METALS IN FISH AND SHELLFISH FROM LAKE ILLAWARRA, NEW SOUTH WALES, AUSTRALIA

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ABSTRACT

Fish (dusky flathead – *Platycephalalus fuscus* and luderick – *Girella tricuspidata*) and shellfish (*Anadara trapezia* and *Saccostrea commercialis*) samples from Lake Illawarra in south-eastern Australia were collected in 1993 and 2000 and analysed for a range of metals. Sediments with which the shellfish were in contact were also examined. The results were compared with shellfish data collected in 1976 and in an independent study in 1993. No reported data were available for comparison with the fish metal results. The results showed that trace metal concentrations in both fish and shellfish were generally low and represented minimal health risk. The dusky flathead, a predator species, had detectable concentrations of mercury, while the luderick, a herbivore, had values below detection limits. Metal concentrations in shellfish were in general agreement with those found in other studies, and showed that no apparent changes were occurring over time, except those that could be explained by changes in the age of the shellfish. Only copper in Lake Illawarra oysters showed greater concentrations than found in other south-eastern Australian estuaries. It is recommended that future studies focus on organic and microbial contamination.

INTRODUCTION

Lake Illawarra is a coastal lagoon located 10 km south of Wollongong on the southeast coast of Australia (Fig. 1), at latitude 34°30'S and longitude 150°50'E. The regional setting of the Lake and some of its conditions have been described by Ellis *et al.* (1977). The Lake averages 1.9 m in depth, its deepest point being 3.7 m (Yassini and Jones, 1987). Wollongong has a heavy industry base and its economy primarily depends upon a large steelworks and associated coke and copper industries. The majority of these industries are in close proximity to, but not within the Lake Illawarra catchment. Airborne pollution from the industry reaches the Lake directly or indirectly via deposition in the catchment area and has been the prime mechanism of heavy metal pollution of the lake (Crisp *et al.*, 1984).

A complete review of pollution and its impacts on Lake Illawarra is detailed in Depers and Yassini (1995). This report discussed urbanisation, industrial activities in the Illawarra, ash and trace metal content in the Lake sediments and a number of other issues relating to the management and quality of the Lake and it's catchment. Historically, in addition to the industries described above, industry in the Illawarra region also includes coal mining, fertiliser production and a power station. The use of leaded petrol and urban runoff have are also sources of anthropogenic pollution to the Lake. Ellis and Kanamori (1977) found elevated concentrations of Pb, Cd, Cu and Zn in Lake sediments. These elevated concentrations were attributed to the industrial operations that commenced at Port Kembla in 1928 with the greatest enrichment of sediment metals in Griffins Bay, the nearest portion of the Lake to the industries of Port Kembla. This paper summarises the findings of a number of studies on metal concentrations in sediments, fish and shellfish from Lake Illawarra.

MATERIALS AND METHODS

Sampling

Sediment and pore water was collected at each site using PVC cores (5 cm diameter and 10 cm length). The sampling for sediment and pore water was conducted at the same time. The PVC cores were inserted into the sediments where the cockles (*Anadara trapezia*) and oysters (*Saccostrea commercialis*) were collected (locations indicated in Fig. 1). The top 10 cm of the sediments was sampled. The samples were covered separately with airtight plastic bags to avoid the loss of pore waters, contact with air and possible contamination. Using this procedure, up to ten sediment and pore water samples were collected from each site on each sampling occasion. The pore waters were collected by centrifugation. A Jouan MR22i centrifuge was used for the extraction of pore waters from fine particle sediments whereas a Hettich EBA 35 centrifuge was used for sandy sediments. The sediments were placed into 0.45 µm Millipore ultrafree-CL filters and centrifuged at 1500 rpm for 15 min. The filtered pore waters were collected from both centrifuging procedures, were transferred to 50 mL vials, and acidified with concentrated HNO^3 to a pH < 2. The separated sediments were wet sieved through a 63 µm plastic mesh and then frozen until analysis whereas the pore waters were stored at 4°C in a refrigerator.

Surface waters were collected from each site in 30 mL polyethylene bottles which had been washed with 10% HCl. The surface waters were filtered through 0.45 µm filter papers and acidified with concentrated HNO^3 in the field. A minimum of two water samples were collected from each site. These samples were stored in a refrigerator at 4°C, for a period of less than five days, until the laboratory analysis.

Shellfish (*A. trapezia* and *S. commercialis*) and fish (*Girella tricuspidata* (luderick) and *Platycephalus fuscus* (dusky flathead)) were collected from various locations within the Lake. In the first sampling event (1993), 76 shellfish samples (*A. trapezia*) were collected from the three locations in Lake Illawarra indicated in Fig. 1. In the second sampling event (2000), ten *A. trapezia* were collected from one of the locations in the 1993 sampling event (Tallawarra). During the first sampling, up to 30 cockles were collected from each of the three sites. In addition, ten *S. commercialis* were sampled from the Tallawarra site during the second sampling period. Both sampling events took place during late autumn to early winter. Twenty fish samples (ten of *G. tricuspidata* and ten of *P. fuscus*) were sampled from the Lake. Nets were used to catch the fish.

The shellfish were depurated in filtered Lake Illawarra surface water for up to ten days following collection. Subsequent to depuration the shellfish were measured (length and breadth) with vernier calipers: the precision of the measurement was ± 0.05 mm. The samples were then frozen for subsequent metal analysis. Upon collection, the fish were immediately frozen. Flesh was sampled from the edible portions of the fish only.

Metal Analysis

All analyses were carried out at the laboratories of the Australian Nuclear Science and Technology Organisation (ANSTO). Sediment samples (< 63 µm fraction), together with a certified reference material (NIST standard reference material 1646a - estuarine sediment), were microwave digested using a mixture of hydrofluoric, hydrochloric and nitric acids (ANSTO method VEC-I-9-01-018). The resulting solutions were diluted and then analysed by either inductively coupled optical emission spectrometry (ICPOES – ANSTO method VEC-I-9-03-002) or mass spectrometry (ICPMS – ANSTO method VEC-I-9-03-007). The ANSTO methods are minor adaptations of those contained in USEPA SW-846 (USEPA, 1998; methods 3051, 6020 and 6010A, respectively). The adaptations included minor variations in the proportions of sample/digester or the internal standard used in the methods.

For shellfish, the soft tissue of each sample was separated from the shell, whereas for the fish a tissue sample (0.5-1.0 g) was obtained from above the pectoral fin. The shellfish and fish samples were then oven dried to a constant weight at 40°C. Both the dry and wet weights of each of the samples were recorded. The samples were then microwave digested using the method outlined above and analysed using either ICPOES or ICPMS. Certified reference materials (NIST standard reference material 1566a - oyster tissue, or DORM-2 standard reference material - dogfish muscle) were also treated in the same manner for quality control.

RESULTS AND DISCUSSION

Quality Control Samples

Measured concentrations were generally within the certified ranges, however, for the sediment reference material, in some instances (Ca, Cu, Fe, Se and Zn) the variability in the measured concentrations was quite high. In addition, the agreement for Cu and Fe between the measured and expected concentrations could be improved. The quality control results are given in Table 1.

Sediments and Pore Waters

The metal concentrations are summarised in Table 2. In the table, the results of this study are compared with previous studies of metals in sediments of Lake Illawarra. No previous results are available for pore waters in Lake Illawarra sediments.

The results of the 2000 sediment sampling (present study) are in good agreement with the sediment concentrations found by Chenhall *et al.* (1992) and are higher or within the background sediment concentrations found by Ellis and Kanamori (1977) who analysed whole sediments, dried and ground to < 150 µm. The 1993 sediment metal concentrations (present study) are very much lower than the

Table 1. Quality control results for standard reference materials. The 95% confidence intervals are given in parentheses for both the certified and recovered results.

Element		Oyster tissue – NIST 1566a (n = 7)	Dogfish muscle – DORM 2 (n = 5)	Estuarine sediment – NIST 1646a (n = 4)
Arsenic	Certified	14.0 (1.2)	18.0 (1.1)	6.2 (0.2)
	Recovered	14.2 (1.2)	17.7 (1.0)	5.6 (1.4)
Calcium	Certified	1690 (190)	Not certified for Ca	5190 (200)
	Recovered	1830 (80)		5070 (560)
Cadmium	Certified	4.15 (0.40)	0.04 (0.01)	0.15 (0.01)
	Recovered	4.24 (0.79)	< 0.1	< 0.1
Copper	Certified	66.3 (4.3)	2.3 (0.2)	10.0 (0.3)
	Recovered	56.9 (3.7)	1.9 (0.4)	16.9 (16.3)
Iron	Certified	539 (15)	142 (10)	20000 (1800)
	Recovered	490 (14)	100 (6)	24500 (9300)
Mercury	Certified	0.06 (0.01)	4.6 (0.3)	0.04
	Recovered	< 0.1	5.4 (0.1)	< 0.1
Lead	Certified	0.37 (0.03)	0.07 (0.01)	11.7 (1.2)
	Recovered	0.36 (0.08)	< 0.1	12.9 (2.3)
Selenium	Certified	2.21 (0.20)	1.4 (0.1)	0.19 (0.03)
	Recovered	2.28 (0.19)	1.46 (0.09)	0.6 (0.4)
Zinc	Certified	830 (57)	25.6 (2.3)	48.9 (1.6)
	Recovered	824 (12)	20.0 (1.7)	44.0 (4.9)

Table 2. Elemental concentrations (mg kg-1 dry weight) found in Lake Illawarra sediments in the present and previous studies. The sediment results are compared with the ANZECC/ARMCANZ low level interim sediment quality guidelines. Also given are the elemental concentrations (in mg L-1 for Ca and Fe, otherwise in g L-1) found in pore waters within the sediments.

Reference	Ca	Fe	Zn	As	Se	Cd	Pb	Cu
Sediments								
Chenhall *et al.* (1992)	ND	ND	65-203	ND	ND	0.01-0.22	21-84	16-122
Ellis and Kanamori (1977)	ND	ND	3-710	ND	ND	< 0.1-4.3	< 0.1-115	1-127
Ellis and Kanamori (1977) - background	ND	ND	16-79	ND	ND	ND	9-19	20-65
Roy and Peat (1974)	ND	ND	900	ND	ND	ND	175	100
This study – 1993 (Range)	534-4670	1033-18758	3-38	ND	ND	< 0.5	< 5-15	2-15
[Mean (Std Dev.)] (n = 15)	1966 (1125)	8070 (7436)	20 (14)	ND	ND	ND	9.3 (4.4)	7.3 (4.0)
This study – 2000 a (Range)	2876-11186	47535-75535	101-139	8.9-14.5	1.5-2.0	< 0.1-0.3	36.1-53.9	40.4-62.2
[Mean (Std Dev.)] (n = 8)	5879 (2730)	57385 (9291)	124 (13)	11.3 (1.6)	1.8 (0.1)	ND	43.5 (5.5)	48.9 (7.7)
ANZECC/ARMCANZ (2000)			200	20		1.5	50	65
Pore Waters								
This study – 2000 (Range)	320-411	0.59-3.03	37-59	56-63	45-60	< 0.2	< 2	< 0.5
[Mean (Std Dev.)] (n = 8)	359 (29)	1.51 (0.79)	42 (10)	62 (3)	55 (5)	ND	ND	ND

ND Not determined
a The analysis performed in 2000 used the < 63 m fraction.

results of previous studies and are towards the lower end of concentrations found by Ellis and Kanamori (1977). No size fractionation was carried out on the samples obtained in 1993 study, whereas samples obtained in 2000 were only analysed for the < 63 µm fraction (this fraction accounted for only 2.8% of the total sediment weight). Although it is difficult to compare studies that have analysed different size fractions, it is important to recognise that the metal concentrations found in sediments in the present study most likely represent background levels and are below the low level interim sediment quality guidelines (ANZECC/ARMCANZ, 2000), except for one sample where the Pb level was slightly higher (53.9 mg kg^{-1}).

Fish and Shellfish

The results of the metal analyses (as concentrations per unit wet weight) are summarised in Table 3. Full data for each individual specimen are available from the authors. Also given in Table 3 are results from previous studies, as well as the Australia New Zealand Food Authority (ANZFA, 1998) maximum permitted concentrations (MPC) in oysters and fish.

The trace metal concentrations in the shellfish and fish sampled in Lake Illawarra were relatively low. In general, the concentrations of trace metals (As, Cd, Cu, Hg, Pb, Se and Zn) were below the MPC in oysters or fish. Of the metals listed, only As and Cu exceeded the MPC limits for a single shellfish or fish sample. However, the concentrations found in this study are similar to those found in other studies for shellfish from Lake Illawarra (Harris, 1976; Scanes and Roach, 1999). In addition, the concentrations of As are similar to those found in other New South Wales estuarine lakes that would be considered to be less impacted, e.g., Burrill Lake (Hafey, 2000; Oku, 2001). Only the concentration of Cu in Lake Illawarra oysters (*S. commercialis*) would appear to be greater than concentrations found in other estuarine lakes.

There were few if any discernable patterns that could be found in the trace metal concentrations within the species sampled within the Lake. This may have been due to the relatively small range in sizes sampled in either 1993 or 2000, particularly for shellfish.

The sampling study performed in 1993 indicated that spatially there was little variation in metal concentrations in *A. trapezia* found within the Lake (Table 2). The results from this sampling study indicated that there was considerable overlap in the concentration range found for each of the trace metals at the three sites. Conversely, there are temporal differences between the 2000 sampling of *A. trapezia* and that conducted in 1993. There is no overlap in the concentration ranges of some elements and only a minor overlap in others (Table 2). The metal concentrations found in *A. trapezia* in 2000 for Ca, Cd and Pb were less than those found in 1993, whereas the concentrations of Cu and Zn were greater in the 2000 sampling study. These differences, however, may be related to differences in the sizes of the animals sampled in the two studies. The shell length of the animals sampled in 1993 ranged from 60 to 76 mm, whereas those in 2000 ranged from 22 to 27 mm. The animals sampled in 2000 are smaller (and younger) than those sampled in 2000. The finding of higher metal

Table 3. Elemental concentrations (mg kg-1 wet weight) found in Lake Illawarra shellfish and fish in the present and previous studies. The Australia New Zealand Food Authority (1998) [ANZFA] maximum permitted concentrations (MPC) in oysters and fish are presented for comparative purposes.

Reference	Species	Site	Year	Ca	Mg	As	Cd	Cu	Fe	Hg	Pb	Se	Zn
Harris, 1976	Mollusc		1976				0.04-1.0	0.04-1.0			0.7-1		210-820
This study	*A. trapezia*	Bevans Island	1993	305-642	501-994		0.66-2.69	0.23-0.55	26.9-140		1.25-4.11		8.00-16.8
This study	*A. trapezia*	Windang	1993	390-678	723-909		1.01-2.84	0.34-0.54	45.6-80.5		1.97-3.80		9.69-17.4
This study	*A. trapezia*	Tallawarra	1993	310-844	708-951		1.82-4.63	0.34-0.77	44.1-102		0.64-2.93		8.24-12.9
This study	*A. trapezia*	Tallawarra	2000	254-354		0.70-0.90	0.93-1.34	1.24-2.29	32.5-116	< 0.02-0.13	0.049-0.15	0.57-0.92	11.6-21.7
Scanes and Roach, 1999	*S. commercialis*		1993			1.07	0.26	34.0		< 0.01	0.18	0.39	261
This study	*S. commercialis*	Tallawarra	2000	268-1150		0.52-1.22	0.29-0.53	34.0-72.1	16.3-86.0	< 0.02-0.042	0.037-0.088	0.38-0.89	106-265
This study	P. fuscus		2000			0.30-1.24	< 0.02	0.12-0.45		0.02-0.07	< 0.02	0.44-0.55	3.97-6.87
This study	*G. tricuspidata*		2000	112-821		0.38-1.18	< 0.02	0.078-0.43	0.68-6.11	< 0.02		0.091-0.38	1.93-5.64
ANZFA MPC	Oysters					1.0	2.0	70.0		0.5	0.5	1.0	1000
ANZFA MPC	Fish					1.0		10.0		0.5	0.5	1.0	150

concentrations in smaller/younger bivalves is consistent with other studies (Boyden, 1977, Hung *et al.*, 2001). This can be explained by a decrease in the metabolic rate with increasing size/age of the animal, where the metal concentration in the flesh decreases as the surface area/volume ratio decreases (i.e., metal content is diluted with an increase in mass). The result is supported by the results of Oku (2001) from other estuarine lakes where both the size range and trace metal concentrations are intermediate between those found in Lake Illawarra during the two sampling studies.

In addition, results for trace metals found in *S. commercialis* in the present study are very similar to those found earlier by Scanes and Roach (1999) for the oyster. The results obtained for *S. commercialis* in the present study and by Scanes and Roach (1999) would suggest that there are no adverse changes in Lake chemistry that could be used to explain the differing trace metal concentrations in *A. trapezia* between 1993 and 2000. Figure 2 indicates the relationship between size and Cu and Ca concentrations found in *A. trapezia* for the Tallawarra site in Lake Illawarra. Also, included in the figure are similar data from other estuarine lakes (St. Georges Basin; Burrill Lake) in New South Wales (Oku, 2001). It is clear from the figure that a significant fit exists in both cases.

There have been no previous studies on the trace metal concentrations in fish from Lake Illawarra. However, the concentrations, on the basis of mg/kg dry weight, are within the range of those found for mullet (*Mugil cephalus*) in other Australian estuaries (Kirby *et al.*, 2001). One of the interesting results of the present study was that the dusky flathead (*P. fuscus*), a predator species, had detectable concentrations of Hg and higher concentrations of Se than the luderick (*G. tricuspidata*), a herbivore. The flathead, however, being a bottom dweller, may be potentially more exposed to Lake sediments and their associated trace metal loads (even though these latter loads would not be considered overly elevated – see Table 1).

CONCLUSIONS

The results of this investigation indicate that there were no obvious metal contamination problems in the biota found in Lake Illawarra. The Cu concentrations in Lake Illawarra oysters were found to be greater than in other non-impacted lakes whereas the concentrations of other metals were found to be similar to trace metal concentrations found in the same species in other lakes. No discernable patterns could be found either between metals for either shellfish or fish or between sites for shellfish. The results of the present study suggested, however, that there may be some temporal differences as a result of differences in sample sizes, and therefore age, for shellfish.

While the present study suggests that there are few health implications associated with the metal concentrations in the fish or shellfish in Lake Illawarra there is little to no information with respect to organic or microbial contamination. It is suggested that studies focussing on organic and microbial contamination be a future research direction.

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