Oysters (*Crassostrea gigas*) in the Hiroshima wide area urban districts concentrate cadmium (Cd) in their shells

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ABSTRACT

To investigate the status of Cd in the oysters available in the Hiroshima wide area urban districts, cultured or wild oysters have been collected from the 7 prefectures in recent 5 years. Concentrations of the two heavy metals, Cd and zinc (Zn), were measured by the sediment detemining methods with the instrument for atomic absorption spectrometry in their shells. Oysters were found to accumulate a certain amount of Cd from sea into shells. The concentration was 0.16 ± 0.07 mg/kg in average with the range of 0.15 ~ 0.25 mg/kg. Since the average Cd was high in the wildlife kidney, present data of Cd concentrated in oyster shells would support the specultion that the accumulation of Cd in wildlife could be caused by the agricultural land, where the fertilizers blended with oyster shells were spred. The human activity to reuse oyster shells as one of the fertilizer components adds burden of Cd on our sanitary environment.

key words: cadmium, oyster, raccoon dog, oyster shell, wild boar

INTRODUCTION

Heavy metals circulating in the environment are accumulated in the tissues of living organizms. We have examined the oyster (*Crassostrea gigas*) as one of the special food stuff in Hiroshima to evaluate its nutrition beneficial to humans[1–3]. The component of nutrients and the composition of free amino acids of the oysters indicated the high concentrations of histidine and Zn[4]. These chatacteristics were explained as the result of evolution beneficial for self-defense against pathogens[5]. Whereas, the oysters collected from the Hiroshima bay between 2014 and 2017 contained Cd in meat as high as that reported in 2002 (Table 1)[6–8]. Since certain amounts of metals were found in their shells constantly[7], the oyster could be a sentinel marine life for the evaluation of the safety of marine food stuff and public health.

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Table 1. Concentrations of Cd in foods.

	Foods	Meat or seed (mg/kg)	Kidney (mg/kg)	Country	Reported year	Reference No.
1	Scallop	3.69	−	Japan	2002	6
2	Wakame	1.65	−	Japan		
3	Hijiki	1.217	−	Japan		
4	Oyster	0.487	−	Japan		
5	Oyster (Hiroshima)	0.53 ± 0.24	−	Japan	2015−2017	1 ~ 3
6	Oyster (Okayama)	0.09 ± 0.06	−	Japan		
7	Oyster (Kagoshima)	1.05 ± 0.25	−	Japan		
8	Cattle beef	0.001 >	−	Japan	2002	6
9	Swine pork	0.001 >	−	Japan		
10	Cattle beef	0.0281	−	Spain	2018	13
12	Wild boar	0.02	3.72	Italy	2015	10
13	Wild boar	0.078	−	Italy	2012	11
14	Wild boar	0.006 ~ 0.018	−	Poland	2010	12
15	Wild boar	−	0.112 ~ 5.400	Spain	2018	13
17	Wild boar	−	1.07 ± 0.70	Japan	2019	14
16	Wild boar	0.05 >	1.97 ± 1.67	Japan	2019	15
18	Wild boar	0.05 >	−	Japan	2018	8
19	Sika deer	0.07, 0.08 and 0.05 >	−	Japan	2018	
20	Red deer	0.006	1.02	Italy	2015	10
21	Cacao	0.90	−	Ecuador	2019	17
22	Cacao	0.303 ± 0.035	−	Itary	2018	18

The EU countries reported the concentrations of Cd in game with the necessity because of the habit to consume their meats with high frequencies[9]. The concentrations of Cd in the wild boar (*Sus scrofa*) meat were 0.02 mg/kg or 0.078 mg/kg in Italy[10, 11] and 0.006 ~ 0.018 mg/kg in Poland[12]. Wild boars accumulated Cd in kidney with the values of 3.72 mg/kg and 0.112 ~ 5.400 mg/kg in Italy and Spain, respectively[10, 13]. The red fox (*Vulpus vulpus*) accumulated Cd of 0.002 ~ 0.260 mg/kg in their bodies[13]. The red deer (*Cervus elaphus*) concentrated 0.006 mg/kg and 1.020 mg/kg of Cd in the muscle and the kidney, respectively[9]. By the screening, some of the game meats commercially aveilable in the Hiroshima wide area urban districts contained more than 0.05 mg/kg of Cd[14]. To assess the contamination of Cd, we set up the narrow areas, captured wildlife and measured the concentrations of Cd in the sentinel animals of satoyama[15]. Comparing the values in the kidney to the soil, there was a discrepancy of the concentrations of Cd, high in wildlife but low in soil[14].

The objective of this study is to investigate the status of Cd in the oyster shells available in the Hiroshima wide area urban districts by the comparison of that in other prefectures of Japan. The data would be helpful to explan the idea that high concentrations of Cd in wildlife coud be caused by taking excess amount of Cd through the crops, fruits or vegetables given the fertilizers blended with oyster shells and grown in their satoyama habitat.

MATERIALS AND METHODS

Oyster shell: Cultured or wild oysters were used. Cultured oyster were collected from the 5 prefectures: Hiroshima, Hyogo, Niigata, Miyazaki and Miyagi from 2014 to 2018. Wild oysters have been collected from the 3 prefectures, Hiroshima, Okayama and Kagoshima for 5 years in every January from 2014 to 2018[1, 7]. After removing the meat, the shells were stored at −20℃ until using.
Measurements of Cd and Zn: The shells were washed with running water, air-dried and ground by a stainless ball mill. The pulverised shells were sieved through 2 mm screen to remove impurities. Concentrations of the two metals were determined by the sediment detemining methods of II-5.1 and II-5.4 for Cd and Zn, respectively, with the instrument for atomic absorption spectrometry (AA-6200, SHIMADZU, Kyoto, Japan)[1, 7]. The mean value of the triplicated measurements was sued as the representative for each sample.
Statistical analysis: Student's *t*-test, F-test and χ^2-test were performed to compare the concentrations of Cd and Zn. Pearson's coefficient of correlation was used to examine the correlation between the values of Cd and Zn. The software, Mac multiple regression analysis, version 3 (ESUMI, Tokyo, Japan) and Kaleida Graph (HULINKS, Tokyo, Japan) were used[16].

RESULTS

Cd concentration in oyster shell: Concentrations of Cd in the oyster shells were shown in Figure 1-A and Table 2. The average concentration of the 24 samples was 0.148 ± 0.055 mg/kg (mean ± SD). The dispersion was 0.003 with the data range from 0.05 to 0.25 mg/kg. There was no sitatisitically significant difference in the concentrations between the shells of cultured and wild.

The concentrations of Zn of the shells cultured in Hiroshima bay were higher than those cultured at the other 5 bays of the 4 prefectures ($p = 0.0197$) (Table 2). The aver-

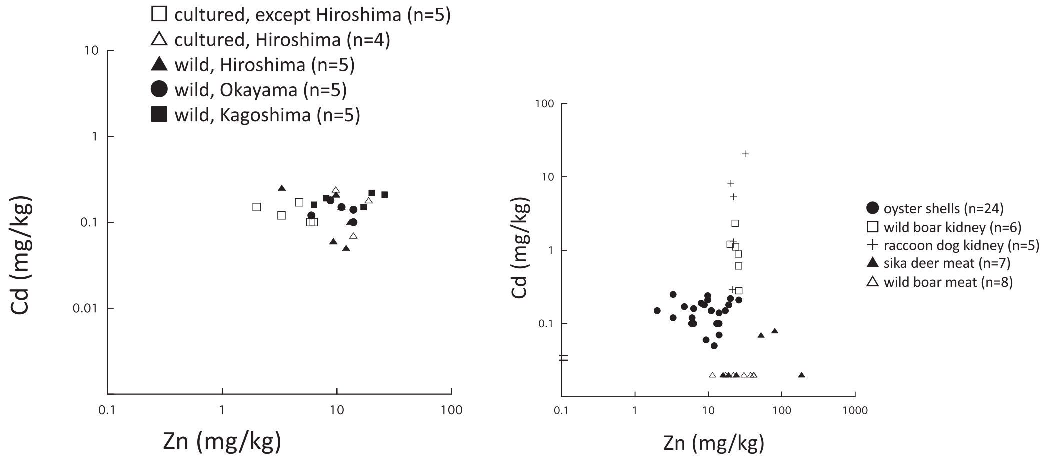

Figure 1. Cadmium concentrations in the environment.

A: Cd concentrations in the shells of cultured or wild oysters. The cultured oyster was from the 5 prefectures Hiroshima, Hyogo, Niigata, Miyazaki and Miyagi from 2014 to 2018, while the wild oyster has been collected from the 3 prefectures, Hiroshima, Okayama and Kagoshima for 5 years in every January from 2014 to 2018. **B**: Comparison of the Cd from sea to land. Samples were purchased or captured in the Hiroshima wide area urban districts[14, 15].

Table 2. Concentrations of Cd and Zn in oyster shells (mean ± SD).

	Cultured oyster		Wild oyster a)		
	Hiroshima	Except Hiroshima b)	Hiroshima	Okayama	Kagoshima
n	4	5	5	5	5
Cd (mg/kg)	0.16 ± 0.07	0.13 ± 0.03	0.13 ± 0.03	0.14 ± 0.03	0.19 ± 0.03
Zn (mg/kg)	15.23 ± 9.10 c)	4.44 ± 1.80	9.48 ± 3.78 d)	10.76 ± 3.45 e)	15.46 ± 8.27 f)

a): Wild oysters were collected at the mouths of the Ootagwa river, Takahashigawa river and Nagatagawa river and measured as the representative values at the Gulf of Hiroshima, Okayama and Kagoshima, respectively, for 5 years in every January from 2014 to 2018. b): Oysters were cultured in the Hyogo, Miyagi (Ishinomaki and Onagawa), Miyazaki and Niigata prefectures. c): $p < 0.0197$ by *t*-test when compared to the Zn value of the oysters cultured in the prefectures except Hiroshima. d): $p < 0.0273$ by *t*-test when compared to the Zn value of the oysters cultured in the prefectures except Hiroshima. e): $p < 0.0066$ by t-test when compared to the Zn value of the oysters cultured in the prefectures except Hiroshima. f): $p < 0.0195$ by *t*-test when compared to the Zn value of the oysters cultured in the prefectures except Hiroshima.

age Zn concentration of the cultured oysters in the prefectures except Hiroshima was lower than those of the three wild oyster groups ($p = 0.0273$, $p = 0.0066$ and $p = 0.0195$ for the wild oysters of Hiroshima, Okayama and Kagoshima, respectively).

Evaluation of Cd in the environment: Concentrations of Cd in the oyster shells and wildlife were shown in Figure 1-B. The data of wildlife schatcherd were quoted from our previous reports[14, 15]. The concentrations of Cd were under the measuremnt limit, < 0.05 mg/kg, in all of the wild boar meat purchased, while the 28.6% of the deer meat commercially available were over the limit. Values of the concentrations of Zn in the game were constant.

When compared the values in kidney, the average Cd was higher in the raccoon dogs (*Nyctereutes procyonoides*) (7.15 ± 8.16 mg/kg) than in the wild boars (1.07 ± 0.70 mg/kg)[15]. The average values of the Zn were similar in the two species, 22.3 ± 3.9 and 23.5 ± 4.7 mg/kg for the wild boars and the raccoon dogs, respectively[14].

When compared the concentration level of Cd between oyster shell and wildlife kidney, the values in the former were as low as the botom levels of the latter.

DISCUSSION

This report is the first to show the Cd concentrations of oyster shells cultured at the 4 different areas in the gulf of Hiroshima. They contained 0.16 ± 0.07 mg/kg of Cd in average. Oyster had an ability to accumulate a certain amount of Cd from sea into shell. The concentration range of Cd in shells was 0.15 ~ 0.25 mg/kg by the measurement of 24 samples from the 7 prefectures all over Japan. We could say from these data that the industrial system to recycle oyster shells from the industrial waste to the soil fertilizer circulates Cd from sea to land in certain concentrations calculable. This human activity adds burden of Cd, one of the heavy metals, on our sanitary environment.

Cd pollution poses a threat to food safety and human health in the world. Plant absorbes Cd. The higher concentrations of Cd have been reported in the soil of cacao plantation worldwide (Table 1). After the establishment of the critical level of Cd (0.6 mg/kg) by EU, concerns of safety in the consumption of cacao-based chocolate has risen[17, 18]. The critical levels of 0.43 mg/kg and 0.5 mg/kg of total Cd in the agricultural soils were also determined by the United States Environmental Protection Agency and Brasil, respectively, based on the scientific evidences[19, 20].

Artificial contamination is the greatest concern for the Cd pollution. Application of phosphate fertilizersis considerd one of the major inputs of Cd into agricultural soils, whose concentration was as high as 130 mg/kg[21]. Other soures of Cd in soils were Zn mining, battery production, planting or smelting[22]. Many studies revealed the several factors such as total metal content, pH, soil organic matter, cation exchangecapacity or cray content, which controled metal bioavailability in soil[23). The oyster shell usage could become one of the factors to increase total metal consumption of humans through the food chain from sea to land.

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広島広域都市圏のマガキ（*Crassostrea gigas*）が蓄積する重金属

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要　　　約

カドミウム（Cd）は食品汚染物質であるが，米と清涼飲料以外の食材に行政は基準値を設定していない。従って，農水産物の Cd 含有の実態を調査して情報提供することは，消費者の Cd 摂取量低減に寄与する。著者らは，広島広域都市圏のカキ（*Crassostrea gigas*）と野性動物を定点観察し，Cd と亜鉛（Zn）の含有量を測定している。本稿では，カキ殻に含まれる Cd と Zn 量を測定し，カキ殻を肥料として用いる場合の Cd の環境循環を，水域と陸域という区分で考察する。**材料及び方法**：2014～2018年に購入または採集した養殖および天然のカキを用いた。原子吸光分析法により，殻中の Cd と Zn の濃度を測定した。**成績**：①養殖カキ殻と野性カキ殻が，いずれも一定量の Cd を含有した（濃度域：0.15～0.25 mg/kg）。②カキ殻の Cd 含有量に日本国内の地域差を認めなかった。③Zn 含有量では，養殖カキ殻の方が野性カキ殻より有意に高かった（$p = 0.0197$）。**考察**：農地への施肥にカキ殻粉末が用いられることは注目に値する。カキ殻が一定量の Cd を含有する知見は，カキ殻を肥料として利用することで Cd を海域から陸域へ循環させることを数値で示すものであり，ヒトの公衆衛生環境への影響を考察するために必須の基礎資料となる。

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