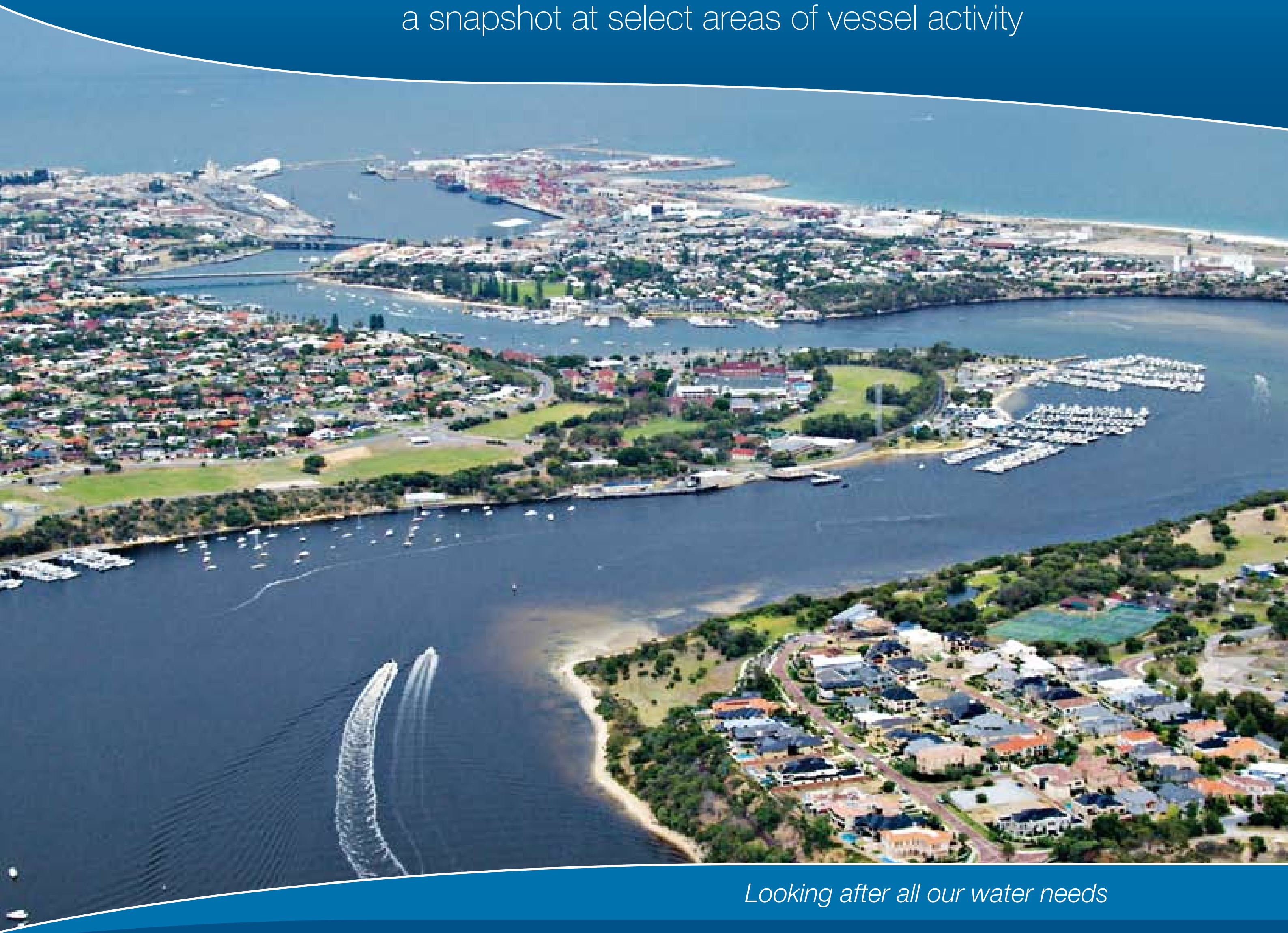
Government of **Western Australia**
Department of **Water**

Antifouling biocides in Perth coastal waters:

a snapshot at select areas of vessel activity



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Antifouling biocides in Perth coastal waters: a snapshot at select areas of vessel activity

Department of Water

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Cover photograph: *Aerial view Lower Swan towards Fremantle Port (*Photo: D. Tracey)

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Summary

This report has been prepared by the Water Science Branch, Department of Water, for the Perth Region NRM (formerly the Swan Catchment Council). In summary, antifouling biocides were found in high concentrations in sediments adjacent to areas of vessel activity and related industrial sites, in particular at two sailing clubs and a boat repair facility. This contamination is probably due to historic usage, and could also be an indication of poor management practice. Further investigation is recommended in order to assess bioavailability of the contaminants and to evaluate potential environmental risk.

In March 2006 a survey of antifouling biocides was carried out in sediments, water and, where possible, mussels in Perth coastal waters. The purpose was to undertake a preliminary scoping study of chemicals that have not usually been included in such investigations, and link these to vessel activity or related industries. Eight sites, including commercial harbours, recreational boat harbours, ship-building facilities, sailing clubs and boatlifts/slipways, were chosen to represent a broad range of intensive vessel activities. Sampling locations were selected where contamination would most likely be found (i.e. directly adjacent to slipways). The paint manufacturers Hempel (Aust) Pty Ltd and International Paints assisted with information regarding the chemicals likely to be found in Perth coastal waters. As a consequence, the following chemicals were selected for analysis: tributyltin (TBT), copper, zinc, diuron, Irgarol 1051, dithiocarbamates (including thiram and zineb), chlorothalonil and dichlofluanid.

The project found significant contamination by unregistered biocides such as TBT and Irgarol 1051 at a number of sites in Perth coastal waters, including two sailing clubs and a boat repair facility. TBT has been banned on vessels <25 m long for 15 years; therefore the gross contamination of sediments at these locations is likely to indicate historic contamination, and raises the possibility of poor environmental management practices. This is particularly evident when comparison is made to the relatively low levels found in sediments of commercial shipyards where TBT is regularly removed from vessels that are scraped down and repainted.

Irgarol 1051 is not currently registered for use in antifouling paints in Australia, and has been banned in several other countries. The presence of this contaminant in the sediments of the same three facilities highlights the need for a more comprehensive follow-up survey. This survey should include parameters to evaluate bioavailability, so that a more complete assessment of environmental risk can be undertaken. This recommendation is further underscored by results for copper and zinc in sediments and water, where these three sites were also well in exceedance of Australia and New Zealand Environment and Conservation Council (ANZECC) guidelines.

Diuron was sampled for the first time in waters, biota and sediments of Perth coastal waters. As diuron is used in almost half of the 49 antifouling products registered in Australia, it is not surprising to find significant concentrations of this herbicide. Concentrations of diuron in sediment and water reflected those of other antifouling biocides, with highest levels at two sailing clubs and a boat repair facility.

In summary, the project found that there are hotspots of contamination by antifouling biocides in Perth coastal waters. Follow-up surveys should be undertaken to assess the extent of contamination at these facilities, as well as other areas of vessel activity and related industries in the region. There is a need to address issues not covered in this study relating to bioavailability, as well as physical factors affecting impact, in order to carry out a full environmental risk assessment. Finally, it is recommended that a review of the environmental management and operating conditions of those premises is undertaken, to assess whether suitable systems are in place to prevent contamination of adjacent water bodies.

1 Introduction

Antifouling paints are used to prevent the growth of fouling organisms on the hulls of submerged surfaces such as the hulls of boats and ships. Fouling reduces hull smoothness, increasing drag with associated loss of speed and increased fuel consumption.

From the 1970s until recent years, tributyltin (TBT) was the predominant biocide used in antifouling paints, due to its high effectiveness over long periods. Concerns about its toxic effects on non-target organisms led to legislation being introduced in Western Australia in 1991 limiting its use to vessels > 25 m, following the lead of similar restrictions elsewhere. In 2001, these types of restrictions were deemed insufficient by the International Maritime Organization, which agreed on a convention that would see a ban on the application of TBT-based paints in 2003, and a ban on the presence of TBT on hulls by 2008.

With the imminent ban on TBT there has been an increase in usage of copper-based paints, which are augmented with so-called booster-biocides. A number of these booster biocides (such as Sea-nine®) have been developed specifically for use in antifouling paints. Others are products such as herbicides like diuron, or fungicides such as the dithicarbamates, thiram and zineb that incorporate well into a paint matrix. These have a diverse range of possible adverse effects on non-target organisms, and few have been assessed for use in the aquatic environment.

1.1 Tributyltin

As mentioned above, TBT has been the most widely used biocide in antifouling agents since the early 1970s. TBT is highly toxic to non-target organisms with a range of adverse effects that vary with bioavailability and the ability of the organism to metabolise it. First reports of environmental impacts of TBT were noted in the early 1980s with the crash of the oyster fishery in Arcachon Bay, France (Alzieu et al.1986). Since then, TBT has been related to numerous toxic effects, from oyster shell malformation and spatfall reductions through to immunotoxic effects in dolphins and seals (Ruiz et al. 1994; Kannan and Tanabe, 1997). For full review see Fent, (1996).

The most sensitive group of organisms to TBT contamination is neogastropods, which respond to concentrations as low as 0.5 ng TBT-Sn L-1 (parts per trillion) with a condition known as imposex (Gibbs et al. 1988). Imposex refers to the development of male characteristics, notably a penis and vas deferens in females (Smith, 1971). Since 1971 more than 140 species of neogastropods have been identified as exhibiting imposex (Matthiessen et al. 1999). Numerous laboratory experiments have shown that a unique, irreversible dose-response relationship exists between TBT and neogastropod imposex. Occasional studies have mentioned other possible causes of imposex (Nias et al. 1993; Evans et al. 2000), but these remain unconvincing and unverified. For this reason, imposex has been shown to be a particularly useful bioindicator of TBT contamination, with surveys still being undertaken throughout the world (Fernandez et al. 2005; Jorundsdottir et al. 2005). Direct chemical analysis of TBT is an expensive, time-consuming process; biological monitoring using the imposex response offers a useful alternative (Ellis and Pattisina, 1990).

The first reported occurrence of imposex in Western Australian waters was in *Conus sp*. sampled at Rottnest Island in 1991, with a clear relationship between boating activity and imposex (Kohn and Almasi, 1993). In a 1993 survey of imposex in *Thais orbita*, Field (1993) found the condition to be widespread in Perth coastal waters, with a strong correlation to both boating activity and TBT concentrations in sediment. These results complemented those of Wilson et al*.* (1993) who used the same species in Sydney waters. In the summers of 1998 and 1999 sites sampled by Field in 1993 were re-sampled in order to investigate the effectiveness of the 1991 restrictions which limited the use of TBT to vessels > 25 m (Reitsema et al. 2003). It was clear that areas such as Hillarys Boat Harbour and Ocean Reef Marina, which are frequented by mainly smaller boats, had improved in the years following the ban, with considerable reductions in the incidence of imposex. Areas near commercial shipping activities and ship repair facilities showed evidence of residual contamination; at most of these locations it is common for 100 per cent of female *Thais orbita* to exhibit the symptoms of imposex.

Surveys of imposex in Western Australia have not been limited to Perth metropolitan waters. A 1997 survey in the Dampier Archipelago demonstrated a relationship between imposex in the tropical species *Morula granulata* and distance to shipping activity, as well as concentrations of butyltins in rock oyster tissue (Figure 1.) (Reitsema and Spickett, 1999). The incidence of imposex ranged from 0-54 per cent, which is low relative to other surveys in areas of shipping done elsewhere in the world.

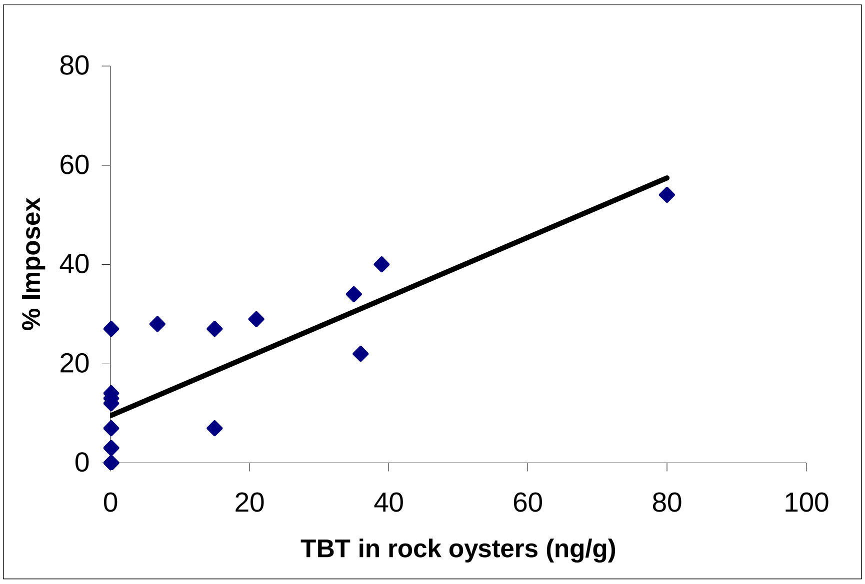

Figure 1 Imposex in *Morula granulata* and concentrations of TBT in its prey, rock oysters

Acceptance of imposex in *Thais orbita* as a biological marker specific to TBT contamination in Perth coastal waters led to its introduction as an environmental *Quality standard in the state environmental policy for Cockburn Sound in 2005* (EPA, 2005). In summary, this means that where the incidence of imposex is found to exceed the standard, these results are reported to the community, tabled in parliament, and management action is required. The use of imposex as a standard adds ecological relevance to the reporting system rather than relying only on chemical analysis of TBT in sediments or water. Chemical analysis has difficulties related to spatial variations in sediment concentrations due to presence of paint chips, as well as the rapid breakdown of TBT in water.

Figures 2 and 3 below show the incidence of imposex at sites in Perth coastal waters using data from 1993, 1999 and 2005 (Reitsema et al. 2003; M Gagnon [Curtin University] 2007 pers. comm.). Areas dominated by commercial shipping and larger vessels continue to have around 100 per cent imposex, whilst areas of recreational vessel activity have seen a reduction in incidence of imposex since the introduction of restrictions on the use of TBT to vessels > 25 m.

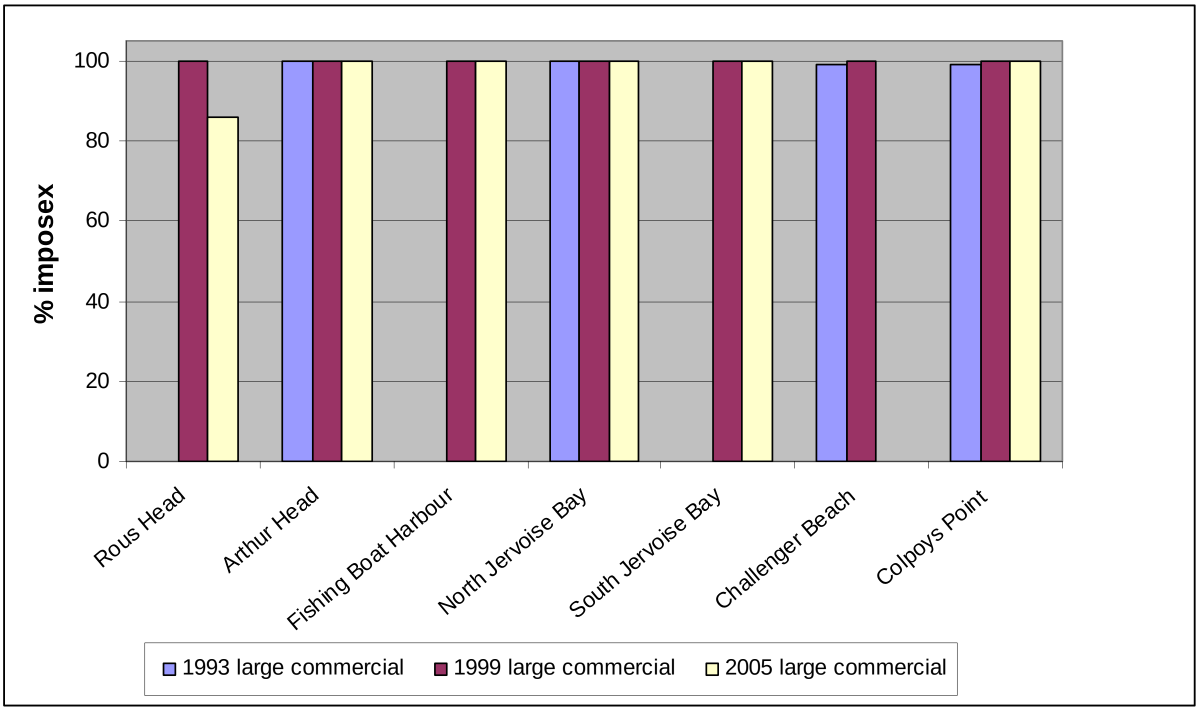

Figure 2 Imposex in *Thais orbita* at sites in Perth coastal waters that are dominated by commercial vessel activity: 1993 to 2005

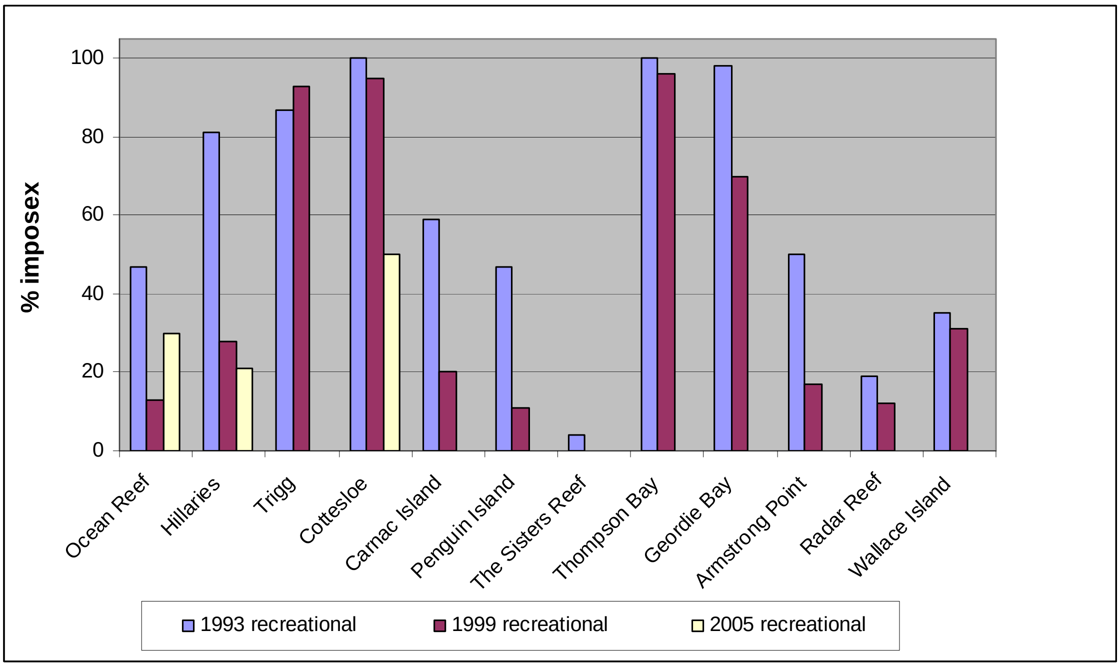

Figure 3 Imposex in *Thais orbita* at sites in Perth coastal waters that are dominated by recreational vessel activity: 1993 to 2005

Whilst the imposex response is a useful indicator of TBT contamination, it does have its limitations. Firstly, there are a number of sites of interest at which gastropod whelks such as *Thais orbita* cannot be found due to lack of suitable habitat. The absence of whelks applies in areas of immediate impact, such as directly under slipways and adjacent to hardstands – areas which would be expected to be hotspots. Secondly, *Thais orbita* can live for a decade or more following exposure to TBT at a sufficient level (parts per trillion) to induce imposex); so it is difficult to determine if the effect is caused by recent or historic contamination. Finally, areas impacted by TBT contamination can have reduced numbers of *Thais orbita*, resulting in the risk of destructive sampling to achieve desired sample sizes.

1.2 Emerging antifouling biocides in Perth waters

With a global ban in 2008 on the application and presence of TBT on the hulls of all vessels, phasing out of TBT-based products has already started. It is no longer registered for use in Australia as a biocide in antifouling paints (Appendix A), and most paint manufacturers use alternative biocides. In its place a range of mostly copper-based paints has emerged which are rendered more potent by the use of so-called ‘booster biocides’.

A survey of local paint manufacturers was undertaken to determine which antifouling paints are likely to be used in Perth coastal waters, and their associated active ingredients. International Marine Coatings (Akzo-Nobel) and Hempel provided the information which is detailed in Appendix B, and which represents most of the market in antifouling paints for Perth. This was supplemented with some information from the

Australian Pesticides and Veterinary Medicines Authority (APVMA) website for other biocides, to generate the following:

- diuron
- copper (cuprous oxide, and cuprous thiocyanate)
- zinc oxide
- zinc pyrithione
- copper pyrithione
- Irgarol 1051
- Sea-nine 211
- dithiocarbamates (including zineb and thiram)
- dichlofluanid
- chlorothalonil.

These biocides were investigated through the existing literature to determine which could be monitored in the scope of this study. Of the biocides listed above, only Sea-nine 211 was specifically manufactured for use as an antifouling biocide (by Rohm-Haas). Most of the chemicals listed were originally developed for other uses, but were found to be suitable for incorporation into a paint matrix, and had the toxicity required to boost copper-based paint. A difficulty with Sea-nine 211 with regard to environmental monitoring is that very few laboratories have the capability to carry out chemical analysis of environmental samples as the use of Sea-nine 211 is so specific, and it has only recently been developed.

Zinc pyrithione was originally used as the active ingredient for anti-dandruff shampoo, so as with Sea-nine 211, few laboratories have existing methods for its analysis. The pyrithione compounds and Sea-nine share other characteristics as well, in that they break down rapidly in seawater and sediments to a range that makes identifying breakdown products difficult (Konstantinou and Albanis, 2004). Given that very few paints currently incorporate these new biocides, the decision was made not to include them in this investigation.

1.3 Aim and scope of this study

The aim of this study was to undertake a preliminary scoping study of emerging antifouling biocides in Perth coastal waters, by sampling water, sediment and biota (where possible) at selected sites. With the global ban on TBT imminent, it was expected that a range of booster biocides and copper will be found in increasing concentrations as their usage increases. The following biocides were analysed in this study: diuron, Irgarol 1051, copper, zinc, dichlofluanid, chlorothalonil, and dithiocarbamates including zineb and thiram. TBT was also included because of its historical usage for recreational vessels, and use on vessels of more than 25 m until the global ban in 2003.

In order to determine whether there are hotspots of contamination in Perth coastal waters, a range of vessel activity and related industrial sites was selected. Where accessing a site required entry onto private premises, permission was sought from the facility manager. In all cases the most likely contaminated area; for example, directly beneath a boat or shiplift facility, or adjacent to a hardstand, was chosen for sampling.

It is important to emphasise that this study is a snapshot of likely hotspots and does not aim to characterise entire sites or facilities. The following sites were selected for this study: Hillarys Boat Harbour, Fremantle Sailing Club, Royal Perth Yacht Club, Fremantle Inner Harbour, Careening Bay, Fremantle Boat Lifters, Austal Ships and Tenix Marine. They represent a broad spectrum of vessel activity, including a recreational boat harbour and sailing clubs with active boatlift and hardstand facilities, a commercial shipping harbour, a naval harbour, a commercial boatlift and repair facility, a ferry manufacturing factory with a slipway, and a shiplift and repair facility.

2 Methods

2.1 Location of the sites

Figure 4 below shows the location of the sampling sites for this study. At all of these locations samples were taken from the area of likely highest impact; for example, directly adjacent to boatlifts or hardstands. Water, sediment and biota samples were all collected at the same time for each site. Details on specific sampling locations are available in Appendix D.

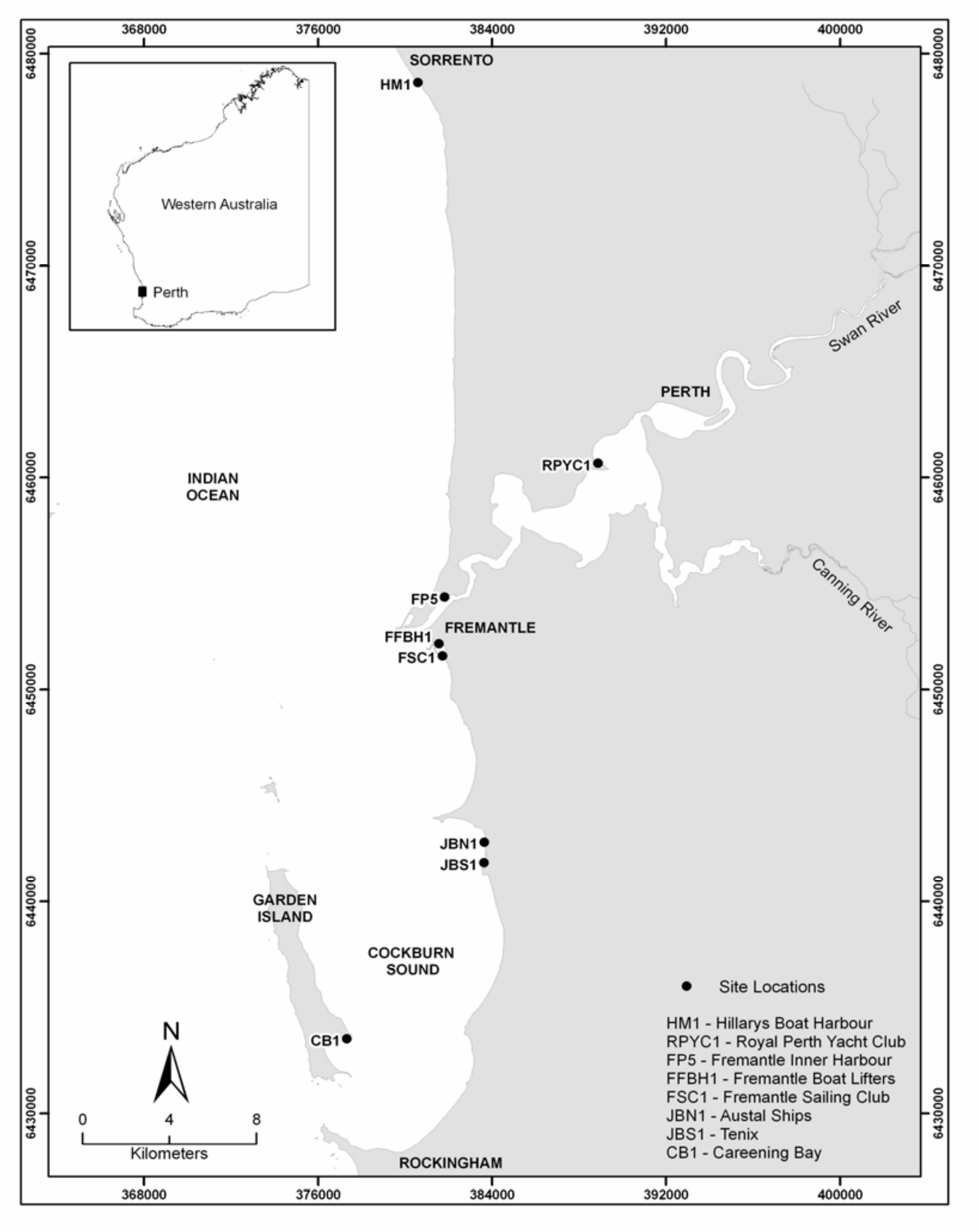

Figure 4 Map showing location of sampling sites

2.2 Methods of collection

Water

Water samples were collected in duplicate at all sites. Surface water was collected by angling the mouth of the bottle to the surface; this was done because many contaminants such as TBT are found at their highest concentrations in water at the surface micro-layer. Prior to sample collection each bottle was rinsed out three times with sample water. Samples were not filtered, as total concentrations were required for this study.

The following bottles were used: two litre plastic for butyltins; one litre amber glass for dithiocarbamates; 200ml plastic for metals (with acid for preservation); and one litre high-density polyethylene for diuron, Irgarol 1051, chlorothalonil and dichlofluanid. Samples were filled to shoulder height in bottles of a volume and type required by the respective laboratories, and kept dark and cold on ice before delivery either to the local laboratory or to the courier in the case of samples analysed in New Zealand. Care was taken to use a courier that guaranteed timely delivery of the samples, and that was able to replace ice to ensure samples were kept chilled.

Sediments

Duplicate sediment samples were collected by use of a polycarbonate sediment core, either through wading at shallow sites, or by snorkelling. Sediment samples were taken from the same location as water samples. The core was approximately 14 cm in diameter and 20 cm in length, and sediment was captured through the use of two rubber bungs. The core was depressed in the sediment to a depth of 10-15 cm, depending on the degree of consolidation of the sediment, with one bung used to seal the top and the other to seal the core when it was removed. Sediment was extruded from the corer, with approximately the top 2 cm collected in sample jars. For samples to be analysed for dithiocarbamates, metals and butyltins, 500 ml plastic jars were used. For samples to be analysed for diuron, Irgarol 1051, chlorothalonil and dichlofluanid, 250 ml glass jars were the designated choice. In all instances the choice of jar type and size followed the recommendations of the respective analytical laboratory. Samples were kept chilled and dark and transported to the laboratory as described for water samples.

Biota

Where wild mussels (*Mytilus edulis*) were found, approximately a dozen were collected and stored in plastic bags on ice. Samples were kept chilled and transported to the laboratory as described for water samples.

2.3 Analytical methods and laboratories

Table 1 summarises the analytical methods and laboratories used in this study. The National Measurement Institute (NMI) was used where possible as it is a local laboratory with existing methods for most of the biocides. However, it did not have existing methods for Irgarol 1051, dichlofluanid or chlorothalonil analysis of water, sediment and biota, so Hills Laboratories in New Zealand were also used. As Hills carried out analysis of diuron using the same method as for Irgarol 1051, it was cost-effective to have both parameters analysed together at the one laboratory.

It is important to note that due to the snapshot nature of this study, water samples were not filtered, and as such total metals are presented in this report. While this is consistent with the ANZECC guidelines (ANZECC & ARMCANZ, 2000), care needs to be taken in interpretation of the results as bioavailability, uptake and toxicity also need to be considered.

Table 1: Summary of analytical methods and laboratories used for this study

Parameter	Method	Laboratory
Butyltins	Sediment and mussels: solvent extraction, SPE cleanup, determination by GC-AED Water: SPE isolation, determination by GC-AED	NMI
Copper	Water, sediment and mussels: acid extraction, determination by ICP-MS	NMI
Zinc	Water, sediment and mussels: acid extraction, determination by ICP-MS	NMI
Dithiocarbamates	Water, sediment and mussels: decomposition by acidified stannous chloride, determination by FPD-GC	NMI
Dichlofluanid	Sediment and mussels: ethylacetate extraction, SPE cleanup, determination by GC-MS Water: SPE isolation, determination by LC-MS	Hills
Chlorothalonil	Sediment and mussels: ethylacetate extraction, SPE cleanup, determination by GC-MS Water: SPE isolation, determination by LC-MS	Hills
Diuron	Sediment and mussels: ethylacetate extraction, SPE cleanup, determination by LC-MS Water: SPE isolation, determination by LC-MS	Hills
Irgarol 1051	Sediment and mussels: ethylacetate extraction, SPE cleanup, determination by LC-MS Water: SPE isolation, determination by LC-MS	Hills

3 Results

All results are presented in Appendix C. It should be noted that no mussels could be found at the Fremantle Sailing Club site. Unless otherwise stated, guidelines for water that are referred to are for a 95 per cent level of protection for marine waters. Royal Perth Yacht Club is in estuarine waters, but these are relatively saline, particularly in summer.

3.1 Butyltins

Butyltins were found in water at two sites: Fremantle Sailing Club and Royal Perth Yacht Club. TBT was detected at Royal Perth Yacht Club at 10 and 12 ng/L, with only its breakdown product dibutyltin found at Fremantle Sailing Club at 3.1 and 3.8 ng/L.

Sediment concentrations of TBT are presented in Figure 5 below. Concentrations (expressed in this report as ng Sn per g dry weight for butyltins in sediment) ranged from 0.9 ng/g at Careening Bay to 89 000 ng/g at Fremantle Sailing Club, with all but three samples falling below 110ng/g. A second core from Fremantle Sailing Club had a significantly lower concentration of 79 ng/g. Royal Perth Yacht Club cores were the second highest, both with 61 000 ng/g. TBT concentrations exceeded the interim sediment quality guideline (ISQG-low is 5 µg/kg) (ANZECC & ARMCANZ, 2000) at five of the eight sites sampled, as well as the ISQG-high value (70 µg/kg) at four of the eight sites.

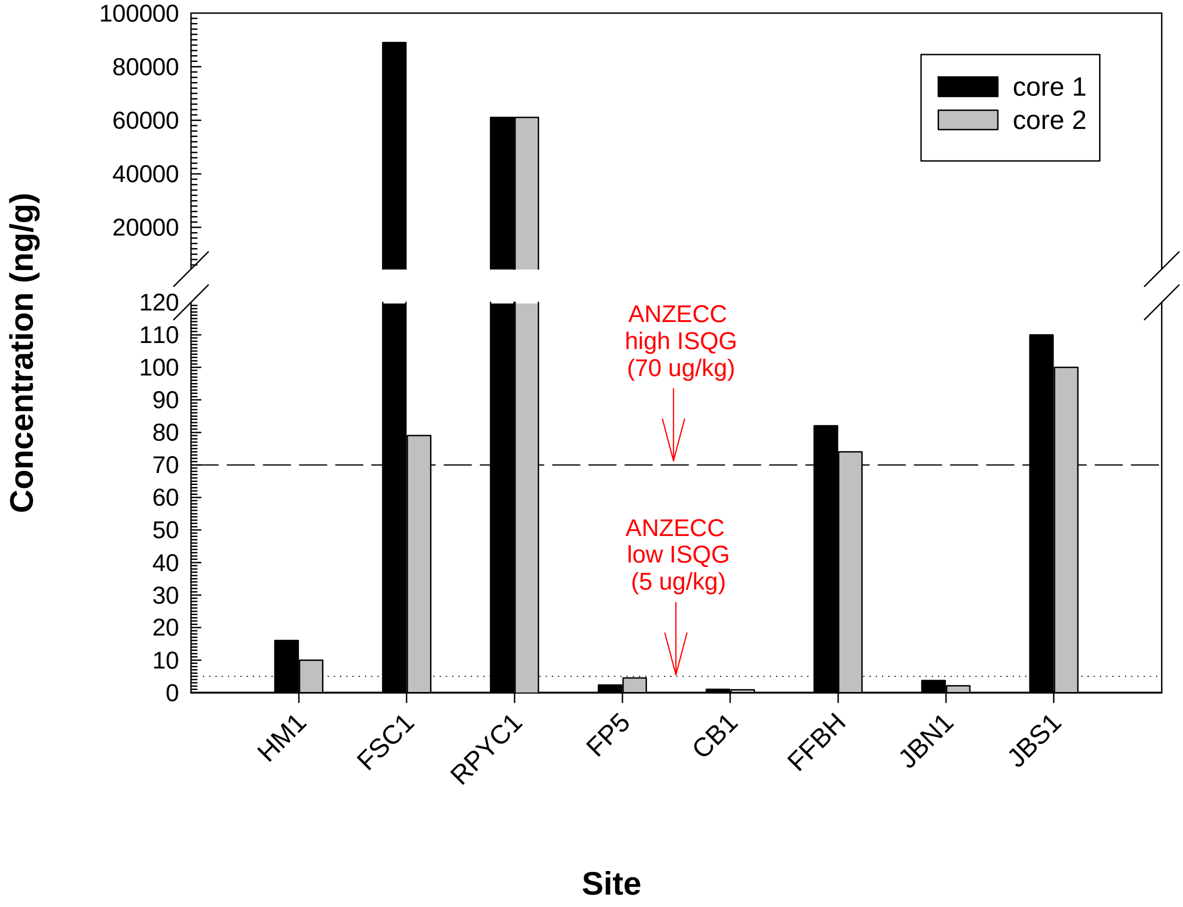

Figure 5 Concentrations of TBT in sediment from Perth coastal waters

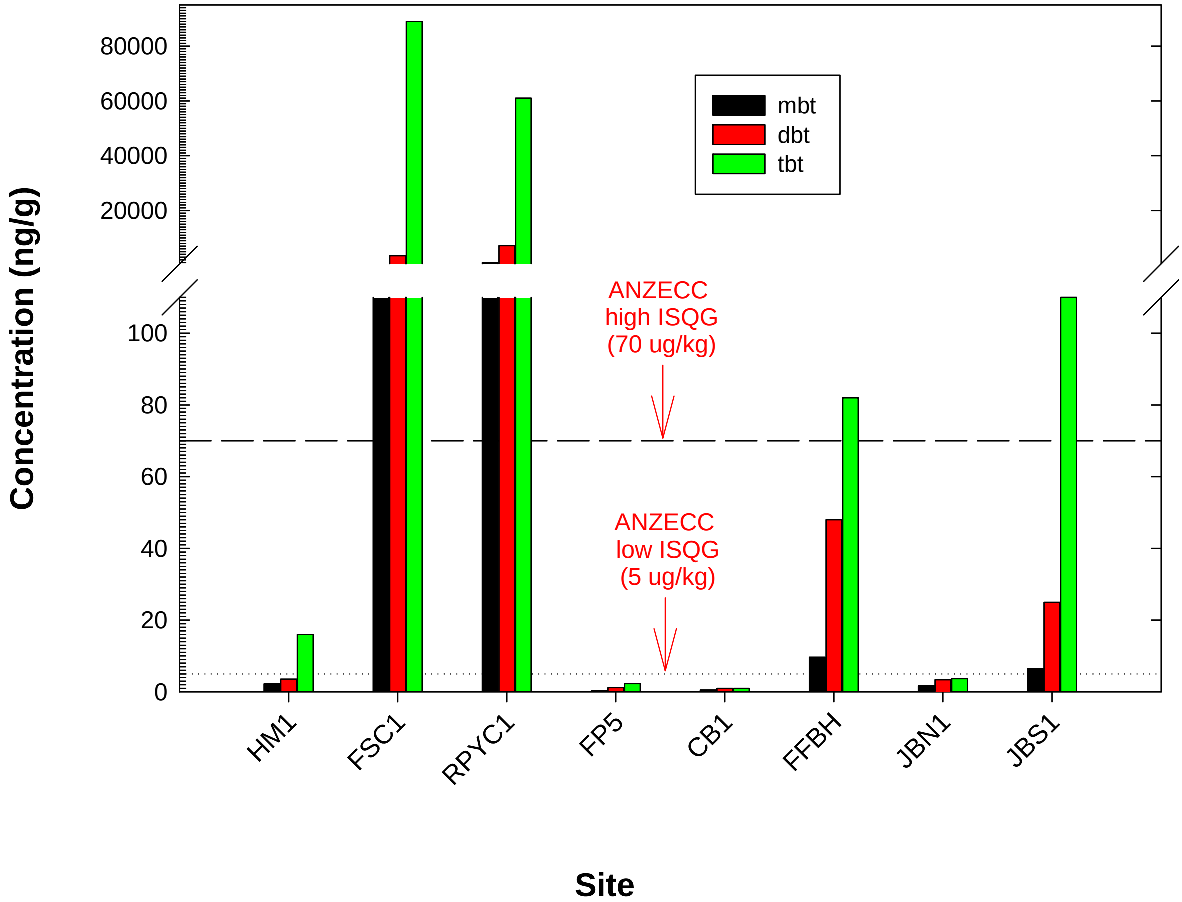

Figure 6 Concentrations of butyltins in sediment from Perth coastal waters (using only core 1)

In general, concentrations of monobutyltin (MBT) and dibutyltin (DBT) were lower than TBT in all cores, with maximum concentrations of 1500 and 7200 ng/g respectively, both at Royal Perth Yacht Club (Figure 6).

All butyltins were detected in mussel samples from all sites where mussels could be found (mussels could not be found at Fremantle Sailing Club site). At five of the seven sites DBT was the butyltin found in highest concentrations, and MBT was the lowest at all sites. Concentrations of TBT ranged from 8.5 ng/g at Fremantle Inner Harbour to 47.0 ng/g at Austal Ships.

3.2 Metals: copper and zinc

The concentrations of copper and zinc in water followed a very similar trend with concentrations for both ranging from below detection (<1 µg/L) at Careening Bay through to maximum concentrations of 3500 µg/L for zinc and 12 000 µg/L for copper, at Royal Perth Yacht Club (Figure 7 and 8). However, seven sites had concentrations below 43 µg/L for both metals; six sites had samples above the ANZECC guideline for copper and four sites exceeding the guideline for zinc.

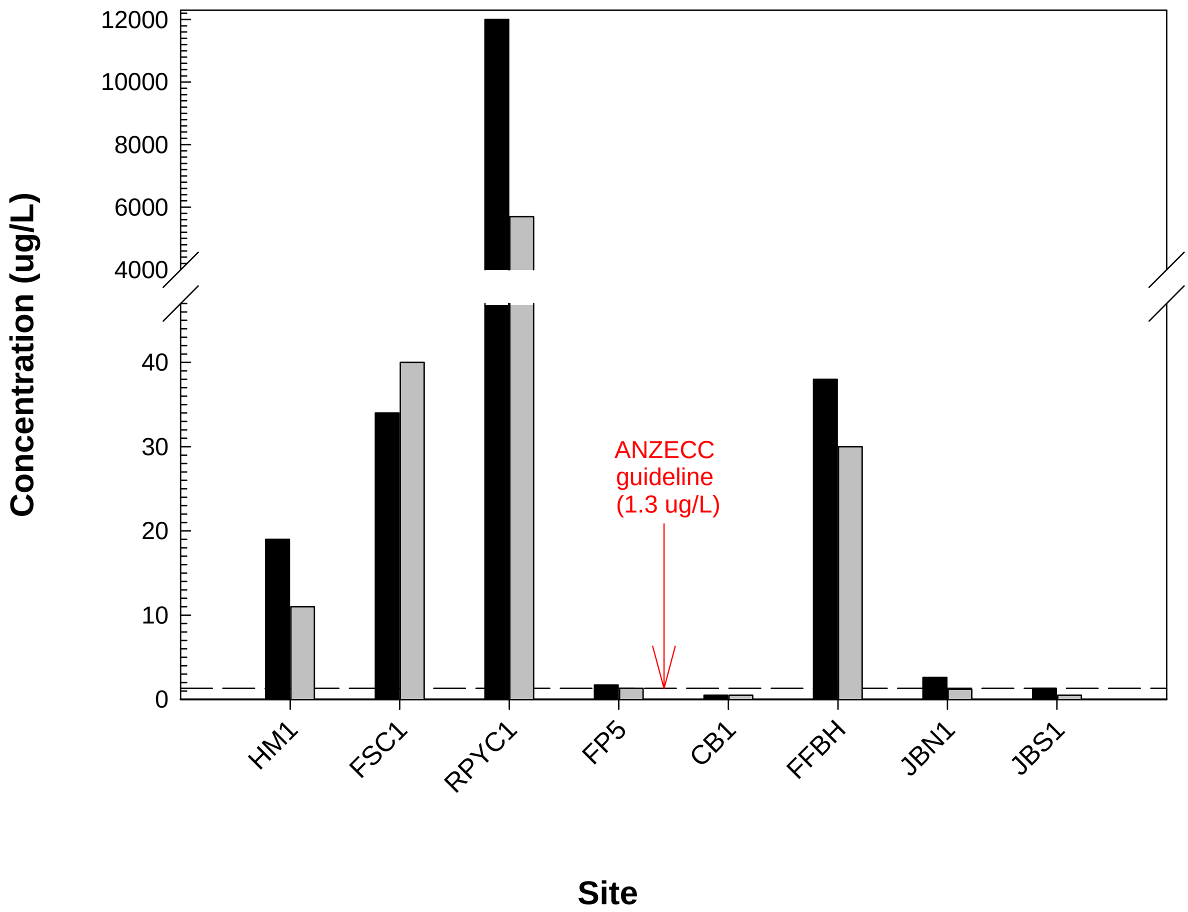

Figure 7 **Concentrations of copper in water at sites in Perth coastal waters**

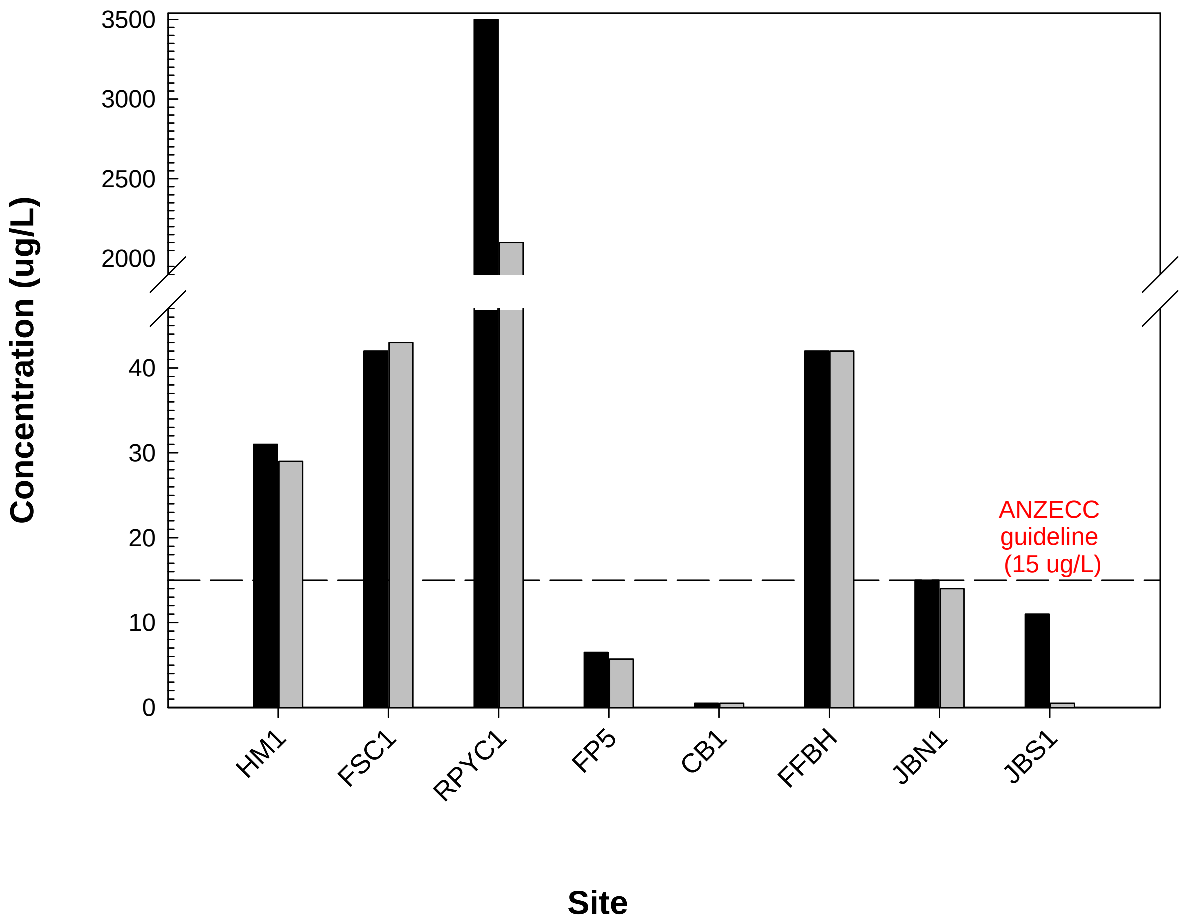

Figure 8 Concentrations of zinc in water at sites in Perth coastal waters

Copper concentrations in sediment (as shown in Figure 9) ranged from 1.5 mg/kg in a core from Careening Bay through to 17 900 mg/kg at Fremantle Sailing Club. That particular core from Fremantle Sailing Club was also the highest for zinc at 6490 mg/kg. Those concentrations were more than an order of magnitude higher than the next highest concentrations which were found in cores from Royal Perth Yacht Club. The ANZECC guideline (ISQG low) for zinc is 200 mg/kg, sediments exceeded that concentration at three sites: Royal Perth Club, Fremantle Sailing Club, and Fremantle Boat Lifters (Figure 9). The guideline (ISQG-low) for copper in sediment is 65 mg/kg. This was exceeded at the same three sites as well as Hillarys Boat Harbour.

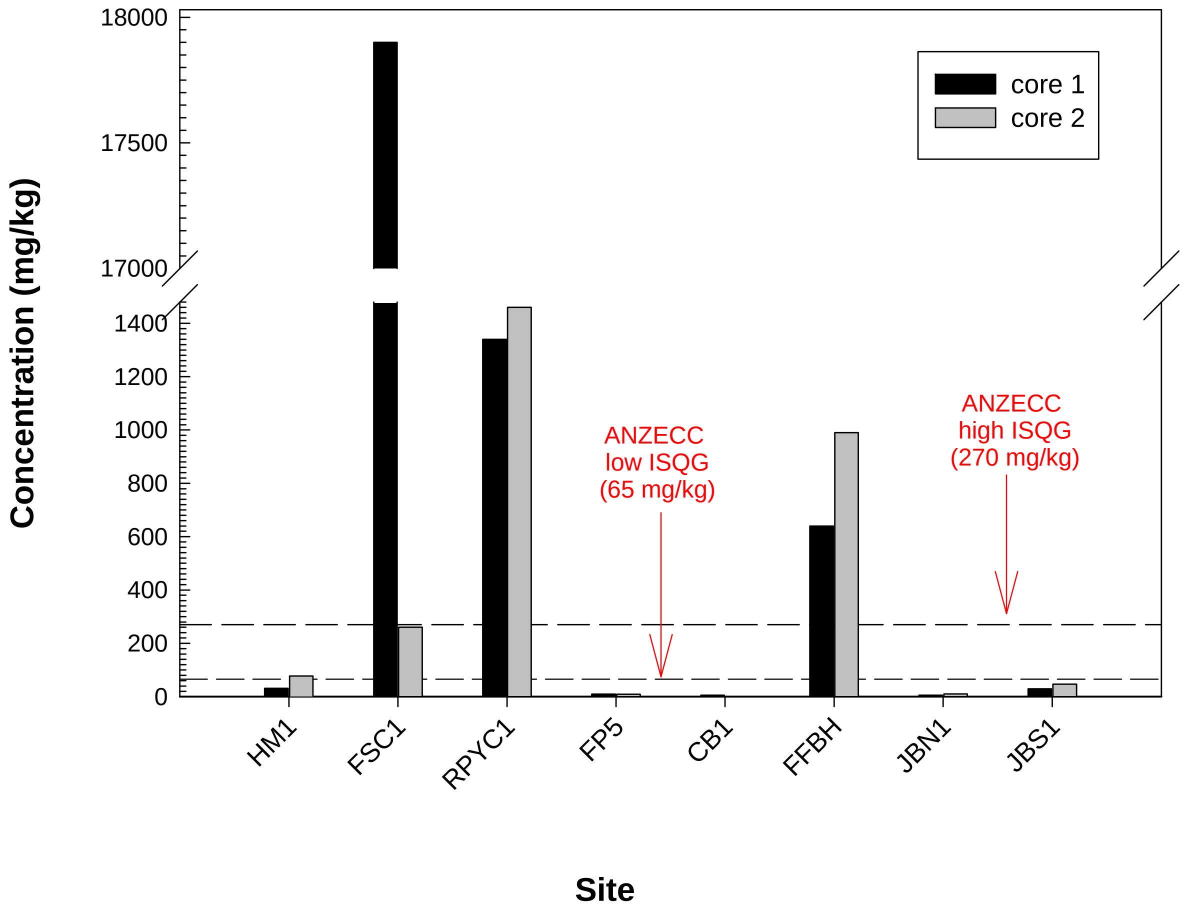

Figure 9 Concentrations of copper in sediment from Perth coastal waters

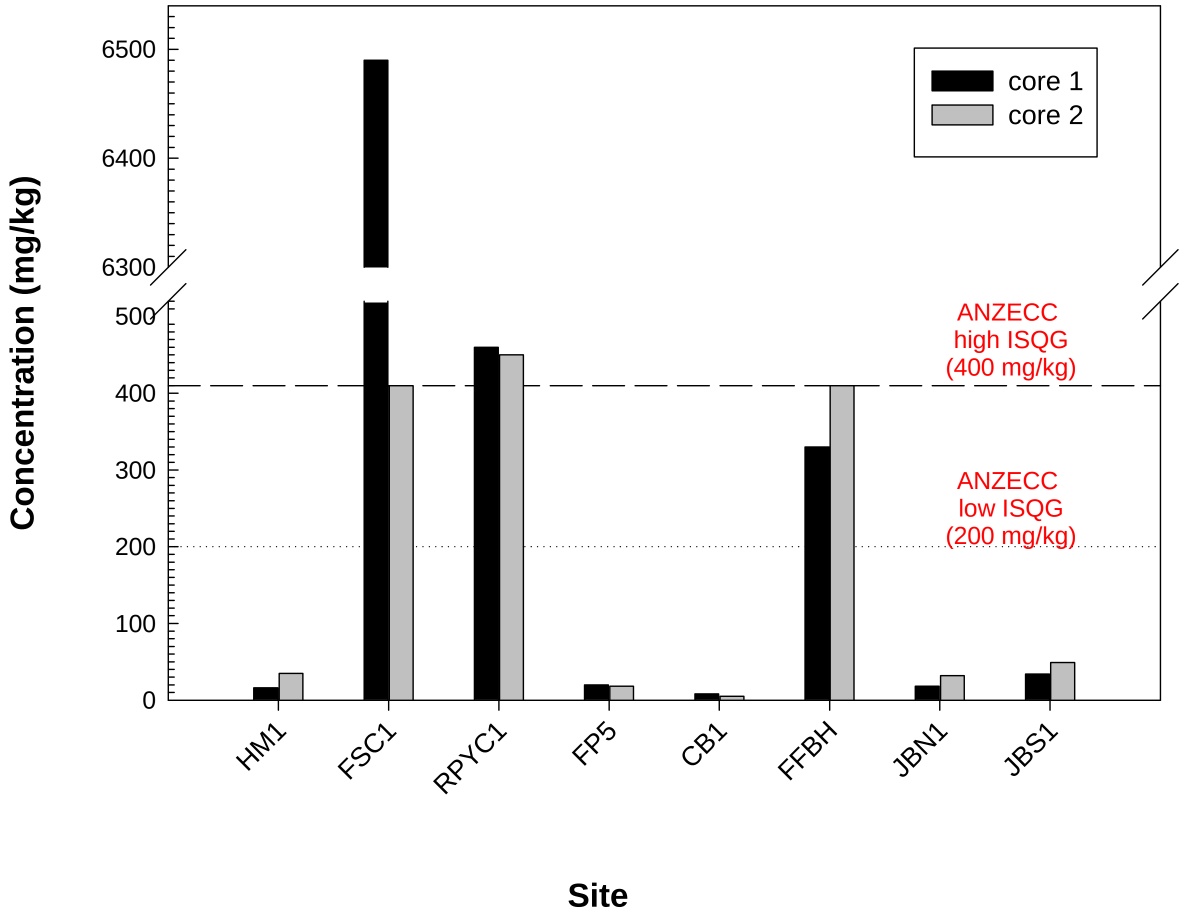

Figure 10 Concentrations of zinc in sediment from Perth coastal waters

Copper concentrations in mussels ranged from 0.83 mg/kg at Austal Ships to 14 mg/kg at Hillarys Boat Harbour. Similarly, the highest concentrations of zinc were found in mussels from Hillarys (83.0 mg/kg), with the lowest (27.0 mg/kg) at Fremantle Boat Lifters (see Appendix C).

3.3 Fungicides: dithiocarbamates, dichlofluanid and chlorothalonil

Dithiocarbamates, dichlofluanid and chlorothalonil were not detectable in water at any of the sites at the limit of detection (0.1 µg/L).

Royal Perth Yacht Club and Fremantle Boat Lifters had dithiocarbamates detectable in both sediment cores, with concentrations ranging from 0.25 to 1.3 mg/kg. One core at Fremantle Sailing Club also had dithiocarbamates present (at 3.4 mg/kg); all other cores were below detection limits. Dichlofluanid was not detectable in sediment cores from any of the sites at the limit of detection (0.01 mg/kg). Chlorothalonil was detected only at cores from Royal Perth Yacht Club, with concentrations of 0.040 and 0.225 mg/kg.

Dithiocarbamates were not detectable in mussels at any of the sites at the limit of detection (0.1 mg/kg). Dichlofluanid and chlorothalonil were not detectable in mussels at any of the sites at the limit of detection (0.01 mg/kg). Australia does not have environmental guidelines for dichlofluanid or chlorothalonil.

3.4 Herbicides: diuron and Irgarol 1051

Diuron was detected in all water samples, with a range of 20 ng/L at Careening Bay, through to 2160 ng/L at Fremantle Sailing Club (the only sample above the ANZECC low reliability trigger value of 1.8 µg/L). Data is presented below in Figure 11. Irgarol 1051 was detected in water samples from Fremantle Sailing Club (both samples 5 ng/L) and Fremantle Boat Lifters (one sample at 6 ng/L). All other samples were below the limit of detection, which was 5 ng/L.

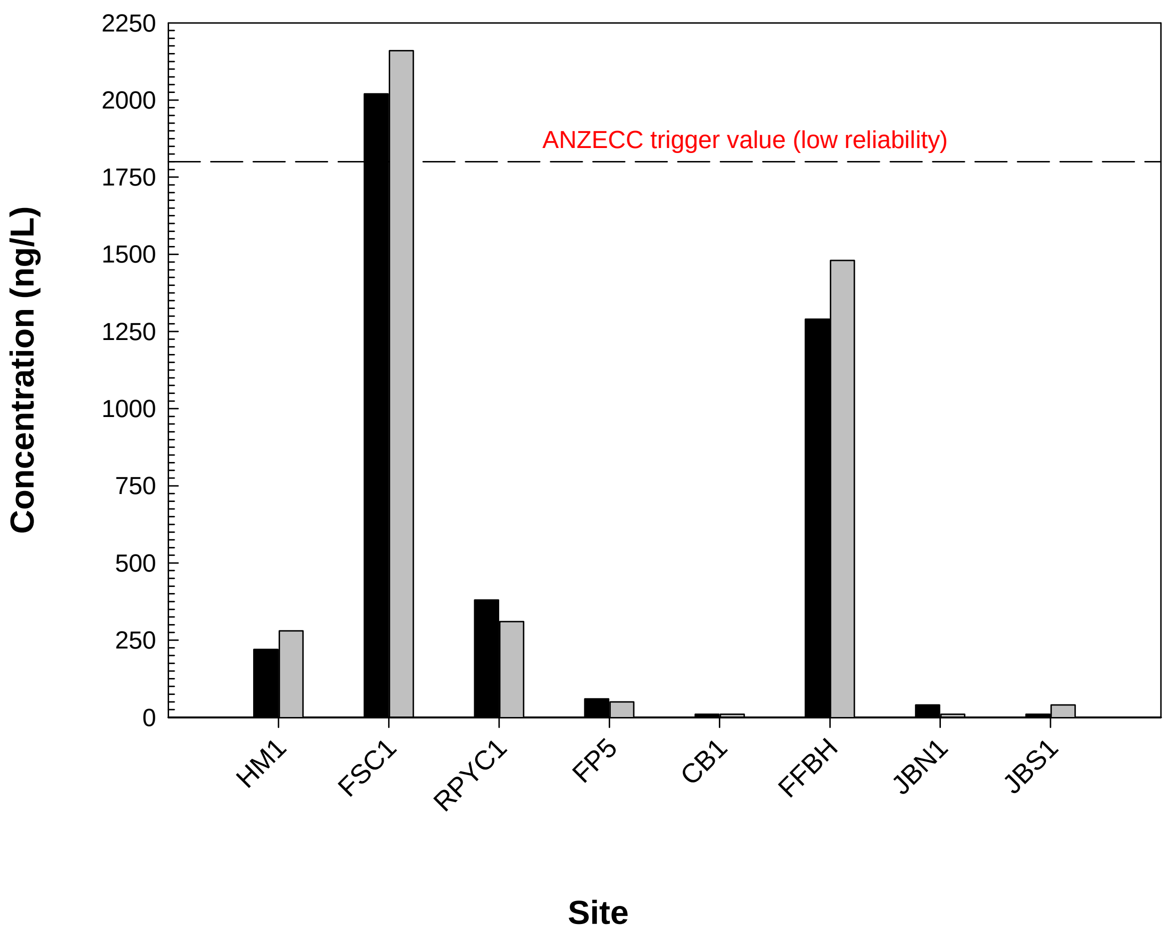

Figure 11 Concentrations of diuron in water at sites in Perth coastal waters

Diuron was not detectable in sediments at three sites: Fremantle Inner Harbour, Careening Bay or Austal Ships. As shown in Figure 12, the site with the highest concentrations was Fremantle Boat Lifters, with 0.555 and 0.367 mg/kg diuron.

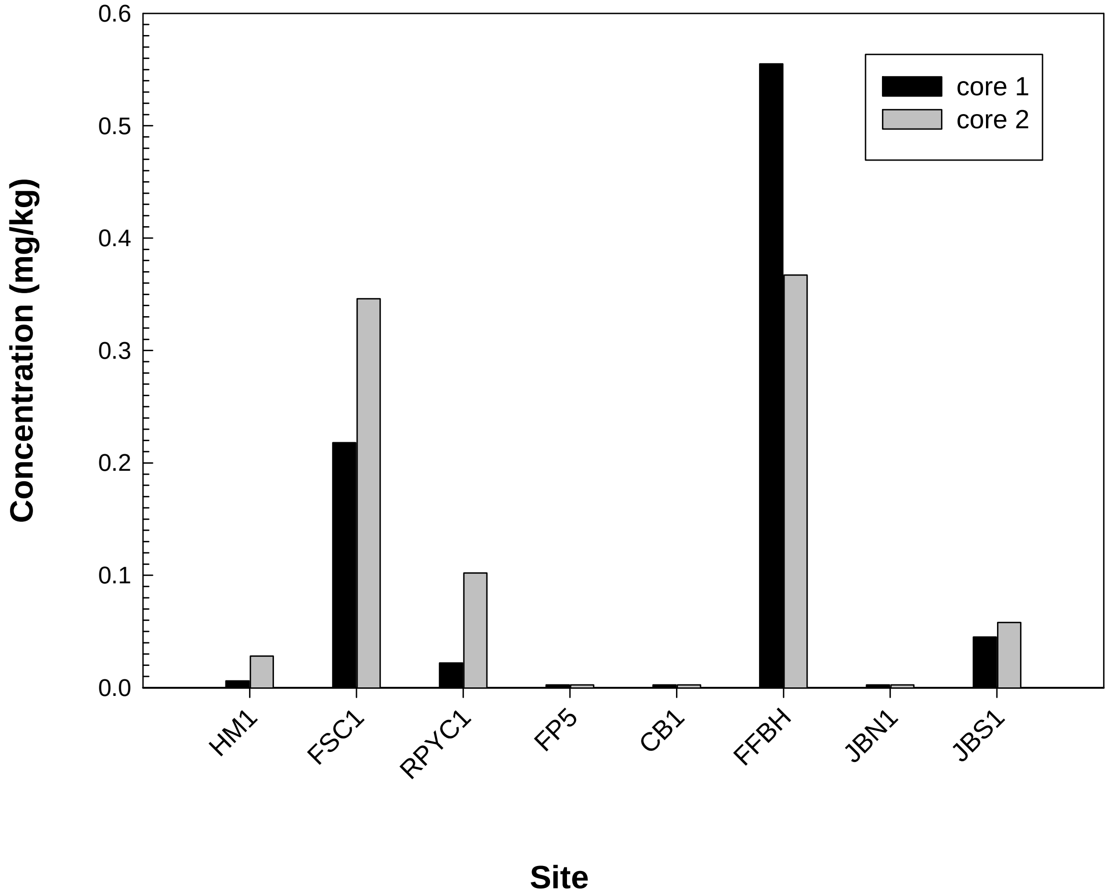

Figure 12 Concentrations of diuron in sediment from Perth coastal waters

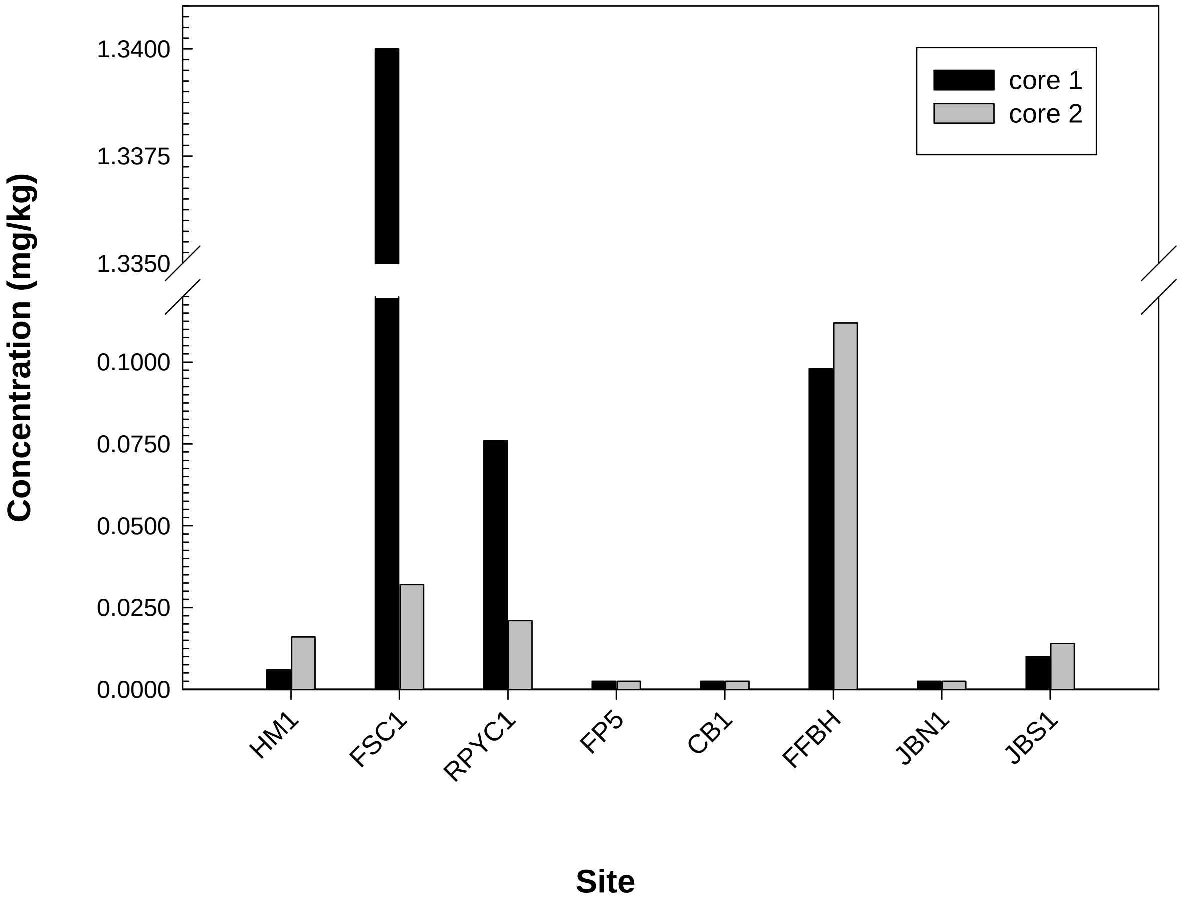

Figure 13 Concentrations of Irgarol 1051 in sediment from Perth coastal waters

Figure 13 shows concentrations of Irgarol 1051 in sediment, with non-detects for only three sites: Fremantle Inner Harbour, Careening Bay and Fremantle Boat Lifters. Concentrations ranged from 0.006 mg/kg in a core from Hillarys Boat Harbour through to 1.34 mg/kg in a core from Fremantle Sailing Club.

Three sites had detectable levels of diuron in mussels: Hillarys Boat Harbour, Fremantle Inner Harbour and Careening Bay, which had the maximum concentration of 9 µg/kg. All of the other sites had levels below the limit of detection, which was 4 µg/kg. Irgarol 1051 was not detected in mussels from any sites at the same limit of detection.

Australia does not have environmental guidelines for diuron or Irgarol 1051.

4 Discussion

These results indicate that there is potential for contamination in Perth coastal waters from the use of a range of antifouling biocides, suggesting that a more extensive survey should be undertaken. Contaminants sampled at several sites were at levels likely to be acutely toxic to marine biota.

This study provides a snapshot of antifouling biocides at selected sites of vessel activity and related industry in Perth coastal waters. It is by no means an assessment of the degree of contamination at each site, as it focuses specifically on worst-case locations such as directly under boatlifts and adjacent to hardstands.

However, the study does raise concerns about the environmental management of a number of the facilities, in particular at Royal Perth Yacht Club, Fremantle Sailing Club, and Fremantle Boat Lifters. The degree of contamination of sediments at these sites by copper and zinc, and apparent gross TBT contamination despite restrictions, highlight the need for urgent follow-up.

Irgarol 1051 is not registered for use in Australia but is found in sediments at all but three sites. While it is possible that vessels painted with Irgarol 1051-based paints could originate from overseas, there is a need for an assessment of the regulations governing possible application of unregistered antifouling paints in Western Australia. In addition to the risk posed by antifouling contamination, biosecurity should also be considered, as untreated wastes from cleaning of vessels from overseas provide a vector for invasive species. Follow-up investigations should determine if the problem is more widespread than just those sites investigated in this study.

It is clear that there is a need for education of sailing clubs and boat repair facility managers in relation to strategies for proper containment of contaminants and environmental management systems, including awareness of the ANZECC code of practice for antifouling (ANZECC,1997).

Given the nature of antifouling contamination and the possibility for paint flakes to be found in sediments close to slipways and hardstands, it is not surprising to find significant differences between adjacent cores. An example is the difference between the cores from Fremantle Sailing Club for concentrations of butyltins, copper and zinc in particular. An alternative is to combine cores into a composite, as was done by the Environment Protection Authority (EPA 1990) in a previous study in Perth waters. That method was not followed in this case as information on the heterogeneity of contamination is lost through such methods.

4.1 Tributyltin

This study has revealed high and at times gross contamination of sites in Perth coastal waters by TBT. Five of the eight sites had concentrations in exceedance of the ANZECC trigger value (5 µg/kg), with samples from Fremantle Sailing Club (89 000 ng/g) and Royal Perth Yacht Club (61 000 ng/g) more than two orders of magnitude higher than other sites. Put into perspective, concentrations of TBT above

500 ng/g have been considered as grossly contaminated in previous studies (Dowson et al. 1993).

TBT contamination to this extent was not expected at sites dominated by recreational vessels because of the restrictions that were imposed in 1991 that limited its use to vessels > 25 m. As detailed in the introduction, since 1993 there has been a reduction in TBT-induced imposex at a range of sites dominated by vessels no longer able to legally use TBT-based paints. However, it should be noted that *Thais orbita* is restricted to environments such as limestone rockwalls, and often cannot be found inside harbours or marinas, or in estuarine conditions. For this reason, it could be said that decreasing levels of imposex at some sites have painted an incorrect picture of diminishing TBT contamination; while this might be true at some sites, it definitely is not the case for the two sailing clubs sampled in this study. Moreover, this study did not capture parameters that would inform on bioavailability, as detailed in the recommendations.

In 1989, the Environmental Protection Authority carried out sampling of sediments from a number of yacht clubs in the Swan River, including Royal Perth Yacht Club (EPA, 1990). Samples were taken from similar areas as in this study, those expected to be hotspots, such as immediately in front of slipways. The maximum concentration reported in that study was 13 353 ng/g; results that supported a move to introduce restrictions on TBT to vessels > 25 m in Western Australia in 1991.

Further investigations in 1991 by Burt and Ebell (1995) in a survey of 64 sites in Perth coastal waters found maximum concentrations of 1350 ng/g. These previous studies have maximum concentrations considerably lower than those found in this study, which was 89 000 ng/g in a core from Fremantle Sailing Club. As locations such as sailing clubs are not likely to be visited by vessels >25m, this is cause for concern, as it indicates ongoing contamination. It is possible that following the restrictions in 1991 there has been a constant demand for vessels coated in TBT-based antifouling paints to be scraped down and repainted. But given that the typical turn-around time for scrape-down and repainting is at most a few years, even for the highly effective TBT, it is reasonable to have expected this source of contamination to have decreased significantly as much as a decade ago.

Historic use of TBT is often put forward as an argument as to why certain sites might still have high concentrations. However, there are a number of factors that need to be considered in relation to this argument. Firstly, it has been demonstrated that degradation of TBT in sediments is a microbially mediated process, with half-life estimates of 1.85 years (de Mora et al, 1989) to five years (Dowson et al, 1993) in other than totally anaerobic sediment, or in cases where paint flakes are common, as demonstrated by Thomas et al, (2003). In the case of Fremantle Sailing Club, for example, the disparity between the two cores appears to indicate that paint flakes are present, with a resultant long half-life for TBT. Secondly, Figure 6 shows the ratio of TBT to its breakdown products dibutyltin (DBT) and monobutyltin (MBT). At all sites TBT is found at higher proportions of total butyltin, which indicates either slow breakdown of TBT due to its presence in the form of paint flakes and/or anaerobic sediment conditions, or alternatively, that fresh inputs of TBT are occurring.

That butyltin concentrations in water were mostly below the level of detection for most sites is not surprising given the rapid breakdown and removal of TBT from the water column by volatisation, photolysis, or adsorption onto suspended sediments. Its half-life is typically short in water, breaking down in a matter of days (de Mora et al.1995)

It is of interest that concentrations of butyltins in mussels were lower than might be expected given the level of contamination of sediments. The maximum concentration of TBT was 47 ng/g at Fremantle Boat Lifters, which is low relative to findings of the EPA study in 1989, in which concentrations as high as 2819 ng/g were reported for Careening Bay. In this study, mussels at Careening Bay were found to have TBT at 17 ng/g, a significant reduction.

Burt and Ebell (1995) found concentrations in mussels from Perth coastal waters as high as 320 ng/g, which is consistent with other studies (Hwang et al. 1999; St-Jean et al. 1999). That the concentrations in mussels in this study are so much lower could be an indication of the nature of TBT contamination; that is, it could be largely due to paint flakes or TBT strongly bound to sediments that are not so readily bioavailable. The data for Fremantle Sailing Club in particular, with the large difference between the two cores, points towards contamination through paint chips. This indicates that poor management practices allowing paint chips to be released into the environment are the likely source of TBT at these locations.

Following the ANZECC guidelines decision tree for the assessment of contaminated sediment, (ANZECC & ARMCANZ, 2000), the four sites that exceeded the upper interim sediment quality guideline for TBT (70 µg/kg) require follow-up to examine bioavailability. This follow-up would include analysis of factors affecting bioavailability, including sediment grain size analysis, total organic carbon concentrations, and if necessary, pore water concentrations.

4.2 Metals: copper and zinc

The majority of antifouling paints registered in Australia have a copper base, and many contain zinc oxide, so it is not surprising to find these metals in all sediment, water and biota samples. Samples from the two sailing clubs and Fremantle Boat Lifters presented the most contaminated sediment samples, with exceedances of high and low interim sediment quality guidelines.

There are alternative sources of these metals into the aquatic environment, particularly for zinc. Bird et al. (1996) demonstrated that sacrificial anodes used on steel and iron structures such as marinas, pylons and vessels to prevent corrosion are a likely, significant source of contamination in marina environments. Recent work by the Department of Water has also found zinc and copper in surface water of stormwater drains, at concentrations of ~ 210 and 9 µg/L respectively (Nice et al., 2009). However, relative to maximum concentrations found in this study of up to 3500 and 12 000 µg/L, this is fairly insignificant.

Stormwater as a source of metals in sediment was also investigated in the Swan estuary by Rate and Robertson (2000) who found concentrations of copper near stormwater outfalls as high as 297 mg/kg. While this indicates that stormwater may explain some of the lower concentrations found, it certainly does not account for the high levels found at Royal Perth Yacht Club, Fremantle Sailing Club and Fremantle Boat Lifters.

As with TBT, there are strong indications that the copper and zinc in sediments at the sites with the highest concentrations appear to be related to paint chips. At Fremantle Sailing Club there is a substantial difference between copper and zinc in the adjacent cores, as was the case with TBT. Heterogeneous contamination by paint chips leading to hotspots has been reported recently in other locations such as England (Turner et al. 2007). The important point to note is that the bioavailability of copper and zinc from sediments contaminated by paint chips is variable according to local conditions; therefore without the follow-up studies recommended below environmental impact is difficult to determine at this stage. Given the toxicity of copper and zinc to a range of marine biota it is important to do further investigations to evaluate environmental impact; there are previous studies that can be used for guidance (Matthiessen et al. 1999).

4.3 Fungicides: dithiocarbamates, dichlofluanid and chlorothalonil

The dithiocarbamates thiram and zineb, as well as dichlofluanid and chlorothalonil, are fungicides that are commonly used in horticulture and agriculture, and only recently have been incorporated into antifouling paints, mostly in conjunction with copper as ‘booster biocides’. Thiram is an active ingredient in five registered products, while the other three are only found in one product each. As a result, it is not surprising to find that none of these were detectable in water or mussels, particularly as they are only sporadically found, even in European waters where they are more widely used (ACE, 2002).

Dithiocarbarmates were detected in sediments of Royal Perth Yacht Club, Fremantle Sailing Club, and Fremantle Boat Lifters. It is difficult to make comment on the concentrations found as there are no environmental guidelines for marine waters in Australia, let alone previous studies.for comparison.

Chlorothalonil was found at Royal Perth Yacht Club at 0.225 mg/kg (225 ng/g). This is substantial, considering concentrations in European sediments of marinas were reported as high as 165 ng/g (Konstantinou and Albanis, 2004). As chlorothalonil is otherwise used as an agricultural chemical, it is safe to assume that antifouling biocides are the source, and given the high levels of copper, zinc, and TBT, the high levels are probably due to the presence of paint chips in sediment.

That dichlofluanid was not detected in sediment is fortunate, as European studies have found it to be more persistent than diuron, Irgarol 1051 and chlorothalonil (Voulvoulis et al. 2000).

4.4 Herbicides: diuron and Irgarol 1051

Diuron is a commonly-used broad spectrum herbicide that is also incorporated into antifouling paints, mainly to boost the toxicity of copper-based paints to algal species such as *Enteromorpha* (Voulvoulis et al. 1999). The maximum levels of diuron reported here for sediments (0.555 mg/kg) and water (2160 ng/L) are relatively high by international standards but not excessive, with higher levels noted in the United Kingdom in 1998; for example (Konstantinou and Albanis, 2004). Levels of diuron in water are in excess of the low reliability guideline, which is 1.8 µg/L (ANZECC & ARMCANZ, 2000). This is also higher than those found in New Zealand marinas by Stewart (2003), who reported levels of up to 830 ng/L.

Part of the concern over diuron is its persistence in water; a half life of 273 days has been determined (ACE, 2002), so it is of little surprise that it was found in all water samples. Given its properties as a herbicide via photosynthesis inhibition, this has implications for non-target organisms such as primary producers (like algae). The breakdown product of diuron is 3,4-dichloroaniline, which is more toxic than diuron and also very persistent (Giacomazzi and Cochet, 2004). Due to its persistence and toxic properties, diuron has been banned in some European countries, and has come under review (but not restricted) by the Australian Pesticide and Veterinary Medicine Authority. In contrast to TBT, diuron is predominantly found in the dissolved phase and only weakly binds to sediments (Konstantinou and Albanis, 2004).

While diuron is widely used in antifouling paints, with 22 registered products in Australia, its use as a herbicide cannot be discounted as a source for Perth waters. Surface water concentrations of 50 ng/l and sediment concentrations of 1.1 ng/g were found in seagrass meadows of Queensland, and this was attributed to agricultural runoff (McMahon *et al*, 2005).

Unlike diuron, Irgarol 1051 is not registered in Australia for use in antifouling paints, so the fact that it is found in sediments of all but three sites is of concern, particularly given its toxicity to algae (Hall et al. 2005). Other than possible illegal use of paints containing Irgarol 1051, or vessels purchased from overseas having Irgarol 1051-based paints on their hulls, it is difficult to pin-point what the source of contamination could be. The concentrations in water at the sites where it was detected (5 ng/L at Fremantle Sailing Club and 6 ng/L at Fremantle Boat Lifters) are relatively low by international standards, particularly in Europe where it is widely distributed (ACE, 2002).

Irgarol 1051 is persistent in water and has a fairly low affinity for sediments, much like diuron (Tolosa et al. 1996). The fact that relatively high concentrations of Irgarol 1051 are found in sediments at sites like Fremantle Sailing Club is consistent with previous findings that such high concentrations are associated with paint chips from hull scrape-down and repair operations (Konstantinou and Albanis, 2004).

5 Conclusions and recommendations

This study provides a snapshot of antifouling biocides at select sites of vessel activity and related industry in Perth coastal waters. It is by no means an assessment of the degree of contamination at each site, as it focuses specifically on 'worst-case' locations such as directly under boatlifts and adjacent to hardstands. However, the study does raise serious concerns about the environmental management of a number of the facilities, in particular at Royal Perth Yacht Club, Fremantle Sailing Club, and Fremantle Boat Lifters.

The degree of contamination of sediments at these sites by copper and zinc, and apparent gross TBT contamination despite restrictions highlight the need for urgent follow-up. Irgarol 1051 is not registered for use in Australia, but is found in sediments at all but three sites. Furthermore, assuming that this trend of contamination is the same for similar sites in Perth coastal waters, there is a need for education of sailing clubs and boat repair facility managers in relation to proper environmental management systems, and in particular waste management.

A number of recommendations can be made as a result of this study:

- A follow-up survey should take place at sites with high levels of contamination, including Royal Perth Yacht Club, Fremantle Sailing Club and Fremantle Boat Lifters, in order to evaluate the full extent of contamination. This survey could form part of a larger investigation of other likely hotspots; and should focus on TBT, copper, zinc, diuron and Irgarol 1051. This study should include a comprehensive literature review, as there are a number of excellent case studies of how a full environmental risk assessment for antifouling biocides should be undertaken.
- Follow-up investigations should include analysis of physical characteristics of sediments in order to determine bioavailability; for example: percentage solids, total organic carbon, sediment grain size analysis, pore water evaluation, acid volatile sulfides (with simultaneously extractable metals), and sediment speciation. Filtered water samples should also be taken to assess potential for impacts from waterborne exposure (as only total metals were determined in this study).
- Monitoring of the abundance and diversity of benthic invertebrates should be undertaken around identified and likely hotspots of antifouling contamination.
- Whole sediment toxicity studies should be carried out on the highly contaminated sediments to determine the intensity and extent of any effects on biota.
- Subsequent surveys that are undertaken should not focus solely on likely hotspots, as antifouling biociodes by their nature leach into water wherever vessels are present. A comprehensive survey of antifouling biocides in Perth coastal waters is recommended.
- Facility managers and end users should be educated on responsible environmental management, and waste management procedures. The

ANZECC *Code of practice for antifouling and in-water hull cleaning and maintenance* should be used as a tool to inform on proper environmental management. Guidelines such as those that have been developed by other states such as Tasmania could be used for the same purpose (DPI, 2003).

- Finally, facility managers in particular need to be made aware of the possible environmental regulations, including legal obligations under the *Environmental Protection Act*, *Unauthorised Discharge Regulations*, and the *Contaminated Sites Act.*

Glossary

ACE	Assessment of antifouling agents in coastal environments
ANZECC	Australia and New Zealand Environment and Conservation Council
APVMA	Australian Pesticides and Veterinary Medicines Authority
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand.
CB	Careening Bay
DBT	Dibutyltin
DoW	Department of Water
EPA	Environmental Protection Agency
FBL	Fremantle Boat Lifters
FP	Fremantle Port
FPD-GC	Flame Photometric Detector – Gas Chromatography
FSC	Fremantle Sailing Club
GC-AED	Gas Chromatography - Atomic Emission Detector
GC-MS	Gas Chromatography – Mass Spectrometry
HM	Hillarys Marina
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ISQG	Interim Sediment Quality Guideline
MBT	Monobutyltin (MBT)
NMI	National Measurement Institute
PUBCRIS	The online database of the Australian Pesticide and Veterinary Medicines Authority
RPYC	Royal Perth Yacht Club
SPE	Solid Phase Extraction
TBT	Tributyltin

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Appendices

Appendix A — Constituents of antifouling paints that are registered in Australia

Constituent	# of Products
CUPROUS OXIDE	40
DIURON	22
ZINC OXIDE	14
HYDROCARBON	12
XYLENE	10
COPPER THIOCYANATE	7
THIRAM	5
ZINEB	1
ZINC PYRITHIONE	1
SEA-NINE	1
DICHLOFLUANID	1
CHLOROTHALONIL	1

(Source: PUBCRIS, which is the online database of the Australian Pesticide and Veterinary Medicines Authority, as of June 2007. The website has more detailed information including suppliers and concentrations of constituents in each of the paint products.)

Appendix B — Antifouling biocides and likely product usage in Perth waters

(Information provided by antifouling paint suppliers: Hempel and International Marine Paints, and supplemented by PUBCRIS, the online database of the Australian Pesticide and Veterinary Medicine Authority. This is not a comprehensive list and is only indicative of the types of active ingredients used.)

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
Chlorothalonil			Transocean Marine Paint Cleanship	Asian Paints	
Copper oxide	001317-38-0	2.5-10	Intersmooth 465 Black	International	Defence vessels Foreign flag vessels Coastal traders Large commercial
Copper(i)oxide aka Cuprous oxide	001317-39-1	25-50	Intersmooth 360 Ecoloflex Black & Red; AND	International	Defence vessels Foreign flag vessels Coastal traders

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
or dicopper oxide			Intersmooth 365 & 465 Black		Large commercial
		25-50	Bottomkote Antifouling Blue	International	
		25-50	Coppercoat Extra A-foul Black[1]	International	Retail pleasure boats
		25-50	Interspeed Tin-free A-F Red Interspeed 642 Red Bulk (and Dark Red Bulk)	International	Foreign flag vessels Coastal traders Commercial fishing boats/ large yachts
		25-50	Interswift 655 Dark Red	International	Foreign flag only
		25-50	Longlife Antifouling Blue	International	Retail pleasure boats
		25-50	Micron Extra Antifouling Black	International	Retail pleasure boats
		25-50	Micron CSC Boatguard Extra Blue	International	Retail pleasure boats
		25-50	Micron 66 Blue	International	Retail pleasure boats

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
		50-100	VC-Offshore Extra A-foul (part B)	International	Retail pleasure boats
		60 (apvma)	Awlcraft	International	Retail pleasure boats
		40-50	Olympic HI 76600	Hempels	Pleasure boats, commercial fishing boats
		30-40	Globic 81920/81950	Hempels	Commercial vessels, tugs, supply vessels, dredges
		40-50	Nautic tin-free	Hempels	Commercial vessels, tugs, supply vessels, dredges
		40-75	Seatech 7820	Hempels	Pleasure boats, commercial fishing boats
		30-40	Mille Dynamic 7170C	Hempels	Pleasure boats, commercial fishing boats
Copper pyrithione	014915-37-8	2.5-10	Interswift 655 Dark Red	International	Foreign flag only

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
aka Copper omadine ®					
Cuprous thiocyanate	001111-67-7	10-25	Cruiser Superior Antifouling Black	International	Aluminum pleasure boats
		10-25	Interspeed 2000 Antifouling Black	International	Aluminum pleasure boats
		15-20	Mille Dynamic 7160C	Hempels	Aluminum pleasure boats
Dichlofluanid			International Trilux for Aluminuim	International	
Diuron		2.5-10	Interspeed Tin-free A-F Red	International	Foreign flag vessels Coastal traders

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
			Interspeed 642 Red Bulk (and Dark Red Bulk)		Fishing boats/large yachts
		2.5-10	Coppercoat Extra A-foul Black[1]	International	Retail pleasure boats
		2.5-10	Cruiser Superior Antifouling Black	International	Aluminum pleasure boats
		2.5-10	Interspeed 2000 Antifouling Black	International	Aluminum pleasure boats
		2.5-10	Interspeed Tin-free A-F Red	International	Aluminum pleasure boats
		2.5-10	Longlife Antifouling Blue	International	Retail pleasure boats
		2.5-10	Micron Extra Antifouling Black	International	Retail pleasure boats
		2.5-10	Micron CSC Boatguard Extra Blue	International	Retail pleasure boats
		1-2.5	VC-Offshore Extra A-foul (part A)	International	Retail pleasure boats
		5	Awlcraft	International	Retail pleasure boats

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
		2-5	Nautic tin-free	Hempels	Commercial vessels, tugs, supply vessels, dredges
		2-5	Mille Dynamic 7170C	Hempels	Pleasure boats, commercial fishing boats
		2-5	Mille Dynamic 7160C	Hempels	Aluminum pleasure boats
			Sigmaplane Ecol (and HA 120)	Wattyl	
			Newport 77/88	Wattyl	Retail pleasure boats
			Trawler Antifouling	Wattlyl	Retail pleasure boats
Irgarol 1051					Foreign flag only
Sea-nine 211® (4,5-dichloro-2-n-octyl-4-isothiazolin-	64359-81-5	1-2	Globic 81920/81950	Hempels	Commercial vessels, tugs, supply vessels, dredges

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
3-one)					
Thiram			ABC 3 Antifouling	Ameron	
			Altex Coatings AF3000	Resene	
			Boero SA633 Yacht Selfpolishing	Resene	
Zinc oxide	001314-13-2	2.5-10	Bottomkote Antifouling Blue	International	
		2.5-10	Coppercoat Extra A-foul Black	International	Retail pleasure boats
		10-25	Cruiser Superior Antifouling Black	International	Aluminum pleasure boats
		10-25	Interspeed 2000 Antifouling Black	International	Aluminum pleasure boats

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
		10-25	Interspeed Tin-free A-F Red Interspeed 642 Red Bulk (and Dark Red Bulk)	International	Foreign flag vessels Coastal Traders Fishing boats/large yachts
		10-25	Interswift 655 Dark Red	International	Foreign flag only
		2.5-10	Longlife Antifouling Blue	International	Retail pleasure boats
		10-25	Micron Extra Antifouling Black	International	Retail pleasure boats
		10-25	Micron CSC Boatguard Extra Blue	International	Retail pleasure boats
		2.5-10	VC-Offshore Extra A-foul (part A)	International	Retail pleasure boats
		10-15	Olympic HI 76600	Hempels	Pleasure boats, commercial fishing boats
		15-20	Globic 81920/81950	Hempels	Commercial vessels, tugs, supply vessels, dredges
		5-10	Nautic tin-free	Hempels	Commercial vessels, tugs, supply vessels, dredges

Chemical	CAS	Concentration (%w/w in paint)	Product	Company	Vessel type
		20-30	Mille Dynamic 7170C	Hempels	Pleasure boats, commercial fishing boats
		15-20	Mille Dynamic 7160C	Hempels	Aluminuim pleasure boats
Zinc pyrithione aka ZPT, Zinc omadine ®	013463-41-7	2.5-10	Intersmooth 360 Ecoloflex Black & Red; AND Intersmooth 365 & 465 Black	International	Defence vessels Foreign flag vessels Coastal Traders Large commercial
		2.5-10	Micron 66 Blue	International	Retail pleasure boats
Zineb			Antifouling Seasafe	Jotun	

Appendix C — Concentrations of antifouling biocides in water, sediment and mussels from Perth coastal waters

Sediment

Butyltins in sediment (LOD: 0.5 ng Sn/g dry weight)

Site	MBT (ng/g)		DBT (ng/g)		TBT (ng/g)	
	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2
Hillarys Boat Harbour	2.2	3.3	3.6	5.2	16	10
Fremantle Sailing Club	420	7.6	3500	79	89000	79
Royal Perth Yacht Club	990	1500	7200	6200	61000	61000
Fremantle Inner Harbour	<0.5	<0.5	1.2	2	2.3	4.5
Careening Bay	0.51	0.53	0.99	0.82	1	0.9
Fremantle Boat Lifters	9.7	1.6	48	37	82	74
Austal Ships	1.7	1.4	3.4	3.5	3.7	2.1
Tenix Marine	6.4	7.2	25	21	110	100

Metals in sediment (LOD: 1 mg/kg dry weight)

Site	Zinc (mg/kg)		Copper (mg/kg)	
	Core 1	Core 2	Core 1	Core 2
Hillarys Boat Harbour	16	35	31	77
Fremantle Sailing Club	6490	410	17900	260
Royal Perth Yacht Club	460	450	1340	1460
Fremantle Inner Harbour	20	18	9.5	9
Careening Bay	8.2	4.9	5.3	1.5
Fremantle Boat Lifters	330	410	640	990
Austal Ships	18	32	5.9	10
Tenix Marine	34	49	29	47

Fungicides in sediment (LOD: 0.1 mg/kg for dithiocarbamates, 0.01 mg/kg for chlorothalonil and dichlofluanid; all dry weight)

Site	**Dithiocarbamates (mg/kg)**		**Chlorothalonil (mg/kg)**		**Dichlofluanid (mg/kg)**	
	Core 1	Core 2	Core 1	Core 2	Core 1	Core 2
Hillarys Boat Harbour	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01
Fremantle Sailing Club	3.4	<0.1	<0.01	<0.01	<0.01	<0.01
Royal Perth Yacht Club	0.42	1.3	0.225	0.040	<0.01	<0.01
Fremantle Inner Harbour	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01
Careening Bay	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01
Fremantle Boat Lifters	0.25	0.42	<0.01	<0.01	<0.01	<0.01
Austal Ships	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01
Tenix Marine	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01

** Dithiocarbamates includes Thiram and Zineb*

Herbicides in sediment (LOD: 0.005 mg/kg dry weight)

Site	**Irgarol 1051 (mg/kg)**		**Diuron (mg/kg)**	
	Core 1	Core 2	Core 1	Core 2
Hillarys Boat Harbour	0.006	0.016	0.006	0.028
Fremantle Sailing Club	1.34	0.032	0.218	0.346
Royal Perth Yacht Club	0.076	0.021	0.022	0.102
Fremantle Inner Harbour	<0.005	<0.005	<0.005	<0.005
Careening Bay	<0.005	<0.005	<0.005	<0.005
Fremantle Boat Lifters	0.098	0.112	0.555	0.367
Austal Ships	<0.005	<0.005	<0.005	<0.005
Tenix Marine	0.01	0.014	0.045	0.058

Water

Butyltins in water (LOD: 2 ng/L)

Site	MBT (ng/L)		DBT (ng/L)		TBT (ng/L)	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Hillarys Boat Harbour	<2	<2	<2	<2	<2	<2
Fremantle Sailing Club	<2	<2	3.8	3.1	<2	<2
Royal Perth Yacht Club	<2	<2	7.7	8.4	10	12
Fremantle Inner Harbour	<2	<2	<2	<2	<2	<2
Careening Bay	<2	<2	<2	<2	<2	<2
Fremantle Boat Lifters	<2	<2	<2	<2	<2	<2
Austal Ships	<2	<2	<2	<2	<2	<2
Tenix Marine	<2	<2	<2	<2	<2	<2

Metals in water (LOD: 1 µg/L)

Site	Zinc (µg/L)		Copper (µg/L)	
	Sample 1	Sample 2	Sample 1	Sample 2
Hillarys Boat Harbour	31	29	19	11
Fremantle Sailing Club	42	43	34	40
Royal Perth Yacht Club	3500	2100	12000	5700
Fremantle Inner Harbour	6.5	5.7	1.7	1.3
Careening Bay	<1	<1	<1	<1
Fremantle Boat Lifters	42	42	38	30
Austal Ships	15	14	2.6	1.2
Tenix Marine	11	<1	1.3	<1

Fungicides in water (LOD: 0.1 µg/L for dithiocarbamates, 40 ng/L for chlorothalonil and dichlofluanid)

Site	**Dithiocarbamates (µg/L)**		**Chlorothalonil (ng/L)**		**Dichlofluanid (ng/L)**	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Hillarys Boat Harbour	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Fremantle Sailing Club	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Royal Perth Yacht Club	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Fremantle Inner Harbour	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Careening Bay	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Fremantle Boat Lifters	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Austal Ships	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0
Tenix Marine	<0.1	<0.1	<40.0	<40.0	<40.0	<40.0

** Dithiocarbamates includes Thiram and Zineb*

Herbicides in water (LOD: 5ng/L for Irgarol 1051, 10ng/L for Diuron)

Site	**Irgarol 1051 (ng/L)**		**Diuron (ng/L)**	
	Sample 1	Sample 2	Sample 1	Sample 2
Hillarys Boat Harbour	<5	<5	220	280
Fremantle Sailing Club	5	5	2020	2160
Royal Perth Yacht Club	<5	<5	380	310
Fremantle Inner Harbour	<5	<5	60	50
Careening Bay	<5	<5	20	20
Fremantle Boat Lifters	<5	6	1290	1480
Austal Ships	<5	<5	40	20
Tenix Marine	<5	<5	20	40

Mussels

Butyltins in mussels (LOD: 1 ng Sn/g wet weight)

Site	MBT (ng/g)	DBT (ng/g)	TBT (ng/g)
Hillarys Boat Harbour	4.1	19.0	9.8
Royal Perth Yacht Club	8.6	32.0	13.0
Fremantle Inner Harbour	1.3	8.0	8.5
Careening Bay	2.8	14.0	9.8
Fremantle Boat Lifters	7.2	21.0	17.0
Austal Ships	9.4	43.0	47.0
Tenix Marine	7.0	20.0	14.0

Metals in mussels (LOD: 0.1 mg/kg)

Site	Zinc (mg/kg)	Copper (mg/kg)
Hillarys Boat Harbour	83.0	14.0
Royal Perth Yacht Club	33.0	1.60
Fremantle Inner Harbour	32.0	0.89
Careening Bay	35.0	3.70
Fremantle Boat Lifters	27.0	1.10
Austal Ships	35.0	0.83
Tenix Marine	33.0	1.30

Fungicides in mussels (LOD: 0.1 mg/kg for dithiocarbamates, 0.01 mg/kg for chlorothalonil and dichlofluanid)

Site	Dithiocarbamates (mg/kg)	Chlorothalonil (mg/kg)	Dichlofluanid (mg/kg)
Hillarys Boat Harbour	<0.1	<0.01	<0.01
Royal Perth Yacht Club	<0.1	<0.01	<0.01
Fremantle Inner Harbour	<0.1	<0.01	<0.01
Careening Bay	<0.1	<0.01	<0.01
Fremantle Boat Lifters	<0.1	<0.01	<0.01
Austal Ships	<0.1	<0.01	<0.01
Tenix Marine	<0.1	<0.01	<0.01

** Dithiocarbamates includes Thiram and Zineb*

Herbicides in mussels (LOD: 4 µg/kg)

Site	Irgarol 1051 (µg/kg)	Diuron (µg/kg)
Hillarys Boat Harbour	<4.0	7.0
Royal Perth Yacht Club	<4.0	<4.0
Fremantle Inner Harbour	<4.0	4.0
Careening Bay	<4.0	9.0
Fremantle Boat Lifters	<4.0	<4.0
Austal Ships	<4.0	<4.0
Tenix Marine	<4.0	<4.0

Appendix D — Sampling locations

Site name	Site code	Site information	Easting	Northing
Hillarys Boat Harbour	HM1	Northern side of the marina, at end of Northside Drive, adjacent to slipway	380596	6478642
Fremantle Inner Harbour	FP5	North eastern end of Fremantle Inner Harbour, access off Swan St. (Mussels sampled by boat)	381821	6454360
Fremantle Sailing Club	FSC1	At slipway adjacent to spray-down booth	381722	6451585
Fremantle Boat Lifters	FFBH1	At northwestern corner of facility, adjacent to slipway	381564	6452161
Royal Perth Yacht Club	RPYC1	At slipway	388870	6460665
Austal Ships	JBN1	Rockwall at southern perimeter of Austal Ships, adjacent to slipway	383649	6442781
Tenix	JBS1	Rockwall adjacent to slipway	383635	6441813
Careening Bay	CB1	Rockwall at Colpoys point at end of the pier	377331	6433513

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