DIOXINS IN FISH AND OTHER SEAFOOD FROM SYDNEY HARBOUR, AUSTRALIA

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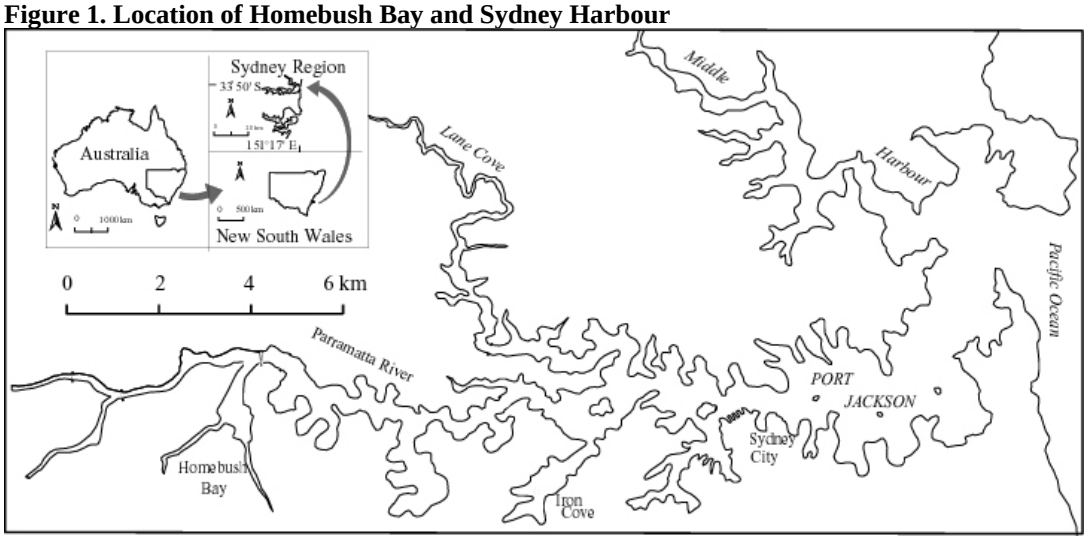
Abstract
Chemical manufacturing was located along the shore of Sydney Harbour and its tributaries in the first half of the twentieth century. One site on Rhodes Peninsula adjoining Homebush Bay (an embayment of the Parramatta River) was used to manufacture herbicides, pesticides and chlorinated organics for about 40 years. Land at this site was also reclaimed using waste materials as part of the fill. On-site practices and the impacts of the contaminated fill material resulted in contamination of land and sediments with dioxins, chlorinated organics and a range of pesticides.

Initial work in 1989 and 1990 showed biota were contaminated in Homebush Bay and surrounding areas. Fishing restrictions were introduced. Remediation is currently underway to allow residential use of the site. Contamination levels in fish and other organisms were checked again in 2005-2006 while preparing for this remediation. Contamination of biota tested recently was similar to 1990 levels in Homebush Bay and Parramatta River but levels in some species caught in eastern parts of Sydney Harbour were higher than found in the earlier work. Recent guidance on acceptable levels of intake of dioxins from WHO was used in interpreting the levels found. Commercial fishing in Sydney Harbour has been stopped and a number of advisories have been issued for recreational fishers.

Introduction
A range of industry including chemical manufacturing was historically located around Sydney Harbour and its tributaries in the early part of the twentieth century. Such locations were not highly sought after for residential purposes at the time and the locations enabled easy transport of materials by boat. Homebush Bay is an embayment of Parramatta River, which forms part of Sydney Harbour, Australia (Figure 1). The Bay is approximately 80 hectares in size. A range of chemical manufacturing and other industry lined its shoreline. Since the 1980s all of this industry has closed down or moved to other locations and the land is now being redeveloped for medium and high density residential uses. This change in land use has required significant remediation of a number of the sites that were heavily contaminated. It has also meant that some heavily contaminated sediments have been removed or will be removed in the near future to minimise the possibility of people coming into contact with them.

Figure 1. Location of Homebush Bay and Sydney Harbour



In the 1920s the manufacture of timber preservatives using coal tars began on the Rhodes Peninsula adjoining Homebush Bay. In the late 1940s and early 1950s the manufacture of chlorophenols, chlorobenzenes, DDT and the herbicides 2,4,5-T and 2,4-D began. Manufacturing at the site ceased in 1986[1]. Between 1940 and the early 1970s land was reclaimed from the Bay using a variety of materials as fill.

Both the land and the sediments remaining in the Bay have been found to be contaminated with dioxins, pesticides and chlorinated organics. In 1989 and 1990 elevated levels of 2,3,7,8-TCDD were measured in biota from the Bay resulting in a ban on all forms of fishing within the Bay. Commercial fishing in Parramatta River was also restricted and recreational fishers were advised to limit their consumption of fish caught in the River.[1]

Remediation of Rhodes Peninsula and the sediments of Homebush Bay is currently underway and is expected to be completed in 2009. Further studies of levels of dioxins in biota were initiated in 2005 as part of the baseline work for the remediation project. This paper provides an initial summary of results with a full description of all the data from the study to be published shortly.

Materials and Methods

Sampling

PHASE 1

School prawns (*Metapenaeus macleayi*) and/or king prawns (*Penaeus plebejus*) were caught by commercial trawlers in mid 2005 at a number of locations throughout Parramatta River and one location in Sydney Harbour. Prawns were prepared for analysis by cleaning and shelling. Bream (*Acanthropagrus australis*) were caught in late 2005 in the same locations as the prawns with the addition of some fish collected in Homebush Bay itself. 50 individuals were collected at each location. Each fish was scaled, skin removed and filleted. The fillets from 10 individuals were composited.

PHASE 2

Additional prawn and bream samples were collected in late 2005 from locations in the eastern part of the Harbour and prepared as described above.

PHASE 3

During the first half of 2006, another 14 species of fish and invertebrates commonly caught by recreational fishers were targeted for collection throughout the Harbour. Species collected included dusky flathead (*Platycephalus fuscus*), tailor (*Pomatomus saltatrix),* sand whiting (*Sillago ciliata*), trumpeter whiting (*Sillago maculata*), trevally (*Pseudocaranx dentex*), yellowtail scad (*Trachurus novaezelandiae),* kingfish (*Seriola lalandi*), silver biddy (*Geres ovatus*), luderick (*Girella tricuspicata*), fan-belly leather jacket (*Monocanthus chinensis*), sea mullet (*Mugil cephalus*), flounder (*Pseudorhombus sp.*), blue swimmer crab (*Portunus pelagicus*), and squid (*Loliotus noctiluca* and *Photololigo* spp.).

Analytical Methods

Samples were prepared and analysed in accordance with USEPA 1613b (dioxins and furans) and USEPA 1668a (dioxin like PCBs) by the National Measurement Institute, Pymble, Australia and Agriquality Ltd, Wellington, New Zealand.

PHASE 1 AND 2

Analysis of lyophilised fish tissue was conducted by the National Measurement Institute (NMI), Sydney, Australia using the technique of isotope dilution High Resolution Gas Chromatography/ High Resolution Mass Spectrometry (HRGC/HRMS) according to their ISO 17025 scope of accreditation. The detailed method has been previously described[2] and is briefly summarised here. A Dionex ASE100 accelerated solvent extractor (ASE) (Dionex Corporation, Sunnyvale, CA, USA) was used to extract all samples. Where available, 20g of fish tissue was accurately weighed into an appropriately sized ASE cell and spiked with a known amount of the respective isotopically labelled 13C12 surrogate solutions and extracted with toluene. The toluene extracts were solvent exchanged with hexanes, extracted with concentrated sulfuric acid and cleaned-up on acid, neutral and base modified silica followed by purification with basic alumina and carbon dispersed on celite. Dioxins and

dioxin-like compounds were analysed by HRGC/HRMS (R≥ 10,000) on a 60m x 0.25mm i.d., film thickness 0.25μm DB-5 (J and W Scientific, Folsom, CA, USA) capillary column with multiple ion detection (MID) experiments performed in the electron impact mode by monitoring of the exact masses of ions for native and labelled compounds.[2]

PHASE 3
Weighed aliquots of the samples (approximately 40g) were blended with sodium sulfate, spiked with isotopically labelled internal standards and extracted with organic solvent (methylene chloride:hexane; 1:1) by Soxhlet extraction 18 hours. The lipid content was determined gravimetrically by evaporating the sample extract to constant weight. Isotopically labelled clean-up standards were added to the extract, which was purified by acid and base modified silica gel, alumina, and carbon column chromatography. The final extract was spiked with recovery standard and evaporated to a reduced volume for HRMS analysis. Analysis was carried out on Micromass Autospec Ultima HRMS (High-Resolution Mass Spectrometer) instrumentation interfaced to Agilent 6890 gas chromatographs, operating in the splitless mode and using Zebron ZB-5 capillary columns. Confirmatory analysis of the 2,3,7,8-TCDF congener was performed on a J&W Scientific DB225 capillary column. HRMS analyses were carried out in the electron impact mode. Native and labelled compounds were detected by Selected Ion Monitoring with the mass resolution being maintained at 10,000 (10% valley) throughout the analysis for mid-range masses.

Results and Discussion

PHASE 1 AND 2
Results for prawns and bream showed that significant levels of dioxin-like compounds were present in all samples caught throughout Sydney Harbour.

In 1989 and 1990 when data on fish tissue concentrations in this area first became available, US FDA guidance was used to determine if the levels of 2,3,7,8-TCDD in biota posed a risk to people. A level of 50 pg 2,3,7,8-TCDD/g wet weight was used to indicate where all forms of fishing should be restricted while a level of 25 pg 2,3,7,8-TCDD/g wet weight was used to indicate where fishing advisories should be issued to recreational fishers and commercial fishing should be restricted.

The National Health and Medical Research Council in Australia adopted the WHO tolerable daily intake of 70pg WHO_{98}-TEQ_{DF+PCB}/kg body weight/month in 2002. Food Standards Australia and New Zealand used this value to develop an action level for use in considering the data from this study. The action level that was recommended was 6 pg WHO_{98}-TEQ_{DF+PCB}/g wet weight[3,4]. All of the results for bream and prawns caught in Sydney Harbour were close to or above this action level.

School prawns were caught from upstream in Parramatta River down to about half way down the Harbour at Drummoyne (approx 6km). They contained levels ranging up to 23 pg WHO_{98}-TEQ_{DF+PCB}/g wet weight.

King prawns were caught in Homebush Bay and then downstream through Parramatta River and throughout Sydney Harbour (approx 20km). They contained levels ranging up to 15 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight.

Bream were caught at all sites throughout the Harbour. They contained levels ranging up to 50 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight in Parramatta River and the Harbour, while fish caught inside Homebush Bay had levels ranging up to 140 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight.

Based on these results, all forms of commercial fishing in Sydney Harbour were restricted in January 2006 and negotiations began with licence holders to buy back their licences. A recreational fishing advisory was also issued recommending that fishers not consume more than 1 meal a month of fish or prawns caught in Sydney Harbour.

PHASE 3
Over 300 samples were analysed from 14 species caught throughout the Harbour.

Samples caught in the areas west of the Sydney Harbour Bridge, including all samples taken in Parramatta River, had levels averaging 38 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight in the various fish species and 19 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight in the blue swimmer crab and squid.

Samples caught in the areas east of the Sydney Harbour Bridge towards the mouth of the Harbour had levels averaging 10 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight in the various fish species and 5.6 pg WHO_{98}-TEQ_{DF+PCB} /g wet weight in the blue swimmer crab and squid.

The level of 2,3,7,8-TCDD in sediments in Homebush Bay was found to range from <100 pg 2,3,7,8-TCDD/g dry weight to >300 000 pg 2,3,7,8-TCDD/g dry weight[1]. Other studies[5,6] have investigated levels of dioxin-like compounds in Parramatta River in a limited way and have found levels ranging from 75 to 510 pg WHO_{98}-TEQ_{DF}/g dry weight. Data on levels in sediments in the eastern part of the Harbour are more limited but show levels ranging from 0.7 to 75 pg WHO_{98}-TEQ_{DF} /g dry weight.

For some species and the average case, levels of dioxin-like compounds decreased along a gradient away from Homebush Bay. This is in line with what would be expected around a point source in an estuary and is in line with the limited information available on sediment levels of dioxin-like compounds in the Harbour. However, other species show levels of dioxin-like compounds that do not appear to follow this gradient. For these fish levels were highly variable throughout the Harbour. Further discussion of the information this provides on life history for the different species will be presented in a separate poster paper.

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