

Contaminants in water, sediment and fish biomonitor species from natural and artificial estuarine habitats along the urbanized Gold Coast, QueenslandNathan J. Waltham,^{†*ab} Peter R. Teasdale^c and Rod M. Connolly^b

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Metal and pesticide contaminants were measured in water, sediment and fish species in various Gold Coast waterways, Queensland. With the exception of Cu, metal concentrations in water, measured using the diffuse gradients in a thin film (DGT) technique, complied with relevant Australian guidelines. Cu concentrations in these waterways have been related to recreational vessel activities previously. All sediment metal concentrations measured were below the national guidelines, although Cu, Zn and Pb were found to vary significantly between habitat types. Evidence of spikes in sediment pesticide concentrations (some banned over 50 years ago) was observed in some artificial residential waterways. Heavy metals and pesticides were measured in the tissue (muscle, gills and liver) of three economically important species of fish, with different feeding strategies (partly herbivore *Arrhamphus sclerolepis*, carnivore *Acanthopagrus australis*, detritivore *Mugil cephalus*). We tested the hypothesis that fish accumulate different amounts of contaminants from wetland habitats affected by different intensities of anthropogenic activities (*i.e.*, marinas, artificial residential canals, artificial residential lakes, estuaries and natural, vegetated waterways). Significantly higher concentrations of Cu were found in the gills of each fish species from marinas compared to fish caught in other waterways. Furthermore, fish caught in canals had the second highest Cu and natural waterways the lowest. These results support the stated hypothesis for Cu and furthermore indicate that these fish species are suitable as biomonitors in estuarine waterways. Metal and pesticide concentrations in the edible muscle tissue of all fish complied with the Australian Food Standard Code recommended limits for human consumption, apart from As which is likely to be due to bioconcentration of lower toxicity organo-As species. These results indicate a low health risk for humans consuming fish, in terms of contaminant levels. The accumulated body of evidence on contaminants within Gold Coast waterways generally suggests that there are no major threats of metal or pesticide contamination, except for marina facilities which are a major source of Cu which also accumulates in fish. Water quality threats are also highlighted in residential canals, presumably as a consequence of their hydrological design.

^aGold Coast City Council, PO Box 5042, Gold Coast Mail Centre, QLD, 9729, Australia. E-mail: nathan.waltham@griffithuni.edu.au

^bAustralian Rivers Institute – Coasts and Estuaries, and School of Environment, Griffith University, Gold Coast Campus, QLD, 4222, Australia

^cEnvironmental Futures Centre and School of Environment, Griffith University, Gold Coast Campus, QLD, 4222, Australia

[†] Present address: Koskela Group PO Box 2965 Southport, QLD 4215, Australia. Fax +61 7 5564 886; Tel: +61 7 5502 8092; E-mail: nathan.waltham@griffithuni.edu.au

Environmental impact

Sediment and water column contamination (heavy metals and pesticides) in natural and artificial estuarine habitats in southern Moreton Bay comply with Australian guidelines. Importantly, this translates to a low health risk for humans consuming local fish species, with all fish, regardless of feeding strategy (carnivore, herbivore, omnivore), shown to be safe to eat. There is evidence of contaminant spikes in sediment in some habitats examined highlighting that some areas of the bay are influenced by proximate land use. For example, highest sediment and water column copper concentrations were found in marinas, and was reflected with the highest copper concentrations in the gill tissue of all fish. Managers face the challenge of human health protection whilst also accommodating further population, urbanization and pollution.

Introduction

The coastal zone supports a large part of global biological productivity yet, at the same time, it is becoming modified by high rates of anthropogenic activity such as residential development, industry, effluent discharge, mining, and shipping facilities.^{1,2} The modern day coastline is subject to a mix of land uses which generate a range of contaminants that are transported following rainfall runoff, usually untreated and unprocessed, to local rivers and estuaries.^{1,3,4} Many major discharge points are located within the coastal zone which has consequently accumulated contaminants and other waste from human activities.³ Coastal managers therefore face solving the juxtaposition of continuing anthropogenic needs with ecosystem conservation, often with limited scientific data.⁵

Routine estuarine water and sediment quality monitoring programs are common but are rarely able to measure disturbance because they focus on water and sediment quality as surrogates for ecosystem health.^{6,7,8} To determine whether poor water and sediment quality equates to reduced ecosystem health and function, a more comprehensive suite of measurements is needed.⁹ Programs that integrate biological measurements with water and sediment surveys are not only useful for demonstrating responses (*e.g.*, accumulation of contaminants) by local fauna to a measured range of abiotic environmental conditions, but also raise public awareness and encourage contaminant assessments and management intervention.^{3,10} In applications where the fate and magnitude of potential contamination is of concern, fish are a useful choice of indicator because:

- 1) they are abundant, easy to identify and process;
- 2) a range of trophic feeding modes can be investigated in a single survey;
- 3) some species are sedentary and provide a direct and continuing biological response to local contamination;
- 4) they have a high public awareness as they are economically and recreationally targeted; and
- 5) their loss can be equated to societal costs.^{9,11}

While sedentary bivalve species are often preferred as biomonitors,^{12,13} there have already been several studies in Gold Coast waterways that have used the local rock oyster,¹⁴ and therefore this project investigates the use of fish as biomonitor species instead.

Like many major coastal wetland systems around the world, Moreton Bay and the connected Gold Coast waterways, in southeast Queensland, Australia, is under pressure from rapidly increasing rates of anthropogenic activities.¹⁵ The 2006 population of 2.7 million (600,000 on the Gold Coast) is expected to increase to approximately 5 million (750,000 on the Gold Coast) people by 2026¹⁶ and this will undoubtedly bring increased waste, sediment, nutrients and other forms of contaminants to local waterways.¹⁵ Large areas of natural coastal wetland habitat have already been lost or claimed for urban development. An obvious feature of the landscape has been the replacement of natural wetland habitat with artificial residential urban waterways (canal estates), which massively extend the opportunity for residential real estate with water frontage while at the same time increasing the amount of fish habitat.¹⁷ These urban waterways also receive high loads of untreated and unprocessed urban stormwater

runoff and, being highly ramified, can be poorly flushed relative to nearby natural estuaries.¹⁸

Routine ecosystem health monitoring in southeast Queensland waterways has been ongoing for the past 10 years (see <http://www.healthywaterways.org>). This program utilises a suite of indicators that provide an understanding of the ecosystem health and response to land use activities. The program focuses largely on physicochemical parameters (*e.g.*, temperature, dissolved oxygen, salinity) along with nutrient and sediment concentrations in the water column, together with seagrass depth/range, nitrogen isotope and coral cover monitoring. However, this regional program does not include heavy metals or pesticides that are available in the water column or accumulated in the sediments, nor does it consider whether fish are safe to eat, which is a more fundamental question for managers and the public. Monitoring that integrates abiotic and biotic parameters are being used more frequently as part of ecosystem health surveillance and operational programs and to guide management intervention (*e.g.*, European Water Framework Directive, Chesapeake Bay).^{19,20} While contaminant studies have been completed in Moreton Bay (Table 1), few have extended beyond water and sediment measurements to include ecological mechanistic processes, which is of greater importance to managers challenged with achieving urban planning targets with conservation and biodiversity outcomes. In addition, these previous studies have also generally focused on one discrete habitat type, and consequently the mosaic of natural and artificial wetland habitats have not been examined.

In this study, we measured the accumulation of contaminants in fish tissue (muscle, gill and liver) to determine whether concentrations vary amongst natural and artificial residential waterway habitats on the Gold Coast. We predicted that contaminant (metals and pesticides) concentrations in fish would differ among habitats because of exposure to different amounts of contaminants, with concentrations higher in fish captured in habitats exposed to higher contaminant concentrations. Contaminants were also measured in sediment and water samples in each habitat to check for concentrations against national guidelines for ecosystem protection and for mechanistic insights into fish contamination. The results of this study are also compared with some more extensive previous studies into water and sediment quality on the Gold Coast and southeast Queensland (Table 1), which are used here to provide an overall impression of ecosystem health.

Materials and methods

Survey design and field sampling

Fish were collected over 3 weeks in austral autumn (April) in 2007 from five different wetland habitats in Gold Coast:

- 1) estuaries;
- 2) open natural vegetated parts of the bay (hereafter referred to as natural habitat);
- 3) artificial residential canals (canals);
- 4) artificial residential lakes (lakes); and
- 5) marina facilities (Fig. 1).

The estuaries and natural habitat sites receive pollutant loads from urban, agricultural, golf courses and industrial areas, but

Table 1 Summary of contaminant studies in the tidal waters of Moreton Bay catchment

Study	Elements	Water sampling	Sediment sampling	Biological sampling	Wetland habitat(s)	Conclusions	Source
1	Trace metals, metalloids, pesticides	—	—	✓Intertidal crabs	Intertidal mud flats	Pesticide were detected in crabs in Brisbane area, small number of individual crabs failed human consumption guidelines	21
2	Trace metals	—	✓	✓Mangroves	Estuary of northern Moreton Bay	Sediment metals in the study area are sourced from the geological bedrock. Disturbed banks within estuary had low levels of metal enrichment due to boating activities. Metals detected in mangrove tissue, particularly so for Cu which was higher in mangroves compared to sediment	22
3	Chlorohydrocarbon pesticides	✓	—	✓	Brisbane Estuary	The banning in 1970's to 1980's of chlorohydrocarbon pesticide use has resulted in consequent reductions in water and marine fish samples many years on, however, there is still the occasional occurrence of relatively high concentrations	23
4	Trace metals	—	✓	—	Flood plain	Geochemistry and mineralogy of samples show the effect of both natural and anthropogenic inputs of heavy metals to the Moreton Bay catchment, however, natural processes are more dominant than anthropogenic inputs	24
5	Trace metals	✓(water and DGT)	—	—	Estuary	Significant correlation between 24 h DGT-labile measurements and 0.45 µm filterable measured, on time-averaged composite samples	25
6	Trace metals	—	✓	—	Estuary, canals and marinas	Sediment metal concentrations undetectable to very low at sites in Southern Moreton Bay, whereas elevated concentrations were observed for sample sites in artificial residential canals and marinas probably due to reduced flushing in canals and boat related activities undertaken in marinas	26
7	Trace metals	✓(water and DGT)	—	—	Estuary vessel anchorages	Correlation between recreational boat numbers at anchorage sites and water column Cu concentrations for Gold Coast waterways	27
8	Trace metals	—	✓	—	Marine and estuary	Overall Moreton Bay has relatively low content metal content in sediments compared to similar studies in other highly populated centres in Australia	28
9	Trace metals	✓(water and DGT)	—	—	Estuary	Use of DGTs enable changes in heavy metal concentrations to be related to various cycle and events within estuaries	29
10	Trace metals	—	—	—	Bay	Modelling of Cu loading to Moreton Bay based on boat number observations and literature leaching rates revealed that boat hulls are a major source of Cu	30

Table 1 (Contd.)

Study Elements	Water sampling	Sediment sampling	Biological sampling	Wetland habitat(s)	Conclusions	Source
11 PCDD/F and PCBs	—	✓	✓(Dugongs and green turtles)	Bay	PCDD/F and PCB contaminants higher in biota in Moreton Bay compared to elsewhere in Australia, but comply with EU maximum limits	31
12 PBDE	—	—	✓(turtles, dugongs, fish)	Bay	PBDEs levels in marine biota were low in Moreton Bay compared to elsewhere	32
13 Trace metals	✓(DGTs)	—	✓(oysters)	Canals, estuary, Bay	Significant positive correlation between oyster Cu uptake and accumulation in DGTs	14
14 Trace metals, pesticides	✓(DGTs)	✓	✓(fish)	Estuary, Bay, marina, canals, lakes	Present study	—

are well flushed and are considered to be in a more natural condition.¹⁵ Both artificial residential waterways receive untreated runoff, mostly from urban development and some industrial areas, but are highly ramified and less well flushed than adjacent estuaries and natural habitat, especially artificial residential lakes.¹⁸ Local marina facilities receive high loads of

contaminants from hard stands, repainting and maintenance outlets, as well as directly from boats and urban run-off.³³ Each wetland habitat had four replicate sites, which were chosen randomly and interspersed over the study, except marinas, which had three replicate sites (total N = 19 sites) that were chosen subjectively based on access. Total rainfall over the 4 weeks prior

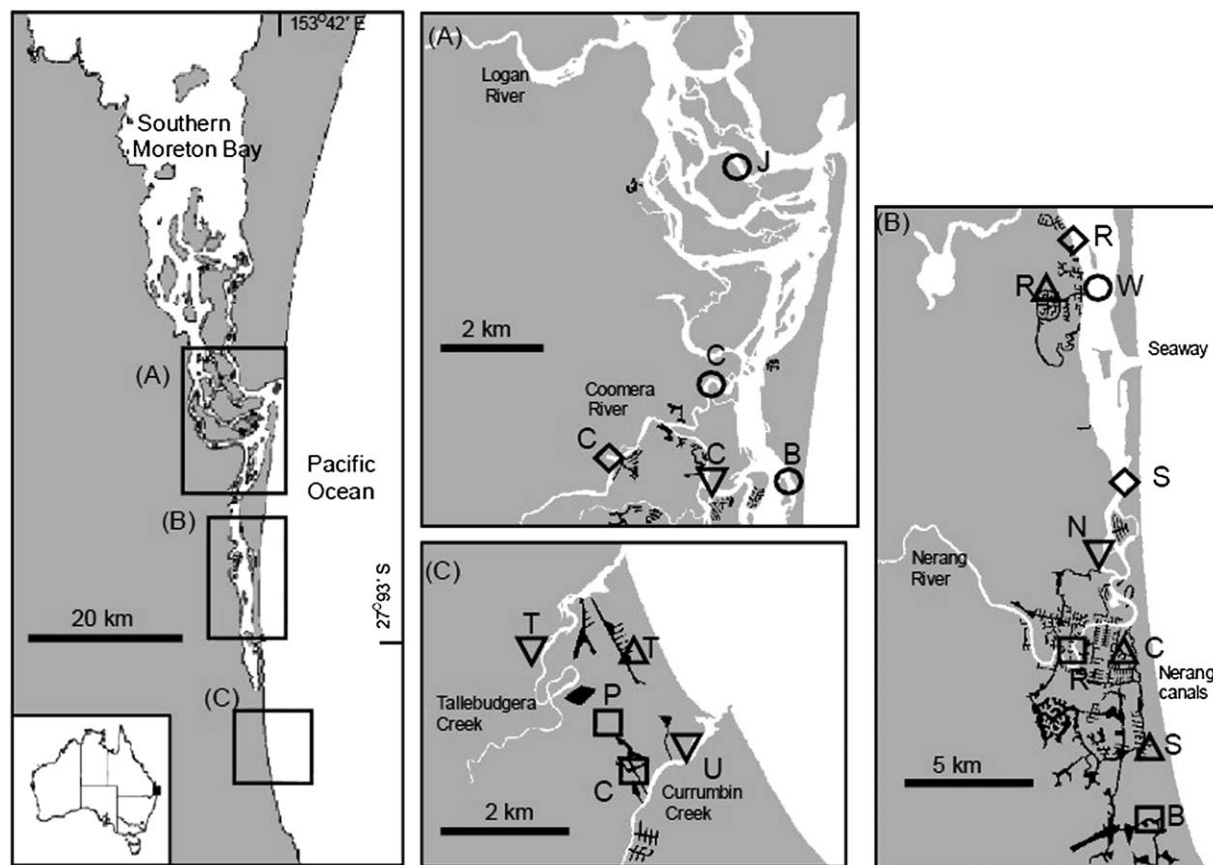


Fig. 1 Southern Moreton Bay showing extent of artificial residential waterways (filled) and natural waterways (open). Artificial residential canal (Δ ; T Tallebudgera Canal, S Sunshine Canal, C Council Canal, R Runaway Bay Canal), estuary (∇ ; U Currumbin Creek Estuary, T Tallebudgera Creek Estuary, N Nerang River Estuary, C Coomera River Estuary), natural (\circ ; W Wave Break Island, B Brown Island, C Coomera River, J Jumpinpin), marina (\diamond ; S Southport Marina, R Runaway Marina, C Coomera Marina), artificial residential lakes (\square ; C Cyclades Lake, P Pine Lake, B Burleigh Lake, R Rudd Lake).

to, and during sampling, was 45 mm (Bureau of Meteorology, Queensland, Gold Coast Seaway station 040764), with one event over 20 mm (38.6mm/24 h, 7 April 2007).

The fish species chosen were widespread and represented different trophic levels within the overall fish assemblage of Moreton Bay; carnivorous yellowfin bream, *Acanthopagrus australis*, detritivorous sea mullet, *Mugil cephalus*, and the largely herbivorous snub nosed garfish, *Arrhamphus sclerolepis*.³⁴ There is local evidence from stable isotope analysis of fish tissue that these species demonstrate high site fidelity over periods of several weeks.³⁵ Up to 5 individuals of each species were collected from each site using a seine net (70 m × 4 m, 18 mm mesh). Fish were placed on ice and returned to the laboratory for dissecting various tissues (liver, gill and muscle; the skin was removed from muscle tissue because it contains lipids which can lead to over-estimation of results).³⁶ There was no effect of fish length on metal concentrations with any tissue type (all *p* values > 0.05), so no adjustment for length was made (size ranges for *A. australis*, *M. cephalus* and *A. sclerolepis* were 15–24, 17–34, and 12–21 cm total length, respectively).

Three replicate sediment grab samples (Eckman sampler) were taken at each site (within 100 m of each other), and were homogenised in a stainless steel bowl using a stainless steel scoop. Given the previous extensive baseline studies that had been carried out in Gold Coast waterways (Table 1), this was considered to be sufficient for the purposes of this project. Sub-samples of sediment grabs were placed into polyethylene bags and returned to the laboratory for analysis.

Sample processing, analysis and quality control

All fish tissue and sediment samples were dried in an oven (60 °C) for >24 h to a constant weight. Dried tissue and sediment were ground with a clean mortar and pestle. Three replicate aliquots of approximately 200 µg dried sediment and fish tissue were placed into 30 mL plastic digestion reflux tubes. 2.0 mL of concentrated HNO₃ (65%) (Suprapur, Merck) followed by 0.5 mL of concentrated (30%) H₂O₂ (Suprapur, Merck) was added to each digestion tube. Samples were microwave-digested on medium/low for 22 min and diluted 1 : 30 prior to analysis by

inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 Series). Certified Reference Materials (CRM) were also digested and measured: PACS-2 sediment CRM from the institute for National Measurement Standards, National Research Council of Canada and SRM 2976 mussel tissue from the National Institute of Standards and Technology, USA. CRM replicates were measured in each run of samples and the summary data are presented in Table 2. Laboratory reference standards were also measured every 10 samples and sufficient blank samples (>5% of overall samples) were measured to allow determination of the limits of detection (LOD). LOD values are not reported for the metals in tissue and sediment as, except for Cd in sediment, the concentrations measured were much higher.

Recovery of the sediment CRM digestion was variable among most metals ranging between 40–100% for As, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn, with Relative Standard Deviations (RSD) all low indicating very good analytical precision. Such a range for metal-sediment studies is not uncommon due to the incomplete digestion of metals within mineral lattices given the somewhat weaker digest conditions used in this study than is typical.^{37,38} Furthermore, the best recoveries were obtained for those heavy metals most commonly measured (Cu, Zn, Pb, Ni, Co). Cd was overestimated, which may be due to the lower concentration present in the CRM. In any case, Cd in sediment was below the LOD (0.1 mg kg⁻¹ dry wt) at each site, so this recovery does not cause any difficulty with interpretation. Al was greatly underestimated, as the matrix aluminosilicate minerals require much stronger digestion conditions before they become measurable. The recoveries for the muscle tissue SRM for As, Cd, Co, Cu, Fe, Ni, Mn, Pb, Se, and Zn were between 85–115%; only Al (75%) and Cr (120%) were outside this range. RSDs were low indicating very good analytical precision.

Sixteen pesticides (organochlorine and organophosphorus) and mercury concentrations were examined in the edible muscle tissue of up to 3 individual fish of each species from each site, at the Pathology and Scientific Services laboratory, Queensland Health, Australia, which is a NATA accredited laboratory. Samples were solvent-extracted with 10% acetone in hexane. Organic extracts were evaporated and cleaned on 5% deactivated florisil. The final extract was prepared in hexane solution. All

Table 2 Summary of Certified Reference Material (CRM) for elements measured in sediment and fish tissue

Element	Sediment (n = 5)			Fish tissue (n = 3)		
	Measured concentration (mg kg ⁻¹ dry weight)	Recovery (%)	RSD (%)	Measured concentration (µg g ⁻¹ dry weight)	Recovery (%)	RSD (%)
Al	9 700	1.47	3.8	99.8	74.5	15
Ar	18.2	69.5	3.7	11.5	86.8	7.6
Cd	5.41	256	3.3	0.84	102	5.9
Cr	37.0	40.1	3.4	0.60	119	32
Co	6.99	60.8	2.9	0.52	84.6	5.4
Cu	257	82.9	2.6	3.85	95.8	9.6
Fe	23 000	56.2	4.1	186	108	4.4
Pb	182	99.2	5.6	1.16	97.8	5.0
Mn	184	41.8	3.2	34.6	105	5.3
Ni	25.1	63.5	3.3	1.07	115	5.2
Se	—	—	—	1.83	102	15
Zn	314	86.2	2.2	122	89.2	8.6

^a (—) not examined. ^b Relative Standard Deviation (RSD).

analysis was by gas chromatography with dual electron capture detection (GC/ECD). Confirmation of peak identity was performed by gas chromatography with mass spectrometric detection. LOD were calculated for each pesticide and in many instances the results are reported as not detected (ND) where they are below the LOD. Recoveries on spiked surrogate substances were measured for each sample and were within an acceptable range (61–96%, mean 88%).

Preparation and measurement of DGT devices

Previous metal uptake studies have collected water samples randomly over the survey period and while these measurements provide information of the spatial variability, they offer limited temporal understanding of the exposure experienced by organisms.³⁹ The use of diffusive gradients in thin films (DGTs) integrates divalent metals over time.⁴⁰ Polyacrylamide hydrogel sheets containing Chelex 100 resin (BioRad) (the binding layer) were prepared and processed in the laboratory.⁴¹ Samples were measured using ICP-MS. Recoveries of multi-element laboratory standards were >90%. All analyses with relative standard deviations >10% of the three replicate measurements were repeated. Sufficient blanks were measured to allow estimation of LODs, which are reported in Table 2. The Zn LOD was very high (23.1 $\mu\text{g L}^{-1}$), which has subsequently been related to a contaminated batch of DGT devices from the commercial supplier. Consequently the Zn DGT data should be interpreted with caution, although we note that the DGT-reactive Zn concentration for the natural sites are not only lower than the LOD, but also all the other site concentrations, which was an expected result. The mass of accumulated metals was calculated for an approximately 72 h deployment, and the average of the three probes from each site was used to calculate the DGT-reactive metal concentration using the DGT equation.^{40–42}

Data analysis

Differences in metal concentrations for fish tissue, sediment and water among habitats, species, and tissue type were analysed using ANOVA. Data were $\log_{10}x$ transformed where necessary to satisfy assumptions of homogeneity of variance and normality. Where significant differences were found, Tukey's multiple comparison was used to examine differences among habitat. Correlations between metal concentrations in water and

sediment with each fish tissue type, for each species, were examined to determine pathway uptake, however, after adjustment for Type I error, no significant correlations were found and results are not therefore reported further. No analysis of fish and sediment pesticide differences among habitats could be performed as the pesticides were usually below the LOD.

Non-metric multidimensional scaling (NMDS) was used to ordinate metal concentrations using Euclidian distances. Differences in metal concentrations in water, sediment and each individual fish tissue type (for each species separately) among habitats were tested for significance using analysis of similarities (ANOSIM).⁴³ When significant differences were detected, the R-statistic was used to determine the extent of the difference, and similarity percentages (SIMPER) elucidated which metal contributed most to the difference (based on high mean:SD ratio).⁴³

Results

Environmental contaminant concentrations

Mean water quality concentrations mostly complied with the national marine water quality guidelines⁴⁴ for the 95% level of aquatic ecosystem protection (Table 3). The exception was Cu concentrations, which exceeded the 95% trigger value at marinas, estuaries and natural habitats. Zn also failed the 95% trigger value in all habitats except natural, though these results should be viewed with caution given that the detection limit in the analysis was higher than that recorded in each habitat except the marinas and canals. There were no significant multivariate differences in water metal concentrations among habitats (ANOSIM, global $r = 0.07$, $p = 0.258$, Stress = 0.02), nor for individual metal elements among habitats (1-way ANOVA, $p > 0.117$; except Zn, though again these results should be viewed with caution).

Mean sediment metal concentrations generally complied with the lower trigger values outlined in the national sediment guidelines⁴⁴ (Table 4). Lead sediment concentrations were significantly higher in both types of artificial residential waterways (1-way ANOVA, $p = 0.021$), with concentrations in several individual systems exceeding the lower trigger values (Fig. 2). Sediment Cu concentrations were significantly higher in marinas than all other habitats, and were intermediate in both artificial residential waterways (1-way ANOVA; $p = 0.010$). Zinc

Table 3 Metal concentrations (mean, \pm SE; $\mu\text{g L}^{-1}$) measured in the water column using DGT in each wetland habitat. Concentrations in bold exceed 95% trigger values.⁴⁴ Values within rows having different superscript lower case letters are significantly different according to Tukey's post hoc test ($p < 0.01$)

Metal	Marina	Estuary	Canal	Lake	Natural	Trigger value	LOD
Cd	0.017 (0.005)	0.012 (0.003)	0.023 (0.010)	0.024 (0.010)	0.009 (0.001)	5.5	0.004
Co	0.078 (0.030)	0.101 (0.020)	0.074 (0.010)	0.087 (0.020)	0.085 (0.020)	1.0	0.004
Cr	1.1 (0.4)	1.1 (0.5)	0.5 (0.2)	0.7 (0.1)	0.6 (0.1)	4.4	0.4
Cu	2.3 (0.8)	1.4 (0.3)	0.8 (0.4)	0.9 (0.3)	1.4 (0.5)	1.3	0.1
Fe	7.4 (0.6)	7.2 (0.8)	8.6 (1.9)	6.3 (1.0)	10.0 (0.9)	—	2.3
Mn	6.7 (2.3)	9.4 (2.6)	7.8 (1.8)	21.9 (16.9)	4.1 (0.8)	—	0.1
Ni	0.5 (0.1)	0.3 (0.1)	0.4 (0.1)	0.5 (0.1)	0.4 (0.1)	70	0.1
Pb	0.019 (0.009)	0.017 (0.005)	0.020 (0.008)	0.037 (0.010)	0.022 (0.005)	4.4	0.009
Zn	23.7^a (7.2)	20.1^a (5.9)	27.0^a (9.5)	22.6^a (7.36)	10.9 ^b (1.8)	15	23.1

^a ANZECC/ARMCANZ Cr VI guideline trigger used here. ^b LOD, Limit Of Detection ($3 \times$ SD of blanks).

Table 4 Sediment contaminant concentrations (mean, \pm SE) and lower trigger values⁴⁴ (metals: mg kg⁻¹ dry weight; pesticide: μ g kg⁻¹ dry weight) in each wetland habitat. Values within rows having different superscript letters are significantly different according to Tukey's post hoc test ($p < 0.01$)

Metal	Marina	Estuary	Canal	Lake	Natural	Trigger value
Al	3170 (730)	2380 (910)	3650 (1030)	4070 (1150)	2440 (861)	—
As	2.1 (0.4)	1.9 (0.3)	3.5 (0.2)	2.6 (0.3)	2.4 (0.4)	20
Cd	0.1 (0.0)	0.1 (0.0)	0.1 (0.0)	0.1 (0.0)	0.1 (0.0)	1.5
Co	3.9 (1.2)	2.9 (1.1)	2.6 (0.4)	2.3 (0.6)	3.3 (0.8)	—
Cr	10.0 (2.8)	4.8 (1.8)	8.1 (2.1)	6.7 (1.7)	6.2 (2.0)	80
Cu	31.5 ^a (16.9)	7.1 ^c (0.9)	12.2 ^b (2.3)	10.6 ^b (2.1)	5.8 ^c (0.3)	65
Fe	9170 (2350)	6980 (2550)	10800 (2680)	8320 (2160)	6250 (1990)	—
Mn	87.0 (31.6)	67.8 (31.2)	62.0 (17.4)	71.2 (21.4)	82.6 (19.0)	—
Ni	3.3 (0.7)	1.6 (0.5)	2.1 (0.4)	1.7 (0.3)	2.6 (0.7)	210
Pb	14.9 ^b (7.0)	8.6 ^b (3.4)	48.4 ^a (18.8)	39.8 ^a (13.7)	5.0 ^b (2.1)	50
Se	1.4 (0.2)	1.6 (0.3)	1.5 (0.2)	1.5 (0.3)	1.6 (0.3)	—
Zn	71.5 ^a (15.4)	47.5 ^b (9.8)	105.1 ^a (24.5)	76.9 ^a (23.9)	32.3 ^c (6.4)	200
Pesticides						
DDE	ND	ND	0.008 (0)	0.005 (0)	ND	2.2
Dieldrin	ND	ND	0.007 (0)	ND	ND	0.02
Bifenthrin	ND	ND	0.015 (0)	0.009 (0)	ND	—

^a ND, Not Detected. ^b (0.00) no variance due to only single data point.

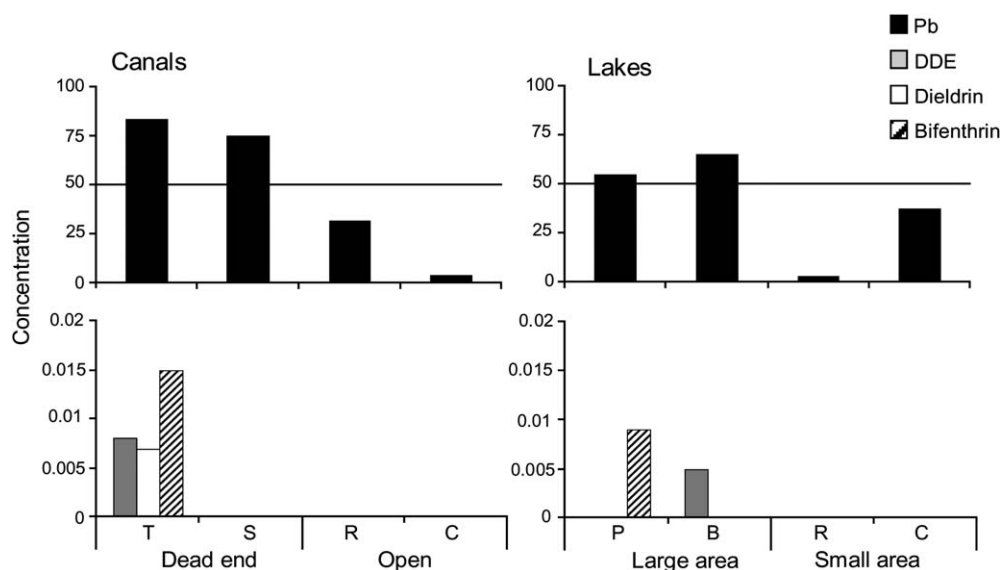


Fig. 2 Lead (mg kg⁻¹) and pesticide (μ g kg⁻¹) concentrations in the sediment of single canal and lake systems in Moreton Bay. Results shown are for a composite sample from three sediment grabs collected in each system. ISQG low trigger value for Pb shown, however, DDE, dieldrin and bifenthrin not shown, as concentrations comply with the guideline.⁴⁴ For canals, dead end and open labels refer to flow characteristics of each system, while large (~280 ha) and small (~20 ha) area refers to the size of the catchment area draining to each lake system. Site labels are same as in Fig. 1.

concentrations were significantly higher in marinas and both artificial residential waterways than in natural habitats, with estuaries intermediate. There were no significant multivariate differences in sediment metal concentrations among habitats (ANOSIM, global $r = 0.13$, $p = 0.912$, Stress = 0.01). DDE, dieldrin and bifenthrin were detected in the sediments of artificial residential waterways only, but remained below the lower guideline values (Fig. 2).

Contaminant concentrations in fish tissue

Overall, metal concentrations were similar among the fish species and habitats (Table 5), with only minor differences detected among habitats. Copper in gills was the only metal

and tissue combination that varied consistently among habitats (nested ANOVA: main factor (habitat), $F_{4, 24} = 13$, $p = 0.001$, main factor (fish) $F_{2, 199} = 6$, $p = 0.003$, nested (sites) $F_{21, 199} = 0.04$, $p = 0.431$; Fig. 3). For all species, except *Acanthopagrus australis*, for which there was some overlap between marinas and canals, highest Cu concentrations occurred in fish from marinas. Fish caught in canals always gave the second highest Cu concentration and the natural habitat always had the lowest concentration, although these differences were not significant. Copper concentrations in the gills of *Mugil cephalus* and *Arrhamphus sclerolepis* were higher than in the gills of *A. australis*. Overall, there was no significant multivariate difference among habitats or among sites within the same habitat for each fish tissue/species combination (two-way

Table 5 Contaminant concentrations (mean, \pm SE; mg kg⁻¹ dry weight) in edible muscle tissue for fish in each wetland habitat in Moreton Bay. Results only reported here for those elements where a guideline exists. Guidelines for metals and pesticide contaminants are wet weight,⁴⁵ however, results in this study are dry weight and have been corrected following Kirby *et al.*,⁴⁶ Total N is the same as Fig. 3

Species	Habitat	Metals						Pesticide Dieldrin
		As ^a	Cd	Cu	Hg	Pb	Zn	
<i>Acanthopagrus australis</i>	Natural	4.8 (0.4)	0.02 (0.01)	4.9 (0.2)	0.13 (0.03)	0.05 (0.01)	18.9 (1.35)	ND ^b
	Marina	4.2 (0.4)	0.03 (0.01)	3.6 (0.1)	0.13 (0.02)	0.04 (0.03)	21.1 (1.24)	ND
	Estuary	4.6 (0.3)	0.04 (0.01)	5.9 (0.4)	0.07 (0.01)	0.09 (0.00)	22.2 (2.1)	ND
	Canal	5.4 (0.8)	0.03 (0.01)	3.2 (0.1)	0.08 (0.01)	0.07 (0.00)	15.8 (0.5)	0.005 (0.000 ^c)
	Lake	9.6 (2.9)	0.05 (0.01)	3.6 (0.1)	0.17 (0.02)	0.06 (0.01)	18.2 (1.0)	0.01 (0.00 ^c)
<i>Mugil cephalus</i>	Natural	2.5 (0.2)	0.02 (0.00)	4.9 (0.1)	0.01 (0.00)	0.06 (0.01)	20.5 (2.2)	ND
	Marina	3.5 (0.6)	0.02 (0.00)	5.4 (0.2)	0.01 (0.00)	0.07 (0.01)	28.7 (2.6)	ND
	Estuary	2.7 (0.3)	0.26 (0.21)	5.9 (0.2)	0.02 (0.00)	0.09 (0.02)	24.9 (3.0)	0.01 (0.00 ^c)
	Canal	3.3 (0.3)	0.1 (0.1)	2.1 (1.0)	0.02 (0.00)	0.08 (0.01)	27.8 (5.4)	0.01 (0.00 ^c)
	Lake	2.3 (0.3)	0.01 (0.03)	7.2 (0.6)	0.01 (0.00)	0.05 (0.00)	23.9 (1.7)	ND
<i>Arrhamphus sclerolepis</i>	Natural	5.6 (1.1)	0.04 (0.01)	2.1 (0.7)	0.01 (0.00)	0.05 (0.01)	23.1 (1.3)	ND
	Marina	3.6 (0.5)	0.21 (0.19)	3.6 (0.1)	0.02 (0.00)	0.05 (0.04)	34.7 (5.4)	ND
	Estuary	3.6 (0.3)	0.03 (0.01)	2.7 (0.0)	0.02 (0.00)	0.08 (0.01)	30.0 (2.2)	ND
	Canal	4.7 (0.5)	0.04 (0.01)	3.2 (0.0)	0.06 (0.04)	0.09 (0.01)	39.8 (1.9)	ND
	Lake	4.8 (0.6)	0.04 (0.01)	2.7 (0.1)	0.02 (0.02)	0.04 (0.01)	21.2 (3.0)	ND
Australian Food Standard Code ⁴⁵		2.0	2.0	10	0.5	0.5	200	0.1

^a inorganic As. ^b ND, Not Detected. ^c (0.00) no variance due to only single data point.

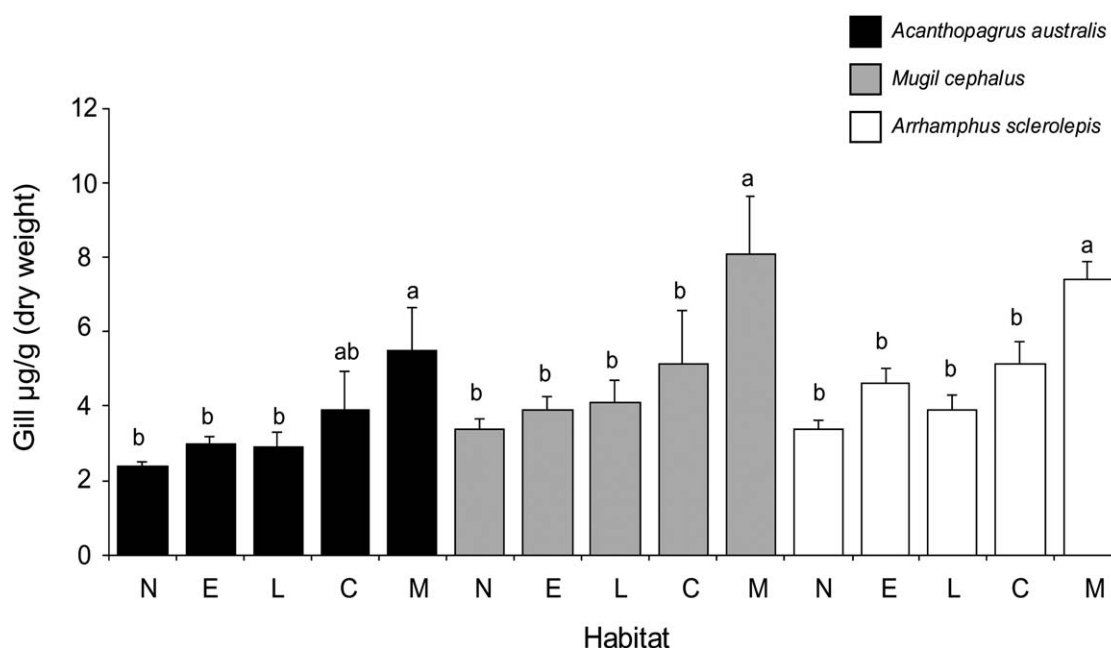


Fig. 3 Copper concentrations in gill tissue of fish in each habitat (mean, \pm SE). N natural, E estuary, L lake, C canal, M marina. Values for each species with different lower case letters differ significantly between habitats according to Tukey's post hoc test ($p < 0.01$). N in habitat, for each species, ranges between 8 and 20.

ANOSIM: habitat, $r < 0.39$, $p > 0.080$; sites, $r < 0.26$, $p > 0.151$; Stress < 0.05).

Arsenic was the only metal that was consistently above the Australian Food Standard Code⁴⁵ recommended limit for human consumption in the muscle tissue of all fish species, and in all habitats. All other metals complied with the guidelines for human health protection. The pesticide dieldrin was detected in the tissue of *Acanthopagrus australis* and *Mugil cephalus*, but complied with the guidelines for safe consumption in all cases.

Discussion

Surficial sediment and water quality in southern Moreton bay

Water and sediment metal concentrations in all wetland habitats generally complied with relevant Australian guidelines for aquatic ecosystem protection. This pattern is consistent with the results of sediment studies in Gold Coast waterways and other regions of Moreton Bay (Table 1) and which suggests an overall low level of contamination for the extent of land use activities in the bay catchments. Some water and sediment site anomalies

have been detected. The most regularly reported is high Cu concentrations near marina facilities (Table 1) and this was also detected in this study, although we demonstrated more widespread contamination with concentrations exceeding guideline levels in the waters of most habitats, despite relatively low rainfall over the weeks preceding collection. Sources of Cu in coastal waters are varied and include vehicle roadway runoff,⁴⁷ discharge from smelting and industrial facilities,⁴⁸ antifouling paints on vessels in marinas,^{49,50} and sewage treatment plants.⁴⁹ Recent research in Moreton Bay has also shown that leaching from antifouling paints on vessel hulls within and around popular recreational anchorages is another major source of Cu contamination.^{27,29} Neither our data nor previous studies show whether a single or multiple anthropogenic sources contribute to high Cu concentrations in Moreton Bay, as urban stormwater run-off has also been shown to increase Cu concentrations at several widespread sites,²⁵ but large marinas are certain to act as point sources of Cu contamination. The above guideline results at the natural and estuary sites may be due to one or more of these locations being affected by a nearby marina or major anchorage, due to water circulation patterns. Surficial sediments in both artificial residential habitats had higher concentrations of several pesticide and metals (Cu, Zn and Pb) than those of the other habitats examined, with some metals even more enriched than in marinas. This pattern is a distinguishing feature of artificial residential waterway developments and is an important consideration for managers given their popularity in the coastal zone.⁵¹ For example, Maxted *et al.*,⁵² in a study in Delaware and Maryland, USA, reported significantly higher sediment-bound metal and pesticide concentrations in canal estates compared to nearby open natural bay areas. In canal estates adjacent to the Port Jackson estuary in New South Wales, Australia, Birch and Taylor⁵³ also found elevated metal concentrations in sediments with a declining gradient with distance away from their opening into the natural estuary. In a more local context, and in several of the same canal estates examined here, Burton *et al.*,²⁶ reported enriched sediment pollutant concentrations compared to nearby natural habitat. This feature of artificial residential waterways probably results from their highly ramified design, which reduces the tidal prism leading to longer residence times and accumulation of organic carbon content and fine sediments, compared to well flushed adjacent estuaries and natural open bay waters. The engineering of artificial residential waterways in this fashion would seem to also explain the detection of sediment-bound pesticides in some artificial residential waterways, and not others, even several decades after deregistration of these contaminants in Australia.²³ Cu and Zn concentrations may be related to recreational boating use as well as urban runoff. The widespread elevated Pb result may be related to historical contamination from leaded petrol. However, the very high results within the artificial residential canals and lakes are most likely to be due to the use of Pb sinkers for recreational fishing. This is supported by the very low water Pb concentrations that indicate low likelihood of Pb transport from the water column to the sediment and *vice versa*.

This study provides the first evidence that the altered design in artificial residential waterways has, in general, not contributed to higher water and sediment contaminant concentrations, with both waterway types (natural and artificial) grouping together in

the ordination plots. This conclusion must be viewed with some caution, however, because the full extent of lake designs was not considered.¹⁸ Rather, the lakes examined were chosen haphazardly within the overall extent in Moreton Bay. What is particularly evident is that some artificial residential systems seem to be more susceptible to contamination than others. This was most evident in dead-end canals where water exchange is low or for systems receiving stormwater runoff from large urban catchments. In these systems, some sediment-bound metals were elevated above the lower trigger value and therefore could pose toxicological risk to estuarine fauna. Fig. 3 indicates that both Pb and detectable pesticides are more likely to be observed in dead-end canals and larger lakes. Based on these findings, it is possible that artificial residential waterways engineered with dead-ends and receiving stormwater from large urban areas could, in fact, be effective in the sequestration of anthropogenic contaminants and protection of natural coastal wetlands. Given their massive extent (~300 km linear), this may be particularly important in the protection of Moreton Bay.¹⁷

Fish contaminants and use as biomonitors

Metal and pesticide guidelines for water and sediment quality have been entrenched in environmental legislation and government planning codes in many places. Trigger values have been established for contaminants in water and sediment in Australia and New Zealand to help managers achieve a prescribed level of ecosystem protection; here we have used the 95% level of ecosystem protection guideline, which assumes that 95% of species will be protected under the corresponding set of trigger values. The inclusion of biomonitors in this study, as a component of water and sediment monitoring and assessment, provided greater insights into biological responses associated with achieving 95% level of ecosystem protection, which would not be determined with water or sediment samples only. Under a 95% level of ecosystem protection, fish across the range of natural and artificial residential wetland habitats surveyed were also safe for human consumption. This is an important result not previously considered in other local studies, particularly given the extent of urban development occurring over the past 30 years and the continued expansion expected in the future for southeast Queensland. Even in marinas where contaminants are higher in water and sediment, and in the organs of fish, the edible muscle tissue was still safe to eat. Fish did however have As concentrations above the maximum permitted concentration for human health. However, this maximum permissible concentration is based on inorganic As, which typically represents only a small proportion of the total As found in marine fauna.⁵⁴ Our method of analysis did not discriminate between inorganic and organic forms of As. Therefore, we cannot confirm whether concentrations in fact satisfy the Australian Food Standards Code. However, the concentrations reported in fish here are generally low in comparison to fish in coastal areas elsewhere that have been exposed to greater As loading (*e.g.*, Lihir gold mine, Papua New Guinea, Brewer *et al.*,⁵⁵). If in fact As concentrations exceed the food standard code then this is of widespread concern given that concentrations are high in all species and across the range of habitats examined. A detailed study of the speciation and bioavailability of As in fish and other marine life is needed to

determine the extent of any threat to human health. For pesticides, concentrations in all fish complied with the Australian Food Standards Code, though trace amounts of were detected in fish in those wetland habitats where pesticides were detected in sediments. This further illustrates that fish are able to signify local accumulation of anthropogenic contaminants.

In general, metal concentrations in fish differed little among natural and artificial residential habitats examined. Copper was the exception with highest concentrations in the gills of fish within marinas. The gills of fish contain many filaments, which increase the surface area in contact with water, which together with a thin epithelium assists the diffusion of oxygen and carbon dioxide.^{56,57} It is through this diffusion that aqueous metals can be absorbed and redistributed to other organs *via* blood circulation. Experiments show that the mechanism of contaminant accumulation in gills is more rapid when water concentrations are higher than food source concentrations.⁵⁸ Accumulation of Cu in fish gills in marinas reflects the availability in the water column, but also bound in the sediment. If the Cu uptake by fish is a function of long-term exposure, this would then imply a high degree of residency by all fish species examined, or that gill tissue takes on the characteristics of environmental Cu concentrations within a very short time following exposure to new concentrations. This mechanism of Cu uptake by fish in marinas is evidence to support the use of fish as a biomonitor species.

There was a tendency for Cu to be higher in the gills of herbivorous and detritivorous species than in the carnivorous species across all habitats. This among species difference probably reflects an ability to regulate and reduce metals after uptake, or feeding strategies contributing to increased exposure to contaminants. Examining which of these accumulation mechanisms underpins uptake of contaminants could be investigated with the use of chemical tracers.⁵⁹ Accumulation of Cu has been shown to occur in epibenthic organisms located within marinas, and this not only contributes to biomarker effects in organisms, for example, reduced gonad development but also accumulation in high order organisms consuming them, such as fish.⁶⁰ This study provides additional evidence of the possible sources and effects of contaminants in marinas.

Exposure and accumulation of contaminants can cause changes in the histological structure and functional efficiency of fish.⁶¹ The liver and gills are susceptible to this damage particularly when exposed to excessive rates of pollution. For example, the liver is the main organ for metal homeostasis in animals whereby it reduces metal toxicity and cellular damage; exposure to excessive pollution will lead to a decrease in liver function and therefore resistance to disease and infection.⁵⁶ This phenomenon has been widely shown in fish. For example, a higher prevalence of liver diseases were found in fish collected over areas with elevated water metal concentrations in the Kola Region, Russia.⁶² A high occurrence of liver pathology was also found in winter flounder (*Pleuronectes americanus*) in Boston Harbour, USA, near major sewage outfall,⁶² though this prevalence reduced rapidly following major plant upgrades.⁶³ At a similar latitude to the present study, a higher prevalence of pathology was found in fish from a sewage-impacted estuary than an adjacent estuary that did not receive direct input from sewage treatment plants.⁶⁴ Their findings are important because it implies that the health of fauna can be impaired even where

animals from waterways comply with food consumption standards. There is an apparent focus on fish health investigation in coastal areas that are exposed to high rates of anthropogenic discharge,⁶⁵ however, a greater level of research is necessary to examine implications of small, pulse, amounts of pollution on local fauna.

Protection of Gold Coast waterways

An extensive monitoring program exists in southeast Queensland estuaries and is intended to provide managers with a set of tools to optimise mitigation strategies, and deliver water quality and ecosystem health protection and enhancement outcomes.¹⁵ While the fundamentals of this program are important, it is driven by an objective determination of controlling nutrient and sediment loads. Despite previous contaminant studies available in the region, this is the first to integrate water and sediment with biomonitors, and that has included a range of natural and artificial habitats. In doing so, it has demonstrated low contamination in most wetland habitats, a response presumably to the low extent of heavy industry. There is still evidence of localised problems from point sources with the most significant contamination source, excluding episodic human induced catastrophes (*e.g.*, oil spills⁶⁶), from marinas where vessel maintenance and repair works contribute high loads of Cu to the waterways. The results here support previous evidence (see Table 1) indicating consistent year to year contamination, but we have demonstrated biological implications with three fish species caught in marinas found to have significantly higher concentrations of Cu on their gills than fish caught in other habitats. At this stage, fish comply with the safe consumption guidelines, but the results are evidence that continued unplanned and unregulated land use changes may have future implications for fish health. Overall, the economic and social value of Gold Coast waterways, and Moreton Bay more broadly, means that a more comprehensive surveillance program which includes contaminants and biomonitors, is necessary. Such data would allow managers to achieve ecosystem health protection and enhancement.

Conclusion

This study has extended the range of data available on contaminants within Moreton Bay (Table 1), with previous studies typically focusing on water and sediment contamination; this is the first study to also investigate uptake in recreational fisheries species, and in a wider range of habitats. It would be useful to further develop the use of such biomonitor species so that the accumulated contaminants could be directly related to water quality guidelines, as shown by Jordon *et al.*,¹⁴ for oysters (*Saccostrea glomerata*) for which Cu uptake was modelled with DGT measurements. Current data affirm which contaminants are entering fisheries food webs and provide new observations beyond existing regional water quality monitoring.¹⁵ There is still a need to understand the ecotoxicological effects of contaminants on local biota, which would provide important data to develop conceptual models. There may also be a need to further determine opportunities to treat stormwater runoff from identified point sources, for example, use of stormwater treatment

engineering in marina facilities to pre-treat stormwater before entering receiving waterways.

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