cd, Pb, Cu and Zn is unclear, other heavy metals (Co, Cr, Ni and Mn) were not considered to be pollutants. Ho et al. (2010) added that the distribution patterns of heavy metals were mainly controlled by organic matter and clay minerals, which might decrease the potential for toxic effects at the studied area.With respect to the sites, M1 and M3 were less influenced by river flow at the Bach Dang estuary. The concentrations of heavy metals in oysters at these sites were identical, except for Cd. The elevated Cd level in M1 compared to M3 might relate to the water and sediment dynamics of the Bach Dang estuary. The river caused southward surface flow, and the near bottom currents were also stronger than northward currents (van Maren 2007). Therefore, the river flow and its suspended sediment influenced the metal accumulation in oysters more at site M1 rather than at site M3. Furthermore, site M1 also obtained metal contamination loads from the Van Uc estuary, which is south of the Do Son peninsula. The Van Uc River is within an important region for agricultural production in northern Vietnam. Therefore, higher concentrations of Cd in oysters from this site might partly be due to the intensive use of fertilisers for agriculture in the region. Because commercial phosphate fertilisers contain a small amount of heavy metal contaminants, runoff represents a potential source of Cd, which is delivered to the rivers from upstream activities (Ngo et al. 2005).

A comparison of metal levels in oysters between the rainy and dry seasons is presented in Fig. 2. Although the levels of Cu, Zn, Cd and Pb in the rainy season tended to be higher than in the dry season at all sites, the level of Cu and Zn in oyster samples from M1 did not show any significant difference between the seasons. As and Cr showed no significant differences in the study sites between seasons, except for Cr at site M2.There was a significant difference of heavy metal levels in the oysters between seasons from the study sites, except for Cr and As. The peak in metal levels of oysters in the rainy season might relate to the pollutants in runoff along riversides and human activities upstream. In the rainy season, the outflow of heavy rainfall washed out the polluted water in the rivers and lakes to the estuarial area. The excessive runoff from land significantly impacted the coastal areas, resulting in decreased salinity, higher turbidity, increased nutrient load, and higher concentrations of heavy metal contaminants. The impact could extend seaward several kilometres offshore from the river mouths (Cao and Nguyen 2009; van Maren 2007). These factors might be the result of the elevated levels of heavy metals in oysters in the rainy season. In contrast, during the dry season, heavy metals tended to be trapped in the site where manufacturing companies were located, because of the lack of water, a slower water flow, and the influence of tidal predominance in the estuarine areas, (Ho and Egashira 2000). Thus, fewer amounts of the metal contaminants were introduced to coastal areas in the dry season.

Unlike other metals, the concentrations of As and Cr did not vary among the sites and seasons. However, elevated levels of As at the Ha Long site and Cr at the Dinh Vu site were noted as effects of local contamination sources. The peak of As at site M4 during the rainy season was likely related to the runoff of coal mining activities, while the elevated level of Cr at the M2 site during the dry season was merely caused by wastewater from the Dinh Vu industrial area. To assess the potential human health risk due to local human consumption, the present data were compared with domestic and international standard levels (Table 2). Because domestic standard levels are presented as wet weight concentrations and the international standard levels are given for different weight bases (dry or wet weight concentration), the present data were converted into the wet weight based on the mean percentage of moisture in oyster tissue (approximately 82%). Except for Cr, for which limited information is available, the concentrations of As, Cd, Cu, Zn and Pb were compared to regulatory standards from Vietnam and various countries. The concentrations of Cd, Cu, and Zn at the high-concentration sites, M1 and M2, during the rainy season were found to exceed all domestic and international standards, whereas these metal levels were below the standard levels during the dry season (Table 2). Among the studied metals, Zn and Cu are considered nutritionally essential to human health as they support necessary metabolic processes. Although excessive concentrations of these metals could be harmful to human consumption, the elevated Zn concentration in oysters might not cause adverse effects if these oysters are included in the local diet because oyster-accumulated Zn occurs in detoxified granules, which have a relatively low bioavailability to subsequent predators (Langstone et al. 1998). The excessive Cd in the oysters at the high-concentration sites in both seasons represents a potential risk for local human health (Castro-González and Méndez-Armenta 2008). Unlike Cd, concentrations of Pb at all sites and seasons were below the standard levels. Although the concentrations of As in the oysters exceeded all of the standard levels, the data showed in this paper represent the total arsenic levels in oysters. Arsenic in marine organisms or seafood is mainly in various organic forms, such as arsenobetaine, arsenoribosides, and arsenocholine, which are effectively non-toxic (Peshut et al. 2008).

CONCLUSIONS

The rock oyster, *Saccostrea glomerata*, accumulates metals in response to contaminated sites along Haiphong-Halong coast. The average levels of As, Zn and Pb in the oysters do not represent a threat to human health, however, the contaminated sites of the coastal area by these metal residues can raise toxicological concerns. Therefore, further studies should be conducted and oysters from the polluted sites should not be consumed.

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