THE PRESENT LEVELS OF HEAVY METALS IN SOME MOLLUSCS OF THE UPPER GULF OF THAILAND

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Abstract. This investigation was carried out as part of Thailand's participation in the global 'Mussel Watch' program. The levels of Cd, Cr, Cu, Pb, and Zn in the green mussel, *Perna viridis*, oyster, *Crassostrea commercialis*, and the cockle, *Anadara granosa*, were studied from July 1982 to November 1982. Comparison was made with the previous study in August 1981 which also included the short necked clam, *Paphia undulata* and moon scallop, *Amusium pleuronectes*. It was found that the metal levels were sufficiently low that the molluscs could be consumed without any danger to health. The salinity of the water appeared to influence the uptake as higher levels of metals were found during the flood season when salinity was lower.

1. Introduction

The most popular bivalve molluscs of Thailand are the Australian oyster, *Crassostrea commercialis*, green mussel, *Perna viridis*, cockle, *Anadara granosa*, short necked clam, *Paphia undulata*, and moon scallop, *Amusium pleuronectes*. The first three bivalves are widely grown commercially in shallow water in the Upper Gulf of Thailand not far from the Bangkok area.

Investigations of the levels of Pb and Cd in green mussels and oysters in Thai waters have already been reported by Huschenbeth and Harms (1975), Menasveta and Cheevaparanapiwat (1981) and Siriruttanachai (1980). The Cd, and especially the Pb, values quoted in the latter two references must be regarded as being much too high, as the analyses were carried out before the introduction into that laboratory of clean room facilities and of the use of deuterium background correction for atomic absorption spectrophotometry. However, year-round sampling by Siriruttanachai of three different oyster farms showed increases of 6 fold, 5 fold, 4 fold, and 3 fold in Cd, Cu, Pb, and Zn, respectively, during the months of November and December, when the salinity levels of the waters are at a minimum. Huggett *et al.* (1975) found that there was an increase in Cu and Zn levels in oysters with decreasing salinity of three river mouth areas in Virginia, and suggested that the reason might be because there was less competition from Ca and Mg in the estuarine waters for the absorbing sites of the oyster tissue.

The purpose of the present survey was to determine current levels of selected heavy metals in shellfish in Thai waters, in order to assess whether any changes are occurring on an annual basis, and to verify whether there are fluctuations in levels during the flood season, when the salinity drops. It is also necessary to have data on the levels of heavy metals in shellfish in order to assess whether there is a health hazard.

2. Experimental

2.1. Sampling

Six to 12 molluscs of the same size were gathered by hand from farms in each of the three coastal areas, namely Ang Sila Bay, Bang Prong Bay, and the Bang Pakong Estuary, from July until the end of November 1982, when the river runoff into the Upper Gulf was at its maximum. July is the beginning of the rainy season in Thailand, and by October–November the river flow may have increased by as much as 8 times. Thus there will be considerable dilution of the estuarine waters in November with a consequent drop in salinity levels.

The sampling was restricted to just these three study areas, as previous work has shown that other areas of Thai waters where molluscs were grown were all less polluted (Siriruttanachai, 1980).

2.2. Sample preparation

The bivalves were washed under running tap water, then drained. The flesh was chucked, using mussel shells for prying the mussels open, and stainless steel oyster chuckers for the cockles and oysters. Care was taken to minimize the contact of metals with the samples. The flesh was placed on filter paper for a short while, then transferred to a small beaker. Samples were dried for 12 hr at 80 °C in an oven and the dry weight then recorded. The beaker was then transferred to a muffle furnace and heated to 450 °C and kept there for 12 hr. A previous experiment* had shown that there was no loss of Cd or Pb under these conditions, but if the combustion was carried out for 24 hr, then up to 60% of the Pb could be lost. After cooling, a mixture of 10% redistilled HNO_3 in double-quartz distilled water was added to dissolve the residue. The solution was filtered through acid washed filter paper to remove any residual grey ash, and then analyzed using atomic absorption spectrophotometry. Cadmium, Cr, and Pb were determined using the graphite furnace method, and Cu and Zn with the air-acetylene flame. Deuterium background correction was used throughout and calibration carried out using the standard addition method.

3. Results

The metal contents of the green mussels, oysters and cockles are summarized in Tables Ia, Ib, and Ic. Table II shows the results of a previous survey by the authors of Cd and Pb levels in these three molluscs as well as the short necked clam *Paphia undulata* and moon scallop *Amusium pleuronectes*. The samples were all obtained in August 1981 from a local market, the analyses being carried out on composite homogenized samples

* Five replicate analyses were carried out using this method, and the results compared with a series of digestions with concentrated redistilled HNO_3 in a teflon decomposition vessel under pressure, whereby it was assumed that no losses occurred with the closed system.

TABLE Ia

The concentration of metals in green mussels, *Pernia viridis* (in μg g^{-1} dry weight)

	July		September		November	
	Bang Pakong	Ang Sila	Bang Pakong	Ang Sila	Bang Pakong	Ang Sila
Cd mean	1.02	0.87	1.05	0.51	0.13	0.23
range	0.15–2.51	0.31–1.13	0.11–2.38	0.31–0.89	0.10–0.19	0.09–0.46
Cr mean	0.44	0.18	0.13	0.12	1.07	0.92
range	0.21–0.60	0.07–0.28	0.01–0.33	0.12	0.11–2.17	0.35–1.60
Cu mean	2.97	4.31	4.01	3.90	7.81	11.48
range	1.47–4.41	2.66–6.23	0.66–9.19	2.69–5.20	5.68–9.38	6.13–17.92
Pb mean	1.28	2.05	1.83	1.77	0.54	0.63
range	0.20–2.61	1.48–3.38	0.56–3.25	0.99–3.80	0.20–1.21	0.19–1.31
Zn mean	78.18	121.39	201.2	191.7	129.5	149.4
range	58.27–119.4	158.9–213.1	142.7–285.7	108.6–157.5	95.78–173.5	100.9–253.7
average wet wt (g)	2.34	2.41	2.05	3.46	4.36	4.40

TABLE Ib

The concentration of metals in Australian oysters, *Crassostrea commercialis* (μg g^{-1} dry weight)

Metal	Bang Prong Bay.		Ang Sila Bay	
	July 1982	September 1982	July 1982	September 1982
Cd mean	1.88	0.76	2.05	5.02
range	0.93–2.73	0.42–1.33	0.33–4.58	2.67–7.44
Cr mean	0.19	0.23	0.24	0.26
range	0.15–0.24	0.19–0.27	0.24	0.22–0.29
Cu mean	70.90	152.8	76.16	185.7
range	5.73–120.06	63.48–276.3	4.89–206.49	109.8–240.5
Pb mean	1.51	3.77	2.15	5.19
range	0.54–2.55	1.25–13.11	0.72–3.88	3.42–9.21
Zn mean	424.13	976	448.01	1347
range	83.07–670.8	631–1256	64.11–698.5	973–1920

TABLE Ic

Metal levels of cockles, *Anadara granosa* from Ang Sila Area ($\mu g\ g^{-1}$ dry weight)

	Large (average length 3.2 cm)	Small (average length 2.7 cm)
Cd mean	2.30	3.36
range	1.88–2.77	3.10–3.71
Cr mean	0.14	0.19
range	0.14	0.14–0.28
Cu mean	1.88	2.07
range	1.36–2.21	1.78–2.44
Pb mean	1.92	2.11
range	1.64–2.16	1.78–2.77
Zn mean	87.75	107.33
range	79.15–92.30	77.75–119.81

TABLE II

Cd and Pb in bivalve molluscs from the local market, August 1981 ($\mu g\ g^{-1}$ dry weight)

Mollusc	Cd	Pb
Perna viridis	0.48	0.49
Crassostrea commercialis	0.26	0.36
Anadara granosa	0.77	0.47
Paphia undulata	0.42	0.26
Amusium pleuronectes (white meat only)	0.36–0.70	0.21–0.79

of from 25 to 54 individuals, except in the case of oysters and moon scallops, where individuals were analyzed. All of these samples were digested with concentrated HNO_3 using the teflon decomposition bomb technique.

The performance of the present analytical procedure, using the dry ashing and leaching technique, was also monitored by analyzing ICES Intercomparison samples for Pb and Cd, to give the following results:

Sample A Acceptable Cd value: $0.79 - 0.81\ \mu g\ g^{-1}$
Found: $0.81 +/- 0.15\ \mu g\ g^{-1}$
Sample B Acceptable Pb value: $2.77 +/- 0.18\ \mu g\ g^{-1}$
Found: $2.71 +/- 0.20\ \mu g\ g^{-1}$.

These results confirmed that the analytical procedure was satisfactory.

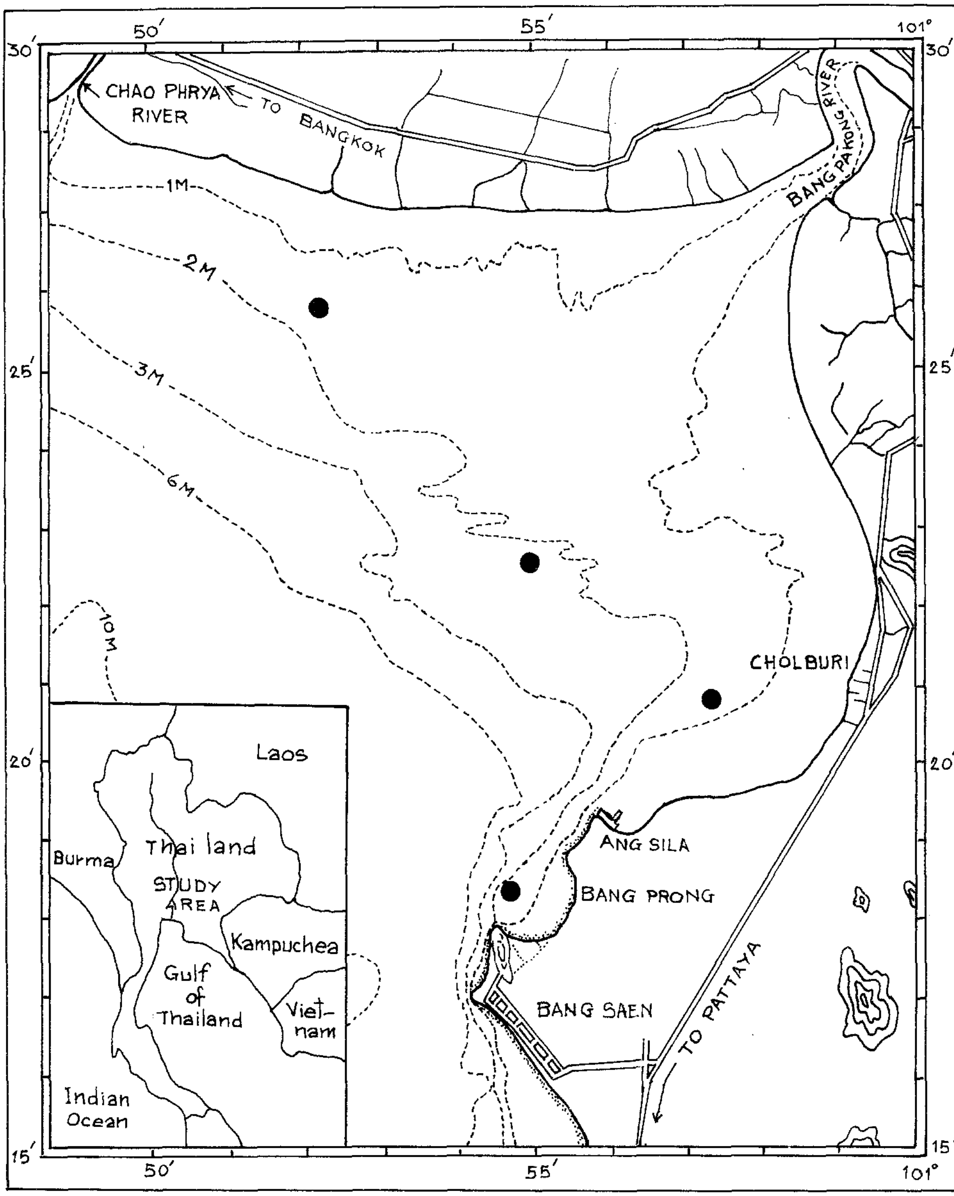

Fig. 1. Sampling Stations. The river shown in the inset is the Chao Phyra.

4. Discussion and Conclusion

4.1. *Perna viridis* (Table Ia)

The three areas studied are adjacent to each other and all come under the influence of the Bang Pakong river, which is quite a 'clean' river compared with most others which drain into the Upper Gulf of Thailand. However, this coastline is fairly densely populated, and the impact of man is considerable. It is also thought that the Chao Phrya river, which enters the Gulf at the northwest of the study area, could have a wide spread impact upon the top section of the Upper Gulf.

The metal content of the mussels in the Bang Pakong and Ang Sila was similar, although the mussels in the Ang Sila area had higher levels during the July and November sampling periods. It is not possible to compare the September figures, as the mussels from Ang Sila were approximately double the size of those at Bang Pakong.

On considering both areas (Bang Pakong and Ang Sila) as one continuous sampling area, a statistical analysis of the Cr content of individual mussles gave, for July, a mean Cr value of 0.3700 with a standard deviation of 0.2098 (n = 8), and for November a mean of 0.9878, S.D. 0.6599 (n = 14). For 95% confidence interval, the range of values for July became 0.1946 to 0.5454, while that for November was 0.6068 to 1.3688. There was no overlap of the ranges, and thus the difference between means is significant.

The same conclusion holds true for Cu whereby the July mean was 3.3231, S.D. 1.1958 (n = 19) while for November the mean was to 10.1013, S.D. 3.3204 (n = 16). For 95% C.I. the range for July was from 2.745 to 3.893 while the range for November was 8.332 to 11.870. There also was no overlap, thus the difference is also real.

We can say that the Cr and Cu contents in mussels in November (flood season) were significantly higher than those for July (beginnng of the rainy season). This agrees with the widely known finding that the metal content in the organisms increases when the water becomes less saline (Huggett *et al.*, 1975).

4.2. *CRASSOSTREA COMMERCIALIS* (Table Ib)

By reference to the Table, a comparison can be made between Bang Prong Bay and Ang Sila Bay, as well as an assessment of the influence of seasonal changes upon heavy metal content. Again it may be observed that at the beginning of the flood season in September there is a general trend of increasing heavy metal content.

The mean values of Cd, Cr, Cu, Pb, and Zn were 0.76 to 5.02, 0.19 to 0.26, 70.9 to 259.2, 1.51 to 5.19, and 424.1 to 1347 $\mu g\ g^{-1}$ dry weight, respectively.

4.3. *ANADARA GRANOSA* (Table Ic)

Samples were only available for the July period, and it would appear that the metal content decreases with increasing weight of the cockles.

The mean values of Cd, Cr, Cu, Pb, and Zn were 2.30 to 3.36, 0.14 to 0.19, 1.88 to 2.07, 1.92 to 2.11, and 87.8 to 107.3 $\mu g\ g^{-1}$ dry weight, respectively.

A general assessment of heavy metal contamination of shellfish in the Upper Gulf in relation to other areas might be made by a comparison of the data of Table Ia, Ib, Ic, and II with that of Table III. It should also be noted that the levels of Cd and Pb listed in Table II, which were obtained in August 1981, appear to be lower than the 1982 data. This might be because in 1981 the flesh of the bivalve molluscs was washed with distilled water and then drained prior to analysis, whereas in 1982, the outside shells only were washed before opening up.

TABLE III

Some reported concentration of metals in bivalves ([1]$\mu g\ g^{-1}$ dry weight, [2]$\mu g\ g^{-1}$ wet weight)

Species	Cd	Cr	Cu	Pb	Zn	Locality/Reference
Anadara granosa[2]	0.28		5.6	0.18	16.2	Rayong, Thailand (Huschenbeth and Harms, 1975)
Anadara subcrenata[1]	0.80	3.2	3.2	0.90	33.3	Hong Kong (Phillips, 1980)
Crassostrea commercialis[2]	0.2		2.0	0.8	27.7	New South Wales, Australia
range	0.1–1.0		3–48	0.3–1.3	80–665	MacKay *et al.* (1975)
Crassostrea commercialis[1]	8.9		117.4	15.2	572	Siriruttanachai (1980)
Crassostrea virginica[1]	1.3–10.7		23–40	0.1–3.5	310–7080	Gulf Coast, U.S.A. (Goldberg *et al.*, 1978)
Crassostrea gigas[1]	0.2–0.6	0.2	3.0	0.4	250	U.K., Pollution Report No. 2 (1977)
Mytilus edulis[2]	2.09		0.73	–	42.7	Australia (Phillips, 1976)
Mytilus edulis[1]	1.7–3.6		6.5–14	2–15	130–170	S.W. Spain & Portugal (Stenner and Nickless, 1975)
Mytilus edulis[1]	0.3–0.5	0.2–0.3	31–33	0.2–0.4	150–240	U.K., Pollution Report No. 2 (1977)
Pecten maximus[1]	13	1.5	3.3	8.3	230	Irish Sea (Segar *et al.*, 1971)
Perna viridis[1]	0.38		7.3	0.11	14.2	Rayong, Thailand
Perna viridis[1]	3.3	–	8.7	83.3–330	54.7	Chao Phrya Estuary, Thailand (Menasveta and Cheevaparanapiwat, 1981)

In conclusion, it would appear from this work that the levels of toxic heavy metals in molluscs of the Upper Gulf are low enough not to present a health hazard if the molluscs are eaten, although due attention should be paid to the maximum acceptable daily intake per kilogram body weight.

In Australia the acceptable limits, per weight of food consumed, as recommended by the National Health and Medical Research Council (1979) are as follows:

Seafood (shellfish)
Cd 1 $mg\,kg^{-1}$
Pb 2.5 $mg\,kg^{-1}$
Cu 70 $mg\,kg^{-1}$
Zn 100 $mg\,kg^{-1}$ (but for oysters the limit is 1000 $mg\,kg^{-1}$).

The WHO Technical Report Series No. 373 (1967) recommends the following maximum acceptable load (in $mg\,kg^{-1}$ body weight per day):

Pb 0.005 Cu 0.5.

No limit for Zn was recommended as it was thought that there is a wide margin between the levels of this element in ordinary diets and the level that could induce toxic effects.

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