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COPPER INTAKE AND HEALTH THREAT BY CONSUMING SEAFOOD FROM COPPER-CONTAMINATED COASTAL ENVIRONMENTS IN TAIWAN

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Abstract—The purpose of this paper is to describe the impact of copper pollution on the main aquaculture coast of Taiwan and the potential risk from eating the green oysters cultured along the polluted coast. Our data show that the highest average concentration of copper ($2,194 \pm 212 \mu\text{g/g}$) in oysters was observed in the Erhjin Chi estuary from 1986 to 1990 (after the “green oyster” incident). The copper concentration in both the seawater and the sediment collected along the Erhjin Chi estuary was also the highest in all sampling locations. Copper concentration in oysters collected from Erhjin Chi, Hsiangshan, and Anping from 1988 to 1990 was, respectively, 61, 29, and 22 times higher than that of 10 years ago. The potential risk from consuming oysters is relatively higher than that of other seafoods due to the high bioaccumulation of oysters. The oysters in the Erhjin Chi estuary had an average concentration of copper of $3,075 \pm 826 \mu\text{g/g}$ during the past three years (1988–1990). The average copper intake from oysters for an adult with 70 kg body weight was 12.6 mg/d. The estimate indicated that the average copper intake from the oysters for female individuals is 14 times more than that of international limits. Based on the average value, long-term intake of copper through consumption of oysters cultured along the Erhjin Chi estuary could be critical, especially for some high-risk groups.

Keywords—Seafood Copper pollution Oyster Health

INTRODUCTION

Taiwan is a modern industrialized island country with a population of about 20 million and a strong economy. However, due to dense population and rapid industrial expansion, the estuarine and coastal environments of Taiwan are suffering an ever-increasing impact from all kinds of human activities [1]. From March 1980 to February 1983, our National Committee for SCOPE/ICSU, with the support of the Academia Sinica and the National Science Council, carried out a three-year mussel watch program for the purpose of establishing local biological monitoring systems. Several species of bivalves, oysters (*Crassostrea gigas*), clams (*Meretrix lusoria*), and blue mussels (*Mytilus smaragdinus*) were collected from various coastal waters around Taiwan (Fig. 1), and their heavy-metal contents were determined [2,3]. Moreover, the background environmental conditions, including BOD, DO, and NH_4 values, of the main aquacultural streams in Taiwan indicated that there is a serious problem of pollution [4].

We monitored for heavy metals in the coastal environment of Taiwan from 1980 to 1992 and found that heavy-metal pollution is the most serious and one of the most studied marine environmental problems in Taiwan. The area around the Erhjin Chi estuary is especially affected by large discharges of heavy metals from acid cleaning of metal scrap on the riverbanks [5]. For example, the first incident of “green oysters”

in the Charting coastal area was observed in January 1986. The green color was found to be due to a high concentration of copper in the oyster tissue. The green oysters collected from the Erhjin Chi estuary on January 26, 1989, gave the highest copper concentration of $4,401 \pm 79 \mu\text{g/g}$ [3,5,6]. Hundreds of millions of dollars was lost because a major sector of aquaculture in this region had to be closed. All seafood industry suffered from the oyster incident because consumers were so afraid of its products.

Most current health risks associated with seafood safety originate in the environment [7]. People's demand for protein increases when their standard of living rises. Oysters are one of the most popular seafoods in Taiwan; some alarm has been expressed concerning possible health implications of copper residues in oysters. Therefore, the main purpose of this study is to describe the copper pollution impact on the main aquacultural coast in Taiwan and to warn consumers who might eat the oysters cultured along the polluted coast.

MATERIALS AND METHODS

Water samples, sediments, and oysters were collected along the western coast of Taiwan from 1980 to 1990. Sampling locations are shown in Figure 1. Besides oysters, clams, blue mussel, Crustacea, and Osteichthyes were collected from the Erhjin Chi estuary over those three years (1988–1990).

Water samples were collected with metal-free Van Dorn bottles aboard either the research vessel *Ocean Researcher I* or fishing boats. Immediately after collection, water samples were analyzed for DO, BOD, and NH_4 . The methods for

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Fig. 1. Sampling locations of seawater, sediments, and oysters (*Crassostrea gigas*) collected from several culture areas (1, Hsiangshan; 2, Lukang; 3, Taishi; 4, Tungshih; 5, Putai; 6, Chiangchun; 7, Anping; 8, Erhjin Chi estuary; 9, Tungkang; 10, Markung).

analysis of all above parameters have already been described [5,8]. Seawater samples were analyzed for copper species at natural pH (labile copper) and after acidification to pH 2 (total copper). The water samples were analyzed by differen-

tial pulse anodic stripping voltammetry (DPASV) following extraction by a C_{18} -bound Sep-Pak® cartridge (Millipore-Waters, Milford, MA) [3]. After filtering water samples through 0.45- μ m Millipore® filters (Milli-Q Corp., Bedford,

MA), filters were subsequently placed in borosilicate test tubes with 5.0 ml concentrated HNO_3 for digestion using a microwave digester. Particulate copper concentrations were also determined [3]. In general, copper speciation (particulate, total dissolved, labile, and nonpolar organic copper) in seawater was determined.

The bulk sediment was collected from different locations. Only the top oxic layer of 0 to 2 cm was collected, and the sediment was wet-sieved in the laboratory. One-half gram sediment was dissolved in a mixture of ultrapure HNO_3 and HF. Copper contents in sediments were determined with a Hitachi Zeeman 8000 AA spectrophotometer.

Marine organisms (bivalves, Crustacea, Osteichthyes, and Mollusca), mainly oysters caught from culture areas, were brought back to the lab and individually scrubbed and shucked, and the oyster flesh was placed in tared acid-washed Teflon® beakers and reweighed to obtain individual wet-weight values. Samples were then oven-dried at 105°C for approximately 24 h for dry-weight determination [8]. Then the samples were digested with a nitric:sulfuric acid (1:1, v/v) solution, and the supernatant was analyzed for copper by AA spectrophotometry [3].

In general, 15 to 20 individual oysters of similar size (3.21 ± 0.40 cm in shell length) were sampled from each location. The 15 individuals in a bulk homogenate (30 g) gave a minimum standard deviation ($\pm 2\%$), indicating that a population of 15 is significant for measuring copper. In other words, the "effect inherent variables" were suppressed by preparing composite samples of 15 individual specimens.

RESULTS AND DISCUSSION

Copper pollution along the western coast

In Taiwan, most industrial areas are located on the western coast, where the main oyster aquaculture areas are also

located. Most pollutants from factories are discharged on the coast or rivers of western Taiwan, causing serious pollution. The results of surveying the water qualities, including DO, BOD, and NH_4 of the main streams in Taiwan, are given by the R.O.C. Environmental Protection Administration (EPA). It was found that the values of BOD ranged from 8.0 to 27.2 mg/L and those of NH_4 ranged from 1.00 to 2.87 mg/L. Both exceed the limits (BOD < 4 mg/L, NH_4 < 0.1 mg/L) for third-class river water set by the EPA [9]. Only the values of DO ranging from 5 to 5.8 mg/L slightly exceed the limit (>4.5 mg/L). The related data reported by the EPA showed that nine major and minor rivers of 297 km total length appeared to be heavily polluted. The Erhjin Chi (river) was particularly affected by heavy metals and was the most polluted of the rivers in Taiwan [9].

The results of analysis for copper contents in seawater, sediment, and oysters collected along the western coast of Taiwan from 1980 to 1990 are listed in Table 1. The highest average concentration of copper ($2,194 \pm 212$ $\mu\text{g/g}$) in oysters was observed in the Erhjin Chi estuary, one of the most important oyster mariculture areas in Taiwan, from 1986 to 1990, after the green oyster incident.

The copper concentrations of both the seawater (10.8 ± 7.21 and 23.3 ± 12.1 $\mu\text{g/L}$) and the sediment (32.9 ± 23.1 and 49.9 ± 46.3 $\mu\text{g/g}$) collected along the Erhjin Chi estuary before and after the green oyster incident, respectively, also were the highest of all sampling locations. This finding indicated that the Erhjin Chi estuary had become so polluted that the oysters were constantly in contact with contaminated water and accumulated undesirable or even dangerous levels of copper. Hsiangshan also contained high copper levels in seawater (15.3 ± 13.1 $\mu\text{g/L}$) and oysters (682 ± 101 $\mu\text{g/g}$) from 1986 to 1990. In general, when the copper content in oysters was over 500 $\mu\text{g/g}$, the color of the oysters became

Table 1. Average copper concentrations in seawater, sediments, and oysters (*Crassostrea gigas*) collected along the western coast of Taiwan from 1980 to 1990

Location	Seawater ^a ($\mu\text{g/L}$)	Seawater ^b ($\mu\text{g/L}$)	Sediments ^a ($\mu\text{g/g}$)	Sediments ^b ($\mu\text{g/g}$)	Oysters ^a ($\mu\text{g/g}$)	Oysters ^b ($\mu\text{g/g}$)
Erhjin Chi estuary	10.8 ± 7.21 ($n = 30$)	23.3 ± 12.1 ($n = 39$)	32.9 ± 23.1 ($n = 31$)	49.9 ± 46.3 ($n = 42$)	214 ± 54.4 ($n = 50$)	$2,194 \pm 212$ ($n = 85$)
Hsiangshan	12.5 ± 7.25 ($n = 24$)	15.3 ± 13.1 ($n = 28$)	9.47 ± 6.56 ($n = 13$)	13.7 ± 12.8 ($n = 17$)	201 ± 51.2 ($n = 15$)	682 ± 101 ($n = 20$)
Lukang	1.92 ± 0.45 ($n = 15$)	2.23 ± 0.77 ($n = 17$)	3.71 ± 2.24 ($n = 5$)	6.35 ± 1.01 ($n = 5$)	309 ± 35.1 ($n = 12$)	392 ± 54.3 ($n = 12$)
Taishi	3.06 ± 1.81 ($n = 11$)	3.57 ± 1.21 ($n = 14$)	17.2 ± 7.61 ($n = 9$)	21.7 ± 8.82 ($n = 12$)	205 ± 50.2 ($n = 9$)	315 ± 65.3 ($n = 9$)
Tungshih	3.11 ± 2.42 ($n = 13$)	3.51 ± 1.43 ($n = 17$)	1.68 ± 5.21 ($n = 10$)	23.7 ± 8.51 ($n = 13$)	208 ± 35.6 ($n = 10$)	386 ± 40.2 ($n = 9$)
Putai	5.72 ± 3.57 ($n = 20$)	7.19 ± 4.58 ($n = 22$)	8.01 ± 5.02 ($n = 10$)	9.88 ± 4.85 ($n = 13$)	233 ± 40.2 ($n = 10$)	303 ± 42.2 ($n = 9$)
Chiangchun	2.84 ± 0.81 ($n = 12$)	3.38 ± 0.94 ($n = 15$)	21.4 ± 8.75 ($n = 7$)	24.8 ± 10.6 ($n = 8$)	198 ± 27.4 ($n = 8$)	230 ± 30.4 ($n = 8$)
Anping	2.89 ± 1.09 ($n = 9$)	3.83 ± 0.94 ($n = 11$)	14.7 ± 3.72 ($n = 5$)	17.8 ± 5.41 ($n = 6$)	49.3 ± 28.9 ($n = 9$)	438 ± 94.0 ($n = 12$)
Tungkang	2.19 ± 0.44 ($n = 8$)	2.44 ± 0.61 ($n = 11$)	24.4 ± 2.01 ($n = 2$)	25.3 ± 2.21 ($n = 3$)	92.7 ± 18.9 ($n = 9$)	127 ± 20.8 ($n = 10$)
Markung	3.41 ± 0.10 ($n = 7$)	3.57 ± 0.13 ($n = 5$)	15.8 ± 2.51 ($n = 5$)	16.3 ± 1.84 ($n = 3$)	25.7 ± 7.05 ($n = 12$)	67.8 ± 20.2 ($n = 14$)

^aBefore the green oyster incident (1980–1986).

^bAfter the green oyster incident (1986–1990).

green [10]. Besides the Erhjin Chi estuary, Hsiangshan also produced green oysters from time to time.

Comparing the copper contents in oysters collected from the Erhjin Chi estuary to those from Hsiangshan, Anping, and Markung (Fig. 2), all except Markung displayed elevated levels of copper in oysters year by year. Generally, a review of data shows that the Erhjin Chi estuary had the highest average concentration of copper in oysters ($3,075 \pm 826 \mu\text{g/g}$) during 1988, but gradually decreasing levels have been observed since then because a program has been implemented by the EPA to reduce the pollution in this area. In addition, the government of Taiwan has allocated some \$200 billion (NT dollars) in controlling the pollution of the Tanshui River (on the outskirts of Taipei city), showing its resolution to improve the polluted streams in Taiwan.

Both Hsiangshan and Anping presented high levels of copper in oysters, but there was a stable and low copper concentration in the oysters collected from Markung, probably because its location is far from pollution sources. In addition, the concentration of copper in oysters collected from each location was below $100 \mu\text{g/g}$ before 1980. As industry and its environmental impact expanded in Taiwan from 1980 to 1990, the copper concentration in the oysters cultured along the Erhjin, Hsiangshan, and Anping increased year by year. The data we obtained showed that the copper concentrations of oysters collected from Erhjin Chi, Hsiangshan, and Anping from 1988 to 1990 were, respectively, 61, 29, and 22 times higher than those of 10 years ago.

A multiple regression equation was developed on the basis of the results of field experiments relating copper accumulation by green oysters and the various copper species in

natural seawater [3]. This equation can be represented as follows:

$$Y = -448 + 562X_1 + 300X_2 - 336X_3 - 21X_4$$

$$(r^2 = 0.7261),$$

where

Y = concentration of copper in green oysters

X_1 = concentration of particulate copper in seawater

X_2 = concentration of total dissolved copper in seawater

X_3 = concentration of nonpolar organic copper in seawater

X_4 = concentration of labile copper in seawater.

There was evidence showing that the copper content in oysters was significantly correlated (at the level of $p < 0.05$) with the concentration of particulate copper [3]. Figure 3 shows that the total dissolved and particulate copper of the Erhjin Chi estuary increased from 1987 to 1989, with some seasonal variation. Moreover, the highest values of total dissolved copper ($22.5 \pm 3.71 \mu\text{g/g}$) and particulate copper ($11.5 \pm 2.85 \mu\text{g/g}$) were much higher than the average copper levels ($< 5 \mu\text{g/L}$) in seawater of other countries [11]. The concentration of total dissolved and particulate copper increased year by year, with no improvement until February 1989.

Copper intake and the health threat of consuming oysters

Some studies have demonstrated that oysters appear to have adapted to the high-metal-level environment without displaying any obvious adverse symptoms [3,12]. A long-term survey for copper contents in shellfish, crustaceans, and

Fig. 2. Time variation of copper concentration in oysters collected from the Erhjin Chi estuary, Hsiangshan, Anping, and Markung.

Fig. 3. Total dissolved and particulate Cu in seawater of the Erhjin Chi estuary from 1987 to 1989.

Osteichthyes collected from the Erhjin Chi estuary showed that the copper concentrations in oysters were much higher than those in the other species by about 20 to 2,500 times (Table 2). This indicates that the ability of oysters to concentrate copper is much stronger than that of other edible shellfish and fish. Although all of the species were collected from the same culture area, the oysters can accumulate copper from surrounding water 20 to 2,500 times more effectively than other species. Therefore, the potential risk of consuming oysters is relatively higher than that of other seafoods due to the high bioaccumulation of oysters. These high concentrations of copper may not affect oysters directly [3], but may transfer toxicity to humans through the food chain and may render people consuming the shellfish more susceptible to bacterial and viral infection [13].

Among the total values and amounts of production of 11 major kinds of seafood in Taiwan during 1990, as reported by the Council of Agriculture, Republic of China, the oyster was not only in the top 10, but also the only shellfish in the top 11. Because oysters are one of the most popular seafoods in Taiwan, and the Erhjin Chi estuary is one of the major oyster-producing areas, we assume that all of the oysters consumed by some high-risk groups were cultured along the Erhjin Chi estuary. The oyster has had an average concentration of copper of $3,075 \pm 826 \mu\text{g/g}$ during the past three years (Table 2), and the average consumption for individuals has been about 4 g/d, as calculated by annual oyster consumption (30,000 t) and population (20,000,000), so the average copper intake from oysters for an adult with 70 kg body weight has been 12.6 mg/d. The safe levels of dietary copper intake for adults suggested by the Food and Agriculture Organization/World Health Organization (FAO/WHO) are 2 to 3 mg/d [14], or 1.2 mg/d for males and 0.9 mg/d for females [15]. The result of the estimation indicated that the

highest average copper intake from oysters for individuals is 14 times more than that of international limits (female). Although copper is an essential trace metal for animal metabolism, it has been reported toxic to humans after the ingestion of as little as 10 to 15 mg at one time [16], although Moeschlin [17] reported 10 mg as a fatal oral dose. Based on the average value, long-term intake of copper through consumption of oysters cultured, for example, along the Erhjin Chi estuary, especially for some high-risk groups, could be dangerous.

In the long term, amelioration and eventual elimination of some hazards require strengthening and more effective application of control measures to prevent the disposal of human and industrial wastes into aquacultural estuarine and

Table 2. Copper concentrations ($\mu\text{g/g}$) in seafood collected along the Erhjin Chi estuary from 1988 to 1990

Organisms	Cu concn. ($\mu\text{g/g}$) (mean $\pm$ 1 SD)	n
Oyster		
<i>Crassostrea gigas</i>	$3,075 \pm 826$	26
Clam		
<i>Meretrix lusoria</i>	39.3 ± 24.9	2
Blue mussel		
<i>Mytilus smaragdinus</i>	24.5 ± 4.61	6
Crustacea		
<i>Parapenaeopsis cornuta</i>	29.8 ± 8.40	3
<i>P. hardwickii</i>	37.0 ± 13.6	3
<i>Portunus sanguinolentus</i>	118 ± 40.4	3
Osteichthyes		
<i>Cynoglossus</i> sp.	0.94 ± 0.51	3
<i>Engypropon</i> sp.	4.80 ± 0.82	3
Mollusca		
<i>Anadara subcrenata</i>	3.95 ± 0.93	4

coastal environments. In addition, public health authorities should instruct consumers through public education to understand the potential and indirect risk of consuming oysters cultured in the polluted areas, and how to avoid the risk. At the same time, we hope that the government and the producers face the consequence of this problem and find a realistic way to resolve it.

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