Australian Government

Department of the Environment and Heritage

Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia

Disclaimer:

This document is one of three reports:

1. **Assessment of concentrations of polybrominated diphenyl ether flame retardants in aquatic environments in Australia**
2. *Assessment of concentrations of polybrominated diphenyl ether flame retardants in indoor environments in Australia*
3. *Assessment of concentrations of polybrominated diphenyl ether flame retardants in the Australian population: levels in blood*

Foreword

Polybrominated diphenyl ethers (PBDEs), a common class of brominated flame retardants, are a ubiquitous part of our built environment, and for many years have contributed to improved public safety by reducing the flammability of everyday goods.

Recently, PBDEs have come under increased international attention because of their potential to impact upon the environment and human health. Some PBDE compounds have been nominated for possible inclusion on the Stockholm Convention on Persistent Organic Pollutants, to which Australia is a Party. Work under the Stockholm Convention has demonstrated the capacity of some PBDEs to persist and accumulate in the environment and to be carried long distances. Much is unknown about the impact of PBDEs on living organisms, however recent studies show that some PBDEs can inhibit growth in colonies of plankton and algae and depress the reproduction of zooplankton. Laboratory mice and rats have also shown liver disturbances and damage to developing nervous systems as a result of exposure to PBDEs.

In 2004, the Australian Government Department of the Environment and Heritage began three studies to examine levels of PBDEs in aquatic sediments, indoor environments and human blood, as knowledge about PBDEs in Australia was very limited. The aim of these studies was to improve this knowledge base so that governments were in a better position to consider appropriate management actions.

Due to the high costs for laboratory analysis of PBDEs, the number of samples collected for each study was limited and so caution is required when interpreting the findings. Nevertheless, these studies will provide governments with an indication of how prevalent PBDEs are in the Australian population and the environment and will also contribute to international knowledge about these chemicals.

The Department of the Environment and Heritage will be working closely with other government agencies, industry and the community to investigate any further action that may be required to address PBDEs in Australia.

Department of the Environment and Heritage
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Glossary/Abbreviations

ANOVA	Analysis of Variance
∑PBDE	Sum total of all PBDE congeners analysed (unless specified otherwise)
ACT	Australian Capital Territory
BDE	Brominated diphenyl ethers (used when specifying the congener or degree of bromination)
BFR	Brominated flame retardant
Congeners	Closely related chemicals derived from the same parent compound.
Dw	Dry weight
EnTox	National Research Centre for Environmental Toxicology
IUPAC	International Union of Pure and Applied Chemistry.
LOD	Limit of detection, the least concentration at which a chemical can be detected in a sample by the analytical method used.
LOD (excluding LOD)	The LOD is assumed to be zero when used to calculate the sum of PBDEs.
LOD (including half LOD)	The LOD is assumed to be 50% of the reported LOD when used to calculate the sum of PBDEs.
MND	Mean Normalised Difference
NDP	National Dioxins Programme
NMI	National Measurement Institute
NSW	New South Wales
NT	Northern Territory
PBDE	Polybrominated diphenyl ether (used to describe all PBDEs when not specifying which congener or degree of bromination)
pg	Picogram
pg g^{-1}	Picogram (10^{-12} g) per gram. Equal to nanogram per kilogram (ng kg^{-1}).
POP	Persistent organic pollutant
QLD	Queensland
SA	South Australia
SEQ	South East Queensland
TAS	Tasmania
TBBP-A	Tetrabromobisphenol-A
VIC	Victoria
WA	Western Australia

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Executive summary

This study was conducted to determine the concentrations of brominated flame retardants (BFRs) in sediment samples from the Australian aquatic environment. To date, there are no published data on the concentrations of BFRs in aquatic sediment in Australia.

The study involved the re-analysis (for BFRs) of sediment samples collected in 2002-03 to ascertain background concentrations of dioxin-like compounds as part of the Australian Government Department of Environment and Heritage (DEH) National Dioxins Programme (NDP). In addition, six sediment samples from up- and downstream of the outfall of sewage treatment plants (STPs) were collected in 2005 to assess contamination from this potential point source. Samples were analysed from 39 locations from all states and territories of Australia. At seven locations, two samples were analysed representing similar sites within the same location. In total, samples from 46 sites were analysed. The locations were chosen to be representative of various land uses – remote (5), remote/agricultural (2), agricultural (7), urban (11), urban/industrial (9), industrial/urban/agricultural (1), industrial (7) and STPs (4) and a range of salinities – freshwater (20), marine (1) and estuarine (25).

The samples were collected by environmental professionals and risk of sample contamination was minimised at all stages of collection, processing and analysis. Chemical analysis of 26 polybrominated diphenyl ethers (PBDEs) congeners was done by the National Measurement Institute (NMI), Sydney, Australia. Quality assurance/ Quality Control included inter-laboratory comparison and sampling replication.

PBDEs were detected in samples from 35 of 46 sites and the ΣPBDE concentration (excluding the LOD (limit of detection)) ranged from non-detect to 60900 pg.g^{-1} dry weight (dw) with an overall mean (± standard deviation) and median of 4707 ± 12580 and 305 pg.g^{-1} dw, respectively. The results were rated as having low, medium or high ΣPBDE concentrations for this report and are listed in Table ES.1.

Table ES.1 Sediment sample sites categorised by ΣPBDE concentration

Low (non-detect to 1000 pg.g^{-1} dw)	La Trobe Industrial, La Trobe agricultural, Lower Werribee, East of Newcastle, Torrens River 'A' and 'B', Upper Serpentine, Upper Derwent, Hobart Derwent, Port of Darwin, Kakadu, Lower Brisbane 'A' and 'B', Lake Illawarra, Lower Hunter, Port Jackson East, Torrens Estuary, Upper Torrens, Canberra Lake Burley Griffin 'A' and 'B', ACT STP upstream, Luggage Point Downstream, Upper Brisbane River, Upper Yarra River, Upper Avon, Upper Swan River, Lower Tamar, Lower Derwent 'A' and 'B', Moreton Bay
Medium (1000 to 10000 pg.g^{-1} dw)	Port Phillip Bay 'B' (Lower Yarra 'B'), Botany Bay, Lower Torrens, Middle Swan 'A' and 'B', Canning River, ACT STP downstream, Brisbane River, Luggage Point Upstream, Bremer River up- and downstream.
High (> 10000 pg.g^{-1} dw)	Port Phillip Bay, Port Phillip Bay 'A' (Lower Yarra 'A'), Port Jackson West, Parramatta River 'A' and 'B'.

As expected, the sites with the highest concentrations were the estuaries with the highest degree of urbanisation and industrialisation. Marine and freshwater locations on the whole had lower PBDE concentrations than estuarine locations. Overall, there was a trend with

land-use which showed the concentrations of ΣPBDEs to be higher in the industrial/urban areas and followed in descending order of ΣPBDE concentration by industrial, STPs, urban, remote, agricultural, agricultural/remote and agricultural/urban/industrial. It should be noted those sediment samples from remote, remote/agricultural, agricultural and agricultural/urban/industrial land-uses had non-detectable or low concentrations of PBDEs. Table ES.2 summarises the results of the ΣPBDE concentrations in Australian aquatic sediment by land-use.

Table ES.2 Summary of ΣPBDE concentrations (pg.g^{-1} dw, excluding LOD) in aquatic sediment by land-use type.

	Number of samples	Mean	Standard Deviation	Median	Range
Remote	5	96	210	n/a	nd-480
Remote/ agricultural	2	47	14	n/a	37-57
Agricultural	7	52	96	2	nd-250
Agricultural/ urban/ industrial	1	n/a	n/a	n/a	33
Urban	11	880	910	530	nd-2800
STPs	4	3400	3400	2700	380-7700
Industrial	7	3900	9100	170	nd-25000
Industrial/ urban	9	17000	23000	1700	nd-61000

Results are reported to two significant figures; nd = non-detect; n/a = not assessable

In 86% of sediment samples the congener profile was dominated by BDE-209 (excluding samples where PBDEs were not detected). The main exceptions were the location at Port Phillip Bay and the STP locations. The profile from the Port Phillip Bay sample had BDE-183 as the dominant congener. This may suggest there is a nearby point source of the octa-BDE commercial product for which BDE-183 is described as a marker. Interestingly, the BDE-183 concentration at this location is one of the highest found in the international literature. The profile of the samples obtained near the outfall of STPs was dominated by BDE-209, however, it differed slightly from other samples with contributions from congeners BDE-17, -47, -49, -99, -206 and -207. This suggests the sources of PBDEs in the outfall from STPs differed from that in other aquatic environment locations.

Overall, with the exception of the samples collected from Port Phillip Bay, the concentrations of PBDEs in Australian sediment were relatively low when compared to studies on PBDEs in sediments in industrialised countries from the northern hemisphere. The concentrations of PBDEs were considerably lower than those found in sediment from North America, Europe and Asia (eg Oros et al 2005, Verslycke et al 2005, Mai et al 2005) with the maximum concentrations comparable to the minimum concentrations from some European and Asian countries. This indicates that aquatic environments in Australia have low levels of PBDE contamination.

1. Introduction

1.1 Background

The incorporation of brominated flame retardants (BFRs) into plastic and other materials is a cost-effective and highly efficient way to reduce flammability and therefore reduce harm caused by fires. They are incorporated into a variety of manufactured products including electronic and electrical equipment, building materials, carpet, clothing and other textiles. It is the bromine molecule that provides the flame retardancy properties of the chemical. Different BFRs are used depending on the application and product requiring flame retardancy. BFRs include among others, the chemicals polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBP-A).

They are relatively persistent, lipophilic chemicals with a tendency to bioaccumulation (ie accumulation in biota including humans) (de Wit 2002). This study focused on one group of BFRs - polybrominated diphenyl ethers (PBDEs) with TBBP-A analysis for 10% of samples. To date, there are no published data on the concentrations of BFRs in aquatic sediment in Australia.

Figure 1.1 shows the structure of PBDEs. They are synthesised by brominating diphenyl ether in the presence of a catalyst. There are 10 hydrogen atoms in the diphenyl ether molecule and any of these are able to be exchanged for bromine. Therefore, there are 209 possible PBDE congeners. These are numbered according to the position of the bromine atoms on the ring using the same IUPAC system as that used for numbering polychlorinated biphenyls (PCBs).

x+y = 1-10
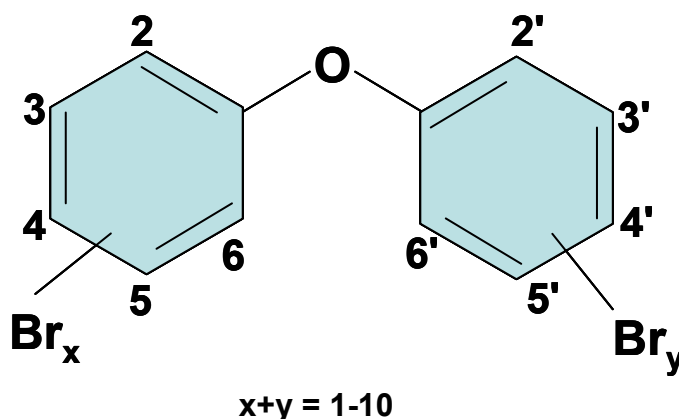
Figure 1.1 The structure of polybrominated diphenyl ethers (PBDEs).

There are two main types of BFR compounds: reactive and additive. Reactive flame retardants form part of the chemical makeup of the polymer and as such are bound to the polymer matrix via covalent bonds, but, some of the reactive flame retardants may not have polymerized and may be released into the environment (de Wit 2002). Additive compounds are mixed with polymers during their production and do not form chemical bonds with the polymer. As a consequence, they are able to separate or leach out of the product over time (de Wit, 2002, Alaee et al, 2003). PBDEs belong to the additive group of

flame retardants while TBBP-A is mostly used as a reactive flame retardant with limited use as an additive flame retardant (Alaee et al, 2003).

PBDEs have been used in three major commercial products: penta-BDE, octa-BDE and deca-BDE. The penta-BDE product mainly consists of the tetra, penta and hexa-BDEs including BDE -47, -99, -100, -153 and -154; the octa-BDE product consists of hexa, hepta, octa and nona-BDEs including BDE -153, -154, -183, -196, -197, -206 and -207; and the deca-BDE product consists primarily of BDE-209. Both penta and octa-BDE formulations contain the hexa-BDEs -153 and -154. The penta-BDE product is used mainly in flexible polyurethane foam for mattresses and cushioning, octa-BDE is used in the plastics industry in computer casings and monitors and deca-BDE is used in high impact polystyrenes and other materials used in electronic and electrical appliances, the automotive industry, construction and building applications as well as textiles (Department of Health and Human Services, 2004). TBBP-A is used, for example, in epoxy resins for printed wiring boards (BSEF, 2005).

PBDEs are imported as such into Australia, and also as constituents in manufactured products. In 2003-04, it was estimated that 180 tonnes of deca-BDE product, 20 tonnes of penta-BDE product, less than 10 tonnes of octa-BDE product and 69 tonnes of TBBP-A were imported into Australia. A decrease in the use of approximately 90% of octa-BDE and approximately 70% of penta-BDE was seen in 2003-2004 compared to 1998-1999 (NICNAS, 2005). The amount of BFRs in manufactured products imported into Australia is unknown. There are currently no restrictions on the use of PBDEs in Australia although since the end of 2005 the penta- and octa-BDE products are no longer sold, coinciding with the worldwide cessation of penta and octa-BDE product manufacture (NICNAS, 2005).

Aquatic sediment provide a final sink for persistent organic pollutants (POPs) such as PBDEs, as the water solubilities and vapour pressures of these chemicals are very low and therefore they adsorb onto solid particles such as sediment (Hyötyläinen and Hartonen 2002). It is noted that the half-lives of PBDEs in sediment are short compared to those of other POPs such as dioxin-like compounds (Ahn et al 2006; Sinkkonen and Paasivirta 2000). However, Ahn et al (2006) showed that in sediment, photodegradation is the main loss process which occurs only on the surface and in environments where the light reaches the sediment. Often this is not the case and therefore, once adsorbed onto sediment, PBDEs are only slowly degraded and can accumulate over time.

Analysis of POPs in aquatic in aquatic sediments can provide information on the contaminant sources and serve as the basis for assessing bioavailability and biomagnification factors of such compounds in biota. Studies from various countries have reported PBDE contamination in sediment. The cause for concern over this contamination is the potential for PBDEs to bioaccumulate and biomagnify. As diet is one of the suggested major routes of human exposure to PBDEs, it is necessary to investigate the presence of these chemicals in sediment. Prior to the current study, no data were available on PBDEs in the Australian aquatic environment. For this reason, it was decided to undertake the present study to investigate the concentration of BFRs in the Australian aquatic environment and also to assess state, land-use and salinity differences.

1.2 Objectives

The overall objective of the project was to provide knowledge about BFRs in the Australian aquatic environment through the investigation of aquatic sediments.

Specific aims of this study were to:
- determine the background concentrations and congener compositions of BFRs in estuarine, freshwater and marine sediments from Australia
- investigate the concentrations found at one type of potential point source – sewage treatment plant outfalls
- evaluate the concentration and congener composition of BFRs in sediment from areas with different land uses *and*
- compare the concentration and congener composition of BFRs in sediments from Australia with international data.

1.3 Scope

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

Stage 1 - Sample collection
Archived sediment samples collected in 2002-03 as part of the National Dioxins Programme (NDP) were selected to include a variety of land uses and salinities from all states and territories of Australia. Additional samples were collected up- and downstream of sewage treatment plants (STP) in 2005. Composite samples were collected from all sampling locations to ensure samples were representative of the background at each location.

Stage 2 - Sample analysis
Analysis of samples was undertaken at NMI to determine the concentrations of the 26 PBDE congeners listed in Appendix B. Quality control and quality assurance were integrated into all phases of the sampling and analysis processes. Inter-laboratory comparisons were undertaken with 10% of the sediment samples sent to eurofins/ERGO Research, Germany for PBDE analysis.

Stage 3 - Review data
Raw data were examined to assess BFR congener profiles in the sediment samples. A review of international literature was conducted and results obtained in the current study compared to those found in international environments.

Stage 4 - Report preparation and presentation
The results of the study of BFRs in Australian aquatic sediment are presented in this report.

2. Project design

An extensive selection of sediment samples representing rivers, estuaries and marine areas in all Australian states and territories was available for analysis. The majority of these samples were originally collected for the NDP. As sampling aquatic sediment is a complex task and organising a nation-wide sampling programme can be time consuming and expensive, the use of archived samples was considered to be efficient and cost-effective.

In the NDP study, sites that may have been subject to specific local contamination were purposely avoided. This was also appropriate for the current study, since the objective was to assess background concentrations of BFRs in the Australian aquatic environment. It was then necessary to collect additional samples to represent potential point sources of exposure, in this case, STPs. The samples originally collected for the NDP are referred to as 2002-03 samples and the newly collected samples as the 2005 samples.

Most estuarine fine-grained sediments on Australian coastal shelves are physically and biologically mixed downward, and thus surface sediment samples usually represent a mixture of the last decade of sediment inputs (Alongi and Christoffersen, 1992; Brunskill et al, 2002; Orpin et al, 2004). Mid and outer shelf Holocene sediments of NE Australia are composed of biogenic marine skeletal carbonate minerals, which are often mixed to sediment depths of >50 cm, and these surface sand/gravel sediments probably have a mean age of thousands of years (Larcombe and Carter, 2004). Accordingly, EnTox believes finding a detectable change in surface sediment concentrations of BFRs between 2002-03 and 2005 would be very unlikely. Therefore, it was considered feasible to use the 2002-03 samples to provide data on current background concentrations of PBDEs in Australia.

Sediment samples were analysed from 39 locations from all states and territories of Australia. At seven locations, two samples were analysed representing similar sites within the same location. In total, samples from 46 different sites were analysed. The locations were chosen to be representative of various land uses – remote (5), remote/agricultural (2), agricultural (7), urban (11), STPs (4), urban/industrial (9), industrial/urban/agricultural (1) and industrial (7) and a range of salinities – freshwater (20), marine (1) and estuarine (25).

2.1 Selection of sampling locations

Samples were selected from a bank of archived NDP sediments at EnTox based on the criteria set out by the Department of the Environment and Heritage (DEH). Table 2.1 lists the region, state and catchment requirements supplied by DEH.

Table 2. 1 Priority catchments for sampling

Region	Jurisdiction	Catchment
Northern Australia	NT	Darwin Harbour and surrounding catchments
Northern Australia	QLD	Logan, Albert and Brisbane
South-east Australia	ACT	Molonglo and Murrumbidgee
South-east Australia	NSW	Port Jackson, Hunter River, Lake Illawarra
South-east Australia	SA	Torrens and estuarine areas adjacent to these metropolitan centres
South-east Australia	TAS	Derwent, Tamar
South-east Australia	VIC	Latrobe-Thomson, Yarra, Werribee and Maribyrnong
South-west Western Australia	WA	Avon, Peel-Harvey, Swan-Canning

The geographical distribution of sampling locations is illustrated in Figure 2.1. The sampling locations were the geographical sampling area, for example, Lower Brisbane River while the sampling sites were the actual site from which the sample was obtained. Hence, Lower Brisbane 'A' and Lower Brisbane River 'B' are two different sites at the same location. Sampling locations were distributed nationally, covering all Australian states and territories and included different land-use types. 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. Table 2.2 lists the state, site, salinity and land-use of the sampling sites.

The selection of the locations for the 2005 samples was based on the need to investigate a possible point source of BFRs. DEH requested the collection of samples from within the vicinity of STPs. Samples were obtained from near the outfall of two STPs in South East Queensland (SEQ) and from near the outfall of one STP in the Australian Capital Territory (ACT).

Table 2.2. List of sampling locations by state, salinity and land-use.

State	Site	Salinity	Land-use	GPS coordinates*
SA	Upper Torrens	F	Agr/ Remote	NA
SA	Torrens River A	F	Agricultural	34.859 138.73637
SA	Torrens River B	F	Agricultural	NA
SA	Lower Torrens	F	Urban	34.915 138.55122
SA	Torrens Estuary	E	Industrial	34.817 138.51138
Tas	Lower Tamar River	E	Agr/ Remote	NA
Tas	Upper Derwent	F	Remote	NA
Tas	Hobart Derwent R	E	Urban	NA
Tas	Lower Derwent A	E	Agricultural	42.52850 146.72885
Tas	Lower Derwent B	E	Agricultural	42.53414 146.73094
Vic	LaTrobe R Industrial	F	Industrial	NA
Vic	LaTrobe R Agricultural	E	Agricultural	NA
Vic	Upper Yarra	F	Remote	NA
Vic	Port Phillip Bay	E	Ind/ Urban	38.0198 145.08251
Vic	Port Phillip Bay A (Lower Yarra A)	E	Ind/ Urban	37.8231 144.9495
Vic	Port Phillip Bay B (Lower Yarra B)	E	Ind/ Urban	37.83117 144.8983
Vic	Lower Werribee	F	Urban	37.750 144.570
WA	Upper Avon	F	Agricultural	NA
WA	Middle Swan A	E	Urban	NA
WA	Middle Swan B	E	Urban	NA
WA	Upper Swan	F	Urban	NA
WA	Upper Serpentine	F	Remote	32.50291 116.292358
WA	Canning R.	F	Industrial	NA
NT	Port of Darwin	E	Urban	12.4701 130.8676
NT	Kakadu	F	Remote	12.4617 132.9538
ACT	Canberra Lake Burley Griffin A	F	Urban	NA
ACT	Canberra Lake Burley Griffin B	F	Urban	35.293167 149.101638
ACT	ACT Downstream STP	F	STP	NA
ACT	ACT Upstream STP	F	Urban	NA
NSW	Port Jackson East	E	Ind/ Urban	33.851133 151.24428
NSW	Port Jackson West	E	Industrial	33.8711166 151.145433
NSW	Parramatta R. A	E	Ind/ Urban	33.8199333 151.0390833
NSW	Parramatta R. B	E	Ind/ Urban	33.8255166 151.059466
NSW	Botany Bay	E	Ind/ Urban	NA
NSW	Lower Hunter	F	Agricultural	NA
NSW	East of Newcastle	M	Ind/ Urban	32.916666 151.826388
NSW	Lake Illawarra	F	Industrial	34.53033 150.8403166
QLD	Moreton Bay	E	Ind/ Urb/ Agr	27.48335 153.21625
QLD	Upper Bris	F	Remote	NA
QLD	Lower Bris A	E	Industrial	27.35095 153.106808
QLD	Lower Bris B	E	Industrial	27.3600997 153.17838
QLD	Brisbane River(city and Indooroopilly)	E	Ind/ Urban	27.48749 152.02903
QLD	Luggage Point Downstream STP	E	STP	NA
QLD	Luggage Point Upstream STP	E	STP	NA
QLD	Bremer R. Downstream STP	E	STP	NA
QLD	Bremer R. Upstream STP	E	Urban	NA

F = freshwater, E = estuarine water, M = marine water * as provided by sampling personnel
NA – not available, not supplied by sampling personnel

Figure 2.1 Australian geographical distribution of sampling locations.

2.2 Sample collection

The sample collection methods are described here for the 2002-03 samples (Müller et al 2004) and the 2005 samples.

2.2.1 Sampling personnel
The nation-wide sampling programme was conducted by environmental professionals from various government departments and research organisations. Sampling personnel were responsible for the selection of 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 and sites. Details of this material can be found in Müller et al (2004).

2.2.2 Sampling strategy

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 gain 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 (eg narrow rivers and creeks), sampling personnel were instructed to collect samples 100m apart and provide details of the configuration used. Samples 'A' and 'B' are referred to as replicates and were collected approximately 1km apart within the same section of the water body and were used for the assessment of the reproducibility of the sampling strategy.
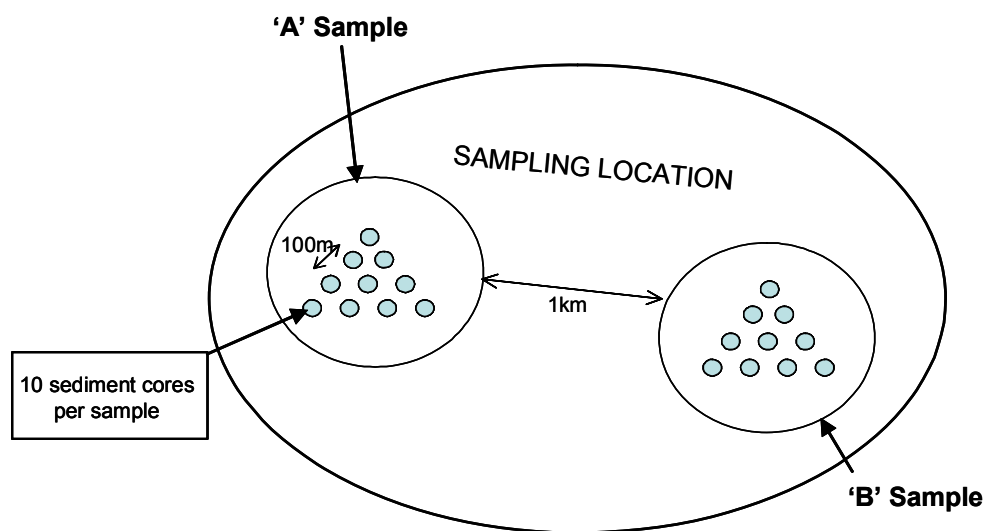
Figure 2.2 Sampling strategy for a given sampling location.

To obtain samples representing the background concentrations of POPs in a particular region or environment, sediment sampling personnel were specifically instructed to avoid potential immediate point sources (with the exception of the sites used for the 2005 sample collections). In the aquatic environment such point sources included but were not limited to:

- areas potentially subject to chemical spills
- wooden structures that may have received chemical treatment (ie jetties, docks) *and*
- drains in general.

Sediment sampling personnel were instructed to avoid sampling in areas that may be directly affected by localised sources in the aquatic environment. Criteria were provided for sampling site selection with sampling 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 *and*
- 50 m proximity of any drain except if the drain was natural (in remote areas) or drains in agricultural sites (ie 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).

The archived 2002-03 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 potential contamination problems associated with the handling of tubes. Upon receipt of a sample by EnTox, sediment was removed from coring tubes, pooled to form a composite sample, and homogenised.

As the 2005 samples were collected to represent point sources, these were obtained within 300 m up- and downstream of the outfall from STPs. These sediment samples were collected using a grab sampler where at each site, one sample was taken from each side of the river and one in the middle. These three cores were mixed in a stainless steel bucket to form one composite sample and placed in a solvent-washed glass jar.

Composite samples were freeze-dried, sieved through a 2 mm sieve and placed in individual solvent washed jars for transportation to NMI and eurofins/ERGO for analysis. All samples were stored in cool, dry, dark conditions between processing and analysis at EnTox or NMI.

3. Analysis, statistics and data quality

3.1 Analytical methodology

Samples were analysed at the National Measurement Institute (NMI), Sydney, Australia. For the purpose of inter-laboratory comparison, duplicate samples were analysed at eurofins/ERGO in Hamburg, Germany. Briefly, NMI used isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) to determine the concentrations of PBDEs in the sediment samples. This method provided data on 26 PBDE congeners listed in Table 3.1. The analytical methodology for the determination of PBDEs was based on the Draft USEPA Method 1614.

Table 3.1 BDE congeners analysed by NMI.

BDE Congener	Abbreviation
2,2',4-Tribrominated diphenyl ether	BDE 17
2,4,4'-Tribrominated diphenyl ether	BDE 28
2',3,4-Tribrominated diphenyl ether	BDE 33
2,2',4,4'-Tetrabrominated diphenyl ether	BDE 47
2,2',4,5'-Tetrabrominated diphenyl ether	BDE 49
2,3',4,4'-Tetrabrominated diphenyl ether	BDE 66
2,3',4',6-Tetrabrominated diphenyl ether	BDE 71
3,3',4,4'-Tetrabrominated diphenyl ether	BDE 77
2,2',3,4,4'-Pentabrominated diphenyl ether	BDE 85
2,2',4,4',5-Pentabrominated diphenyl ether	BDE 99
2,2',4,4',6-Pentabrominated diphenyl ether	BDE 100
2,3',4,4',6-Pentabrominated diphenyl ether	BDE 119
3,3',4,4',5-Pentabrominated diphenyl ether	BDE 126
2,2',3,4,4',5'-Hexabrominated diphenyl ether	BDE 138
2,2',4,4',5,5'-Hexabrominated diphenyl ether	BDE 153
2,2',4,4',5,6'-Hexabrominated diphenyl ether	BDE 154
2,3,3',4,4',5-Hexabrominated diphenyl ether	BDE 156
2,3,4,4',5,6-Hexabrominated diphenyl ether	BDE 166
2,2',3,4,4',5',6-Heptabrominated diphenyl ether	BDE 183
2,2',3,4,4',6,6-Heptabrominated diphenyl ether	BDE 184
2,3,3',4,4',5',6-Heptabrominated diphenyl ether	BDE 191
2,2,3,3',4,4',5,6'-Octabrominated diphenyl ether	BDE 196
2,2,3,3',4,4',6,6'-Octabrominated diphenyl ether	BDE 197
2,2,3,3',4,4',5,5',6-Nonabrominated diphenyl ether	BDE 206
2,2,3,3',4,4',5,6,6-Nonabrominated diphenyl ether	BDE 207
Decabromodiphenyl ether	BDE 209

The BDE congeners investigated in this study were reported on a pg.g^{-1} dry weight (dw) basis. For positive identification and quantification, the concentration of PBDE congeners in a sample had to be greater than three times any level found in the corresponding laboratory blank analysed. The ΣPBDE concentration in the laboratory blanks (n=4) ranged from 71 to 110 pg/g dry weight with a mean ± standard deviation of 81 ± 19 pg/g dry weight. The ΣPBDE concentration is the sum of the 26 congeners excluding the limit of detection (LOD) values unless specified otherwise. For all samples, data for quantified analytes were reported to 2 or 3 significant figures, and the limit of detection data for non-quantified analytes were reported to 1 significant figure. The mean concentration is expressed ± the standard deviation. Further details of the analytical methodologies for NMI and eurofins/ERGO are included in Appendix B.

The samples sent to eurofins/ERGO for inter-laboratory comparison were also analysed for TBBP-A.

3.2 Database and statistical analysis

Statistical analysis was undertaken using XL Stat (supplementary Microsoft Excel 2000 package). The Kruskal-Wallis non-parametric test was used to assess differences between strata as the data were not normally distributed. The results were considered statistically significant if the p-value was less than the alpha value of 0.05. In this study, the median concentration 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 increased or reduced substantially by a single high or low sample result.

3.3 Quality Control and Quality Assurance

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. Contact between samples and with plastics was avoided at all stages. Direct contact with the sediment by sampling personnel was avoided by use of the coring tubes. Coring tubes were thoroughly cleaned with acetone and toluene at EnTox and sealed with aluminium foil prior to distribution to sampling personnel. Sediment-filled coring tubes were resealed in aluminium foil at the point of collection, and returned as quickly as practical to EnTox in the original packaging. Following receipt by EnTox, tube contents were removed promptly under clean laboratory conditions. All items of equipment involved in sediment core handling were rinsed clean in a detergent solution and solvent rinsed (acetone) between samples. Once removed from coring tubes, samples were stored in aluminium foil packets prior to homogenisation. Once placed in solvent-washed foil containers and covered with foil, the samples were frozen over night and then freeze dried for 24-48 hours. The dried samples were sieved through a 2 mm sieve and the sieved material was transferred to solvent-washed glass jars for transport to NMI for analysis.

Grab samples comprising the STP sediment collected in 2005 were placed in solvent washed glass jars at the point of collection. Following receipt by EnTox, the same procedures areas detailed above for the coring tubes were used for processing the sediment.

The study design allowed for the determination of inter-laboratory comparison as well as sampling reproducibility.

3.3.1 Inter-laboratory comparison

An inter-laboratory comparison (laboratory quality control) was conducted in which five samples were re-analysed by an independent second laboratory – eurofins/ERGO, Hamburg, Germany. The comparisons between inter-laboratory data were assessed by calculating the normalised differences (ND) between the original sample and the re-analysed sample for all detectable congeners (see Box 1). The ND was then averaged for each sample to obtain the mean normalised difference (MND) which gives an indication of whether or not there were systematic differences between the two laboratories (ie either laboratory was consistently higher or lower for any compounds) in a given sample. The samples were Darwin, Upper Brisbane River, Canberra Lake Burley Griffin 'B', Parramatta 'A' and Port Jackson East.

The congeners determined by both laboratories were: BDE- 17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -197, -207 and -209 (see Appendix C, Table C.1).

For the sample from Darwin it was not possible to calculate a MND as the sample analysed by NMI resulted in no PBDE congeners detected while the analysis at eurofins/ERGO found low concentrations of BDEs -85, -207 and -209. For the Upper Brisbane River, it was not possible to calculate a MND as the analysis by NMI resulted in the detection of only low concentrations BDEs-85, -183 and -207 while the analysis at eurofins/ERGO detected only low concentrations of BDE-209. For the sample from Canberra Lake Burley Griffin 'B', BDE-209 was detected by both laboratories with a ND of 43% (MND not applicable since only one congener detected), in addition, eurofins/ERGO detected BDE-207. The sample from Parramatta 'A' was found by both laboratories to have detected concentrations of PBDEs and the MND was 46%. For the sample from Port Jackson, BDE-207 and -209 were detected by both laboratories and the MND was 20%.

It would have been preferable to determine which samples had detected PBDE concentrations prior to sending samples for inter-laboratory comparison. However, due to the project timeframe this was not possible and therefore five samples were randomly chosen. It should be noted that typically for inter-laboratory comparisons the differences can be relatively high particularly for congeners that are found in low concentrations, close to the LOD.

3.3.2 Sampling replication

As explained in Section 2.2.2, two samples ('A' and 'B') were obtained from each site. From the 39 locations, seven 'B' samples were randomly chosen to be analysed for the assessment of sampling replication. This was undertaken to assess the reproducibility of

the sampling strategy, that is, whether or not using the prescribed sampling criteria and reproducing the sampling procedures identically at both sites by the same sampling personnel was carried out successfully. For each sampling location the normalised difference (ND) between 'A' and 'B' samples was determined for the congeners detected in both replicates (see Box 1). The normalised differences were then averaged to achieve a mean normalised difference (MND) between the two samples collected at one location. Full details are listed in Appendix C.

A comparison between 'A' and 'B' samples is complicated by the fact that many of the samples chosen had relatively low contamination. Notably, this was usually consistent between sampling replicates. For example, in the Torrens River location PBDEs were not detected in either the 'A' or the 'B' sample. Similarly in the locations Lower Brisbane, Lower Derwent, Lake Burley Griffin and the Middle Swan only few congeners were detected at relatively low concentrations in one or both samples and usually with good reproducibility (if detected in both samples). The reproducibility between 'A' and 'B' samples was lowest in the samples from the most contaminated locations, Parramatta River and Port Phillip Bay (Lower Yarra). For example, the results from Parramatta River 'A' were consistently higher (2-4 fold) than the results from the 'B' site. The lowest reproducibility was observable in samples collected from Port Phillip Bay where the concentration of most congeners were more than an order of magnitude higher in the samples from the 'A' site. These lower reproducibilities in samples from more contaminated sites may indicate proximity to sources and/or inhomogenous distribution of PBDEs.

Box 1. 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.

Sample A (pg g^{-1} dw)	Sample B (pg g^{-1} dw)	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 (MND) expresses the average normalised difference for all detected congeners.

4. Brominated flame retardant concentrations in Australian aquatic environments

The following section provides an analysis of BFRs in the aquatic environment in Australia. Individual results of the PBDE analysis from samples collected in 2002-03 and 2005 are listed in Appendix D. Results from samples collected in 2005 are indicated by an asterisk (*). Results of the TBBP-A analysis from five samples are detailed in Section 4.4.

BDEs were detected at 35 of 46 sites with the ΣPBDE concentrations ranging from 1.3 to 60900 pg.g^{-1} dw. The mean and median ΣPBDE concentrations were 4707 ± 12580 and 305 pg.g^{-1} dw excluding the LOD, respectively. The sample from Newcastle East was analysed twice and the mean of the two results was used in the summary results of all samples. Overall, 24 out of 26 congeners were detected in the Australian sediment samples. BDEs -126 and -156 were not detected in any samples. Site concentrations of PBDEs were rated as low, medium or high for this report (Table 4.1).

Table 4.1 Sites rated as low, medium or high concentrations of ΣPBDEs.

Low (non-detect to 1000 pg.g^{-1} dw)	La Trobe Industrial, La Trobe agricultural, Lower Werribee, East of Newcastle, Torrens River 'A' and 'B', Upper Serpentine, Upper Derwent, Hobart Derwent, Port of Darwin, Kakadu, Lower Brisbane 'A' and 'B', Lake Illawarra, Lower Hunter, Port Jackson East, Torrens Estuary, Upper Torrens, Canberra Lake Burley Griffin 'A' and 'B', ACT STP upstream, Luggage Point Downstream, Upper Brisbane River, Upper Yarra River, Upper Avon, Upper Swan River, Lower Tamar, Lower Derwent 'A' and 'B' and Moreton Bay
Medium (1000 to 10000 pg.g^{-1} dw)	Port Phillip Bay 'B' (Lower Yarra 'B'), Lower Torrens, Middle Swan 'A' and 'B', Canning River, ACT STP downstream, Brisbane River, Luggage Point Upstream and Bremer River up- and downstream.
High (> 10000 pg.g^{-1} dw)	Port Phillip Bay, Port Phillip Bay 'A' (Lower Yarra 'A'), Port Jackson West and Parramatta River 'A' and 'B'.

In 86% of samples (where PBDEs were detected) BDE-209 made the highest contribution to the ΣPBDE concentration. BDE-209 was also found to be dominant in studies from various other countries (eg Eljarrat et al 2005, Verslycke et al 2005, Mai et al 2005). The preferential accumulation of BDE-209 over the lower brominated diphenyl ethers can be attributed to the difference in hydrophobicity, that is, the log K_{ow} of BDE-209 is ~ 9.97 while for BDE-47 it is ~ 6.1 (Strandberg et al 2001; Tomy et al 2001).

An exception was the sample from Port Phillip Bay which had a profile dominated by BDE-183 with elevated levels of a range of other BDEs that are typical for octa-BDE commercial product. In contrast the typical components of the penta-BDE product were below the LOD and the key component of deca BDE (BDE 209) was about a factor 13 lower than BDE-183. The sample from Port Phillip Bay was the only sample with such a BDE profile in the current study. The site at Port Phillip Bay was classified as industrial/urban with a high urban density, that is, greater than 500 000 inhabitants. The area is tidal and subject to flooding with minimal flow velocity. The sample was sandy sediment, obtained from around 1km off-shore and around 1.5 km from the Mordialloc Estuary mouth. The sampling area is described as the east side of Port Phillip Bay, Victoria. As stated in Section 2.2.2, sampling was avoided near possible point sources.

These instructions concerned primarily point sources of dioxin for the NDP study. The result from this study suggests a point source or spill of the octa-BDE commercial product in the proximity to this sampling location.

The concentration of BDE -183 at 31 000 pg.g^{-1} dw from Port Phillip Bay is to the authors' knowledge, the highest ever reported. Oros et al (2005) found BDE-183 to be 200 pg.g^{-1} dw in one sample from San Pablo Bay in the San Francisco Estuary in the USA. While in Spain, Eljarrat et al (2004) found BDE-183 to range from 100 to 23000 pg.g^{-1} dw where the sample with the highest concentration was obtained from a site described as 30km downstream of a heavily industrialised town with a very significant chemical industry. Wang et al (2005) found the concentration of BDE-183 to be 3810 pg.g^{-1} in sediment collected in the vicinity of an open electronic waste disposal and recycling facility in China. Accordingly, the Port Phillip Bay site data may warrant further monitoring of PBDE concentrations.

The congener profile of samples collected near the outfall of STPs also showed BDE-209 made the highest contribution to the ΣPBDE concentration, but, there was also some contribution by lower brominated congeners BDE-17, -47, -49, -99, as well as higher brominated congeners BDE-206 and -207. This suggests the sources of PBDEs in the outfall from STPs may differ from those in the other aquatic environment locations.

The congener profile can be used to consider possible sources of PBDE exposure to the aquatic environment. However, identification of sources is complicated by degradation from higher to lower brominated diphenyl ethers and differences in chemical half-lives, metabolic activity and bioaccumulation ability. In addition, it is difficult to ascertain from where the actual commercial product contamination is originating and how it is reaching the aquatic environment. Certain land-use types have been suggested as potential sources based on use or processing of PBDEs or PBDE contaminated waste and are discussed further in Section 4.3.

4.1 Concentration of brominated flame retardants in sediments in different states and territories of Australia

The analytical results of PBDEs in sediment are presented here on the basis of regional distribution. The concentrations of PBDEs in $pg.g^{-1}$ dw are presented in Figures 4.1 to 4.7 for each state and territory. Note that the scale for the axes may differ between graphs. The graphs include the congeners BDE-47, -99, -100, -153, -154, -183 and -209 where detected.

4.1.1 Queensland

Nine samples obtained in Queensland were analysed, comprising, four from the Brisbane River and one from Moreton Bay (Figure 4.1, top graph) and four from the vicinity of STP outfalls (Figure 4.1, bottom graph). The concentrations of PBDEs were greatest in the Brisbane River (City and Indooroopilly) sample with only low concentrations detected in the Upper Brisbane River, and Lower Brisbane River 'A' and 'B' samples. Lower Brisbane River 'B' had small concentrations of BDE-209 as did the sample obtained from Moreton Bay. The Lower Brisbane River 'A' sample was collected in 2002-03 near the Luggage Point sample site yet no PBDEs were detected at this site whereas, both the up- and downstream Luggage Point samples collected in 2005 had detectable concentrations of BDE-209 and relatively low concentrations of lower brominated congeners. However these results should not be used to assess temporal trends since the deposition rate of sediments was not assessed in this study. Also the area at the mouth of the Brisbane River is subject to intensive maritime activity including dredging and sedimentation including resuspension of sediments and dilution is very complex.
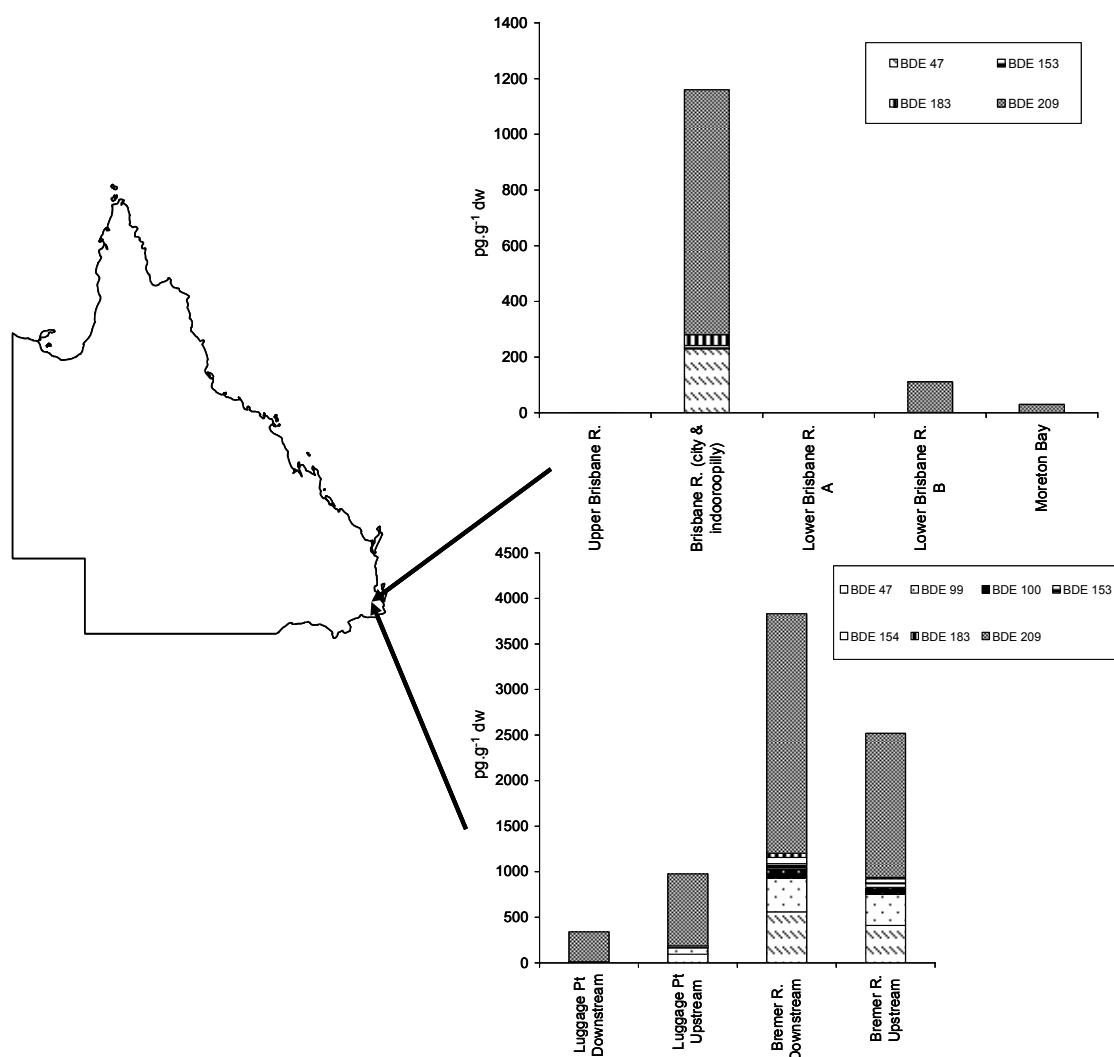
Figure 4.1 ΣPBDE concentrations from sites in Queensland

4.1.2 New South Wales

Seven samples were analysed from NSW with low or non-detectable concentrations of PBDEs found in the east of Newcastle, Lower Hunter and Lake Illawarra samples. The ΣPBDE concentrations in the samples from Port Jackson East and West and the Botany Bay ranged from 900 to 25000 pg.g^{-1} dw while the greater concentrations were found in the Parramatta River at over 35000 pg.g^{-1} dw.

4.1.3 Australian Capital Territory

Four samples of sediment from the Australian Capital Territory were analysed. Two from Lake Burley Griffin and two from the outfall of the Lower Molonglo Water Quality Control Centre (referred to as STP ACT). The STP samples were targeted as a possible point source (downstream) and a control (upstream) and these samples had greater concentrations of ΣPBDEs than the Lake Burley Griffin samples. The ΣPBDE concentrations in the lake samples were less than 210 pg.g^{-1} dw while the upstream and downstream STP concentrations were 360 and 7700 pg.g^{-1} dw, respectively. Figure 4.2 depicts the PBDE results from New South Wales and the Australian Capital Territory.
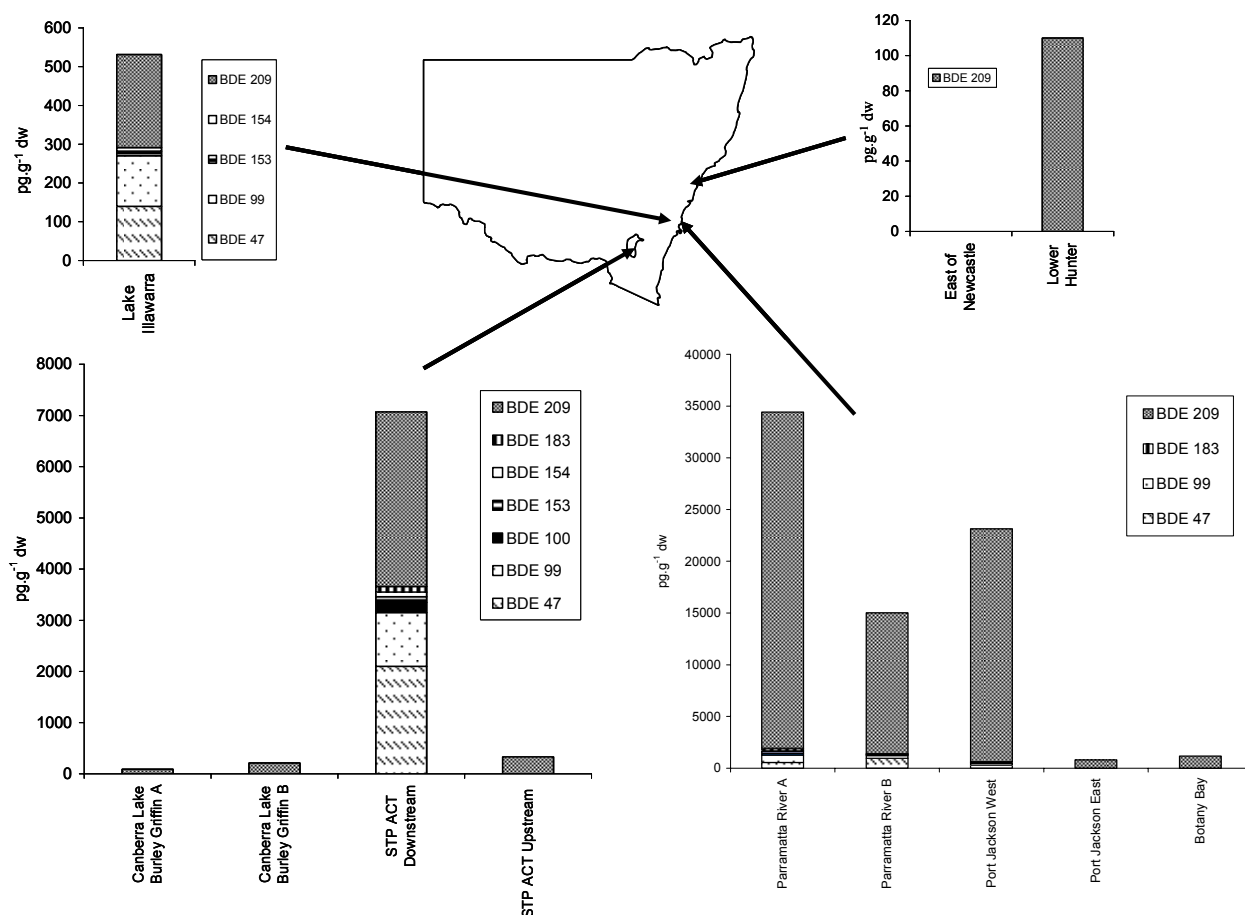
Figure 4.2 ΣPBDE concentrations from sites in NSW and the ACT

4.1.4 Victoria

Seven samples of sediment were analysed from Victoria. There were no detectable PBDE concentrations at either the industrial or the agricultural sites from the La Trobe region. The samples obtained from Port Phillip Bay showed variable results with the central Port Philip Bay sample having the highest concentration of ΣPBDEs found in this study. Other Victorian samples were obtained from the Lower Werribee River where no PBDEs were detected and the Upper Yarra River where the concentration of ΣPBDEs was 480 pg.g^{-1} dw. The results are presented in Figure 4.3. The inset shows the result of the congeners BDE-196, -197, -206 and -207 which were found in Port Phillip Bay and Port Phillip Bay 'A' (Lower Yarra 'A') samples.
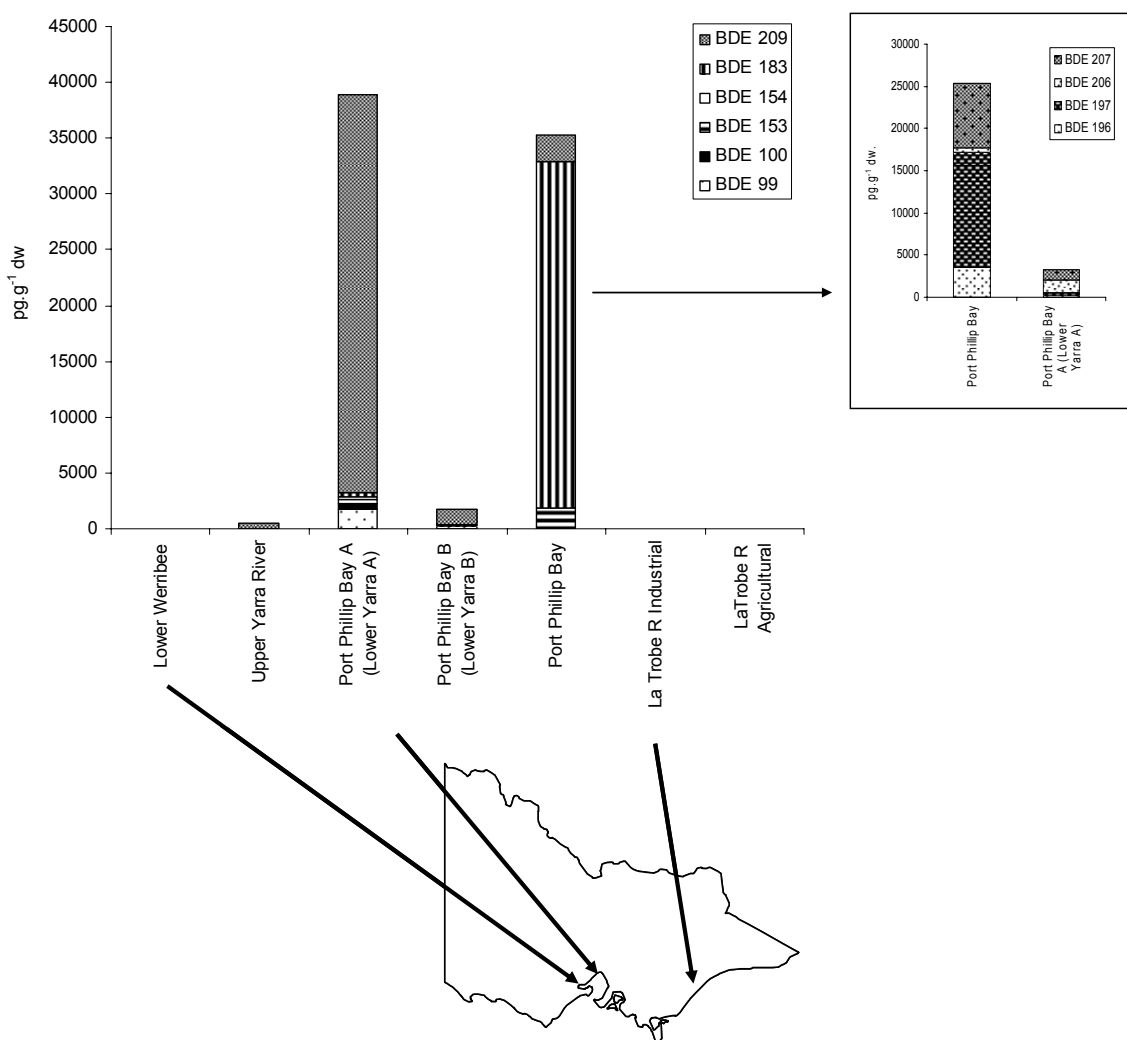
Figure 4.3 ΣPBDE concentrations from sites in Victoria

4.1.5 Tasmania

Five samples of sediment were analysed from Tasmania and either no or relatively low concentrations of PBDEs were detected. The sample with the greatest concentration was from the Hobart Derwent River, while the other samples from the Derwent River had the lowest concentrations ranging from nd to 37 pg.g^{-1} dw. The results are presented in Figure 4.4.
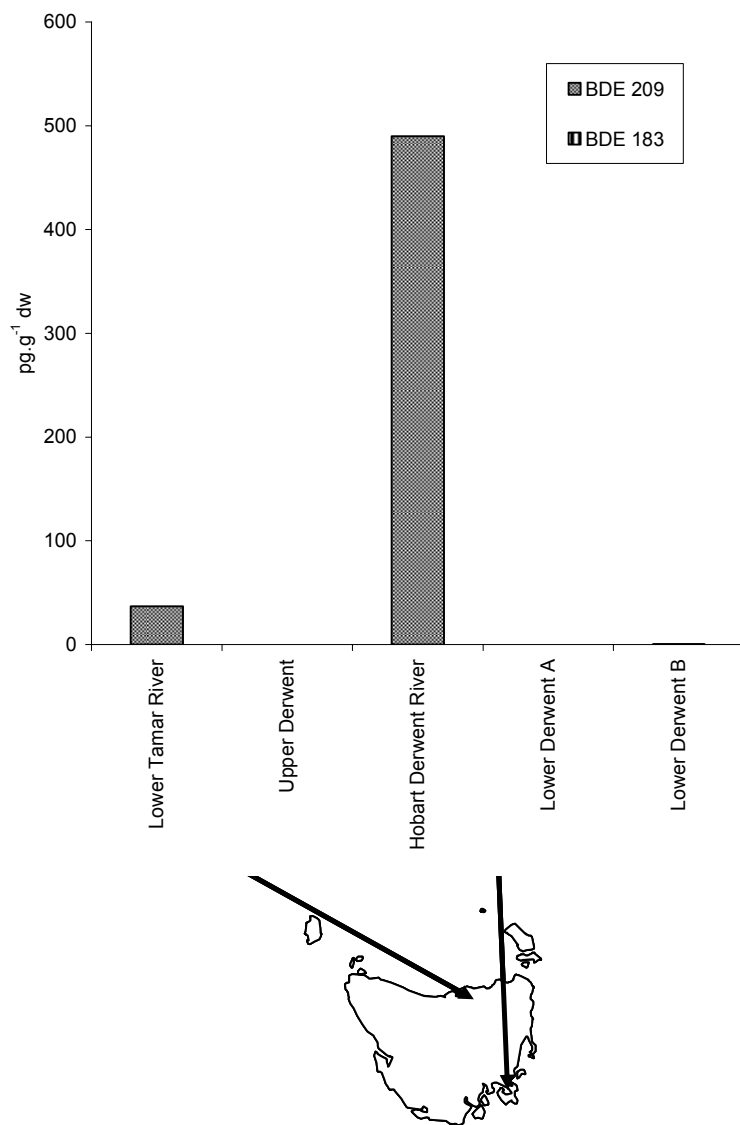
Figure 4.4 ΣPBDE concentrations from sites in Tasmania

4.1.6 South Australia

Five samples of sediment from South Australia were analysed. The concentration of ΣPBDEs ranged from nd to 1878 $pg.g^{-1}$ dw. The greatest concentration was from the Lower Torrens River. The results are presented in Figure 4.5.
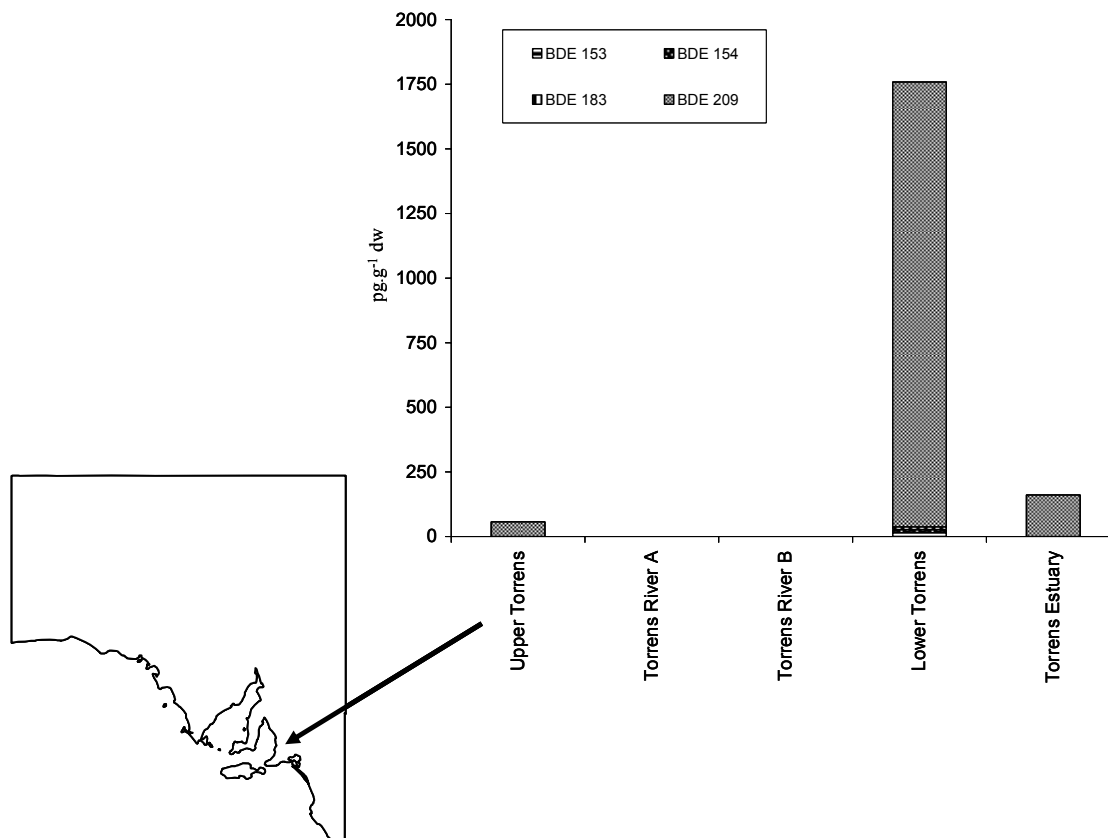
Figure 4.5 ΣPBDE concentrations from sites in South Australia

4.1.7 Western Australia

Six samples of sediment from Western Australia were analysed. The concentrations of ΣPBDEs ranged from nd to 1640 pg.g^{-1} dw. The greatest concentration was found in the Canning River and was followed closely by the concentration found at the Middle and Upper Swan River locations. There were no PBDE congeners detected in the Upper Serpentine River. A congener pattern different from the other samples was found in the Upper Avon River with BDE-47 and -28 + 33 making the highest contribution to the ΣPBDE concentration as opposed to BDE-209. This suggests that the Upper Avon may be contaminated by a point source different to the other sites such as a STP as this is similar to the profile seen in samples from STPs from Queensland and the ACT. The results are presented in Figure 4.6.
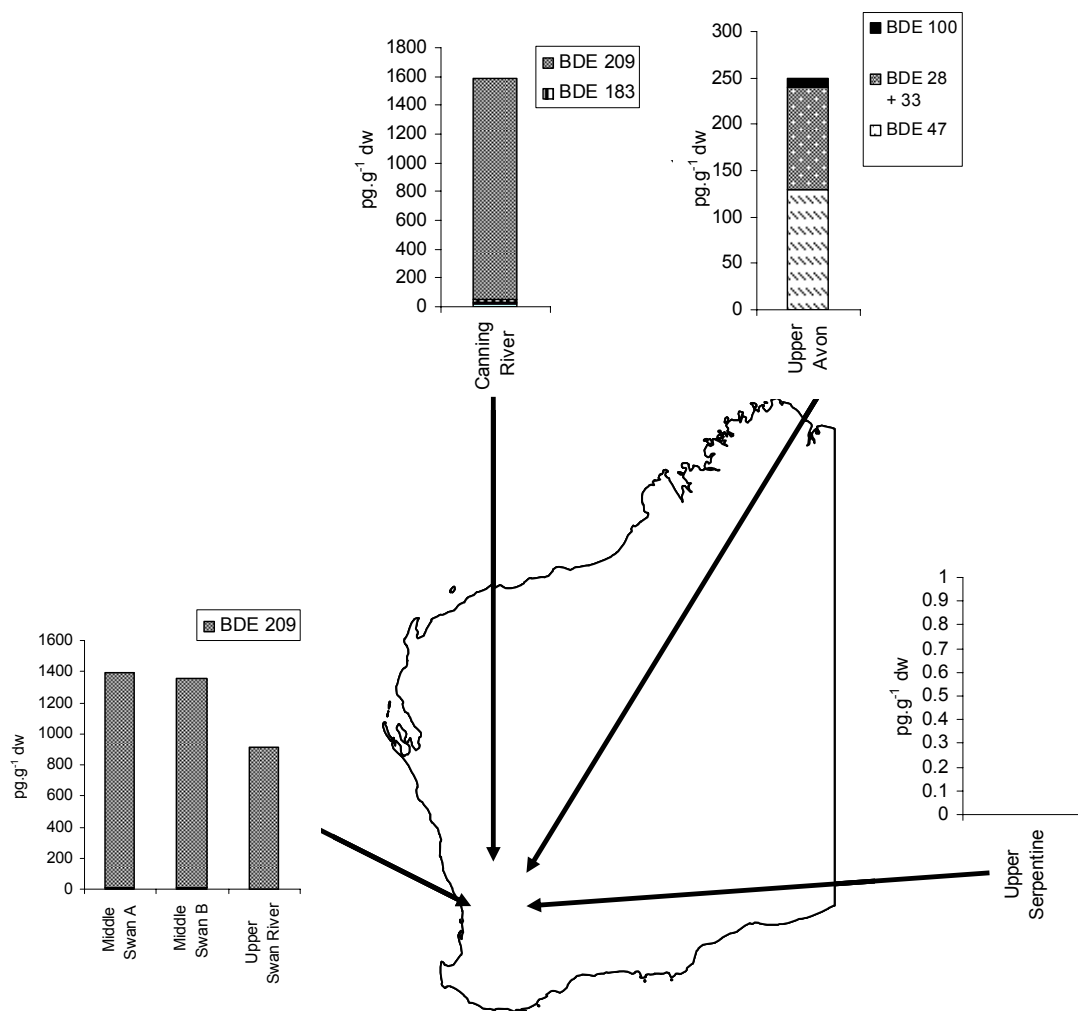
Figure 4.6 ΣPBDE concentrations from sites in Western Australia

4.1.8 Northern Territory

Sediment was obtained and analysed from the Port of Darwin, an urban area and from Kakadu, a remote area of the Northern Territory. No PBDEs were detected in either of these samples. Figure 4.7 is a map of the Northern Territory.
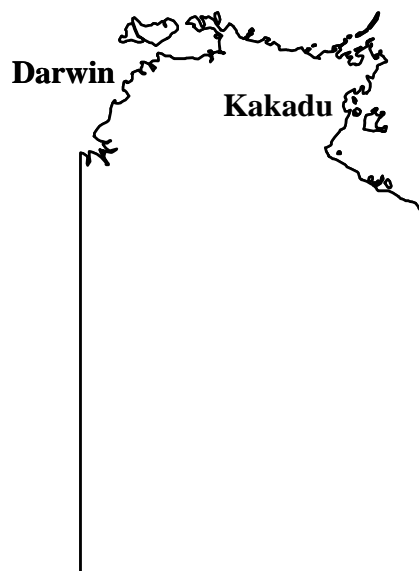
Figure 4.7 Map of Northern Territory.

4.2 Concentration of PBDEs by salinity

This study determined background concentrations of PBDEs in sediment on the basis of salinity. The sampling locations were differentiated as fresh, estuarine and marine waters and the locations and corresponding salinity classifications are listed in Table 2.2. It should be noted that the mean, median and range are calculated including both the 'A' and 'B' samples where applicable.

Overall, the results of this study found that PBDE concentrations were around 10 times higher in estuarine water than freshwater (Table 4.2). Only one marine location was sampled and PBDEs were not detected at this location. For this reason, this salinity type was removed from the analysis with only fresh and estuarine waters compared. A statistically significant difference was found between the concentrations of ΣPBDEs in fresh and estuarine waters (p=0.02) (Kruskal-Wallis test).

The higher concentrations of PBDEs in estuaries relates to the proximity to potential diffuse urban inputs and point sources such as industry or STPs that are typically situated in Australia's estuaries. In contrast, fresh water environments are typically inland and thus distant to the major metropolitan and industrial centres. In this study, freshwater locations included the following land-use types: remote (5), agricultural (4), urban (6), STPs (1), industrial (3) and agricultural/remote (1). Estuarine locations included the following land-use types: industrial (4), industrial/urban (8), urban (5), STPs (3), agricultural (3), agricultural/remote (1) and industrial/urban/agricultural (1). Section 4.3 discusses PBDE concentrations by land-use type. Briefly, higher concentrations were found at industrial, industrial/urban, near the outfall of STPs and urban locations than at remote, agricultural and agricultural/remote locations.

Table 4.2 Summary of ΣPBDE results by salinity expressed as pg.g^{-1} dw excluding LOD (mean, standard deviation, median and range).

Salinity	Number of samples	Mean	Standard deviation	Median	Range
Freshwater	20	720 (890)	1740 (1710)	100 (320)	nd - 7730 (40-7750)
Estuarine	25	8090 (8200)	16400 (16300)	1060 (1140)	nd - 60900 (96-60940)
Marine	1	n/a	n/a	n/a	nd
Total	46	4700 (4900)	13000 (13000)	310 (480)	nd-61000 (40-61000)

Results including the LOD are included in parenthesis. Where a result was non-detect it was considered to be zero for summary results. All results are reported to two to three significant figures. n/a = not assessable nd = non-detected

In agreement, in the USA, higher PBDE concentrations were found in estuarine sediment than in freshwater sediment (eg Oros et al 2005, Hale et al 2001, Zhu and Hites 2005, Song et al 2005). In Spain, Eljarret et al (2005) found the most contaminated samples were from the Barcelona river mouth while the least contaminated were the marine sediment samples. In Denmark, sediment samples from freshwater had higher concentrations of PBDEs than the marine sediment from all sites except in the Copenhagen harbour which the authors describe as highly trafficked (Christensen and Platz 2001). The current study also found the freshwater sediment to contain higher concentrations than the marine, however, only one marine location was investigated in the current study.

4.3 Concentration of PBDEs by land-use types

This study determined background concentrations of PBDEs in sediment from locations that were influenced by various land-use types. For the aquatic environment in particular it is difficult to differentiate between land-use types that influence concentrations of contaminants in sediments at a particular location. Nevertheless, for the purpose of this study sampling locations were classified as remote, agricultural/remote, agricultural, agricultural/urban/industrial, urban, near the outfall of STPs, industrial and industrial/urban based on the dominant land-use type situated near the sampled locations. The sites and corresponding land-use types are listed in Table 2.2. A summary of the measured concentrations of PBDEs collected in sediment from the different land-use types are presented in Table 4.3 and Figure 4.8. It should be noted that the mean, median and range are calculated including both the 'A' and 'B' samples where applicable.

Table 4.3 Summary of results by land-use type expressed as pg.g^{-1} dw excluding LOD (mean, standard deviation, median and range).

	Number of samples	Mean	Standard Deviation	Median	Range
Remote	5	96 (230)	210 (210)	n/a (170)	nd-480 (40-590)
Remote/ agricultural	2	47 (220)	14 (35)	n/a (220)	37-57 (200-250)
Agricultural	7	52 (230)	96 (110)	2 (230)	nd-250 (96-420)
Agricultural/ urban/ industrial	1	n/a	n/a	n/a	33 (120)
Urban	11	880 (1100)	910 (880)	530 (740)	nd-2800 (240-2800)
STPs	4	3400 (3500)	3400 (3300)	2700 (2800)	380-7700 (590-7800)
Industrial	7	3900 (4000)	9100 (9100)	170 (340)	nd-25000 (210-25000)
Industrial/ urban	9	17000 (18000)	23000 (23000)	1700 (2200)	nd-61000 (170-61000)
TOTAL	46	4700 (4900)	13000 (13000)	310 (480)	nd-61000 (40-61000)

Results are reported to two significant figures; nd = non-detect; n/a = not assessable. Results including the LOD are included in parenthesis.

Analysis of the data found a statistically significant difference in ΣPBDE concentrations between the land-use types (p=0.007, Kruskal-Wallis test). The data indicate concentrations are generally greater in sediment samples collected from industrial/urban, industrial STPs and urban locations while the lowest concentrations were from the remote, agricultural and remote/ agricultural areas.

As was the trend in the current study, proximity to industrial and urban areas was identified as a possible source of PBDE contamination to aquatic environments in other studies (eg Samara et al 2006, Mai et al 2005, Christensen and Platz 2001). Oros et al (2005) suggested that the lower PBDE concentrations in a non-urbanised area of the estuary were due to the high levels of freshwater inflow, dilution and short residence times.

Conversely, Rayne et al (2003) sampled sediment from sites chosen to surround potential point sources such as automobile 'wrecking' operations, landfills, major industry, forest fire sites, sewage outfalls and agricultural sites where biosolids may have been applied. No clear trends were observed in PBDE concentrations compared to any of these potential

sources. Allchin et al (1999) suggested that landfill leachate was not a likely source of PBDEs to the aquatic environment, however suggested that industrial waste influenced PBDE concentrations.

The non-detected and low concentrations of PBDEs in remote, remote/ agricultural and agricultural/urban/industrial locations suggests that if PBDEs are released in urban and industrial locations there is not yet movement of PBDEs via long range transport to these Australian locations.

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 EnTox 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).

Maximum value

80000

Closed circle: outliers > 3 times the inter-quartile range

Open circle: outliers < 3 times the inter-quartile range

Q3: represents the third quartile

Median value

Q1: represents the first quartile

Whiskers: 1½ times the inter-quartile range

0.1   Minimum value

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.

na   96   Remote

na   47   Remote/Agricultural

2   52   Agricultural

530   880   Urban

2700   3400   STPs

170   3900   Industrial

2160   18000   Industrial/Urban

0   20000   40000   60000   8000

sum PBDE concentration (pg.g^{-1}dw)

Figure 4.8 Box and whisker plot (see Box 2) of ΣPBDE concentrations by land-use type expressed as pg.g^{-1} dry weight.
The number on the left hand side of the box is the median and on the right is the mean. (The agricultural/urban/industrial site is not on this graph as there was only one data point. The ΣPBDE concentration in this sample was 33 pg.g^{-1} dry weight.)

4.3.1 Potential point source – outfall of sewage treatment plants (STPs)

Sediment samples were obtained from sites up- and downstream near the outfall of STPs to investigate the possibility of STPs acting as point sources for PBDEs. As the samples obtained from upstream of the outfall of STPs were not likely to be contaminated by the outfall of the STP, these sites were included in the urban land-use type and were used as a comparison for the samples obtained from downstream of the outfall. Overall the ΣPBDE concentrations were higher at sites downstream of a STP than upstream (Figure 4.9).

The highest ΣPBDE concentrations at the outfall of STPs were found at the ACT site. The ACT downstream site had a ΣPBDE concentration of 7730 pg.g^{-1} dw compared to 360 pg.g^{-1} dw found at the upstream site. The difference between downstream and upstream was expected at this site as the water body below the outfall is completely distinct from that above the outfall and other studies have found higher PBDE concentrations downstream of a potential source than upstream (eg de Wit 2002). The same was found at the Bremer STP where the ΣPBDE concentration was higher downstream at 4420 pg.g^{-1} dw than upstream at 2760 pg.g^{-1} dw. The Bremer STP discharges only on outgoing tides, and so particulate matter would settle out to the sediments mainly in the downstream direction. It is possible that sediment would be resuspended and carried back upstream of the discharge point, but most would be deposited and remain downstream.

It should be noted that at the Luggage Point STP location, it was not possible to distinguish between an upstream-downstream effect and a dilution effect on PBDE concentrations. The outfall at Luggage Point has no distinct 'downstream' as the river takes on open bay characteristics below this point, and therefore the high dilution would help explain the lower ΣPBDE result from downstream (380 pg.g^{-1} dw) compared with upstream (1060 pg.g^{-1} dw) which has more contribution from urban runoff and includes discharges from other STPs further upstream. The Upper Brisbane River site which had a ΣPBDE concentration of 1.3 pg.g^{-1} dw was used as a comparison for the Luggage Point sites as it is a remote site further upstream and unlikely to be affected by discharges from STPs.
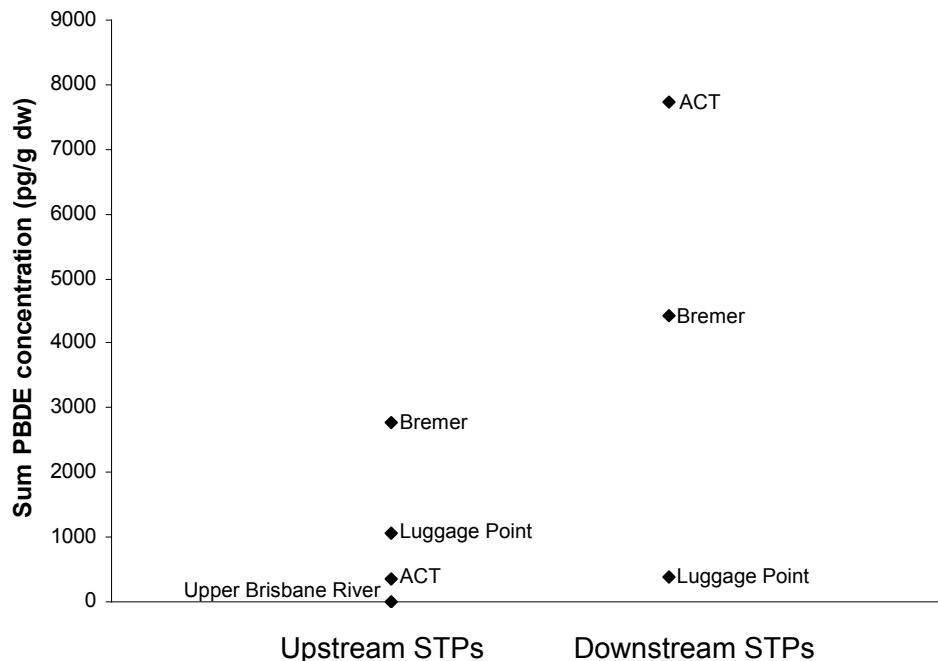
Figure 4.9 ΣPBDE concentration at sites up- and downstream of sewage treatment plants (STPs)

4.4 TBBP-A

In the current study, five samples were analysed for TBBP-A although a detectable concentration was found in only one sample (Table 4.5). This sample was the Parramatta River 'A' with a concentration of 0.13 ng.g^{-1} dw. The other samples all had concentrations below the limit of detection at <0.1 ng.g^{-1} dw. Due to the small sample size, the TBBP-A results are not compared by state, salinity or land-use type.

Table 4.4 Concentration of TBBP-A (ng.g^{-1} dw)

Site	TBBP-A (ng.g^{-1} dw)
Darwin	<0.1
Upper Brisbane River	<0.1
Canberra Lake Burley Griffin 'B'	<0.1
Parramatta 'A'	0.13
Port Jackson East	<0.1

4.5 Comparison with international data – PBDEs

In this section the data obtained in this study are compared with international data. It should be noted that this comparison is limited by a number of factors including the following:

- differences between the aims of studies, for example determining background levels versus identification of contamination and potential hotspots
- differences in the sampling design including sampling depth, criteria for sampling, number of samples that are pooled, sampling equipment and methodology
- difference in sampling time (year) *and*
- differences in interpreting or summarising results (ie mean, median, range of results, congeners and/or ∑PBDE values may or may not be provided).

Nevertheless, the results from selected studies are summarised here with further details in Appendix E. All concentrations are expressed as pg.g^{-1} dw for ease of comparison with the Australian data.
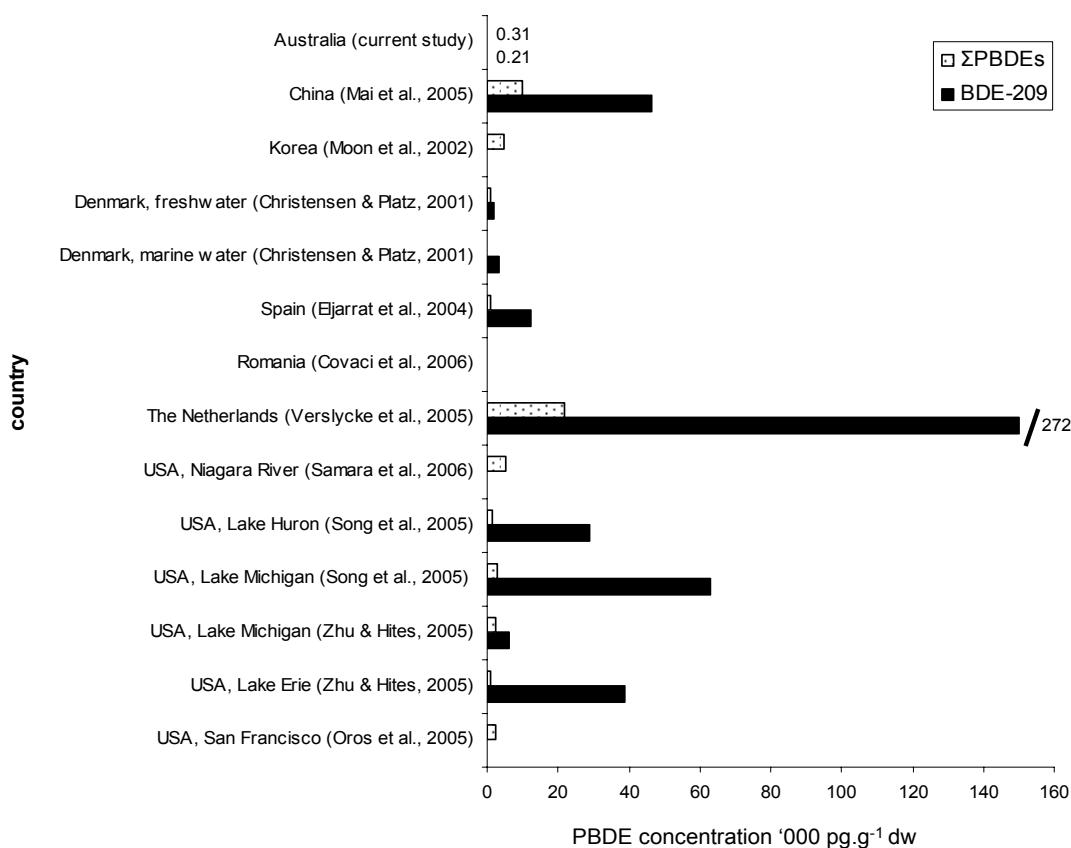
Figure 4.10 ΣPBDE (excluding BDE-209) and BDE-209 concentrations (median, pg.g^{-1} dw) from Australia, North America, Europe and Asia.

4.6 Comparison with international data – TBBP-A

In the current study, five samples were analysed for TBBP-A and only one sample had detectable concentrations. This was the Parramatta River 'A' sample with a concentration of 0.13 ng.g^{-1} dw. The other locations all had concentrations below the limit of detection <0.1 ng.g^{-1} dw. There is currently limited data on TBBP-A concentrations in sediment. Overall, the concentrations in the Australian sample were similar to or lower than that found in Europe and North America.

Verslycke et al (2005) analysed sediment samples collected at three sites in the Scheldt Estuary in The Netherlands. The concentrations of TBBP-A were below the limit of detection (<0.1 ng.g^{-1} dw) in all samples. In Sweden, considerably higher concentrations were found in sediment collected up- and downstream from a plastics industry where TBBP-A was used. The TBBP-A concentration was 50 ng.g^{-1} dw upstream and 430 ng.g^{-1} dw downstream (Sellström and Jansson 1995).

Quade et al (2003) reported the concentrations of TBBP-A in river sediment from 8 sites of the Great Lakes region, Canada. The levels reported represented dimethyl-TBBP-A (mTBBP-A) and TBBP-A together. TBBP-A was detected at all eight Detroit River stations sampled. The concentrations ranged from 0.06 to 1.84 ng.g^{-1} dw with a median concentration of 1.3 ng.g^{-1}. Another study of the Great Lakes area collected sediment at Lake Erie (Chu et al 2005). TBBP-A was detected in only three out of 55 sediment samples and only one sample could be quantitatively determined with the concentration of 0.51 ng.g^{-1} dw.
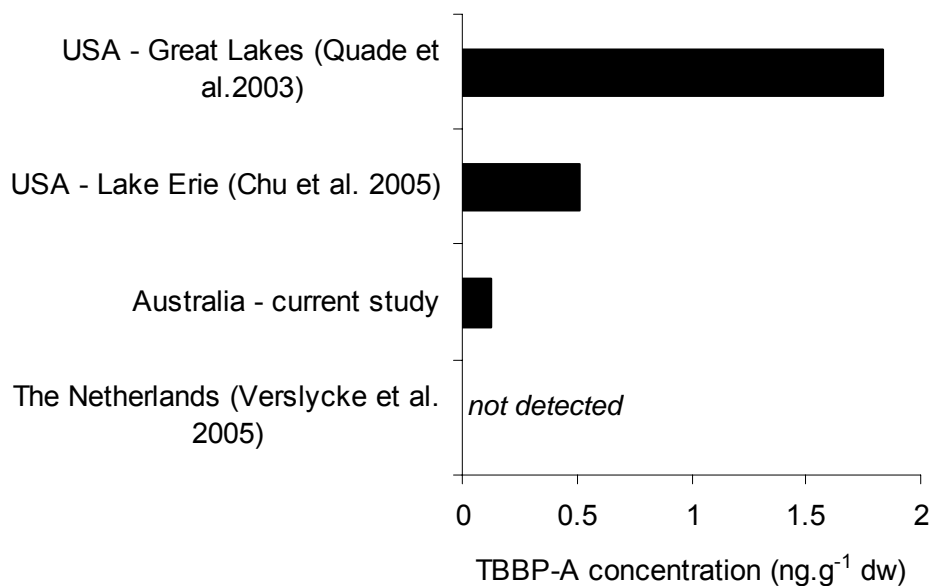
Figure 4.11 TBBP-A concentrations (ng.g^{-1} dw) in sediment from USA, Australia and the Netherlands

5. Summary of findings

This study was conducted to determine the concentrations of brominated flame retardants (BFRs) in sediment samples from the Australian aquatic environment. To date, there are no published data on the concentrations of BFRs in aquatic sediment in Australia.

The study involved the re-analysis (for BFRs) of sediment samples collected in 2002-03 to ascertain background concentrations of dioxin-like compounds as part of the Australian Government Department of Environment and Heritage (DEH) National Dioxins Programme (NDP). In addition, six sediment samples from up- and downstream of the outfall of sewage treatment plants (STPs) were collected in 2005 to assess contamination from this potential point source. Samples were analysed from 39 locations from all states and territories of Australia. At seven locations, two samples were analysed representing similar sites within the same location. In total, samples from 46 sites were analysed. The locations were chosen to be representative of various land uses – remote (5), remote/agricultural (2), agricultural (7), urban (11), urban/industrial (9), industrial/urban/agricultural (1), industrial (7) and STPs (4) and a range of salinities – freshwater (20), marine (1) and estuarine (25).

PBDEs were detected in samples from 35 of 46 sites and the ΣPBDE concentration (excluding the LOD (limit of detection)) ranged from non-detect to 60900 pg.g^{-1} dry weight (dw) with an overall mean (± standard deviation) and median of 4707 ± 12580 and 305 pg.g^{-1} dw, respectively. The results were rated as low, medium or high concentrations for this report.

Low 30 sites with ΣPBDE concentrations ranging from less than the limit of detection to 1000 pg.g^{-1} dw. These sites included all remote, remote/ agricultural, agricultural and agricultural/ urban/ industrial sites.

Medium 11 sites with ΣPBDE concentrations ranging from 1000 to 10000 pg.g^{-1} dw and included most of the sites near STP outfalls, urban/industrial and urban sites.

High The sites with the highest concentrations (> 10000 pg.g^{-1} dw) were Port Phillip Bay, Port Phillip Bay (Lower Yarra 'A'), Port Jackson West and Parramatta River 'A' and 'B'.

As expected the sites with the highest concentrations were the estuaries with the highest degree of urbanisation and industrialisation. Marine and freshwater locations on the whole had lower PBDE concentrations than estuarine locations. Overall, there was a trend with land-use which showed the concentrations of ΣPBDEs to be higher in the industrial/urban areas and followed in descending order of ΣPBDE concentration by industrial, STPs, urban, remote areas, agricultural, agricultural/remote and agricultural/urban/industrial. It should be noted that sediment samples from remote, remote/agricultural, agricultural and agricultural/urban/industrial land-uses had non-detectable or low concentrations of PBDEs.

In 86% of sediment samples, BDE-209 made the highest contribution to the ΣPBDE concentration (excluding samples were PBDEs were not detected). The main exceptions

were the location at Port Phillip Bay and the STP locations. The profile from the Port Phillip Bay sample differed with BDE-183 the dominant congener. This may suggest there is a nearby point source of the octa-BDE commercial product for which BDE-183 is described as a marker. Interestingly, the BDE-183 concentration at this location was one of the highest found in the international literature. The profile of the samples obtained near the outfall of STPs was also dominated by BDE-209, however, it differed slightly from other samples with contributions from congeners BDE-17, -47, -49, -99, -206 and -207. This suggests the sources of PBDEs in the outfall from STPs differed from that in other aquatic environment locations.

TBBP-A was assessed in five sediment samples with detectable concentrations in only one sample. The concentrations in Australian sediment were similar to or lower than that found in Europe and North America. Overall, the concentrations of PBDEs in Australian sediment were relatively low with the exception of the Port Phillip Bay location. The Australian concentrations of PBDEs were considerably lower than those found in sediment from North America, Europe and Asia (eg Oros et al 2005, Verslycke et al 2005, Mai et al 2005). The maximum Australian results were comparable with the minimum results from some European and Asian countries. This indicates that aquatic environments in Australia have low levels of PBDE contamination.

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Appendix A – Details of sampling device

The picture below shows four parts. From bottom to top they have the following function:
- The coring device is a 15 cm aluminium tube (2.8 cm internal diameter) that holds the sediment sample together. The tube also acts as a storage container for the individual sub-samples.
- The plastic joint holds the coring tube (only by friction) and screws into the valve
- The one-way valve (brass) lets the air out of the tube after inserting it into the sediment - creating the vacuum to remove the sediment sample.
- The plastic joint screws into the top of the valve and is manufactured to fit directly into a swimming pool cleaning rod.

Appendix B – Analytical methodology

NMI Method Précis - Polybrominated diphenyl ethers (PBDE) in sediments
High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) was used to determine the levels of PBDEs in environmental matrices. This method provided data on 26 PBDE congeners determined by the isotope dilution HRMS quantification technique. The detection limits and quantification levels in this method were usually dependent on the level of interferences rather than instrumental limitations. The method is 'performance based'. The analytical methodology for the determination of PBDEs was based on USEPA Draft Method 1614.

Clean up was effected by partitioning with sulfuric acid then distilled water. Further purification was performed using column chromatography on acid, base and neutral modified silica gels and basic alumina. After cleanup, the extract was concentrated to near dryness. Immediately prior to injection, internal standards were added to each extract, and an aliquot of the extract was injected into the gas chromatograph. The analytes were separated by the GC and then detected by a high-resolution ($\geq$10,000) mass spectrometer. The quality of the analysis was assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

PBDE Analyses
The following standards were all purchased from Wellington Laboratories (Ontario, Canada) and were used for calibration, quantification and determination of recovery of PBDEs:
- MBDE-MXE labelled surrogate spiking solution
- MBDE-138 internal standard solution *and*
- BDE-CVS-E calibration and verification solutions (CS1-CS5)

Acetone, dichloromethane, hexanes, and toluene were all OmniSolv® grade sourced from Merck KgaA (Darmstadt, Germany). Anhydrous sodium sulfate (granular) were both AR grade sourced from Mallinckrodt (Kentucky, USA). AnalaR® sulfuric acid S.G. was sourced from Merck (Victoria, Australia). All chromatographic columns were purchased from Fluid Management Systems Inc. (Watertown, MA, USA) and were used without any further treatment. They comprised multi-layer (acidic/basic/neutral) silica and basic alumina which are packed in individual Teflon® columns and vacuum sealed in Mylar® packages.

Sample preparation
A Dionex ASE100 accelerated solvent extractor (ASE) (Dionex Corporation, Sunnyvale, CA, USA) was used to extract all samples operated under the conditions listed in Table B.1. Where available, 50g of sediment was accurately weighed into an appropriately sized ASE cell and spiked with a known amount of the respective isotopically labeled $^{13}C_{12}$ PBDE surrogate solutions. Moisture determination on a separate portion was then calculated gravimetrically after drying overnight in an oven set at 105°C.

Table B.1. ASE Operating Conditions

Solvent	Toluene
Temperature	150°C
Equilibration time	5 minutes
Static	5 minutes
Flush volume	60%
Purge time (Nitrogen)	180 seconds
Static cycles	2
Pressure	1750 psi

Toluene extracts were concentrated under vacuum using a BÜCHI Syncore® Analyst (BÜCHI Labortechnik AG, Flawil, Switzerland) and solvent exchanged into hexanes. The hexanes solutions were subjected to multiple extractions with concentrated sulfuric acid until the acid layer remained colourless and then washed several times with water and dried through cleaned anhydrous sodium sulfate. The extracts were then concentrated prior to clean-up on a Fluid Management Systems, Inc. (FMS, Watertown, MA, USA) Power-Prep System™. The Power-Prep System™ consists of a number of chromatography panels comprising a valve module, a valve drive module and pump modules which are all computer controlled. The chromatographic columns used are disposable silica (acid, base, and neutral mix) and basic alumina columns also manufactured by FMS. These columns are made of Teflon® and individually sealed in Mylar® packaging.

Elution through the different columns is computer controlled and requires applying the hexane extract first onto the multi-layer silica and using hexane at a flow rate of 10 mL/min directly onto the alumina column. Dichloromethane:hexane (2:98) at 10 mL/min is used initially and then the solvent strength is modified to dichloromethane:hexane (50:50) in the forward direction at 10 mL/min. The fraction containing the PBDEs is collected from the alumina column directly into 200 mL BÜCHI Syncore® Analyst tubes. This fraction is concentrated to near dryness and the recovery standard (MBDE-138) is added and then further concentrated using clean dry nitrogen to a final volume of 40 µL prior to HRGC/HRMS analysis.

High-Resolution Gas Chromatography High-Resolution Mass Spectrometric (HRGC-HRMS) Analysis

All experiments were conducted on a MAT95XL HRMS (ThermoFinnigan MAT GmbH, Bremen, Germany) coupled to an Agilent 6890 GC (Palo Alto, CA, USA) equipped with a CTC A200S auto sampler. A DB-5 (J and W Scientific, Folsom, CA, USA) capillary column (15m x 0.25mm i.d., film thickness 0.25µm) was used as the primary analytical column with ultra-high purity Helium as the carrier gas. A flow rate of 1.0 mL/min was maintained throughout the chromatographic run. The temperature programme for the PBDE analysis was: 100°C (isothermal for 2 min.) then ramp 1 to 230°C at 15°C/min, ramp 2 to 270°C at 5°C/min and then ramp 3 to 320°C at 10°C/min (isothermal 5 min). A 1µL splitless injection with an injector temperature of 280°C for PBDE analysis were employed for standards and sample extracts. The mass spectrometer operating conditions were: ion source and transfer line temperatures, 240°C and 280°C, respectively; ionisation energy 45eV, filament current 0.7mA and electron multiplier voltage set to produce a gain of 10^6. Resolution was maintained at 10 000 (10% valley definition) throughout the sample

sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of the exact masses of appropriate ions for native and labelled compounds. Individual congeners are identified using the GC retention time and ion abundance ratios with reference to internal standards.

Table B.2 gives a list of the PBDE congeners included in this method. Table B.3 shows the theoretical ion abundance ratios and QC limits and Table B.4 shows the MID windows for the PBDEs.

Table B.2. List of PBDE Congeners Analysed

BDE Congener	Abbreviation
2,2',4-Tribrominated diphenyl ether	BDE 17
2,4,4'-Tribrominated diphenyl ether	BDE 28
2',3,4-Tribrominated diphenyl ether	BDE 33
2,2',4,4'-Tetrabrominated diphenyl ether	BDE 47
2,2',4,5'-Tetrabrominated diphenyl ether	BDE 49
2,3',4,4'-Tetrabrominated diphenyl ether	BDE 66
2,3',4',6-Tetrabrominated diphenyl ether	BDE 71
3,3',4,4'-Tetrabrominated diphenyl ether	BDE 77
2,2',3,4,4'-Pentabrominated diphenyl ether	BDE 85
2,2',4,4',5-Pentabrominated diphenyl ether	BDE 99
2,2',4,4',6-Pentabrominated diphenyl ether	BDE 100
2,3',4,4',6-Pentabrominated diphenyl ether	BDE 119
3,3',4,4',5-Pentabrominated diphenyl ether	BDE 126
2,2',3,4,4',5'-Hexabrominated diphenyl ether	BDE 138
2,2',4,4',5,5'-Hexabrominated diphenyl ether	BDE 153
2,2',4,4',5,6'-Hexabrominated diphenyl ether	BDE 154
2,3,3',4,4',5-Hexabrominated diphenyl ether	BDE 156
2,3,4,4',5,6-Hexabrominated diphenyl ether	BDE 166
2,2',3,4,4',5',6-Heptabrominated diphenyl ether	BDE 183
2,2',3,4,4',6,6-Heptabrominated diphenyl ether	BDE 184
2,3,3',4,4',5',6-Heptabrominated diphenyl ether	BDE 191
2,2,3,3',4,4',5,6'-Octabrominated diphenyl ether	BDE 196
2,2,3,3',4,4',6,6'-Octabrominated diphenyl ether	BDE 197
2,2,3,3',4,4',5,5',6-Nonabrominated diphenyl ether	BDE 206
2,2,3,3',4,4',5,6,6-Nonabrominated diphenyl ether	BDE 207
Decabromodiphenyl ether	BDE 209

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Table B.3. Theoretical Ion Abundance Ratios and QC Limits

No. of Bromine Atoms	*m/z's forming the ratio (R/Q)	Theoretical Ratio	QC limits Lower	Upper
1	M/(M+2)	1.03	0.88	1.18
2	(M+2)/(M+4)	0.51	0.43	0.59
2	M/(M+2)	0.43	0.47	0.59
3	M-Br_2/(M+2)-Br_2	1.06	0.82	1.22
3	(M+2)/(M+4)	1.03	0.88	1.18
4	M-Br_2/(M+2)-Br_2	0.53	0.41	0.61
4	(M+2)/(M+4)	0.70	0.60	0.81
4	(M+4)/(M+6)	1.54	1.31	1.77
5	(M+2)-Br_2/(M+4)-Br_2	1.06	0.82	1.22
5	(M+4)/(M+6)	1.03	0.88	1.18
6	(M+2)-Br_2/(M+4)-Br_2	0.71	0.54	0.82
6	(M+4)/(M+6)	0.77	0.65	0.89
6	(M+6)/(M+8)	1.37	1.16	1.58
7	(M+4)-Br_2/(M+6)-Br_2	1.06	0.82	1.22
7	(M+6)/(M+8)	1.03	0.88	1.18
8	(M+6)/(M+8)	0.82	0.70	0.94
9	(M+8)/(M+10)	1.03	0.88	1.18
10	(M+8)/(M+10)	0.73	0.86	0.99

Table B.4. The MID Windows for PBDEs

MID Window	Accurate Mass	Ion Id	Analyte (I= internal standard)
1	245.9675	M-Br$_2$	TriBDE
	247.9655	(M+2)-Br$_2$	TriBDE
	258.0077	M-Br$_2$	TriBDE(I)
	260.0057	(M+2)-Br$_2$	TriBDE(I)
2	323.8780	M-Br$_2$	TeBDE
	325.8760	(M+2)-Br$_2$	TeBDE
	335.9182	M-Br$_2$	TeBDE(I)
	337.9162	(M+2)-Br$_2$	TeBDE(I)
	483.7106	M+2	TeBDE
	485.7085	M+4	TeBDE
3	561.6231	M+2	PeBDE
	563.6211	M+4	PeBDE
	565.6190	M+6	PeBDE
	573.6634	M+2	PeBDE(I)
	575.6613	M+4	PeBDE(I)
	577.6593	M+4	PeBDE(I)
4	481.6976	(M+2)-Br$_2$	HxBDE
	483.6956	(M+4)-Br$_2$	HxBDE
	485.6937	(M+6)-Br$_2$	HxBDE
	493.7372	(M+2)-Br$_2$	HxBDE(I),(IS)
	495.7352	(M+4)-Br$_2$	HxBDE(I),(IS)
	497.7331	(M+6)-Br$_2$	HxBDE(I),(IS)
5	559.6082	(M+2)-Br$_2$	HpBDE
	561.6062	(M+4)-Br$_2$	HpBDE
	563.6042	(M+6)-Br$_2$	HpBDE
	571.6477	(M+2)-Br$_2$	HpBDE(I)
	573.6457	(M+4)-Br$_2$	HpBDE(I)
	575.6436	(M+6)-Br$_2$	HpBDE(I)
6	639.5160	(M+2)-Br$_2$	OcBDE
	641.5140	(M+4)-Br$_2$	OcBDE
	643.5120	(M+6)-Br$_2$	OcBDE
	651.5562	(M+2)-Br$_2$	OcBDE (I)
	653.5542	(M+4)-Br$_2$	OcBDE (I)
	665.5521	(M+6)-Br$_2$	OcBDE (I)
7	717.7265	(M+2)-Br$_2$	NoBDE
	719.4245	(M+4)-Br$_2$	NoBDE
	721.4225	(M+6)-Br$_2$	NoBDE
	729.4667	(M+2)-Br$_2$	NoBDE (I)
	731.4647	(M+4)-Br$_2$	NoBDE (I)
	733.4626	(M+6)-Br$_2$	NoBDE (I)
7	797.3350	(M+2)-Br$_2$	DeBDE
	799.3329	(M+4)-Br$_2$	DeBDE
	801.3308	(M+6)-Br$_2$	DeBDE
	809.3752	(M+2)-Br$_2$	DeBDE (I)
	811.3732	(M+4)-Br$_2$	DeBDE (I)
	813.3711	(M+6)-Br$_2$	DeBDE (I)

TriBDE- Tribrominated diphenyl ether; TeBDE- Tetrabrominated diphenyl ether; PeBDE- Pentabrominated diphenyl ether; HxBDE-Hexabrominated diphenyl ether; HpBDE-Heptabrominated diphenyl ether; OcBDE-Octabrominated diphenyl ether; NoBDE-Nonabrominated diphenyl ether; DeBDE-Decabrominated diphenyl ether

Analyte identification and quantification criteria

For positive identification and quantification, the following criteria must be met:

- the retention time of the analyte must be within 1 second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard;
- the ion ratio obtained for the analyte must be ±20% of the theoretical ion ratio;
- the signal to noise ratio must be greater than 3:1;
- levels of PBDE congeners in a sample must be greater than 3 times any level found in the corresponding laboratory blank analysed; and
- surrogate standard recoveries must be in the range 25-150%.

Quantification using the Isotope Dilution Technique

The naturally occurring (native) compound was determined by reference to the same compound in which one or more atoms were isotopically enriched. In this method, all carbon atoms for selected PBDE molecules were substituted with carbon-13 to produce $^{13}C_{12}$-labelled analogs of the brominated diphenyl ethers. The $^{13}C_{12}$-labelled PBDEs were spiked into each sample and allowed identification and correction of the concentration of the native compounds in the analytical process. The proprietary chromatographic integration package supplied with the Thermo Finnigan instrument, (Xcalibur®), was used to target all monitored compounds and create a text file that was further manipulated in Excel to produce the final certificate of analysis.

Quality Assurance

In order to manage quality assurance batch sizes were typically 6-8 samples. A laboratory blank was analysed with each batch of samples. The HRMS resolution, performance and sensitivity were established for each sequence and the recoveries of all isotopically labelled surrogate standards were calculated and reported. The sum PBDE concentration in the laboratory blanks ranged from 71 to 110 pg/g dry weight with a mean ± standard deviation of 81 ± 19 pg/g dry weight.

Data reporting

The basis of reporting for primary and quality control samples is as follows: pg/g on a dry weight basis; PBDEs data were corrected for recovery of $^{13}C_{12}$ surrogate standards; for all samples, data for quantified analytes were reported to 2 or 3 significant figures; and limit of detection data for non-quantified analytes were reported to 1 significant figure.

Eurofins/ERGO - Method Précis - polybrominated diphenyl ethers (PBDE) in sediments

The following method was applied for the determination of PBDEs in sediment. The method may be subject to certain changes depending on the individual sample properties. Before the extraction the following ^{13}C-UL-labeled internal standards were added to the sample:

IUPAC-code	Internal standards (^{13}C-UL) PBDE	
3	4-	Mono-BDE
15	4,4'-	Di-BDE
28	2,4,4'-	Tri-BDE
47	2,2',4,4'-	Tetra-BDE
99	2,2',4,4',5-	Penta-BDE
153	2,2',4,4',5,5'-	Hexa-BDE
154	2,2',4,4',5,6'-	Hexa-BDE
183	2,2',3,4,4',5',6-	Hepta-BDE
197	2,2',3,3',4,4',6,6'-	Octa-BDE
207	2,2',3,3',4,4',5,6,6'-	Nona-BDE
209	2,2',3,3',4,4',5,5',6,6'-	Deca-BDE

After the spiking, the sample was extracted by means of toluene (soxhlet 20 h). For the determination of polybrominated diphenyl ethers the sample extract was taken up in n-hexane and treated by a clean-up including H_2SO_4/SiO_2. After addition of the syringe standard 2,2',3,4,4',6-Hexabromdiphenylether (Hexa-BDE 139 ^{13}C-UL labelled) the PBDEs were measured by high resolution gas chromatography and mass spectrometry. The measurement was done by means of HRGC/HRMS (high resolution gas chromatography/ high resolution mass spectrometry, VG Autospec resp. Finnigan MAT 95 XL) using a DB 5 column for gas chromatographic separation. The quantification was performed by means of internal/external standards (isotope dilution).

Eurofins/ERGO - Method Précis – TBBP-A (tetrabromobisphenol A) in sediment

Before the extraction the following ^{13}C-UL-labelled internal standard was added to the sample:

[13]C-TBBP-A   (^{13}C-UL-labelled)

After the spiking, the sample was extracted with appropriate solvents for ultratrace-analyses (eg nanograde), afterwards a column clean up was performed. The measurement was done by means of high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) with VG-AutoSpec and/or Finnigan MAT 95 XL using DB-5 capillary columns.

The detection limit for the batch of five samples analysed for this study was 0.1 ng.g^{-1} dw.

Appendix C – Quality Control/ Quality Assurance

Table C.1 PBDE concentrations (pg.g^{-1} dw) and normalised difference (%) of samples analysed for inter-laboratory comparison.
1 – eurofins/ERGO, 2 – National Measurement Institute

n.c. not possible to calculate < not detected and detection limit value

	Port of Darwin A			Upper Brisbane River			Canberra Lake Burley Griffin B			Parramatta River A			Port Jackson East		
	1	**2**	**Norm. diff.**	**1**	**2**	**Norm. diff.**	**1**	**2**	**Norm. diff.**	**1**	**2**	**Norm. diff.**	**1**	**2**	**Norm. diff.**
BDE #17	<10	<5	n.c.	<10	<0.1	n.c.	<10	<5	n.c.	232	130	56%	<10	<5	n.c.
BDE #28	<10	<20	n.c.	<10	<7	n.c.	<10	<10	n.c.	16	<50	n.c.	<10	<9	n.c.
BDE #47	<41	<60	n.c.	<29	<10	n.c.	<34	<30	n.c.	599	550	8%	<37	<40	n.c.
BDE #49	<10	<5	n.c.	<10	<0.1	n.c.	<10	<5	n.c.	304	230	28%	<10	<5	n.c.
BDE #66	<10	<5	n.c.	<10	<0.09	n.c.	<10	<5	n.c.	49	39	23%	<10	<5	n.c.
BDE #71	<10	<5	n.c.	<10	<0.02	n.c.	<10	<5	n.c.	51	<10	n.c.	<10	<5	n.c.
BDE #77	<10	<5	n.c.	<10	<0.1	n.c.	<10	<5	n.c.	<10	<5	n.c.	<10	<5	n.c.
BDE #85	18	<5	n.c.	<10	0.43	n.c.	<10	<5	n.c.	171	34	134%	<10	<5	n.c.
BDE #99	<25	<40	n.c.	<20	<10	n.c.	<28	<20	n.c.	1218	710	53%	<27	<30	n.c.
BDE #100	<10	<8	n.c.	<10	<2	n.c.	<10	<5	n.c.	327	170	63%	<10	<6	n.c.
BDE #119	<10	<5	n.c.	<10	<0.4	n.c.	<10	<5	n.c.	<10	<20	n.c.	<10	<5	n.c.
BDE #126	<10	<5	n.c.	<10	<0.2	n.c.	<10	<5	n.c.	267	<5	n.c.	<10	<5	n.c.
BDE #138	<10	<5	n.c.	<10	<0.2	n.c.	<10	<5	n.c.	18	19	5%	<10	<5	n.c.
BDE #153	<10	<5	n.c.	<10	<0.8	n.c.	<10	<5	n.c.	212	170	22%	<10	<5	n.c.
BDE #154	<10	<5	n.c.	<10	<0.6	n.c.	<10	<5	n.c.	241	150	46%	<10	<5	n.c.
BDE #156	<10	<5	n.c.	<10	<0.1	n.c.	<10	<5	n.c.	<10	<5	n.c.	<10	<5	n.c.
BDE #183	<10	<5	n.c.	<10	0.3	n.c.	<10	<5	n.c.	102	170	50%	<10	<5	n.c.
BDE #197	<10	<5	n.c.	<10	<1	n.c.	<10	<5	n.c.	86	98	13%	<10	<5	n.c.
BDE #207	56	<5	n.c.	<23	0.5	n.c.	33	<7	n.c.	1261	640	65%	70.1	49	35%
BDE #209	94	<60	n.c.	64	<4	n.c.	136	210	43%	13407	32500	83%	842	810	4%
Sum of PBDE congeners															
Excluding LODs	**169**	**0**	**n.c.**	**64**	**1**	**n.c.**	**169**	**210**	**22%**	**18560**	**35610**	**63%**	**912**	**859**	**6%**
Mean normalised difference			**n.c.**			**n.c.**			**n.c.**			**46%**			**20%**

Table C.2 PBDE concentrations (pg.g^{-1} dw) and normalised difference (%) of 'A' and 'B' samples for sampling replication
n.c. not possible to calculate < not detected and detection limit value

	Torrens River A	Torrens River B	Norm. diff.	Lower Brisbane River A	Lower Brisbane River B	Norm. diff.	Middle Swan A	Middle Swan B	Norm. diff.	Lower Derwent A	Lower Derwent B	Norm. diff.
BDE 17	<5	<5	n.c.	<5	2	n.c.	5.1	<5	n.c.	0.48	0.37	26%
BDE 28 + BDE 33	<20	<10	n.c.	<10	<20	n.c.	<20	<20	n.c.	<20	<30	n.c.
BDE 47	<50	<30	n.c.	<30	<40	n.c.	<100	<40	n.c.	<40	<50	n.c.
BDE 49	<5	<5	n.c.	<5	2.6	n.c.	12	<5	n.c.	0.52	0.49	6%
BDE 66	<5	<5	n.c.	<5	0.31	n.c.	<0.9	<5	n.c.	<0.2	<0.2	n.c.
BDE 71	<5	<5	n.c.	<5	0.22	n.c.	<0.5	<5	n.c.	<0.1	<0.03	n.c.
BDE 77	<5	<5	n.c.	<5	<0.06	n.c.	<0.4	<5	n.c.	<0.3	0.082	n.c.
BDE 85	<5	<5	n.c.	<5	<0.9	n.c.	<2	<5	n.c.	0.35	0.71	68%
BDE 99	<30	<20	n.c.	<20	<20	n.c.	<50	<20	n.c.	<10	<20	n.c.
BDE 100	<5	<5	n.c.	<5	<5	n.c.	<10	<5	n.c.	<4	<6	n.c.
BDE 119	<5	<5	n.c.	<5	<0.7	n.c.	<2	<5	n.c.	<1	<0.2	n.c.
BDE 126	<5	<5	n.c.	<5	<0.09	n.c.	<0.9	<5	n.c.	<0.4	<0.1	n.c.
BDE 138 + BDE 1	<5	<5	n.c.	<5	<0.2	n.c.	<0.8	<5	n.c.	<0.6	<0.4	n.c.
BDE 153	<5	<5	n.c.	<5	<2	n.c.	<7	<5	n.c.	<0.8	<2	n.c.
BDE 154	<5	<5	n.c.	<5	<2	n.c.	<4	<5	n.c.	<0.5	<1	n.c.
BDE 156	<5	<5	n.c.	<5	<0.03	n.c.	<0.07	<5	n.c.	<0.07	<0.04	n.c.
BDE 183	<5	<5	n.c.	<5	1	n.c.	6.5	5	26%	<0.2	0.27	n.c.
BDE 184	<5	<5	n.c.	<5	<0.06	n.c.	<4	<5	n.c.	<0.2	<0.2	n.c.
BDE 191	<5	<5	n.c.	<5	<0.2	n.c.	<4	<5	n.c.	<0.6	<0.1	n.c.
BDE 196	<5	<20	n.c.	<5	0.51	n.c.	<2	<5	n.c.	<3	<0.6	n.c.
BDE 197	<5	<20	n.c.	<5	0.56	n.c.	<5	5.6	n.c.	<2	<0.09	n.c.
BDE 206	<5	<5	n.c.	<5	3.1	n.c.	36	37	3%	1.3	<0.4	n.c.
BDE 207	<5	<5	n.c.	<5	3.2	n.c.	60	51	16%	<4	0.41	n.c.
BDE 209	<30	<50	n.c.	<50	110	n.c.	1390	1350	3%	<5	<9	n.c.
Sum of PBDE congeners						n.c.						n.c.
Excluding LOD values	0	0	n.c.	0	120	n.c.	1500	1450.0	3%	3	2	12%
Mean normalised difference (detected congeners)			n.c.			n.c.			12%			33%

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Table C.2 cont.

	Canberra Lake Burley Griffin A	Canberra Lake Burley Griffin B	Norm. diff.	Parramatta River A	Parramatta River B	Norm. diff.	Port Phillip Bay A (Lower Yarra A)	Port Phillip Bay B (Lower Yarra B)	Norm. diff.
BDE 17	<5	<5	n.c.	130	45	97%	510	9.4	193%
BDE 28 + BDE 33	<6	<10	n.c.	<50	<40	n.c.	120	<20	n.c.
BDE 47	<30	<30	n.c.	550	950	53%	2050	230	160%
BDE 49	7.4	<5	n.c.	230	200	14%	1070	26	191%
BDE 66	<5	<5	n.c.	39	9.1	124%	87	6.5	172%
BDE 71	<20	<5	n.c.	<10	14	n.c.	50	2.3	182%
BDE 77	<5	<5	n.c.	<5	<3	n.c.	<3	<0.1	n.c.
BDE 85	<5	<5	n.c.	34	13	89%	100	12	157%
BDE 99	<20	<20	n.c.	710	260	93%	1780	210	158%
BDE 100	<5	<5	n.c.	170	63	92%	510	51	164%
BDE 119	<5	<5	n.c.	<20	<0.6	n.c.	5.8	0.45	171%
BDE 126	<5	<5	n.c.	<5	<3	n.c.	<2	<0.03	n.c.
BDE 138 + BDE 1	<5	<5	n.c.	19	<3	n.c.	28	<7	n.c.
BDE 153	<5	<5	n.c.	170	42	121%	300	23	172%
BDE 154	<5	<5	n.c.	150	39	117%	240	21	168%
BDE 156	<5	<5	n.c.	<5	<0.5	n.c.	<0.8	<0.07	n.c.
BDE 183	<5	<5	n.c.	170	57	100%	450	14	188%
BDE 184	<5	<5	n.c.	7.4	<2	n.c.	18	1	179%
BDE 191	<5	<5	n.c.	5.1	1.6	104%	20	0.6	188%
BDE 196	<5	<5	n.c.	64	31	69%	220	7	188%
BDE 197	<5	<5	n.c.	98	43	78%	330	8.8	190%
BDE 206	<5	<8	n.c.	720	410	55%	1460	68	182%
BDE 207	<5	<7	n.c.	640	360	56%	1300	57	183%
BDE 209	86	210	84%	32500	13600	82%	35600	1420	185%
Sum of PBDE congeners Excluding LOD values	**93**	**210**	**77%**	**36400**	**16200**	n.c. **77%**	**46200**	**2160**	**182%**
Mean normalised difference (detected congeners)			**84%**			**84%**			**177%**

Appendix D – PBDEs in Australian sediments

Table D.1 Concentrations of PBDEs (pg.g^{-1} dw) in Australian sediment samples collected in 2002-03 and 2005 (* indicates sample collected in 2005). < not detected and detection limit value

State	VICTORIA						
Location	La Trobe R Industrial	Lower Werribee	Port Phillip Bay	Port Phillip Bay 'A' (Lower Yarra 'A')	Port Phillip Bay 'B' (Lower Yarra 'B')	Upper Yarra River	LaTrobe R Agricultural
PBDE congeners							
BDE 17	<5	<5	<5	510	9.4	<0.2	<5
BDE 28 + BDE 33	<60	<30	<10	120	<20	<20	<20
BDE 47	<100	<50	<30	2050	230	<50	<30
BDE 49	<5	<5	<5	1070	26	0.63	<5
BDE 66	<5	<5	<5	87	6.5	<0.1	<5
BDE 71	<5	<5	<5	50	2.3	<0.4	<5
BDE 77	<5	<5	<5	<3	<0.1	<0.08	<5
BDE 85	<5	<5	<5	100	12	0.99	<5
BDE 99	<40	<40	<30	1780	210	<30	<10
BDE 100	<5	<5	<5	510	51	<7	<5
BDE 119	<5	<5	<5	5.8	0.45	<0.5	<5
BDE 126	<5	<5	<5	<2	<0.03	<0.03	<5
BDE 138 + BDE 166	<5	<5	34	28	<7	0.24	<5
BDE 153	<5	<5	1830	300	23	4.9	<5
BDE 154	<5	<5	91	240	21	3.2	<5
BDE 156	<5	<5	<5	<0.8	<0.07	<0.03	<5
BDE 183	<5	<5	31000	450	14	25	<5
BDE 184	<5	<5	96	18	1	0.18	<5
BDE 191	<5	<5	21	20	0.6	<0.04	<5
BDE 196	<5	<5	3590	220	7	2.8	<5
BDE 197	<5	<5	13600	330	8.8	2.7	<6
BDE 206	<5	<5	520	1460	68	16	<5
BDE 207	<5	<5	7700	1300	57	14	<5
BDE 209	<20	<20	2340	35600	1420	410	<40
Sum of PBDE congeners							
Excluding LOD values	**0**	**0**	**60900**	**46200**	**2160**	**480**	**0**
Incl. half LOD values	**160**	**120**	**60882**	**46252**	**2182**	**535**	**101**

Incl. LOD values	**320**	**240**	**60942**	**46255**	**2195**	**589**	**201**

State	NEW SOUTH WALES						
Location	Lake Illawarra	East of Newcastle I (II)	East of Newcastle (mean of I and II)	Lower Hunter	Port Jackson West	Port Jackson East	Parramatta River 'A'
PBDE congeners							
BDE 17	<5	<5 (<5)	<5	<5	37	<5	130
BDE 28 + BDE 33	<40	<8 (<20)	<14	<10	<50	<9	<50
BDE 47	140	<20 (<30)	<25	<60	290	<40	550
BDE 49	8.2	<5 (<5)	<5	<5	81	<5	230
BDE 66	<5	<5 (<5)	<5	<5	8.8	<5	39
BDE 71	<5	<5 (<5)	<5	<5	<5	<5	<10
BDE 77	<5	<5 (<5)	<5	<5	<5	<5	<5
BDE 85	<5	<5 (<5)	<5	<5	7.9	<5	34
BDE 99	130	<10 (<20)	<15	<40	170	<30	710
BDE 100	<8	<5 (<6)	<6	<6	44	<6	170
BDE 119	<10	<5 (<5)	<5	<5	<5	<5	<20
BDE 126	<5	<5 (<5)	<5	<5	<5	<5	<5
BDE 138 + BDE 166	<5	<5 (<5)	<5	<5	<5	<5	19
BDE 153	12	<5 (<5)	<5	<5	36	<5	170
BDE 154	9.3	<5 (<5)	<5	<5	28	<5	150
BDE 156	<5	<5 (<5)	<5	<5	<5	<5	<5
BDE 183	<5	<5 (<5)	<5	<5	71	<5	170
BDE 184	<5	<5 (<5)	<5	<5	<5	<5	7.4
BDE 191	<5	<5 (<5)	<5	<5	<5	<5	5.1
BDE 196	<5	<5 (<5)	<5	<5	57	<5	64
BDE 197	<5	<5 (<5)	<5	<5	62	<5	98
BDE 206	8.4	<5 (<5)	<5	<5	590	36	720
BDE 207	7.1	<5 (<5)	<5	<5	600	49	640
BDE 209	240	<10 (<20)	<15	110	22500	810	32500
Sum of PBDE congeners							
Excluding LOD values	**560**	**0 (0)**	**0**	**110**	**24500**	**890**	**36400**
Incl. half LOD values	**617**	**74 (96)**	**85**	**216**	**24628**	**980**	**36454**
Incl. LOD values	**678**	**148 (191)**	**170**	**321**	**24673**	**1065**	**36502**

State	NSW cont.	SOUTH AUSTRALIA					
Location	Parramatta River 'B'	Botany Bay	Torrens Estuary	Lower Torrens	Torrens River 'A'	Torrens River 'B'	Upper Torrens
PBDE congeners							
BDE 17	45	<5	<5	<5	<5	<5	<5
BDE 28 + BDE 33	<40	<10	<8	<20	<20	<10	<20
BDE 47	950	<50	<40	<80	<50	<30	<40
BDE 49	200	7.1	<5	6.8	<5	<5	<5
BDE 66	9.1	<5	<5	<5	<5	<5	<5
BDE 71	14	<5	<5	<5	<5	<5	<5
BDE 77	<3	<5	<5	<5	<5	<5	<5
BDE 85	13	<5	<5	<5	<5	<5	<5
BDE 99	260	<20	<30	<90	<30	<20	<30
BDE 100	63	<5	<5	<8	<5	<5	<5
BDE 119	<0.6	<5	<5	<5	<5	<5	<9
BDE 126	<3	<5	<5	<5	<5	<5	<5
BDE 138 + BDE 166	<3	<5	<5	<5	<5	<5	<5
BDE 153	42	<5	<5	15	<5	<5	<5
BDE 154	39	<5	<5	12	<5	<5	<5
BDE 156	<0.5	<5	<5	<5	<5	<5	<5
BDE 183	57	<5	<5	11	<5	<5	<5
BDE 184	<2	<5	<5	<5	<5	<5	<5
BDE 191	1.6	<5	<5	<5	<5	<5	<5
BDE 196	31	<5	<5	5.8	<5	<20	<5
BDE 197	43	<5	<5	6.1	<5	<20	<5
BDE 206	410	29	4.4	52	<5	<5	<5
BDE 207	360	26	5.9	49	<5	<5	<5
BDE 209	13600	1170	160	1720	<30	<50	57
Sum of PBDE congeners							
Excluding LOD values	**16200**	**1230**	**170**	**1880**	**0**	**0**	**57**
Incl. half LOD values	**16164**	**1315**	**254**	**2004**	**115**	**120**	**154**
Incl. LOD values	**16200**	**1397**	**338**	**2131**	**230**	**240**	**247**

State	WESTERN AUSTRALIA					
Location	Upper Serpentine	Upper Avon	Middle Swan 'A'	Middle Swan 'B'	Upper Swan River	Canning River
PBDE congeners						
BDE 17	<5	<5	5.1	<5	2.5	2.3
BDE 28 + BDE 33	<8	110	<20	<20	<20	<40
BDE 47	<20	130	<100	<40	<40	<100
BDE 49	<5	<5	12	<5	<2	7.3
BDE 66	<5	<5	<0.9	<5	0.49	1.1
BDE 71	<5	<5	<0.5	<5	<0.6	1.2
BDE 77	<5	<5	<0.4	<5	<0.08	<0.7
BDE 85	<5	<5	<2	<5	0.67	<3
BDE 99	<10	<40	<50	<20	<20	<80
BDE 100	<5	9.6	<10	<5	<5	<20
BDE 119	<5	<5	<2	<5	<0.2	<0.6
BDE 126	<5	<5	<0.9	<5	<0.2	<1
BDE 138 + BDE 166	<5	<5	<0.8	<5	<0.5	<2
BDE 153	<5	<5	<7	<5	<3	16
BDE 154	<5	<5	<4	<5	<2	10
BDE 156	<5	<5	<0.07	<5	<0.2	<0.8
BDE 183	<5	<5	6.5	5	2	20
BDE 184	<5	<5	<4	<5	<0.2	<3
BDE 191	<5	<5	<4	<5	<0.4	<1
BDE 196	<5	<5	<2	<5	2.2	<40
BDE 197	<5	<5	<5	5.6	1.9	<8
BDE 206	<5	<5	36	37	8.6	20
BDE 207	<5	<5	60	51	7.6	27
BDE 209	<10	<40	1390	1350	910	1540
Sum of PBDE congeners						
Excluding LOD values	**0**	**250**	**1500**	**1450**	**940**	**1640**
Incl. half LOD values	**74**	**337**	**1616**	**1529**	**983**	**1795**
Incl. LOD values	**148**	**425**	**1723**	**1609**	**1030**	**1945**

State	AUSTRALIAN CAPITAL TERRITORY				TASMANIA		
Location	Canberra Lake Burley Griffin 'A'	Canberra Lake Burley Griffin 'B'	ACT STP Downstream*	ACT STP Upstream*	Lower Tamar River	Hobart Derwent	Upper Derwent
PBDE congeners							
BDE 17	<5	<5	65	<5	<5	0.91	<5
BDE 28 + BDE 33	<6	<10	61	<10	<10	<20	<20
BDE 47	<30	<30	2100	<40	<30	<100	<30
BDE 49	7.4	<5	99	<5	<5	4	<5
BDE 66	<5	<5	57	<5	<5	0.76	<5
BDE 71	<20	<5	14	<5	<5	<0.2	<5
BDE 77	<5	<5	<5	<5	<5	<0.2	<5
BDE 85	<5	<5	25	<5	<5	<2	<5
BDE 99	<20	<20	1050	<30	<20	<60	<20
BDE 100	<5	<5	200	<5	<5	<10	<5
BDE 119	<5	<5	<5	<5	<5	<1	<5
BDE 126	<5	<5	<5	<5	<5	<0.2	<5
BDE 138 + BDE 166	<5	<5	6.9	<5	<5	<0.3	<5
BDE 153	<5	<5	110	<5	<5	<4	<5
BDE 154	<5	<5	90	<5	<5	<3	<5
BDE 156	<5	<5	<5	<5	<5	<0.07	<5
BDE 183	<5	<5	110	<5	<5	<0.5	<5
BDE 184	<5	<5	<5	<5	<5	<1	<5
BDE 191	<5	<5	<5	<5	<5	<0.8	<5
BDE 196	<5	<5	33	<5	<5	<7	<8
BDE 197	<5	<5	53	<5	<5	<6	<7
BDE 206	<5	<8	140	15	<5	13	<10
BDE 207	<5	<7	100	13	<5	16	<5
BDE 209	86	210	3410	330	37	490	<40
Sum of PBDE congeners							
Excluding LOD values	**93**	**210**	**7730**	**360**	**37**	**530**	**0**
Incl. half LOD values	**176**	**293**	**7739**	**443**	**117**	**633**	**110**
Incl. LOD values	**259**	**368**	**7754**	**528**	**197**	**741**	**220**

State	TASMANIA cont.		NORTHERN TERRITORY		QUEENSLAND		
Location	Lower Derwent 'A'	Lower Derwent 'B'	Port of Darwin	Kakadu	Lower Brisbane River 'A'	Lower Brisbane River 'B'	Moreton Bay
PBDE congeners							
BDE 17	0.48	0.37	<5	<5	<5	2	<0.2
BDE 28 + BDE 33	<20	<30	<20	<10	<10	<20	<20
BDE 47	<40	<50	<60	<30	<30	<40	<40
BDE 49	0.52	0.49	<5	<5	<5	2.6	<0.4
BDE 66	<0.2	<0.2	<5	<5	<5	0.31	0.31
BDE 71	<0.1	<0.03	<5	<5	<5	0.22	0.042
BDE 77	<0.3	0.082	<5	<5	<5	<0.06	<0.04
BDE 85	0.35	0.71	<5	<5	<5	<0.9	<0.8
BDE 99	<10	<20	<40	<10	<20	<20	<20
BDE 100	<4	<6	<8	<5	<5	<5	<6
BDE 119	<1	<0.2	<5	<5	<5	<0.7	<0.2
BDE 126	<0.4	<0.1	<5	<5	<5	<0.09	<0.05
BDE 138 + BDE 166	<0.6	<0.4	<5	<5	<5	<0.2	<0.1
BDE 153	<0.8	<2	<5	<5	<5	<2	<2
BDE 154	<0.5	<1	<5	<5	<5	<2	<1
BDE 156	<0.07	<0.04	<5	<5	<5	<0.03	<0.03
BDE 183	<0.2	0.27	<5	<5	<5	1	0.77
BDE 184	<0.2	<0.2	<5	<5	<5	<0.06	<0.07
BDE 191	<0.6	<0.1	<5	<5	<5	<0.2	<0.03
BDE 196	<3	<0.6	<5	<5	<5	0.51	0.25
BDE 197	<2	<0.09	<5	<5	<5	0.56	0.42
BDE 206	1.3	<0.4	<5	<5	<5	3.1	1.1
BDE 207	<4	0.41	<5	<5	<5	3.2	1.2
BDE 209	<5	<9	<60	<20	<50	110	29
Sum of PBDE congeners							
Excluding LOD values	**3**	**2**	**0**	**0**	**0**	**120**	**33**
Incl. half LOD values	**49**	**62**	**142**	**85**	**105**	**168**	**79**
Incl. LOD values	**96**	**123**	**283**	**170**	**210**	**215**	**124**

State	QUEENSLAND cont.					
Location	Brisbane River (city and Indooroopilly)	Upper Brisbane River	Luggage Point STP Downstream*	Luggage Point STP Upstream*	Bremer R. STP Downstream*	Bremer R. STP Upstream*
PBDE congeners						
BDE 17	1.4	<0.1	6.3	14	68	31
BDE 28 + BDE 33	<10	<7	<20	<20	61	<30
BDE 47	230	<10	<70	94	560	410
BDE 49	47	<0.1	11	20	150	63
BDE 66	<0.6	<0.09	<5	<5	34	22
BDE 71	<1	<0.02	<5	<5	8.6	<5
BDE 77	<0.4	<0.1	<5	<5	<5	<5
BDE 85	<2	0.43	<5	<5	8.5	13
BDE 99	<50	<10	<50	70	370	340
BDE 100	<50	<2	<5	<5	95	79
BDE 119	<0.2	<0.4	<5	<5	<5	<5
BDE 126	<1	<0.2	<5	<5	<5	<5
BDE 138 + BDE 166	<2	<0.2	<5	<5	<5	5.1
BDE 153	12	<0.8	5.6	7.5	63	48
BDE 154	<4	<0.6	5.1	8.1	70	45
BDE 156	<1	<0.1	<5	<5	<5	<5
BDE 183	38	0.33	<5	5.7	44	15
BDE 184	<1	<0.3	<5	<5	<5	<5
BDE 191	<0.7	<0.2	<5	<5	<5	<5
BDE 196	<6	<1	<5	<5	25	8
BDE 197	15	<1	<5	<5	39	14
BDE 206	<20	<1	12	29	100	49
BDE 207	30	0.51	9.6	19	92	36
BDE 209	880	<4	330	790	2630	1580
Sum of PBDE congeners						
Excluding LOD values	**1260**	**1**	**380**	**1060**	**4420**	**2760**
Incl. half LOD values	**1328**	**21**	**485**	**1100**	**4433**	**2791**
Incl. LOD values	**1403**	**40**	**590**	**1142**	**4453**	**2823**

Appendix E - International comparisons

North America

Oros et al (2005) investigated the concentration of PBDEs in surface sediment samples collected from San Francisco. The samples were collected in 2002 at 40 spatially randomised and eight fixed sampling stations located throughout the San Francisco Estuary. In order of concentration, the five congeners detected were BDE-47, -99, -205, -204 and -183.   The sum concentration of these PBDE congeners ranged from below the limit of detection to 212 000 pg.g^{-1} dry weight (excluding LOD). BDE-47 ranged from <500 to 100 000 pg.g^{-1} dry weight, while BDE-100 and BDE-209 were below the limit of detection. The following congeners were targeted for determination: BDEs-17, -28, -33, -47, -66, -82, -85, -99, -100, -138, -153, -154, -166, -183, -190, -203, -204, -205, -206, -207, -208 and -209. BDEs-204 and -205 are not assessed in many other studies however the authors do not provide an explanation of whether or not there is any relevance to the detection of these congeners. Notably, this was the only study which analysed for BDE-209 and found it to be below the limit of detection in sediment. The authors suggest a more sensitive spectrometric method could be used to better determine low level PBDE congeners.

Three years earlier in 1998/99, Hale et al (2001) determined the concentrations of PBDEs in sediment samples collected in Virginia. Samples were collected at 133 sites from two large watersheds including the largest bodies of freshwater in Virginia. Exact point sources are not specified but it is noted that the southern Virginian/ northern North Carolina region is home to significant textile and furniture manufacturing, but not polyurethane foam production. After preliminary analysis, the 17 sediment samples with the highest PBDE concentrations were re-analysed. The total ΣPBDE concentration (the sum of BDE-47, -99, -100, -153, -154 and -49) ranged from below the limit of detection (<500 pg.g^{-1}) to 52300 pg.g^{-1} dry weight. The congener profile was dominated by BDE-47, -99 and -100. Data on individual congeners are not provided and BDE-209 was not determined.

Zhu and Hites (2005) investigated the concentration of PBDEs in surficial freshwater sediment from Lakes Michigan and Erie in the north east of the USA. The surficial concentrations of ΣPBDEs (BDE-28, -47, -49, -66, -99, -100, -153, -154, and -183) and BDE-209 were 2600 and 63000 pg.g^{-1} dw in Lake Michigan and 1100 and 39000 pg.g^{-1} dw in Lake Erie, respectively.

Also in the USA, Song et al (2005) sampled sediment from Lakes Michigan and Huron in 2002. Lake Michigan borders the Chicago-Milwaukee metropolitan area, an urbanised area with about 8 million people while the northern part of Lake Huron is sparsely populated and lacks a large river input. Both lakes received discharges from rivers and harbours. Three locations each from Lakes Michigan and Huron were sampled to obtain 75 samples. The mean concentration of ΣPBDEs (BDEs-28, -47, -66, -85, -99, -100, -153, -154 and -183) and BDE-209 in sediment in Lake Michigan was 3000 pg.g^{-1} dw and 63100 pg.g^{-1}

dw, respectively. In Lake Huron, the mean ΣPBDE concentration and BDE-209 in sediments was 1500 pg.g^{-1} dw and 28800 pg.g^{-1} dw. PBDEs were detected in all samples with BDE-209 the predominant congener.

Sediment samples from the Niagara River in the USA were analysed for PBDEs (Samara et al 2006). Samples were obtained from 11 sites and the sites with the highest PBDE concentrations were those in close proximity to industrial and urban areas. The congener profile was dominated by BDE-47 and then -99. BDE-209 was not measured in these samples. The concentration of BDE-47 ranged from 720 to 56 000 pg.g^{-1} dw while the ΣPBDE (BDEs -28, -47, -66, -99, -85, -100, -138, -153, and -154) ranged from non-detect to 148000 pg.g^{-1} dw with a median of 5400 pg.g^{-1} dw.

United Kingdom

Allchin et al (1999) investigated sediment and fish in the UK in estuaries with potential exposure from the manufacture and handling of BFRs. The sites were the Rivers Skerne and Tees, Rivers Calder and Ribble, River Nith, Great Ouse, Avonmouth and Bristol Channel, Leeds and River Humber and River Tweed. The latter was used as the control as there were no known sources of BFRs in this estuary. There were 29 sediment samples collected between November 1995 and January 1996, intertidally and from river and stream beds. The data were presented as equivalent concentrations of three commercial PBDE formulations (Great Lakes DE-71, DE-79 and DE-83) and as concentrations of three individual PBDE congeners (BDEs-47, -99 and -85). The highest concentration was found at the River Calder, downstream of a sewage treatment plant, suggesting a local source was responsible for the contamination. The range of concentrations for BDE-47, BDE-99 and BDE-85 were <300 to 368 000, <600 to 898 000 and <400 to 72 000 pg.g^{-1} dw, respectively.

Europe

In The Netherlands, the concentration of BFRs and other possible endocrine disrupting contaminants were investigated in the Scheldt estuary (Verslycke et al 2005). In 2001, one sample was collected from each of three locations in the estuary which in addition to being ranked as among the most polluted estuaries worldwide, was characterized as a long and well mixed estuary with large intertidal areas. The authors do not mention if these locations were in the vicinity of point sources. The concentration of ΣPBDEs (BDE -28, -47, -66, -71, -75, -77, -85, -99, -100, -119, -138, -153, -154 and -190) ranged from 14000-22000 pg.g^{-1} dw while the concentrations of BDE -209 ranged from 240 000-1 650 000 pg.g^{-1} dw. The median ΣPBDE concentration excluding BDE-209 was 22 000 pg.g^{-1} dw and the median concentration of BDE-209 was 272000 pg.g^{-1} dw.

In Spain, Eljarrat et al (2005) collected 13 coastal sediment samples from several hotspots on the Spanish coast and the mouths of rivers in Barcelona. Samples were collected in 2002. The concentration of ΣPBDEs (BDE-28, -33, -47, -66, -77, -100, -99, 118, -154, -153, -183 and -209) ranged from 2700 to 134000 pg.g^{-1} dw. BDE-209 contributed 50-99% to the total PBDE contamination followed by -47, -99, -100 and -153. Of the 12 BDEs detected (BDE-28, -33, -47, -66, -77, -100, -99, -118, -154, -153, -183 and -209), BDE-47

and -209 were detected in all samples. BDE-47 ranged from 50 to 130 pg.g^{-1} dw and BDE-209 ranged from 2500 to 132000 pg.g^{-1} dw. The authors state the most contaminated samples were from the Barcelona river mouth while the least contaminated were the coastal samples from Andalusia and Tarragon. Different congener patterns were observed at each site indicating that the sites may have differing commercial mixtures as the potential sources.

Also in Spain, Eljarrat et al (2004) collected one sample of freshwater river sediment at each of four sites up- and downstream from Monzon, a heavily industrialised town which drains to the river. The concentration of ΣPBDEs (BDE-47, -100, -118, -154, -153, -183 and -209) found in sediment ranged from 2000 to 42000 pg.g^{-1} dw. The mean concentrations of BDE-47 and BDE-209 were 120 and 12500 pg.g^{-1} dw, respectively. The median ΣPBDE (BDEs- 47, -100, -118, -153, -154 and -183) concentration was 1150 pg.g^{-1} dw. The lowest concentrations for sediment were found upstream of the industry, while PBDE concentrations were greater near the site of industrial impact. The samples were dominated by congeners BDE-209, -183 and -153.

In Denmark, sediment samples were collected from Danish marine territory (n=10); lakes (=5) and a river (n=1) in 2000 (Christensen and Platz 2001). The ΣPBDE concentrations (47, 99, 100, 153 and 209) ranged from 60-24700 and 70-10600 pg.g^{-1} dw in marine and freshwater sediment, respectively. The median ΣPBDE concentration (excluding BDE-209) in marine water was 250 pg.g^{-1} dw and in freshwater was 880 pg.g^{-1} dw. The median BDE-209 concentration (excluding limit of detection) in marine water was 3350 pg.g^{-1} dw and in freshwater was 2050 pg.g^{-1} dw. The samples from freshwater had higher concentrations of PBDEs than the marine sediment from all sites except in the Copenhagen harbour which the authors describe as highly trafficked. The highest concentrations of PBDEs were found in populated areas such as harbours and lakes in urban areas. BDE-209 dominated the congener profile followed by BDE-99, BDE-47, BDE-100 and BDE-153. The authors state that PBDEs are not produced, nor are there point sources, in Denmark, rather they state that PBDEs enter the Danish environment by long range transport and by emission due to washout, evaporation and incineration of products imported to Denmark such as textiles, television and computer screens and from polyurethane foam applications.

In Romania, sediment samples were collected in 2001 from three different lakes situated in the Danube Delta (Covaci et al 2006). PBDEs (BDEs-28, -47, -99, -100, -153, -154 and -183) were not detected in any samples with the concentration in each sample found to be <100 pg.g^{-1} dw.

Asia

Moon et al (2002) sampled marine sediment from 89 stations in south eastern parts of Korea. The mean concentration of ΣPBDEs (BDE-28, -47, -99, -153 and -154) ranged from 1800 to 5900 pg.g^{-1} dw. The median ΣPBDE concentration was 4500 pg.g^{-1} dw. The mean concentrations of BDE-47 and -99 were in the range 1000-2000 pg.g^{-1} dw and 900-2200 pg.g^{-1} dw, respectively. BDE-209 was not measured.

In China, Mai et al (2005) determined the concentrations of PBDEs in sediments of the Pearl River Delta and Adjacent South China Sea. In 2002, 66 sediment samples were collected from three major rivers of the Pearl River Delta, including both rural and urbanised areas. The concentration of ΣPBDEs (BDE-28, -47, -66, -85, -99, -100, -138, -153, -154 and -183) ranged from 40 to 94700 pg.g^{-1} with a mean of 9900 pg.g^{-1} dw. The concentration of BDE-209 ranged from 400 to 7341000 pg.g^{-1} dw with a mean of 465000 pg.g-1 dw. PBDEs were detected in all samples. The sample with the highest concentration was from Dongjiang River which the authors state is the world's largest manufacturing base for electronics and electrical products. The dominant congener was BDE-209 contributing 73 to 99.7% of the total PBDEs with the exception of four samples that had relatively low BDE-209 (31-53%) abundances. Following BDE-209 in most samples was BDE-99, -47, -153 and -100.

Middle East
In Kuwait, Gevao et al (2006) determined the concentrations of PBDEs in coastal marine sediment receiving industrial and municipal effluents. The congener profile was dominated by BDE-183 followed by BDE-154 and -153. PBDEs were detected in all sediment samples at concentrations ranging from 50 to 3700 pg.g^{-1} dw. The authors do not mention is BDE-209 was detected. Gevao et al (2006) found that PBDE concentrations decreased with increasing distance from the shoreline.