

Review of Sediment Sampling Program

Tasmanian Boat Maintenance and Repair Facilities



Prepared for Environmental Policy, Environment
Division DTAE

October 2007



Aquatic Science

Facilitating environmental solutions

Table of Contents

| | |
|---|----|
| Executive Summary..... | 2 |
| Introduction..... | 4 |
| Scope and purpose of this report..... | 4 |
| Background information..... | 4 |
| Environmental impacts of TBT & heavy metals in marine ecosystems..... | 5 |
| International and National response to TBT | 7 |
| Tasmanian policy..... | 7 |
| Investigations of TBT contamination in Tasmania | 8 |
| Sediment sampling program design | 9 |
| Analytical measurements..... | 9 |
| Assessment against guidelines..... | 9 |
| Uncertainties..... | 10 |
| Normalising sediment data | 10 |
| Summary of the Tasmanian sediment survey | 12 |
| TBT data..... | 13 |
| Heavy metals data..... | 18 |
| Discussion..... | 21 |
| Source of contaminants | 21 |
| Emerging issues: Diuron and other biocides..... | 21 |
| Recommendations..... | 22 |
| Summary and Conclusions..... | 24 |
| .References | 25 |
| Appendix 1 DTAE Sediment Coring Protocol..... | 29 |
| Appendix 2 AST Analytical Methods | 35 |

A word on units.....

The measuring and reporting of tributyltin (TBT) based compounds have historically been done in a number of ways. The consensus method is to report TBT as tin (Sn). Concentrations are expressed as the mass (nanograms) of tin per gram of sediment that has been dried to a constant weight, commonly referred to as dry matter basis (DMB)

e.g. TBT as ng Sn/g DMB

1 ng Sn/g DMB is equivalent to 1 µg Sn/kg DMB, therefore these units can be used interchangeably. Biota results are usually expressed as a wet matter basis (WMB).

The Australian and New Zealand Environment and Conservation Council (ANZECC) Interim Sediment Quality Guidelines (ISQG) use the units µg Sn/kg DMB. Where references cited in this report have used different conventions, they have been converted to TBT as ng Sn/g DMB using the conversion factors described in Blakley 2005.

TBT concentrations in water are commonly reported as nanograms of tin per litre (L) of water, or TBT as ng Sn/L.

Heavy metals are expressed as the mass (milligrams) of metal per kilogram (kg) of sediment, on a dry matter basis

e.g. mg/kg DMB

Executive Summary

A sampling program designed to assess the degree of tributyltin (TBT) and heavy metal contamination present in sediments adjacent to Tasmanian boat repair and maintenance facilities was conducted by Environment Division, Department of Tourism, Arts and Environment DTAE, from July 2006 to March 2007. This sampling program was not intended to be a comprehensive survey of all boat repair and maintenance facilities, but rather provide a broad indication of the degree of TBT and heavy metal contamination associated with slipway activities. A mix of private, commercial, and club facilities undertaking a range of maintenance and construction activities were included for assessment.

Aquatic Science was commissioned to review the analytical data, summarise key trends, identify limitations of the data and provide recommendations to the Environment Division on areas for further investigation. The predominant focus of this review is the impact of TBT, firstly because of its acute toxicity to marine organisms; and secondly because it is a unique indicator of the “environmental footprint” associated with the use of antifouling agents in general .

The Australian and New Zealand Environment Conservation Council Interim Sediment Quality Guidelines (ISQG) were used as a screening tool to evaluate sediment data, identify areas with elevated levels of contaminants associated with boat repair and maintenance activities, and to prioritise sites for further investigation. Survey results should be viewed only as broadly indicative of contaminant levels due to high contaminant variability in the sediment samples and limited replication.

The composition of new paint formulations is briefly discussed, with particular reference to booster-biocides that are incorporated into many new paint products.

Key findings

- Sediment cores collected at boat repair and maintenance facilities indicated that all such locations had detectable levels of tributyltin in the sediments in the immediate vicinity of the slipway.
- All 26 sites exceeded the ANZECC ISQG-Low trigger value of 5 ng Sn/g. Concentrations above this level are characterized by frequent occurrences of adverse biological effects, and should trigger further investigation into causes or mitigating factors.
- At 80% of sites, the measured concentration of TBT also exceeded the ISQG-High trigger value of 70 ng Sn/g, often by a large margin, indicating significant contaminant levels and an expectation of adverse effects on biota.
- Boat repair and maintenance facilities that serviced the greatest number of boats (> 100 /year) generally had the highest levels of TBT in sediments, exceeding 5,000 ng Sn/g DMB.
- Elevated levels of TBT are highly associated with areas of maritime activities such as harbours, marinas, ship repair facilities and ship building. Generally impacts and effects decrease rapidly as distance away from potential sources increases. Although it is not possible to define the zone of impact in the DTAE study, it is likely that the areas impacted by TBT contamination are localised.
- High tributyltin values may be indicative of recent inputs into the surface sediments. However, they may also be the result of the minimal breakdown of

TBT from past activities. In both instances, TBT may continue to exert toxicity on marine and estuarine organisms. Long term recovery of the sediments ultimately depends on the decomposition of the TBT.

- Inputs of TBT into the marine environment are expected to decline as a result of legislative conditions resulting in the prohibition of TBT products. However TBT is relatively persistent and under certain environmental conditions historical loads may be slow to degrade to less toxic forms.
- Sediments with elevated levels of TBT also contained high loads of heavy metals, notably copper, nickel, lead and zinc. Copper and zinc are common active agents in many modern anti-fouling paint formulations and can also enter the marine environment from a number of other point and diffuse sources. This needs to be considered when interpreting the heavy metal data.
- The use of alternative biocides such as Diuron is an emerging issue for slipway management and operation. Containment and management of paints containing such biocides is critical due to their greater potential to be transported in the water column. This may result in a wider zone of impact from their point of use.

Introduction

Scope and purpose of this report

The purpose of this report is to:

- review heavy metal and TBT data collected by the Environment Division, DTAE, during the 2006-2007 survey of 26 slipways located around Tasmania;
- prepare a general summary of the data to provide information to stakeholders on the level of heavy metal and TBT contamination associated with slipways facilities;
- provide recommendations on the appropriateness of the sampling program for assessing the level of impact of historical and /or current use of antifouling paints at slipway facilities around the State; and
- identify areas for priority investigation.

Background information

Antifouling paints were developed to protect the hulls of vessels from settlement and growth of fouling organisms such as barnacles, shellfish, bacteria, macro and microalgae. Failure to remove or control hull fouling organisms leads to increased drag, with a subsequent increase in fuel consumption. Fouling of hulls has also been identified as a potential vector for the transfer and introduction of marine pests (NHT, 2004). Antifouling paints are an effective way of preventing fouling on boat hulls for long periods of time as a result of continued slow release of active agents such as copper, zinc, or organotins. These active agents are non-selective in terms of their toxicity to aquatic organisms, and can persist in the environment, with potential to accumulate in sediment and biota. The effectiveness of antifouling surfaces is eventually reduced due to the continual release of the active agent from the paint.

Around Tasmania, some 2700 boats are permanently moored in the water and therefore require the application of antifouling paints on a regular basis (Powell, DTAE *pers comm.*). Boats are generally slipped every 12 -18 months, for the purposes of removing fouling organisms and the re-application of antifouling products. Approximately 65 facilities were identified in Tasmania during the Slipways Management Framework Project (DPIWE, 2000b). The removal of antifouling paints at slipways can result in the accumulation of paint debris, sludge, dust and other particles that typically still contain high concentrations of the active ingredients and continue to exert a toxic effect once removed from the boat (DTAE, 2007).

TBT

Tributyltin (TBT) is the active agent in organotin-based antifouling paints. The toxic impact of TBT in particular on the aquatic environment has been widely recognised since work in France by Alzieu *et al* (1980) demonstrated the link between oyster deformities and TBT exposure in the Pacific oyster *Crassostrea gigas*. This and subsequent research resulted in increasing international effort to reduce, and then eliminate, the use of TBT based paints for antifouling purposes.

Other Formulations

Arsenic, lead, DDT and mercury were commonly-used additives to paint formulations prior to 1970 (DTAE, 2007). Boats constructed before 1970 may still have remnants of these paints still intact, most likely barrier coated with more recent products. New paint formulations currently available in Australia as an alternative to TBT based products, almost without exception, contain copper or zinc, or a mixture of both as the active agent. Like TBT, copper and zinc can bioaccumulate in aquatic biota, leading to chronic and acute effects in the organism. These metals may accumulate to such a degree in some recreationally-targeted species that consumption can result in illness if recommended safe consumption levels are exceeded (ANZFA, 2000). An increasing number of products also incorporate the anti-slime herbicide Diuron, referred to as a “booster biocide” (Boxhall *et al*, 2000).

TBT as a Marker

Whilst heavy metals may enter the marine environment from a number of sources, including the application, use and removal of antifouling products, TBT is considered a unique marker of the impact of these activities. It is highly unlikely that elevated levels of TBT detected in sediments in the vicinity of boat maintenance and construction activities are due to other diffuse sources. Whilst it is recognised that the use of TBT has been reduced due to legislative change, its persistence in the environment makes it a key contaminant to monitor to track the impact of activities typically undertaken at slipways, and to monitor the recovery of the marine environment as better practices are implemented.

Environmental impacts of TBT & heavy metals in marine ecosystems

Toxicity and Persistence of TBT

Numerous studies around the world have confirmed that organotin antifouling agents are highly toxic to a wide range of non-target marine organisms (Reitsema *et al*, 2003; Noller, 2003; Bellas *et al*, 2005; Negri *et al*, 2002; Reitsema and Spickett, 1999). Incidences of TBT exposure and contamination are highly correlated with areas of maritime activities such as harbours, marinas, ship repair facilities and ship building (Bhosle *et al*, 2006). Generally impacts and effects decrease rapidly as distance away from potential sources increases (Barakat *et al*, 2001).

In order for toxic effects to be detected in marine organisms, there must be a sustained or continual source of TBT into the aquatic environment (Noller 2003). Sustained sources may include sediment contaminated by TBT material through accumulation of paint material (e.g. at washdown or slipping facilities) or a cluster or high density of ships or surfaces treated with TBT in a harbour or marina. TBT in the water column either rapidly adheres to the surface microlayer, or partitions to fine sediments and particulate material. For this reason, sediment samples are generally preferred over water column samples for assessing TBT exposure.

Occasional exposure to TBT does not generally cause long term effects unless the toxic threshold concentration is exceeded (Noller 2003). TBT may bioaccumulate in biota and flesh and concentrations as low as 18 ng Sn/g have been shown to limit growth of shellfish. Regoli *et al* (2001) showed a strong correlation between the concentration of TBT measured in sediments and that accumulated by the zebra mussel, with greatest accumulation occurring in marinas and coastal harbours.

Tributyltin in the marine environment is subject to degradation processes known as debutylation that breakdown TBT to dibutyltin (DBT) and monobutyltin (MBT). Generally the tri-substituted form (TBT) is more toxic than di- or mono- forms (Gadd,

2000). Degradation can be due to light (photodegradation) or by microorganisms (biodegradation). Long term recovery of the sediments ultimately depends on the decomposition of the TBT (de Mora *et al*, 1995). The half life of TBT in sediments in a New Zealand marina has been estimated to be approximately 2 years (de Mora *et al*, 1995), with several other studies in Australian and New Zealand showing estimates with calculated half-life between 2 and 5 years (Batley, 1995).

Despite the ability of many organisms to excrete TBT, significant biological effects are commonly observed. The most widely monitored impact is the development of male reproductive organs on female gastropods, known as imposex (Anderson, 2004). Many populations continue to survive despite high incidences of imposex, however at extremes it can lead to complete sterilization of populations. Evidence of imposex is still recorded many years after the introduction of TBT restrictions (Gibson and Wilson, 2003; Reitsema *et al*, 2003). It has recently been proposed as an indicator of estuarine, coastal and marine habitat integrity at the state and national level (NRM, 2006).

Marine biota can bioaccumulate significant concentrations of TBT from both the water column and sediments. TBT is lipophilic and readily taken up by living organisms. Bioconcentration factors (i.e. the ratio between concentration in the environment and in the flesh) in oysters have been estimated to be as high as 2000 (Noller, 2003) for TBT. Shell deformities in oysters has been used with some success to indicate TBT exposure in wild populations, and the use of deployed oysters has been suggested as a management action for site specific investigations in Tasmania (Scammel, 2002).

Toxicity of Heavy Metals

Heavy metals such as copper and zinc have been incorporated into antifouling paint formulations as a result of their acute toxicity to a range of aquatic organisms, and can enter waterways through the same pathways outlined above for TBT, i.e. accumulation of removed material or active leaching from vessel surfaces. Heavy metals may also enter the marine environment through a variety of sources other than antifouling products. Copper, lead and zinc are commonly elevated in run-off in urban and industrial areas, and may also be associated with effluent from sewage treatment plants. Mining and mineral processing industries can also contribute significant concentrations of heavy metals to the environment. Heavy metals in the sediments and pore waters are usually several orders of magnitude higher than the overlying water column due to their tendency to adsorb onto particulate matter (Stark, 1998; Danis *et al*, 2004). For example, zinc levels in Derwent estuary sediments may be in excess of 10,000 mg/kg DMB, while overlying waters are typically in the range of 5 – 40 µg/L. These high levels of zinc in sediments correspond to areas of significant organic enrichment.

Unlike TBT, heavy metals cannot be degraded by biotic or abiotic processes and sediment investigations should therefore include factors that may ameliorate or reduce metal toxicity. The toxicity of heavy metals depends upon their bioavailability, and this is principally controlled by the geochemistry of the sediments (Peng *et al*, 2004). The presence of sulphide is one of the major factors controlling the interaction between metals in the sediments, and the biota that live in and above the sediments. Metals such as copper and zinc can form insoluble complexes with sulphide, which limits mobility and effectively renders them unavailable to biota while redox conditions remain stable (Naylor *et al*, 2004). Other controlling factors include the organic carbon content, pH, the particle size distribution, the oxic status of the sediments and various other geochemical phases (Peng *et al*, 2004). Biological effects associated with heavy metals range from acute toxicity, to chronic impacts such as deformations and reduced reproductive capacity. Ecosystem effects such as shifts in community

structure, and associated changes in functional groups have also been observed (Macleod and Helidoniotis, 2005; Scammel and Biddulph in Noller, 2003).

Heavy metals are also known to bioaccumulate in marine organisms, particularly shellfish. This has led to a permanent ban on the consumption of shellfish in some highly contaminated estuaries in Australia, including the Derwent (DEP, 2006).

International and National response to TBT

In 1990, the International Maritime Organisation (IMO) adopted a resolution to ban the use of organotin based antifouling paints on vessels less than 25m, with the exception of hulls constructed from aluminium (IMO, 2002). The IMO also specified the maximum leaching rate acceptable for TBT based paints. In 1999, the IMO extended this action to call for a global ban on the application or re-application of TBT based antifouling paints, on all vessels, from January 1, 2003 and complete prohibition by January 1, 2008 (IMO, 2002). This requires vessels to remove and replace TBT based products with a non-organotin based product, or apply an effective barrier coat such that organotin compounds cannot leach from non-compliant coatings.

At the national level, the Australian and New Zealand Environment and Conservation Council (ANZECC) developed a *Code of Practice for Antifouling and In-water Hull Cleaning and Maintenance* (1997) which has been adopted by all States and Territories. All antifouling residues are identified as contaminated wastes in the Code, and are therefore treated as controlled (hazardous) wastes under Tasmania's Environmental Management and Pollution Control (Waste Management) Regulations 2000 (DPIWE, 2002). The Code requires slipways and hardstands to implement waste management actions to remove toxic substances, turbidity and discolouration from liquid wastes. Management measures must include the prevention of discharge of slipway waste to the aquatic environment.

Tasmanian policy

Tasmania was the first Australian State to act on international concern about the environmental impacts of TBT, banning the use of TBT on vessels less than 25 m in the late 1980's. In 2001, local issues linking TBT usage to shellfish mortality and deformities resulted in a Ministerial Order being gazetted to remove TBT based paints from points of sale. Following the Ministerial Order, TBT could only be sold to "approved persons" for application on vessels greater than 25 m in length (DPIWE, 2002a). There are currently no permits for the use of TBT in Tasmania (Powell, DTAE, *pers comm.*). In 2003, the Australian Pesticides and Veterinary Medicines Authority cancelled the registration of all TBT products in Australia, and undertook not to grant any new registrations for these types of products. This effectively prohibited the sale of TBT based products in Australia.

The State Policy on Water Quality Management 1997 requires that pollutants are reduced as far as is reasonable and practical, by implementing best practice environmental management. DTAE is currently in the processing of finalising Draft Environmental Best Practice Guidelines for Boat Repair and Maintenance Facilities (DTAE, 2007). These guidelines aim to limit the impact of contaminants associated with the use of antifouling products, by protecting the environmental quality of coastal, marine and estuarine environments.

Documents prepared as part of the Tasmanian Slipways Management Framework should be consulted for a more detailed assessment of the regulatory issues associated with managing boat wastes in Tasmania (DPIWE, 2002a; 2002b).

Investigations of TBT contamination in Tasmania

Several investigations into the level of TBT contamination in coastal "hotspots" have been undertaken in Tasmania. The majority of this work was comprehensively reviewed by Professor Barry Noller (NRCET), who in 2003 undertook a consultancy to provide the Tasmanian government with an analysis of the TBT monitoring programs, with particular emphasis on assessing potential toxicological effects on the Pacific oyster in selected growing areas. A summary of the concentrations of TBT previously found in water, sediment and oysters in Tasmanian studies is presented in Table 1. Studies by DPIWE in Spring Bay/Triabunna found the highest levels of TBT (22 ng Sn/g) were associated with slipway and wharf facilities. Similarly, sediments sampled in the vicinity of slipways in the Georges Bay/St Helens area contained up to 1400 ng Sn/g with a high degree of variability between samples taken either side of the slip. Oysters sampled from contaminated slipways in Georges Bay and Spring Bay were found to concentrate excessive levels of TBT. Other studies in Tasmania include an audit of boat hulls for the presence of TBT, monitoring associated with offshore dredge spoil disposal, marina development applications, and assessments of encapsulation technologies for sludge and grit wastes generated by boat repair and maintenance facilities.

| Location | Biota (TBT as ng Sn/g WMB) | Sediment (TBT as ng Sn/g DMB) | Water (TBT as ng Sn/L) | Comments |
|-----------------------------|-------------------------------|----------------------------------|---------------------------|--|
| St Helens* | 1.2 - 91 | <0.8 - 1400 | <2 | Oyster flesh, slips and leases around St Helens |
| Devonport ‡ | - | 12 - 2900 | - | Dredge disposal application, included sites adjacent to slipways |
| Tasman Peninsula* | <0.5 -18 | - | - | |
| Spring Bay* | 7.6 - 460 | <0.8 - 22 | <2 | Oyster flesh, slips and leases around Triabunna |
| Hobart^{*,‡} | 89 - 121 | <10 - 1060 | - | 2 commercial slips, marina development survey |

*Table 1 Summary of TBT data from previous Tasmanian studies (*from Noller, 2003; ‡ from NHT, 2004).*

Sediment sampling program design

Sediment sampling was undertaken according to protocols developed by the Environment Division, which are included as Appendix 1. Sites located on Crown Land were sampled by staff from the Marine Structures Assessment Project, Crown Lands Services (DPIW), while all other facilities were sampled by Environment Division (DTAE) staff. Sampling commenced in July 2006, and was completed in March 2007. Samples were collected from 26 facilities, located in 15 coastal municipalities around Tasmania. The facilities sampled included a number of sailing clubs, and a mix of private, and commercial facilities undertaking construction and maintenance activities.

At each location, a transect consisting of 4 sites was sampled across the base of the slipway to give an indication of the spread of contaminants of interest. Samples were collected at low tide to the immediate left and right of the base of slipway, and at a point 100m either side of the "left" and "right" samples (referred to as "Controls"). Sediment cores were collected at each site by pushing a Perspex tube into the sediment, placing a bung in the top and gently removing the tube. The overlying water was carefully siphoned off and the top 50 mm of the core extruded into a clean glass sample jar. Three replicate cores were composited for each of the 4 sites in the transect. Due to rocky or unfavourable conditions at some sites, Control samples were not always collected.

Where available, estimates of number of boats slipped annually at each facility were provided by DTAE.

Analytical measurements

The analysis of heavy metals, Total Characteristic Leaching Procedure (TCLP), TBT, and organic carbon content in the sediments was undertaken by Analytical Services Tasmania (AST), Hobart. TCLP results are not included in this report (see later). Details of methods employed by AST are provided in Appendix 2. Particle size analysis was undertaken by Aquenal (Hobart) using a wet sieving technique.

Heavy metal, organic carbon content and particle size analysis were measured in each of the 4 composited samples collected from each facility. TBT analysis was only undertaken on a composite prepared at the laboratory, consisting of the left and right sample, and not on the control samples. Thus a single TBT result is available for each facility. TCLP analysis was conducted on a limited number of samples.

Assessment against guidelines

Contaminant levels in the top 50 mm of sediments were assessed using the ANZECC/ARMCANZ Interim Sediment Quality Guidelines (ISQG), as set out in the Australian Water Quality Guidelines for Marine and Freshwaters (NWQMS, 2000). The National Ocean Disposal Guidelines for Dredged Material were also consulted since this document provides additional guidance on the assessment of contaminant levels in sediments (Environment Australia, 2002). The guidelines are based on observed biological effects and are used here as a screening tool to assess sediment data and identify areas that require further investigation (Long *et al*, 1995). The Interim Sediment Quality Guidelines (ISQG) Low and High are shown in Table 2.

| Contaminant | ISQG-Low "Screening Level" (mg/kg DMB) | ISQG-High "Maximum Level" (mg/kg DMB) |
|--------------------------------|--|---|
| Arsenic (As) | 20 | 70 |
| Cadmium (Cd) | 1.5 | 10 |
| Chromium (Cr) | 80 | 370 |
| Copper (Cu) | 65 | 270 |
| Lead (Pb) | 50 | 220 |
| Nickel (Ni) | 21 | 52 |
| Zinc (Zn) | 200 | 410 |
| Tributyltin (TBT as Sn) | 5 µg Sn/kg | 70 µg Sn/kg |

Table 2 Sediment quality assessment criteria for contaminants monitored in this sampling program from Australian Water Quality Guidelines for Marine and Freshwaters (NWQMS,2000).

Uncertainties

In 2000, the Australian Government funded an extensive study to develop standardized methodologies for the sampling and analysis of TBT contaminated sediments from coastal and estuarine locations around the country (NHT, 2004). No single analytical method was identified as superior, or could be recommended as a standard protocol. Recommendations included that laboratories should use a published method that had been evaluated in appropriate studies, and seek NATA accreditation for the analysis. Established analytical methods were deemed to give comparable results when performed by competent laboratories.

A key finding of the NHT study was that, where laboratories were able to demonstrate competency with the analysis, large variations in TBT concentrations in sediments meant that replication and compositing of large numbers of cores still required very broad confidence limits when comparing results to guidelines or standards. Due to the limited compositing that took place, the concentrations reported in this survey should therefore be compared to guidelines with acknowledgement of the potential for large uncertainties in the dataset.

Normalising sediment data

Organic carbon content is an important variable to consider when assessing sediment contaminant levels. Data for TBT in sediments may be adjusted or "normalised" to 1% organic carbon (OC) content, since higher and lower levels of OC can decrease or increase bioavailability respectively (NWQMS, 2000). In this process, values are adjusted down or up dependent upon whether they contain more or less than 1% OC. The correction is valid over the range 0.2 – 10% OC (Environment Australia, 2002). Normalisation of TBT data is commonly used in assessing contaminated sites because it allows a more reliable comparison with sediments at reference sites, or with action or trigger levels. Unless otherwise specified, all TBT results reported here are normalised results.

Sediments may be described or characterized by the particle or grain size distribution on the basis of separations using various size sieves. The fraction of the sample that consists of particles >2 mm generally consist of shells, rocks, wood, etc that are not usually considered a source of bioavailable contaminants (NWQMS, 2000). This may be complicated by the presence of paint flakes in slipway sediments that may skew the particle size distribution to suggest a higher component of inactive material, when in fact it is a concentrated source of bioavailable material.

The clay/silt fraction (i.e. < 63 μm) has a high surface area and is more likely to adsorb organic and heavy metal contaminants. It is not unusual to normalise contaminant analyses on the basis of the fraction < 63 μm for better comparison between sites, however for the purposes of assessment against guidelines, raw heavy metal data was used.

Summary of the Tasmanian sediment survey

Figure 1 shows a breakdown of facilities sampled by type during the DTAE survey. Commercial facilities (62 %) make up the majority of locations sampled, followed by club (27%), large private (8%) and small private (4%).

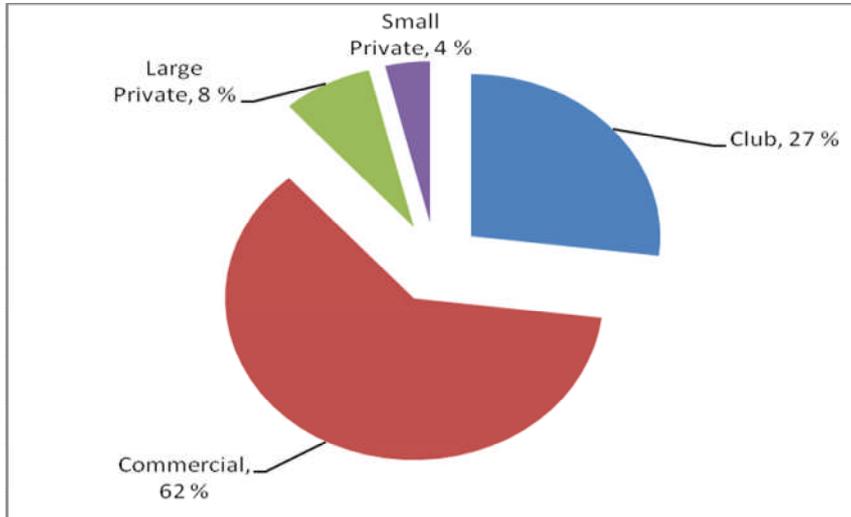


Figure 1 Type of facility sampled (% of total) during DTAE sediment survey.

The contaminant levels at each location were assessed against the ANZECC ISQG shown in Table 2. The ISQG-Low is referred to as a Trigger value or Screening Level, whereby some investigation into causes or mitigating factors is required if the value is exceeded. Below this concentration, adverse effects are seldom observed. It is not a cut-off point below which no toxicity will occur (O'Connor, 2004). The ISQG-High value, alternatively referred to as a Maximum Level, is a level above which it is very likely that adverse effects will occur (Environment Australia, 2002).

| Category | Description | Interpretation |
|-----------------------------------|--|--|
| Uncontaminated √ | Concentrations < ISQG-Low or Screening Level | "Adverse biological effects are seldom observed." |
| Contaminated √√ | Concentrations are > ISQG-Low threshold, but < ISQG-High or Maximum Level. | "Possible effects range. Frequent occurrence of adverse biological effects." |
| Highly Contaminated √√√ | Concentrations > the ISQG-High or Maximum Level. | "Indicates significant contamination and sediments are expected to have an adverse effect on biota." |

Table 3 Classification system for sediments based on ISQG values.

Applying the ISQG allows sediment data to be classified into three principle categories. The categories are, "*Uncontaminated*", "*Contaminated*" and "*Highly Contaminated*" and the definition of these categories is shown below in Table 3 (NWQMS, 2000; Birch and Taylor 2004; O'Connor, 2004). Since the trigger values

presented in Table 2 are based on observed biological effects reported in the scientific literature, levels in excess indicate an increased likelihood of environmental impact. Further studies are required to demonstrate whether actual impact has occurred, or mitigating factors have reduced expected effects.

TBT data

A summary of the contaminant category for TBT from composite samples collected at each location are presented in Table 4.

| Municipality | Location | Uncontaminated [‡] | Contaminated | Highly contaminated |
|-----------------------------|-------------|-----------------------------|--------------|---------------------|
| <i>Break O'day</i> | Facility 1 | | | JJJ |
| <i>Circular Head</i> | Facility 2 | | | JJJ |
| <i>Clarence</i> | Facility 3 | | | JJJ |
| | Facility 4 | | | JJJ |
| | Facility 5 | | | JJJ |
| | Facility 6 | | | JJJ |
| <i>Devonport</i> | Facility 7 | | | JJJ |
| | Facility 8 | | | JJJ |
| <i>Glamorgan-Spring Bay</i> | Facility 9 | | | JJJ |
| | Facility 10 | | JJ | |
| <i>Glenorchy</i> | Facility 11 | | | JJJ |
| | Facility 12 | | JJ | |
| <i>Hobart</i> | Facility 13 | | | JJJ |
| <i>Huon Valley</i> | Facility 14 | | | JJJ |
| | Facility 15 | | | JJJ |
| <i>Kingborough</i> | Facility 16 | | | JJJ |
| | Facility 17 | | | JJJ |
| <i>Latrobe</i> | Facility 18 | | | JJJ |
| | Facility 19 | | JJ | |
| <i>Launceston</i> | Facility 20 | | | JJJ |
| <i>Sorell</i> | Facility 21 | | | JJJ |
| <i>Tasman</i> | Facility 22 | | | JJJ |
| <i>West Coast</i> | Facility 23 | | | JJJ |
| | Facility 24 | | JJ | |
| <i>West Tamar</i> | Facility 25 | | JJ | |
| | Facility 26 | | | JJJ |

Table 4 Summary of the contaminant category for TBT detected in marine sediments during the DTAE survey. Based on results normalised to 1 % OC. [‡]No facilities in the "Uncontaminated" category. See Table 3 for category definitions.

The classification of each facility into a particular contaminant category in Table 4 is based on the combination of 6 individual cores collected at each slipway i.e. the samples from left and right of slip were further composited in the laboratory to produce a single sample. Individual facilities are identified only by their general location and/or municipality.

All locations recorded significant concentrations of TBT, with the majority (21 locations, 81%) found to be in the *Highly Contaminated* category with levels in excess of the ISQG-High or Maximum Level of 70 ng Sn/g. Five locations fell in the *Contaminated* category. No categories fell in the *Uncontaminated* category. Concentrations ranged from 18 – 54,000 ng Sn/g DMB (12 – 22,500 ng Sn/g DMB after normalisation to 1% OC). The average concentration over all locations was 4,617 ng Sn/g DMB (2,187 ng Sn/g DMB after normalisation to 1% OC).

Figure 2 shows the cumulative % of facilities plotted against the normalised TBT concentration in the sediment. The majority of facilities fall in the range 10 – 1000 ng Sn/g DMB, with 5 facilities showing extreme concentrations of TBT, in excess of 1000 ng Sn/g DMB.

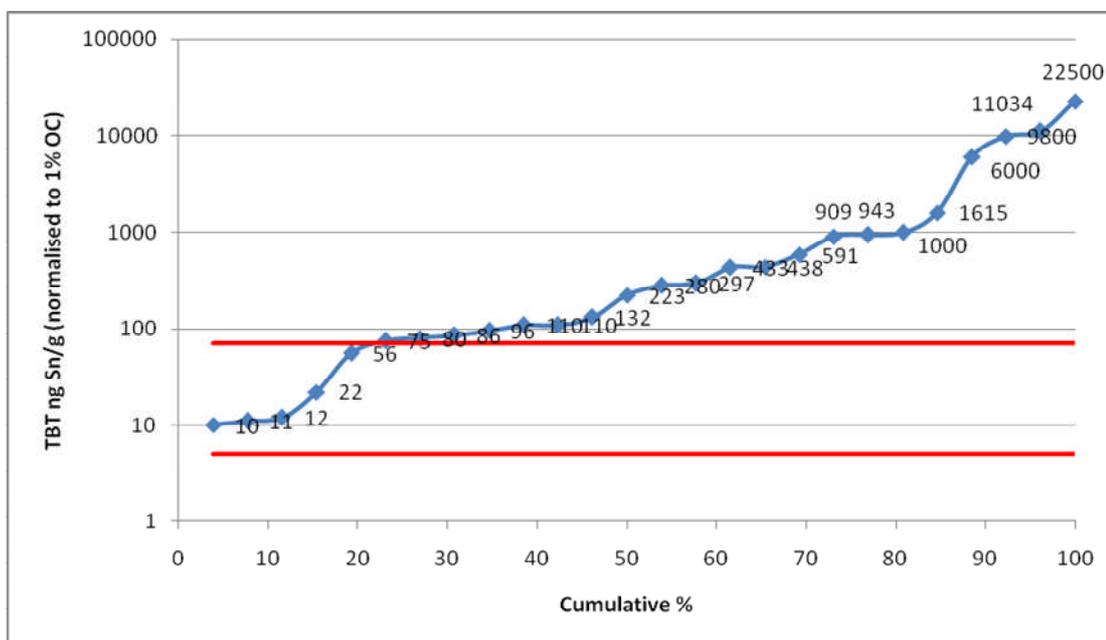


Figure 2 Cumulative total (% of facilities) plotted against normalised TBT concentration in sediments for all facilities. ISQG Low and High plotted for reference.

It has been well documented in the literature that the impact of TBT contamination in the environment is often extremely localized around areas of boating activity. For example, the studies of Bhosle *et al* (2006), Fernandez *et al* (2005), Diez *et al* (2002), Axiak *et al* (2000) and Barakat *et al* (2001) all recorded a strong correlation between the incidence of TBT in sediments and proximity to marinas and ship repair facilities. It is not possible to define the zone of impact in the DTAE study as no TBT measurements were made on the control samples. Despite the absence of complete transect data, it is likely that a similar trend to those studies cited above occurs in Tasmania i.e. the area impacted by TBT contamination is localised. Noller (2003) concluded in his review of environmental impacts of TBT in Tasmania that significant accumulation of TBT at slipways and wharfs was restricted to 200m from source, with the presence of residual material in sediment containing TBT from boat hull scrapings the “clearly established long-term source”.

The number of comparable studies focusing exclusively on slipway facilities in Australia is extremely limited. The most recent nationwide survey conducted by the Department of Environment and Heritage (summarised in Table 5) are used here to provide broad comparisons to typical TBT levels measured in sediments from coastal environments around Australia (NHT, 2004). While the number of sites reported for each State is limited, all samples were collected from areas used by high tonnage shipping or small craft (< 25m). An intensive sampling protocol included the collection of hundreds of replicate cores over an area of 20 m radius, or approximately 1250 square metres. Results from 25 - 50 composited cores were used to generate data for the two Tasmanian sites, one the base of a large commercial slipway (also sampled in this study), the other within a large recreational marina.

Sediment investigations in New Zealand focusing on the distribution of TBT found significant contaminant levels in areas around dry docks and washdown facilities (de Mora *et al*, 1995; Shaw and Hickey, 1999). Sediment samples from a naval base drydock showed a “plume of serious contamination extending in an arc approximately 150m” from the drydock outfall and entrance.

Figure 3 shows the spread of TBT results for facilities grouped by type for this study (note logarithmic scale). The range of concentrations of TBT detected at club facilities was 56 – 11,034 ng Sn/g DMB (normalised to 1% OC), while the concentration range for commercial facilities was 10 – 22,500 ng Sn/g DMB (normalised to 1% OC). There was no clear trend between TBT concentrations and whether slipway facilities serviced vessels greater than or less than 25 m in length.

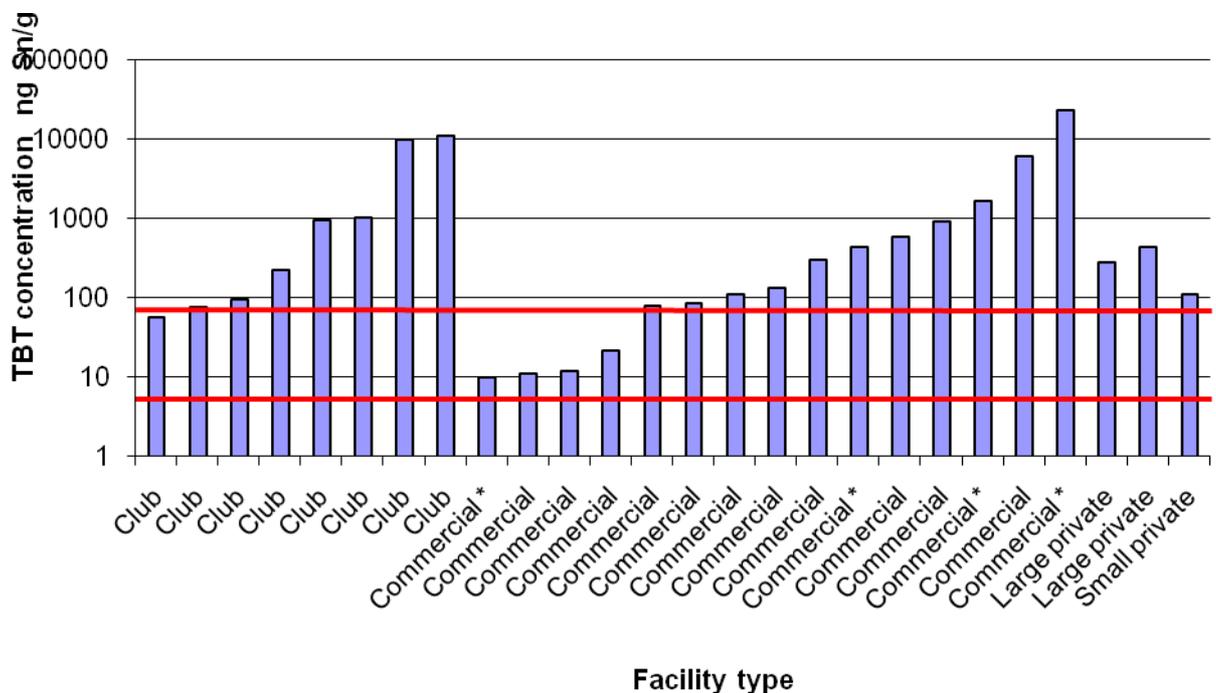


Figure 3 Normalised TBT concentration at club, commercial and private slipway facilities. Lines indicate the ISQG-Low (5 ng Sn/g) and ISQG-High (70 ng Sn/g) values. * indicates facility services vessels > 25 metres.

| State | Concentration range (raw) TBT as ng Sn /g | Concentration range (normalised*) TBT as ng Sn /g | Comments |
|---------------------------|---|---|--|
| South Australia | <0.4 - 13.3 | 20 | Marina and small slipways, shipping channel and commercial fishing vessels |
| Northern Territory | 5.03 | 8.1 | Small commercial shipping wharves and slipway |
| Tasmania | 770 | 255 | Base of commercial slipway |
| | 44.7 | 41.7 | Recreational marina |
| Tasmania | 18 – 54,000 | 12 – 22,500 | This study, base of slipways, single result for each facility |
| Tasmania † | 0.8 – 2,900 | Not reported | Noller 2003; NHT 2004 |
| Western Australia | <1 - 1 | * | Passenger ferry terminal, commercial boat building marina |
| Victoria | < 25 - 214 | not reported | 1 recreational boating and 2 commercial shipping sites |
| New South Wales | < 23 | * | Oil terminal, recreational vessel moorings, container and bulk shipping berths |
| Queensland | 1.7 -251 | 2.9 - 137 | Recreational vessel marina, wharves and slipways |

Table 5 Summary of Australian TBT results for sediment samples collected as part of the project "TBT analysis protocol development and current contamination assessment" (NHT, 2004). Samples from all States were collected in the vicinity of recreational boating and commercial shipping facilities. Results are the range of calculated means for a number of sites. *Normalisation not applied to results below detection. † see Table 1 for more detail.

The range of concentrations recorded in the DTAE study are significantly higher than concentrations recorded in Table 5. Contributing factors may include:

- TBT in sediments is highly heterogeneous, particularly with respect to particulate TBT associated with paint flakes and fine paint particles. Observations by field staff and laboratory analysts indicate that samples yielding the highest concentrations of TBT contained visible paint material. (M. Rushton DTAE, A. Featherstone AST *pers. comm.*). This effect will be exacerbated with a sample design using low numbers of composites and no replicate sampling.
- In instances where appropriate containment and collection of solid and liquid wastes are not in place, high levels of contaminants will accumulate in the immediate vicinity of the slipway. Samples collected in areas where wastes are properly managed, or more distant from sources of particulate material, would be expected to have lower concentrations of TBT. Excessively high levels of TBT are indicative of practices that have not prevented solid waste from entering the marine environment.
- Samples in the NHT study were collected by divers and were therefore in deeper water more distant from the base of the slipway.

TCLP results were not obtained for TBT due to the incompatibility of marine sediments for the TBT-TCLP procedure. The acidification and subsequent derivitisation step resulted in the explosion of several samples, as a result TCLP analyses were discontinued (N.Kerr, AST *pers. comm.*). TCLP is generally used as a laboratory test to simulate leaching in municipal landfill and is not routinely used for inferring bioavailability in sediments in marine environments. More appropriate methods for understanding bioavailability in sediments include determining pore water concentrations, degradation studies, and seawater elutriate tests. These tests may provide useful information on the potential for uptake, bioaccumulation and toxicity however they are most relevant when used in combination with toxicity testing and/or biological monitoring. For example, studies on TBT and heavy metal contamination in New Zealand navy dockyards found that there was little dissolution of heavy metals or TBT into the water column when seawater elutriate tests were performed, however toxicity tests showed significant toxicity compared to control sites (Shaw and Hickey, 1999).

Other approaches available for investigating trends in TBT usage and impact on marine sediments include using profiles collected from sediment cores. Batley and Scammell (1991) found reduced TBT concentrations in the upper 1-3 cm of sediment following restrictions on the use of TBT. It is also possible to examine degradation rates by measuring TBT, DBT, and MBT in down-core profiles. This was considered outside the scope of this study. Extremely high concentrations recorded at some locations in this study are assumed to be indicative of significant past use, and/or minimal degradation processes operating in the sediments. Given the restrictions on the availability of TBT based products, any current contributions to TBT in sediments are most likely to be associated with removal of old organotin material, rather than the application of new paint.

Figure 4 shows, with the exception of one facility, that the highest TBT concentrations are associated with the slips that service the greatest number of boats. Slipways that slipped more than 100 boats/year had the highest concentrations of TBT in sediments, with levels exceeding 5,000 ng Sn/g DMB. Facilities that slipped less than 100 boats/year had TBT concentrations < 2,100 ng Sn/g DMB.

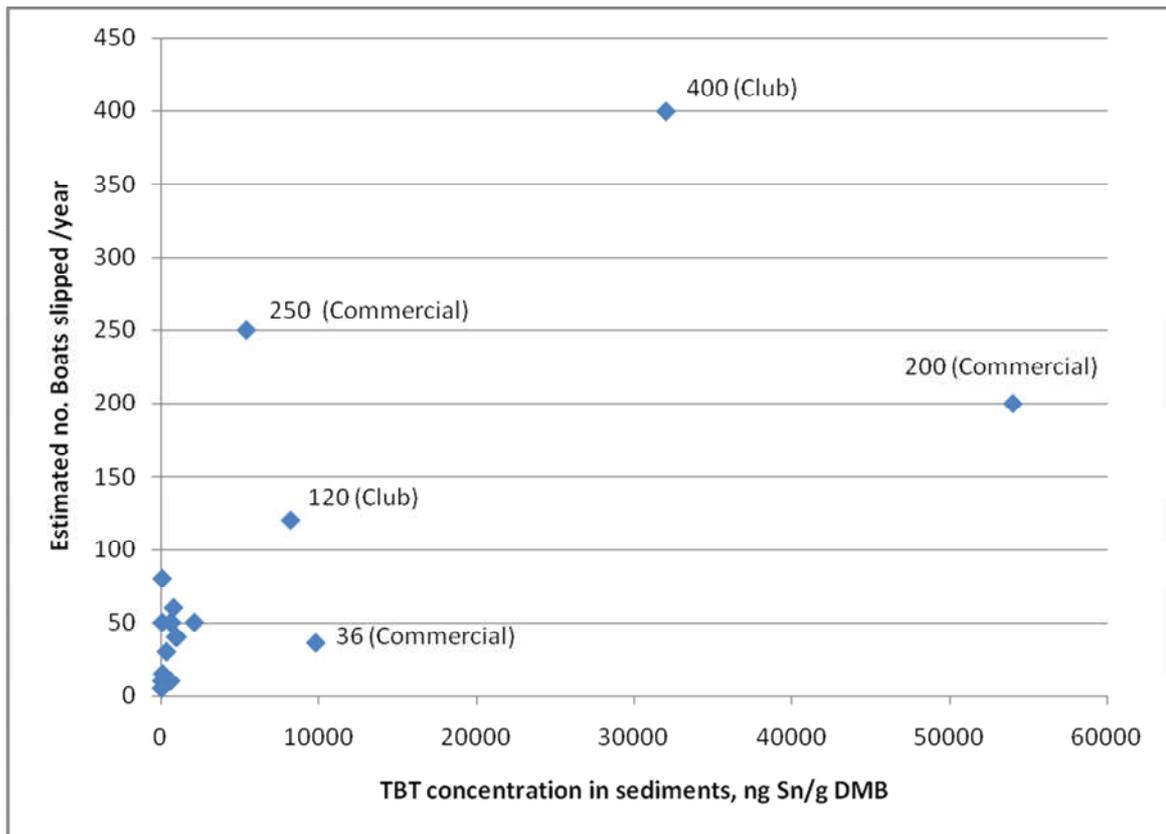


Figure 4 TBT concentration (raw data, not normalised to 1% organic carbon) in sediments as a function of the estimated number of boats slipped each year.

Heavy metals data

A summary of the sediment heavy metal results grouped by contaminant category is presented in Table 6. As with TBT, data is summarised using the classification system presented in Table 3. The results from all sites sampled along each transect are included in the comparison against guideline values in Table 6. Data were not normalised, however particle size analysis and organic carbon content were considered when examining trends in the data. There were no strong correlations between OC or particle size and individual metals (Cd, Cu, Pb, As or Zn). Particle size data may be considerably influenced by the presence of paint flakes in samples.

Copper concentrations measured in sediments ranged from < 1 to 13,500 mg/kg, with an average concentration of 1670 mg/kg. Zinc concentrations ranged from 5 to 17,000 mg/kg, with an average of 1670 mg/kg. Lead and nickel were also elevated at a number of sites, particularly those with elevated copper and zinc.

Cadmium was generally below detection, and only sites immediately adjacent to the zinc smelter in the Derwent estuary had concentrations in excess of the ANZECC ISQG-High trigger. Excessive cadmium concentrations in this area are well documented (DEP 2007). Chromium and arsenic levels exceeded the ISQG-Low in a number of locations.

| Municipality * | Matrix | As | Cd | Cr | Cu | Ni | Pb | Zn | Overall ranking |
|-----------------|---------------------|-----|-----|----|-----|-----|-----|-----|---------------------|
| Break O'day 1 | Shell grit and sand | ✓ | ✓ | ✓ | ✘✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Circular Head 2 | Sand | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | Uncontaminated |
| Clarence 3 | Sandy silt | ✘✘ | ✓ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Clarence 4 | Gravel | ✘✘ | ✓ | ✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Clarence 5 | Sand | ✓ | ✓ | ✓ | ✘✘ | ✓ | ✓ | ✓ | Contaminated |
| Clarence 6 | Shell grit and sand | ✘✘ | ✘✘ | ✓ | ✘✘✘ | ✓ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Devonport 7 | Sandy silt | ✓ | ✓ | ✓ | ✘✘ | ✘✘ | ✘✘ | ✘✘✘ | Highly contaminated |
| Devonport 8 | Muddy sand | ✓ | ✓ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Glamorgan SB 9 | Shell grit and sand | ✓ | ✓ | ✓ | ✘✘✘ | ✓ | ✓ | ✘✘✘ | Highly contaminated |
| Glamorgan SB 10 | Sand | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✘✘ | Contaminated |
| Glenorchy 11 | Shell grit and sand | ✓ | ✘✘ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Glenorchy 12 | Mud | ✘✘✘ | ✘✘✘ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Hobart 13 | Shell grit and sand | ✘✘ | ✓ | ✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Huon Valley 14 | Muddy sand | ✓ | ✓ | ✓ | ✘✘✘ | ✓ | ✘✘ | ✘✘✘ | Highly contaminated |
| Huon Valley 15 | Gravel and sand | ✘✘✘ | ✓ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Kingborough 16 | Rocks and sand | ✓ | ✓ | ✓ | ✘✘ | ✓ | ✓ | ✓ | Contaminated |
| Kingborough 17 | Shell grit and sand | ✓ | ✓ | ✓ | ✘✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Latrobe 18 | Shell grit and sand | ✓ | ✓ | ✓ | ✘✘ | ✓ | ✓ | ✓ | Contaminated |
| Latrobe 19 | Shell grit and sand | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | Uncontaminated |
| Launceston 20 | Mud | ✓ | ✘✘ | ✘✘ | ✘✘ | ✘✘ | ✘✘ | ✘✘ | Contaminated |
| Sorell 21 | Muddy sand | ✓ | ✓ | ✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| Tasman 22 | Muddy sand | ✓ | ✓ | ✓ | ✘✘✘ | ✓ | ✘✘ | ✘✘ | Highly contaminated |
| West Coast 23 | Sand | ✘✘ | ✘✘ | ✓ | ✘✘ | ✓ | ✓ | ✓ | Contaminated |
| West Coast 24 | Muddy sand | ✓ | ✓ | ✓ | ✘✘✘ | ✓ | ✘✘ | ✓ | Highly contaminated |
| West Tamar 25 | Mud | ✘✘ | ✘✘ | ✓ | ✘✘ | ✘✘ | ✘✘✘ | ✘✘✘ | Highly contaminated |
| West Tamar 26 | Muddy sand | ✘✘ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | Contaminated ? |

Table 6 Summary of heavy metal contamination in sediments at slipway facilities. Matrix descriptions based on particle size data provided by Aquenal. ✓ indicates results in the "Uncontaminated" category, ✘✘ the "Contaminated" category & ✘✘✘ the "Highly Contaminated" category.. * indicates facility number as per Table 4.

Almost without exception, sediments to the immediate left and right of the slipway were found to contain elevated concentrations of copper, lead and zinc. The presence of copper and zinc are likely to be due to antifouling products replacing TBT, however they are also typically present in urban stormwater, industrial and sewage effluents. Land-use categories influence the concentration of heavy metals entering the aquatic environment and thus the metal data in locations near major urban centres or industrial activity need to be carefully examined. For example, it should be noted that two of the facilities in the *Contaminated* category are situated in Macquarie Harbour, and widespread sediment contamination is primarily due to historical loads of copper and lead entering the harbour from the Queen River, associated with mining activities. Similarly, those facilities located in urban estuaries (e.g Derwent and Tamar) typically have elevated concentrations of arsenic, copper, cadmium, nickel, lead, and zinc in both the slipway and control samples. Widespread and significant levels of heavy metals in sediment are well documented throughout the Derwent estuary (Green and Coughanowr, 2003; Macleod and Helidoniotis, 2006).

At more remote locations, it would be expected that heavy metal inputs from other anthropogenic sources such as stormwater would be minimal. Locations in the *Uncontaminated* category are facilities in small coastal centres, servicing an estimated 10 boats/year or less. As with TBT, the highest concentrations of copper were associated with high turnover facilities servicing in excess of an estimated 120 boats/year. The trend is less clear for zinc, suggesting sources of zinc are more ubiquitous.

A small number of facilities had localised heavy metal contamination, particularly copper and zinc, in the slipway samples, but not the control samples. These are mid-size facilities in typically rural areas where it is most probable that the heavy metals are due to slipway activities. Where available, data on number of vessels slipped/year suggested that up to 60 vessels year were serviced.

Heavy metal bioavailability

In the absence of ecotoxicological data, it is important to proceed cautiously when interpreting the effects of heavy metals on the aquatic environment at these locations. Results in excess of the guideline values should trigger further investigation into the speciation, bioavailability, and toxicity of the sediments. For example, toxicity testing of Derwent sediments at heavy metal concentrations similar to those reported here showed the sediments were highly toxic (DEP, 2006), however infaunal community studies suggested that toxicity was likely to be significantly reduced if sediments were not mixed or disturbed. Elutriate tests showed low concentrations of metals were mobilized using seawater, however dilute acid released significant concentrations of metals. Routine monitoring of shellfish showed that despite significant reductions in metal loads to the estuary, (reflected in large reductions in water column concentrations), modeling and laboratory experiments suggesting limited efflux of metals from the sediments, the levels of metals in oysters and mussels remain high.

TCLP analyses were conducted on a sub set of the 26 locations sampled in this study, with the intention of estimating the bioavailability of the metals bound to the sediments. The TCLP test is designed to model a theoretical scenario in which a solid or liquid waste is placed in an unlined landfill containing municipal solid waste. The infiltration and leaching of rainwater through landfill containing putrescibles is simulated by the addition of an acetic acid solution to the sample. It is an arbitrary (method defined) waste characterisation measurement. It can be used to assess the suitability of contaminated marine sediments for disposal in contained waste facilities, however it is not a test commonly used to evaluate the mobility or

bioavailability of contaminants in the marine environment (S. Simpson, CSIRO, *pers. comm.*).

Established methods for estimating bioavailability in marine sediments *in situ* include seawater and weak acid elutriate tests, determining pore water concentrations, speciation studies, sequential extraction schemes and measurement of acid volatile sulfide and simultaneously extracted metals (AVS/SEM). Details are provided in the 'National Ocean Disposal Guidelines for Dredged Material (Environment Australia, 2002). As mentioned previously, these are best coupled with direct biological measurements.

Discussion

Source of contaminants

In light of current restrictions on the use of TBT based paints, concentrations of TBT present in Tasmanian sediments around slipways are most likely due to two major sources:

- (i) water-borne TBT that enters the waterway through run off from high pressure blasting of pre-existing paint during hull stripping; and
- (ii) sludge and particulate material, particularly paint flakes that enter the waterway during hull stripping via unbanded slips, facilities without washdown containment and separation systems, or slips that are located below the high tide mark (Thomas *et al*, 2003).

The presence of paint flakes and particles in sediments can significantly increase TBT and heavy metal concentrations. Obvious paint flakes and garnet were observed to occur in several samples, notably those that had extremely high concentrations of TBT. Because the samples are taken from the top 5 cm of sediment, it is possible that the elevated concentrations observed are associated with past, rather than current practices. If this is the case, a slow or minimal rate of degradation of TBT in the sediment is evident. Either way, significant contaminant levels are evident at all slipways sampled, and the trend will be continued by copper, zinc and biocides such as Diuron, present in current paint formulations.

Emerging issues: Diuron and other biocides

The inclusion of herbicide formulations such as Diuron, and Irgarol 1051 in antifouling paints is based on their "broad-spectrum" toxicity to a wide range of aquatic plants. A growing body of information exists as to its environmental impacts in coastal and estuarine waters. Diuron has been observed to suppress photosynthesis in seagrass, corals, and is also implicated in mangrove dieback where sediment concentrations were elevated (Moss *et al*, 2005). There are also reports in the literature of impacts on marine phytoplankton community structure.

Diuron is moderately water soluble, and noted for its high level of persistence in the marine environment. It is unlikely to partition to particulate material and sediments unless there are very high concentrations of suspended solids (Stewart, 2006). Monitoring in New Zealand to determine the extent of Diuron and Irgarol-1051 contamination identified water column samples as important since the contaminants are likely to be transported some distance from the point source. The implication for slipway management is that zone of impact of antifouling activities is likely to be

much wider than for TBT. Stewart (2006) also noted that co-biocides associated with paint flakes and particles in the sediment have increased persistence, and accumulation of Diuron was observed when point source inputs of untreated boat hull washing wastewaters occurred. There is some suggestion that the degradation products of Diuron may be more toxic than the parent compound. Diuron has been identified as carcinogenic, so there are also potential implications for bioaccumulation and human health (Evans *et al*, 2000). Thomas *et al* (2002) reported that Diuron had its approval for use as an active ingredient in antifouling paints revoked in 2000, and may not be applied to vessels of any size in the UK. Other countries have restricted its use to vessels greater than 25 metres (APVMA, 2005).

Thiram is a co-biocide also present in a number of commercially available paint formulations. Little is known about the impact and level of thiram contamination in the marine environment, however it has been demonstrated to be toxic to algae, fish, crustacea and amphibian at concentrations less than 1 µg/L (ANZECC Water Quality Guideline database, NWQMS 2000).

Recommendations

The data collected during the sediment survey can be used to prioritise areas for further investigation. The fact that no facilities had concentrations of TBT below the ANZECC trigger level is indicative that unacceptable levels of waste associated with slipway activities have entered the marine environment in the immediate vicinity.

Modifications to sediment sampling techniques

The intent of this sampling program was to provide a broad indication of the degree of sediment contamination in areas that have active slipway facilities. The design was therefore not intended to provide an accurate measure of the concentration of each contaminant in the sediment. Sediments are inherently heterogeneous, which leads to high spatial variability, and sampling programs with low replication or limited compositing of samples are at risk of large uncertainties in the data. Any further sampling undertaken should use a higher degree of replication (i.e multiple samples from the same site) and a much higher number of cores collected for compositing for each of the replicate samples. The study conducted by the Australian Government (NHT 2000) was specifically designed to address these issues and should be consulted prior to any further sediment sampling programs being undertaken. The results of the current study can however be confidently used to identify hotspots, and sites of further interest.

The use of "control" sites was included in the sample design to identify how locally these contaminants are distributed. TBT was not measured in these samples, however, it has been clearly demonstrated in the literature that impacts are usually localised, and tend to drop off rapidly with increasing distance from the facility. Control samples for heavy metals could not be collected at all sites for a variety of reasons, however results showed widespread contamination at facilities close to urban and industrial areas. In general, areas more removed from other anthropogenic point sources tended to show elevated levels of copper and zinc in the immediate vicinity of the slip. It would be useful to include a range of sediment types collected away from anthropogenic sources to establish the natural background range of heavy metals of interest. Arsenic for example may exceed ANZECC guidelines due to natural sources and this is important when applying the "decision tree" investigative approach in the ANZECC guidelines. Increasing the transect distance would also help define the extent of elevated contaminant levels at

sites targeted for further investigation. Transects moving away from the shoreline may also be beneficial.

Choice of indicator

Despite limited availability and bans in recent years, it is still important to monitor environmental concentrations of TBT to determine its fate and environmental behavior (Yang and Maguire, 2000). TBT can degrade to less toxic forms, the rate of degradation dependent upon environmental conditions. Measurement of breakdown products DBT and MBT can provide a clearer picture of how TBT is being processed in the environment and would be pertinent for those sites where TBT concentrations are excessively high.

Understand the new products

The data presented here confirms that active agents associated with antifouling products lead to significant contaminant levels in the marine environment. The use of products containing the biocide Diuron has potential to follow the same, if not greater pattern of impact, since it is more water soluble than TBT, has a long half-life, and there is evidence that the breakdown products are more toxic than the active agent itself. The increased risk of more widespread contamination via the water column should be considered when options for upgrades or improved practices are proposed for individual facilities: high pressure hosing to clean painted surfaces, for example, is demonstrated to lead to significant levels of Diuron entering the environment.

Diuron is present in almost half the formulations currently available in Australia (25 out of a total of 53), therefore a survey of the type and quantity of paints being sold in Tasmania is recommended. This could be conducted with the assistance of chandleries and boat yards that may supply antifouling products to customers. A review of other potential sources of Diuron should be conducted to identify if Diuron is a suitable marker for current practices at Tasmanian facilities. If this is the case, monitoring for the occurrence of Diuron in water and sediment samples at high turnover facilities should be undertaken to establish contamination levels in worst-case scenarios.

The level of usage of products containing thiram should also be investigated, as little is known about the environmental fate and toxicity in the marine environment. The survey of product sales at ship chandleries and slipway facilities would be a useful first step in establishing the relative application of these products.

Assess bioavailability using biota

The question of bioavailability of contaminants is an important one. TCLP testing was judged to be difficult to interpret due to its non-specificity to marine sediments, unknown correlations with bioavailability or toxicity, and incompatibility with TBT. The use of biological indicators such as imposex is recommended to determine both the bioavailability of TBT and the long-term recovery of sediments. A broad spatial survey of imposex in selected mollusc species is recommended to a) determine biological availability of TBT and b) provide a measure to monitor ecosystem health and recovery in the coming years. Numerous studies have shown that biological monitoring needs to be conducted over a long time period (> 10 years) to determine changes, however intervals of 5 years between surveys is not uncommon.

Alternatively, biological monitoring using deployed oysters in areas of concern as previously proposed by Scammel (2002) would provide a measure of bioavailability. A transect approach would be useful as it has been clearly demonstrated that TBT concentrations measured in oyster flesh are positively correlated with distance from the point source (Noller, 2003). Suitable endpoints include incidence of shell deformities and body burden of TBT and heavy metals. Seawater elutriate tests, toxicity testing, bioaccumulation studies and measurement of pore- water concentrations are some of the other complimentary techniques available for understanding the bioavailability of metals in the marine environment. A small subset of sites selected to cover a range of sediment/habitat/facility types would be proposed.

Summary and Conclusions

This report summarises the results of the first systematic assessment of sediment contamination at Tasmanian boat repair and maintenance facilities. Despite some limitations in sampling design, the results clearly show that TBT and heavy metals are an issue at the majority of facilities sampled. Sediments containing elevated concentrations of contaminants pose a risk of reintroduction of toxicants back into the water column by physical disturbance (i.e. re-suspension, dredging etc), direct exposure to benthic and pelagic organisms, or bioaccumulation up through the food chain. The environmental impact of TBT is beyond doubt, and presence of TBT can be confidently linked to activities associated with the use of antifouling paints at boat maintenance and construction facilities. In this respect TBT is a unique marker for the impact of antifouling products. The presence of heavy metals may be attributed to these same activities, however, they may also be present due to other urban or industrial inputs. Despite this caveat, it is not unreasonable to assume that slipways have contributed significant quantities of metals to the marine environment.

The paint formulations that have been developed to replace TBT are by nature also highly toxic. The use of Diuron in a high percentage of paint formulations presents new challenges in environmental management due to its greater solubility in water and potential for wider distribution through the marine environment. Monitoring programs and slipway management practices should consider these factors.

It is recognised that there are significant costs associated with the proposed environmental monitoring programs, however they are important to define the extent of the problem and, if designed carefully, can serve the dual purpose of demonstrating the effectiveness of continual improved management practices. The sediment monitoring and biological monitoring proposed should not preclude the adoption of best practice management at slipway facilities, but rather complement and target key issues likely to be faced by slipway operators.

Priority sites are the facilities handling the greatest number of boats, (particularly those facilities lacking adequate control measures), and those with potential to impact negatively on nearby sensitive operations such as aquaculture, and areas identified as having a high conservation value.

References

- Alzieu C, Thibaud Y, Heral M, Boutier B (1980) *Evaluation des risques des a l'emploi des peintures antisalissures dans les zones conchylicoles. Rev. Trav. Inst. Pech. Marit. 44, 301-348.*
- Anderson L (2004) *'Imposex in the City: A Survey to Monitor the Effects of TBT Contamination in Port Curtis, Queensland.'* Cooperative Research Centre for Coastal Zone Estuary and Waterway Management, Technical Report 16.
- ANZECC (1997) *'Code of Practice for Antifouling and In-water Hull Cleaning and Maintenance.'* Maritime Safety Authority of New Zealand, Australian and new Zealand Environment and Conservation Council, Australian Transport Council and Australian Maritime Safety Authority
- ANZFA (2000) *'The establishment of guideline levels for contaminants (metals) in food: Generally Expected Levels (GELs).'* Australian and New Zealand Food Authority.
- APVMA (2005) *'The Reconsideration of Approvals of the Active Constituent Diuron, Registrations of Products containing Diuron and their Associated Labels"* Preliminary Review Findings Volume 1 Review Summary July 2005 Australian Pesticides & Veterinary Medicines Authority Canberra Australia
- Axiak V, Vella AJ et al (2000) *"Evaluation of environmental levels and biological impact of TBT in Malta (central Mediterranean)" Science of the Total Environment 258, 89-97.*
- Barakat AO, Kim M, Qian Y, Wade TL (2001) *Butyltin compounds in sediments from the commercial harbor of Alexandria City, Egypt. Environ Toxicol Chem 20, 2744-8.*
- Batley G, Scammel M (1991) *Research on tributyltin in Australian estuaries. Applied Organometallic Chemistry 5, 99-105.*
- Batley G (1995) *Heavy metals and tributyltin in Australian coastal and estuarine waters. In 'State of the marine environment report for Australia: Pollution-Technical annex 2'. (Department of the Environment and Water Resources)*
- Bellas J, Beiras R, Marino-Balsa JC, Fernandez N (2005) *Toxicity of organic compounds to marine invertebrate embryos and larvae: a comparison between the sea urchin embryogenesis bioassay and alternative test species. Ecotoxicology 14, 337-53.*
- Bhosle NB, Garg A, Harji R, Jadhav S, Sawant SS, Krishnamurthy V, Anil C (2006) *Butyltins in the sediments of Kochi and Mumbai harbours, west coast of India. Environ Int 32, 252-8.*
- Birch GF, Taylor SE (2004) *'The contaminant status of Sydney Harbour sediments.'* Environmental, Engineering and Hydrogeology Specialist Group (EEHSG) Geological Society of Australia, 1.

Boesch DF, Burroughs RH, Baker JE, Mason RP, Rowe CL, Siefert RL (2001) *Marine Pollution in the United States*. In 'America's Living Oceans: Charting a Course for Sea Change'. (Ed. PO Commission)

Boxhall ABA, Comber SD, Conrad AU, Howcroft J, Zaman N (2000) *Inputs, monitoring and fate modelling of antifouling biocides in UK estuaries*. *Marine Pollution Bulletin* 40, 898-905.

Clarke MW, McConchie D, Lewis DW, Saenger P (1998) *Redox stratification and heavy metal partitioning in Avicennia-dominated mangrove sediments; a geochemical model*. *Chemical Geology* 149, 147-171.

Danis B, Wantier P, Dutrieux S, Flammang R, Dubois P, Warnau M (2004) *Contaminant levels in sediment and asteroids (Asterias rubens L., Echinodermata) from the Belgian coast and Scheldt estuary: polychlorinated biphenyls and heavy metals*. *Science of the Total Environment* 333, 149-165.

de Mora SJ, Stewart C, Phillips D (1995) *Sources and rate of degradation of Tri(n-butyl)tin in marine sediments near Auckland, New Zealand*. *Marine Pollution Bulletin* 30, 50-57.

DEP (2006) *'Water Quality Improvement Plan for the Derwent estuary.'* Derwent Estuary Program, DTAE

Diez S, Abalos M, Bayona JM (2002) *Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation*. *Water Res* 36, 905-18.

DPIWE (2002a) *'Tasmanian Slipways Management Framework Issues and Options Paper.'* Environment Division, Department of Primary Industries, Water and Environment.

DPIWE (2002b) *'Tasmanian Slipways Management Framework Issues and Options Paper Public Consultation Summary Report.'* Environment Division, Department of Primary Industries, Water and Environment.

DTAE (2007) *'Draft Environmental Best Practice Guidelines for Boat Repair and Maintenance Facilities.'* Environment Division, Department of Tourism, Arts and the Environment.

Environment Australia (2002) *'National Ocean Disposal Guidelines for Dredged Material.'*

Evans SM, Nicholson GJ (2000) *The use of imposex to assess tributyltin contamination in coastal waters and open seas*. *Sci Total Environ* 258, 73-80.

Fernandez MA, de Luca Rebello Wagener A, Limaverde AM, Scofield AL, Pinheiro FM, Rodrigues E (2005) *Imposex and surface sediment speciation: a combined approach to evaluate organotin contamination in Guanabara Bay, Rio de Janeiro, Brazil*. *Mar Environ Res* 59, 435-52.

Gadd GM (2000) *Microbial interactions with tributyltin compounds: detoxification, accumulation, and environmental fate*. *Sci Total Environ* 258, 119-27.

Gibson CP, Wilson SP (2003) *Imposex still evident in eastern Australia 10 years after tributyltin restrictions. Mar Environ Res 55, 101-12.*

Green G, Coughanowr C (2003) *'State of the Derwent report 1999-2003.'* Derwent Estuary Program, Department of Tourism, Arts and the Environment.

IMO (2002) *International convention on the control of harmful anti-fouling systems on ships. International Maritime Organisation*
http://www.imo.org/Conventions/mainframe.asp?topic_id=529

Long ER, MacDonald DD, Smith S, Calder FD (1995) *Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management 19.*

Macleod CK, Helidoniotis F (2005) *'Ecological status of the Derwent and Huon Estuaries.'* Tasmanian Aquaculture & Fisheries Institute, Hobart, Tasmania, Australia, NHT/NAP Final Report (Project No.46928),.

Moss A, Brodie J, Furnas M (2005) *Water quality guidelines for the Great Barrier Reef World Heritage Area: a basis for development and preliminary values. Marine Pollution Bulletin 51, 76-88.*

Naylor C, Davison W, Motelica-Heino M, Van Den Berg GA, Van Der Heijdt LM (2004) *Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediments measured using a combined metal/sulfide DGT probe. Science of the Total Environment 328, 275-286.*

Negri AP, Smith LD, Webster NS, Heyward AJ (2002) *Understanding ship-grounding impacts on a coral reef: potential effects of anti-foulant paint contamination on coral recruitment. Mar Pollut Bull 44, 111-7.*

NHT (2004) *'Tributyltin (TBT) analysis protocol development and current contamination assessment.'* Natural Heritage Trust (Coast and Clean Seas), Project no 25425.

Noller BN (2003) *'Critical review of the environmental fate of TBT and its toxicological effects on the Pacific oyster Crassostrea gigas including at Georges Bay and other Tasmanian locations.'* National Research Centre for Environmental Toxicology.

NRM (2006) *Estuarine, coastal and marine habitat integrity indicators Occurrence of imposex. <http://www.nrm.gov.au/monitoring/indicators/index.html>*

NWQMS (2000) *Australian and New Zealand Guidelines for Fresh and Marine Water Quality, ANZECC/ARMCANZ*

O'Connor TP (2004) *The sediment quality guideline, ERL, is not a chemical concentration at the threshold of sediment toxicity. Marine Pollution Bulletin 49, 383-385.*

Peng S, W. W, Li X, Yen Y (2004) *Metal partitioning in river sediments measured by sequential extraction and biomimetic approaches. Chemosphere 57, 839-851.*

Regoli L, Chan HM, de Lafontaine Y, Mikaelian I (2001) Organotins in zebra mussels (*Dreissena polymorpha*) and sediments of the Quebec City Harbour area of the St. Lawrence River. *Aquatic Toxicology* 53, 115-126.

Reitsema TJ, Spickett JT (1999) Imposex in *Morula granulata* as bioindicator of tributyltin (TBT) contamination in the Dampier Archipelago, Western Australia. *Marine Pollution Bulletin* 39, 280-284.

Reitsema TJ, Field S, Spickett JT (2003) Surveying imposex in the coastal waters of Perth, Western Australia, to monitor trends in TBT contamination. *Australasian Journal of Ecotoxicology* 9, 87-92.

Scammel, M (2002) Tributyl Tin Contamination of Shellfish Growing Areas Field Investigation: 25th to 28th March 2002. Report to DPIWE (Appended in Noller, 2003)

Scammel, M and Biddulph, S "Intertidal biological assemblages as a tool for measuring the health of a waterway" (Appended in Noller, 2003)

Shaw, P and Hickey, B (1999) "The Legacy of 110 years of Dockyard Operations" 10th International Congress on Marine Corrosion and Fouling University of Melbourne, February 1999, Additional Papers

Stark L (1998) Heavy metal pollution and macrobenthic assemblages in soft sediments in two Sydney estuaries, Australia. *Marine and Freshwater Research* 49, 533-40.

Stewart C (2006) 'Antifouling co-biocides in New Zealand coastal waters: 2006 resurvey.' New Zealand Ministry of the Environment.

Thomas KV, Mc Hugh M, Hilton M, Waldock M (2003) Increased persistence of antifouling paint biocides when associated with paint particles. *Environmental Pollution* 123, 153-161.

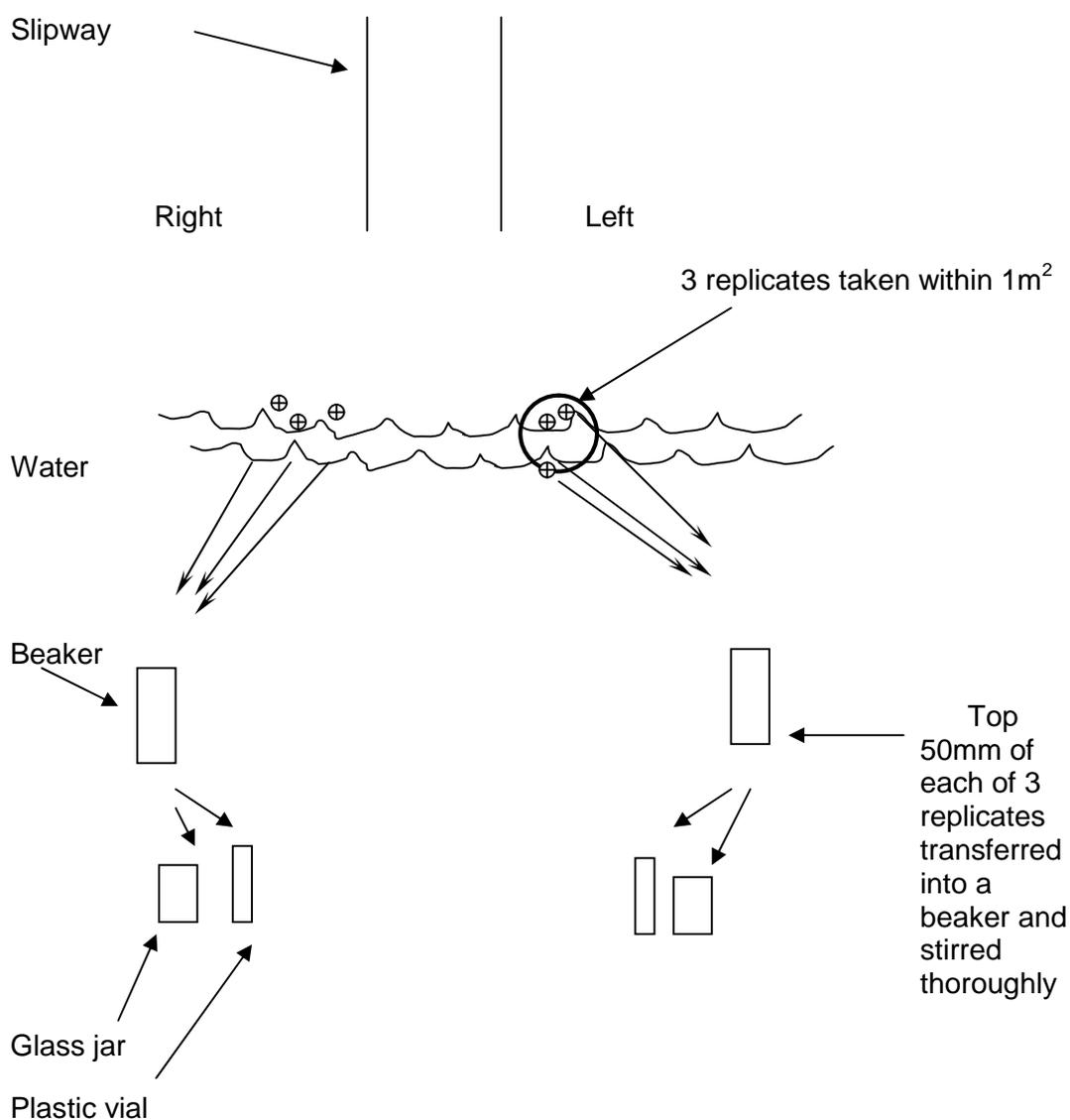
Yang F, Maguire RJ (2000) Occurrence and seasonal variation of tributyltin in Marinas on Lake Ontario, Canada. *Water Quality Research Journal of Canada* 35, 681-691.

Appendix 1 DTAE Sediment Coring Protocol

Introduction

To get a good handle on the degree of contamination of each slipway site it is necessary to sample the top 50mm of the sediment in an area around the bottom of the slip. A core tube is a useful tool for reliably doing this in soft sediments. For our purposes we need to take two samples on either side of the bottom of the slip. Each of these samples will consist of the top 50mm of each of three replicate cores taken within a metre or so (see diagram below). Two control samples are to be taken approx. 100m on either side of the slipway as well. Coring is best undertaken on a low tide.

Sampling site diagram:



Once the sample is stirred a small plastic vial and glass jar are filled per site.

Nomenclature

To avoid confusion and possible sample loss or mix-ups I recommend that the following labelling protocol be used:

Location and Site

Location: is the name of the slipway.

Site: Each slipway (location) has two sample sites to be identified logically as: Left (L) and Right (R). These sites are to be chosen from left to right looking down the slipway. Left: to the left of the slip and Right to the right of the slip. To make life easier you can abbreviate these when identifying the sample.

Three replicate cores are taken at each site, the top 50mm of each of these are combined in a single sample for that site.

Label each site sample with these details as well as the date and time of sampling and the initials of the sampler.

So each site bottle will be labelled with the following information:

(Example only)

Client: DTAE

Project: Marine Structures

Location: Mersey Slipway

Site: Left

Date/time: 7/6/06 @0945

Initials: MJR

Each control site bottle will be labelled with the following information:

(Example only)

Location: Mersey Slipway

Site: Left Control (and identifier approx. distance. North/South . upstream/downstream)

Date/time: 7/6/06 @ 0945

Initials: MJR

This information will be transferred to the sample submission form when the samples are delivered to the laboratories.

QA/QC

Duplicate analysis will need to be done on three samples. A second analysis can be performed on chosen samples, these to be identified on the sample submission form.

Coring Method

As mentioned above three cores are to be taken at two sites on the seaward side of the slipway and two control sites approx. 100m either side of the slip. To minimise the chances of cross contamination the control samples should be taken before the slip samples where possible. Sampling should (hopefully) proceed as follows:

- Wade into the water to a depth slightly below the knee
- Push core tube vertically into sediment to a depth of ~ 150mm
- Insert rubber bung firmly into the top end of the core tube (this creates a vacuum when the tube is removed from the sediment and stops the sediment from falling out)
- Lift the core tube slowly, and as soon as the bottom of the core is clear of the mud firmly insert a second rubber bung into the bottom end of the tube
- At this stage it is important to keep the tube vertical and treat it as gently/smoothly as you can. The surface of the sediment is generally very loose and can be mixed and disturbed very easily
- The water on top of the sediment in the tube needs to be removed before the sediment sample is transferred to the bag. This can be done by either sucking with a syringe with a tube attached (see diagram below - being careful not to suck up any of the sediment from the top of the core), or by pushing the sediment up the core with the 'core pusher', so the excess water will spill over the top of the tube
- Using the 'core pusher' extrude the core 5cm out of the tube into the plastic beaker provided. If the sediment is 'firm' 5cm can be measured from the top of the tube with a plastic ruler. If the sediment is 'loose' its best to measure from the bottom of the core tube
- Repeat the above steps for the second and third cores of that site (all three cores to be taken within a square metre) extruding the sediment into the one plastic beaker. You must take care to avoid coring an area that has been disturbed

while taking earlier samples (ie don't take a core in an area you have just walked over)

- Once the third core has been deposited into the beaker the contents is to be stirred thoroughly with the plastic spoon
- A small plastic vial is to be filled from this mixture labelled and put aside (this sample is to be taken to Aquenal lab. for particle size analysis)
- A glass jar is to be filled with the mixture, labelled and put into an eski with ice (this sample goes to the AST lab for all other analysis)
- Proceed to the next site at that location
- Make field notes recording the site and time details and any other information relevant to the coring process
- Clean core tube with bottle brush between sites

On completion of each slipway 4 glass jars and 4 plastic vials should have been filled

Materials Check List

You will need the following:

- Core tubes x2
- Bungsx3
- Core Pusher
- 50 ML Plastic vials and Glass Jars
- Plastic ruler
- Plastic zip lock bags
- Syringe and tubing
- Felt pens (water proof) pencils
- Field sheets
- Sample submission forms (for AST)
- Eski and ice
- Note pad and pencil/pen
- Bottle brush

Sample Handling

Samples taken for Particle Size (small plastic vials) analysis may be stored at room temperature and are to be dropped off at Aquenal Pty, at Huon Quays. They can be contacted on 6234 3403 and its recommended that they be contacted before dropping samples in.

All other samples are to be stored in an eski with ice and be delivered to the Analytical Services Tasmania laboratories that are located in the Chemistry building of the University of Tasmania in Sandy Bay, Hobart.

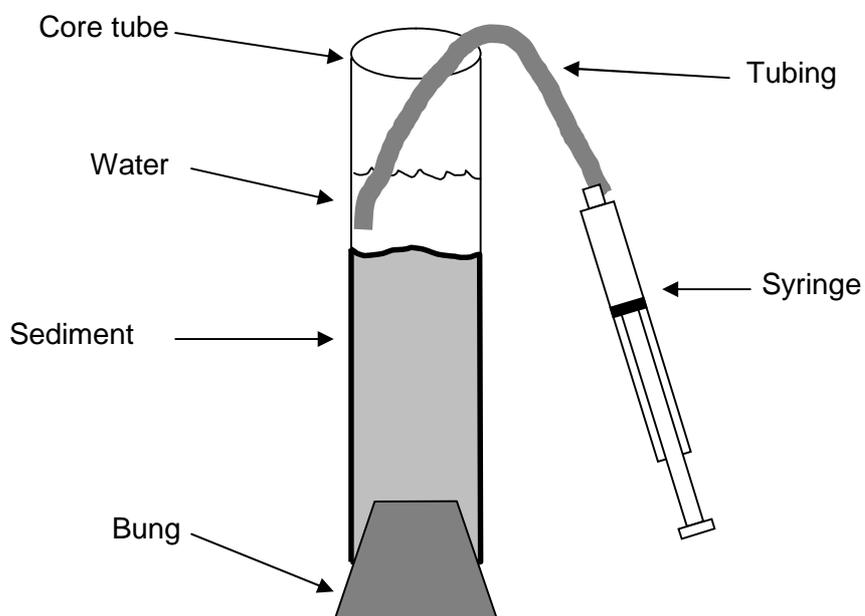
A good contact at AST is Damien Norman on ph: 03 6226 7175

I have included a number of sample submission forms for AST for your use and attached an example form.

Things to watch out for

- Coring over rocks is difficult, its best to hunt around a bit until you find a useful bottom
- If there is only a thin layer of fine sediment over a harder substrate, then use your judgement in accepting a lesser volume in the core. On that issue, the lab only needs about 10g-20g of sample so less than 50mm in the core tube is ok if you can't get any more. (50mm is preferred though)
- Document in your field notes any non standard events eg. Shallow cores, rocky sediment, aggressive slip operators etc

Diagram of syringing overlying water off core:



Analyte Selection

We are collecting Left, Right and two control samples per slip 30 slips.

Proposed analytes: Total Metals (TM)
Organic Carbon (OC)
Tributyl Tin (TBT)
Particle size (PS)

Explanatory Notes:

TBT

The laboratories minimum reporting level for tin is 200 times that of the guideline levels for TBT. Therefore Tin cannot be relied on as an indicator of TBT as there may be TBT present but the Tin levels are below detection levels.

As TBT analysis is very expensive (\$216.00 per analysis) it is proposed that a subsample is taken of the two samples per slip and a subsample of the controls. These are then combined to give a single composite sample per slipway and control. The remainder of the cores are to be stored for further analysis if hot spots are identified and investigation is required.

Particle Size

It is generally accepted that sediments with smaller particle sizes have a greater capacity to bind with metals. Given the same contamination sources you would expect a sandy sediment to have a lower metal content than a silty sediment. To conduct between site comparisons of sediment contamination it is necessary to correct for differing particle size distribution in the sediments. This analysis is to be conducted by Aquenal Pty Ltd.

OH&S

You are going to be dealing with possibly contaminated sediments in a marine environment so I suggest that you consider the following Personal Protection Equipment (PPE):

- Waders, Personal Flotation Device (PFD), hat , sunglasses and sunscreen
- Long gloves/gauntlets to keep hands dry and out of the sediments when sampling is being conducted
- Disposable gloves, clean water for washing hands with and towels for drying

Extreme care must be taken when entering these facilities and it is important to recognise that you will be visiting an industrial site albeit a submarine one. So care must be taken to avoid debris (old paint tins, steel rails, mooring blocks etc) that may be in the water and unseen because of the often turbid nature of the water in these areas. This visibility problem will be increased as sampling is conducted and the loose sediments get stirred up by foot traffic etc.

Sediments in these areas are often highly variable in nature ranging from super soft where 'getting stuck in the mud' is a real issue to slippery and stony where tripping or slipping is a hazard or it could be a combination of the two.

Among other hazards to be considered are the tripping hazard caused by the slip rails and bearers below the water surface, it may be that there is a depression between these that has been caused by boating activity. Also, if the slip is on the edge of an underwater bank eg the rails head down into a river, then it could get very deep very quickly. Best practice would be to have someone observe you while you sample.

A wader safety course is recommended.

Personal Protection Equipment Check List

- Waders
- PFD
- hat
- sunscreen
- sunglasses
- gauntlets
- disposable gloves
- water and towel

Appendix 2 AST Analytical Methods

2105-Soil Organic Carbon in Soil by NEPC Method 105*

2201-Soil Metals in Soil, Sediment and Dust by ICPAES

2302-Soil TCLP Metals by ICPAES*

Metals are leached from the sample using an extraction fluid, the composition of which varies as a function of the alkalinity of the solid sample. Where the sample pH < 5, extraction fluid 1 (acetic acid-sodium acetate buffer, pH 4.93) is used. Where sample > 5, hydrochloric acid is added to adjust the pH. If the pH is now < 5 extraction fluid 1 is used. If pH > 5 extraction fluid 2 (diluted acetic acid pH 2.88) is used. Samples are tumbled for 18 hours before the liquid is decanted off and filtered followed by analysis by ICPAES

2311-Soil Alkyltin Compounds in Soil by GCMS*

Organotins are extracted using an organic solvent (alkaline methanol) followed by a one-step derivitisation of the alkyl tin compounds to their hydride adducts using sodium borohydride. Hydride adducts are extracted in hexane, concentrated and analysed by GCMS. The method can quantify TBT and the primary degradation product DBT. Only TBT reported in this study. Method Reporting Limit for TBT is 0.8 ng Sn/g DMB. Blank recoveries reported as 80 - 111%, sample recoveries 69 - 107%.

*NATA accreditation does not cover this analyte.