National Dioxins Program

Technical Report No. 6
Dioxins in Aquatic Environments in Australia

A consultancy funded by the Australian Government Department of the Environment and Heritage

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2. Dioxins emissions from Motor Vehicles in Australia
3. Inventory of Dioxin emissions in Australia 2004
4. Dioxins in Ambient Air in Australia
5. Dioxins in Soils in Australia
6. **Dioxins in Aquatic Environments in Australia**
7. Dioxins in Fauna in Australia
8. Dioxins in Agricultural Commodities in Australia
9. Dioxins in the Australian Population: Levels in Blood
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Foreword

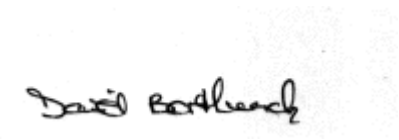
When the Australian Government established the four year National Dioxins Program in 2001, our knowledge about the incidence of dioxins in Australia was very limited.

The aim of the program was to improve this knowledge base so that governments were in a better position to consider appropriate management actions. Starting in mid 2001, a range of studies were undertaken which involved measuring emissions from sources such as bushfires, as well as dioxin levels in the environment, food and population. The findings of these studies were used to shed light on the risk dioxins pose to our health and the environment.

This work has been completed and the findings are now presented in a series of twelve technical reports.

Having good information is essential if there is to be timely and effective action by governments; these studies are a start. Our next step is to foster informed debate on how we should tackle dioxins in Australia, as this is an obligation under the Stockholm Convention on Persistent Organic Pollutants. The Department of the Environment and Heritage will be working closely with other Australian Government, State and Territory agencies to take this step.

Ultimately, the effective management of dioxins will be the shared responsibility of all government jurisdictions with the support of the community and industry.



David Borthwick
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Department of the Environment and Heritage

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- the Department of Agriculture, Fisheries and Forestry, who assessed the levels of dioxins in agricultural commodities
- Food Standards Australia New Zealand and the Department of Health and Ageing and who assessed the levels of dioxins in foods and assessed the health effects of dioxins
- officers of the Chemical Assessment Section in DEH who assessed the ecological effects of dioxins
- members of the National Dioxins Project Team which included representatives from the State and Territory environment protection agencies, the Australian Health Ministers Conference and the Primary Industries Ministers Council
- members of the National Dioxins Consultative Group which included representatives from industry and agricultural sectors, environment and public health groups and research institutions.

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Executive summary

This study was a component of the National Dioxins Program tasked to quantify and assess the concentrations and relative chemical compositions of dioxin-like chemicals in Australia's aquatic environment.

The project involved the collection and analysis for dioxin-like chemicals in aquatic sediment cores from 62 sampling locations. Collections were made by a team of sampling personnel using a standard sampling protocol, from locations representative of major catchments based on the National Pollution Inventory. The study was deliberately designed to avoid collecting samples in immediate proximity to known or likely sources of contamination with dioxin-like chemicals. A range of samples was collected from each of freshwater, estuarine and marine locations. Where practical, samples were collected from locations within the same catchment from the non-impacted upper catchment through estuary to marine environment, covering different land-use influences classified as remote, agricultural and urban/industrial. In addition to sediment samples, bivalve samples were collected, when available from the locations from which sediment samples were collected. Fish were also obtained through local commercial fishing industries with an emphasis on local catch of table species.

Chemical analysis of sediment and biota samples was conducted by the Australian Government Analytical Laboratories (AGAL), and a series of quality assurance/quality control (QA/QC) procedures were incorporated into the study, including replicate sampling, replicate analysis and an interlaboratory comparison of analysis using an overseas laboratory highly regarded for its experience in the analysis of dioxin-like chemicals in environmental samples. The QA/QC procedure suggested that the reproducibility of the chemical analysis was good, and that the identification of individual dioxin-like chemicals and quantification of their concentrations in sediment samples was reliable. The analysis of sampling replicates, or samples collected at different sites within the same water body representing similar exposure to dioxin-like chemicals, demonstrated that the greatest uncertainty in the results is likely to relate to variability at specific sampling locations rather than uncertainty in chemical analysis.

The concentrations of dioxin-like chemicals in the sediment and biota samples were assessed both in terms of the concentrations of PCDD/PCDF and PCB and their toxic equivalents. In addition, the patterns of component chemicals were evaluated, and assessments of concentration and patterns were made with respect to geographic location and land-use types.

Dioxin-like chemicals were found in all Australian aquatic sediments analysed, with middle bound concentrations ranging from 0.002 to 520 pg TEQ g^{-1} dm. Highest concentrations were found in the sediments sampled from the Parramatta River estuary (100 and 520 pg TEQ g^{-1} dm) and the western section of Port Jackson (78 and 130 pg TEQ g^{-1} dm), in close proximity to historical manufacturing point sources around Homebush Bay. In addition, elevated concentrations were also found in other estuarine waters of Sydney (Botany Bay) as well as the estuaries in or near Brisbane, Melbourne, Hobart, Perth and Wollongong.

Considering all sediment samples, the median concentrations were 0.2, 2.3 and 0.12 pg TEQ g^{-1} dm in sediments from freshwater, estuarine and marine locations, respectively. However, statistical analysis showed that median concentrations across marine, freshwater and estuarine sampling locations did not differ significantly. By contrast, urban/industrial sampling locations had significantly greater concentrations of dioxin-like chemicals than samples from remote and agricultural locations. It is also noteworthy that the elevated concentrations in urban/industrial areas were also evident if data were expressed on a total organic carbon basis.

Homologue and congener profiles for the PCDD/PCDF were strongly dominated by OCDD with the 1,2,3,4,6,7,8-heptachloro dibenzodioxin usually the congener with the second highest concentration. The source or formation processes by which such a higher chlorinated dominance could occur remains unresolved despite intensive studies by others. For most sediment samples, PCDD/PCDF dominated the mixture of dioxin-like chemicals present, accounting for more than 80% of the total TEQ. However, a range of samples such as those from the Brisbane River, the Torrens River or from Western Australia showed contributions of PCB exceeding 50%. This suggests local sources of PCB have influenced the compound profiles at those sampling locations.

The middle bound concentrations of dioxin-like chemicals in 18 bivalves samples ranged from 0.0043 pg TEQ g^{-1} fm to about 1.2 pg TEQ g^{-1} fm when expressed using fish toxic equivalent factors, with the greatest concentrations in samples from Port Jackson and the Yarra estuary.

Dioxin-like chemicals were also analysed in 23 fish samples from around the country and middle bound concentrations ranged from 0.0053 pg TEQ_{FISH} g^{-1} fm to about 0.49 pg TEQ_{FISH} g^{-1} fm. The level of dioxin-like chemicals was highest in a fish sample obtained from the Sydney/Port Jackson area.

Overall, the results from this study showed that the concentrations of dioxin-like chemicals in the aquatic environment (sediments, bivalves and fish) are in most cases less than published levels for other industrialised countries. However, the concentrations in sediments at a few areas and particularly in the lower Parramatta estuary and the western part of Port Jackson are substantially elevated. The bivalve results followed a similar pattern to the sediment results confirming the existence of areas with elevated environmental exposure levels of dioxin-like chemicals. However, the fish analysed in this study were unaffected, with consistently low levels of dioxin-like chemicals found.

Glossary/Abbreviations

AGAL	Australian Government Analytical Laboratories.
ANOVA	Analysis of Variance.
ANZECC	Australian and New Zealand Environmental Conservation Council, now replaced by the Environment Protection and Heritage Council. Representation includes environment ministers from Australia and New Zealand.
Congeners	Closely related chemicals derived from the same parent compound.
CSIRO	Commonwealth Scientific and Industrial Research Organisation.
Bivalve	Two shelled mollusc.
Dioxin	Common name for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF).
Dioxin-like	For the purpose of this study, 2,3,7,8-chlorine substituted PCDD/PCDF and non-ortho and mono-ortho PCB.
dm	Dry mass.
Furan	Polychlorinated dibenzofuran (PCDF).
ENTOX	National Research Centre for Environmental Toxicology.
fm	Fresh mass.
GC	Gas Chromotography.
Homologue	A group of structurally related chemicals that have the same degree of chlorination.
Isomer	Chemical compound where the overall composition of the molecule is the same but the structure is different.
IPCS	International Programme on Chemical Safety.
I-TE	Toxicity equivalencies using NATO-CCMS (1988) toxicity equivalency factors. Most data prior to 1998, including the NZ studies reported in I-TEs did not include PCB.
I-TEF	See TEF but factors developed earlier by NATO-CCMS (1998).
IUPAC	International Union of Pure and Applied Chemistry.
LOD	Limit of detection, the lowest level at which a chemical can be measured in a sample by the analytical method used.
Lower bound TEQ	Toxic equivalencies (TEQ) for which the concentration of a non-detected congener is assumed to be zero. The remaining detected values are multiplied by the corresponding TEF value then summed to achieve the lower bound TEQ (TEQ excluding LOD values).

Middle bound TEQ	Toxic equivalencies (TEQ) for which the concentration of a non-detected congener is assumed to be half the limit of detection. All values are multiplied by the corresponding TEF value then summed to achieve the middle bound TEQ (TEQ including half LOD values).
MS	Mass Spectrometer.
NATO	North Atlantic Treaty Organisation.
NDP	National Dioxins Program.
NPI	National Pollution Inventory.
OCDD	Octachlorodibenzo-*p*-dioxin.
OCDF	Octachlorodibenzofuran.
PCB	Polychlorinated biphenyl
∑PCB	Summed total of all PCB congeners that were analysed and detected.
PCDD/PCDF	Polychlorinated dibenzo-*p*-dioxin and furan.
∑PCCD/PCDF	Summed total of all tetra-octachlorinated PCDD/PCDF congeners that were analysed and detected.
pg g^{-1}	Picogram (10^{-12} g) per gram. Equal to nanogram per kilogram (ng kg^{-1}).
TCDD	Tetrachlorodibenzo-*p*-dioxin.
TEF	Toxic equivalency factor of a specific dioxin, furan, or PCB. Defines the toxicity of each congener with dioxin-like biochemical and toxic responses, relative to the toxicity of the dioxin 2,3,7,8-TCDD (van den Berg et al., 1998).
TEQ	Abbreviation of WHO_{98}-TEQ (this document).
TOC	Total Organic Carbon (considered the sorption phase for hydrophobic substances such as dioxin-like chemicals in sediments).
WHO	World Health Organization.
WHO_{98}-TEQ	World Health Organization toxic equivalent: the quantified level of each individual congener multiplied by the corresponding TEF. TEQs of each congener are summed to achieve and overall toxic equivalents for a sample (van den Berg et al., 1998). In this document WHO_{98}-TEQ is abbreviated to 'TEQ'.
WHO_{98}-TEQ_{DF}	WHO_{98}-TEQ for PCDD and PCDF.
WHO_{98}-TEQ_{PCB}	WHO_{98}-TEQ for PCB.
WHO_{98}-TEQ_{DF+PCB}	WHO_{98}-TEQ for all analytes.

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1. Introduction

1.1 Background

The first Australian inventory of dioxin emissions to air "Sources of Dioxins and Furans in Australia: Air Emissions" was published in 1998 (Environment Australia, 1998). As there were few Australian data on dioxins, the preparation of that inventory relied heavily on overseas data, using release estimation methodology. The limited monitoring data available indicated that environmental concentrations were generally low, but that there was insufficient information to assess the impact of dioxins in Australia.

At its meeting in December 2000, the Australian and New Zealand Environment and Conservation Council (ANZECC) requested the development of a discussion paper on dioxins for use in consultation with stakeholders. In April 2001, public meetings were held in several cities across Australia to seek public input into the development of a possible national dioxins program. These workshops noted the lack of information on dioxins in Australia and recommended that data be obtained on concentrations in the environment and the human population. Following on from these consultations, a proposal for a National Dioxins Program was tabled at the meeting of ANZECC in June 2001. At this meeting, Council noted that the Australian Government would fund a National Dioxins Program (NDP) with $5 million over four years and that this program would generate data over the following two years which could be used to determine whether a specific regulatory approach would be required to manage dioxins.

The NDP is being implemented by the Australian Government Department of the Environment and Heritage (DEH) in three phases:

- information gathering about the current concentrations of dioxins in Australia
- risk assessment using the information gathered as a basis to assess the potential risks of dioxins to the environment and human health
- development of measures to reduce, and where feasible, to eliminate the release of dioxins in Australia.

Under the information gathering phase, DEH commissioned organisations to undertake the following studies:

- Determination of ambient environmental levels (ambient air, aquatic, soils and fauna) of dioxin and dioxin-like compounds in Australia
- Determination of the levels of dioxin emissions from bushfires in Australia
- Determination of the levels of dioxin emissions from motor vehicles in Australia
- Determination of the levels of dioxins in the Australian population by analysis of blood serum
- Determination of the levels of dioxins and dioxin-like compounds in pooled human milk samples.

Studies of dioxins in food by Food Standards Australia and New Zealand (FSANZ) and dioxins in agricultural commodities under the National Residues Survey by the Australian Government Department of Agriculture, Fisheries and Forestry (DAFF) also contributed valuable information on dioxins.

"Dioxins" refer to the group of persistent chlorinated chemical compounds, polychlorinated dibenzodioxins (PCDD), which share certain similar chemical structures, properties and biological characteristics, including toxicity. For the purpose of the NDP the term "dioxins" is used in the broader sense and is also taken to include the closely related polychlorinated dibenzofurans (PCDF or furans) and co-planar polychlorinated biphenyls (PCB). Several hundred of these compounds or congeners exist, of which 29 are considered by the World Health Organization (WHO) to have significant toxicity (WHO, 1998). It is these 29 closely related toxic chemicals that are the subject of this report and they are listed in Table 1.1. The general formulae for PCCD and PCDF are presented in Figure 1.1; numbers 1-9 indicate the possible positions of the chlorine atoms. The general formulae for PCB is presented in Figure 1.2, numbers 2-6 (2'-6') indicate the possible positions of the chlorine atoms at ortho(o), meta(m) and para(p) positions, respectively.

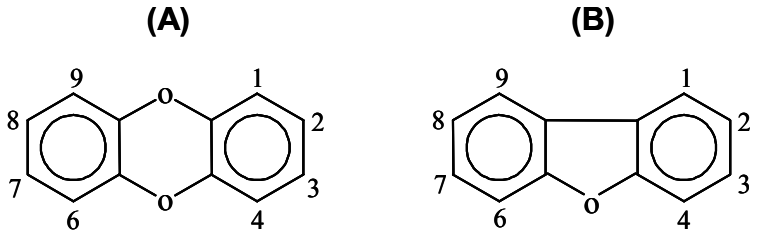


Figure 1.1 The structures of polychlorinated (A) dibenzo-*p*-dioxins and (B) dibenzofurans.

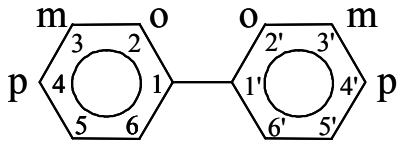


Figure 1.2 The structures of polychlorinated biphenyls.

Since dioxins occur as complex mixtures of congeners in most environmental media (air, water, soil), the concept of toxic equivalents (TEQs) has been developed. This concept allows the toxicity of a complex mixture to be expressed as a single number. Available animal-based toxicological data have been used to generate a set of weighting factors, each of which expresses the toxicity of a specific congener relative to an equivalent mass of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most studied and most toxic PCDD. Multiplication of the mass of the congener by its weighting factor (or toxic equivalents factor, TEF) yields the corresponding TCDD mass (or TEQ). The total toxicity of any mixture is then simply the sum of the individual congener TEQs.

$$TEQ = ([PCDD_i \times TEF_i]_n) + ([PCDF_i \times TEF_i]_n) + ([PCB_i \times TEFi]_n)$$

The most widely adopted system of TEQs is that proposed by the North Atlantic Treaty Organisation (NATO) and known as the International Toxic Equivalents Factors (I-TEFs). This system has been updated and expanded by the WHO into a scheme that includes factors for humans and other mammals as well as fish and birds. The TEFs for humans and fish for the 29 closely related chemicals that are the subject of this report are listed in Table 1.1.

Table 1.1 Dioxin, furan and PCB toxic equivalents factors.

Congener	IUPAC No.	NATO CCMS or $WH0_{94}$-TEF	WHO_{98}-TEF HUMAN [3]	WHO_{98}-TEF FISH [3]
Dioxins				
2,3,7,8-TetraCDD [a]	-	1 [1]	1	1
1,2,3,7,8-PentaCDD	-	0.5	1	1
1,2,3,4,7,8-HexaCDD	-	0.1	0.1	0.5
1,2,3,6,7,8-HexaCDD	-	0.1	0.1	0.01
1,2,3,7,8,9-HexaCDD	-	0.1	0.1	0.01
1,2,3,4,6,7,8-HeptaCDD	-	0.01	0.01	0.001
OctaCDD	-	0.001	0.0001	0.0001
Furans				
2,3,7,8-TetraCDF [b]	-	0.1	0.1	0.05
1,2,3,7,8-PentaCDF	-	0.05	0.05	0.05
2,3,4,7,8-PentaCDF	-	0.5	0.5	0.5
1,2,3,4,7,8-HexaCDF	-	0.1	0.1	0.1
1,2,3,6,7,8-HexaCDF	-	0.1	0.1	0.1
1,2,3,7,8,9-HexaCDF	-	0.1	0.1	0.1
2,3,4,6,7,8-HexaCDF	-	0.1	0.1	0.1
1,2,3,4,6,7,8-HeptaCDF	-	0.01	0.01	0.01
1,2,3,4,7,8,9-HeptaCDF	-	0.01	0.01	0.01
OctaCDF	-	0.001	0.0001	0.0001
Non-ortho PCB[c]				
3,3',4,4'-tetrachlorobiphenyl	PCB#77	0.0005 [2]	0.0001	0.0001
3,4,4',5-tetrachlorobiphenyl	PCB#81	-	0.0001	0.0005
3,3',4,4',5-pentachlorobiphenyl	PCB#126	0.1	0.1	0.005
3,3',4,4',5,5'-hexachlorobiphenyl	PCB#169	0.01	0.01	0.0005
Mono-ortho PCB				
2,3,3',4,4'-pentachlorobiphenyl	PCB#105	0.0001	0.0001	0.000005
2,3,4,4',5-pentachlorobiphenyl	PCB#114	0.0005	0.0005	0.000005
2,3',4,4',5-pentachlorobiphenyl	PCB#118	0.0001	0.0001	0.000005
2',3,4,4',5-pentachlorobiphenyl	PCB#123	0.0001	0.0001	0.000005
2,3,3',4,4',5-hexachlorobiphenyl	PCB#156	0.0005	0.0005	0.000005
2,3,3',4,4',5-hexachlorobiphenyl	PCB#157	0.0005	0.0005	0.000005
2,3',4,4',5,5'-hexachlorobiphenyl	PCB#167	0.00001	0.00001	0.000005
2,3,3',4,4',5,5'-heptachlorobiphenyl	PCB#189	0.0001	0.0001	0.000005

[1] NATO CCMS (1989) From Kurtz et al., (1990)
[2] WHO-TEF (1994) From Ahlborg et al., (1994)
[3] WHO-TEF (1998) From van den Berg et al., (1998)

[a] CDD – chlorinated dibenzo-*p*-dioxin
[b] CDF – chlorinated dibenzofuran
[c] PCB – polychlorinated biphenyl

1.2 Objectives

This study formed part of the Ambient Environmental Levels section of the Data Gathering and Consolidation phase of the National Dioxins Program. The overall objective of the project was to characterise levels of dioxin-like chemicals in Australian aquatic environments across a range of ecosystems, climates and land-uses.

Specific aims of this study were to:

- Increase understanding of background dioxin levels in Australian aquatic environments by direct sampling of aquatic biota and sediments
- Consolidate the current state of knowledge concerning dioxin levels in Australian aquatic environments (freshwater, estuarine and marine)
- Compare analytical results with previous Australian studies and international data.

1.3 Scope

A four-stage project plan was implemented in order to achieve the project aims:

Stage 1 - Sample collection.

Composite samples were collected from all sampling locations to ensure samples were representative of the background at each location, and in the case of biota, to achieve sufficient material for analysis. Sampling was conducted within airsheds and catchments selected according to priorities identified by the National Pollution Inventory (NPI).

Stage 2 - Sample analysis.

Analysis of samples was undertaken at AGAL to determine the concentrations of the 29 PCDD/PCDF and PCB as outlined in the analysis methodology at Appendix B.

Quality control/quality assurance was integrated into all phases of the sampling and analysis process. Duplicate samples (i.e. 'A' and 'B') were collected at each location to allow sampling reproducibility to be determined through the analysis of 20% of 'B' samples. Analytical reproducibility was determined for the parallel NDP soil study and, thus, considered unnecessary for the aquatic study. The evaluation of the analytical reproducibility in the soil study clearly demonstrated that the error related to the analytical reproducibility is smaller than the error related to replication/representativeness of the sampling site selection.

Stage 3 - Collation and statistical analysis of the data.

A database was prepared to include all site information recorded at the time of sample collection, and to store analytical results for the corresponding sites. Information included: GPS readings (latitude, longitude and altitude), vegetative cover, soil type, temperature range, average annual rainfall, possible PCDD/PCDF and/or PCB sources near the sampling location. The database was utilised for statistical analysis of results.

The current state of knowledge on dioxin concentrations in Australian aquatic environments was consolidated through a literature review of studies previously undertaken in Australia. A review of international literature was conducted and results obtained in Australian studies compared to those found in international environments. Data are also compared with international regulatory guidelines.

Stage 4

Report preparation and presentation.

2. Project design

The sampling protocol was designed to determine background concentrations of dioxin and dioxin-like chemicals across a range of environments and land-uses. Sites that may have been subject to specific local contamination were specifically avoided.

Samples were collected in metropolitan (urban and industrial), agricultural and remote areas and from freshwater, estuarine and marine environments. Aquatic sediment samples were collected from 62 locations nationally. Two replicate samples were collected at each location, allowing the overall reproducibility of the sampling to be determined through analysis of a proportion of the 'B' samples. Where available, bivalves were collected in conjunction with sediment samples at sampling locations, allowing assessment of aquatic bioavailability and potential human exposure to dioxin-like chemicals. A total of 75 sediment samples and 18 bivalve samples were analysed. In addition, 23 samples of commercially available fish species were obtained from 15 mainly coastal locations. However, it was not practical for all of these to be associated with a specific sediment sampling location.

2.1 Selection of sampling locations

A key task of the project was to develop a meaningful and representative sampling regime for collection of the sediment and biota samples. Sampling sites were selected with consideration of the following:

- Covering the key regions including those defined by Environment Australia (now the Australian Government Department of the Environment and Heritage) (for details see Request for Tender, Environment Australia 2002).
- Covering aquatic environments where the concentrations of dioxin-like chemicals are influenced by three 'broad environments' (i.e. urban, agricultural and remote reference areas). Where possible, urban and industrial sections of rivers were differentiated.
- Providing information on exposure of humans to dioxin-like chemicals from the consumption of aquatic organisms.
- Providing data that could be integrated with other components of the National Dioxins Program, and thus potentially allow assessment of sources and fate of dioxin-like chemicals within the environment.

Sampling locations were distributed between the regions, covering all Australian States and Territories and included at least four each of a given land-use type in each region (i.e. industrial, urban, agricultural and remote). Sampling sites are listed in Table A1.

Sampling locations were situated throughout a catchment and in most cases, where practical and applicable, samples were collected from a remote site at the top of each catchment, an agricultural site within the mid-catchment and urban and industrial sites lower in the catchment. A number of remote marine samples were also collected.

The geographical distribution of catchments where sediment, bivalve and fish samples were collected is illustrated in Figure 2.1.

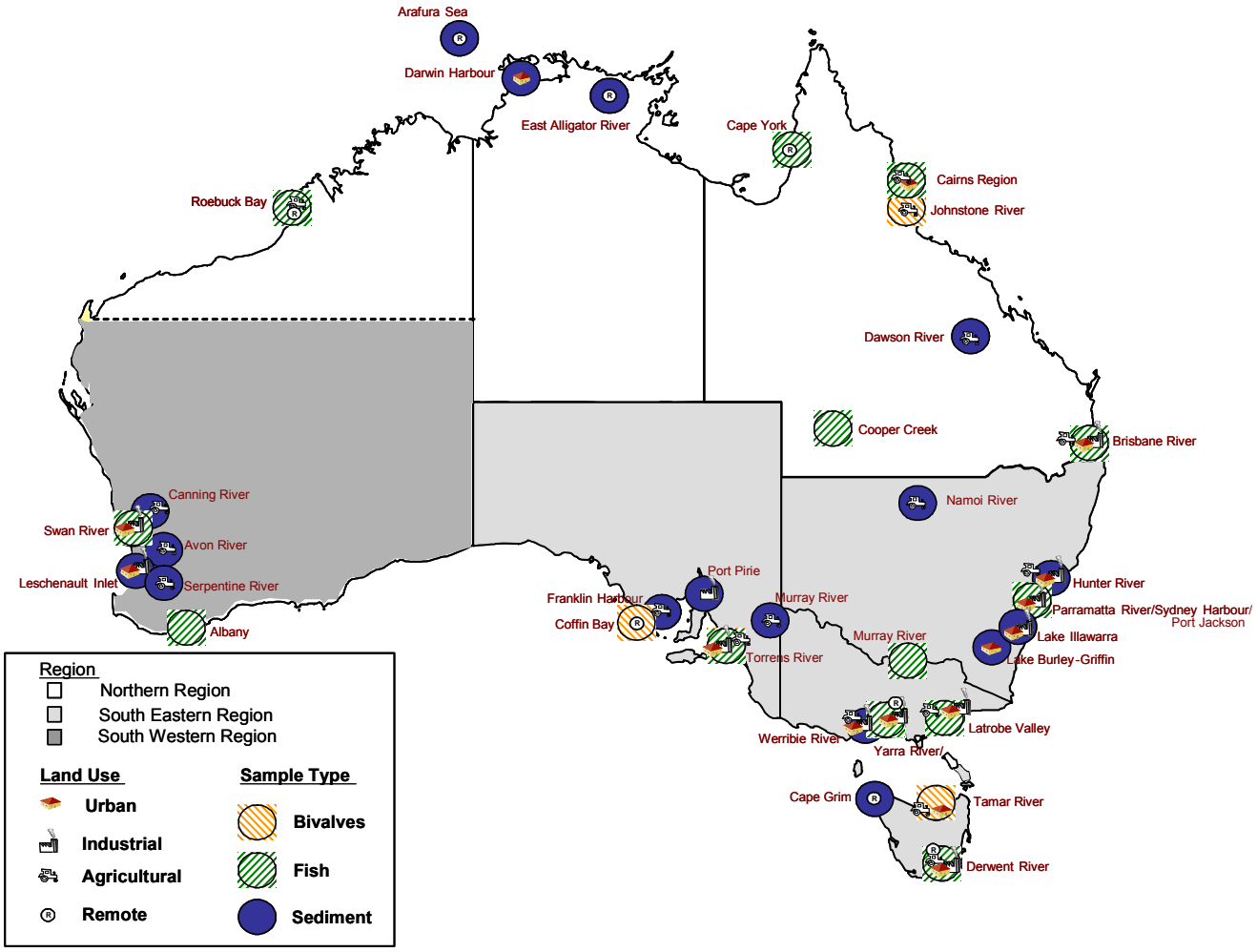


Figure 2.1 Geographical distributions where samples were collected.

2.2 Sample collection

2.2.1 Sampling personnel

The nation-wide sampling program was conducted by environmental professionals from various government departments and research organisations. Sampling personnel were responsible for the selection of sub-sampling sites at each sampling location according to prescribed study criteria.

Sampling personnel were provided with instructions specific to land-uses in catchments relevant to the allocated sampling location. This comprised audiovisual material along with

extensive instructions and detailed sampling site data sheets to ensure the sampling technique remained consistent between locations (refer to Appendix A).

2.2.2 Sampling strategy - sediment

A sampling strategy based on that used by Buckland et al. (1998) was employed. At each location two composite samples, 'A' and 'B', were collected. Each composite sample consisted of 10 pooled sediment cores (Figure 2.2). Composite sampling was used in order to cover the greatest possible area and thereby gaining a representative sample for a given site. The triangular sampling configuration was used to ensure the samples were randomly distributed. Where it was not practical to collect cores in this manner (e.g. narrow rivers and creeks), sampling personnel were instructed to collect samples 100 m apart and provide details of the configuration used. Replicate samples 'A' and 'B' were collected approximately 1 km apart within the same section of the water body and were used for the assessment of the reproducibility of the sampling strategy.

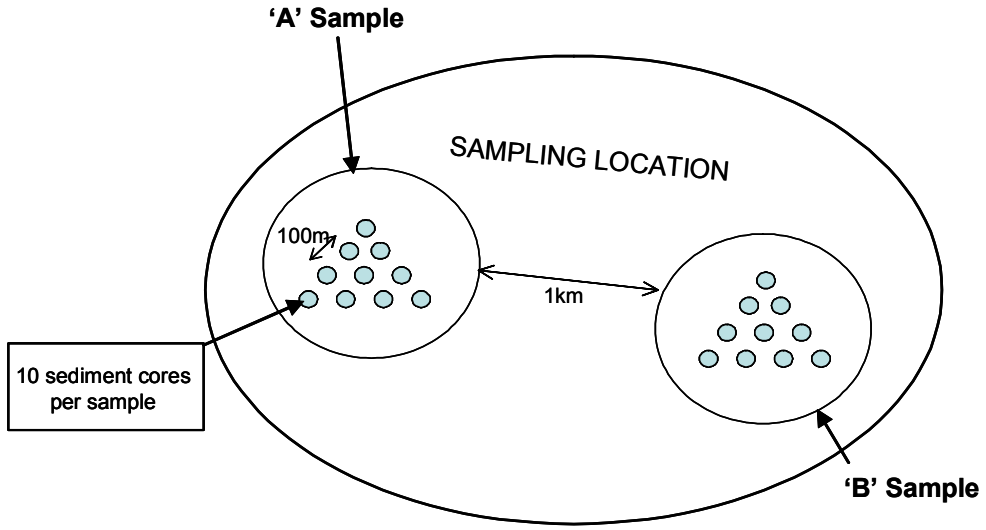


Figure 2.2 Sampling strategy for a given location.

Near-surface aquatic sediments represent the recent deposition of dioxin-like chemicals, and provide information on the present concentrations of these chemicals in the benthos and adjacent aquatic layer. However, the exact accumulation period is difficult to determine (and beyond the scope of this study) since the deposition rates or net flux of sediments is highly variable throughout Australia, even within a given bay, river or lake. Sediment samples were collected using a standardised coring device comprising aluminium tubes (15 cm length, 2.8 cm diameter) attached to a sediment coring device which collected a shallow profile (10 cm depth) of surface sediment (Appendix A). This design maintained a consistent methodology between sampling personnel and minimised the potential contamination problems associated with the handling of tubes (see Appendix C for details).

To obtain samples representing the background concentrations of dioxin-like chemicals in a particular region or environment, sediment sampling personnel were specifically instructed to avoid potential immediate point sources. In the aquatic environment such point sources include but are not limited to:

- Areas potentially subject to chemical spills
- Wooden structures that may have received chemical treatment (i.e. jetties, docks)
- Drains in general.

Sediment sampling personnel were instructed to avoid sampling in areas that may be directly affected by such localised sources in the aquatic environment. Criteria were provided for sampling site selection; sampling was avoided in areas within:

- 200 m proximity of any specific major industrial plant, chemical factory or major port facility that serves activities other than passenger transport
- 50 m proximity of jetties and moorings
- 50 m proximity of wooden structures, buildings, fences, poles or any man-made structures
- 50 m proximity of any drain except if the drain is natural (in remote areas) or drains in agricultural sites (i.e. no buildings or paved areas).

Dredged areas were also avoided where possible. Where dredged areas could not be avoided, samples were collected along the edge of the dredged area rather than directly within the dredged channel (which may provide sediment representative of a different depositional timeframe).

In order to avoid sampling bias, sample collectors were specifically instructed to select aquatic sampling sites irrespective of the availability of biota.

2.2.3 Sampling strategy - biota

Where available, bivalves were collected in conjunction with the 'A' sample at each of the sampling locations. Bivalves were chosen to represent chemical concentrations in aquatic biota since they are well established as practical sentinel organisms for monitoring aquatic contaminants (Phillips and Rainbow 1993). Approximately 30 individuals or a minimum of 200 g of flesh (fm) was collected and pooled to make one composite sample for chemical analysis. A total of 18 bivalve composite samples were analysed for this study.

Evaluation of dioxin-like chemicals in commercially available fish samples was also included in this study. A total of 23 fish composite samples were collected, and were preferentially sampled from sediment sampling locations, however, this was not always achievable. Each fish sample consisted of flesh from five adult fish caught in the same location. Where available, flathead (*Platycephalus spp*.) were obtained, along with another one or two locally caught and consumed species (see Table E2). Fisheries agencies or commercial fishers collected the fish samples for this study.

2.3 Analysis, statistics and data quality

2.3.1 Analysis

Upon receipt of a sample by ENTOX, sediment was extracted from coring tubes, pooled to form a composite sample, and homogenised. Composite samples were freeze-dried, sieved through a 2mm sieve and placed in individual solvent washed jars for transported to AGAL for analysis. Precautions taken to avoid contamination of samples are detailed at Appendix C.

The analytical methodology for the determination of PCDD/PCDF and PCB is based on quantification of the analytes through isotopic dilution techniques and is modified from those described by the US EPA methods 1613B and 1668A, respectively. For further details on the analytical methodologies and list of analytes see Appendix B.

Total organic carbon (TOC) was determined in the Queensland Health Scientific Services (QHSS) laboratory according to a standardised procedure (QHSS, 1996) (see Appendix B).

For all samples, data with quantified analytes were reported to two or three significant figures, whereas limit of detection data for non-quantified analytes were reported to one significant figure only. Where censored data (non-detects) were involved, total TEQs were calculated both with below limit of detection values excluded and also with half limit of detection values substituted.

2.3.2 Database and statistical analysis

A database (Microsoft Access) was developed for storage and retrieval of data pertaining to the sampling location and chemical analysis.

Statistical analysis was carried out using XL-Stat (supplementary Microsoft Excel 2000 package) and SYSTAT V7.0 statistical analysis package (Wilkinson, 1996). In this study, the median concentration or TEQ is often presented rather than the mean, since the median is a "resistant" measure that is not sensitive to extreme observations, whereas the mean may be raised or lowered substantially by a single high or low sample result (Box 1).

Box 1. Means and medians

Means and medians are two alternative ways to define the middle or "average" value for a set of samples.

The arithmetic **mean** is the sum of all values divided by the number of samples.

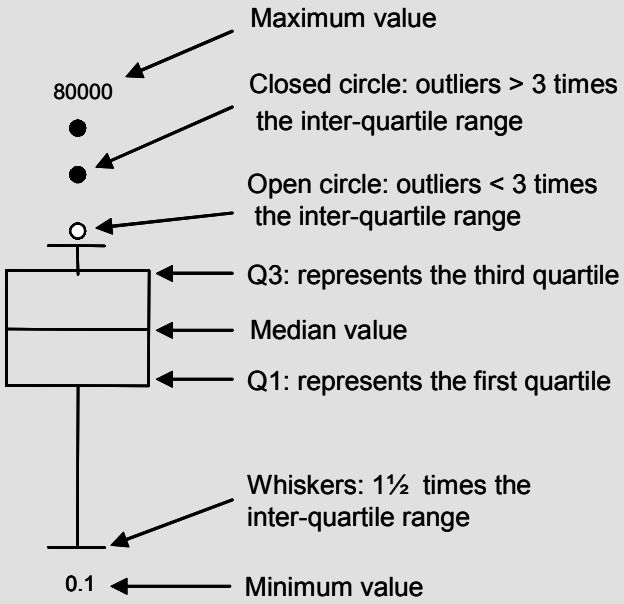
The **median** is the middle value of a set of samples arranged in order from the lowest to the highest. If there is an even number of samples then the median is the mean of the centre two values in the ordered list.

Standard box and whisker plots were used for data presentation (Box 2). Two-way analysis of variance (ANOVA) was used to explore differences in mean TEQ_{DF+PCB} concentrations between sampling sites (freshwater, estuarine and marine sites) and adjacent land-use type (urban/industrial, agricultural and remote). Data were inspected for gross deviations from normality prior to analysis and where necessary, Log_{10} transformed.

Box 2. Box and whisker plots

Box and whisker plots are a widely accepted way of presenting environmental data. They show where the data points are concentrated (the box) and the outlying values (the whiskers, open and closed circles). Box plots are often used to compare several sets of data.

Here we use a plot where the boxes represent the 25th and 75th percentiles. The top of the box in these plots is the 75th percentile (75% of the data fall below this line), while the bottom of the box represents the 25th percentile (25% of the data fall below this line). The line in the middle of the box represents the median (50% of the data fall above and 50% below this number).



The whiskers on the box extend to data points that are up to 1½ times the Inter Quartile Range (IQR). The IQR is defined as the difference between the 75th and the 25th percentiles, and is equal to the range of about half the data. Outliers which are less than three times the IQR are shown as open circles, while those greater than three times the IQR are shown as closed circles. The statistical and graphical package XL-Stat was used to produce all box plots and calculate percentiles.

2.3.3 Data quality

A number of procedures were implemented to avoid sample contamination. A chain of custody was established with a suitable labelling system to ensure that no samples were mixed up or misplaced. For a detailed description of sample handling and quality assurance refer to Appendix C.

The study design allowed for the determination of both sampling and analytical reproducibility. The overall reproducibility of the sampling was determined through analysis of a selection of the replicate 'B' samples collected at each sampling location. A total of thirteen replicate 'B' samples were selected for analysis. Half of these were selected randomly, covering each environment (freshwater, estuarine and marine). The remaining replicates were selected from samples that were found to have unusual results from the analysis of the 'A' sample (for example, high concentrations or unusual congener profiles). It is important to note that 'B' samples corresponding to any 'A' samples that showed very low concentrations of dioxin-like chemicals were excluded from selection for

re-analysis, because re-analysis was unlikely to provide additional information. Hence, the selections of 'B' samples were strongly biased towards urban and industrial sites where point sources are more likely to be present.

For each sampling location the normalised difference (Box 3) between 'A' and 'B' samples was determined for corresponding congeners detected in both replicates. The normalised differences were then averaged to achieve a mean normalised difference between the two samples collected at one location (Table C3 for results and Tables D1, D2 and D3 for the mean and standard deviations of the replicate analyses). This comparison demonstrated that the sampling reproducibility was highly variable and the average of all thirteen mean normalised difference values was approximately 67%. This suggests that A and B samples are grossly different in contamination levels and may indicate that a historical or current point source exists near one of the sites where paired 'A' and 'B' samples were collected. If this is the case, it may indicate spatial variation in the levels found that reflect insufficient designation of sampling locations away from the influence of point sources, and consequently implications for conclusions drawn from the data generated by the study regarding the background concentrations of dioxin-like chemicals.

Box 3. Normalised differences

In this report, comparisons between replicate samples or replicated analysis have been made using the normalised difference. The normalised difference between two samples is mathematically defined as:

$$\text{normalised difference (\%)} = \frac{\left|\text{value a} - \text{value b}\right|}{\frac{(\text{value a} + \text{value b})}{2}} \times 100$$

The table below provides a demonstration of the normalised difference (ND) values that would result from a range of differences in sample values.

Examples of normalised differences (ND) that would result from different sample values.

Sample A (pg g^{-1} dm)	Sample B (pg g^{-1} dm)	ND %
1.0	1.2	18
1.0	1.5	40
1.0	2.0	67
1.0	3.0	100
1.0	10.0	160
1.0	100.0	200

The mean normalised difference expresses the average normalised difference for all 29 congeners.

The analytical reproducibility was determined through a combination of methods. Firstly, the reproducibility of analysis conducted for the parallel National Dioxins Program soil study was considered applicable to the aquatic study since chemical analysis of soil and sediment samples are analogous laboratory procedures. In the soil study, the analytical reproducibility was determined through the re-analysis of six 'A' soil samples. Each of the 'A' samples, selected for re-analysis, was split into two where both portions were analysed by AGAL but at different times. The results indicated good agreement in the repeated

analysis of the samples with respect to the concentration expressed as TEQ, ∑PCDD/PCDF or ∑PCB, although the number of detectable congeners varied substantially between the replicate analyses in two of the samples. Overall the mean normalised difference between congeners detected in both the original and duplicate varied between 14% and 39%. For details see Müller et al. (2003).

Secondly, an interlaboratory calibration (laboratory quality control) was conducted in which eight 'A' samples analysed by AGAL were re-analysed by an independent second laboratory (Ministry of the Environment, Laboratory Services Branch, Toronto, Ontario, Canada). The comparison between interlaboratory data was assessed by calculating the normalised differences between the original sample and the reanalysed sample for all detectable congeners. The overall mean normalised difference was approximately 33% (see Table C4 for the results of the analysis). It can be noted that there was no systematic differences between the two laboratories (i.e. neither laboratory was consistently higher or lower for any compounds) in a given sample (refer to Table F1 for the congener profiles of the eight samples from the two laboratories). The criteria used to select samples for re-analysis were the same as those used for sampling reproducibility (see above, this section).

A comparison of the uncertainty related to the reproducibility of sampling (mean normalised difference ranging from 17% to 167%) against the reproducibility of chemical analysis (mean normalised difference ranging from 12% to 62%) suggests that the error associated with the chemical analysis is comparatively minor and not as relevant in the overall interpretation of the data as the potential for uncertainty relating to variability attributed to sampling effects such as insufficient designation of sampling locations away from the influence of point sources.

3. Dioxin concentrations in Australian aquatic environments

The following section provides an analysis of the concentrations of dioxin and dioxin-like chemicals in the aquatic environment in Australia. In particular, the concentration of dioxin and dioxin-like chemicals and the contamination profiles (i.e. concentrations of the different congeners) in sediment, bivalve and fish samples representative of freshwater, estuarine and marine environments.

3.1 Dioxin-like chemicals in Australian aquatic sediments

Seventy five different sediment samples were analysed for 29 individual dioxin-like chemicals as well as the sum of the tetra- to octachlorinated PCDD/PCDF homologues. In all aquatic sediment samples PCDD/PCDF and PCB chemicals were detectable and a summary of the results is presented in Table 3.1. This includes the sum and the respective WHO_{98}-TEQs for all samples combined, for the different environments and for the different regions. The distribution of dioxin-like chemicals across Australian aquatic sediments was evaluated with consideration of different aquatic environments (fresh, estuarine, marine), geographical distribution (States and Territories) as well as land-uses (urban/industrial, agricultural and remote). In addition, patterns were evaluated using congener and homologue profiles (see Box 4) and levels of dioxin-like chemicals in Australian environments found in this study are compared with previous Australian studies and published international data. Notably, this study found relatively large variability in the concentration of dioxins betweens different samples representing the same location. Few studies of environmental levels of dioxin-like chemicals have evaluated sampling reproducibility, particularly studies of background levels, as distinct from studies relating to the influence of known point sources. Accordingly, it is likely that data from other studies of background levels would be similarly affected in terms of high spatial variability attributable to the influence of point sources close to sampling locations.

Table 3.1 Summary of PCDD/PCDF and PCB concentrations

		All samples[1]	Salinity			Region		
			Freshwater (n=33)	Estuarine (n=30)	Marine (n=12)	N	SE	SW
∑PCDD/F Exc. LOD values	Min.	ND	ND	7.6	ND	ND	ND	0.40
	Max.	110000	3500	110000	2500	4900	11000	1600
	Median	250	150	1500	33	270	340	24
	Mean	5700	490	14000	460	960	8400	250
WHO_{98}-TEQ_{DF} Exc. LOD values	Min.	0.0000018	0.00054	0.0038	ND	0.0020	0.0000018	0.0014
	Max.	520	2.2	510	3.2	6.4	520	5.4
	Median	0.21	0.072	2.0	0.0067	0.17	0.38	0.10
	Mean	13	0.32	30	0.45	0.85	19	1.2
WHO_{98}-TEQ_{DF} Inc. ½ LOD values	Min.	0.029	0.039	0.063	0.025	0.029	0.030	0.066
	Max.	520	2.5	510	3.5	6.8	520	5.5
	Median	0.46	0.18	2.2	0.11	0.25	0.51	0.19
	Mean	**13**	**0.44**	**30**	**0.59**	**0.98**	**19**	**1.4**
∑PCB Exc. LOD values	Min.	ND	ND	ND	0.018	ND	ND	ND
	Max.	28000	1300	28000	440	6100	28000	1400
	Median	13	6.2	170	8.1	1.1	39	40
	Mean	1300	160	3200	79	440	1900	350
WHO_{98}-TEQ_{PCB} Exc. LOD values	Min.	ND	ND	ND	0.0000018	ND	ND	ND
	Max.	14	0.88	14	0.66	1.9	14	0.88
	Median	0.0032	0.0012	0.11	0.0011	0.00021	0.0070	0.0093
	Mean	0.72	0.087	1.7	0.075	0.14	1.0	0.23
WHO_{98}-TEQ_{PCB} Inc. ½ LOD values	Min.	ND	0.0014	0.0026	0.00084	0.0018	ND	0.0024
	Max.	14	0.88	14	0.66	1.9	14	0.88
	Median	0.014	0.011	0.11	0.0090	0.0062	0.016	0.013
	Mean	**0.73**	**0.093**	**1.7**	**0.080**	**0.14**	**1.0**	**0.23**
WHO_{98}-TEQ_{DF+PCB} Exc. LOD values	Min.	ND	0.0020	0.0038	0.0000018	0.0016	ND	0.0014
	Max.	510	2.9	520	3.9	4.5	510	4.6
	Median	0.18	0.072	2.1	0.0085	0.16	0.30	0.10
	Mean	12	0.41	32	0.53	0.71	18	0.99
WHO_{98}-TEQ_{DF+PCB} Inc. ½ LOD values	Min.	0.025	0.042	0.066	0.029	0.025	0.029	0.063
	Max.	510	3.1	520	4.2	4.9	510	4.8
	Median	0.34	2.0	2.3	0.11	0.25	0.48	0.18
	Mean	**12**	**0.53**	**32**	**0.67**	**0.84**	**19**	**1.2**

[1] concentrations in pg g^{-1} dm.

3.1.1 Concentration of dioxin-like chemicals in sediments from fresh, estuarine and marine waters.

The sampling locations for the aquatic study were differentiated on the basis of salinity into locations categorised as freshwater, estuarine and marine waters. For the purpose of this report, the aquatic sediment data are expressed predominantly as dry mass (dm) concentrations. Expression of concentration on a total organic carbon (TOC) basis was used in some examples to evaluate outliers and overall trends. A summary of the measured concentrations of dioxin and dioxin-like chemicals on a dm and a TOC basis collected in sediments from freshwater, estuarine and marine locations are presented in Table 3.2.

Table 3.2 Summary of measured concentrations of PCDD/PCDF and PCBs

	Freshwater (n=33)		Estuarine (n=30)		Marine (n=12)	
	Dry mass basis (dm)	TOC basis	Dry mass basis (dm)	TOC basis	Dry mass basis (dm)	TOC basis
TEQ_{DF+PCB} Inc.½ LOD values (pg TEQ g^{-1})	0.2 (0.042-3.1)	42 (1.5-340)	2.3 (0.66-520)	200 (4-16000)	0.12 (0.029-4.2)	92 (18-540)
TEQ_{DF+PCB} Exc. LOD values (pg TEQ g^{-1})	0.072 (0.002-2.9)	16 (0.22-310)	2.1 (0.0038-520)	170 (1.4-16000)	0.0085 (0.000002-3.9)	8.4 (0.0030-525)
∑PCDD/PCDF Exc. LOD values (pg ∑PCDD/-F g^{-1})	150 (<4-8500)	15 000 (<240-300000)	1 500 (7.6-110000)	130 000 (2700-3400000)	33 (<3-2500)	21 000 (<5000-440 000)
∑PCB Exc. LOD values (pg ∑PCB g^{-1})	6.2 (<7-1300)	510 (<1800-210000)	170 (<14-28000)	17 000 (<5000-3600000)	8.1 (<8-140)	4 200 (<13000-100000)

A 2-way ANOVA (Table 3.3) followed by a Tukey (HSD) test showed that significant differences exist between levels of TEQ values of dioxin-like chemicals across sampling locations with different catchment-associated land uses, with urban/industrial sites having significantly higher TEQ levels than samples collected adjacent to remote or agricultural regions (Table 3.4). However, TEQ values of samples collected from freshwater, estuarine and marine sites were not significantly different from each other.

Table 3.3 Results of 2-way ANOVA, expressed as TEQ_{DF+PCB}.

Factor	df	F ratio	P
Sample type (marine, estuarine, freshwater)	2	1.7	0.19
Sample location (remote, agricultural, urban/industrial)	2	4.2	0.019
Interaction	4	0.65	0.63

Table 3.4 Results of Tukey, multiple comparison of TEQ_{DF+PCB}[1]

Land-use	
Remote Agricultural	Urban/Industrial

Median concentrations of dioxin-like chemicals expressed as TEQ values (including half LOD values) in sediments from freshwater, estuarine and marine regions were 0.2, 2.3 and 0.12 pg TEQ g^{-1} dm and 42, 200 and 92 pg TEQ g^{-1} TOC, respectively (Table 3.2, Figure 3.1 and Figure 3.2). It is important to note that the datasets incorporate a few higher values or outliers, and these were included in the statistical analyses, and associated figures and tables. Such values are to be expected since the contamination of the environment varies spatially depending on the proximity to a point source, even though these were avoided during sampling so far as possible. These outliers also indicate that the data population is not normally distributed (i.e. the mean and median are not equal). Analysis of estuarine samples identified a range of outliers all being sampled from locations in the Sydney area, with the greatest concentration of 520 pg TEQ g^{-1} dm in the samples from the lower Parramatta River estuary. The estuarine data are more coherent if expressed on a TOC basis although the sample from the lower Parramatta River estuary remains an outlier with 16,000 pg TEQ g^{-1} dm TOC. The analysis of the freshwater samples showed that both 'A' and 'B' samples from the Canning River in WA were the highest in concentration when expressed on a dry mass basis (2.2 and 3.1 pg TEQ g^{-1} dm). By contrast, if data are expressed on a TOC basis the sample from the lower Torrens River in Adelaide is the highest value in the dataset with levels of 340 pg TEQ g^{-1} TOC. For the Marine locations the key outlier originates from the central part of Port Phillip Bay near Melbourne with 4.2 pg TEQ g^{-1} dm or if expressed on a TOC basis, 540 pg TEQ g^{-1} TOC.

The data can also be evaluated by investigating the sum of the PCDD/PCDF. Both on a dry mass and a TOC basis the results show elevated levels of PCDD/PCDF in estuaries compared to the freshwater and marine samples (Figure 3.3 and 3.4). Interestingly, on a dry mass basis a range of outliers are again identified, including samples from the Lower Torrens and Parramatta rivers for the freshwater samples, the Parramatta River estuary for the estuarine samples and the Port Phillip Bay for the marine sample. Notably, if data are expressed on a TOC basis no major outliers are observable indicating that the contamination is in part correlated to TOC levels.

For dioxin-like PCB the estuarine sediment samples also showed elevated levels compared to the samples from freshwater and marine locations (Figure 3.5 and 3.6). In freshwater samples, the sample from Lake Burley-Griffin (Canberra) showed the highest concentrations of PCB irrespective of whether results were expressed on a dry mass or TOC basis (1,300 pg $\sum$PCB g^{-1} dm and 210,000 pg $\sum$PCB g^{-1} TOC). When the PCB data are expressed on a TOC basis the highest concentrations of PCB from all samples is a sample collected from the lower Brisbane River near the centre of Brisbane with a value of 3,600,000 pg $\sum$PCB g^{-1} TOC (Figure 3.6).

[1] Those joined by a thick underline were not significantly different.

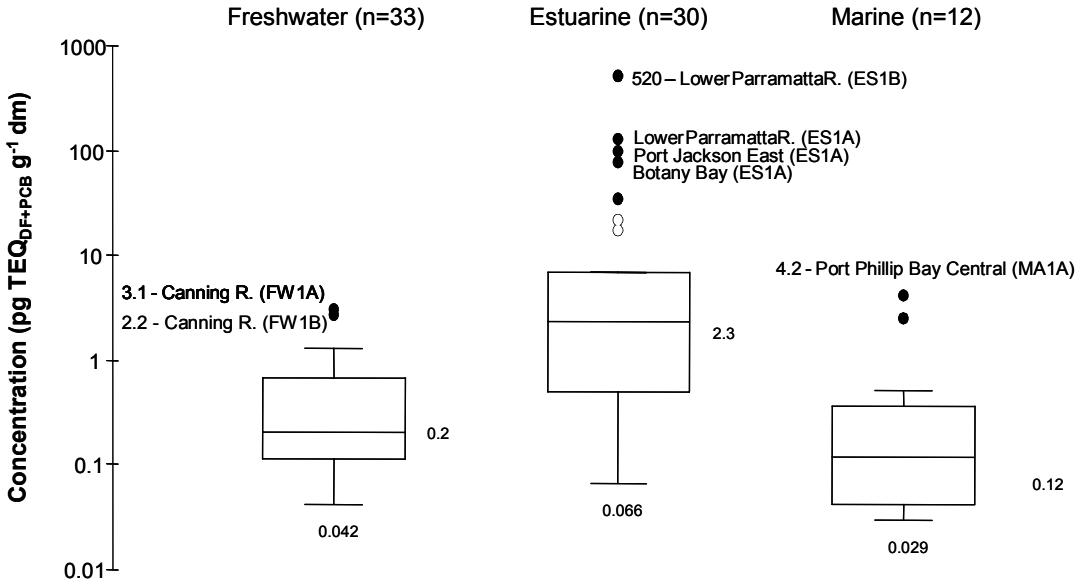


Figure 3.1 Concentration for PCDD/PCDF and PCB[2].

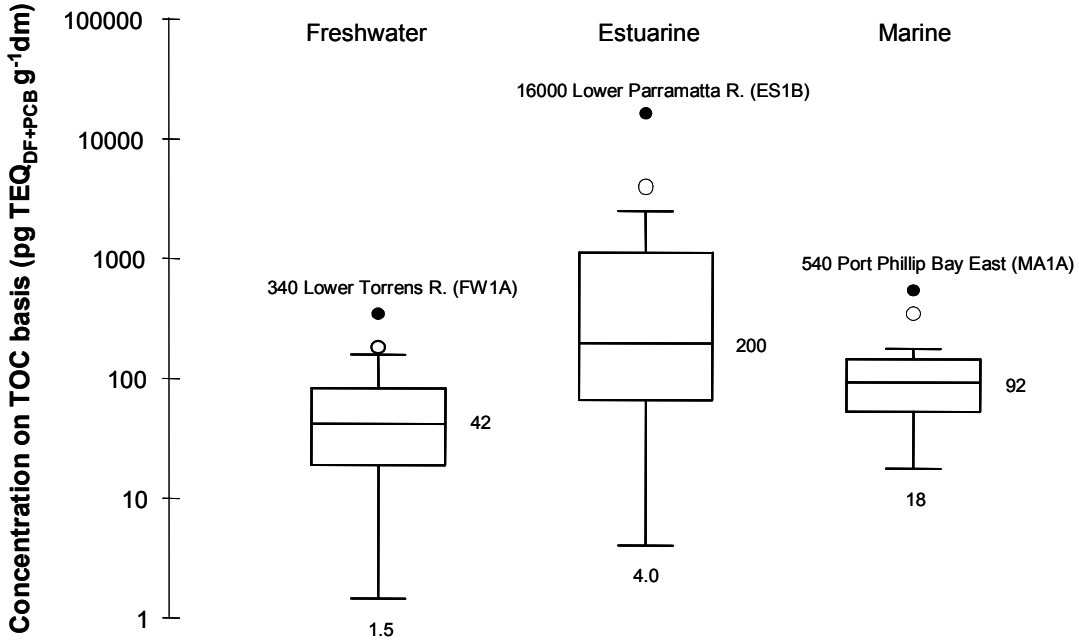


Figure 3.2 Concentration of PCDD/PCDF and PCB on a TOC basis[2].

[2] Including half LOD values.

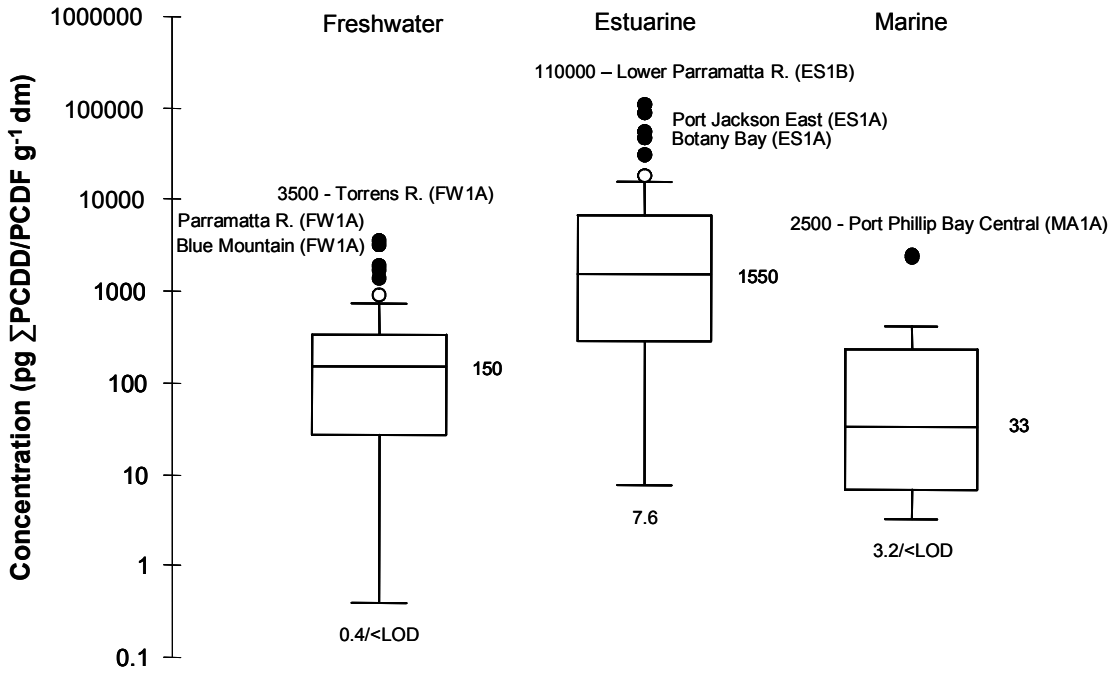


Figure 3.3 Concentration of ∑PCDD/PCDF expressed on a dry mass basis[3].

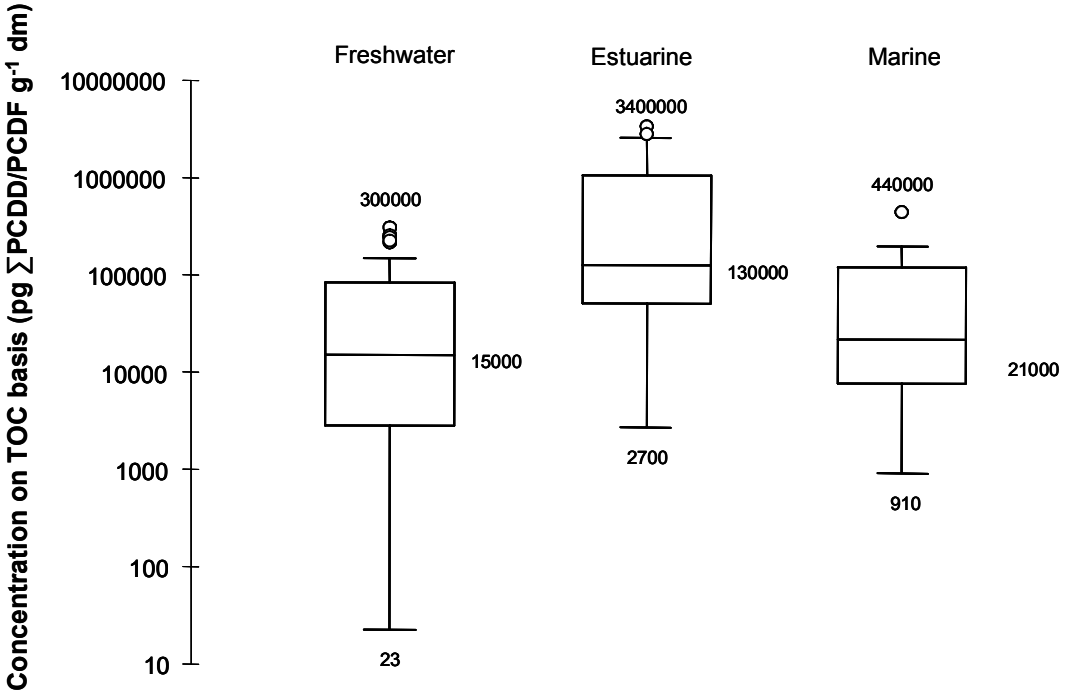


Figure 3.4 Concentration of ∑PCDD/PCDF on a TOC basis[3].

[3] **Excluding LOD values.**

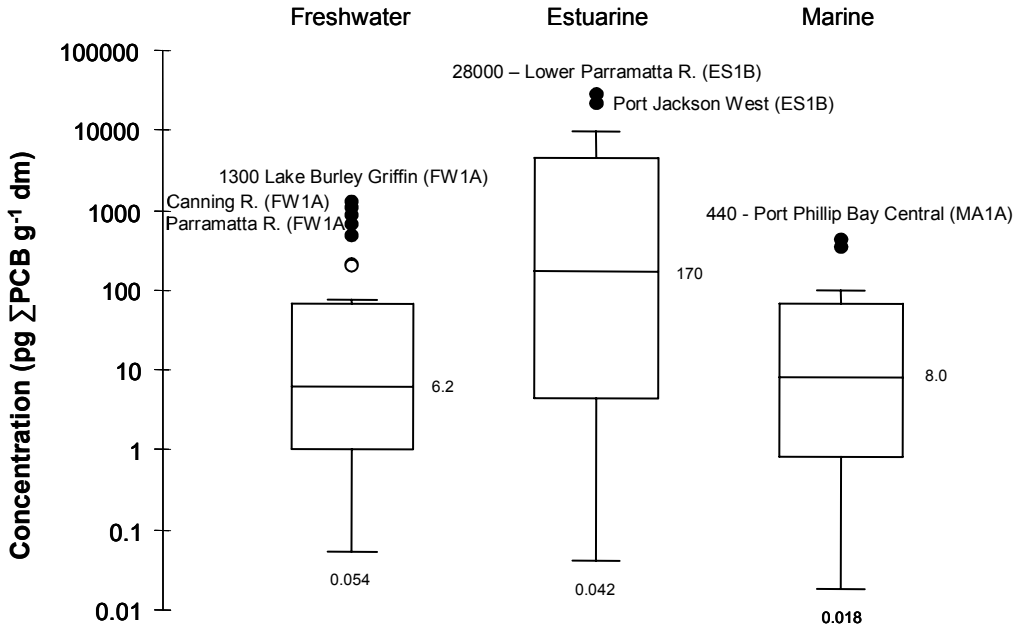


Figure 3.5 Concentration of ∑PCB expressed on a dry mass basis[3].

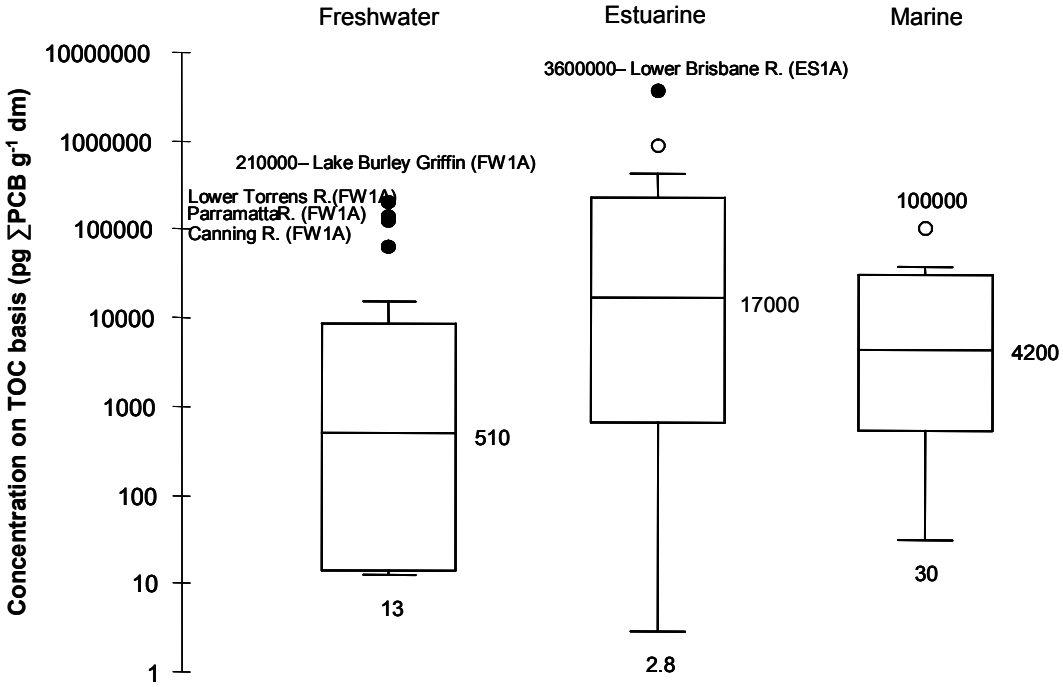


Figure 3.6 Concentration of ∑PCB expressed on a TOC basis[3].

3.1.2 Concentration of dioxin-like chemicals in different land-use types

An aim of the study was to determine the typical background concentration of dioxin-like chemicals in environments that are influenced by various land-use types. For the aquatic environment in particular it is difficult to differentiate between land-use types that influence sediment concentrations at a particular location. For the purpose of this study we broadly differentiated sampling locations into remote, agricultural and urban/industrial land-use types based on the dominant land-use type situated near the sampled locations. The data indicate concentrations are generally higher in sediment samples collected from urban/industrial locations with a median level (1.3 pg TEQ g^{-1} dm) about one order of magnitude greater than those in sediments collected from remote or agricultural locations irrespectively if data are expressed on a dry matter basis (Figure 3.7) or total organic carbon basis.

Concentrations of dioxin-like chemicals (expressed as TEQ) in sediments collected from urban and industrial locations were significantly higher than TEQ concentrations in samples collected from agricultural and remote environments (see Table 3.3 and 3.4 for statistical results).

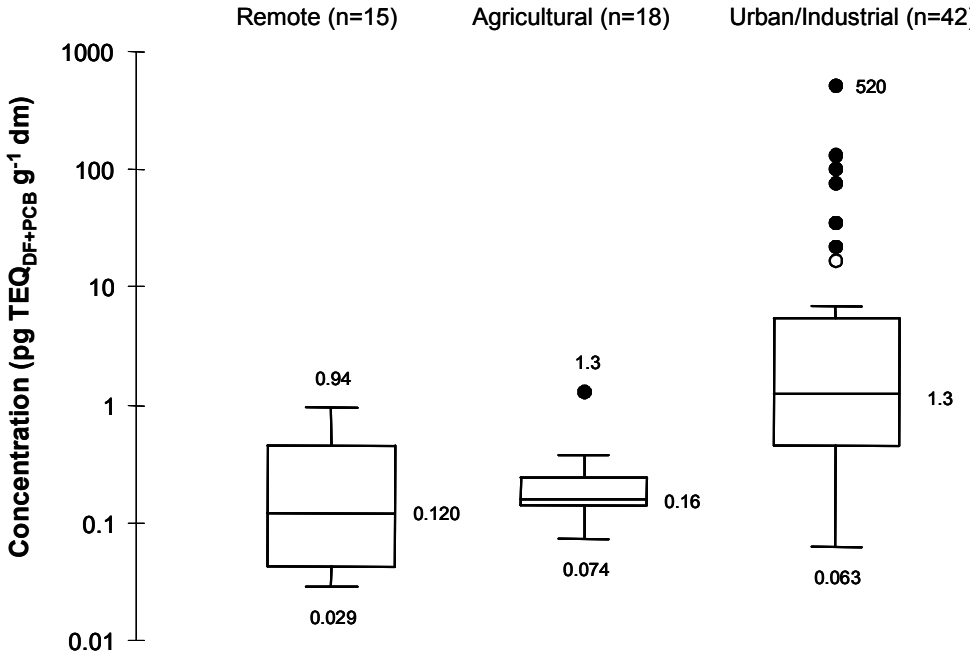


Figure 3.7 Concentration of PCDD/PCDF and PCB in sediment samples.

3.1.3 Sediment concentration of dioxin-like chemicals in different States & Territories of Australia

Sediment concentrations can also be investigated on the basis of regional distribution. In Figure 3.8 to Figure 3.14 the concentrations of PCDD/PCDF and PCB, expressed as TEQs on a dry mass basis, are presented for each state. Samples within each box are from the same catchment. Note that axes differ for one figure to the next and in Figures 3.10 and

Figure 3.11 the axes are different for different catchments. All TEQs have been calculated excluding LOD values.

Three samples were analysed from the Northern Territory including the Arafura Sea, the Port of Darwin and the East Alligator River. Concentrations were relatively low with highest levels in the Port of Darwin with 0.89 pg TEQ g^{-1} dm.

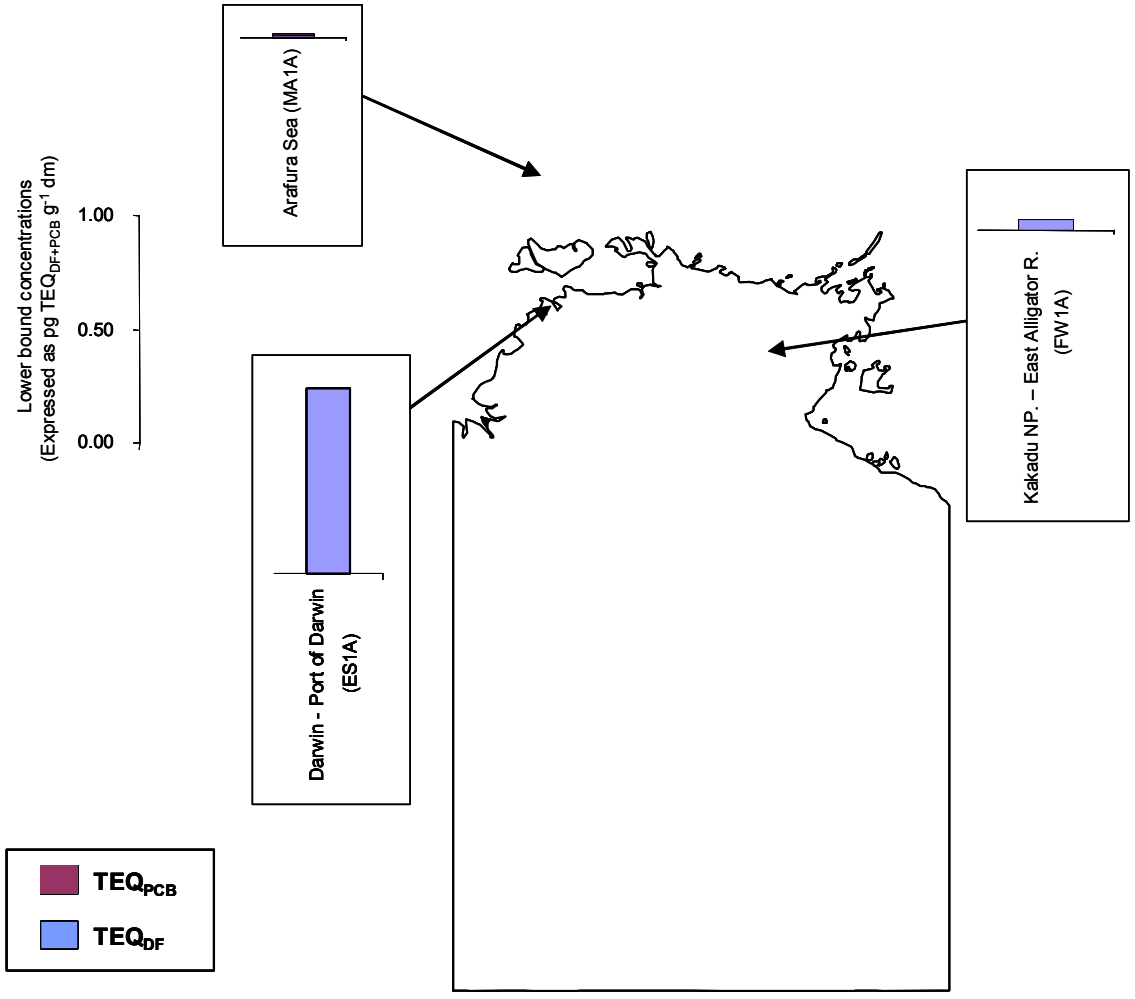


Figure 3.8 NT sediment sampling locations and the corresponding TEQ.

Eleven sediment samples from Queensland were analysed, including samples from the Johnstone River catchment, in the wet tropics, and the Brisbane River catchment from the upper Brisbane River to Moreton Bay in the urbanised south-eastern part of the state.

Concentrations of dioxin-like chemicals were generally low in samples from the remote locations (Heron Island, Upper Johnstone and Endeavour River) as well as the agricultural regions including cotton growing area and the Johnstone River. However, the Lower Johnstone River location, where agriculture is the dominant land-use, showed elevated levels when compared to the remote Upper Johnstone River location.

The highest levels of dioxin-like chemicals in sediment samples in Queensland were found in the city reaches of Brisbane with about 4.9 pg TEQ g^{-1} dm. It is interesting to note that dioxin-like PCB contributed significantly to the total TEQ value for the sample from the Brisbane River indicating a local source of dioxin-like chemicals exists in the lower Brisbane River.

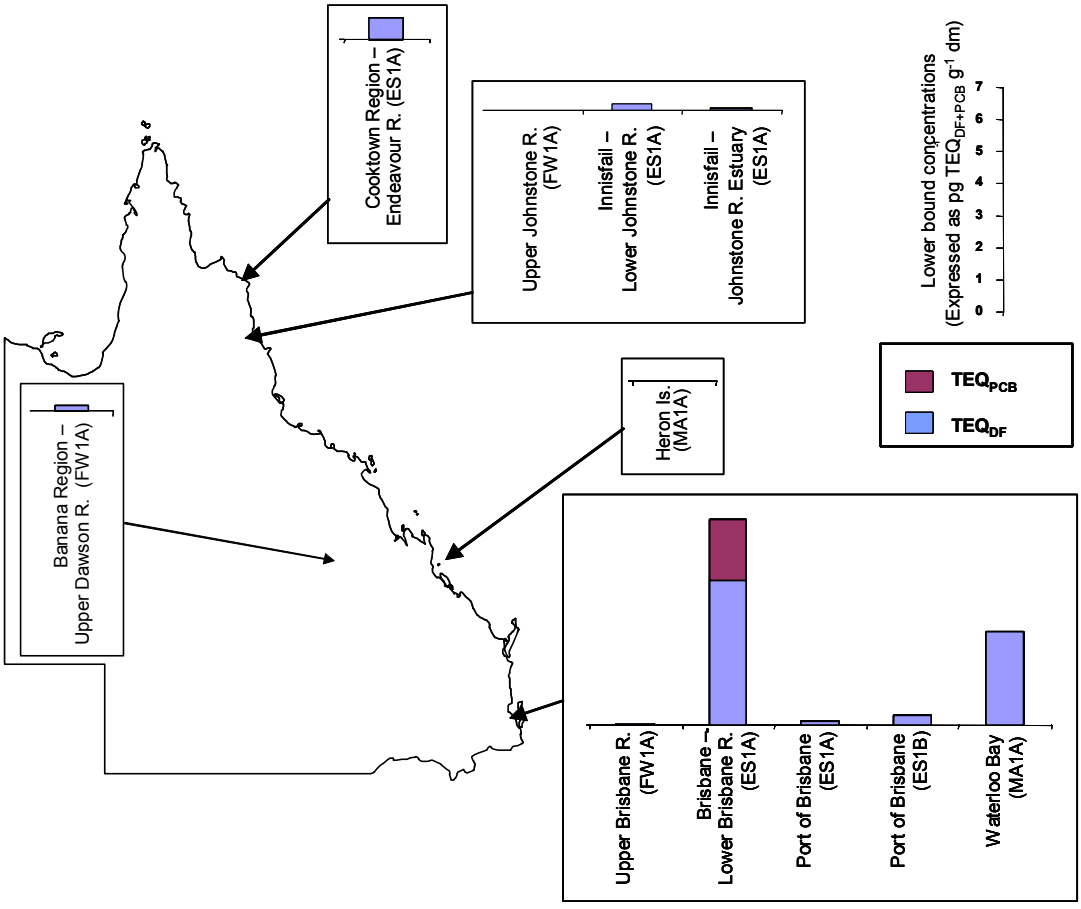


Figure 3.9 Qld sediment sampling locations and the corresponding TEQ.

Seventeen sediment samples were analysed from New South Wales and the Australian Capital Territory, including the Hunter River catchment from the Upper Hunter to the Port Hunter near Newcastle and from the relatively remote rivers in the Blue Mountains west of Sydney and the Parramatta River to Port Jackson (Sydney Harbour).

Concentrations were generally low in the sample from the cotton growing region as well as the samples from the Hunter River catchment. The highest concentrations within the Hunter River were found in the estuary. The levels in the sample from Lake Burley Griffin in Canberra showed low levels of PCDD/PCDF with PCB contributing about 80% of the total TEQ (lower bound). Levels of dioxin-like chemicals in samples from Lake Illawarra near Wollongong were about 6 pg TEQ g^{-1} dm.

As expected, the sediments analysed from the Parramatta River catchment showed that the upper Parramatta River was relatively low in comparison to the highest concentrations

found in the highly industrialised lower estuary of the Parramatta River and the western parts of Port Jackson. It is likely that the sediment concentrations found in the Parramatta River reflect the influence of heavily contaminated sediments of Homebush Bay. Much lower concentrations were seen again at the mouth of Port Jackson. Notably, levels of dioxin-like chemicals in sediments from the lower Parramatta River and western section of Port Jackson were consistently high (between 70 and 520 pg TEQ g^{-1} dm). Concentrations in samples from Botany Bay were also relatively high (35 and 22 pg TEQ g^{-1} dm) when compared to all other samples except those from the Parramatta/Port Jackson estuary.

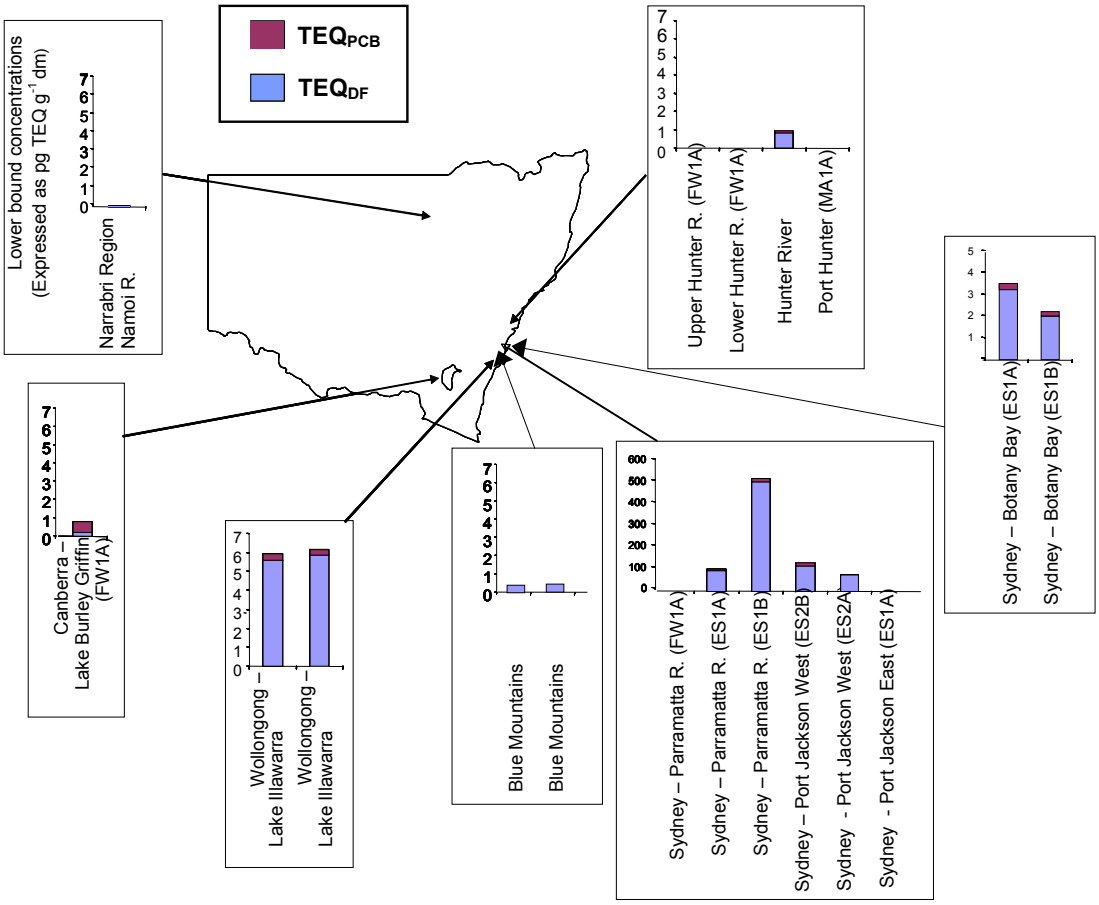


Figure 3.10 NSW and ACT sediment sampling locations and the corresponding TEQ.

Victorian sediment samples were collected from three catchments: the Latrobe River and Gippsland Lake, as well as the Yarra and Werribee Rivers into Port Phillip Bay. For the Latrobe River/Gippsland Lake transect, the highest concentrations were determined in the estuarine Lower Latrobe River with concentrations up to about 2.9 pg TEQ g^{-1} dm. In the Yarra River, the highest concentrations were detected in the Lower Yarra River near the City of Melbourne (17 and 1 pg TEQ g^{-1} dm) but levels were also elevated in the central

part of Port Phillip Bay (3.2 and 2.5 pg TEQ g^{-1} dm) compared, for example, to the eastern part of Port Phillip Bay (0.52 pg TEQ g^{-1} dm).

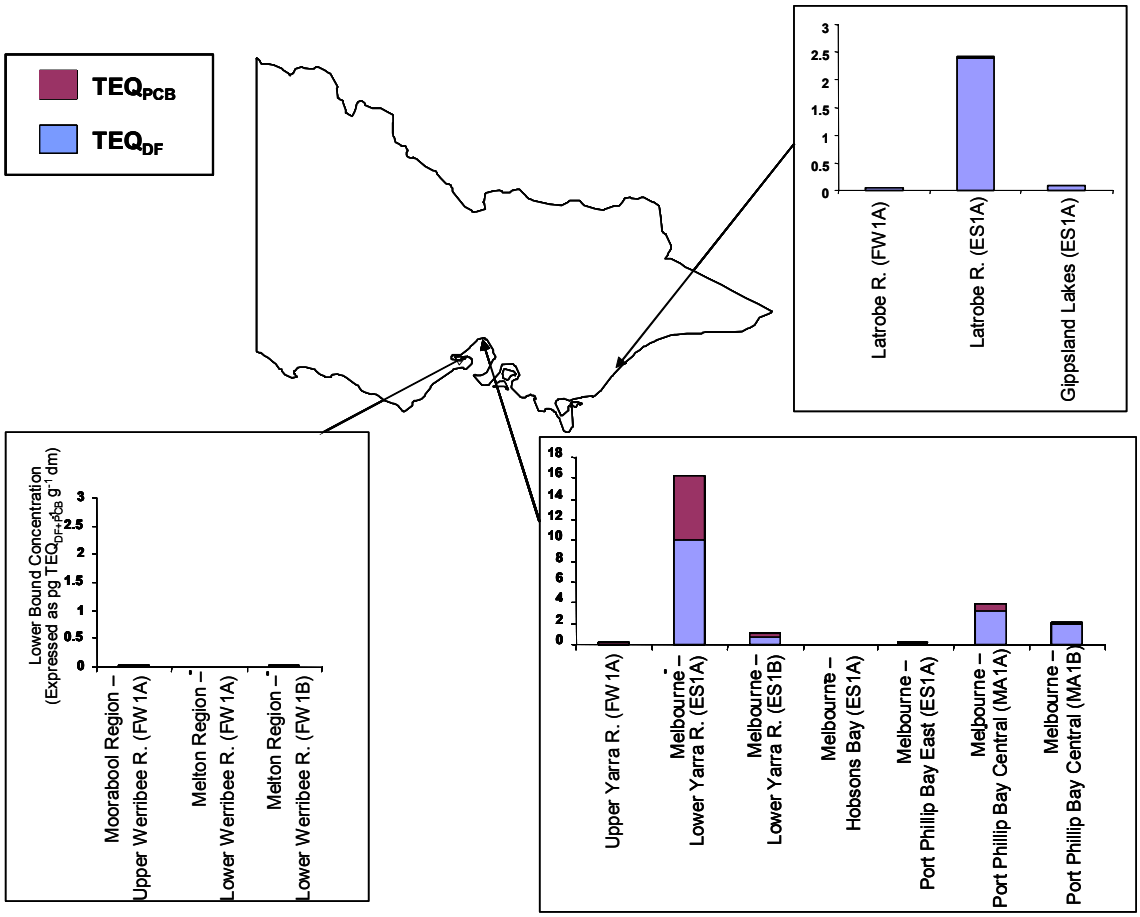


Figure 3.11 Vic sediment sampling locations and the corresponding TEQ[4].

In Tasmania, samples were collected from remote Cape Grim, and a freshwater dam and estuarine site in the Tamar near Launceston, as well as from remote Lake St. Clair, and from the Upper Derwent River down to the Derwent estuary. Concentrations of dioxin-like chemicals were generally low in all samples with the highest levels in the Lower Derwent River (upper estuary) near Hobart (4.9 pg TEQ g^{-1} dm).

[4] Note that the y-axis scale varies for different histograms within the figure

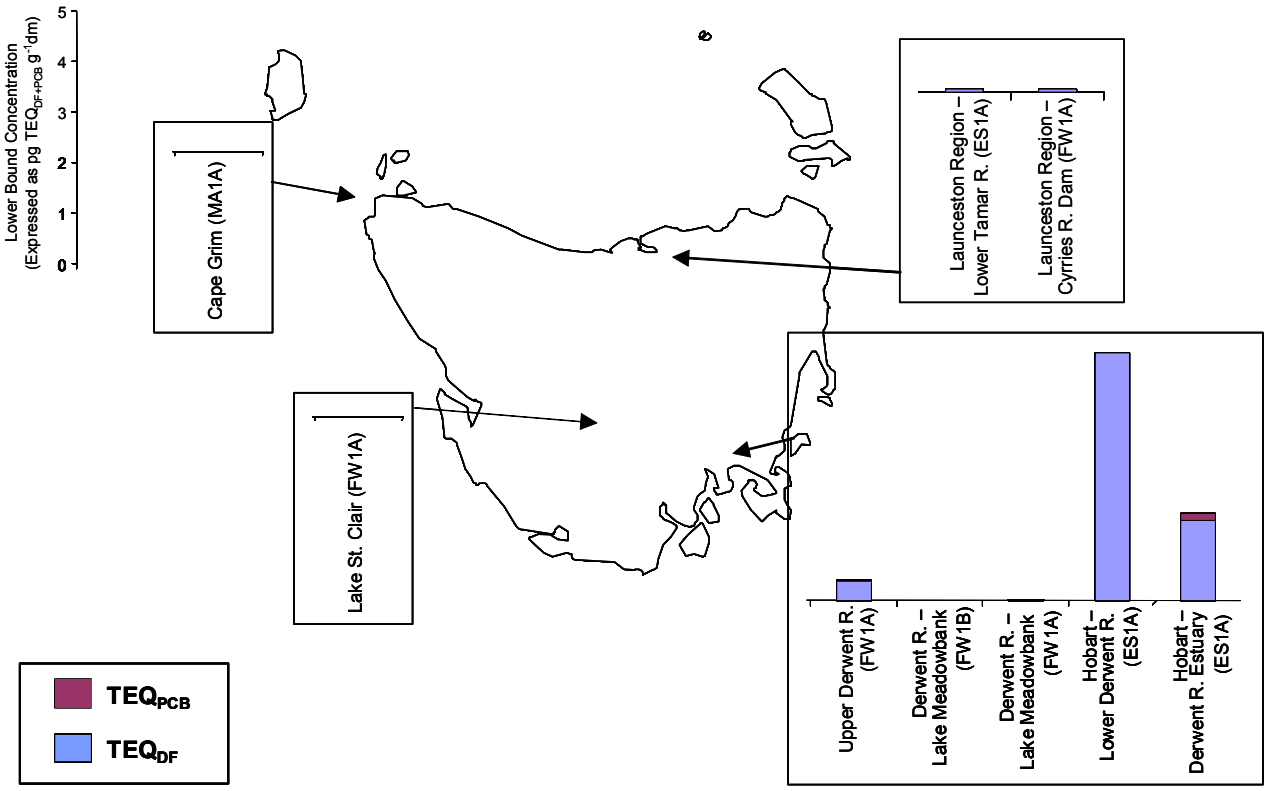


Figure 3.12 Tas sediment sampling locations and the corresponding TEQ.

In South Australia, sediments were collected from a range of sites in or near Spencer Gulf, as well as a freshwater site in the Murray River near Renmark and the Torrens River catchment from the Upper Torrens River to the Torrens Estuary. The concentration of dioxin-like chemicals in sediment samples from Adelaide were relatively low compared to those from other states with the highest concentrations between 1.0 and 1.5 pg TEQ g^{-1} dm in samples collected in the Torrens River near Adelaide.

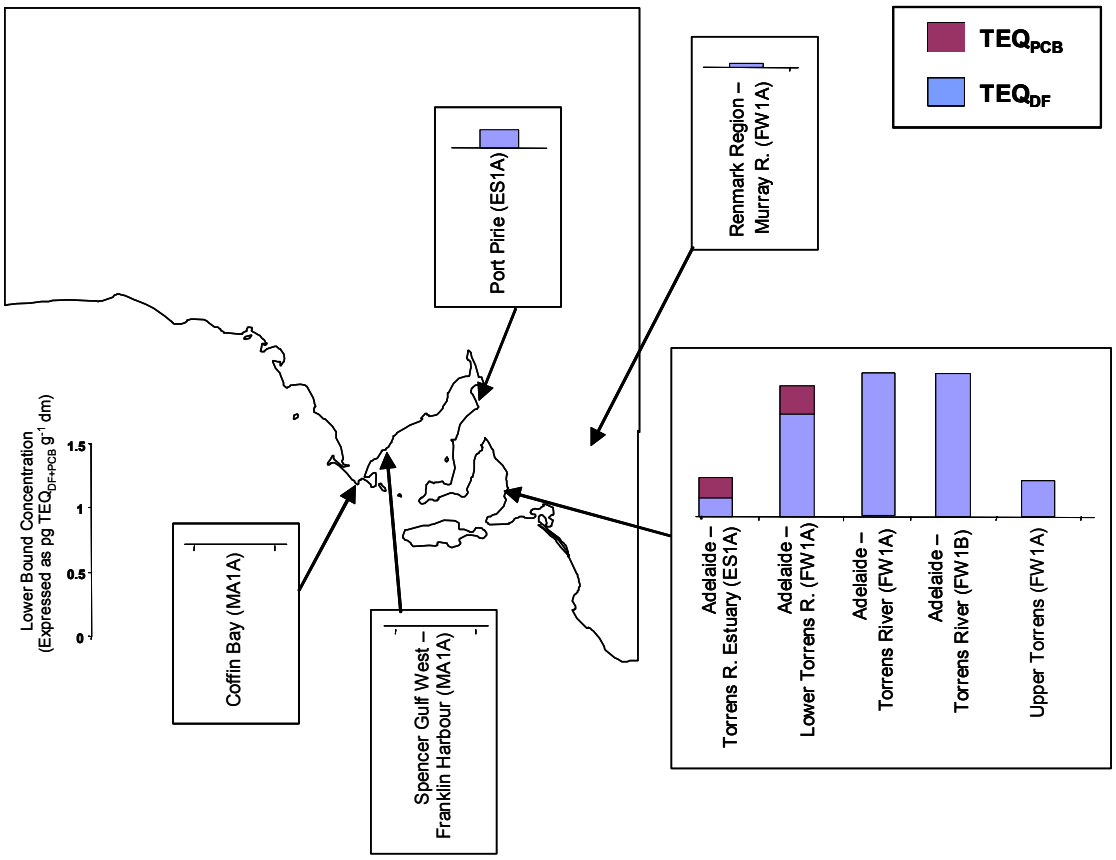


Figure 3.13 SA sediment sampling locations and the corresponding TEQ.

For Western Australia, sediment sampling focused on the south-eastern aquatic environment near Perth. Highest concentrations (5.5 pg TEQ g^{-1} dm) were found in samples from the Swan and the Canning River that were selected to represent aquatic environments influenced by urban and industrial sources.

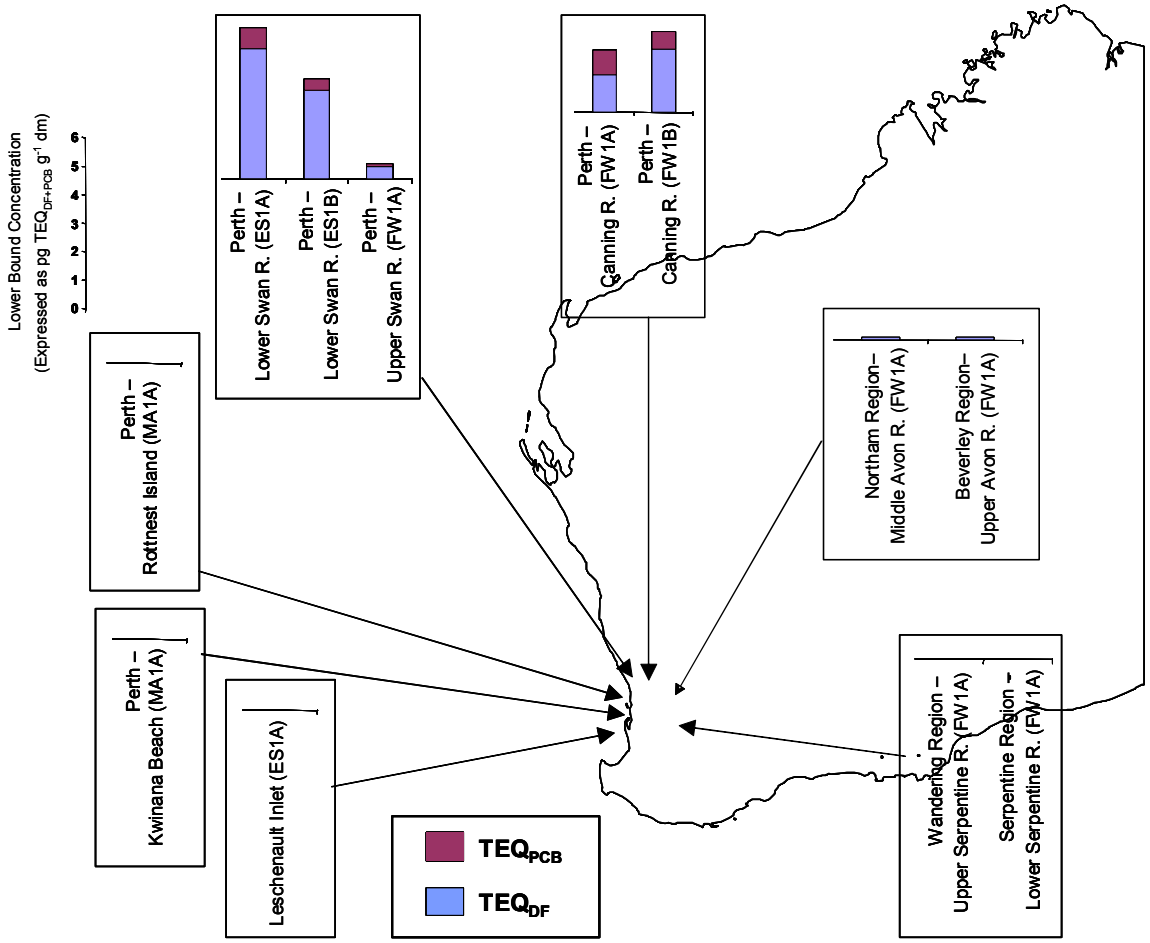


Figure 3.14 WA sediment sampling locations and the corresponding TEQ.

3.1.4 Characteristic patterns for dioxin-like chemicals in Australian aquatic environments.

Sources and fate processes of dioxin-like chemicals are often evaluated by comparing PCDD/PCDF homologue and/or PCDD/PCDF and/or PCB congener profiles (see Box 4). In most samples that were collected in this study, the PCDD/PCDF homologue profile as well as the congener profiles are overwhelmingly dominated by the highest chlorinated PCDD: octachlorodibenzodioxin (OCDD).

In samples where OCDD was detected, this congener contributed between 50% and greater than 99% of the ∑PCDD/PCDF (mean and median contribution 83% and 86%, respectively). The dominance of PCDD over PCDF was highest in samples including the Torrens River freshwater sampling location, the lower estuary of the Endeavour River, the Johnstone River, and the Brisbane River and also from Lake Illawarra and Botany Bay (for comparative purposes, note that only samples where more than 50% of PCDD/PCDF homologues are detected are considered) (Figure 3.15).

In contrast, the contribution of PCDF to the total ∑PCDD/PCDF was more than 10% in samples from the Upper Derwent River Estuary and the freshwater location of the Derwent River, the Torrens Estuary, the Upper Hunter River and almost all sediment samples from WA.

Box 4. Congener homologue and profiles

Congener and homologue profiles are useful tools for the determination of source and fate processes of dioxin-like chemicals, which may lead to accumulation in humans. Sometimes these profiles are compared to a "fingerprint", where the focus is not on the concentration but on the ratio of different dioxin-like chemicals to each other. Accordingly, in this document, profiles are presented by plotting the individual congener or homologue as the percent contribution it makes to the sum of a range of congeners or homologues.

Congeners and congener profiles
Congeners are individual compound members of the same chemical family. There are 75 possible different congeners of PCDD and 135 different congeners of PCDF. They differ according to their degree of chlorination (i.e. tetra-, penta-, hexa-, hepta- and octachlorinated compounds) and the position of chlorines in the molecule (i.e. 2,3,7,8-substituted compounds). There are a total of 7 PCDD and 10 PCDF congeners that are substituted in the 2,3,7,8-position. The congener profiles in this report show the percent contribution of each 2,3,7,8-substituted congener to the sum of the 15 2,3,7,8-chlorine substituted, tetra-heptachlorinated PCDD/PCDF concentration.

Homologues and homologue profiles
Homologues are a group of structurally related chemicals that have the same degree of chlorination (i.e. the same number of chlorines in the molecule). Within the PCDD/PCDF, each of the mono- to octachlorinated groups represents a homologue (i.e. there are 8 PCDD and 8 PCDF homologue groups, however, since only PCDD/PCDF with > 3 chlorines the profiles are of concern, only 5 PCDD and 5 PCDF homologue groups are used). The homologue profiles in this report show the percent contribution of each tetra- to heptachlorinated homologue to the sum total PCDD/PCDF concentration.

With respect to the overall homologue profiles, the OCDD domination, which has been shown previously by studies from Queensland (Müller et al. 1999; Gaus et al. 2001), remains unusual when compared to many studies overseas. For example, in the Estuarine Study from NZ (Scobie et al. 1999), OCDD was only detectable in 16 of the 24 samples and the contribution of OCDD was consistently less than 70% of the ∑PCDD/PCDF (unless only OCDD and/or one or two other homologues were detected).

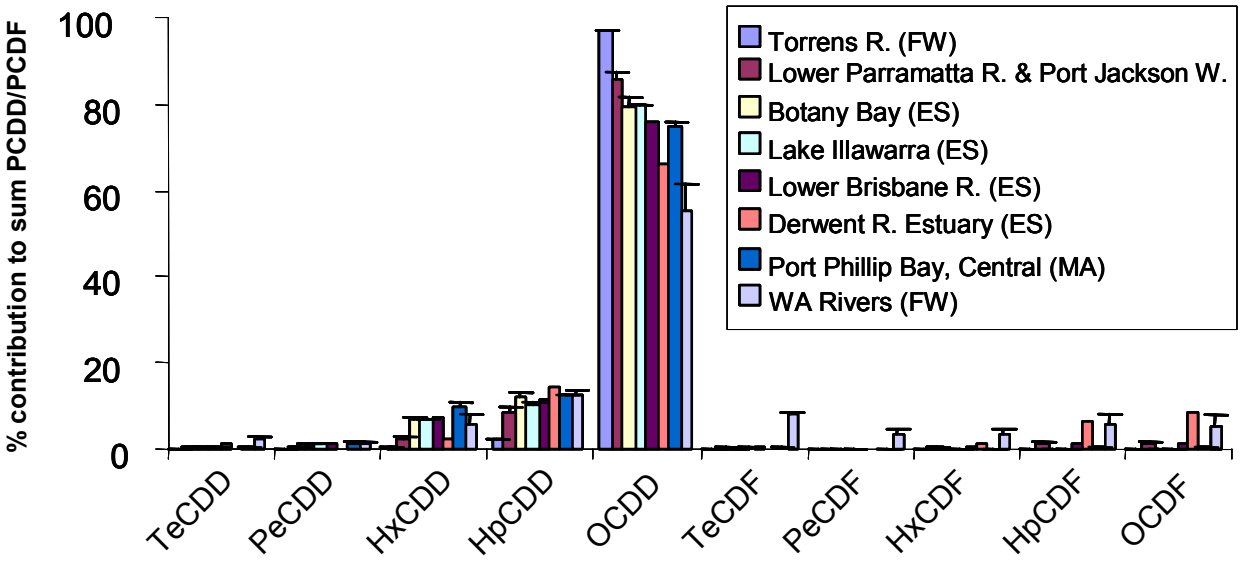


Figure 3.15 PCDD/PCDF homologue profile for sediments sampled from various locations.[5]

Congener profiles presented represent tetra-heptachlorinated 2,3,7,8-chlorine substituted PCDD/PCDF congeners (i.e. OCDD is omitted). As with homologues profiles, domination is exhibited by the highest chlorinated PCDD: 1,2,3,4,6,7,8-heptachloro dibenzodioxins, which contributed on average 85% to the sum of the 2,3,7,8-chlorine substituted tetra - heptachlorinated PCDD/PCDF (Figure 3.16).

This result is in good agreement with other studies on aquatic sediments from Australia, which have found unexpected high levels of higher chlorinated PCDD (Müller et al. 1999, Gaus et al. 2001, Prange et al. 2002). Despite intensive efforts examining soil cores and studies into a range of formation processes, including bush fire and natural formation processes, the source or process remain uncertain (Prange, 2003 submitted).

For the PCB congener 118 dominated the profile whereas the most toxic PCB contributed less than 1% to the PCB congener profile (Figure 3.17).

[5] Samples from Torrens R. (FW) (n=2); Lower Parramatta R. and Port Jackson West (ES) (n=4); Botany Bay (ES) (n=2), Lake Illawarra (ES) (n=2); Lower Brisbane R. (ES) (n=1) Derwent R. Estuary (ES) (n=1); Port Phillip Bay Central (MA) (n=2); Upper Swan R., Canning R. and Middle Avon R. all (FW) near Perth (n=4).

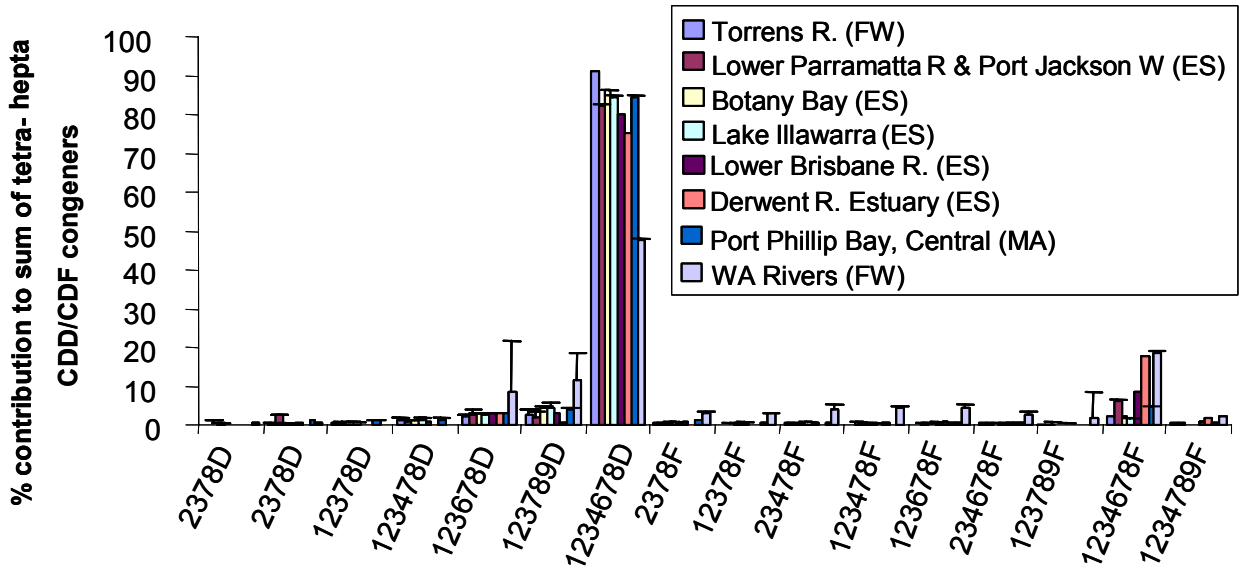


Figure 3.16 PCDD/PCDF congener profile for sediments sampled from various locations.[6]

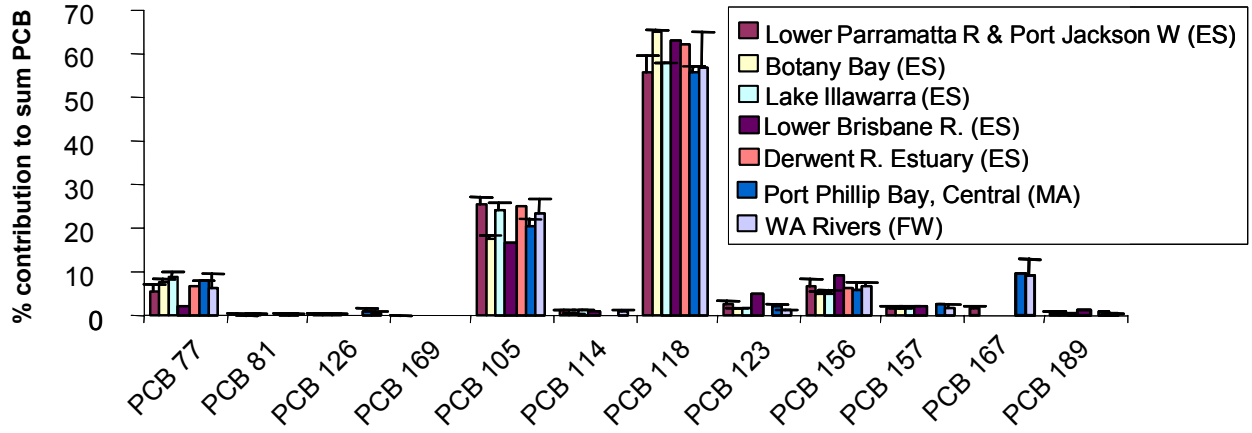


Figure 3.17 PCB congener profile for sediments sampled from various locations.[7]

[6] Samples from Torrens R. (FW) (n=2); Lower Parramatta R. and Port Jackson (ES) (n=4); Botany Bay (ES) (n=2), Lake Illawarra (ES) (n=2); Lower Brisbane R. (ES) (n=1) Derwent R. Estuary (ES) (n=1); Port Phillip Bay Central (MA) (n=2); Upper Swan R., Canning R. and Middle Avon R. all (FW) near Perth (n=4).

[7] Samples from Lower Parramatta R. and Port Jackson West (ES) (n=4); Botany Bay (ES) (n=2), Lake Illawarra (ES) (n=2); Lower Brisbane R. (n=1), Derwent R. Estuary (ES) (n=1); Port Phillip Bay Marine Central (n=2); Upper Swan R., Canning R. and Middle Avon R. all (FW) near Perth (n=4).

3.1.5 Comparison of data from this study with other studies in Australia and overseas

In this section the data obtained in this study are compared with both previous Australian studies and international publications. It should be noted that this comparison is always limited by a series of factors including the following:

- Differences in the aims of the study, for example determining background levels versus identification of contamination and potential hotspots
- Differences in the sampling, particularly for sediment (including sampling depth, criteria for sampling, number of samples that are pooled, sampling equipment and methodology)
- Differences in the expression of results and the basis of the expression of results (i.e. ∑PCDD/PCDF, individual congeners, TEQ values; type of TEF used - human or fish, basis of expression - dry mass versus organic carbon basis for sediments, fresh mass, dry mass or lipid mass basis for biota)
- Difference in sampling period
- Differences in reporting or summarising results (i.e. mean, median, range of TEQ, congeners and/or ∑PCDD/PCDF values may or may not be provided)
- The age and period of exposure for biota
- Seasonal variations, particularly in bivalves - see Wenning et al. (2003)
- Mobility of biota (i.e. fish in this study) and to some extent also of sediments.

It is particularly noteworthy that the results from this study demonstrate that concentration data do often not follow normal distribution patterns (in the statistical sense) and the maximum value or few high values can often be regarded as outliers with respect to background concentration. In other words, results can be highly dependent on the sample location, highly spatially variable and subject to potential localised contamination.

Few countries have carried out comprehensive sediment surveys, although biota surveys have become more common. Here an attempt is made to compare the results from this study with results from some previous key studies with priorities given to those conducted in Australia, and also to provide a summary of some of selected recent studies from overseas countries, particularly New Zealand.

Comparison with other Australian results

A few studies have been carried out on the concentration of dioxin-like chemicals in Australian sediments and as part of the present study some of the locations were revisited. For example, samples in this study were collected at four locations that were in the general vicinity of locations described in the Port Phillip Bay study (Bremner et al. 1990). In addition, two locations from the estuary of the Brisbane River that have been subject to a study in the mid 1990s have also been included in this study. Figure 3.18 displays a plot of

the result from the previous studies compared with the result from this study and shows an overall good agreement. Differences can be attributed to:

- sampling locations being similar but not identical
- samples were collected in some cases more than a decade apart
- all samples were analysed by different laboratories.

Note that the site Lower Yarra R. (ES1B) was used as the B sample, however, it was approximately 5 km downstream of the A site sampled for the Port Phillip Bay study.

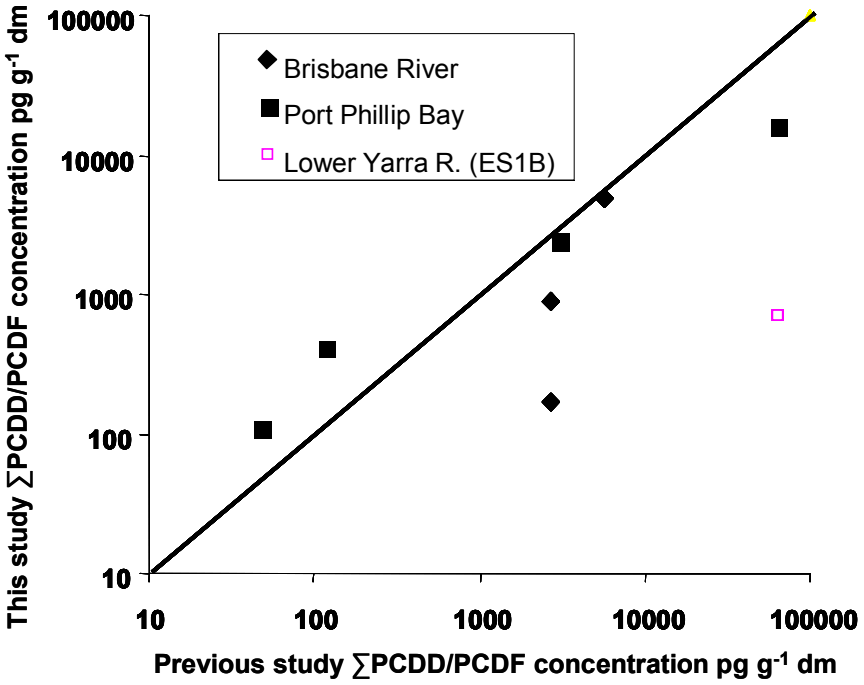


Figure 3.18 Comparison of this study with previous studies in 1990 & 1996.

Besides the sampling locations that were revisited, a series of data is available of dioxin-like chemicals in aquatic sediments in Australia. Specifically, Bremer et al. (1990) reported results for 17 sediment samples from the Port Phillip Bay region and reported levels ranging from 0.13-32 pg I-TE g^{-1} dm. Mosse and Haynes (1993) analysed sediments from inshore waters off Bass Strait adjacent to the Victorian coastline and detected only low levels (LOD - 0.4 pg I-TE g^{-1} dm). Müller et al. (1999) found between 4.6 and 9.9 pg I-TE g^{-1} dm in sediment samples collected from the Brisbane River and coastal sediments along the Queensland coast. Although the results were not particularly elevated in terms of toxic equivalents, the results of this study were surprising as they demonstrated a substantial and very widespread dioxin contamination of the marine environment, with elevated levels in seagrass and dugongs (Haynes et al. 1999; McLachlan et al. 2001). This work lead to probably the most comprehensive study on dioxin-like chemicals in the aquatic environment of Australia before the NDP. It was carried out by Gaus as part of her PhD

thesis (Gaus 2003; Gaus et al. 2001, 2002, 2003; Müller et al. 2001). Gaus collected more than 50 sediment samples along a range of transects including in coastal rivers such as the Herbert River and also offshore. In addition, she investigated levels of dioxins in slices of two sediment cores from inshore regions of the Great Barrier Reef World Heritage Area (GBRWHA). The data demonstrated contamination of the entire coastline with higher chlorinated PCDD. Concentrations were elevated in sediment core slices that were dated to the period prior to European settlement, which indicated natural formation of the OCDD (Gaus et al. 2001). In a further analysis of this data, Gaus et al. (2002) discussed the source and fate of the dioxins in the core and proposed that in addition to the natural formation hypothesis, a diffusion of polar precursors through the sediments and subsequent formation of OCDD from these precursors could also explain these findings. Despite intensive work by Prange and co-workers, the source of the elevated levels of higher chlorinated PCDD remains unclear (Prange et al. 2003; Prange submitted).

Data from overseas

New Zealand's organochlorines program included the evaluation of dioxin-like chemicals in estuarine sediments from 26 locations with median and maximum values of 0.28 and 2.7 pg I-TE_{DF} g^{-1} dm (½ LOD), respectively, (Buckland et al. 1999). Using the sum of PCDD/PCDF, the authors found a medium concentration of 31 pg ∑PCDD/PCDF g^{-1} dm with a maximum concentration of 720 pg ∑PCDD/PCDF g^{-1} dm. In contrast, this Australian study found substantially higher levels (up to 520 pg TEQ_{DF+PCB} g^{-1} dm) with a median concentration of dioxin-like chemicals in estuaries not much lower than the maximum value in the NZ study and a maximum concentration more than 2 orders of magnitude higher, both in terms of TEQ as well as ∑PCDD/PCDF, than the maximum concentration in the NZ study.

In Europe, a wide range of studies has been carried out on dioxin-like chemicals in sediments and some of these data have been compiled by Fiedler et al (1999). For sediments the compilations consisted of three exposure categories ranging from background to contaminated sites. In essence the levels of PCDD/PCDF in sediments of the category background ranged from about 0.07-19 pg TEQ_{DF} g^{-1} dm in central and southern Europe, whereas Fiedler et al. quoted background levels in Finland range from 0.7-100 pg TEQ_{DF} g^{-1} dm and in Sweden from 0.8-207 pg TEQ_{DF} g^{-1} dm. For urban environments the compilation suggested that the levels of PCDD/PCDF in Europe range from 0.2-123 pg TEQ_{DF} g^{-1} dm (note that no urban data were included from Scandinavian countries). For contaminated sediments Fiedler et al. (1999) stated single values for individual countries but they ranged from 570 pg TEQ_{DF} g^{-1} dm in Italy up to 80,000 pg TEQ_{DF} g^{-1} dm in sediments from Finland. Furthermore, Jimenez et al. (1999) reported a median concentration of about 4 pg I-TE g^{-1} dm for sediments collected from the Venice Lagoon with a maximum level in a sample from an industrial area of up to 27 pg I-TE g^{-1} dm. Other studies from the Venice Lagoon and the northern Adria found levels of between 0.27 and 5 pg I-TE g^{-1} dm (Miniero et al. 2003a and Miniero et al. 2003b). In a transect study that evaluated dioxin-like chemicals in sediments of the River Po, Fattore et al. (2002) found between about 1 and 12 pg TEQ g^{-1} dm (only PCDD/PCDF). In Spain Eljarrat, Caixach and Rivera (2001) detected levels of up to about 8 pg I-TE g^{-1} dm in sediments

from two rivers and similar maximum levels in marine sediments from the Catalan coast. From Germany Knoth et al. (2003) recently reported dioxin-like chemicals (only PCDD/PCDF) in sediments from the River Elbe and found levels up to about 150 pg TEQ g^{-1} dm in sediments from a tributary with a highly industrialised catchment. Concentrations were much lower upstream from the industrial region (i.e. <25 pg TEQ g^{-1} dm) and decreased rapidly in the estuary to about 7 pg TEQ g^{-1} dm near the mouth of the Elbe. Koistinen et al. (1997) published data from the northern Baltic Sea with levels between 26 and 71 pg I-TE g^{-1} dm. In contrast to the Baltic Sea, the concentrations in the North Sea appear to be substantially lower. For example, Tyler et al. (1994) reported levels between 0.6 and 2.8 pg I-TE g^{-1} dm for North Sea estuaries although up to more than an order of magnitude higher levels can be found in sediments from estuaries that have a high industrialized activity such as the Humber Estuary (Tyler and Millward, 1996).

Few data are available from Africa and it is noteworthy that recently Vosloo and Bouwman (2003) analysed aquatic sediment samples from 22 locations in South Africa and found levels of dioxin-like chemicals from about 0.2-22 pg TEQ g^{-1} dm (median 0.34 pg TEQ g^{-1} dm).

In North America, the US-EPA Dioxin Reassessment document summarised that for PCDD/PCDF sediment levels typically range from <1-20 pg TEQ_{DF} g^{-1} dm with a mean level of 5.3 pg TEQ_{DF} g^{-1} dm (n=11). In addition the report suggested that for PCBs the average level is 0.53 pg TEQ_{DF} g^{-1} dm and hence PCBs contribute on average about 10% of the total TEQ in sediment samples. Further, Hemming et al. (2003) recently reported levels of dioxin-like chemicals (PCDD/PCDF) in marine bays in Florida with levels between 0.5 and 78 pg TEQ g^{-1} dm. Marvin et al. (2002) found mean values of between 3.3 and 18 pg TEQ g^{-1} dm in sediments from three locations in the Lower Great Lakes, North America. Litten et al. (2003) analysed about 5,000 samples from various parts of New York Harbor with mean levels ranging from 23 to 880 pg TEQ g^{-1} dm. Similarly Wallin et al. (2002) reported between 310 and 1,400 pg TEQ g^{-1} dm in the Passaic River, New Jersey that is part of the New York/New Jersey Harbour Estuary (only PCDD/PCDF TEQ values). In comparison, PCDD/PCDF levels in sediments from Casco Bay, Maine showed levels ranging from about 1 to 27 pg TEQ g^{-1} dm. Tysklind et al. (2002) carried out intensive studies on the levels of PCDD/PCDF in the lower Roanoke River Basin, North Carolina and found between 0.3 and 34 pg TEQ g^{-1} dm where downstream locations where substantially influenced by a tributary which showed sediment concentration of up to 1,200 pg TEQ g^{-1} dm. Also, highly polluted sediments have been reported from Guanara Bay, Rio de Janeiro with up to 2,000 pg TEQ g^{-1} dm (Carvalhaes et al. 2001, 2002), however, little information is available on the specific study aims and the individual results.

In Asia, Müller et al. (2002) found between 4 and 33 pg TEQ g^{-1} dm (only PCDD/PCDF) in sediments from Hong Kong Harbour and between 3 and12 pg TEQ g^{-1} dm at sampling locations that were considered as representative background for the region. From Japan, a 1998 survey found levels of dioxin-like chemicals in bottom sediments of public waters ranging from <LOD to 206 pg TEQ g^{-1} dm with a median concentration of 0.41 pg TEQ g^{-1} dm (Environment Agency, Japan, 1999). Hosomi et al. (2003) report PCDD/PCDF levels in Tokyo Bay of between 3.3 and 52 pg TEQ g^{-1} dm which is very similar to previous

reports from Sakurai et al. (2000) in sediments from the same bay (i.e. 11-52 pg I-TE g^{-1} dm). Ohsaki et al. (1995) analysed river and offshore sediments from southern Japan (Fukuoka) and found on average about 8, 38 and 21 pg TEQ g^{-1} dm in the upper and lower reaches of the river and offshore, respectively. Nineteen samples of surface sediments from coastal zones around Korea were collected by Moon et al. (2001) who reported levels from 0.01 pg TEQ g^{-1} dm to 5.5 pg TEQ g^{-1} dm. Finally, Yu et al. (2002) evaluated dioxin-like chemicals in the northern Caspian Sea in Russia and found between 0.7-28 pg I-TE g^{-1} dm where most of the TEQ values were due to contamination with 2,3,7,8-TCDD. A summary of all these results is represented in Figure 3.19.

Note that individual data of the figure is discussed in the text below and presented in Table G1.

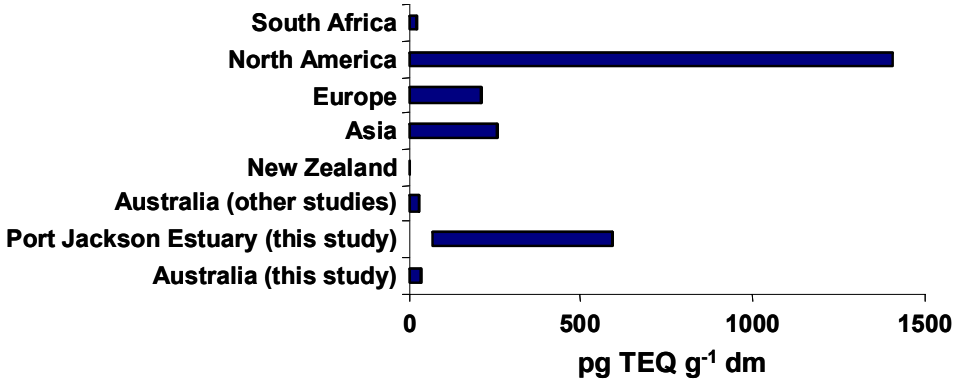


Figure 3.19 Comparison of levels of dioxin-like chemicals in sediments samples from different regions and continents.

3.2 Dioxin like chemicals in Australian aquatic biota

In this study, 18 bivalve and 23 fish samples were investigated. Bivalves were collected at sediment sampling sites and fish samples, where possible, were caught from sediment sampling locations.

3.2.1 Dioxin-like chemicals in bivalves

Dioxin-like chemicals were detected in all 18 bivalve samples collected from freshwater, estuarine and marine locations covering the different regions and various environments of Australia, and a summary of the results is provided in Table 3.5 (refer to Table E1 for the analytical results). The levels, expressed as TEQ, ranged from 0.0043 to 1.2 pg TEQ_{FISH} g^{-1} fm or 0.0068 to 3.4 pg TEQ_{HUMANS} g^{-1} fm. Note that the TEQ_{FISH} reflects toxicity to fish and bivalves, whereas the TEQ_{HUMANS} is relevant with respect to human consumption and human body burden. Consistent with the sediment results, the highest levels of dioxin-like chemicals were found in a bivalve sample collected from Port Jackson. However, it should be noted that the data are too few to evaluate clear trends with respect to regions or land-use. The geographical distribution of the dioxin-like chemicals in bivalve samples (TEF_{FISH}) is shown in Figure 3.20.

Table 3.5 Summary of result of dioxin-like chemicals in bivalves samples.

	Total (18)		Freshwater (1)		Estuarine (11)		Marine (6)	
	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis	Fresh mass basis	Lipid basis
TEQ_{DF+PCB} FISH Inc. ½ LOD values (pg TEQ g^{-1})	**0.16** (0.0043-1.2)	**12** (0.32-50)	**0.023**	**1.3**	**0.20** (0.0043-1.2)	**12** (0.86-50)	**0.080** (0.012-0.90)	**10** (0.32-38)
TEQ_{DF+PCB} HUMAN Inc. ½ LOD values (pg TEQ g^{-1})	**0.36** (0.0068-3.4)	**22** (0.59-140)	**0.035**	**2.0**	**0.45** (0.0068-2.7)	**24** (1.4-140)	**0.087** (0.022-3.4)	**24** (0.59-140)
∑PCDD/PCDF Inc. ½ LOD values (pg ∑PCDD/-F g^{-1})	**26** (0.43-230)	**2100** (27-9900)	**9.8**	**540**	**29** (0.43-230)	**2400** (86-9600)	**26** (1.0-90)	**2000** (27-6800)
∑PCB Inc. ½ LOD values (pg ∑PCB g^{-1})	**180** (2.7-7300)	**13000** (150-300000)	**19**	**1100**	**320** (4.7-5600)	**21000** (150-290000)	**89** (2.7-7300)	**8200** (300-300000)

Results are expressed as median, minimum and maximum values.

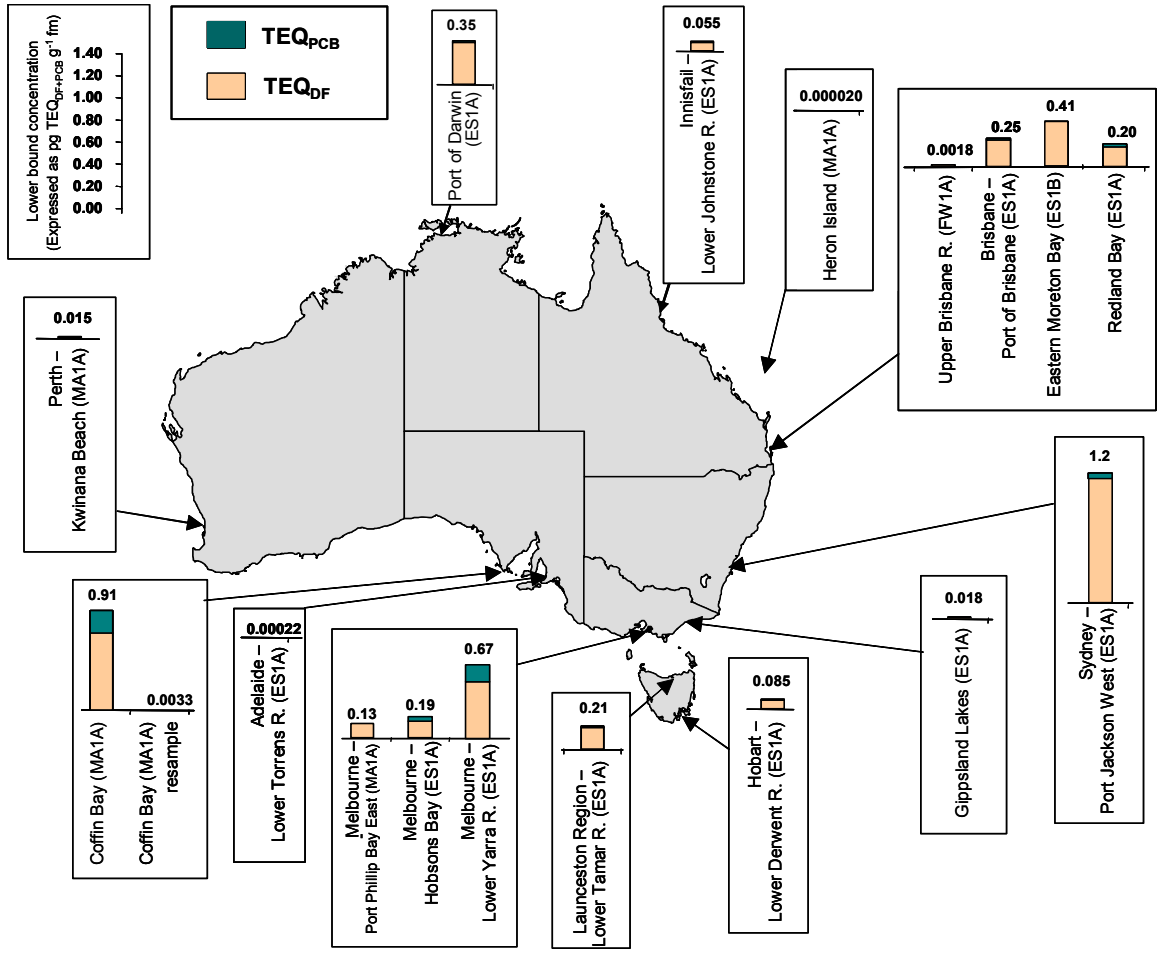


Figure 3.20 Geographical distribution of the dioxin-like chemicals in bivalve samples.

Overall, levels of dioxin-like chemicals in bivalves were well below both the benchmark concentrations for dioxins in fish, identified as a concentration with no serious health effects (25 pg g^{-1} fm), and the fresh weight action concentration (50 pg g^{-1} fm) set by the US Food and Drug Administration (US FDA) (US EPA, 1985 quoted in Wenning et al. 2003). Also none of the samples exceeded the European guideline of 4 pg TEQ g^{-1} fm recently set for fish (Codex Committee on Food Additives and Contaminants 2002).

However, it should be noted that 3 of the 18 bivalve samples exceeded 1 pg TEQ g^{-1} fm (based on TEQ_{HUMANS}), a level that according to information obtained by Wenning et al. (2003) from the US FDA warrants further investigation. Notably, one of these samples originated from the relatively pristine area near the southern part of Spencer Gulf (Coffin Bay) where levels of dioxin-like chemicals in sediments were extremely low. Re-sampling and analysis of bivalves from this location showed much lower levels in the second oyster sample from this area. The elevated results in the first sample remain unexplained.

Hydrophobic persistent chemicals tend to accumulate in the hydrophobic phases of the environment, such as the organic carbon of the sediment and the lipid in biota. A plot of the concentration in the biota (lipid basis) versus the concentration in the sediment (on a TOC basis) again indicates a general trend of increasing concentration in biota with increasing levels in sediments (Figure 3.21). Note that the line on the figure represents unity (x=y).

However, the levels in biota are, tentatively, less than what would be expected from the sediment concentration for 16 of the 18 sampling sites. This may be indicative that the sediments have become a secondary source for the dioxin-like chemicals in most of these environments and that the sediment/water system may not reach equilibrium. Considering the accumulation of individual congeners, the data clearly demonstrates a higher accumulation of the lower chlorinated PCB and PCDD/PCDF in biota compared to sediments. For example, using bivalve and sediment samples from the Lower Yarra River, the biota/sediment concentration ratio (pg g^{-1} lipid / pg g^{-1} TOC) range from greater than 1 (lower chlorinated PCB and TCDF) to below 0.05 for hepta- and octachlorinated PCDD/PCDF.

If the accumulation of dioxin-like chemicals in aquatic biota is sourced from historical accumulations in the sediments, then the lower chlorinated compounds, which tend to be more water-soluble, may be more easily remobilised from the sediments and thus be proportionally more bioavailable. If this hypothesis were correct, it would help explain the higher accumulation of the lower chlorinated PCB and PCDD/PCDF in biota compared to sediments.

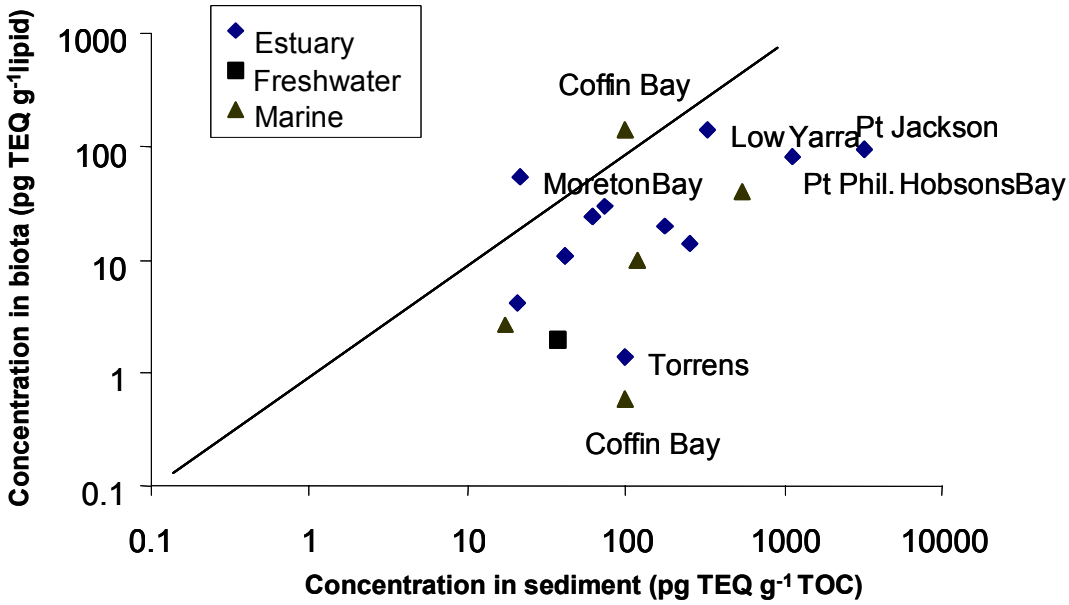


Figure 3.21 Plot of the concentration of dioxin-like chemicals in biota versus the concentration in sediments.

3.2.2 Dioxin like chemicals in bivalves - comparison with previous studies and overseas data.

Bivalves have been widely used for biomonitoring in Australia (Mortimer 2000). However, to date, limited data is available on dioxin-like chemicals in bivalves from Australia. Mosse and Haynes (1993) collected samples from inshore waters off Bass Strait adjacent to the Victorian coastline but these were only analysed for TCDD and TCDF, which were not detectable. Haynes and Toohey (1995) evaluated the temporal variation of PCDD/PCDF in cultured mussels from Port Phillip Bay, Victoria and reported levels between 0.23 and 0.71 pg I-TE g^{-1} fm which is slightly higher than the concentration that was found in this study in bivalves from Hobsons Bay and Eastern Port Phillip Bay (i.e. 0.19 and 0.13 pg TEQ g^{-1} fm using human TEFs).

In the New Zealand Organochlorines Program Scobie et al. (1999), levels of dioxin-like chemicals in bivalves were reported from 26 sites in estuaries around New Zealand. The authors reported a median level of 0.032 pg I-TE g^{-1} fm with levels ranging from 0.015 to 0.26 pg I-TE g^{-1} fm (½ LOD).

Europe Bayarri et al. (2001) found between 0.07 and 0.13 pg I-TE g^{-1} fm in bivalves collected from a north-south transect of the western Adriatic Sea. Karl et al. (2002) report 0.39 pg TEQ g^{-1} fm in pooled mussel samples from Denmark and Knutzen et al. (2003) found between 1.6 and 3.0 pg TEQ g^{-1} fm in mussels collected from Norway's south coast. The German Umweltbundesamt summarises in the report that PCDD/PCDF in 13 mussel samples from the River Elbe showed levels ranging from 0.55-0.96 pg I-TE g^{-1} fm (Umweltbundesamt, 2002). Most recently Abad et al. (in press) reported 0.11-0.54 pg TEQ g^{-1} fm (PCDD/PCDF only) in bivalves collected from three locations including the Mediterranean and two Atlantic shores in the north and south of Spain.

From North America, levels of dioxin-like chemicals in bivalves have been presented by Marvin et al. (2002) but only on a dry mass and lipid mass basis. If we assume that the fm/dm ratio in mussel is about 5.5, as described by Abad et al. (in press), the levels in the mussels from the lower Great Lakes range from mean values of 0.16 to 0.54 pg TEQ g^{-1} fm (only PCDD/PCDF). Wenning et al. (2003) reported levels of PCDD/PCDF in commercial Oysters from Arcata Bay, California with highest mean levels up to 2.1 pg TEQ g^{-1} fm in June 2002 in Pacific Diploids and up to 0.22 pg TEQ g^{-1} fm in samples of the same species collected four months later.

From China, Wu et al. (2001) analysed PCDD/PCDF in mussels from a lake and found 0.34 and 0.43 pg I-TE g^{-1} fm. The Japanese survey study (Environment Agency, Japan, 1999) also included bivalves in their study however in their reporting combined all biota results including fish with levels from 0.002-30 pg TEQ g^{-1} fm (median 1.1 pg TEQ g^{-1} fm). Tsutsumi et al. (2003) determined the levels of PCDD/PCDF in oysters and short-necked clams and found concentrations ranging from 0.22-1.1 and 0.07-0.14 pg TEQ g^{-1} fm respectively. Finally, Choi et al. (2001) analysed oysters and mussels from marine locations in Korea and reported levels from 0.001-1.2 pg TEQ_{DF} g^{-1} fm.

The plot at Figure 3.22 shows the relative levels of dioxin-like chemicals in bivalves across a series of geographic regions relative to Australia and New Zealand (see Table G2 for summary of the literature). However, this should be interpreted with caution due to the limited amount of Australian data available.

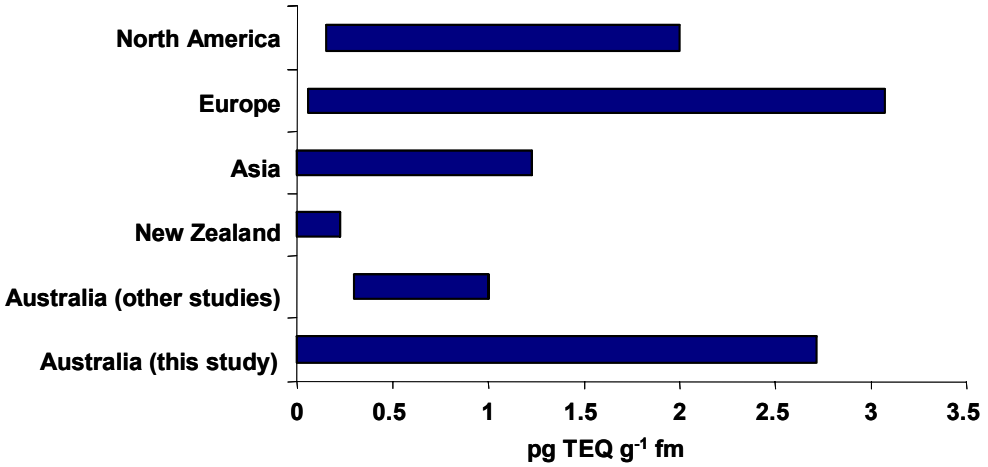


Figure 3.22 Comparison of levels of dioxin-like chemicals in bivalve samples from different continents.

3.2.3 Dioxin-like chemicals in fish samples

Dioxin-like chemicals were evaluated in 23 fish samples collected from around Australia. A summary of the results is provided in Table 3.6 (see Table E2 for analytical results). Overall, PCDD/PCDF and/or PCB were detectable in all 23 fish samples with levels ranging from 0.0053 to 0.49 pg TEQ_{FISH} g^{-1} fm or if based on the mammal TEFs, from 0.054 to 0.85 pg TEQ_{HUMANS} g^{-1} fm. Accordingly, none of the fish samples exceeded the

European guideline of 4 pg TEQ g^{-1} fm recently set for fish (Codex Committee on Food Additives and Contaminants 2002).

Also, all fish samples were less than guideline values set or discussed by the US FDA. These thresholds are a fresh weight action level concentration of 50 pg TEQ g^{-1} fm (US EPA, 1985 quoted in Wenning et al. 2003), and a benchmark value 25 pg TEQ g^{-1} fm and also the 1 pg TEQ g^{-1} fm value that was recently cited as a value that if exceeded warrants further investigations (see Wenning et al. 2003).

The regional distributions of the results (TEF_{FISH}) are presented in Figure 3.23. The levels of dioxin-like chemicals on a fresh mass basis were highest in a fish sample that was caught in the Port Jackson area with about 0.49 pg TEQ_{FISH} g^{-1} fm (0.85pg TEQ_{HUMANS} g^{-1} fm). The bream sample from Port Jackson showed relatively elevated levels of the PCB and the PCDF (i.e. about one order of magnitude higher level of PCDF and PCB than any other fish sample analysed in this study). Whiting and flathead samples obtained from the Port Jackson showed levels of PCDD/PCDF and PCB that were not elevated compared to other samples. This may be related to the mobility patterns and/or feeding habits of these fish.

Overall, the data does not allow evaluation of the differences in the accumulation between different species, partly as the age of the samples that were analysed were not controlled or assessed. Nonetheless, with respect to the risks associated with the exposure of fish to dioxin-like chemicals or to consumers of these fish, the data suggests little concern. However, the analysis of such a small sample and range of species indicates a need for caution in basing a risk assessment on the fish data from this study.

Table 3.6 Summary of result of dioxin-like chemicals in fish collected.

	Total (n=23)		**Freshwater (n=3)**		**Estuarine (n=8)**		**Marine (n=12)**	
	Fresh mass basis	**Lipid basis**	**Fresh mass basis**	**Lipid basis**	**Fresh mass basis**	**Lipid basis**	**Fresh mass basis**	**Lipid basis**
TEQ_{DF+PCB} FISH Inc. ½ LOD values (pg TEQ g^{-1})	**0.034** (0.0054-0.49)	**2.6** (0.36-55)	**0.089** (0.034-0.36)	**2.6** (1.4-18)	**0.044** (0.0054-0.49)	**4.3** (0.42-55)	**0.027** (0.0054-0.095)	**1.5** (0.36-9.3)
TEQ_{DF+PCB} HUMAN Inc. ½ LOD values (pg TEQ g^{-1})	**0.054** (0.011-0.85)	**4.1** (0.72-68)	**0.11** (0.075-0.45)	**5.8** (1.7-23)	**0.054** (0.015-0.85)	**5.4** (1.2-68)	**0.042** (0.011-0.19)	**3.0** (0.72-9.7)
∑PCDD/PCDF Inc. ½ LOD values (pg ∑PCDD/F g^{-1})	**0.73** (0.17-4.4)	**42** (8.8-930)	**0.75** (0.37-3.6)	**28** (12-180)	**1.1** (0.17-4.4)	**87** (13-930)	**0.48** (0.22-1.0)	**35** (8.8-77)
∑PCB Inc. ½ LOD values (pg ∑PCB g^{-1})	**29** (4.5-1100)	**1500** (400-24000)	**63** (21-73)	**1100** (1100-4800)	**11** (4.5-1100)	**1100** (450-24000)	**30** (5.6-190)	**1700** (400-4800)

Results are expressed as median and minimum and maximum values.

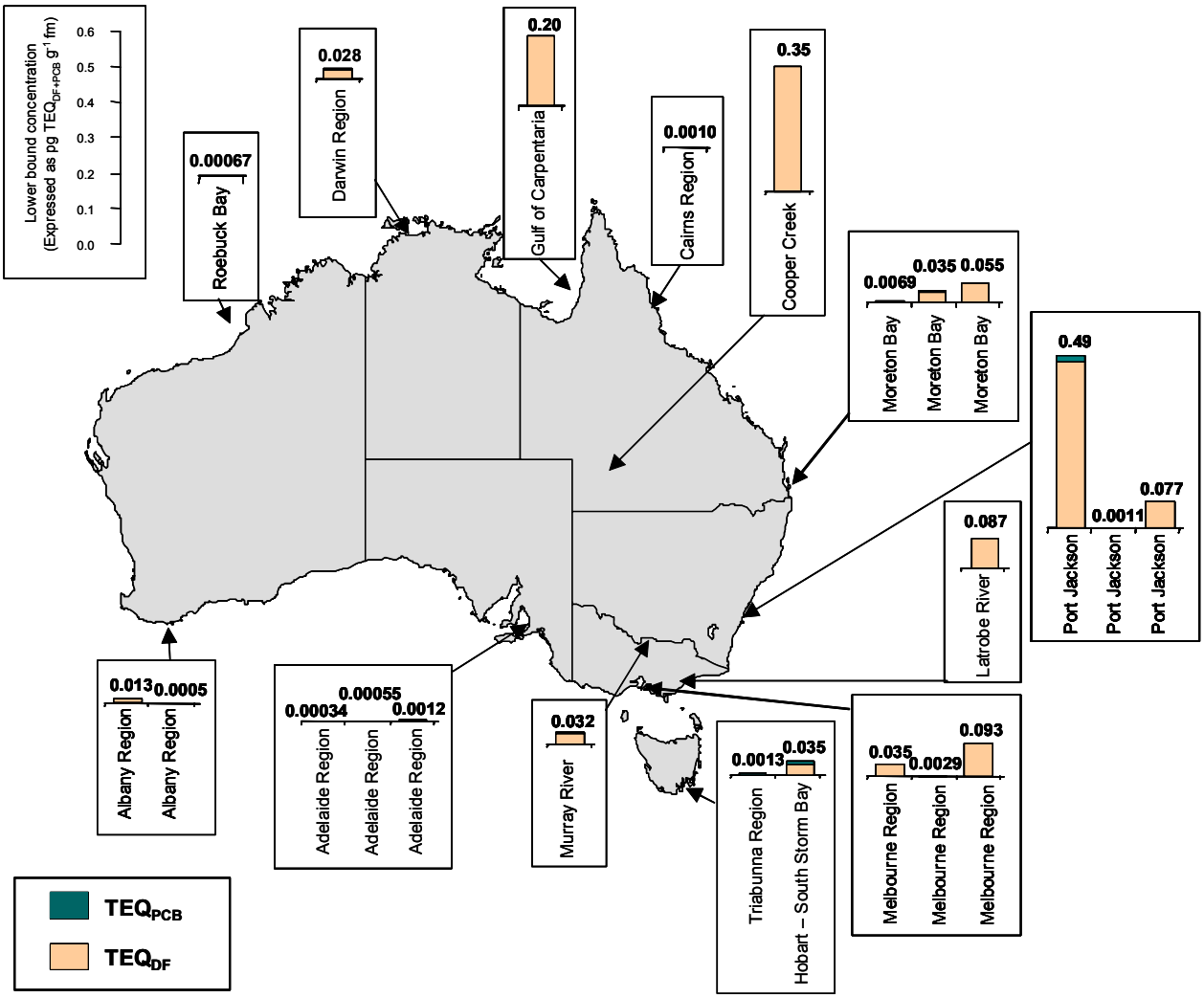


Figure 3.23 Geographical distribution of the dioxin-like chemicals in fish samples[8].

3.2.4 Dioxin-like chemicals in fish - comparison with previous studies and overseas data.

Much work has been carried out in respect to contamination of food by dioxin-like chemicals in Australia and overseas and the data are summarised in Figure 3.24 and Table G3. In Australia, it is noteworthy that parallel with the NDP study, a food study was also carried out which included an analysis of fish samples for dioxin-like chemicals. Also, it is our understanding that fish have been analysed for the Australian tuna industry. However, to our knowledge results from these studies have not been published. Elsewhere, Mosse and Haynes (1993) found 0.05 and 0.15 pg I-TE g^{-1} fm, respectively, in a whiting and a flathead sample caught in the Bass Strait. An Victorian EPA study reported PCDD/PCDF levels in mullet and flathead caught in Port Phillip Bay with levels between 1 and 1.7 pg I-TE g^{-1} fm (Victorian EPA 1991). Ahokas et al. (1994) reported results from the analysis of

[8] Expressed as lower bound TEQ_{DF+PCB}.

carp samples from Lake Coleman, which received treated effluent from a treated pulp and paper mill, with concentrations in the four carp samples between 0.48-4 pg I-TE g^{-1} fm.

The New Zealand Organochlorine Study sampled and analysed 16 eel and 12 trout samples taken from 12 freshwater locations around the country (Buckland et al. 1998). However, no PCDD/PCDF was detected in the majority of the 16 eel samples and in only six of the 12 trout samples. For the remaining samples, the study found maximum concentration of 0.2 and 0.39 pg I-TE g^{-1} fm (incl. half LOD) in trout and eel samples, respectively.

From Europe, the European Union compilation of data shows that PCDD/PCDF levels in fish range from about 2-214 pg TEQ_{DF} g^{-1} fat (Buckley-Golder 1999). When calculated on a fresh mass basis, assuming a 3% lipid content, the maximum value is approximately 10 pg TEQ_{DF} g^{-1}. In addition, Fiedler et al. (1999) in their compilation of data, suggested levels of PCDD/PCDF in fish in Sweden and the UK exceeded this with reported maximum levels of 420 and 700 pg TEQ_{DF} g^{-1} lipid, respectively. Again, assuming a 3% lipid content, this would suggest that the highest level is approximately 20 pg TEQ g^{-1} fm when calculated on a fresh mass basis. Knutzen et al. (2003) reported levels from 1.5 pg TEQ g^{-1} fm in cod fillets to about 30 pg TEQ g^{-1} fm in eel fillets from fish caught in the Fjordlands in the southern parts of Norway. The German Umweltbundesamt summary of levels in fish (perch and bream) from the Elbe to be typically in the range of 1-5 pg I-TE g^{-1} fm, however, with outliers up to about 13 pg I-TE g^{-1} fm (Umweltbundesamt, 2002). Karl et al. (2002) reported analytical results from 184 pooled seafood samples purchased on the German market, but with reference to the origin of the sample. They reported the highest levels of contamination in herring from the Baltic Sea with a mean concentration of 1.9 pg TEQ g^{-1} fm (PCDD/PCDF) and a maximum concentration of 3.2 pg TEQ g^{-1} fm. In contrast to the herring from the Baltic Sea, herring from the North Sea and from Irish fishing areas were about three to four times less contaminated and herring from Norway about half as contaminated (both mean and maximum levels). However, with the exception of the herring samples and halibut samples from various regions of the North Sea and North Atlantic, they found levels of PCDD/PCDF expressed as TEQ were consistently less than 1 pg TEQ g^{-1} fm. Karl et al. (2002) also analysed six samples of farmed salmon and found levels ranging from 0.26-0.74 pg TEQ g^{-1} fm. Kiviranta et al. (2003) analysed 120 pooled herring samples comprising material from 1570 individual herring, and reported levels of PCDD/PCDF ranging from about 1 to 27 pg TEQ g^{-1} fm (PCDD/PCDF) depending on the age and source area of the herring. Furthermore, they also reported levels of dioxin-like PCB between 1-23 pg TEQ g^{-1} fm, hence a total TEQ of up to about 50 pg TEQ g^{-1} fm. The relatively high contamination in herring from the Baltic Sea is confirmed by the results from a range of other studies including those from Finland (Isosaari et al. 2003), Sweden (Bjerselius et al. 2003) and Estonia (Roots et al. 2003). In contrast to the high levels in fish from the Baltic Sea, Abad et al. (2003) reported maximum levels of up to about 2.2 pg TEQ g^{-1} fm in consumer fish from the Mediterranean Sea, 2.4 pg TEQ g^{-1} fm in consumer fish from the Atlantic Ocean and 0.37 pg TEQ g^{-1} fm in consumer fish from the Pacific Ocean that are sold in Spain.

From the USA Litten et al. (2003) reported results on levels of PCDD/PCDF in fish from the New York Harbour waters with mean levels in striped bass fillets in different areas

ranging from 1.9 to 29 pg TEQ g^{-1}. Iannuzi et al. (2003) presented levels from the analysis of fish with values up to 110 pg TEQ g^{-1} fm in adult striped bass, between 5.1 and 23 pg TEQ g^{-1} fm in American eel and up to 370 pg TEQ g^{-1} fm in white perch from the Passaic River. It is noteworthy that despite the very high levels the authors concluded that the PCDD/PCDF do not pose a substantial risk to fish (and blue crabs) in the Passaic River. Elsewhere in the USA, Fairey et al. (1997) reported levels of PCDD/PCDF from 0.12-1.8 pg I-TE g^{-1} fm in sportfish (white croaker, leopard shark, halibut etc.) caught in the San Francisco Bay.

From Asia, a survey by the Environment Agency in Japan included the analysis of aquatic biota from 368 sites and reported a median concentration of 1.1 pg TEQ g^{-1} fm (0.0022-30 pg TEQ g^{-1} fm). Tsutsumi et al. (2003) analysed about 65 fish samples from Tokyo Bay and reported a maximum concentration in a tuna sample of 23 pg TEQ g^{-1} fm. However, this seems to be an outlier, since the median concentration in tuna was 0.18 pg TEQ g^{-1} fm. Overall in the Tokyo Bay study, the median levels across different species ranged from 0.3 to 3.3 pg TEQ g^{-1} fm and the maximum level, other than in the tuna sample outlier, was 4.6 pg TEQ g^{-1} fm in a sample of Yellowtail.

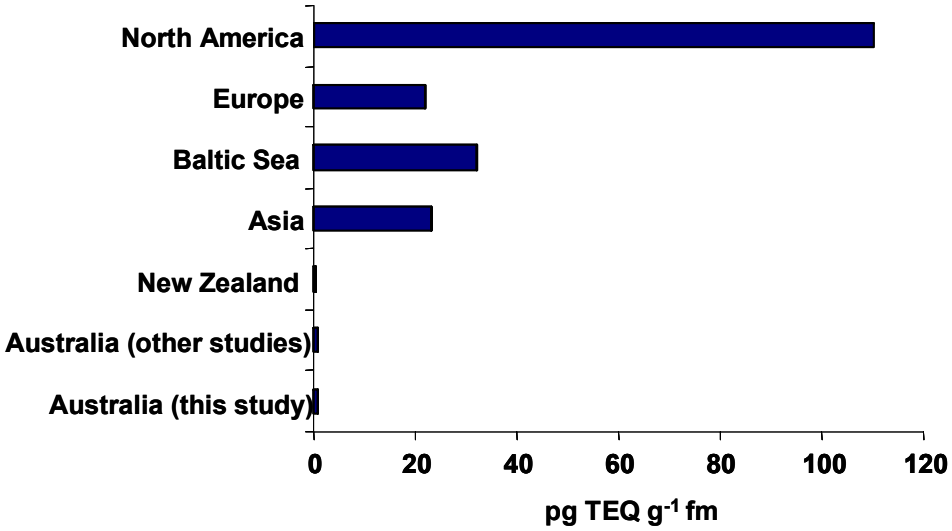


Figure 3.24 Comparison of levels of dioxin-like chemicals in fish samples from different continents.