F I N A L R E P O R T

Q27/2006 Sediment and Antifoul Monitoring Program

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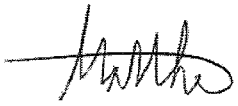

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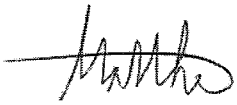

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Section 1 Introduction

1.1 Background

URS Australia Pty Ltd (URS) was commissioned by Hornsby Shire Council to assess the contaminant status of the estuaries within Hornsby Shire, identify which contaminants are present and establish baseline data on levels of contamination to allow an assessment of the risks posed by contamination to human use and amenity, and ecological values of the Lower Hawkesbury River. The work was undertaken by URS in accordance with a proposal dated 29 August 2006. This report details the findings of the Sediment Study (Stage 1) (Appendix A) and the Antifoul Study (Stage 2) (Appendix B) investigations. The findings of the Stage 1 and Stage 2 investigations have been previously submitted to Hornsby Shire Council and presented at the Estuary Management Committee Meetings on 8 February and 26 July 2007. The Final Reports for the Stage 1 Sediment Study and the Stage 2 Antifoul Study are presented in Appendices A and B, respectively.

1.2 Study Area

The study area is identified as the primary waterways of the Lower Hawkesbury River which include the Hawkesbury River, from the upstream limit of Wisemans Ferry to the downstream limit of Parsley Bay/Croppy Point, Marramarra Creek, Berowra Creek and Cowan Creek. Mooney Mooney and Mullet Creeks on the northern side of the river were also sampled during the Sediment Study (Stage 1). The overall study area incorporates the two study areas defined in the Berowra Creek and Brooklyn Estuary Process Studies (Coastal & Marine Geosciences, 1998); UNSW, 2002) with adjustments and includes the connecting water body from the mouth of Berowra Creek to the Freeway Bridge (see Figure 1 in Appendix A).

1.3 Scope of Work (Sediment and Antifoul Studies)

During the Sediment Study (Stage 1) sediment grab samples were collected at 52 locations. Samples were analysed for the following:

- Total Kjeldahl nitrogen (TKN), Total organic carbon (TOC), nitrate and nitrite (NOX); Reactive phosphorus;
- Ca, Mg, Be, Al, V, Cr, Mn, Fe, Co, Cu, Zn, As, Sr, Ba, Pb, Cd, Hg;
- Polychlorinated biphenyls (PCBs);
- Polycyclic aromatic hydrocarbons (PAHs);
- Organochlorine Pesticides (OCs);
- Organophosphate Pesticides (OPs);
- Total petroleum hydrocarbons (TPHs) (C6-C36); and
- BTEX.

Section 1 Introduction

Based on the outcomes of the Sediment Study (Stage 1) (Appendix A), 16 priority locations were identified and agreed upon for the Antifoul Study (Stage 2) (Appendix B). The 16 sampling locations were a subset of the 52 sampling locations visited during the Sediment Study (Stage 1) and were considered to adequately represent the areas of potential sediment contamination, in particular with respect to tributyltin (TBT), other organic contaminants and paint booster biocides (i.e. diuron, chlorothalonil, Irgarol 1051 and dichlofluanid). Paint booster biocides were considered at only four locations due to limitations of resources for the specialized analytical requirements pertaining to these compounds (Locations H37 – Brooklyn; H9 - Berowra Creek Marina; H38 - Sandbrook Inlet; and H31 - Refuge Bay).

Sediment grab samples were collected at each sampling location and the homogenized sediment samples were analysed for the following:

- TBT;
- Organic contaminants at Ultra Trace levels of analytical detection (polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organochlorine pesticides, organophosphorus pesticides, total petroleum hydrocarbons (C6-C36) and BTEX); and
- Silver (locations H3, H5 and H7 only).

The regional sediment geochemical data was displayed spatially on a GIS system (Mapinfo^{TM}) and the data screened against ANZECC/ARMCANZ (2000) sediment quality guideline values.

Three additional sampling locations adjacent to the proposed Sewage Treatment Plant (STP) outfall beneath the Peats Ferry Bridge were also included in the Antifoul Study (Stage 2) investigation (i.e. locations H40, H41 and H42 – see Figure 1 in Appendix B). Sediment samples from these three sampling locations were analysed for:

- TKN, TOC, NOX;
- Al, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, Sr, V, and Zn;
- Polychlorinated biphenyls (PCBs);
- Polycyclic aromatic hydrocarbons (PAHs);
- Organochlorine pesticides (OCs);
- Organophosphorus pesticides (OPs);
- Total petroleum hydrocarbons (TPHs) (C_6-C_{36}); and
- BTEX.

Grainsize was determined by wet sieving (4 fractions: <0.063 mm; 0.063 mm-0.25 mm; 0.25 mm-2 mm; >2 mm) in all sediment samples.

Section 1 Introduction

1.4 Objectives (Sediment and Antifoul Studies)

The overall project Q27/2006 was divided into two stages (Sediment Study - Stage 1 (Appendix A) and Antifoul Study - Stage 2 (Appendix B)) with distinctly different objectives. The objectives of the Stage 1 investigation were to:

- Determine the distribution of contaminated sediments within the study area;
- Compare current levels of sediment contamination with levels established in previous studies to identify areas of accumulation;
- Assess sources of contemporaneous contaminants in the sediments;
- Assess potential anthropogenic contributions to sediments; and
- Provide recommendations for remedial management actions based on the findings of Stage 1 assessment.

The objectives of the Antifoul Study (Stage 2) investigation were to:

- Determine whether or not the use of antifouling products in the Lower Hawkesbury River has resulted in contamination of the estuaries within Hornsby Shire;
- Identify which contaminants are present in the estuaries within Hornsby Shire as a result of the use of antifouling products;
- Look at a range of commercially available antifouling products and document current research;
- Establish a set of baseline data, and compare to recognised standards, on the level of contamination resulting from the use of antifouling products in the sediments of the estuaries within Hornsby Shire;
- Provide recommendations and remedial management actions based on results arising from the above objectives;
- Establish baseline sediment quality data prior to the commencement of discharge from the Brooklyn and Dangar Island Sewerage Scheme outfall (locations H40, H41 and H42 - Hawkesbury River east, beneath and west of Peats Ferry Bridge); and
- Assessment of particulate matter contributions from sewage or stormwater discharges to sediments in lower Berowra Creek based on analysis of silver in surficial sediments at three sampling locations (H3, H5 & H7) in Berowra Creek.

Section 2 Methodology

2.1 Sediment Sampling

Fifty-two sampling locations (H1 to H55, excluding H40-H42)) were sampled during the Sediment Study (Stage 1), which included 19 of the 20 locations that were sampled during the Berowra Creek Estuary Process Study (1998). The 32 new sampling locations were selected in collaboration with Hornsby Shire Council, using existing information of sources of contamination and previous sediment data.

Sediment sampling was undertaken by Dr Carsten Matthai (URS) and Kristy Guise and Peter Coad (Hornsby Shire Council) using a tall Ekman grab sampler, except at two locations, where a Ponar grab sampler was deployed because the sediment was too sandy to be sampled with the Ekman grab sampler. Sampling was conducted from a small motorized boat supplied by Hornsby Shire Council on 13, 14 and 21 December 2006 (Sediment Study - Stage 1) and on 26 March 2007 (Antifoul Study (Stage 2). A Global Positioning System (GPS) was used to locate the sampling locations throughout the study area.

2.1.1 Sampling Rationale

It is important to have an understanding of the field variance because if small-scale spatial variance (SSSV) in the concentration of contaminants is excessive, regional trends may be of limited value. However, many studies of SSSV indicate that field variance is related to ambient energy and the type of sedimentological environment. Total (analytical plus field) variance is approx. 10% Relative Standard Deviation (RSD) for depositional parts in estuaries but increases to about 20-35% RSD for more dynamic parts of a fluvial system. Although multiple samples at multiple locations may be of statistical importance to demonstrate SSSV at each location and across a region, it would substantially curtail the scope of a regional contaminant study of sediments. Essentially, the hierarchical approach used in the Sediment Study (Stage 1) and Antifoul Study (Stage 2) allowed a cost efficient assessment of sampling locations across a regional area without compromising the comparison with previous studies.

Given that the field variance is likely to be higher in sandy sediments in the Hawkesbury River main channel due to a higher energy environment, multiple samples may have been warranted in that area, although the potential for contamination in these sandy, non-depositional sediments is substantially reduced, as exemplified by the data in the Sediment Study (Stage 1) (Appendix A). Multiple sampling at each sampling location in this environment (Hawkesbury River main Channel) would only confirm a higher variance of generally low concentrations. In contrast, the SSSV in muddy depositional areas, such as the tributary creeks, is generally small enough to warrant single samples, as shown in Birch et al. (1998, 1999, 2001).

Multiple replicate sediment samples (n=5) collected at two shallow and two deep locations in the vicinity of Spectacle Island over a spatial scale of about 400 m per replicate "nest" (URS, 2006 – unpubl. data) shows that there is little information gained from replicating the sampling in the main Hawkesbury River channel. Even over spatial scales of several hundred metres the concentrations of heavy metals in sediments are similar (<20% RSD), negating the requirement for replicate sampling, even in a high energy fluvial environment. RSD's <20%, even in sandy sediments, and including analytical variability at low concentrations, are acceptable and justify a single sample methodology.

In addition, the Sediment and Antifoul Studies (Appendices A and B) actually confirmed the presence of elevated concentrations of contaminants near marinas and low concentrations in remote areas and in sandy sediments, which supports the employed sampling rationale. The sampling methodology is therefore a defensible, robust and cost efficient way to establish the required objectives, namely assess sediments across a regional area for likely anthropogenic impacts.

Section 2 Methodology

2.1.2 Sediment Subsampling

At each sampling location, one sediment sample was collected to a maximum depth of 10 cm at each sampling location. Following retrieval, samples were photographed and homogenized using a clean stainless steel spoon and bowl. Homogenized samples were transferred into laboratory-supplied sampling containers for geochemical analyses and one 500 ml resealable plastic bag for grain size analyses. Sample containers were prelabelled and filled with zero headspace. Samples were then stored in eskies on ice. All eskies were filled to capacity and sealed with adhesive tape.

Samples collected from each sampling location were given unique sample numbers (H1 to H55). A CoC form was included in the esky. The samples were delivered to the laboratory within 48 hours of sampling for processing and analysis.

Essentially, all sample handling and processing were performed to minimize contamination and possible cross-contamination of the samples. The workspace on the boat was frequently washed down with ambient seawater to clean all surfaces and minimize dust contamination of samples. Nitrile gloves were worn by the sampling personnel.

2.1.3 General Field Activities Documentation

Field activity records and observations were noted in bound field logbooks. The aim of the documentation within the field logbooks was to allow future reconstruction of field activities without relying on the memory of field team members. To supplement the information and data collected during sample collection and field testing, field data sheets were also completed.

2.2 Sample Handling, Processing and Analysis

This section outlines the general procedures necessary for sample custody that were performed by the analytical laboratory. It is understood that the laboratory (ALS) acted in full accordance with the terms of its NATA Registration for Chemical Testing.

The National Measurement Institute (NMI) performed the analyses of the paint booster biocide compounds (diuron and chlorothalonil - quantitative analysis; Irgarol 1051 and dichlofluanid - semi-quantitative analysis). These analyses are not NATA-accredited and the analytical methodology needed to be developed by NMI because these analytes are not routinely determined by the laboratory.

2.2.1 Chain of Custody Protocols

A chain of custody (CoC) record was utilised by field personnel to document possession of all samples collected for chemical analysis. The eskies containing the samples were sealed with tape and secured with a signed custody seal. The custody seal provided an indication of whether the cooler was opened by unauthorised personnel. The temperature that the samples were stored at following transit to the lab and upon receipt was noted on the CoC forms.

Section 2 Methodology

2.2.2 Laboratory Receipt of Samples

Field samples for this project were delivered to the laboratory pre-contained and pre-preserved (as appropriate) in accordance with laboratory procedures. Sample containers used for the collection of field samples were supplied by ALS Environmental and NMI (booster biocide analyses only), pre-cleaned and inspected.

2.2.3 Pre-and Post-analysis Storage

Samples collected during the Sediment Study (Stage 1) and Antifoul Study (Stage 2) were transported to the laboratory within 48 hours of sample collection. After the Sample Custodian logged in the samples, they were placed in temporary refrigerated storage until analyses were performed. Sample analyses were scheduled as soon as practicable following delivery to the laboratory and extractions and analyses were consistent with the analyte holding times specified by the laboratory.

2.2.4 Sediment Analyses

Whole sediment samples from each of the sampling locations were conducted by ALS Environmental for analysis of the analytes listed in Section 1.3. All analytical methods are NATA accredited for all of the tests, except for particle size distribution. Analyses of organic booster biocide compounds were performed by the National Measurement Institute (NMI).

2.2.5 Analytical Quality Assurance/Quality Control (QA/QC)

Specific mechanisms for checking the accuracy and precision of analytical data in order to ensure that data quality objectives were met involve the analysis of laboratory and field QA check samples, including blanks, calibration check standards, Laboratory duplicates, matrix spikes and surrogates.

2.2.6 Data Handling

All analytical data generated by the analytical laboratory was appropriately reduced and has undergone comprehensive validation prior to reporting. Records and numerical calculations are legible and complete enough to permit reconstruction of the work by a qualified individual other than the originator. Following completion, the final report was signed by the appropriate NATA signatory and submitted to URS.

2.2.7 Data Validation

The validity of all analytical data reported was assessed by URS by critical review of the QC check sample results. This was performed in general accordance with guidance by US EPA guidelines as presented in the document “National Functional Guidelines For Organic Data Review, Multimedia, Multiconcentration (OLMO 1.0) and Low Concentration Water (OLCO 1.0), June 1991”, where appropriate (USEPA, 1991).

Section 2 Methodology

2.3 Geographic Information System

Geochemical data was imported into a GIS database (Mapinfo™ Professional) for generation and interpretation of spatial data.

2.4 Independent Peer Review

The Draft Report for the Antifoul Study (Stage 2) was reviewed by Dr Stuart Simpson (Principal Research Scientist, Centre for Environmental Contaminants Research, CSIRO) whose constructive comments have all been addressed and incorporated in the Final Report.

Section 3 Results

3.1 Sediment Chemistry (Sediment and Antifoul Studies)

The results of the geochemical investigations are provided in the Final Reports for the Sediment Study (Stage 1) (Appendix A) and the Antifoul Study (Stage 2) (Appendix B) and summarized briefly below.

3.1.1 Concentrations of Inorganic Contaminants

The concentrations of some inorganic analytes were highly variable, one order of magnitude or greater (i.e. aluminium, cobalt, copper, lead, manganese, strontium, vanadium, zinc, total organic carbon, calcium and TKN). Concentrations of copper, lead and zinc are highly variable and elevated concentrations (compared to regional concentrations) are present in sediments at locations near marinas and in headwaters of Cowan Creek and Berowra Creek and Sandbrook Inlet and Cottage Point. In contrast, concentrations of inorganic contaminants in the main Hawkesbury River channel are generally low and a spatial concentration gradient is not apparent. Total organic carbon (TOC) contents in sediments are variable (0.9%-13%) and organic-rich sediments (>10% TOC) are present in Berowra Creek.

3.1.2 Concentrations of Organic Contaminants

The majority of organic contaminants were below analytical detection limits in all or most samples and a regional distribution pattern could not be established. However, the concentrations of PAH compounds exceeded the analytical limit of reporting in one or more samples for almost all compounds. Low molecular weight PAHs varied between 65-420 μg/kg and high molecular weight PAHs varied between 165-3,960 μg/kg. Total PAH concentrations in sediments varied between 405-7,040 μg/kg. Total PAH concentrations <1,000 μg/kg were present in Cowan Creek (Smiths Creek, Refuge Bay, Akuna Bay marina and Cottage Point). In contrast, total PAH concentrations >2,000 μg/kg were present in sediments from Sandbrook Inlet, Hawkesbury River marina, Cowan Creek marina, Apple Tree Bay, and Akuna Bay marina refuelling station.

Concentrations of TBT were above the analytical limit of reporting (0.5 μgSn/kg) at all 16 sampling locations (1.4-125 μgSn/kg). Concentrations of TBT in sediments in Berowra Creek decrease from 6.6 μgSn/kg to 1.6 μgSn/kg. Sediments in Sandbrook Inlet have TBT concentrations that vary from 1.6-4.5 μgSn/kg. The concentration of TBT in sediments at the marina at Brooklyn (H37) is 10.4 μgSn/kg. In Cowan Creek and its tributary creeks, the concentrations of TBT are highly variable, with concentrations of <2 μgSn/kg at Waratah Bay, Smiths Creek and Refuge Bay, compared to concentrations of up to 114 μgSn/kg at Akuna Bay marina, 41.5 μgSn/kg at Cottage Point, 10.4 μgSn/kg at Apple Tree Bay and 125 μgSn/kg at Bobbin Head marina.

3.1.3 Organic Booster Biocides

Concentrations of four organic booster biocide compounds (diuron, chlorothalonil, Irgarol and dichlofluanid) in sediments from four sampling locations (Berowra Creek marina, Refuge Bay, Hawkesbury River marina and Sandbrook Inlet) were <0.1 mg/kg. However, inspection of chromatograms allowed a greater sensitivity of analysis with a detection limit of 0.001 mg/kg and revealed low concentrations of diuron between 0.009-0.040 mg/kg in sediments at three of the four sampling locations, except Refuge Bay. An effort was made to sample both marina and non marina areas with high boat use for comparison.

Section 3 Results

3.1.4 STP Site Sediment Chemistry

The concentration ranges of inorganic analytes are summarized in Appendix B. The concentrations of analytes in the three samples were below the analytical limit of reporting for organic contaminants and generally low for most inorganic analytes, except Hg (0.20 mg/kg) at location H40.

3.1.5 Silver Concentrations in Sediments in Berowra Creek

The concentrations of silver in surficial sediments at the three sampling locations in lower Berowra Creek (H3, H5 and H7) were <0.1 mg/kg, 0.1 mg/kg and 0.2 mg/kg, respectively.

Section 4 Discussion

4.1 Sediment Quality

The sediment geochemical data was screened against ANZECC/ARMCANZ (2000) sediment quality guideline values (ISQG-L (Trigger Value) and ISQG-H). The general approach outlined in the ANZECC/ARMCANZ (2000) sediment quality guidelines stipulates that if the lower sediment quality guideline values for a contaminant (i.e. ISQG-L – Trigger Value) is not exceeded, it is unlikely that it will result in any biological disturbance for organisms inhabiting that sediment. If the trigger value is exceeded, either management (including remedial) action is taken, or additional site-specific studies may be conducted to determine whether this exceedence poses a risk to the ecosystem.

Four inorganic contaminants (arsenic, copper, lead and mercury) exceeded the ISQG-L sediment quality guideline value in at least one sample, whereas the ISQG-H sediment quality guideline value is exceeded for copper and zinc at Bobbin Head marina only. The largest number of sediment quality guideline value exceedences (maximum of 3) is present at Bobbin Head marina and Akuna Bay marina, suggesting that anthropogenic contributions from marina activities may have resulted in a contamination of the surficial sediments. Two sediment quality guideline exceedences are present in sediments at Berowra Creek marina, Apple Tree Bay, Cottage Point kiosk and Hawkesbury River marina.

There are no sediment quality guideline exceedences in sediments in the Hawkesbury River between Wisemens Ferry and Mooney Mooney, in Marramarra Creek and in Berowra Creek between Calabash Bay and the confluence with the Hawkesbury River.

Normalization of the concentrations to 1% TOC is required for organic compounds and TBT. All concentrations of all organic contaminants were below the ANZECC/ARMCANZ sediment quality guideline values, except for TBT (5 μgSn/kg) at Bobbin Head marina, Akuna Bay marina and Cottage Point kiosk, where a high density of recreational boating activity exists.

Although PAH compounds are ubiquitous in sediments in the lower Hawkesbury River estuary, the concentrations of PAH compounds were below sediment quality guideline values at all sampling locations. The presence of PAHs in these sediments is likely to be of anthropogenic origin, in particular at locations adjacent to increased boating activity. However, PAHs are also produced by combustion of wood during bushfires and the widespread distribution of these compounds suggests that natural contributions from burnt organic matter originating from bushfires over long periods of time may have contributed to the regional contaminant contribution to sediments.

4.2 Potential Sources of Contaminants to Sediments

Contaminant concentrations in sediments of the Lower Hawkesbury River estuary are elevated at a number of sampling locations adjacent to potential point sources (e.g. marinas). These results are consistent with previous sediment chemistry investigations in the Hawkesbury River (Birch et al., 1998, 1999), which have also highlighted high density boating activities as significant but localized contributors of contaminants to sediments. However, stormwater and urban runoff from diffuse sources within the Berowra and Cowan Creek catchments are overprinted by local sources, such as marinas.

Upper Cowan Creek and Berowra Creek sediments display elevated concentrations of inorganic and organic contaminants, thereby demonstrating the potential for water-related recreational facilities to affect pristine environments. Increased urbanisation and industrialisation in the upper Berowra Creek catchment provide a source of heavy metals and nutrients, possibly from sewage treatment plant contributions and stormwater drainage. Sewage effluent discharges from isolated urban areas (Berowra Waters, Brooklyn)

on the Hawkesbury River are also likely to contribute to the observed anthropogenic enrichment of inorganic contaminants.

Although the current sediment investigation did not address the potential for bioavailability of these contaminants, it is likely that the contaminants are bioavailable, an aspect that may require future investigations. The presence of several contaminants exceeding sediment quality guideline values (Section 4.1) establishes that there is a distinct relationship between proximity to recreational centres (marinas) and urban centres and elevated concentrations of trace metal contaminants and some organic contaminants in surficial sediments.

4.3 Temporal Changes in Contaminant Concentrations

The temporal changes in the concentrations of contaminants were assessed for selected contaminants at 18 sampling locations that were revisited in the Sediment Study (Stage 1) (Appendix A).

Possible factors that may confound a direct comparison of the previous chemical data with the data obtained in the current investigation include the following:

- Triplicate sediment samples were collected during the Brooklyn Estuary Process Study (UNSW, 2002) compared to the current investigation, where single sediment samples were collected. Analytical data for the three sediment samples were therefore compared to the data from the single sample obtained in the current investigation; and
- Analytical data for the Berowra Creek Estuary Process Study (Coastal & Marine Geosciences, 1998) were reported for aqua regia and total sample digests. Only the aqua regia digest data were compared to the current data because it is more compatible with the data extraction used in the current study.

Analytes which have been compared for sediment data obtained during the Brooklyn Estuary Process Study (UNSW, 2002) and the Berowra Creek Estuary Process Study (Coastal & Marine Geosciences, 1998) and the current investigation include silt & clay content, arsenic, chromium, copper, lead, nickel, zinc, total organic carbon and total Kjeldahl nitrogen.

Whole sediment concentrations are substantially greater in 2007 in the upper sections of Berowra Creek from Bobbin Head to Calabash Bay for a number of analytes, including copper, chromium, lead and zinc. In contrast, the relative differences in the concentrations of nickel, arsenic and TKN in the upper Berowra Creek are minimal, suggesting no measurable change in the surficial sediment concentrations of these analytes between 1998 and 2007 and confirming a contribution of anthropogenic trace metal contaminants to sediments in the upper sections of Berowra Creek.

In contrast, TOC contents have substantially decreased in the upper sections of Berowra Creek between 1998 and 2007, from a range of 7-15% to 3-6%. Sediments downstream of Calabash Bay contained between 6-13% TOC in 2007 compared to <3% in 1997, which may be the result of a change in organic carbon contributions to the sediment throughout the Berowra Creek.

The temporal changes in the concentrations of TBT were assessed in the Antifoul Study (Stage 2) (Appendix B). Locations in upper Berowra Creek, Sandbrook Inlet and Cowan Creek (Akuna Bay) displayed elevated concentrations of TBT in sediments in both the EPA (1996) sediment investigation and the current investigation. The concentrations of TBT in 2007 were substantially higher compared to 1990-1991 (EPA, 1996). However, sediment TBT heterogeneity is often high and that there is always much uncertainty in TBT analyses, which makes a comparison of TBT data with differences of less than 1-2 orders of magnitude problematic (S. Simpson, CSIRO, pers. comm., 2007).

Section 4 Discussion

TBT concentrations in Berowra Creek sediments, as determined in 2007, exhibit a distinct gradient, with concentrations decreasing from 6.6–1.6 μgSn/kg. These concentrations are substantially greater than the mean concentrations of 0.1-0.4 μgSn/kg in that area in 1990-1991 (EPA, 1996). Similarly, the mean concentrations of TBT in sediments in Sandbrook Inlet and at Brooklyn varied from 0.8–2.1 μgSn/kg in 1990-1991 (EPA, 1996), compared to 1.6-10.4 μgSn/kg in 2007. The mean concentrations of TBT in sediments in Cowan Creek (including Coal and Candle Creek) were <2.8 μgSn/kg (EPA, 1996) compared to 1.4-125 μgSn/kg in 2007.

The temporal increase in the concentrations of TBT in sediments in Berowra Creek, Sandbrook Inlet/Brooklyn and Cowan Creek between 1990/91 and 2007 is likely to be a result of the different sampling methodologies used in the two studies. Whereas the EPA (1996) investigation utilized a random grit sampling methodology, the 2007 Antifoul Study (Stage 2) (Appendix B) followed a hierarchical sampling approach with the intention to establish contaminant concentrations at likely point sources of contaminants (i.e. marinas and urban developments). The outcomes of these substantially different approaches are therefore not directly comparable, although it should be noted that TBT has been banned in NSW and Australia since the late 1980s and that it would be expected that a period of 16 years between the two sampling programmes results in substantially lower concentrations of TBT in surficial sediments in 2007 compared to 1990-1991.

The presence of elevated concentrations of TBT in surficial sediments adjacent to marinas in 2007 suggests that the deposition of present-day TBT-free particulate matter is consistently bioturbated and mixed with underlying TBT-enriched sediments. This continuous mixing process results in only slight dilutions near existing recreational boating facilities, which have been operating for many years prior to the implementation of the TBT ban, and where the presence of high concentrations of TBT in the sediments is likely to be a legacy of past shore-based activities and hull cleaning operations at slipways.

Although temporal changes in the concentrations of TBT and other contaminants in sediments are unlikely to be discernible in the bioturbated surface layer of sediments (i.e. approximately the upper 0.5 m of sediment), deep sediment cores (>1m depth) would allow an assessment of long-term variations of TBT concentrations beyond the currently assessed 16 year period. It is possible that although the concentrations of TBT are relatively high and possibly constant throughout the bioturbated sediment layer there may be even higher concentrations of TBT in sediments below the mixing zone. This would reflect the past widespread use of TBT in marine boating and result in peak concentrations of TBT in sediment at a depth that corresponds to the time prior to the commencement of the TBT ban (i.e. pre-1989). However, unless additional core data is obtained, especially at some locations where the concentrations of TBT in the sediments exceed ISQG-L concentrations, it is not possible to ascertain the vertical extent and lateral distribution of the elevated TBT concentrations.

An important finding is the presence of TBT at least three times greater than the analytical detection limit at all sixteen sampling locations, despite the absence of any apparent point sources of TBT at some locations (e.g. Berowra Creek (Calabash Bay); Waratah Bay; Smiths Creek; Refuge Bay). This suggests a regional presence of TBT in sediments due to resuspension and downstream transport of particulates from the upper reaches of the two major Creeks and the dispersion and transport of TBT from recreational vessel movements into pristine areas. Although concentrations of <5 μgSn/kg are unlikely to result in adverse biological effects in benthic biota, the widespread presence of TBT, albeit at low concentrations, is an indication of an enlarged anthropogenic footprint beyond the immediate proximity of marinas, due to increasingly common recreational boating activity in this region.

Section 4 Discussion

4.4 Organic Booster Biocides in Hawkesbury River Sediments

Organic booster biocides are not routinely assessed in environmental media in Australia, although some studies have been conducted in Australia (Konstantinou and Albanis, 2004 and references therein). Given the relative scarcity of data and analytical costs and uncertainties, an assessment of organic booster biocides necessarily required a compromise approach both in terms of the number of sample locations and the number of analytes to be assessed. It was decided that diuron and Irgarol 1051 should be included in the suite of organic booster biocide analytes due to their relative non-biodegradability (Amog Consulting, 2002). Although Irgarol 1051 is not registered with the National Registration Authority (NRA) in Australia (Amog Consulting, 2002), precluding its use in marine and other products, the presence of this compound in sediments would indicate that contributions from overseas vessels may be responsible. In addition, dichlofluanid and chlorothalonil were considered to be of value in the assessment of sediments at some locations in the Hawkesbury River system because these compounds are present in registered antifoul products in Australia.

The concentrations of paint booster biocide compounds dichlofluanid, Irgarol 1051, diuron, and chlorothalonil were below the specified analytical limit of reporting (<0.1 mg/kg) in all four sediment samples, which makes a determination of the presence of these compounds in sediments of the Lower Hawkesbury River system inconclusive. Although the analytical detection limits of these compounds in the international scientific literature in both water and sediments are routinely reported in the low μg/kg range (1-10 μg/kg), the quantitative analytical determination of these compounds is not routinely performed by any of the major commercial and NATA-accredited laboratories in Australia. However, the analysis of the detailed mass spectrometry data from the analyses provided a more sensitive analytical detection limit, which resulted in the detection of diuron in three of the four samples with concentrations of up to 0.04 mg/kg, except at Refuge Bay.

Diuron is the most common (in Australia) of the four booster biocide compounds assessed in the Antifoul Study (Stage 2), which explains its presence in sediments at concentrations of up to 0.04 mg/kg. In contrast, dichlofluanid and chlorothalonil are registered in only one antifoul product in Australia and Irgarol 1051 is not legally registered in any antifoul compounds, which corresponds to the absence of these compounds in sediments at these four locations in the Hawkesbury River system.

The low concentrations of both diuron and TBT in sediments in Refuge Bay confirm that the sediments at that location are uncontaminated, which is most likely due to the absence of marinas and only temporary mooring for small recreational vessels in the Bay. In contrast, the higher TBT concentrations of up to 10.4 μgSn/kg and diuron concentrations of up to 0.04 mg/kg at the other three locations corresponds to the substantially higher boating activity at marinas in upper Berowra Creek, Sandbrook Inlet and Brooklyn Harbour. Diuron concentrations of 0.009-0.040 mg/kg in sediments in the Lower Hawkesbury River are generally lower than in sediments at marinas and in estuaries in the Europe (Appendix B).

4.5 Contaminants in Sediments at Proposed STP Site

The concentrations of inorganic analytes in sediments at the three sampling locations in the vicinity of the proposed STP site are low (below ISQG-L sediment quality guideline values), and similar to the concentrations in sediments in the main Hawkesbury River channel (Appendix A). However, the concentration of mercury at sampling location H40 (0.2 mg/kg) slightly exceeds the ISQG-L value for mercury, which may be due to contributions from road runoff. All organic contaminants (PCBs, OC pesticides, OP pesticides, PAHs, TPHs and BTEX) in sediments from sample locations H40, H41 and H42 were below the analytical detection limits.

Section 4 Discussion

4.6 Silver Concentrations in Sediments in Berowra Creek

The concentrations of silver in surficial sediments at three locations in Berowra Creek (H3, H5, and H7) were determined to assess possible sewage and stormwater contributions to these sediments, based on elevated TOC contents in Berowra Creek sediments (Appendix A). The low silver concentrations of up to 0.2 mg/kg suggest that sewage particulate matter concentrations and stormwater contributions are unlikely to be linked to the elevated TOC contents in Berowra Creek sediments. However, a more detailed assessment of the spatial distributions of silver and the vertical concentration gradients in sediments adjacent to stormwater discharge points in Berowra Creek would be required to provide a more conclusive outcome.

Section 5 Conclusions

The Sediment Study (Stage 1) (Appendix A) has resulted in the following outcomes:

- Sediment texture is generally muddy (>80% mud) in deep waters of the creeks (Cowan Creek, Berowra Creek, Marramarra Creek, Mullet Creek, Mooney Mooney Creek) and sandier in the main Hawkesbury River channel and the headwaters of the major creeks;
- Normalized contaminant concentrations (using the lithogenic element aluminium) generally decrease from upper Berowra Creek and upper Cowan Creek towards the main Hawkesbury River channel, with locally elevated concentrations in the vicinity of marinas and areas of increased recreational boating activity. Normalized contaminant concentrations in sediments of Sandbrook Inlet (the Gut) are generally higher than in the main Hawkesbury River channel, where normalized contaminant concentrations are low from Wisemans Ferry to the confluence with Cowan Creek;
- Concentrations of inorganic contaminants (copper, lead, zinc, mercury, arsenic) exceed ANZECC/ARMCANZ (2000) sediment quality guideline values in sediments of upper Berowra Creek, Cowan Creek, Sandbrook Inlet (the Gut), mainly adjacent to marinas, and at some locations in the Hawkesbury River (southwest of Spectacle Island and south of Dangar Island). Nineteen of the 52 sampling locations exceed at least one sediment quality guideline value;
- Concentrations of organic compounds are below the limits of reporting in sediments at most sample locations and below ANZECC/ARMCANZ (2000) sediment quality guideline values where present above the limits of reporting. Total petroleum hydrocarbons are present at concentrations above the limits of reporting in sediments at Waratah Bay, Mooney Mooney Creek, Cowan Creek and Smiths Creek. Fluoranthene and Pyrene, were detected in sediments in Mooney Mooney Creek and at Bobbin Head marina and PCBs were detected in sediments at Bobbin Head marina; and
- Whole sediment concentrations of copper, chromium, lead and zinc are higher in upper Berowra Creek sediments in 2007 compared to 1998, possibly reflecting increased contaminant contributions to receiving waters from the upper Berowra Creek catchment. In contrast, total organic carbon contents in sediments are lower in upper Berowra Creek sediments when compared over the same 9 year period, which suggests that elevated contaminant concentrations in upper Berowra Creek sediments may be related to sources other than stormwater discharge.

The Antifoul Study (Stage 2) has resulted in the following outcomes:

- Concentrations of TBT (normalized to 1% TOC) in sediments exceed the ISQG-L (Trigger Value) of the ANZECC/ARMCANZ (2000) sediment quality guidelines (5 μgSn/kg) at four locations in the vicinity of marinas (i.e. Akuna Bay marina - H25 and H26; Bobbin Head marina - H21) and other points of high recreational boating activity (i.e. Cowan Creek – Cottage Point - H28);
- The occurrence of TBT in the Hawkesbury River estuary system is widespread, albeit at low concentrations in areas other than in close proximity to marinas. Concentrations of >1.4 μgSn/kg in sediments were found at each of the 16 locations assessed in the current study, including locations remote from marinas (i.e. Calabash Bay, Refuge Bay, and Smiths Creek);
- TBT concentrations in sediments at marinas and in areas of high recreational boating activity in the lower Hawkesbury River system are substantially lower compared to many other harbours and coastal areas worldwide, indicating that antifoul-related contamination is comparatively minor and localized to areas of known boating activity;
- Concentrations of organic compounds in surficial sediments are generally below the analytical limits of reporting (i.e. TPH, OP pesticides, BTEX, OC pesticides (except for DDE at four sampling locations), and PCBs (except for Aroclor 1254 at two locations)). However, PAH compounds are generally ubiquitous in sediments in the lower Hawkesbury/Nepean River system and the concentrations of most PAH compounds quantified in this investigation are generally above the analytical limits of reporting at all sampling locations and likely to be at least partially due to natural PAH contributions from burnt organic matter generated during bushfires;

Section 5 Conclusions

- Organic paint booster biocides Irgarol 1051, chlorothalonil and dichlofluanid have not been detected in sediments in the lower Hawkesbury River system at concentrations at or above 0.1 mg/kg. However, the presence of diuron at concentrations between 0.009 mg/kg and 0.04 mg/kg at three locations (Berowra Waters marina, Brooklyn Harbour, Sandbrook Inlet) suggests that these compounds (and other antifoul compounds not assessed in the current investigation, e.g. zinc pyrithione, thiram) may be present at lower concentrations;
- Sediments in the vicinity of the proposed Sewage Treatment Plant discharge point at the Hawkesbury River road bridge have shown to be uncontaminated, except for an exceedance of the ISQG-L (Trigger Level) for mercury at one location (H40), which may be due to road runoff in the vicinity of that location. Contaminant concentrations at these locations are similar to the levels found in other parts of the main Hawkesbury River channel; and
- Concentrations of silver in surficial sediments in lower Berowra Creek are low (<0.2mg/kg), suggesting that the high total organic carbon concentrations in sediments in Berowra Creek are unlikely to be associated with stormwater and sewage discharges.

Section 6 Recommendations

The Sediment and Antifoul Study (Hornsby Shire Council Project Q27/2006) has resulted in important findings, as summarized in Section 5. Additional assessments may be considered by Hornsby Shire Council in the ongoing environmental management of the waterways of the Lower Hawkesbury River estuary. In particular, the following issues may be considered further:

1. Elevated concentrations of TBT in sediments at several sampling locations in the Hawkesbury River system indicate that there is a residual environmental effect, even 18 years after the ban on TBT-based antifoulants. This confirms the assessment by Gibson and Wilson (2003) who established that imposex phenomena in gastropods were still evident in eastern Australia 10 years after the implementation of TBT restrictions. Additional data is needed to ascertain the vertical extent and variability of TBT concentrations in sediments at locations where the surficial sediment concentrations (<10 cm depth) exceed the ISQG-L (Trigger value) of 5 μgSn/kg (ANZECC/ARMCANZ (2000). These locations are H8, H9, and H10 (upper Berowra Creek), H21 and H22 (upper Cowan Creek), H25 and H26 (Akuna Bay marina in Coal and Candle Creek), H28 (Cottage Point) and H37 (Hawkesbury River marina). Vertical contaminant concentration profiles (TBT, heavy metals and organic compounds) are likely to establish the thickness of contaminated sediments, which may have direct implications for future management of sediments at these locations, including maintenance dredging, trawling, relocations of moorings, and other types of sediment disturbances.

2. The abundance and spatial distribution of organic booster biocides in antifouling paints, such as Irgarol 1051, diuron, dichlofluanid, and chlorothalonil (and other booster biocide compounds that were not assessed in the current investigation, such as zinc pyrithione and thiram) near marinas and other areas of high recreational boating activity in the Hawkesbury River system, has not been satisfactorily resolved. Due to the well-known toxicity of these TBT-replacement antifoulants, the demonstrated presence of diuron, and the likelihood of the presence of other booster biocide compounds, aquatic biota in the vicinity of these areas may be adversely affected. It may be possible that toxicity effects to aquatic biota in the vicinity of marinas that are not due to the presence of elevated concentrations of TBT, heavy metals or other commonly analysed organic compounds (i.e. PAHs, PCBs, OC pesticides), are the result of the presence of organic booster biocides in water and sediments. However, this link has not been established in the current investigation and would require additional assessments that identify these compounds and quantify their concentrations in water and sediments in the Hawkesbury River system. A hierarchical assessment, culminating in the determination of ecological risk of these compounds to the environment in the Hawkesbury River system may be warranted, based on the demonstrated prevalence of environmental effects in other areas of intense boating activity throughout the world.

Additional assessments would require substantially lower analytical limits of reporting (0.001 mg/kg in sediments and 0.001 μg/l in water) to allow direct comparisons with results from other studies worldwide and assess the potential ecological implications of the presence of organic booster biocides in environmental media in the Hawkesbury River system. Zinc pyrithione and thiram, which are both registered compounds in Australia, but which have not been assessed in the current investigation may also be included in future environmental assessments of marinas in the Hawkesbury River system.

3. The concentrations of contaminants in sediments at the proposed STP site at the Hawkesbury River road bridge are low, with the exception of mercury (0.2mg/kg) at one location (H40) (possibly due to road runoff), and generally similar to the concentrations of contaminants in the main Hawkesbury River channel. It is recommended to obtain additional sediment grab samples at these sampling locations (H40, H41 and H42), following the commissioning of the STP, at various time-points (e.g. 3 months, 6 months and 12 months post-commissioning) and analyse these samples for an identical suite of contaminants compared to the current investigation. This post-commissioning monitoring programme would allow an assessment of possible contaminant accumulation in sediments in the vicinity of the STP diffusers, as a result of particulate matter contributions from the STP discharge. However, based on the findings of the current investigation it is unlikely that fine particulate matter from the STP discharge would accumulate in the vicinity of the Hawkesbury River road bridge because of the high energy environment prevalent in the

Section 6 Recommendations

centre of the Hawkesbury River channel. Large tidal movements and high velocity currents in the main river channel has resulted in generally sandy substrate with abundant shells and corals and few fine particulates.

4. The presence of high total organic carbon contents in excess of 12% in sediments in lower Berowra Creek downstream of Calabash Bay (H3 to H7) is unlikely to be due to organic-rich contributions of particulate matter from sewage or stormwater discharges, because the concentrations of contaminants, in particular heavy metals, in these sediments are generally low. Concentrations of silver in surficial sediments in lower Berowra Creek have shown to be at or below the analytical limit of reporting (0.1mg/kg), which suggests that the elevated TOC contents in these sediments may be the result of natural organic matter contributions from the surrounding National Park. However, the source of the organic carbon and a confirmation of its natural origin would require additional sampling and analysis of sediments in the vicinity of known stormwater discharge points in Berowra Creek, to establish if there is a spatial gradient in the TOC content in surficial sediments and a decrease in TOC content with distance from the inferred discharge source.

5. The bioavailability of TBT and other inorganic and organic contaminants in sediments in the vicinity of known point sources (i.e. marinas) and the potential effects on aquatic biota are currently poorly understood in the Lower Hawkesbury River estuary. Further research into the ecotoxicological effects of bioavailable contaminant sources near marinas would therefore provide additional information and maximize the efficiency of estuary management of the Lower Hawkesbury River.

6. Analytical procedures for the quantification of booster biocide compounds in sediments need to be further developed before a more detailed spatial assessment of the distribution of these compounds in sediments of the Lower Hawkesbury River estuary can be undertaken.

7. A compilation of the usage profiles and availability of booster biocide compounds in registered antifoulant products available in Australia may provide further information about the likelihood of these compounds to be present in sediments and water near marinas and other areas of high commercial and recreational boating within the Lower Hawkesbury River estuary.

8. Long-term monitoring in high priority oyster lease areas via sampling and analysis of sediments for inorganic and organic contaminants may be necessary to ascertain that contaminants do not accumulate in these areas over time.

Section 7 References

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Section 8 Limitations

URS Australia Pty Ltd (URS) has prepared this Final Report in accordance with the usual care and thoroughness of the consulting profession for the use of Hornsby Shire Council and only those third parties who have been authorised in writing by URS to rely on the Final Report. It is based on generally accepted practices and standards at the time it was prepared. No other warranty, expressed or implied, is made as to the professional advice included in this Final Report. It is prepared in accordance with the Proposal dated 29 August 2006 and the Sampling and Analysis Plans for the Sediment Study (Stage 1) and Antifoul Study (Stage 2).

The methodology adopted and sources of information used by URS are outlined in this Final Report. URS has made no independent verification of this information beyond the agreed scope of works and URS assumes no responsibility for any inaccuracies or omissions. No indications were found during our investigations that information contained in this Final Report as provided to URS was false.

This Final Report was prepared between 15 April and 8 October 2007 and is based on the conditions encountered and information reviewed at the time of preparation. URS disclaims responsibility for any changes that may have occurred after this time.

This Final Report should be read in full. No responsibility is accepted for use of any part of this report in any other context or for any other purpose or by third parties. This Final Report does not purport to give legal advice. Legal advice can only be given by qualified legal practitioners.

Appendix A Sediment Study (Stage 1) – Final Report

Appendix B

Sediment Study (Stage 1) - Sampling and Analysis Plan