

## RESEARCH ARTICLE

# Mercury cycling in Australian estuaries and near shore coastal ecosystems: Triggers for management

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Mercury (Hg) sources to estuaries (natural and anthropogenic) as well as Hg concentrations in Australian nearshore marine environment fish are reviewed herein. The question of whether Australian estuaries have a Hg contamination problem is addressed. The Hg concentrations in fish, excluding sharks, tuna, barramundi and some stingrays, in estuaries and near-shore ecosystems with no discernable pollution sources are typically below 0.5 mg/kg wet weight, the level of health concern. There is no relationship of Hg concentration with fish size or age nor any evidence of biomagnification. In locations with historic large discrete Hg input sources (e.g. Derwent Estuary, Tasmania, Princess Royal Harbour WA, Port Phillip Bay Vic, Sydney sewage outfalls NSW), Hg concentrations in some sediment-dwelling fish such as flatheads exceed the health limit of 0.5 mg/kg. In this paper, we also review, within an Australian context, the biogeochemical processes controlling the formation and accumulation of methyl mercury (MeHg). On entering waterways, Hg rapidly partitions to particulate matter and deposits into sediments. The remobilisation of Hg from sediment is dependent on the formation of MeHg by bacteria and ultimately the interplay of S, Fe and Se cycling. Fish species that move and feed in different areas have Hg concentrations that do not reflect the sediment Hg concentrations where they are caught, i.e. there is an uncoupling of diet and potential Hg exposure.

Concluding remarks focus on management interventions: source reduction, preventing eutrophication and promoting system biodiversity and biodiverse diets to mediate the accumulation of Hg in marine organisms and limit the intake of Hg by humans when consuming fish.

**Keywords:** Mercury marine ecosystems; Fish; Accumulation; Speciation

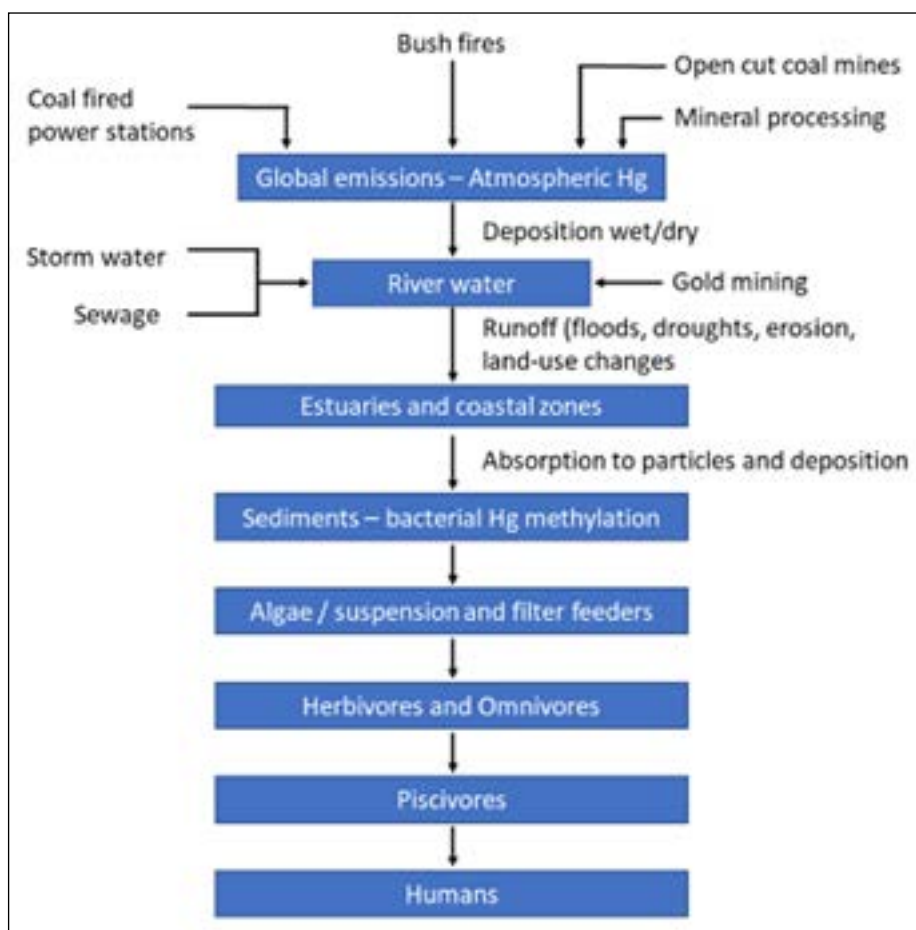
## Introduction

Environmental mercury (Hg) problems first became apparent in the 1950's due to the release of methyl mercury (MeHg) into Minamata Bay Japan. Mercury was discharged in wastewater from 1932–1968 from the production of acetaldehyde and vinyl chloride in which Hg was used as a catalyst (Normile, 2013). Over 200 people were poisoned, the majority of whom died due to the consumption of MeHg contaminated fish. Fish had over 50 mg/kg wet weight Hg. “Minamata Disease” is now recognised as the chemical and pathological characteristics of the neurological disorders caused by Hg poisoning. There is also a link between MeHg intake and acute myocardial infarction (Lambert et al., 2012). The mention of Hg causes hysteria and articles appear regularly in the press (Supplementary **Figure 1**) mainly because of the concern for pregnant women consuming seafood and Hg being maternally transferred. Higher Hg concentrations are found in the placenta and breast milk (Pitkin et al., 1976). In wildlife,

there are links to decreased reproductive success, changes in blood chemistry, neurochemistry, hormones and chromosome structure, aberrant behaviour and abnormal histopathology for fish, birds and other animals (Lambert et al., 2012).

Mercury is mainly emitted to the environment from mining activities, the combustion of coal and industrial activities (**Figure 1**). Historically, the gold rushes in Spanish America (16<sup>th</sup> Century) and the USA and Australia (19<sup>th</sup> Century) resulting in significant Hg inputs into the surrounding environments. Hg can also enter aquatic environments through runoff from weathering, agriculture, wildfires, sewage and municipal wastewater (**Figure 1**). It is estimated that 20% of anthropogenic Hg in the environment results from current industrial activity, while 60–70% is from legacy activities (Sonke et al., 2013).

Mercury concentrations in the Australian environment are low as indicated by the relatively low Hg concentrations measured in the hair of Sydney and Darwin residents (Airey, 1983). In Australia, the National Pollutant Inventory reported that in 2008–2009, over 1188 Australian industrial facilities emitted 25,000 kg of Hg compounds. Natural sources account for approximately 1800 kg/year. Nelson et al. (2012) found that the Hg emissions flux from



**Figure 1:** Mercury sources to the environment and accumulation through food chains. DOI: <https://doi.org/10.1525/elementa.425.f1>

vegetation is between 70–210 tonnes/year, from fires is between 21–63 tonnes/year and from anthropogenic sources is 15 tonnes/year. Overseas, coal-fired burning is considered to be a major source of Hg to the environment; however, Australian brown and black coals contain relatively low Hg concentrations (0.03–0.08 mg/kg and 0.01–0.13 mg/kg respectively) (Nelson, 2007). It is unclear if Hg emissions have substantially increased across Australia and whether Hg emissions from natural and anthropogenic sources need to be further quantified.

Mercury as Hg<sup>0</sup> entering the atmosphere from natural sources, is relatively unreactive and reaches the Earth's surface mainly through dry deposition while Hg<sup>2+</sup> reaches the earth mainly through wet deposition (rain and snow) because Hg<sup>2+</sup> is easy to dissolve in water (Harris et al., 2007). Mercury emitted from coal-fired power stations that is in an oxidised and particulate form (Hg<sup>2+</sup>), is relatively reactive and deposited within hours and generally within 100–200 km of emission sources (Harris et al., 2007). In recognition of Hg being a global problem, efforts have been made to reduce Hg emissions. For example, in the USA, Hg emissions have been cut by 60% since 1990 (Schmeltz et al., 2011). In lakes, when Hg emissions have been reduced, a significant decrease in MeHg concentrations in fish occurs within ~3 years; however, this does not always occur because of residual Hg stored in sediments, which is remobilised over time (Harris et al., 2007, Hutcherson et al., 2014).

This paper was presented at a workshop held in Australia, 7–8 November 2019 to inform Australian scientists and managers of the status of MeHg concentrations in Australian fish, the major pathways of MeHg formation and accumulation within the fish, and the factors controlling MeHg formation. This paper provides an evaluation of Hg concentrations in fish as an issue and management interventions that should be considered. Thus views expressed in this paper are based on local data for MeHg measurements in fish and is based on what is known about the biogeochemical cycling of Hg in Australian marine ecosystems. It is supported by examples from the international literature. The objectives of this paper are:

- 1 To describe the potential sources of Hg to Australian estuaries and nearshore coastal waters;
- 2 To report Hg concentrations in fish commonly consumed in Australia and assess if they are comparable to other regions of the world;
- 3 To describe the major pathways of MeHg formation and accumulation by fish and the factors controlling MeHg formation;
- 4 To suggest management interventions to ameliorate the production and accumulation of MeHg in fish and limit the uptake of Hg by humans when consuming fish.

## Sampling and pretreatment

### Sample locations

Fish samples ( $n = 130$ ) were collected by commercial fisherman from nearshore coastal waters of New South Wales to St Vincents Gulf South Australia over 2017–2018 (**Figure 2**). Barramundi ( $n = 12$ ) were obtained from the Sydney fish market and sourced from the Northern Territory. All fish were immediately frozen on collection. These areas are designated as having no discrete Hg sources with Hg coming from natural weathering, bushfires and drainage of agricultural land. The locations with published Hg data for estuaries with known historic discrete Hg sources (e.g. Derwent River, Tasmania; Port Phillip Bay, Victoria; Sydney NSW sewage outfalls and Princess Royal Harbour Western Australia) are also indicated (**Figure 2**).

### Materials

#### Equipment

Total mercury concentrations in digests were measured using a Perkin Elmer SCIEX Elan DRC-e ICPMS. Mercury species were measured using a Perkin Elmer series 200 HPLC pump coupled to a Perkin Elmer Sciex Elan DRC-e ICPMS.

#### Standards

A stock solution ( $1000 \text{ mg l}^{-1}$ ) of mercury (II) was prepared by dissolving the appropriate amount of mercuric chloride (BDH chemicals Ltd, England) in ultrapure deionised water ( $18.2 \text{ M}\Omega$ ) obtained from a Sartorius arium 611 system. The MeHg stock solution ( $1000 \text{ mg l}^{-1}$ ) was prepared by dissolving the appropriate amount of methyl mercury (II) chloride (Aldrich Chemical Company Inc., USA) in the smallest possible volume of methanol and diluting it to volume with deionised water. The stock solutions were stored in airtight bottles and refrigerated.

Working standards ( $3, 6, 12, 25, 50, 100 \text{ mg l}^{-1}$ ) were prepared daily from the stock solutions by serial dilution using deionised water.

#### Reagents

All reagents were of analytical grade and used without further purification. Enzyme Protease type XIV (*Streptomyces griseus* Protease A, *Streptomyces griseus*, Protease B and *Streptomyces griseus* Trypsin) was obtained from Sigma-Aldrich, Australia. A phosphate buffer was prepared by dissolving ammonium di-hydrogen phosphate (Suprapur, Merck, Germany) and L-cysteine (Sigma-Aldrich, Japan) in deionised water with the pH adjusted to 7.5 with ammonia (Pronalys, May and Becker, Australia).

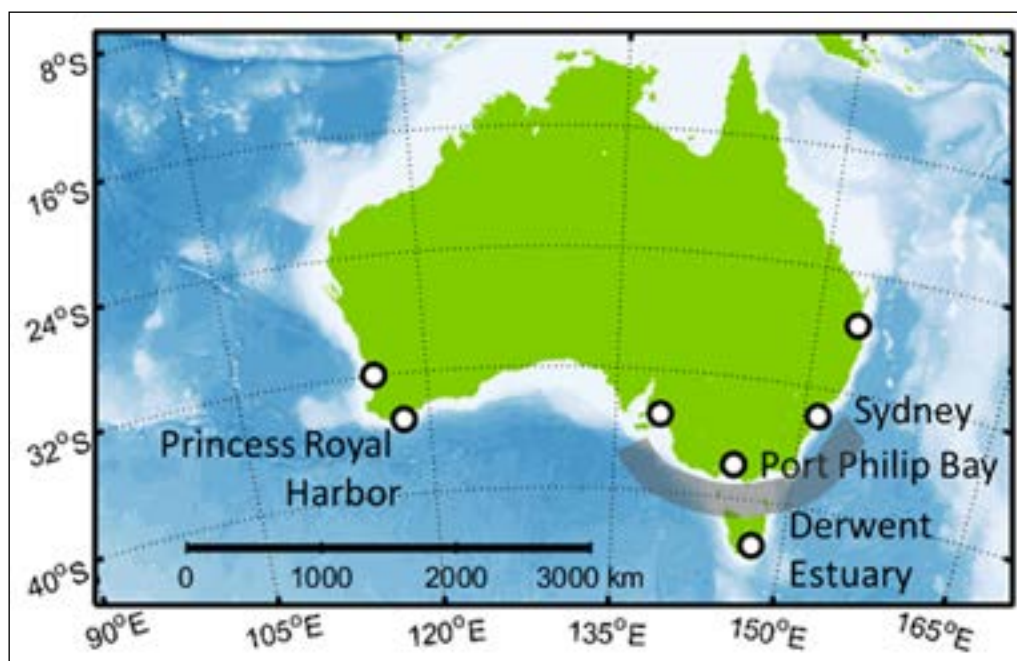
### Measurement of Hg concentrations

#### Sample preparation

Samples were thawed and the muscle tissues between gills and tails excised. All samples were freeze-dried for approximately 24 hours (Labconco, Australia) and ground to a homogenous powder using a IKA A11 basic analytical mill (Germany).

#### Measurement of Total mercury concentrations

Total mercury concentrations were determined after nitric acid digestion (Baldwin et al., 1994). Freeze-dried tissue samples ( $70 \text{ mg}$ ) were weighed into  $7 \text{ ml}$  polytetrafluoroacetate digestion vessels (A.I. Scientific, Australia) and  $1.0 \text{ ml}$  of concentrated nitric acid (Suprapur, Merck KGaA, Germany) was added to the sample. Samples were digested in a microwave oven (CEM MDS 2000, USA) at  $600 \text{ W}$  for  $2 \text{ min}$ ,  $0 \text{ W}$  for  $2 \text{ min}$  and  $450 \text{ W}$  for  $45 \text{ min}$ . After cooling, sample digests were diluted to  $10 \text{ ml}$  with  $1\% \text{ v/v}$   $\text{HNO}_3$  containing internal standards (Ho, In, Tb, Rh;  $10 \mu\text{g l}^{-1}$ ) in  $10 \text{ ml}$  polyethylene vials (Sarstedt, Australia).



**Figure 2:** Map of sampling locations indicating non-contaminated area trawled in grey (Figure 3) and point Hg sources of published data presented in Figure 4. DOI: <https://doi.org/10.1525/elementa.425.f2>

Total mercury concentrations for digests were measured by ICPMS (standard mode, ELAN DRC-e, Perkin Elmer).  $^{181}\text{Ta}$  and  $^{184}\text{W}$  isotopes were also measured as polyatomic oxides that can interfere with the quantification of mercury (Maher et al., 2001). Blanks, spikes and certified fish tissue reference materials (CRMs) were used for quality assurance/control purposes.

Analysis of CRMs, NRCC DORM –2 Dogfish muscle ( $n = 20$ ), NRCC Dolt – 3 Dogfish liver ( $n = 20$ ), NIST RM 50 Albacore Tuna ( $n = 20$ ) and IRMM IMEP-20 Tuna fish ( $n = 20$ ) gave recoveries for total Hg ( $4.6 \pm 0.3 \text{ mg kg}^{-1}$ ,  $3.4 \pm 0.4 \text{ mg kg}^{-1}$ ,  $0.95 \pm 0.04 \text{ mg kg}^{-1}$ ,  $4.3 \pm 0.3 \text{ mg kg}^{-1}$ ) in agreement with the certified values ( $4.64 \pm 0.26 \text{ mg kg}^{-1}$ ,  $3.37 \pm 0.14 \text{ mg kg}^{-1}$ ,  $0.94 \pm 0.01 \text{ mg kg}^{-1}$ ,  $4.32 \pm 0.16 \text{ mg kg}^{-1}$ ).

#### Measurement of Mercury species concentrations

Freeze-dried samples (0.1 g) were weighed into 50 ml fluorinated ethylene propylene tubes (Oakridge, Selby Scientific) with 10 mg of protease type XIV and 4 ml of  $0.1 \text{ mol l}^{-1}$  phosphate buffer (pH = 7.5) containing 0.05% w/v cysteine. The tubes were incubated for 2 h in a hybridisation oven (XTRON HI 200, Bartlett Instruments) at  $37^\circ\text{C}$  with a sample rotation speed of 20 rpm. Extracts were transferred to acid-washed 10 ml polypropylene centrifuge tubes (Sarstedt, Australia), made up to a final volume of 5 ml with buffer and centrifuged for 20 min at 3000 rpm (Eppendorf) (Rai et al., 2002). All supernatants were syringe filtered through a 0.2 mm membrane (Ministart RC 15, Sartorius, Germany) before analysis. 0.1 mL of sample extract was speciated by HPLC-ICPMS. The system consisting of a Phenomenex Luna  $5 \mu\text{m}$  C18 ( $250 \text{ mm} \times 4.6 \text{ mm}$ ) with a mobile phase consisting of 5% v/v  $\text{CH}_3\text{OH}$ ,  $0.06 \text{ mol l}^{-1}$   $\text{NH}_4\text{COOH}$  and 0.1% w/v L-cysteine, pH 6.8, flow rate,  $1.0 \text{ ml min}^{-1}$ ; temp,  $25^\circ\text{C}$ . Mercury species were quantified by external calibration using the standards ( $3\text{--}100 \mu\text{g l}^{-1}$ ). The chromatography package Totalchrom Navigator (Perkin Elmer, Australia) was used to quantify mercury species by peak area.

Blanks, spikes and certified fish tissue reference materials (CRMs) were used for quality assurance/control purposes. Extraction of the certified fish tissue reference materials NRCC DORM –2 Dog fish muscle ( $n = 20$ ), NRCC Dolt – 3 Dogfish liver ( $n = 20$ ), NIST RM 50 Albacore Tuna ( $n = 20$ ) and IRMM IMEP-20 Tuna fish ( $n = 20$ ) gave recoveries for MeHg ( $4.4 \pm 0.8 \text{ mg kg}^{-1}$ ,  $1.55 \pm 0.09 \text{ mg kg}^{-1}$ ,  $0.89 \pm 0.08 \text{ mg kg}^{-1}$ ,  $3.9 \pm 0.6 \text{ mg kg}^{-1}$ ) in agreement with the certified values ( $4.47 \pm 0.1 \text{ mg kg}^{-1}$ ,  $1.4 \pm 0.0 \text{ mg kg}^{-1}$ ,  $0.85 \pm 0.0 \text{ mg kg}^{-1}$ ,  $4.24 \pm 1.0 \text{ mg kg}^{-1}$ ).

#### Statistical measurements

Analysis of results was undertaken using Microsoft Excel 2019 to determine means and standard deviations and using SAS 9.1.3 to produce ANOVA and simple linear regression outputs. Data below detection limits was replaced by the value of half the detection limit ( $0.01 \mu\text{g/g}$ ). The data was log-transformed to meet the requirements of normality and homogeneity of variances. Kruskal-Wallis test was used when data was not normally distributed.

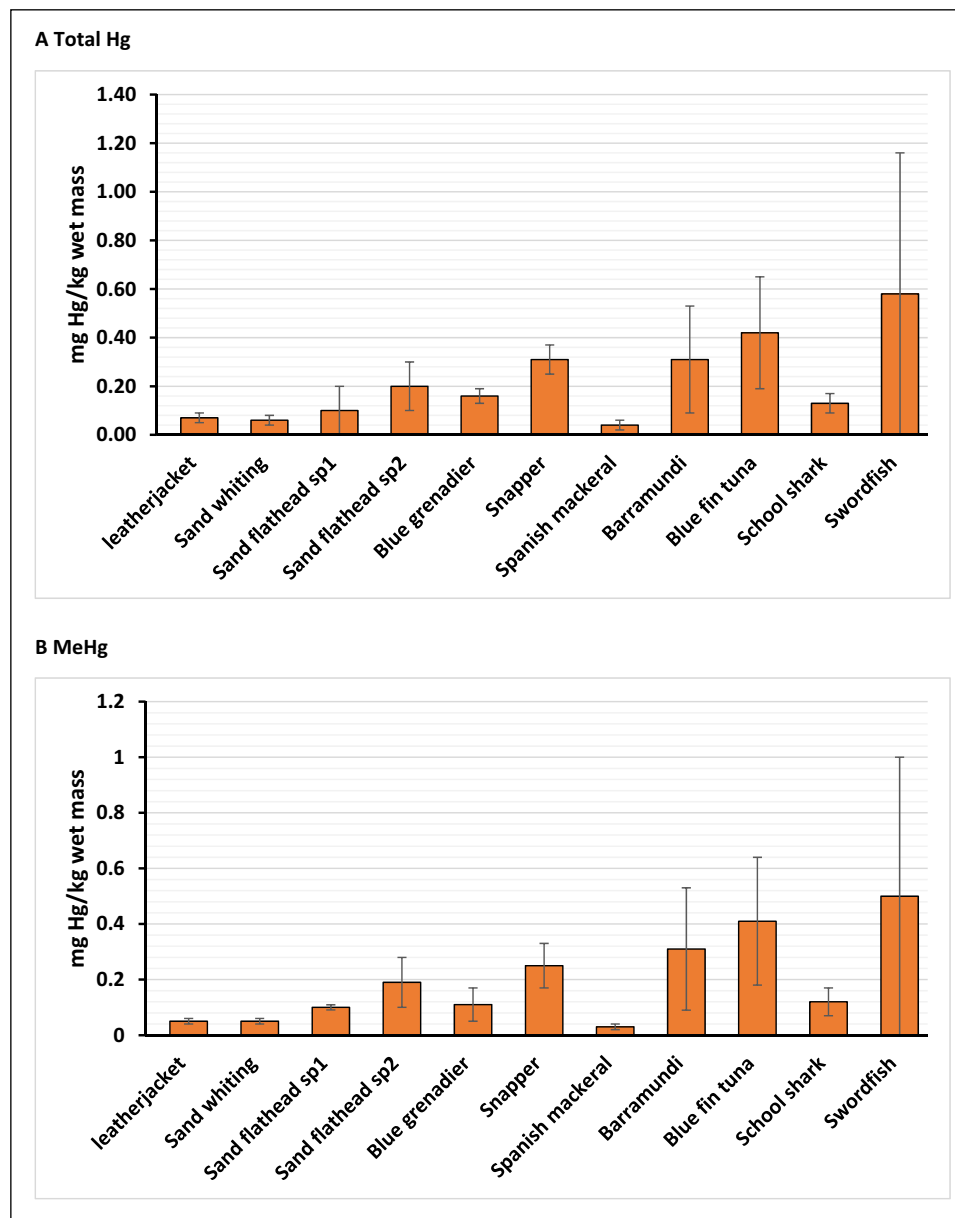
## Mercury concentrations in fish

### No major Hg sources

Most of Australia's estuaries and nearshore coastal ecosystems have no major sources of Hg. Published studies of Hg concentrations in estuaries and coastal areas with no obvious point sources indicate that most water samples have  $<0.1 \mu\text{g/L}$  and sediments range between  $<0.1$  and  $0.2 \text{ mg/kg}$  (Jardine et al., 2012, Walker, 1982, Langlois et al., 1987, Ayling et al., 1975, McLean et al., 1991). Mercury entering these systems comes from natural weathering, bushfires and non-point source drainage of agricultural land. For example, Hg-based fungicides (2-methoxyethyl mercury chloride) used in the catchment of the Great Barrier Reef are associated with sugar cane farming resulting in sediment Hg concentrations increasing by a factor of 3 since 1850 (Jardine and Bunn, 2010). Notably, fish Hg concentrations have not significantly increased in this region (Jardine and Bunn, 2010). Likewise, in Northern Australia, 30% of the landscape has been burned, resulting in marginally higher sediment Hg concentrations (Jardine and Bunn, 2010). Based on our measurements, typical mean Hg concentrations found in small carnivorous fish (15–40 cm length) range from  $0.02\text{--}0.37 \text{ mg/kg}$  wet mass (Figure 3A, Supplementary Table S-1). There are significant differences ( $p < 0.001$ ) in the Hg concentrations between benthic and pelagic fish (mean  $0.09 \pm 0.06 \text{ mg/kg}$  and  $0.31\text{--}0.18 \text{ mg/kg}$ , respectively), but this is attributed to the larger fish being pelagic species. Generally, for fish  $<40 \text{ cm}$  in length, as the size of the fish increases, the Hg concentration of it does not increase ( $r^2 = 0.11$ ,  $P > 0.5$ ). Larger carnivorous fish (40–300 cm) tend to have higher mean Hg concentrations ( $0.14\text{--}0.51 \text{ mg/kg}$ ) (Figure 3A, Supplementary Table S-1) and Hg concentrations are significantly related to length ( $r^2 = 0.81$ ,  $p < 0.05$ ). Hg is present mainly as MeHg (MeHg%: mean,  $86 \pm 12$ ; range, 60–100 in all fish species (Figure 3B, Supplementary Table S-1).

These concentrations are in accordance with published Australian studies with smaller fish collected from areas with no point sources having lower Hg concentrations ( $0.03\text{--}0.47 \text{ mg/kg}$ ) than larger carnivorous fish ( $0.09\text{--}3.41 \text{ mg/kg}$ ) (Walker, 1988, Walker, 1981, Plaskett and Potter, 1979, Chvojka and Williams, 1980, Denton and Breck, 1981, Thomson, 1985, Walker, 1976). Most commercially caught fish, except larger fish such as sharks, tuna, barramundi and some stingrays, have Hg concentrations well below  $0.5 \text{ mg/kg}$  wet weight, the level of health concern (Supplementary Table S-3). Food chains are complex in coastal ecosystems, and fish have opportunistic diets. As well, diets change as fish grow and variable rapid growth rates can reduce Hg concentrations. Fish also are transitory and feed in different locations to where they are caught, so sediment Hg concentrations (if localised contamination) are probably not reflected in fish Hg concentrations.

Comparisons with other locations around the world is difficult as Hg concentrations in fish are dependent on species, latitude, size, age, sex, trophic level, season and feeding depth (Blum et al., 2012, Davis et al., 2016,



**Figure 3:** Mercury concentrations in fish from Australian estuaries and near coastal waters with no Hg point sources. All concentrations are wet mass, mean  $\pm$  standard deviation. DOI: <https://doi.org/10.1525/elementa.425.f3>

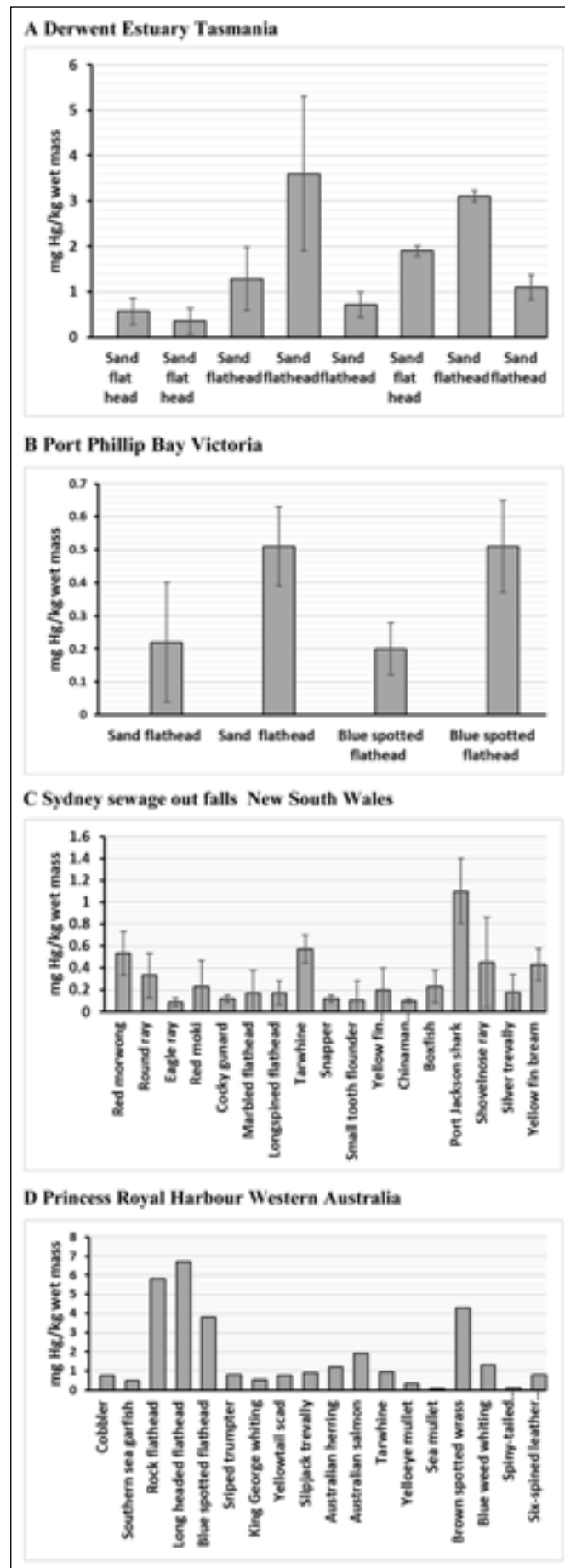
Diop and Amara, 2016, Baumann et al., 2017, Choy et al., 2009). Since 2016, over 90 papers have been published in Google Scholar reporting Hg concentrations in marine fish. These published results are similar to those reported here. In essence, in the published literature, small fish (<40–50 cm length) mostly have Hg concentrations well below 0.5 mg/kg (Mason et al., 2012, Di Lena et al., 2017, Chen et al., 2017, Henry et al., 2017, Anual et al., 2018, Filippini et al., 2018, Rumbold et al., 2018) while large fish such as sharks, tuna and swordfish can greatly exceed 0.5 mg/kg (Bosch et al., 2016, van Hees and Ebert, 2017, Lacerda et al., 2017, O'Bryhim et al., 2017, Madigan et al., 2018) with Hg concentrations reported up to 3.15 mg/kg (Heo et al., 2020, Lee et al., 2016).

Long-lived fish such as sharks, tuna and swordfish worldwide have high Hg concentrations that generally exceed 0.5 mg/kg (Branco et al., 2007, Storelli et al., 2002). In

Australia, the commercial school shark (*Galeorhis australis*) catch size is limited in Victoria to 112 cm, set to limit fish Hg concentrations to below 0.5 mg/kg. In Northern Queensland, however, sharks >51 cm regularly exceed this concentration (Denton and Breck, 1981).

#### **Estuaries with discrete Hg sources**

Elevated Hg concentrations in fish and other organisms have been reported in several estuaries in Australia (Figure 4, Supplementary Table S2). The mean Hg concentrations of the contaminated estuaries are significantly different ( $p < 0.001$ ) to those measured in fish from the non-point source locations and are in the order Princess Royal Harbour ( $1.8 \pm 1.9$  mg/kg) > Derwent Estuary ( $1.6 \pm 1.2$  mg/kg) > Port Phillip Bay ( $0.36 \pm 0.15$  mg/kg) = Sydney sewage outfalls ( $0.30 \pm 0.24$  mg/kg) > Non-point source locations ( $0.17 \pm 0.15$  mg/kg).



**Figure 4:** Mercury concentrations in fish from Australian estuaries and near coastal waters with Hg point sources. All concentrations are wet mass, mean  $\pm$  standard deviation. References are given in Supplementary Table S-2. DOI: <https://doi.org/10.1525/elementa.425.f4>

#### Derwent Estuary Tasmania

The Derwent Estuary historically received Hg inputs from a zinc refinery at Risdon, Tasmania. During the roasting of sulphide concentrates, most Hg was volatilised and the sulphur-rich gas stream used to produce sulphuric acid and wet scrubbers-electrostatic precipitators used to remove Hg. Prior to 1975, recovered Hg was discharged. Now aluminium is used to remove Hg from this stream. Water discharged from the refinery contained up to 16–20 µg/L of Hg and sediments near the refinery up to 1100 mg/kg (Langlois et al., 1987, Plaschke et al., 1997).

A survey of 16 finfish in 1972–1973 measured Hg concentrations of non-detectable to 2 mg/kg with 51% of piscivores and 7% of herbivores containing >0.5 mg/kg. (Ratkowsky et al., 1975). Surveys of sand flathead (*Platycephalus bassensis*) reported Hg concentrations of 0.03–3.1 mg/kg (Jones et al., 2013b, Ratkowsky et al., 1975, Langlois et al., 1987, Ayling et al., 1975) with 63–100% as MeHg (Jones et al., 2013b). At Ralphs Bay, 2.3% of fish contained >1 mg/kg and with a mean of 0.6 mg/kg (Langlois et al., 1987). After treatment of the effluent stream was implemented, flathead Hg concentrations decreased from 0.6–0.9 mg/kg in 1973 to 0.28–0.6 mg/kg in 1983, a 28% decline (Langlois et al., 1987).

#### Port Phillip Bay Victoria

Historically, the Yarra River acted as a point source of Hg to Port Phillip Bay. A survey conducted in 1975–1978 (14 sites) highlighted that water contained up to 0.059 µg/l while the flatheads *Platycephalus bassensis* and *Platycephalus caruleopunctus* contained Hg concentrations between 0.06–0.97 mg/kg, with a mean of 0.51 mg/kg and 0.01–0.99 mg/kg with a mean of 0.51 mg/kg, respectively (Walker, 1982). By 1990, water concentrations were below 0.02 µg/L and mean flathead Hg concentrations had reduced to 0.22 and 0.20 mg/kg, respectively with fish sampled from deeper sites with finer sediments having higher Hg concentrations (Fabris et al., 1992).

#### Sydney New South Wales sewage outfalls

Before the deep ocean outfalls were constructed in 1990–1991, large quantities of sewage and wastewater were discharged relatively close to the shore. For example, Malabar discharge was 600 million L per day (Gibbs and Miskiewicz, 1995). Near discharge points, sediments contained 0.6–5 mg/kg (McLean et al., 1991) and Hg concentrations in 6 fish species were >0.5 mg/kg (Gibbs and Miskiewicz, 1995). Tarwhine (*Cheilodactylus fuscus*) contained Hg concentrations between 0.06–1.07 mg/kg with a mean of  $0.53 \pm 0.2$  mg/kg (McLean et al., 1991).

#### Princess Royal Harbour Western Australia

Princess Royal Harbour is a semi-enclosed marine bay that received Hg contaminated effluent from a superphosphate plant over a 30-year period between 1954–1984 (Francesconi and Lenanton, 1992). Within the bay, Hg concentrations within sediments were up to 1.7 mg/kg. The analysis of 18 species of fish sampled from 1985–1986 had Hg concentrations between 0.01–10.3 mg/kg with means of 0.08–6.7 mg/kg. Fifteen species had mean Hg concentrations exceeding 0.5 mg/kg. After cessation

of the effluent discharge, of the 8 fish species monitored, 5 species had Hg concentrations <0.5 mg/kg while the other 3 species had 0.6–2 mg/kg (Francesconi et al., 1997).

#### Health implications

The recommended safe Hg concentrations for the consumption of fish by various organisations and countries are given in Supplementary Table S-3. Most countries, except Australia and Canada, recommend a limit as MeHg of 0.5 mg/kg wet weight for all fish except long-lived predatory fish, such as sharks and tuna, which is set at 1 mg/kg. In Australia, the same levels are set as total Hg concentrations based on the implicit assumption that Hg is present as MeHg. As previously discussed, all fish from areas with no point sources, except sharks, tuna, barramundi (>40 cm) and some stingrays, have Hg concentrations well below the 0.5 mg/kg limit. Predatory fish such as sharks are below the 1 mg/kg limit if the fish size is below 50–100 cm.

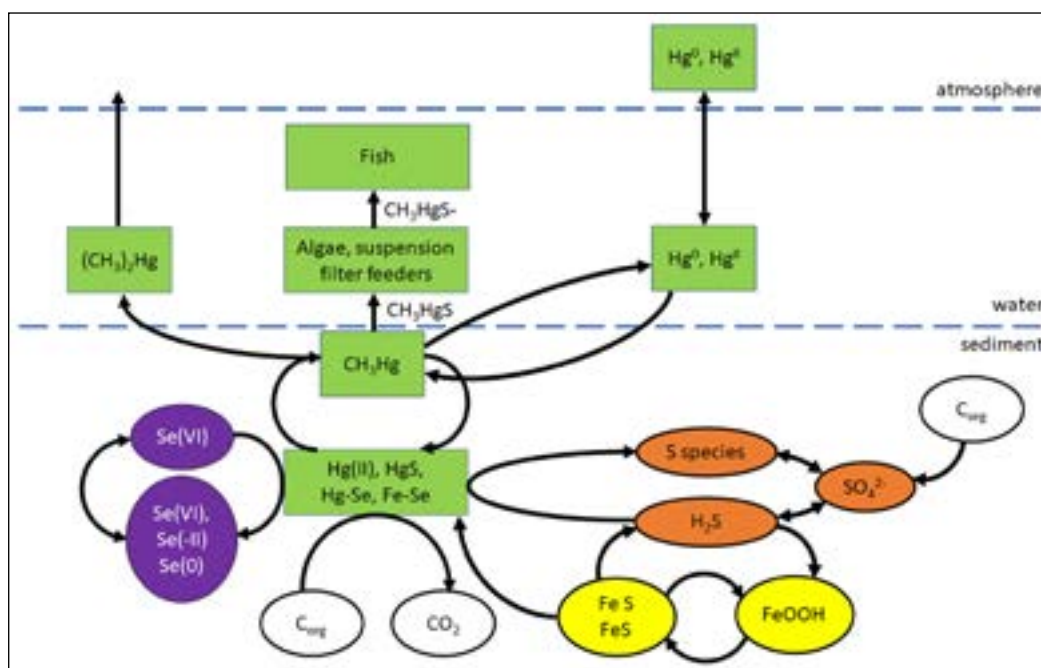
In 2010, the joint FAO/WHO expert committee for food additives derived a limit of 0.11 mg/kg body weight per day as Hg<sup>II</sup> chloride. This limit corresponds to a limit of 0.06 mg/kg body weight per day as Hg, adjusted for a 5 day per week dosing schedule. After the application of a 100-fold uncertainty factor, a provisional tolerable weekly intake (PTWI) for inorganic Hg of 4 µg/kg body weight (FAO/WHO, 1989) was established.

The PTWI of commonly consumed fish from estuaries and coastal zones with no point sources of Hg are between 0.5–4 µg/kg body weight. Consumption of some species of tuna and swordfish may marginally exceed this limit. In contaminated areas, PTWI of flathead species may exceed this limit.

An extensive body of literature indicates that selenium (Se) has protective effects against Hg toxicity (Jones et al., 2013b, Berry and Ralston, 2008). The specific mechanism(s) of protection is not known, but it is hypothesised that Hg selenide complexes are formed (Jones et al., 2013b) or that Se promotes demethylation of MeHg (Bravo et al., 2015). To assess the nutritional benefits of Se in terms of ameliorating MeHg exposure risks associated with seafoods, the Se Health Benefit Value (HBV) was proposed by (Kaneko and Ralston, 2007) whereby  $HBV = \text{Se/Hg molar ratio} \times \text{total Se} - \text{Hg/Se molar ratio} \times \text{total Hg}$ . The sign of the calculated HBV indicates the expected health benefits (positive values) or health risks (negative values). The magnitude of the HBV value is proportional to the expected benefits or risks. Individuals with a poor dietary Se status are more likely to suffer adverse effects from consuming fish with a negative HBV (Kaneko and Ralston, 2007). The range of HBV for Australian fish from estuaries and coastal areas with no known Hg point sources based on data in Supplementary Table S-1 are 6–210. For comparison at Minamata Bay, HBV values were as low as –5000. In the contaminated Derwent Estuary, where Se concentrations were also measured, the HBVs values are highly negative (Jones et al., 2013b).

#### Biogeochemical cycling

The biogeochemical cycle proposed below (**Figure 5**) is based on what is known about the biogeochemical cycling of Hg in Australian marine ecosystems (Jones et al., 2003,



**Figure 5:** Biogeochemical cycling of mercury in nearshore marine environments. DOI: <https://doi.org/10.1525/elementa.425.f5>

Jones et al., 2013a, b, c, Jones et al., 2014a, b) supported by the international literature. The major cycling of Hg in estuaries and nearshore coastal ecosystems consists of its partitioning into sediments, release from sediments as either inorganic Hg or MeHg formed by bacteria, uptake by microalgae and sediment-dwelling organisms, and transfer through the food web (**Figure 5**). The production of MeHg in the water column mainly occurs in oceanic systems (Mason et al., 2012, Faganeli et al., 2012, Sonke et al., 2013). There is no evidence at this time to suggest that MeHg formed by bacteria in the water column is a major pathway in Australian nearshore marine ecosystems. Some formation of MeHg may occur in the water column where decomposition of organic matter is occurring (Heinburger et al., 2010), but most MeHg present in the water column is likely to be derived from exports from sediments (Kim et al., 2006).

#### Mercury partitioning to sediments

On entering waterways, Hg rapidly partitions to particulate matter and deposits into sediments. Thus, little Hg is available to be taken up from the dissolved phase by organisms, except near major point sources. In Australian estuarine sediments, Hg concentrations are usually correlated with total organic carbon, mud, S and Fe content (Jones et al., 2014b) indicating multiple adsorption mechanisms in sediments. Deeper environments that accumulate fine sediments have greater Hg concentrations (Fabris et al., 1992). In estuaries, the addition of  $\text{NO}_3^-$  or oxidation promotes the formation of Fe/Mn oxyhydroxides and the adsorption of Hg (Driscoll et al., 2013). The addition of organic matter causes low oxygen/reducing conditions with the release of inorganic Hg from adsorptive phases (Driscoll et al., 2013).

#### Role of sediment chemistry and microbial processes

The composition and redox state of sediments determines the fate of sediment adsorbed Hg. The remobilisation of Hg from sediments is primarily dependent on the formation of MeHg by bacteria and ultimately the interplay of S, Fe and Se cycling. Mercury in sediments can bind with Fe and Se (Hg-Se) while dissolved organic matter binds with  $\text{Hg}^{2+}$  thus immobilising it (Chen et al., 2008) and prevents its methylation. Iron also binds with S (FeS,  $\text{FeS}_2$ ) and Se (Fe-Se) (Peters et al., 1997). Like inorganic Hg, the percentage of MeHg in sediments has been found to be correlated with TOC, mud, Fe and Se content (Jones et al., 2014b, McLean et al., 1991).

Bacteria that contain the two genes, *hgcA* (that encodes a protein that donates a methyl group) and *hgcB* (that encodes a FeS protein that provides electrons for efficient uptake of Hg), can methylate Hg (Merritt and Amirbahman, 2009b, Regnell and Watras, 2019). Although sulphate reducing bacteria are primarily responsible for Hg methylation (Regnell and Watras, 2019), over 52 bacteria and archaea have been found to have these genes (Sonke et al., 2013). Bacteria can demethylate MeHg if they have the *merB* gene to form volatile Hg species (Merritt and Amirbahman, 2009b, Regnell and Watras, 2019). The *merB* gene encodes an organo Hg lyase for  $\text{CH}_3$  cleavage and formation of  $\text{CH}_4$  and  $\text{Hg}^{2+}$  and a mercuric reductase that causes oxidative demethylation with  $\text{CH}_3^- \rightarrow \text{CO}_2 + \text{Hg}^{2+} \rightarrow \text{Hg}^0$  (Merritt and Amirbahman, 2009b).

The formation of gaseous Hg species  $(\text{CH}_3)_2\text{Hg}$  and  $(\text{CH}_3)_2\text{Hg}_2$  are common in intertidal flats that accumulate large quantities of organic matter (Cesário et al., 2017, Zhu et al., 2018). Phytoplankton do not methylate Hg (Regnell and Watras, 2019).



It has been postulated that bacteria accumulate Hg by passive diffusion of neutral complexes such as HgS nanoparticles (Merritt and Amirbahman, 2009b) or active transport of Hg-L complexes where L = amino acids such as cysteine (Merritt and Amirbahman, 2009b, Regnell and Watras, 2019, Graham et al., 2012). Mercury complexed with cysteine or other thiols has been shown to promote Hg uptake by bacteria (Sonke et al., 2013). Microbes quickly release MeHg from cells, possibly as a detoxification mechanism and probably form complexes such as MeHgS when released (Regnell and Watras, 2019).

The factors influencing Hg methylation-demethylation processes are complex but can be divided into two groups, 1) Hg bioavailability (Hg species, S species and organic matter) and 2) bacterial activity (substrate, temperature and pH). The methylation potential is very variable as methylation is affected by abiotic and biotic factors, some favouring methylation, some factors are synergistic while some counteract the process. At a local scale heterogeneity exists for Hg, Fe and other metals, dissolved organic matter, pH, redox and temperature in sediments and the overlying water column, Hg methylation and demethylation will be site-specific. As well all these factors can vary with season so Hg methylation and demethylation will vary seasonally. These factors can be summarised as:

**-Hg speciation:** Partitioning of Hg between particulate and dissolved phases controls the availability of Hg for methylation; less pore water Hg, less uptake by bacteria and methylation (Hammerschmidt and Fitzgerald, 2004). Major solid-phase complexes in oxic sediments are Hg<sup>2+</sup>-Fe/Mn oxyhydroxides and Hg<sup>2+</sup>-thio groups in organic matter (Jonsson et al., 2014, Sonke et al., 2013). Major solid-phase complexes in anoxic sediments are Hg<sup>2+</sup>-organic matter, Hg<sup>2+</sup>-FeS minerals and HgS minerals. As well, large amounts of Hg<sup>0</sup> can be present (Lei et al., 2019). Reduction of Hg<sup>2+</sup> by humic acids and Fe<sup>2+</sup> favour the formation of Hg<sup>0</sup> under reducing conditions (Colombo et al., 2013, Zhu et al., 2018). In sediments, the pool of dissolved Hg must be replenished by dissolution/desorption of surface sorbed Hg (Jonsson et al., 2012, Sonke et al., 2013). MeHg formation is correlated with dissolved Hg concentrations (Jonsson et al., 2012). In low S<sup>2-</sup> and oxygenated pore waters, Hg<sup>2+</sup>-organic matter species will dominate (Faganeli et al., 2012, Merritt and Amirbahman, 2009b) and at high organic matter concentrations Hg methylation can be inhibited. When sediment pore water concentrations of S<sup>2-</sup> are high, Hg<sup>2+</sup>-FeS and HgS species are present thus Hg is not bioavailable (Colombo et al., 2013, Zhu et al., 2018). Waters with S<sup>2-</sup> concentrations greater than >10 mM tend to inhibit Hg methylation (Merritt and Amirbahman, 2009a, Regnell and Watras, 2019). As well, stable MeHgSH<sup>0</sup> and MeHgS<sup>-</sup> species can be formed (Zhu et al., 2018). MeHg is possibly complexed by HS<sup>-</sup> produced by sulphate reducing bacteria forming stable MeHgS species (Regnell and Watras, 2019). MeHg can persist for decades in sediments suggesting complexes formed with S<sup>2-</sup>, thiols or S minerals

prevent demethylation and Hg from entering food webs (Sonke et al., 2013).

**-Sulphide:** S provides binding sites for both Hg<sup>2+</sup> and MeHg. At low oxygen concentrations, S<sup>0</sup>, FeS, FeS<sub>2</sub> and H<sub>2</sub>S are formed (Lei et al., 2019). At low S<sup>2-</sup> concentrations more bioavailable neutral Hg species such as HgS nanoparticles are formed that diffuse through bacterial membranes and promote the formation of MeHg (Lei et al., 2019, Hammerschmidt and Fitzgerald, 2004). As SO<sub>4</sub><sup>2-</sup> reduction increases, however, more S<sup>2-</sup> is produced and less bioavailable Hg species such as HgS<sub>2</sub><sup>2-</sup>, HgHS<sub>2</sub><sup>-</sup> are formed and Hg<sup>2+</sup> can be sorbed to FeS and FeS<sub>2</sub> thus hindering methylation (Sonke et al., 2013, Merritt and Amirbahman, 2009b, Hammerschmidt and Fitzgerald, 2004, Zhu et al., 2018). Where SO<sub>4</sub><sup>2-</sup> availability is not limiting, the major factor controlling S<sup>2-</sup> formation is organic matter availability (Merritt and Amirbahman, 2009b). The optimum S<sup>2-</sup> concentration for Hg methylation is <10 μM (Merritt and Amirbahman, 2009b). As previously mentioned, the rate of microbial methylation of Hg depends on the Hg species present in the order of HgS(s) < Hg<sup>2+</sup>-FeS < Hg<sup>2+</sup>-OM < Hg<sup>2+</sup> (Jonsson et al., 2012).

**-Organic matter:** Remineralisation of organic matter is the main energy source for bacteria responsible for methylation and promotes oxygen utilisation causing reducing conditions that favour sulphate reduction (Zhu et al., 2018, Sonke et al., 2013). The type (source) of organic matter is important. Organic matter derived from phytoplankton is generally more bioavailable than terrestrial organic matter (Lei et al., 2019), probably as it has a lower C/N ratio (Zhu et al., 2018). Organic matter can reduce MeHg production by complexing with and reducing the availability of Hg<sup>2+</sup> (Chen et al., 2008, Lei et al., 2019, Hammerschmidt and Fitzgerald, 2004). Less MeHg is produced as indicated by the inverse relationship of MeHg and C, N and S (Driscoll et al., 2012). Organic matter can mediate both the reduction and oxidation of Hg<sup>2+</sup> (Zheng et al., 2012). Organic matter also stabilises nanoparticle HgS that is taken up by bacteria, thus promoting Hg methylation. As well, increased organic matter loads stimulate microbial activity as organic material is oxidised by bacteria (Jones et al., 2014b, McLean et al., 1991).

**-Salinity:** An increase in salinity promotes coagulation and precipitation of suspended materials and colloids depositing Hg to sediments (Lei et al., 2019). At high salinities, lower MeHg formation has been reported possibly as higher salinity correlates with higher SO<sub>4</sub><sup>2-</sup> concentrations and increased S<sup>2-</sup> formation (Lei et al., 2019).

**-Iron and other metals:** High MeHg production occurs in sewage affected sediments with high Fe and organic matter concentrations (Bravo et al., 2015). It is postulated that Fe keeps the S<sup>2-</sup> concentration low by the formation of FeS or FeS<sub>2</sub>, (Bravo et al., 2015, Faganeli et al., 2012, Jones et al., 2013b) and more Hg<sup>2+</sup> is available. This illustrates the complexity of the biogeochemical cycle; as mentioned about it is thought that Hg<sup>2+</sup> sorbs to these minerals and should

reduce  $\text{Hg}^{2+}$  bioavailability. Additionally, it is thought that there are low rates of demethylation because sulphate reducing bacteria are outcompeted by Fe reducing bacteria that do not demethylate MeHg. Selenium can also play a critical role in the methylation process. The formation of Hg-Se in sediments will make Hg less bioavailable for methylation (Jones et al., 2013a). Competitive inhibition of the uptake of Hg in bacteria by  $\text{Zn}^{2+}$  has been shown thus suggesting that Hg is actively taken up by essential metal transporters (Regnell and Watras, 2019).

-Nutrients: Increased P and N loading may alter Hg cycling, especially if eutrophication occurs (Verburg et al., 2014). Increased phytoplankton growth causes an increase in the supply of biodegradable organic carbon promoting methylation and the formation of MeHg. At high C, N and S concentrations near sewage outfalls, fish Hg concentrations have been found to be lower than other areas possibly because of inhibition of methylation or increased demethylation because of the abundance of Fe that have changed microbial communities (Driscoll et al., 2012).

-Resuspension of sediments: As Hg is distributed amongst dissolved, colloidal and particulate phases, resuspension of sediments can lead to changes in binding phases influencing Hg speciation and methylation (Kim et al., 2006, Lei et al., 2019). It has been suggested that transient oxidation of sediments and associated porewaters may promote the formation of MeHg in oxic waters (Faganeli et al., 2012). Sediment oxidation will oxidise reduced  $\text{S}^{2-}$  thereby releasing S bound Hg and making it available for methylation (Kim et al., 2008, Kim et al., 2006). Oscillating redox conditions also promotes the degradation of organic matter (Bouchet et al., 2011). Photodecomposition of MeHg can also be reduced if light penetration is less (Denkenberger et al., 2012, Driscoll et al., 2012). As well,  $\text{Hg}^0$  concentrations in water may increase as less oxidation to  $\text{Hg}^{2+}$  occurs (Cesário et al., 2017).

-Bioturbation: Bioturbation affects sediment microbial activity, organic matter decomposition and cycling of S, Fe, Se etc (Lei et al., 2019). Bioturbation is important as it introduces oxygen, enhances sulphate reduction and prevents sulphide build up enhancing Hg methylation.

-Oxic-Anoxic conditions: As mentioned above, oxic conditions promote the degradation of organic matter promoting methylation; however, the formation of oxic Fe/Mn phases may reduce the bioavailability of Hg. Permanent anoxia limits the mobility and bioavailability of Hg due to the formation of HgS and other adsorptive phases such as pyrites (Faganeli et al., 2012, Lei et al., 2019). In contrast, Hg methylation may be favoured in reducing conditions as sulphate reducing bacteria activity is enhanced (Lei et al., 2019). Demethylation is also eliminated under reducing conditions and low pH (Faganeli et al., 2012, Merritt and Amirbahman, 2009b).

-Temperature: microbial activity and methylation increases with increasing temperature (Lei et al., 2019, Merritt and

Amirbahman, 2009b, Hammerschmidt and Fitzgerald, 2004). The activity of bacteria is responsible for the rate of methylation (Schartup et al., 2014) thus, MeHg formation increases with temperature (Chen and Wilcox, 2008). There is also a positive correlation of gaseous  $\text{Hg}^0$  production and temperature as increased temperatures promote Hg volatilisation (Cesário et al., 2017). The effects of temperature and solar radiation are confounded as solar radiation reduces  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  while temperature controls volatilisation (Cesário et al., 2017).

-pH: organic matter degradation lowers pH releasing  $\text{Hg}^{2+}$  from sediments favouring methylation and reduces demethylation (Bravo et al., 2015, Sonke et al., 2013).

-Microbial activity: The rate of methylation depends on the activity of bacteria that is dependent on factors such as substrate, temperature and pH (Schartup et al., 2014). The activity of sulphate reducing bacteria, the bacteria thought to be primarily responsible for most Hg methylation is limited by the amount of organic matter available (Hammerschmidt and Fitzgerald, 2004, Merritt and Amirbahman, 2009b). The two genes required for methylation seem to be restricted to anaerobes. Bacteria such as sulphate reducing species have the ability to methylate and demethylate Hg (Colombo et al., 2013, Colombo et al., 2014, Bravo et al., 2015). Reductive/oxidative demethylation, where  $\text{MeHg} \rightarrow \text{Hg}^{2+}$  or  $\text{Hg}^0$ , is an active detoxification process. Other bacteria groups such as Fe reducing bacteria cannot demethylate MeHg (Bravo et al., 2015). Thus the amount of MeHg/ $\text{Hg}^{2+}$  present will depend on the type of bacteria present and their relative activity.

#### **Bioaccumulation, trophic transfer and biomagnification**

Coastal fish species that move and feed in different areas have Hg concentrations that do not reflect the sediment Hg concentrations where they are caught, i.e. there is an uncoupling of diet and potential Hg exposure (Jardine et al., 2012). Generally, in areas with no point sources of Hg, bioaccumulation is low and little, or no biomagnification occurs. Higher diversity, higher numbers of omnivores, shorter food chains and opportunistic diets also result in less Hg accumulation. There is also no correlation of Hg concentrations with fish size or age (Ayling et al., 1975). The exception is predators that occupy the highest trophic levels such as sharks, tuna, barramundi and stingrays, that grow to large sizes and have long life spans. For example, sharks, 50–100 cm long invariably exceed the 0.5 mg/kg wet weight level of concern (Denton and Breck, 1981b).

Accumulation and trophic transfer of Hg is affected by digestive solubilisation, membrane transport and gut passage time (Dang and Wang, 2010). Mercury uptake by cells is thought to be passive. It, however, has been postulated that MeHg cysteine is formed in fish (George et al., 2011) and its transfer across membranes is energy-dependent and occurs by L-amino acid channels (Dang and Wang, 2010).

The presence and coaccumulation of Se is also important. Organisms living in Se poor environments have lower

MeHg elimination rates (Jones et al., 2014b, McLean et al., 1991). MeHg concentrations in fish decrease with increasing Se concentration (Wang and Wang, 2017). It is thought that Se induces demethylation in fish intestines (George et al., 2011) or that the formation of the MeHg-Se complex in the gut lumen decreases Hg bioavailability at the intestine epithelium (Wang and Wang, 2017). A significant amount of demethylated Hg is deposited in intestines as the Hg-Se complex (Wang and Wang, 2017). Where clear food chains have been delineated, MeHg but not  $\text{Hg}^{2+}$  is biomagnified. This is attributed to MeHg being in the cell cytoplasm while  $\text{Hg}^{2+}$  is associated with cell membranes and debris (Dang and Wang, 2010, Onsanit and Wang, 2011); thus the assimilation efficiency of MeHg is higher (Metian et al., 2019).

MeHg can be biomagnified within food webs as it is transferred through various trophic levels. Most aquatic ecosystems have 3 trophic levels (primary producers-omnivores-carnivores). Tertiary carnivores, e.g. sharks, stingrays, tuna and barramundi have consistently been shown to contain elevated Hg concentrations (Storelli et al., 2002, Branco et al., 2007). An example of the importance of trophic structure is the work conducted on Lake Murray Papua New Guinea (PNG), the largest freshwater lake in PNG (Bowles et al., 2002). Very high Hg concentrations were measured in piscivorous fish such as barramundi (up to 1.4 mg/kg wet weight) and in the hair of local fish-eating inhabitants of Lake Murray. This system is in a relatively pristine area with no industrial Hg sources but has extensive organic-rich marshes that promote Hg methylation. This system is unique in that it has four trophic levels (plankton-planktivore-carnivore-top carnivore-barramundi) that results in the biomagnification of MeHg (Bowles et al., 2001), with barramundi containing over 88% as MeHg. Fish over 80 cm in length accumulated very high Hg concentrations.

#### **Factors influencing Hg cycling in Australian estuaries and nearshore ecosystems**

The Australian environment is characterised by extremes of droughts and floods and by frequent bush fires in catchments ((Leivesley, 1984)). Similar to other marine environments, any dissolved Hg rapidly partitions to sediments and Hg content of sediments is correlated to total carbon, mud, S and Fe content (Jones et al 2014), phases that bind  $\text{Hg}^{2+}$ . Most Hg exported from catchments will already be adsorbed to sediments, but the export of sediments is episodic depending on if drought or flood conditions are prevailing. Estuaries and nearshore environments are also known to have highly variable salinity with high salinities promoting coagulation and precipitation of suspended material; thus, the spatial distribution of sediments (and associated Hg) will be highly variable.

As previously discussed, the main driver of Hg cycling in sediments is the remineralisation of organic matter that lowers pH releasing  $\text{Hg}^{2+}$  from sediments, alters redox conditions stimulating microbial activity and promotes the formation of MeHg that accumulates through food chains. Thus, the formation of MeHg will critically depend on the delivery of labile organic matter to these

environments. Export of organic matter will also be episodic, again depending on if drought or flood conditions prevail. In addition, recent bushfires will further promote the export of organic matter, nutrients and Hg from catchments promoting the formation of MeHg.

As microbial activity and methylation increase with temperature (Lei et al., 2019), the formation of MeHg in temperate regions of Australia will also be different depending on the season. In tropical regions, temperature extremes are less thus seasonal influences should be less as well.

Overall, the distribution of Hg in sediments and MeHg formation is expected to be heterogeneous in both space and time.

In areas subject to point sources of Hg, the presence of Se needs to be considered. The formation of Hg-Se in Australian sediments has been shown to make Hg less available for methylation (Jones et al., 2013a), and although sediments may have high Hg concentrations, MeHg concentrations may not be as high as expected in food webs.

#### **Effect of accelerated climate change**

Accelerated climate change is causing increased  $\text{CO}_2$  concentrations and related vegetation changes, global temperature rises, changed precipitation patterns and increased incidents of biomass burning (wild and bush fires). These changes will influence the transport, partitioning and fate of Hg. The combined effects of accelerated climate change are expected to change the inputs of Hg to the environment and alter the Hg biogeochemical cycle in unpredictable ways; changes will be both on regional and global scales.

Most Hg transfer to soils comes from atmospheric deposition (Obrist et al., 2016). Hg can be directly transferred to soils by rain. Plants take up Hg and transfer it to sediments through two processes: a) deposition by litterfall where plants take up Hg then release it via senescence shedding leaves and; b) throughfall deposition where Hg is taken up by plant surfaces and deposited by rainfall wash off. Hg accumulation correlates with soil organic matter, latitude, annual precipitation, leaf area and vegetation density; thus soil sequestration is related to vegetation cover and productivity (Obrist et al., 2016). Land cover and land use control Hg inputs into terrestrial systems and subsequent inputs into estuaries through waterways (Denkenberger et al., 2012). Fish Hg concentrations are typically higher in water draining forests than agricultural land (Driscoll et al., 2013).

Increased  $\text{CO}_2$  concentrations will promote denser vegetation in some areas and increase soil  $\text{Hg}^0$  sequestration (Krabbenhoft and Sunderland, 2013). Evasion of  $\text{Hg}^0$  from soils is low when covered by plants and litter (Obrist et al., 2018). Landuse changes from forests to pastures is expected to result in more evasion of  $\text{Hg}^0$  from landscapes due to greater incidence of solar radiation and soil matter turn over (Denkenberger et al., 2012).

Increased temperatures are predicted to increase the deposition of  $\text{Hg}^0$  to surfaces as higher air temperatures cause large perturbations in atmospheric Hg chemistry.  $\text{Hg}^0$  oxidation by bromine in air is expected to decrease

as oxidation rates fall by 11% for each 1K increase and increases in-cloud and aqueous  $\text{Hg}^{2+}$  photoreduction occurs (Zhang et al., 2016). Evasion of deposited  $\text{Hg}^0$  depends on air temperature and winds. Increased global temperatures are likely to result in more evasion of  $\text{Hg}^0$  from landscapes and waterways. Other effects of increased air temperatures that will increase  $\text{Hg}^0$  evasion are permafrost melting, declining sea cover and humification (Krabbenhoft and Sunderland, 2013). Increased temperatures also alter transpiration rates and cause water stress thus altering the pathways of Hg to soils as litterfall and throughfall may increase or decrease (Blackwell et al., 2014).

Large-scale changes in meteorological patterns, such as El-Nino/ENSO, influence interannual variability in rainfall. Changes in deposition patterns of Hg will also occur. In areas with increased rainfall, wet deposition will increase  $\text{Hg}^{2+}$  inputs while in drier areas  $\text{Hg}^0$  inputs will increase. Increased storm events will result in more runoff, erosion and deposition of terrestrial soils containing Hg to nearshore coastal zones. Changes in precipitation patterns and amounts will also cause other watershed disturbances such as floods changing organic matter inputs, altering methylation and trophic transfer as for example, increases in fish Hg concentrations have been shown to be associated with increased inputs of dissolved organic matter (Åkerblom et al., 2012). These changes will be hard to predict.

The increased incidence of biomass burning (wild and bush fires) will release Hg sequestered in soils and vegetation (Sigler et al., 2003, Friedli et al., 2003). Drier climate regimes e.g. droughts cause more severe fires and increased burn areas with emissions of mainly  $\text{Hg}^0$  although substantial release of particulate Hg can occur (Obrist et al., 2018, Obrist et al., 2016). Mercury emission by fires are also hard to predict as they depend on pre-fire accumulation, vegetation types, area, and the severity of burning. Post-fire deposition of Hg into waterways can occur through erosional processes, together with warmer waters and organic matter/nutrient enrichment that increase organic matter mineralisation and formation of MeHg in waterways (Obrist et al., 2018, Krabbenhoft and Sunderland, 2013).

Finally, increased water temperatures and decreased pH from  $\text{CO}_2$  increases may fundamentally alter aquatic food webs. Some effects postulated and summarised by (Alava et al., 2017) are that acidification, hypoxia, anoxia and increased microbial activity with increase MeHg formation while increased temperatures will increase fish metabolic rates, feeding rates and maximum body sizes thus more MeHg uptake and less growth dilution. As well, predator-prey interactions may change as temperature changes influence feeding preferences (Ng and Gray, 2011). Changes in primary production from increased temperatures and possibly land-based nutrient inputs may also alter food webs and ultimately change MeHg production and bioaccumulation.

### Management interventions

Three intervention strategies to reduce Hg accumulation in marine organisms and limit the intake of MeHg by humans consuming fish have been identified with the

only strategy being employed at this time being external Hg source reduction.

#### **External Hg source reduction**

A direct management intervention to reduce Hg concentrations in fish is to reduce the amount of Hg entering an aquatic ecosystem. All the locations in Australia, where Hg inputs in waters were historically high, have been substantially reduced (Derwent Estuary, Port Phillip Bay and Princess Royal Harbour) resulting in reduced fish Hg concentrations (Francesconi et al., 1997, Langlois et al., 1987, Fabris et al., 1992). As previously discussed, a well-documented example is Princess Royal Harbour in Western Australia (Francesconi et al., 1997, Francesconi and Lenanton, 1992) where a superphosphate plant was discharging large quantities of Hg to a poorly flushed estuary. On eliminating this point source, the Hg concentrations in four commonly caught fish dropped by 25–95% over a 4-year period. This is in accordance with published reports that show a rapid decrease in fish Hg concentrations in response to decreases in atmospheric Hg deposition over short periods, i.e. <3 years (Harris et al., 2007, Hutcheson et al., 2014). At some locations, however, such as the Derwent River Estuary, Tasmania, only minor reductions in fish Hg concentrations were seen after source reduction (Jones et al., 2013c). Mercury concentrations in fish do not normally decrease to background values because Hg is stored in the sediments. Thus Hg continues to enter food chains through sediment remobilisation processes as previously described.

Sewage plants are often overlooked as sources of low-level continuous Hg inputs, but given the large volumes of treated effluent discharged, they potentially provide substantial loads of Hg to the environment. The use of iron to remove phosphorus from effluents also keeps  $\text{S}^{2-}$  low, potentially making Hg more bioavailable, while bioavailable carbon within the effluent promotes biomethylation and the lower pH of effluent reduces demethylation rates (Bravo et al., 2015).

#### **Internal Hg source reduction-Prevent Eutrophication**

Eutrophication has been shown to cause a substantial increase in Hg concentrations in biota (Verburg et al., 2014). Initially, eutrophication causes higher algal growth and biomass and growth dilution lowers algal Hg concentrations (Lambert et al., 2012, Driscoll et al., 2013), however, because sediments are enriched in nitrogen, phosphorus and carbon from algal exudates (Regnell and Watras, 2019), sediments become anoxic and microbial methylation of Hg is enhanced. The efficient transfer and retention of MeHg results in substantial increases in MeHg concentrations in fish (Willacker et al., 2017). Prevention or reducing eutrophication essentially reduces the conversion of Hg into MeHg and its mobilisation from sediments in a form that is readily bioaccumulated.

#### **Enhance biodiversity**

In estuaries and nearshore ecosystems, some fish, e.g., sand flathead, sharks, tuna, barramundi and swordfish will contain elevated Hg concentrations. While many types of

fish are consumed, only a few species contain elevated Hg concentrations, e.g. in the Derwent River estuary sand flathead (Jones et al., 2014b, Jones et al., 2013c). Biodiversity can be enhanced by maintaining and rehabilitating aquatic environments such that a variety of habitats are available to support varied species. This will also support a biodiverse diet and lower the overall intake of Hg as large numbers of single species containing elevated Hg concentrations will not be consumed.

### Conclusions

Mercury contamination of fish in nearshore Australian marine environments is not evident except at several locations with historical Hg contamination. At these locations, Hg concentrations in fish are decreasing as point sources have ceased. Mercury concentrations in fish collected from non-point source locations are consistent with previous Australian and worldwide data in that fish with lengths <40 cm have Hg concentrations below the 0.5 mg/kg wet weight health guidelines. Se HPV ratios are 6–210, indicating positive health benefits. Larger fish such as sharks, tuna, barramundi and swordfish can greatly exceed this level. Thus consumption of these larger fish needs to be controlled.

The major cycling of Hg in estuaries and nearshore coastal ecosystems consists of its partitioning into sediments, release from sediments as either Hg<sup>2+</sup> or MeHg formed by bacteria, uptake by phytoplankton and sediment-dwelling organisms, and transfer through the food web. Accelerated climate change is causing increased CO<sub>2</sub> concentrations and related vegetation changes, global temperature rises, changing precipitation patterns and increased incidents of biomass burning (wild and bush fires) and will influence the transport, partitioning and fate of Hg. The combined effects of accelerated climate change are expected to change the inputs of Hg to the environment and alter the Hg biogeochemical cycle in unpredictable ways; changes will be both on regional and global scales. At Hg contaminated locations, the only strategy being employed at this time to reduce fish Hg concentrations is external Hg source reduction. Prevention or reducing eutrophication will reduce the mobilisation of MeHg from sediments that is readily bioaccumulated. Enhancing biodiversity by maintaining and rehabilitating aquatic environments will also support a biodiverse diet and lower the overall intake of Hg as large numbers of single species containing elevated Hg concentrations will not be consumed.

### Data Accessibility Statement

Data is presented in Supplementary Table S4.

### Supplemental files

The supplemental files for this article can be found as follows:

- **Figure S-1.** Mercury articles in newspapers and magazines. DOI: <https://doi.org/10.1525/elementa.425.s1>
- **Table S-1.** Mercury concentrations in fish consumed from Australian estuaries and near coastal waters with

no Hg point sources. DOI: <https://doi.org/10.1525/elementa.425.s1>

- **Table S-2.** Mercury concentrations in fish from Australian estuaries and near coastal waters with Hg point sources. DOI: <https://doi.org/10.1525/elementa.425.s1>
- **Table S-3.** The recommended mercury concentrations in fish by country and organisation. DOI: <https://doi.org/10.1525/elementa.425.s1>
- **Table S-4.** Mercury concentrations in fish consumed from Australian estuaries and near coastal waters with no Hg point sources-data. DOI: <https://doi.org/10.1525/elementa.425.s1>

### Competing interests

The authors have no competing interests to declare.

### Author contributions

- Contributed to conception and design: WM, FK, ME
- Contributed to acquisition of data: WM, FK
- Contributed to analysis and interpretation of data: WM, FK, ME
- Drafted and/or revised the article: WM, FK, ME
- Approved the submitted version for publication: WM, FK, ME

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