CHLORINATED ORGANICS IN WHOLE FISH FROM ESTUARINE AND COASTAL HABITATS IN SOUTH AUSTRALIA

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Introduction

Concern about chlorinated organic contaminants in the environment has increased over the past several decades with a number of publications regularly highlighting the latest detections found water, sediments or wildlife such as fish and mussels. The latest figures from the USA totaling 4,249 fish consumption advisories covering 43% of the nation's total lake acreage and 39% of the nation's total river miles[1]. Although mercury contamination was responsible for about 80% of the advisories, polychlorinated biphenyls (PCBs), chlordane, dioxins and furans, and DDT were mostly responsible for the rest. Stahl et al.[2] confirmed these same chemicals were commonly detected in fish from 500 lakes and reservoirs selected randomly from 48 states of the USA, and that PCBs and dioxins/furans were particularly widespread.

Müller et al.[3] provides a summary of published papers and data from Europe that highlights a number of countries that have recorded dioxin concentrations in fish over 6 pg/g TEQ/g fm, including the UK, Sweden, Norway, Germany, Finland and Estonia. This concentration is the temporary action level for dioxin and dioxin-like PCBs in seafood used in Australia[4, 5] whereas the European Union's maximum level for fish and fish products is slightly higher, at 8 pg TEQ/g fm[6].

In Australia, the national dioxins study showed that dioxin-like chemicals were found in all Australian aquatic sediments analysed, with the highest concentrations recorded from the estuarine waters of Sydney, Brisbane, Melbourne, Perth and Wollongong[3]. Samples of molluscs and fish with the highest concentrations came from the Sydney/Port Jackson area and molluscs from the Yarra estuary were also elevated, however, none of the biotic samples were at the temporary action levels that required issuing fish consumption advisories. However, further samples of fish and prawns caught from Sydney Harbour and Parramatta River had sufficient dioxin present for the government to issue an advisory in 2006 for the consumption of seafood, ban commercial fishing in the harbour and recommend that fish west of the bridge should not be consumed[4]. In the lower Yarra River, Victoria, a public health advisory was issued in 2005 (based on PCB concentrations) that recommended limiting the consumption of eels to one serve per month and a maximum of only one 150 g serve per week for all other fish caught from from the Maribyrnong and Yarra estuaries. Additional advice was also given limiting consumption of fish by pregnant women and children up to the age of 15 years[7]. More recent data from Black Bream (Acanthopagrus butcheri) samples collected in 2009 indicated that the contaminant levels were essentially unchanged and that the existing health advisory should remain in place[7]. Other published studies from Australian waters have included generally low levels of dioxins and dioxin-like PCBs in fish fillets with values of 0.05-0.15 pg I-TE/g fm in whiting and flathead caught in Bass Strait[8] and 0.48-4 pg I-TE/g fm from carp samples taken from Lake Coleman that was receiving effluent from a pulp and paper mill[9].

The data for South Australian mussels and fish reported in the national dioxins study were largely unremarkable[3]. Three fish species collected from the Adelaide area had low concentrations of dioxin-like chemicals, including 0.011 (flathead), 0.023 (garfish) and 0.018 (King George Whiting) pg/g TEQDF+PCB. None of these values were high from either a national or international perspective[3]. Studies in South Australia have previously shown that PCBs were detected in the blubber of 12 dolphins that had been found dead in various locations around the state[10]. The highest levels were recorded from dolphins found in the Largs Bay and Port River areas but were lower than most values reported in the scientific literature from around the world.

The objectives of this study were to quantify concentrations of dioxins, furans and dioxin-like PCBs in fish collected from a range of estuarine and coastal locations in South Australia. The design was to sample locations that included limited industrial and urban effects through to locations with considerable industrial development, to provide data across a broad human disturbance gradient. These included industrial areas (Port River and Port Pirie); urban and agricultural (West Lakes, Patawalonga and Onkaparinga estuary); and minor agricultural (Middle and Western rivers from Kangaroo Island). Additional data from an earlier unpublished study on Lake Bonney in the South East were also included to extend the dataset for locations receiving effluent from paper pulp and wastewater treatment plant effluents.

Materials and methods

Whole fish samples were analysed in this study to provide an assessment of the overall body burden posed by the selected contaminants, rather than using just fish fillets for the determination of risk from a human consumption perspective or major organs for the determination of maximum concentrations.
The sampling program focused on the collection of separate composited fish samples from two commonly occurring, target estuarine species (Black Bream *Acanthopagrus butcheri* and Yellow-eyed Mullet *Aldrichetta forsteri*) from each location and site. Black Bream were present at each location but where Yellow-eyed Mullet were not present other species of mullet were collected. In addition, Estuary Catfish (*Cnidoglanis macrocephalus*) were taken from the Port Pirie estuary and additional collections of Common Galaxias (*Galaxias maculatus*) were also taken from Lake Bonney SE where it occurs in large numbers.

Each sample consequently comprised 3-5 adult to sub-adult fish, with the exception of the Common Galaxias samples that required 54-61 fish from the 53-165 mm size range to reach the weight requirement using field measuring scales. Fish were collected in 2007-08 using a range of different nets (seines and fyke nets). The total body length (mm) and weight (g) of each collected fish was recorded. Individual whole fish were wrapped in aluminium foil (rinsed in acid and oven dried), sealed in food grade polyethylene bags and transported to the laboratory in a cold esky. The collections of over 50 Common Galaxias individuals were wrapped together in foil and subsequently treated as the other larger fish samples.

Whole fish samples were composited, freeze-dried, ground and homogenized at the National Measurement Institute (NMI) in Pymble, New South Wales. The determination of tetra- through to octa-chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), and "dioxin-like" PCBs in fish samples was carried out using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The samples were spiked with a range of isotopically labelled surrogate standards and then exhaustively extracted with an organic solvent with clean-up carried out by partitioning using sulphuric acid and distilled water. Further purification was performed using column chromatography on acid and base modified silica gels, basic alumina and carbon dispersed on celite.

The dioxin toxicity equivalent (WHO_{05}-TEQDF/TEQP) of each sample was calculated using World Health Organization toxic equivalency factors (WHO_{05}-TEFs). All results given were corrected for labeled surrogate recoveries and reported on a fresh and lipid weight basis in pg/g.

Results and discussion

The results from this sampling survey indicate that overall the contamination of dioxins, furans and dioxin-like PCBs of estuarine and coastal fish in South Australia does not warrant any food advisories. Figure 1 illustrates both the TEQ for each sample and the proportions of dioxins/furans and dioxin-like PCBs that contributed to the TEQ for the 30 samples reported in this study. Around 46% of the samples collected had a total TEQ of less than 1pg/g and only three samples had TEQ greater than 6pg/g (with a maximum of 11.7pg/g) indicating that these contaminants are not a risk to human health from fish consumption. This is especially the case given these TEQ have been generated from whole fish samples and not just fillets. A conservative approach to better compare the whole fish TEQ to human health risk from consumption is to halve the whole fish TEQ which brings the maximum TEQ recorded in this survey below the temporary action level for dioxin and dioxin-like PCBs in seafood used in Australia.

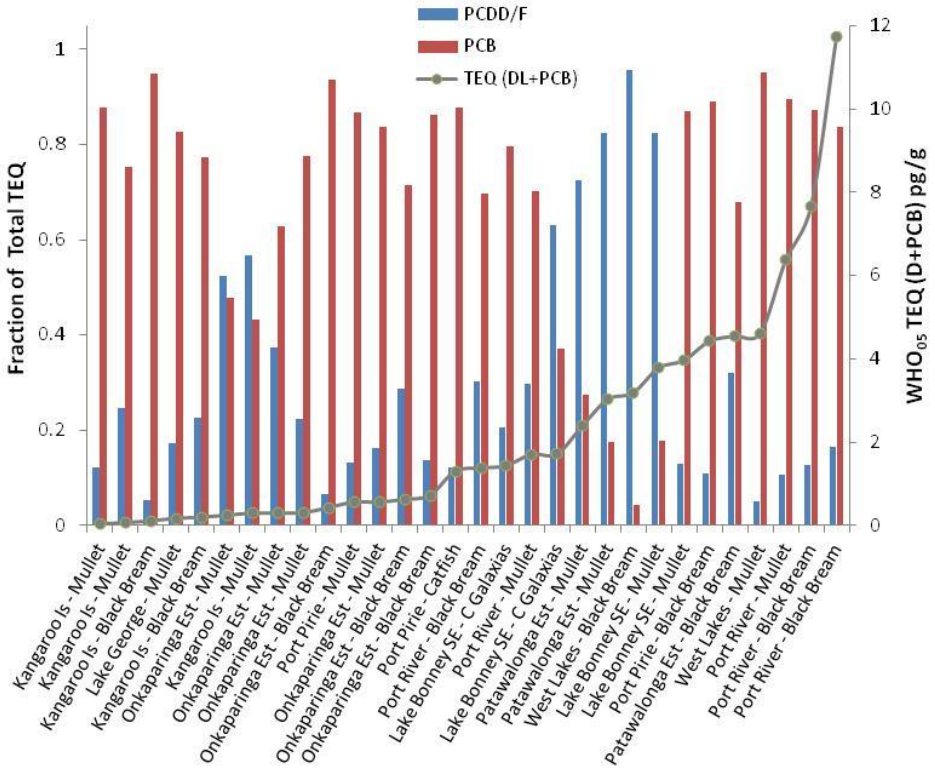

Figure 1 – Pattern of dioxin/furan and PCB contamination of fish samples from South Australia. Samples are ranked left to right from lowest to highest TEQ (.

The results from this survey indicate that fish from waters receiving run-off from agricultural landuses are relatively unimpacted . These results are consistent with Phua et al.[11] who recorded TEQs in 0.16-1.18 pg/g range for Southern Bluefin Tuna (*Thunnus maccoyii*) using fillets from wild-caught and farmed fish off Port Lincoln in South Australia. The TEQs steadily increase as the degree of human impact on run-off increase with the highest TEQ recorded in the Port River which has been impacted historically from both urban and industrial pollution. Another feature of the data in Figure 1 is the dominance of the PCB contribution to the overall TEQ. Over 75% of the samples collected had a TEQ where the contribution from PCB was 65% or greater. The samples where dioxins had the greater contribution tended to be due to slightly elevated results for dioxin and furan congeners with high TEFs.

A comparison of the congener homologue pattern for both dioxins/furans and dioxin-like PCBs provided some interesting results (Figure 2). The patterns for dioxins/furans were generally highly variable (as indicated by the large error bars) although the OCDD congener was most often dominant. Although at low levels, the variable pattern indicates a wide range of possible sources of dioxins with impacts from bushfires and other combustion sources possible given the occasional dominance of OCDD. The pattern for PCBs however was very consistent across all samples collected. As seen in Figure 2(b), the dominance of the congener pattern consistently followed PCB118 >> PCB105 > PCB156 > PCB167 ~ PCB77~PCB157 which are considered to be the most long lived congener homologues. This indicates that there is likely to be a single source type for PCBs across South Australia. Although Sources and pathways of exposure are poorly defined, Aroclor formulations and their use are considered to be the most likely sources of PCB congeners 118, 105 and 156[12].

Further work is planned to differentiate the distribution of PCBs fillets compared with the whole fish for at the sites where the highest TEQs were found. This will allow the assumption of 50% of the total fish TEQ to be explored. This work will also include a range of emerging persistent organic pollutants including brominated

flame retardants as well as fluorinated organic compounds to provide a baseline for these compounds in South Australia.

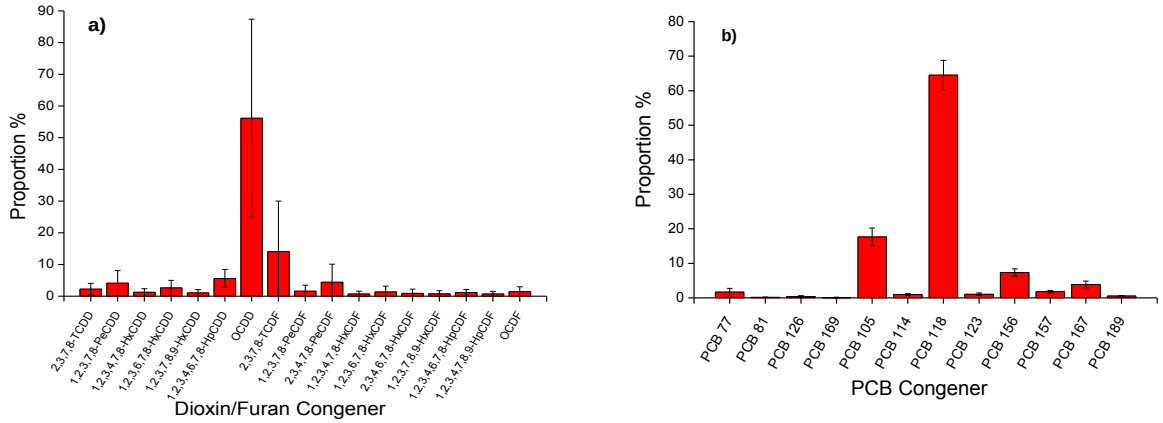

Figure 2 - Congener profile pattern of mean data for both a) dioxins/furans and b) dioxin-like PCBs. Error bars are 1 standard deviation in the data set.

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