Large scale surveys suggest limited mercury availability in tropical north Queensland (Australia)

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Abstract

Little is known about the threat of mercury (Hg) to consumers in food webs of Australia’s wet-dry tropics. This is despite high concentrations in similar biomes elsewhere and a recent history of gold mining that could lead to a high degree of exposure for biota. We analysed Hg in water, sediments, invertebrates and fishes in rivers and estuaries of north Queensland, Australia to determine its availability and biomagnification in food webs. Concentrations in water and sediments were low relative to other regions of Hg concern, with only four of 138 water samples and five
of 60 sediment samples above detection limits of 0.1 µg L⁻¹ and 0.1 µg g⁻¹, respectively. Concentrations of Hg in fishes and invertebrates from riverine and wetland food webs were well below international consumption guidelines, including those in piscivorous fishes, likely due to low baseline concentrations and limited rates of biomagnification (average slope of log Hg vs. δ¹⁵N = 0.08). A large fish species of recreational, commercial, and cultural importance (the barramundi, *Lates calcarifer*), had low concentrations that were below consumption guidelines. Observed variation in Hg concentrations in this species was primarily explained by age and foraging location (floodplain versus coastal), with floodplain feeders having higher Hg concentrations than those foraging at sea. These analyses suggest that there is a limited threat of Hg exposure for fish-eating consumers in this region.

**Keywords:** stable isotopes, barramundi, Cape York, floodplain, fishery, gold mining

1. Introduction

Understanding biogeochemical hotspots and biological factors that lead to high concentrations of toxic metals in fish is critical in identifying where the health of humans and fish-eating wildlife might be compromised (Mergler et al., 2007; Munthe et al., 2007). Our global understanding of one such metal, mercury (Hg), is focused in north temperate latitudes (e.g. Europe, North America) where much of the research has been conducted, and the neotropics (e.g. the Amazon River) where human activities, particularly artisanal gold mining, have lead to elevated concentrations in water, sediment, fish and humans (Malm et al., 1995). Data for other tropical floodplain regions is currently limited despite the significant commercial, recreational
and cultural fisheries that exist in these locations and the resultant high levels of fish consumption by humans, as well as wildlife (Welcomme, 2001).

The threat of Hg to aquatic ecosystems in one of these tropical floodplain regions, northern Australia, is poorly understood (Jardine and Bunn, 2010). Low atmospheric deposition rates (Nelson, 2007), coupled with rapid growth rates of biota and subsequent growth dilution of contaminants (Karimi et al., 2007), likely leads to low Hg concentrations in consumers. However, certain features of the landscape (e.g. seasonal flooding) could promote localised Hg hotspots (Guimaraes et al., 2000). Furthermore, alluvial gold mining that reworks sediments possibly containing residual Hg from past extraction procedures may lead to concentrations in water, sediments and fish that are above acceptable levels (Akagi et al., 1995; Telmer et al., 2006; Dominique et al., 2007). In Cape York, Queensland, the hosting of the Mitchell River Conference by Kowanyama Aboriginal Council in 1990, and the subsequent formation of Queensland’s first watershed management group, originated from Aboriginal community concerns relating to the potential impacts of past and contemporary upper watershed mining operations upon the health of the Mitchell River system and downstream communities (Sinnamon 1998, Strong 2001).

Various factors are known to influence Hg concentrations in fish independently of point sources. Typically, larger, older fish have higher concentrations than smaller, younger fish due to longer exposure times, consumption of larger, more contaminated prey, and lower prey assimilation rates (Trudel and Rasmussen, 2006). Animals situated higher in the food chain exhibit higher Hg concentrations due to strong biomagnification through the food web (Cabana and Rasmussen, 1994). Also, dietary sources of organic matter for consumers can affect Hg concentrations. For example, some fishes that feed in the marine environment
have been shown to have lower Hg concentrations compared to their freshwater 
counterparts (Swanson and Kidd, 2010). Therefore coastal species that move between 
and feed in different areas could exhibit different concentrations if methylation 
potential and resultant Hg availability differs among habitats (Hall et al. 2008). One 
such transient species is barramundi (*Lates calcarifer*), also known as Asian sea bass, 
a common predator in estuaries and the lower reaches of rivers throughout the 
Australasian region. The commercial barramundi fishery in northern Australia 
supplies southern markets for table consumption with catches between 1000 and 2000 
tonnes annually (Blaber 2000). This species is also consumed by traditional fishers 
in Aboriginal communities (Rae et al. 1982), as well as being a popular target for 
anglers, the latter having catches as high as 30% of the commercial catch (Griffin 
1979). In Lake Murray of neighbouring Papua New Guinea, Hg concentrations in 
barramundi are often well above consumption guidelines (Sorentino, 1979); as a result 
there are severe health implications for local communities where barramundi is eaten 
regularly (Abe et al., 1995). High Hg concentrations in barramundi in Lake Murray 
are due to efficient transfer of methyl Hg from water to plankton and high rates of 
biomagnification through the food web leading to this top predator (Yoshinaga et al., 
1992; Bowles et al., 2001). Despite the importance of this species in the diet of 
humans and its ubiquity across the Australasian region, rarely have Hg concentrations 
been reported for locations other than Papua New Guinea (Jones et al., 2005).

This study characterises Hg concentrations in river and wetland ecosystems of 
northern Australia (Lyle, 1984; Jardine and Bunn, 2010) by combining data from 
three sub-projects to yield a comprehensive picture for the region. The first study 
conducted a broad scale survey of rivers, wetlands and estuaries in Cape York and 
measured total Hg in filtered and unfiltered waters and total Hg in sediments to
determine if concentrations were high or low relative to other comparable ecoregions (e.g. Amazonia, Papua New Guinea). The second study used stable isotope analysis (SIA) of nitrogen to characterize Hg biomagnification rates in food webs (invertebrates and small fishes) of the Mitchell River, a large floodplain river of Cape York. The trophic level of animals can accurately be determined using stable isotopes of nitrogen because the heavier isotope increases in a predictable fashion with each level of the food chain (Post, 2002). The third study combined SIA with measures of size and age in two populations of barramundi to determine if Hg concentrations posed threats to human health, and to determine the factors responsible for variation (trophic level, and the relative use of marine and freshwater environments, Doucett et al., 1999; Post, 2002). Sources of organic matter are traceable with stable isotope ratios of carbon and sulphur because ratios of these elements differ among habitats and food sources and change little once they enter food webs (Vander Zanden and Rasmussen, 1999). We predicted that barramundi from the Mitchell River, which has current and historical alluvial gold mining in a portion of its catchment, would have concentrations that were higher than those from an adjacent catchment, the Flinders River, where this type of mining is limited. We expected that concentrations would increase with body size, and largest individuals would have concentrations above acceptable consumption guidelines (Jones et al., 2005). We also predicted that fish feeding and growing in saltwater would have higher Hg concentrations than those in freshwater, as would be expected due to growth dilution in the latter habitat which is believed to be more productive than the former in tropical regions (Gross et al., 1989; Davies et al., 2006; Milton et al., 2008). All of these measurements were made to identify possible Hg risks to humans and wildlife and better understand sources of variation in Hg concentrations in this remote tropical landscape.
2. Materials and Methods

2.1 Water and sediment sampling

Water and sediment grab samples were collected from 11 river catchments in three principal regions across Cape York between 2005 and 2010 (Figure 1). A total of 138 water samples (91 freshwater and 47 estuary) and 60 sediment samples (17 freshwater and 43 estuary) were collected during both ambient flow and flood conditions. Estuary water samples were collected on the out-going tide across a range of saltwater/freshwater mixes, with the measured salinity of estuary water samples ranging from 0 ppt to 35.8 ppt at the mouths of rivers where minimal mixing had occurred. Water samples are representative of both wet season flood event and dry season baseflow conditions. Samples were collected by boat or from the edge of the waterbody directly into the sample bottle, or using a 3m extended sampling pole sample collection bottle.

Polypropylene water sample bottles were lab-sterilised and preserved with nitric acid to a pH <2 (APHA 2005). Dissolved Hg samples were filtered at the site through 60cc/ml Terumo brand plastic syringes fitted with a 0.45 µm Sartorius brand cellulose acetate filter. These filters have low adsorption characteristics. Sediment samples were collected using a stainless steel sediment grab sampler or stainless steel spoon and placed in sterilised glass sample jars. Sediments containing clay and silt were targeted for analysis and sediment type was documented for each sample.

All non-dedicated equipment including sample collection bottles, sediment grab sampler and spoons was decontaminated between each use using a scrub brush and distilled water and rinsate samples were collected to test for potential cross-contamination. Field duplicate, blank and rinsate samples were collected with each
sample batch or at a frequency of approximately 1 per 10 primary samples. Rinsate and blank samples were collected using reagent grade Hg-free blank water which had been purified through a reverse osmosis system coupled with an ultra-filtration system. All samples were placed immediately on ice and sent via refrigerator truck to a laboratory (ALS Group) in Brisbane, QLD, for analysis. Samples were submitted and analysed within the recommended holding time of 28 days for sediments and nitric acid-preserved water samples (APHA 2005).

2.2 Food web and barramundi sampling

Biotic samples to test for food-web biomagnification were collected from 16 sites in the Mitchell River in June 2008 (early dry season) (Figure 1). These samples included fish (99 samples) collected by backpack and boat-mounted electrofishing and invertebrates (64 samples) captured by electrofishing and dip netting. Capture and retention methods were biased towards smaller and more common species which enabled comparisons across sites; however the full range of functional feeding groups was collected including top predators (barramundi and long tom *Strongylura kreffiti*). Sites included two in the Palmer River, a location of historic alluvial mining that yielded 40 tonnes of gold largely in the period 1872-1900 (Bell, 1987) but is still in small-scale production today.

To examine Hg concentrations in larger, older fish that were under-represented in the biomagnification study, barramundi samples were collected from two river systems in the state of Queensland (Figure 1). In the Mitchell River (15º 13’ S, 141º 36 E, n = 46 analysed for Hg and isotopes, n = 38 analysed for Hg only), samples were from recreational fisherman in the lower river collected throughout the dry season (May to October), and in the Flinders River (17º 31’, 140º 44’, n = 41 analysed...
for Hg and isotopes, n = 22 analysed for Hg only, n = 11 analysed for isotopes only), samples were from commercial fishermen that were caught during the late wet season (February to April) in the lower river. An additional estuarine species, king threadfin (*Polydactylus macrochir*) was also collected from the Mitchell River (n = 14 analysed for Hg and isotopes) from recreational anglers during the dry season to compare concentrations and feeding patterns with those of barramundi. For all fish, muscle tissue was removed from the head end of the fillet above the operculum and stored on ice and frozen.

2.3 Water and sediment laboratory processing and analysis

Mercury concentrations were measured in filtered and unfiltered water samples and sediment samples by the NATA accredited ALS Laboratory in Brisbane using a PE (Perkin Elmer) FIMS-400 Flow-Injection Mercury-Atomic Absorption Spectrometer (FIM-AAS) according to Method AS3550 and 3112 Hg-B (APHA 2005). Sediment samples were first prepared using a hot block acid digestion (USEPA Method 200.2), where 1.0 g of sediment sample was heated with nitric and hydrochloric acids then cooled. Peroxide was added and samples were heated and cooled again before being filtered and bulked to a volume of 250 uL for analysis. A 500 uL sample volume was analysed for water samples. FIM-AAS is an automated flameless atomic absorption technique. A bromate/bromide reagent was used to oxidise any organic mercury compounds in the sample. The ionic mercury was reduced online to atomic mercury vapour by SnCl₂ which was then purged into a heated quartz cell. Concentrations were quantified by comparing absorbance against a calibration curve. This method is compliant with NEPM (1999) Schedule B(3).
Field duplicate water samples (n=10) and sediment samples (n=5) were analysed for Hg alongside primary samples and showed no differences; all differences between duplicate samples were below the laboratory detection limit (0.1 µg/L or 0.1 ug g⁻¹). Aqueous field blank (n=13) and equipment rinseate samples (n=18) all contained less than 0.1 µg/L Hg. Laboratory control spike (LCS), matrix spike (MS) and method blank samples were analysed by ALS with every sample batch in accordance with NEPM 1999 Schedule B(3). Water samples were spiked by adding 0.1 mL of spiking solution (1.0 mg/L Hg) to 10.0 mL of sample yielding 0.01 mg/L of Hg. Soil samples were spiked with 0.5 mL of a multi-element spiking solution (concentration = 10 mg/L Hg) added to a 50mL digest yielding 0.1 mg/L Hg. Recovery rates on MS and LCS samples were within the acceptable limits (84% - 116% as per USEPA SW846) and method blank samples contained no Hg above the detection limit; however spike amounts were significantly higher than environmental values and recovery rates may have been lower at lower spike concentrations. Mercury concentrations in these water sediment samples were compared to guidelines for the protection of aquatic life (Gaudet et al. 1995, MacDonald et al. 2000) and those reported for areas contaminated by mining activities (Suchanek et al. 2008).

2.4 Biotic sample laboratory processing and analysis

Invertebrate and fish samples were freeze dried, ground to a fine powder, and analysed for total Hg on a Direct Mercury Analyzer (DMA-80, Milestone, Inc.). Recovery of certified reference materials analysed alongside samples was high (TORT-2: 110 ± 3% S.D., DORM-2: 92 ± 7% S.D.) as was recovery for an intralab standard (KJ-19: 100 ± 5% S.D.). Samples analysed in duplicate had an average
difference of 0.04 ± 0.07 ug g⁻¹ S.D. (n = 29). Blanks (empty weigh boats) always contained less than 0.02 ug g⁻¹ Hg so data were not blank corrected.

For stable isotope analysis of carbon and nitrogen, samples were weighed to approximately 0.8 mg, combusted in an EA 3000 elemental analyser (Eurovector, Milan, Italy) and sample gases delivered to an Isoprime mass spectrometer (GV Instruments, Manchester, UK). Working standards were dried solutions calibrated against IAEA CH6, CH7, N1 and N2, and had elemental composition that matched the samples (44% C and 11% N). A single sample of fish (muscle from spangled perch, Leiopotherapon unicolour) analysed repeatedly to measure precision over time yielded δ¹³C = -21.9 ± 0.2‰ S.D. and δ¹⁵N = 5.5 ± 0.4‰ S.D. (n = 29). The average difference between duplicate samples within runs was 0.3‰ for C and 0.4‰ for N (n = 97).

For sulphur isotope analysis, samples were weighed to approximately 6 mg and combusted as above. Working standards were dried solutions calibrated against NBS 127. The precision of δ³⁴S analysis was monitored using a working standard (Qprawn) that had δ³⁴S = 13.7 ± 0.3‰ S.D. (n = 21). The average difference between duplicate samples within runs was 0.7‰ (n = 11).

2.5 Statistics

All statistical analyses were conducted using NCSS software (Kaysville, UT). To assess biomagnification in the food web samples from the Mitchell River, we ran regressions of log-transformed Hg concentrations against δ¹⁵N as an indicator of trophic level. Two sites were excluded from this analysis because the δ¹⁵N range within the site was too small (<1 trophic level) to assess biomagnification. Using log-transformed slopes of Hg versus δ¹⁵N allowed linear regressions and comparisons to
previous biomagnification studies with stable isotopes (Bowles et al. 2001; Campbell et al. 2003, 2008; Kidd et al. 2003). Non-zero slopes were considered indicative of biomagnification (Jardine and Kidd, 2011). For those sites with non-zero slopes, trophic magnification factors (TMFs, Jardine et al., 2006) were calculated according to: TMF = 10^m, where m is the slope of log Hg vs δ^{15}N multiplied by 3.4 (the average increase in δ^{15}N per trophic level, Post, 2002). To further determine if Hg concentrations differed within different compartments in the food web, we grouped invertebrates and fishes into five categories based on their assumed diet (Pusey et al., 2004). These categories were: herbivorous invertebrates (shrimps Atyidae), omnivorous invertebrates (crayfish Cherax spp., prawns Macrobrachium spp., mussels Hyriidae), herbivorous fishes (bony bream Nematalosa erebi), omnivorous fishes (mouth almighty Glossamia aprion, rainbowfish Melanotaenia splendidida, sleepy cod Oxyeleotris lineolatus, and spangled perch Leiopotherapon unicolor), and piscivorous fishes (barramundi, longtom). These categories were deemed to provide an appropriate level of resolution because of the generalist nature of consumers in the Australian wet-dry tropics (Pusey et al. 2010) compared with more specialized niches occupied by fishes in the Neotropics (McIntyre et al. 2008). They were grouped across sites and a one-way ANOVA was run, followed by a Bonferroni post-hoc test to determine if there were differences among groups in log-transformed Hg concentrations. Differences were considered significant if p < 0.05.

For the barramundi samples, the proportion of the diet derived from three sources (marine, floodplain, river) was calculated for all fish using methods outlined in Jardine et al., (in press) and using IsoError software for three sources and two isotopes (δ^{13}C and δ^{34}S, Phillips and Gregg, 2001). Neither of these isotopes undergoes significant trophic fractionation (McCutchan et al. 2003) so values in top
predators are reflective of underlying food sources available in the different habitats.

For these analyses, values for the mixing model end members were derived from marine predatory fish (“marine”: $\delta^{13}C = -17.1 \pm 1.2\%o$, S.D., n = 16; $\delta^{34}S = 19.6 \pm 0.8\%o$, S.D., n = 15), small floodplain-resident fish (“floodplain”: $\delta^{13}C = -22.8 \pm 2.1\%o$, S.D., n = 43; $\delta^{34}S = 13.6 \pm 1.0\%o$, S.D., n = 45), and invertebrates from dry season freshwater refuges (“river”: $\delta^{13}C = -27.4 \pm 6.0\%o$, S.D., n = 16; $\delta^{34}S = 20.9 \pm 1.9\%o$, S.D., n = 16). We assumed that end-members in the mixing model were similar for the Flinders River where we did not have sulphur isotope data for prey from the floodplain or the river. A multiple regression model was used to evaluate the relative effect of river of capture, barramundi age (determined from otoliths using standard methods, Staunton-Smith et al. 2004), body size, % marine feeding and $\delta^{15}N$ (as an indicator of trophic level) on Hg concentrations, using $p < 0.05$ as criteria for inclusion of a variable in the final model. We focused on those barramundi that had recruited to the fishery, excluding five small fish that were captured in a floodplain lagoon in the food web biomagnification survey. These latter fish were excluded because they were captured at a single site and were considerably smaller (29 to 38 cm) than the smallest fish (55 cm) from the fishery. Prior to running the model that included data from both catchments, we tested for seasonal variation in barramundi Hg in the Mitchell because these samples were collected over a four month period and Hg has been shown to vary seasonally in tropical fishes (Dorea et al. 2006). This preliminary model that included the other variables found no effect of sampling date ($F = 0.537, p = 0.470$), so we ran the remaining full model for both catchments without it.

3. Results
3.1 Water and sediments

Mercury concentrations in water (dissolved and unfiltered) and sediment across Cape York were low compared to known threshold effects levels – 0.1 µg L$^{-1}$ for water and 0.17 µg g$^{-1}$ for sediment. Of 138 fresh and brackish water samples analysed from the three regions that spanned the peninsula, only four samples contained Hg at or above the detection limit of 0.1 µg L$^{-1}$ (Table 1). The maximum concentration detected in water was 1.0 µg L$^{-1}$ in the Wenlock River. Similarly, of 60 sediment samples from five different catchments, only 5 had detectable concentrations (≥ 0.1 µg g$^{-1}$, Table 2). The maximum concentration of Hg detected in sediments was 1.1 µg g$^{-1}$ in a sample from the Endeavour River.

3.2 Food web biomagnification

Biomagnification of Hg through food webs in the Mitchell River was low, with an average slope of log Hg versus $\delta^{15}$N of 0.08 (Table 3). At only three of the 14 sites were slopes significantly different to zero (Table 3). At the three sites with significant regressions, slopes ranged from 0.14 to 0.36, corresponding to trophic magnification factors of 2.9 to 16.3 (TMFs at the remaining sites were effectively zero). When taxa were pooled across sites, only slight increases in Hg with trophic level were observed, and all groups, including top predators (piscivorous fishes) had concentrations that were well below typical international consumption guidelines of 0.5 µg g$^{-1}$ wet weight (Figure 2). There were significant differences in Hg among trophic categories ($F = 30.78$, $p < 0.001$, $n = 188$) and a general trend of increasing Hg from primary to tertiary consumers as expected, but post-hoc analyses could not differentiate between the two groups that should have had most divergent Hg.
concentrations, the herbivorous invertebrates and piscivorous fishes (p > 0.05, Figure 2).

3.3 Barramundi

Of all barramundi samples analysed for Hg (n = 142, Figure 3), only one was above the recommended consumption guideline of 0.5 ug g⁻¹ wet weight (or 2.5 ug g⁻¹ dry weight assuming 80% moisture). Likewise all king threadfin (n = 14) were below the consumption guideline (data not shown).

There was a significant correlation between δ¹³C and δ³⁴S (r = 0.62, p < 0.001), likely due to both elements reflecting to some degree the location of foraging for barramundi and king threadfin (freshwater vs. marine). All of the data points for the Mitchell River fell inside the mixing space created by the three isotopic end-members (marine, floodplain, river, Jardine et al. in press), while several of the Flinders barramundi had δ¹³C that was higher than the presumed marine end-member (δ¹³C = -17.1‰), resulting in estimates of % marine feeding greater than 100.

The multiple regression model identified key factors determining Hg in barramundi (adjusted model r² = 0.52, n = 67, F = 15.02, p < 0.001). Barramundi age accounted for the most variation in Hg concentrations (F = 15.47, p = 0.002, Figure 4a). Body size surprisingly did not account for significant variation in the model (F = 2.58, p = 0.113, Figure 3). Likewise, δ¹⁵N as a measure of trophic level was not significant in the model (F = 0.34, p = 0.561, Figure 4b). Instead, % marine feeding explained a significant proportion of the variation (F = 4.92, p = 0.030, Figure 5) that was independent of fish size or age; fish with high δ³⁴S and δ¹³C values indicative of marine feeding had lower Hg concentrations than those that were feeding in freshwater. Location of capture (Mitchell vs. Flinders River) was not a significant
predictor of Hg concentrations ($F = 0.20$, $p = 0.659$), even though mean concentrations in the Mitchell were higher (ANOVA, $F = 142.79$, $p < 0.001$). This discordance is likely because Mitchell fish had a stronger connection to freshwater production that drove differences in fish Hg between the catchments.

4. Discussion

Our broad scale survey of Hg in water and sediments coupled with first results from fish and other biota at the site and catchment level suggests that Hg is not a major environmental concern in north Queensland, Australia (Jardine and Bunn, 2010). Mercury trophic magnification factors within food webs were low relative to other regions of the world and few fish approached or exceeded consumption guidelines, suggesting that the health of humans and wildlife consuming fish such as barramundi from these rivers is unlikely to be compromised because of exposure to this toxic element. This includes Aboriginal communities that harvest riverine resources, and contrasts with several other tropical locations where natural sources of Hg (e.g. Papua New Guinea, Bowles et al. 2001) or point sources such as artisanal gold mining (e.g. Brazil, Akagi et al., 1995; Ghana, Hilson et al., 2007; Indonesia, Kambey et al., 2001) have led to considerable Hg exposure in local communities largely via fish consumption.

Concentrations measured in the broad scale survey of water and sediments were generally below known thresholds for biological effects (Gaudet et al. 1995, MacDonald et al. 2000) and low relative to sites that have been contaminated by Hg point sources such as mining discharges. For example, Telmer et al. (2006) found Hg concentrations in unfiltered water from an Amazonian tributary impacted by gold mining that ranged from 2 to 27 ug/L, well above the highest detected concentration.
in the current study. This suggests that historical mining inputs in many Cape York
catchments are not significantly contributing to Hg availability. Likewise, Suchanek
et al. (2008) report Hg concentrations in surficial sediments for Clear Lake, California
impacted by a Hg mine, that range from 0.3 µg g⁻¹ to 425 µg g⁻¹; only one value in the
current study was within that range of values (from the Endeavour River estuary).
Other contaminated sites worldwide also typically have sediment concentrations
above those detected in the current study, while uncontaminated sites have
concentrations that range from 0.001 to 0.4 µg g⁻¹ (summarized in Suchanek et al.,
2008). Cape York rivers therefore have water and sediment Hg concentrations that
are consistent with those expected for un-impacted river catchments.

Low Hg concentrations in abiotic compartments such as water and sediment
do not preclude exposure to high concentrations for consumers in food webs because
uptake of metals by biota can be high (Stewart et al., 2010). For example, Bowles et
al. (2001) found extremely low concentrations of Hg in water (1.4 ng L⁻¹ – well below
detection limit in the current study) and in sediment (0.1 µg g⁻¹ – at the detection limit
in the current study) in Lake Murray, Papua New Guinea, but efficient uptake into
plankton and subsequent food web biomagnification led to concentrations in fish that
were above recommended guidelines. For this reason, we extended our study to
include food web Hg biomagnification, measured using stable isotopes of nitrogen
(Kidd et al., 1995).

Trophic magnification factors (TMFs) for Hg, as measured by log Hg-δ¹⁵N
regressions, were lower than those typically reported in other tropical waterbodies.
Food webs in African lakes had log Hg-δ¹⁵N regression slopes ranging from 0.12 to
0.22 (Campbell et al., 2003, 2008; Kidd et al., 2003) and biota from Lake Murray in
Papua New Guinea had a slope of 0.28 (Bowles et al., 2001), considerably higher than
the average value of 0.08 ± 0.18 S.D. for the current study. However, fishes and
invertebrates from a coastal freshwater lagoon in Brazil also showed no evidence of
Hg biomagnification (slope = 0.08, Pereira et al., 2010), suggesting that biotic factors
such as growth dilution could limit Hg biomagnification (Karimi et al., 2007). While
the low slopes in the current may be a function of the use of total Hg that does not
biomagnify as strongly as the methyl fraction alone (Mason et al. 1996), one
alternative explanation is a decoupling of consumers from their resources (Jardine et
al. 2006). Many of the larger fishes derive biomass from the floodplain and carry it
back into dry season refugia (main channel and waterholes) (Jardine et al., in press).
As such, non-mobile consumers with low δ¹⁵N such as shrimps and bivalves are
inappropriate baselines with which to measure biomagnification because larger fishes
have δ¹⁵N and Hg concentrations reflective of habitats external to the location of
capture (Jardine et al., 2006). This uncoupling of diet information from contaminant
information violates the assumption of steady-state when calculating biomagnification
(Borga et al. 2011).

A second possibility for the low TMFs is artificially high δ¹⁵N in some
herbivorous consumers that leads to a dampening of log Hg-δ¹⁵N slopes. Herbivorous
fishes have been shown to have δ¹⁵N diet-tissue fractionation that is higher than
average values for other taxa (Mill et al., 2007). Bony bream in the current study
have relatively high δ¹⁵N yet they are known to be strict herbivores (Sternberg et al.,
2008). Similarly, prawns (Macrobrachium spp.) and rainbowfish (M. splendida) are
both omnivores as suggested by past dietary studies (Pusey et al., 2004) and have
similar δ¹⁵N when they co-occur (8.4‰ vs. 8.6‰), yet prawns have far lower Hg
concentrations (mean = 0.01 µg g⁻¹) compared with rainbowfish (mean = 0.24 µg g⁻¹).
Eliminating prawns from the biomagnification analysis resulted in a higher average
slope (0.12 versus 0.08) and typically improved $r^2$ for the Hg-$\delta^{15}$N regressions within sites, leading to significant TMFs in four of seven sites where prawns were excluded (Table 3). This suggests that prawns feed at a lower trophic level than suggested by their $\delta^{15}$N, they eliminate Hg during moulting of their exoskeletons, or simple metabolic differences between fishes and invertebrates confound comparisons across taxa. Regardless of the sources of error associated with measuring Hg biomagnification (Borga et al. 2011), there is little evidence to suggest that these food webs significantly biomagnify Hg to tertiary (small barramundi and longtom) and apex (large barramundi) predators.

Mercury concentrations in barramundi from the coastal fishery, with one exception, were below the recommended consumption guideline of 0.5 µg g$^{-1}$ wet weight (approximately 2.5 µg g$^{-1}$ dry weight assuming 80% moisture) suggesting that consumption of this popular recreational and commercial species poses no threat to human health. This is in contrast with measurements made on barramundi and other species in Lake Murray of Papua New Guinea, where 23% of all samples were above the consumption guideline (Sorentino, 1979; Bowles et al., 2001). Other top predator fish in tropical locations have Hg concentrations that are greater than the guideline level (e.g. 10 to 45% of samples in Indonesian gold mining areas, Castlihos et al., 2006, 34% of samples of *Cichla* spp. in Brazil, Kehrig et al., 2008).

Body size explained little of the variation in barramundi Hg concentrations ($r = 0.02$, Figure 3). This is surprising given the strong positive relationship between barramundi size and Hg observed in prior studies (Sorentino, 1979; Jones et al., 2005) and generally strong correlations between these variables for a broad range of predatory fish species in tropical and temperate locations (e.g. Wiener et al., 1990; Lange et al., 1994; Da Silva et al., 2005; Desta et al., 2008). Relationships between
body size and Hg can be highly variable among species depending on a myriad of other factors known to influence fish Hg (Jackson, 1991). In our analysis, age was the most important determinant of Hg concentrations in barramundi. Separation of the effects of body size and age on barramundi Hg is possible because these two variables are only weakly correlated, particularly in the Flinders River ($r = 0.20$), suggesting considerable variability in growth rates among individuals. High growth rates are associated with lower Hg accumulation because of growth dilution (Simoneau et al., 2005), but in the current study there was no negative correlation between body size and Hg within the 2-year old age class even though 2-year-olds ranged in size from 549 mm to 932 mm in the Flinders River. Furthermore, there was no negative correlation between size at age 2 and % marine feeding, even though barramundi are expected to grow more rapidly in productive freshwaters (Gross et al., 1988; Milton et al., 2008). The increase in Hg concentrations with barramundi age is likely due to a combination of reduced feeding efficiency and higher Hg concentrations in prey in older fish (Trudel and Rasmussen, 2006).

Trophic level, while correlated with Hg concentrations, was not a significant predictor of Hg in the multiple regression model. Barramundi are known to feed more heavily on fish as they grow, switching from a diet dominated by macrocrustaceans as juveniles (80-400 mm total length) to a diet dominated by fish as adults (>400 mm) (Pusey et al., 2004), however subtle dietary changes do occur within the latter size class that was examined here (Davis, 1985). Stable N isotope data suggest that trophic level continues to increase within the size range for the Mitchell River fish ($r = 0.72$, $p < 0.001$) but not the Flinders River fish ($r = 0.21$, $p = 0.279$). The appearance of large-bodied species such as clupeid, ariid and mugilid fishes in the diet of barramundi > 600 mm and the strong correlation between barramundi size and the
size of its fish prey (Davis, 1985) likely explains the higher δ¹⁵N with increasing size in the Mitchell River. The δ¹⁵N for clupeids (8.9 ± 1.1‰ S.D., n = 35) and mugiliids (8.0 ± 0.6‰ S.D., n = 9), as more strictly herbivorous species, are low compared to ariids (10.5 ± 0.4‰ S.D., n = 30) that are omnivorous (T.D. Jardine, unpublished data), so differences between catchments in barramundi length-δ¹⁵N associations may be due to differential consumption of those taxa. A consistent diet across a range of size classes in African sharptooth catfish (Clarias gariepinus) resulted in no change in δ¹⁵N or Hg with size (Desta et al., 2007) while another species, the straight fin barb (Barbus paludinosus) exhibited increases in both δ¹⁵N and Hg with size (Desta et al., 2008), suggesting that when body size affects Hg in fish it is likely due to larger individuals occupying higher trophic levels (i.e. increased gape). Some tropical fishes decrease their trophic level as they age, yet their Hg concentrations do not show a corresponding decrease (Da Silva et al., 2005), suggesting that Hg continues to accumulate with age or is efficiently retained in the organism with a long half life, despite eating less-contaminated prey (Trudel and Rasmussen 2006). This may be the case for barramundi, where age is a more important determinant of Hg than trophic level, and Hg is accumulated more strongly than can be explained by differences in δ¹⁵N alone.

The strong negative correlation between % marine feeding and Hg concentrations suggests that there is lower Hg in prey in marine habitats compared to floodplains and dry season freshwater refugia. These latter habitats have locations for Hg methylation, with the roots of floating macrophytes having the highest methylation potential compared with flooded soils and sediments (Guimaraes et al., 2000). The lower Mitchell River has waterholes containing floating macrophytes, many of which are non-native weeds such as water hyacinth (Eichornia crassipes)
that can dominate the vegetation assemblage. While concentrations in biota measured at one such waterhole, Fish Hole Creek, were not higher than others in the catchment, the spread of these invasive weed species with enhanced methylation potential may have biogeochemical implications for Hg cycling in these catchments.

The data from this study that included multiple environmental matrices (water, sediment, invertebrates and small and large fish) from a broad geographic region suggests that Hg does not pose a threat to the health of humans or wildlife in this region of Australia (Jardine and Bunn 2010). However, focused investigations of methyl Hg dynamics in various compartments of these floodplain systems and their uptake into food webs would help draw more comprehensive comparisons to other tropical regions (Guimaraes et al. 2000, Bowles et al. 2001). Advocates of future water resource development that is expected in this region should remain wary of the possibility that subtle changes to hydrology or geomorphology could lead to enhanced Hg risks as are observed elsewhere (Akagi et al., 1995; Bowles et al., 2001; Kambey et al., 2001).

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Yalanji; The Mulliridgee; The Barbarum, The Kuku Djungan and Gugu Mini). This study was funded by a Griffith University New Researcher Grant to TDJ and the Tropical Rivers and Coastal Knowledge (TRaCK) Research Hub. TRaCK received major funding for its research through the Australian Government’s Commonwealth Environment Research Facilities initiative; the Australian Government’s Raising National Water Standards Program; Land and Water Australia; the Fisheries Research and Development Corporation and the Queensland Government’s Smart State Innovation Fund.

References


Blaber SJM. Tropical estuarine fishes: ecology, exploitation and conservation.


Griffin RK. Recreational barramundi fishing – how important is it to the Northern Territory. Australian Fisheries 1979; 38: 25-26.


Milton, D., Halliday, I., Sellin, M., Marsh, R., Staunton-Smith, J. and Woodhead, J. Otolith microchemistry of barramundi Lates calcarifer can provide insight


Rae CJ, Lamprell VJ, Lion RJ, Rae AM. The role of bush foods in contemporary Aboriginal diets. Proceedings of the Nutrition Society of Australia 1982; 7: 45-49.


Swanson HK, Kidd KA. Mercury concentrations in Artic food fishes reflect the presence of anadromous Arctic charr (*Salvelinus alpinus*), species, and life history. Environmental Science & Technology 2010; 44: 3286-3292.


Vander Zanden MJ, Rasmussen JB. Primary consumer $\delta^{13}$C and $\delta^{15}$N and the trophic position of aquatic consumers. Ecology 1999; 80: 1395-1404.

Table 1. Number of samples analysed for unfiltered and dissolved total mercury in water at locations across Cape York, Queensland, and the number of those samples above the analytical detection limit of 0.1 µg L⁻¹.

<table>
<thead>
<tr>
<th>Region</th>
<th>River Catchment / Wetland Site</th>
<th>Number of Aqueous Hg Samples</th>
<th>Number at or above Det. Limit (0.1 µg/L)</th>
<th>Detected Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Freshwater</td>
<td>Estuary</td>
<td>Unfiltered</td>
</tr>
<tr>
<td>Pormpuraaw</td>
<td>Christmas Cr. Chillagoe Lagoon</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Kowanyama</td>
<td>Joe's Lagoon Magnificent Cr. Meggara Lagoon Penambl Swamp Crayfish Lagoon Red Lily Lagoon</td>
<td>7</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Cooktown</td>
<td>Endeavour River</td>
<td>20</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Annan River</td>
<td>25</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Jeannie River</td>
<td>7</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Starke Inlet</td>
<td>4</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Laura-Normanby R.</td>
<td>26</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Laura-Normanby-Jack Lakes</td>
<td>8</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Bathurst Bay</td>
<td>Muck River</td>
<td>1</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Mapoon</td>
<td>Wenlock River Turtle Creek Alligator Creek Big Swamp Fish Creek Scorpion Lagoon</td>
<td>10</td>
<td>10</td>
<td>4*</td>
</tr>
<tr>
<td>Weipa</td>
<td>Albatross Bay</td>
<td>4</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td>91</td>
<td>43</td>
<td>47</td>
</tr>
</tbody>
</table>

* Detection Limit 0.5 µg L⁻¹
Table 2. Number of samples analysed for total mercury in sediment at locations across Cape York, Queensland, and the number of those samples above the analytical detection limit of 0.1 µg g⁻¹.

<table>
<thead>
<tr>
<th>Region</th>
<th>River / Wetland Site</th>
<th>Number of Sediment Samples</th>
<th>No. at or above the Det. Limit (0.1 µg g⁻¹)</th>
<th>Detected Concentration (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kowanyama</td>
<td>Joe’s Lagoon</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnificent Cr.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Meggara Lagoon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Penambl Swamp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Annan River</td>
<td>3</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Endeavour River</td>
<td>32</td>
<td>3</td>
<td>0.2, 0.3, 1.1</td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Starke Inlet</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Southeast CYP</td>
<td>Laura-Normanby</td>
<td>7</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Weipa</td>
<td>Albatross Bay</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td><strong>15</strong></td>
<td><strong>43</strong></td>
<td><strong>5</strong></td>
</tr>
</tbody>
</table>
Table 3. Slopes of mercury biomagnification (Hg vs. δ¹⁵N) and corresponding trophic magnification factors for significant slopes at 14 sites in the Mitchell River, Queensland, Australia. Italicized text in parentheses indicates values calculated after removing Macrobrachium spp. from the analysis (see Discussion).

<table>
<thead>
<tr>
<th>Site</th>
<th>Latitude</th>
<th>Longitude</th>
<th>n</th>
<th>Slope ± S.E.</th>
<th>r²</th>
<th>p</th>
<th>TMF ± S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>McLeod River</td>
<td>-16.50</td>
<td>145.00</td>
<td>15 (12)</td>
<td>0.24 ± 0.14</td>
<td>0.17</td>
<td>0.113</td>
<td>~0</td>
</tr>
<tr>
<td>Emu Creek (Petford)</td>
<td>-17.34</td>
<td>144.95</td>
<td>14 (11)</td>
<td>-0.16 ± 0.30</td>
<td>0.02</td>
<td>0.598</td>
<td>~0</td>
</tr>
<tr>
<td>Palmer River (Goldfields)</td>
<td>-16.10</td>
<td>144.78</td>
<td>16 (13)</td>
<td>0.14 ± 0.19</td>
<td>0.06</td>
<td>0.351</td>
<td>~0</td>
</tr>
<tr>
<td>Fish Hole Creek</td>
<td>-15.48</td>
<td>141.79</td>
<td>14 (11)</td>
<td>0.34 ± 0.05</td>
<td>0.85</td>
<td>&lt;0.001</td>
<td>14.3 ± 1.5</td>
</tr>
<tr>
<td>Hodgkinson River</td>
<td>-16.72</td>
<td>144.82</td>
<td>12</td>
<td>-0.01 ± 0.16</td>
<td>&lt;0.01</td>
<td>0.973</td>
<td>~0</td>
</tr>
<tr>
<td>Ten Mile Lagoon</td>
<td>-16.34</td>
<td>143.04</td>
<td>11</td>
<td>0.14 ± 0.04</td>
<td>0.62</td>
<td>0.004</td>
<td>2.9 ± 1.4</td>
</tr>
<tr>
<td>Saltwater Creek</td>
<td>-17.82</td>
<td>144.42</td>
<td>9</td>
<td>0.22 ± 0.11</td>
<td>0.36</td>
<td>0.083</td>
<td>~0</td>
</tr>
<tr>
<td>Mitchell River (Koolatah)</td>
<td>-16.54</td>
<td>143.03</td>
<td>10</td>
<td>0.21 ± 0.03</td>
<td>0.85</td>
<td>&lt;0.001</td>
<td>5.0 ± 1.3</td>
</tr>
<tr>
<td>Mitchell River (Gamboola)</td>
<td>-15.95</td>
<td>142.38</td>
<td>15 (13)</td>
<td>0.13 ± 0.05</td>
<td>0.36</td>
<td>&lt;0.001</td>
<td>2.8 ± 1.5</td>
</tr>
<tr>
<td>Magnificent Creek</td>
<td>-15.48</td>
<td>141.75</td>
<td>12 (9)</td>
<td>-0.01 ± 0.06</td>
<td>0.01</td>
<td>0.839</td>
<td>~0</td>
</tr>
<tr>
<td>Walsh River (Nullinga)</td>
<td>-17.17</td>
<td>145.30</td>
<td>13</td>
<td>0.02 ± 0.02</td>
<td>0.09</td>
<td>0.309</td>
<td>~0</td>
</tr>
<tr>
<td>Cairo Lagoon</td>
<td>-16.46</td>
<td>143.22</td>
<td>9</td>
<td>-0.01 ± 0.03</td>
<td>&lt;0.01</td>
<td>0.860</td>
<td>~0</td>
</tr>
<tr>
<td>Kingfish Lagoon</td>
<td>-16.17</td>
<td>142.83</td>
<td>7</td>
<td>0.02 ± 0.04</td>
<td>0.05</td>
<td>0.648</td>
<td>~0</td>
</tr>
</tbody>
</table>
**Figure captions**

**Figure 1.** Map of the study area, showing the regions where water and sediment samples were collected (shaded bubbles), the sites where food web samples were collected in the Mitchell River (open circles), and where barramundi samples were obtained from commercial fisheries (solid circles).

**Figure 2.** Mercury concentrations (mean ± 1 S.E.) in various food web compartments from sites in the Mitchell River, QLD, Australia. See methods for taxa included in each category.

**Figure 3.** Mercury concentrations in relation to body size for barramundi from the Mitchell (open circles) and Flinders (solid circles) Rivers, QLD, Australia. The best-fit regression line for barramundi from Port Curtis, QLD, Australia (solid line) is shown for comparison (Jones et al. 2005, data converted from wet weight to dry weight assuming 80% moisture) as well as the typical maximum guideline for human consumption (hatched bar).

**Figure 4.** Barramundi age vs. mercury (A) and $\delta^{15}N$ vs. mercury (B) in the Mitchell (open circles) and Flinders (solid circles) Rivers.

**Figure 5.** Mercury concentrations in relation to % marine feeding for barramundi from the Mitchell (open circles) and Flinders (solid circles) Rivers, and king threadfin salmon (shaded squares) from the Mitchell River, North Queensland, Australia. % marine feeding estimates are derived from mixing models using $\delta^{13}C$ and $\delta^{34}S$ (Jardine et al. in press).
Figure 1.
Figure 2.

![Graph showing Mercury (μg g⁻¹ dry weight) for different taxonomic and feeding groups. The graph includes bars indicating different feeding groups: herbivorous invertebrates, omnivorous invertebrates, herbivorous fishes, omnivorous fishes, and piscivorous fishes. The consumption guideline is also shown.]
Figure 3. 

Log Hg (μg g⁻¹ d.w.) vs. Total Length (mm) according to Jones et al. (2005) with consumption guidelines indicated.
Figure 4

(A) Log Hg (μg g⁻¹ d.w.) vs. Barramundi age (years)

(B) Log Hg (μg g⁻¹ d.w.) vs. δ¹⁵N
Figure 5.