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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 $\mu g\,L^{-1}$ and 0.1 $\mu g\,g^{-1}$, 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. $\delta^{15}N = 0.08$). 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 vs. 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.

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 lead 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

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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 differ 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 characterise 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., 1988; Davies et al., 2008; 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 (Fig. 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 3 m extended sampling pole and sample collection bottle.

Polypropylene water sample bottles were lab-sterilised and preserved with nitric acid to a pH <2 (American Public Health Association (APHA), 2005). Dissolved Hg samples were filtered at the site through 60 cm^3/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 (American Public Health Association (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) (Fig. 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 biassed 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 krefftii*). Sites included

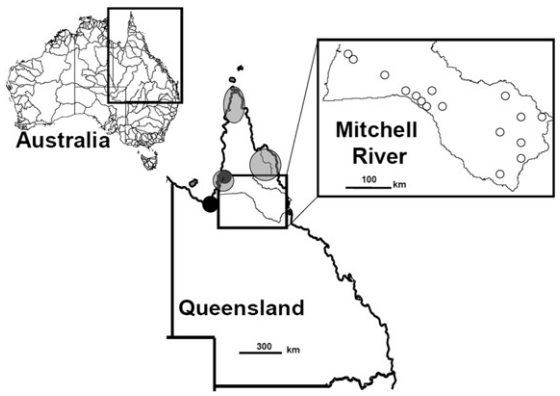

Fig. 1. Map of the study area, showing the regions where water and sediment samples were collected (shaded bubbles), the sites where food web samples were collected in the Mitchell River (open circles), and where barramundi samples were obtained from commercial and recreational fisheries (solid circles).