Environmental Pollution xxx (2017) 1–7

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# Levels of PCDD/Fs and dioxin-like PCBs in seafood from Sydney Harbour, Australia☆

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ARTICLE INFO

*Article history:*
Received 23 December 2016
Received in revised form
16 February 2017
Accepted 19 February 2017
Available online xxx

*Keywords:*
Dioxins
Dioxin-like PCBs
Fish
Fish consumption
Contamination
Seafood

ABSTRACT

Sydney Harbour, Australia is contaminated with polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) due to a historical Union Carbide chemical manufacturing facility. We measured levels of PCDD/Fs and dl-PCBs in over 400 seafood samples (covering 20 species) collected throughout Sydney Harbour. Concentrations ranged from 0.1 to 193 pg total TEQ ($WHO_{05}$)/g wet weight. These concentrations were above those considered safe for human consumption in many cases. Dioxin accumulation varied among species and was associated with life history traits. Mobile species had elevated concentrations throughout Sydney Harbour whereas accumulation in species likely to move less widely was dependent on the distance they were caught from the point source. This large scale study on multiple species of recreationally caught seafood resulted in the implementation of human consumption advisories for recreational fishing based on individual species and distance from point source. In addition, all forms of commercial fishing in Sydney Harbour were banned.



## 1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) are groups of chemicals that are regulated under the Stockholm Convention on Persistent Organic Pollutants (www.pops.int). The Stockholm Convention was developed a decade ago to enable better global management of persistent organic chemicals. These chemicals are highly toxic, persistent and bioaccumulative environmental contaminants (Mandal, 2005; Hites, 2011).

PCDD/Fs and dl-PCBs are by-products of certain industrial and combustion processes (e.g. production of pesticides, bleaching of paper and waste incineration) (Cleverly et al., 1997; USEPA, 2003). They enter aquatic environments through either point or diffuse sources. Once they enter waterways they will bind to sediments and bioaccumulate in organisms. Dioxin contamination in aquatic organisms is of concern to human health due to the potential for exposure through the consumption of seafood. In various locations around the world with elevated levels of dioxins in seafood, fishing bans or advisories have been introduced to control human exposure (Knutzen et al., 2003; Williams and Cseh, 2007; Wang et al., 2015). Most of these advisories have been based on small scale studies on limited species. Studies assessing the risk of dioxin exposure to humans from consumption of several seafood species within an estuarine system are lacking.

Port Jackson (including Sydney Harbour and Middle Harbour, Fig. 1) is a well-regarded natural harbour and is surrounded by Australia's largest city, Sydney (with over 4 million residents). The harbour is renowned for its biological diversity and prior to this study, supported both recreational and commercial fishing industries. Homebush Bay, an embayment in the upper reaches of Port Jackson, has shown very high dioxin contamination in sediments and water due to historical chemical manufacturing on the shoreline and reclamation activities using chemical manufacturing waste (Birch et al., 2007; Roach et al., 2009a, 2009b). Union Carbide Australia Ltd and its related companies manufactured chemicals from the 1920s until the mid-1980s (Parsons-Brinckerhoff, 2002) at the site. A wide range of chemicals were manufactured including the pesticides 2,4,5-T, 2,4-D and DDT.

From the mid 1980s until the early 2000s the land adjoining Homebush Bay was largely vacant. Since then, remediation of the

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

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http://dx.doi.org/10.1016/j.envpol.2017.02.042
0269-7491/

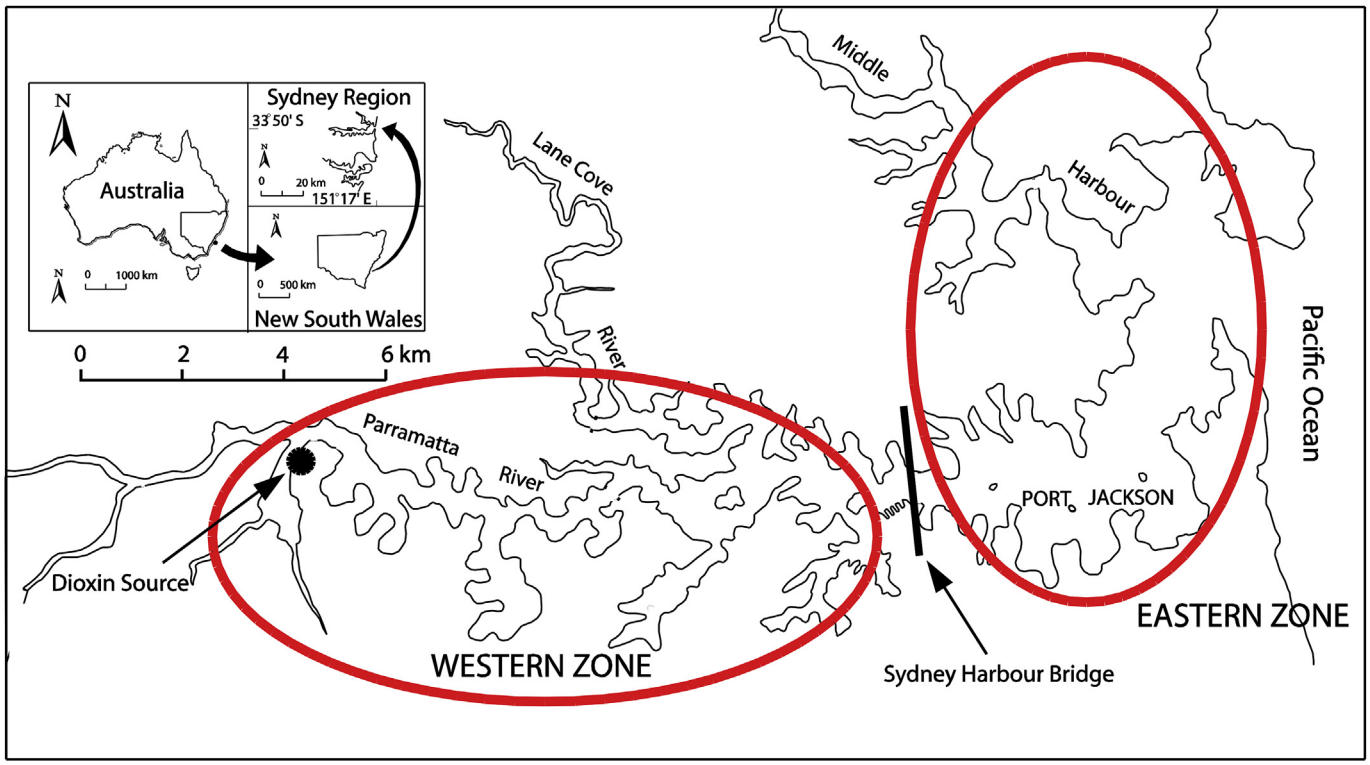


**Fig. 1.** Map of Port Jackson estuary (including Sydney Harbour and Middle Harbour).

land has occurred to enable high density residential apartments to be constructed. As a result, the population of the area has increased dramatically. These changes in land use have resulted in a potential for an increased risk of exposure of dioxins to people and has drawn attention to the accumulation of these chemicals in seafood from Port Jackson.

Previous studies have detected high concentrations of PCDD/Fs as well as a range of common urban contaminants in organisms from Port Jackson (Roach and Runcie, 1998; Losada et al., 2009; Roach et al., 2008; Dafforn et al., 2012). Furthermore, dioxins have been detected in blood in fishers from the estuary (Rudge et al., 2008). We measured dioxin concentrations in a broad range of seafood from Port Jackson to assess the risk to human health from consumption. Further, this study considered the influence of species-specific differences on total TEQ levels in seafood.

## 2. Methods and materials

### 2.1. Sampling

Twenty species of seafood were collected at various locations throughout Port Jackson (including Sydney Harbour and Middle Harbour) between June 2005 and June 2006 (Fig. 1, Table 1). Targeted species were those commonly caught by recreational or commercial fishers. Seafood was sampled using commercial fishing methods including trawling, gill or seine netting. Samples were immediately transferred to the laboratory and frozen at −20 °C until subsampling for tissues. Fish were filleted and muscle (with skin) was targeted for analysis, replicating how the seafood is consumed. For prawns, the animals were shelled, veined and the body tissue was sampled. For crabs, the muscle and hepatopancreas were sampled and for squid the soft tissue was sampled. Up to five composite samples of ten individuals of each species were taken from five regions within Port Jackson, three regions on the western side of the Sydney Harbour Bridge and two regions on the east. For prawns, crabs and squid, the composite samples included enough individuals to obtain sufficient fresh tissue for analysis (approximately 200–300 g).

### 2.2. Chemical analysis and quality control

To enable a rapid throughput of samples, two laboratories accredited for dioxins analysis were used for sample preparation and analysis (National Measurement Institute, Pymble, Australia and Agriquality, Auckland, New Zealand). Both laboratories were accredited for the analysis. Samples were prepared for analysis either using solvent extraction according to US EPA 1613b (USEPA, 1994) and US EPA 1668a (USEPA, 2010) or accelerated solvent extraction according to US EPA 3545 (USEPA, 2007) depending on the laboratory. All samples were analysed for 17 individual PCDD/F and 12 dl-PCB congeners. Chemical analysis was performed using the isotope dilution method and high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) according to US EPA 1613b and US EPA 1668a (USEPA, 1994, 2010). Lipid levels were determined gravimetrically.

One of the laboratories used a standard solvent extraction technique. The technique involved blending the sample with sodium sulfate, spiked with $^{13}C_{12}$ isotopically labelled internal standards and then extracting it with methylene chloride:hexane (1:1) using Soxhlet extraction for 18 h.

The other laboratory used accelerated solvent extraction performed on lyophilised samples that had been mixed with Hydromatrix using an ASE 100 (Dionex, Utah, USA) with toluene at 150 °C and 1500 psi. Between 1 and 10 g of the extracted lipid was spiked with PCDDs/PCDFs and dioxin-like PCB isotopically labelled $^{13}C_{12}$ surrogates. The extracts were then purified on the Power-Prep system (Fluid Management Systems USA) using standard elution programs as supplied by the manufacturer.

Please cite this article in press as: Manning, T.M., et al., Levels of PCDD/Fs and dioxin-like PCBs in seafood from Sydney Harbour, Australia, Environmental Pollution (2017), http://dx.doi.org/10.1016/j.envpol.2017.02.042