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Methyl mercury concentrations in edible fish and shellfish from Dunedin, and other regions around the South Island, New Zealand

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ABSTRACT

Methyl mercury (MeHg) concentrations were determined in edible fish and shellfish available in local markets in Dunedin, New Zealand. While most of the fish species were sourced in Dunedin, some specimens of fish were also collected from waters off Picton, around Stewart Island and also off-shore of the South Island in the Puysegur and Subantarctic regions. The concentrations of MeHg were analysed in 25 different fish species and shellfish (103 muscle tissue samples). Total mercury (Hg_T) levels were also analysed in a few ($n = 12$) selected fish samples. Most of the Hg was in the form of MeHg (≥96%). Higher MeHg concentrations were found in fish at higher trophic levels, particularly in predatory fish species such as ling, school shark, spiny dogfish and albacore tuna. Concentrations of MeHg in all samples ranged from 0.002 to 2.515 μg MeHg/g.

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Fish and shellfish are important for a healthy human diet because they are high in protein and contain omega-3 fatty acids (WHO, 2011; USEPA, 2004). The health benefits and risks generally differ according to the fish species, fish size, as well as the amount of fish consumed (WHO, 2011). Most fish and shellfish contain trace amounts of MeHg, which is a neurotoxin. In particular, it can damage the human nervous system, hinder brain development in newborn and young children, and can also cause a variety of adverse health effects such as impaired vision and ataxia, the lack of voluntary coordination of muscle movements, and cardiovascular disease (Mergler et al., 2007; Choi and Grandjean, 2008; Hong et al., 2012; Karagas et al., 2012).

The major source of mercury (Hg) to the open ocean is through the atmosphere. Mercury enters the atmosphere from both anthropogenic and natural sources. The major input of Hg to the atmosphere due to human activities is the combustion of oil and coal for societal needs. Natural Hg sources to the atmosphere include atmospheric emanations from volcanoes, continental degassing, and Hg evasion from the oceans (Kim and Fitzgerald, 1986; Pirrone et al., 2010; Mason et al., 2012). Elemental mercury (Hg^0) enters in the atmosphere as a gas, and thus can be transported long distances through the atmosphere to the open ocean. Elemental Hg can be converted to divalent mercury (Hg^{2+}) species through oxidative processes and this form of Hg is removed from the atmosphere to the ocean by dry deposition and rain (Fitzgerald et al., 2007; Driscoll et al., 2013).

In freshwater systems, sulphate-reducing bacteria in the sediment are mainly responsible for the methylation of Hg^{2+}, (Gilmour et al., 1992). Most recently, the genes responsible for Hg methylation in these bacteria have been indentified (Parks et al., 2013). In coastal regions, this process may also occur in conjunction with iron-reducing bacteria (Fitzgerald et al., 2007; Driscoll et al., 2013). However, in the open ocean the production of MeHg is associated with the decomposition of particulate organic matter in the oxygen minimum zone below the thermocline (Mason et al., 2012), possibly in marine snow (Mason, personal communication).

Methyl Hg enters the aquatic food chain and is bio-accumulated in fish, particularly in the upper trophic levels (Fitzgerald et al., 2007; Mason et al., 2012; Driscoll et al., 2013). The major pathway of chronic exposure of MeHg in humans is through the consumption of fish and shellfish. A world-wide concern of MeHg concentrations in edible fish began with the notorious Minamata Bay tragedy in Japan during the 1950s, where Japanese fishermen and their families were poisoned by MeHg through consumption of seafood (Takizawa, 1979). Since then, considerable attempts have been made to monitor Hg concentrations in marine and freshwater fishes, here in New Zealand (Van den Broek et al., 1981; Mitchell et al., 1982; Kim, 1995; Kim and Burggraaf, 1999; Love et al., 2003); in Australia (Thomson, 1985; Walker, 1988; Pethybridge et al., 2010, 2012) and in many other countries. In this investigation, we report MeHg concentrations in edible fish and shellfish

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available from retail fish outlets in Dunedin, and other regions around the South Island, New Zealand. These results reveal a wide range of MeHg concentrations in fish which may be due to their size, their trophic position in the fish food web or their habitat.

A total of 103 samples from 25 different fish species were analysed in our investigation. Fresh fish, fish fillets and canned fish were purchased from local fish retailers and supermarkets in Dunedin. Most of the fresh fish were sourced locally, but albacore tuna ($n = 1$) which was bought in Dunedin, was imported from Fiji. Ling specimens ($n = 7$) in the ling^{1A} and the ling^{1B} groups were obtained from the Dunedin market. The fish in the ling^{2} group ($n = 6$) were caught from the Subantarctic area, southeast of the South Island, whereas ling in the ling^{3} group ($n = 6$) were from the Puysegur region, situated southwest of the South Island. The spiny dogfish specimens in the dogfish^{1} group ($n = 7$) were obtained from Dunedin, while the fish in the dogfish^{2} group ($n = 7$) were from Picton, situated off the northern coast of the South Island. Lastly, the specimens in the dogfish^{3} group ($n = 7$) were from Stewart Island, located at the bottom of the South Island. Fish in the school shark^{1} group ($n = 6$) were obtained from around Stewart Island and fish samples in the school shark^{2} group ($n = 6$) were from Picton, respectively. The other fish specimens were obtained from the local Dunedin market (Fig. 1). The canned yellowfin tuna, skipjack tuna, red salmon and pink salmon were products of Thailand and Canada, respectively.

The fish samples were prepared with extreme care under "trace metal clean" conditions (Bloom, 1992). Fish muscle tissue was carefully dissected from each sample by first cutting out a piece of fish muscle tissue and discarding the outer sections of *ca.* 0.5 cm of muscle prior to preparation of the final sample. A section of about 30 g of "clean" muscle tissue was minced into *ca.* 1 mm pieces, and placed in acid-cleaned glass vials with Teflon®-lined lids. These samples were kept frozen at −20 °C until further processing and analysis. A portion of fish muscle tissue from the canned fish samples was also placed in the vials and preserved as described above.

Methyl mercury concentrations in fish muscle tissue (μg MeHg/g) were determined using an ethylation method (Bloom, 1989; Liang et al., 1994). This involved an alkaline methanol digestion (25% weight per volume, *w*/*v*, KOH in methyl alcohol) of 1 g of minced muscle tissue (*ww*) in an acid-cleaned, screw-capped Teflon® vial, which was heated

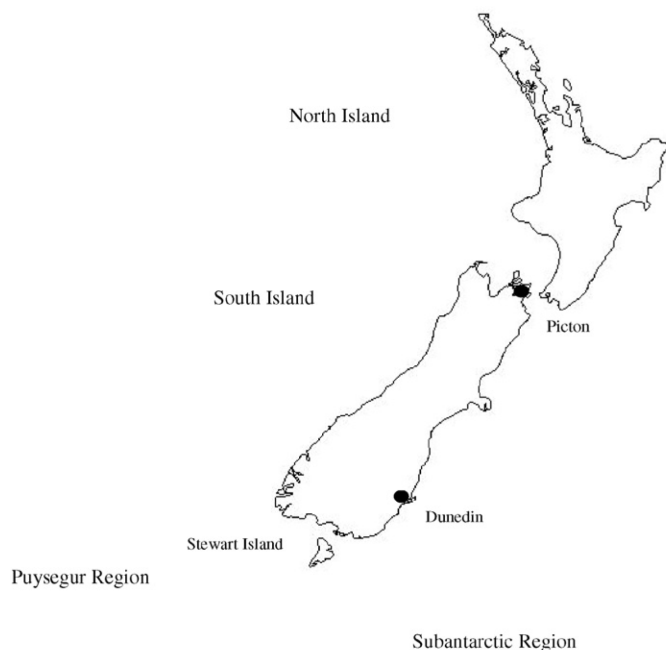

Fig. 1. Geographical locations of the fish specimens caught around the South Island, New Zealand.

at 60 °C for at least 12 h. After cooling to room temperature, an aliquot of digestate (25 μL) was pipetted into a buffered aqueous solution of 150 mL of ultrapure deionised water (18.2 MΩ cm) and 0.2 mL of 4 molar (M) acetate buffer. Ethylation of $MeHg^{+}$ and inorganic Hg^{2+} species to methyl ethyl Hg and diethyl Hg, respectively, were accomplished by the addition of 75 μL of sodium tetraethyl borate solution ($NaBEt_4$, 1% weight per weight, *w*/*w*). These derivative compounds were then stripped from solution; trapped on a carbon substrate (Carbotrap®) and transferred by quick heating to 400 °C into a packed GC column (15% OV-3 on Chromosorb W; i.d: 4 mm; length: 1.5 m) for resolution by gas chromatography (Tracor 550, oven temperature 100 °C). The separated Hg species were then converted into Hg^0 by pyrolysis at 700 °C and subsequently detected by atomic fluorescence spectrometry (Tekran 2500). The detection limit for this method was 0.001 μg MeHg/g.

The yield recoveries, accuracy and precision for the MeHg determination were evaluated by multiple analyses of certified reference material DORM-2 (dogfish muscle) obtained from the National Research Council of Canada. Our average yield recovery was 102%, and the measured average value for the DORM-2 reference material was 4.57 ± 0.44 μg/g ($n = 19$); compared to the certified value of 4.47 ± 0.32 μg/g.

Total mercury was determined by the dissolution of fish tissue with a modified acid digestion method (Louie, 1983). This procedure consisted of an acid digestion (10 mL of concentrated HNO_3/H_2SO_4 mixture, 2:1, *w*/*w*) of *ca.* 1 g of fish tissue in acid-cleaned glass test tubes, covered with glass tear drops and heated (100 °C for 3 h). After cooling and dilution with ultrapure water to 100 mL, the mercury was reduced with $SnCl_2$, stripped from solution and determined by two-stage gold amalgamation with detection by cold vapour atomic fluorescence spectrometry (Gill and Bruland, 1990).

The detection limit for Hg_T in fish is 0.01 μg Hg/g (Louie, 1983). Our average yield recoveries for Hg_T in the DORM-2 certified reference material was 105.9% and the measured mean value was 4.91 ± 0.24 μg Hg/g ($n = 3$) compared to the certified value of 4.64 ± 0.26 μg Hg/g.

The MeHg concentrations in 25 edible fish and shellfish commonly available in the South Island, New Zealand are presented in Table 1. Although fish were obtained from five locations (Picton, Dunedin, Stewart Island, Puysegur and Subantarctic) around the South Island; most of the fish samples were obtained in Dunedin (Fig. 1).

Our results show that MeHg concentrations in these fish varied considerably. The highest mean MeHg concentration was found in large ling (ling^{1A}) caught off of Dunedin (2.404 μg MeHg/g, length *ca.* 130 cm). The mean values of MeHg in some of our fish samples (*e.g.* ling^{2}, spiny dogfish^{1} and spiny dogfish^{2}) were above 0.5 μg MeHg/g. However, most of the MeHg concentrations in all other fishes were below this level. Some fish, such as in the spiny dogfish^{3} group, albacore tuna^{a}, the school shark^{1} and school shark^{2} groups, groper, sea perch, skate, red cod, red gurnard, hoki and monk fish had MeHg levels between 0.1–0.5 μg MeHg/g. Flounder, blue cod, spotty, yellowfin tuna^{b}, tarakihi, salmon^{c}, sole, skipjack tuna^{b}, red salmon^{b}, lemon fish, whitebait, greenbone, pink salmon^{b} and bluff oyster had very low (<0.1 μg MeHg/g) concentrations. Similar Hg levels in fish have been observed for ling, school shark, spiny dogfish, grouper, red cod, hoki, blue cod, flounder, and tarakihi from New Zealand and Australia.

In New Zealand, Hg in takeaway fish (shark) in Dunedin during 1977 had Hg levels between 0.28–1.8 μg Hg/g (Mitchell et al., 1982). For the following fish caught off of Dunedin between 1976 and 1980; ling (*Genypterus blacodes, G. blacodes*) had between 0.03–1.92 μg Hg/g; red cod (*Pseudophycis bacchus, P. bacchus*) had values that ranged from 0.02–0.26 μg Hg/g and Hoki (*Macruronus novaezelandiae, M. novaezelandiae*) 0.03–0.38 μg Hg/g (Van den Broek et al., 1981). A later investigation of the same fish species above, but caught off Wellington and other areas around the South Island in 1972 and 1988 reported similar Hg concentrations (Love et al., 2003). There is no apparent historical increase of Hg in these fish species from the prior New Zealand studies and our investigation.

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