Scientific Report

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### Executive summary

The Yarra Estuary is located in the City of Melbourne and contains the major operating Port of Melbourne in its lower section. The estuary catchment is diverse, with natural vegetation in the upper areas, agriculture in the mid sections and a highly urbanised environment in the lower catchment. The estuary is a narrow, permanently open, salt-wedge system that discharges into Port Phillip Bay.

This report is a literature review outlining the current state of knowledge on the origin, fate and dispersion of toxicants within the Yarra Estuary. In terms of this review toxicants have been defined in accordance with ANZECC and ARMCANZ (2000) as:

'Chemicals capable of producing an adverse response (effect) in a biological system at concentrations that might be encountered in the environment, seriously injuring structure or function or producing death'.

This includes both naturally occurring chemicals as well as those manufactured or introduced to the environment by human activities. Examples include heavy metals, pesticides, herbicides and aromatic hydrocarbons.

Toxicants within the Yarra Estuary have been studied for over three decades. Although there is some spatial bias in the sampling, the following conclusions can be made:

- Concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc, PAH, PCB, TBT and DDT in sediments have each exceeded the ANZECC and ARMCANZ Interim Sediment Quality Guidelines (ISQG) -Low levels on occasion.
- Concentrations of arsenic, lead, mercury, nickel, zinc and DDT in sediments have exceeded ISQG-High levels in the last decade.
- Concentrations of some metals (arsenic, cadmium, chromium, lead, mercury nickel and zinc) in the water column have exceeded SEPP objectives on at least one occasion in the last decade. However, on average they are generally within SEPP objectives.
- The majority of metals in the water column are in particulate form, with the exception of arsenic and nickel which are mostly in dissolved forms.
- Concentrations of organic toxicants in the water column are below detection or reporting limits.
- Concentrations of metals within fish are within guideline levels.
- Concentrations of organic toxicants in fish are mostly within guideline levels, with the exception of a few short-finned eels sampled that exceeded guideline values for PCBs.
- Compared to other estuaries nationally and globally, the Yarra Estuary contains comparable concentrations of most toxicants. However, compared to results reported for estuaries worldwide, the Yarra contains higher concentrations of arsenic and nickel, and higher concentrations of DDT in the sediments.
- Urban and industrial stormwater entering the estuary from the city and the catchment is the dominant source of toxicants. Most of the toxicants enter during high flow events following heavy rainfall.
- Natural sources are likely for arsenic (and possibly nickel) rather than human activities in the catchment.
- The sediment is the major sink of toxicants in the estuary with the greatest concentrations in the surficial fine, unconsolidated sediments. Evidence from the lower estuary indicates that disturbance of the sediment does not result in the release of high concentrations of bioavailable toxicants into the water column.
- Results of toxicity testing indicate that surficial sediments (in the lower estuary) are toxic to marine biota. However, the sediments that were tested were largely removed from the estuary during the Channel Deepening Project (CDP).

Given the large amount of data available for the system, recommendations for future monitoring and investigation are limited. While there is not a complete understanding of all aspects of toxicant presence and behaviours within the system, recommendations for extensive scientific studies to fully model loads or processes are not warranted. Evidence to date suggests a low risk to the beneficial uses and values of the Yarra Estuary from toxicants, and as such, continued intensive monitoring is not justified. Recommendations related to the state of knowledge of toxicants within the Yarra Estuary are to:

- investigate the status and likelihood of the release of toxicants in the upper and mid estuary
- continue periodic assessments of toxicants within the Yarra Estuary, adopting a multiple lines and levels of evidence approach. Methods to be considered in the design of such a monitoring program include deployed mussels, fish, sediment, groundwater and water column measures.

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### 1. Introduction

### 1.1 Background

The Yarra River is a major waterway and natural feature of Melbourne's landscape. It has shaped Melbourne's development and growth, supports industry and tourism, and is highly valued as an environmental and recreational asset.

In 2006 the Environment Protection Authority (EPA) Victoria developed the Yarra River Investigation and Response Program (YRIRP). This program was aimed at increasing our understanding of water quality in the Yarra River and reducing pollutant inputs, particularly from industrial and commercial sources. Over the four years of YRIRP (2006 to 2010) the program focused on scientific analysis and investigations, social research, knowledge transfer and partnerships with statutory enforcement, all aimed at improving the amenity of the Yarra River.

This report is a literature review outlining the current state of knowledge on the origin, fate and dispersion of toxicants in the lower sections of the Yarra River, henceforth referred to as the Yarra Estuary.

### **1.2 Objectives**

The objectives of this review were to:

- summarise the current state of knowledge with respect to toxicants in the Yarra Estuary
- explore the potential sources of the toxicants found within the Yarra Estuary
- determine the likely fate of those toxicants with respect to physical and biological processes
- benchmark this knowledge with similar urban estuarine environments
- identify any potential issues relating to toxicants within the Yarra Estuary and recommend future actions to address knowledge gaps.

### 1.3 Scope and definitions

For the purposes of this review the Yarra Estuary is defined as the extent of the lower Yarra River that is under tidal influence. The estuary can be considered to start downstream of Dights Falls, a weir across the Yarra that causes pooling of freshwater upstream and forms an effective barrier against salt water intrusion and tides. The estuary extends some 22 kilometres downstream to Williamstown, where the river discharges into Hobsons Bay (Figure 1).

Toxicants are defined in accordance with ANZECC and ARMCANZ (2000) as:

'Chemicals capable of producing an adverse response (effect) in a biological system at concentrations that might be encountered in the environment, seriously injuring structure or function or producing death'.

This includes both naturally occurring chemicals as well as those manufactured or introduced to the environment by human activities. Examples include heavy metals, pesticides, herbicides and aromatic hydrocarbons.

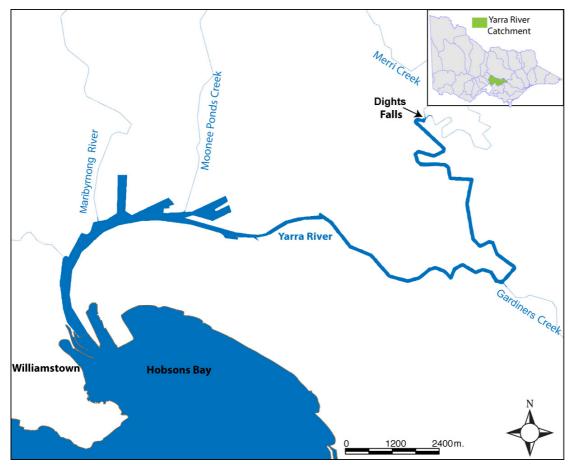


Figure 1: Yarra River Estuary, extending from Dights Falls to Hobsons Bay.

### 1.4 Structure of this report

To meet the objectives as provided in section 1.2 above this report has been structured as follows:

#### Section 2: The Yarra Estuary

Describes the location, catchment setting and physical attributes of the Yarra Estuary.

#### Section 3: Toxicants in the Yarra Estuary

Provides a summary of the historical and current data related to the state of toxicants in the sediments, water column and biota of the Yarra Estuary. Comparisons are made to relevant guideline values and other estuaries within Australia and internationally.

#### Section 4: Origin of toxicants

Provides an overview of the evidence related to potential sources of toxicants within the Yarra Estuary including from catchment, industry, stormwater and atmospheric inputs.

#### Section 5: Fate of toxicants

Describes the potential pathways for toxicant storage and dispersal within the Yarra Estuary, drawing on direct evidence from the site and elsewhere. Known ecological effects of toxicants of concern in the system are presented and the potential impact to ecosystem health discussed.

#### Section 6: Toxicants in the Yarra Estuary in context

Compares the toxicants within the Yarra Estuary to other comparable systems both within Australia and internationally.

#### Section 7: Key issues and recommendations

Highlights the key findings, identifies knowledge gaps and provides recommendations to fill important knowledge gaps.

### 2. The Yarra Estuary

### 2.1 Catchment and influences

The Yarra is the major river flowing through the city of Melbourne. The catchment lies to the northeast of the city and covers approximately 4000 km<sup>2</sup> (Sokolov and Black 1999; Carty and Pierotti 2010). Land use is variable, with around 40% of the total area retaining natural vegetation cover, mostly in the upper catchment. The mid sections are predominantly agricultural land (grazing and cropping) and over 20% of the catchment area is urbanised, mostly in the lower sections, including all of the area immediately adjacent to the estuary (Carty and Pierotti 2010). The Yarra River is a regulated watercourse with major water storages on the main stem and major tributaries. There is also significant extraction via pumping and interception of water by farm dams (Carty and Pierotti 2010).

There are a number of tributaries to the Yarra River, three of which join the main stem within the estuary area: Gardiners Creek, Moonee Ponds Creek and the Maribyrnong River (see Figure 1 above). The estuary also receives direct stormwater discharge from the adjacent industrial and urban areas (Beckett et al. 1982).

### 2.2 Hydrology and physical characteristics

The Yarra Estuary is narrow (30 to 120 m wide) and naturally shallow (maximum depth of 8 m) (Bruce et al. 2011). For most of the length of the estuary, the banks have been rock-stabilised, and little remains of the natural bank and riparian zone (SKM 2005). The lower portion of the estuary has been physically modified into a series of docks and wharves, with the first major modifications occurring in the 1880s, which included straightening the course and dredging to increase depth, making it navigable for shipping (PoMC 2011). Various modifications have been made since that time to accommodate shipping in the downstream end of the estuary. In 2008 and 2009 the navigable depth was increased to a maximum of 15.5 m under the Channel Deepening Project, which removed approximately five million m<sup>3</sup> from the estuary and berths (PoMC 2009).

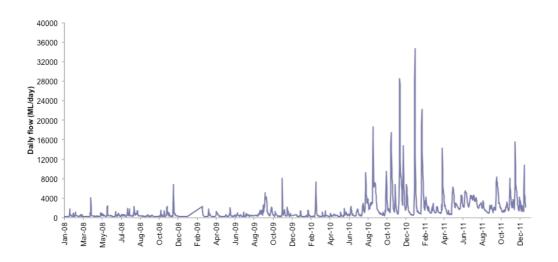
The sediments of the Yarra Estuary vary from upstream to downstream sections with fluvial and marine influences reflected in grain size and composition. The upper estuary (nearest to Dights Falls) has a higher proportion of coarser sediments with eight to 30 per cent fine clays and silt. The proportion of fine sediments increases as you move downstream to over 90 per cent silts and clays just upstream of the port areas (Ellaway et al. 1982). Within the lower estuary, there is a layer of unconsolidated, fine grain sediment that is thin in mid-channel (< 0.5 m depth) but thicker in the edge silt traps (up to 2 m depth) (URS 2007). Closer to Hobsons Bay marine influences can be seen, with an increase in shell fragments and sand (Poore and Kudov 1978).

The defining characteristic of estuarine systems is the dual influences of freshwater flows from the catchment and tidal intrusion of saline, marine waters. The interactions between these two major sources of water in the Yarra Estuary were first comprehensively described by Beckett et al. (1978 and 1982). This was expanded on by SKM (2005) to include changes in hydrology due to water resource development in the catchment, and a three-dimensional, hydrodynamic model of the estuary was developed by Lawson and Treloar (2004). In addition, Bruce et al. (2011) used a three-dimensional, open source General Estuarine Transport Model to explore aspects of the hydrodynamics and water quality of the Yarra Estuary, and models have been developed for the catchment and receiving waters of Port Phillip Bay (Lawson and Treloar 2004; Carty and Pierotti 2010; EPA 2012).

The Yarra Estuary is a permanently open, river dominated estuary that discharges into a sheltered Bay. River flow is permanent, but highly variable over seasonal and longer climatic scales. River flow is generally higher in winter and spring, and lower in summer and autumn (Beckett et al. 1982). Total annual flow from 1979 to 2008 in the Yarra River varied from less than 150 GL to over 1000 GL (Carty and Pierotti 2010). However, these measurements were recorded upstream and did not account for flow entering the estuary from the Maribyrnong River, which over the same period varied from less than 10 GL to over 200 GL per annum (DSE 2011). The variability in flow is illustrated in Figure 2, which shows the difference in daily flow during drought conditions, followed by above average rainfall.

While Figure 2 includes flow from both the Yarra and Maribyrnong Rivers entering the estuary, it does not provide an indication of stormwater inputs from the adjacent city area (downstream of flow gauging stations), for which there are no estimates.

Water enters the estuary from Port Phillip Bay on semidiurnal tidal cycles. Port Phillip Bay is a large basin with a narrow connection to the Southern Ocean through the Heads in the south at some distance from the Yarra Estuary, which discharges into the north of the Bay. As such, tidal fluctuations are smaller in the estuary than the open ocean and than those experienced within southern parts of the Bay. Tides at the estuary mouth have an average range of around 0.5 m but can vary from 0.3 to 0.8 m (Beckett et al. 1978).

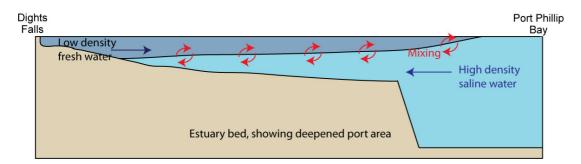


## Figure 2: Total flow (Yarra and Maribyrnong Rivers) from June 2008 to December 2011 (EPA 2012).

The interaction of fresh river flow and saline marine tides creates a salt wedge within the Yarra Estuary. The three dimensional hydrodynamic model of Lawson and Treloar (2004) described three distinct layers (Figure 3):

- an upper layer of fresh, river water constantly flowing downstream
- a lower layer of denser, saline water, moving upstream on the flood tide and downstream on the ebb tide
- a middle, mixed layer of intermediate density that moves downstream with the freshwater layer, gradually thickening until the freshwater layer disappears.

The position and behaviour of this salt wedge is affected by both flow volume and tidal magnitude (Lawson and Treloar 2004). During periods of low and medium flows (< 2000 ML/day), the thin (1-2 m deep) freshwater (< 5 ppt) layer does not extend much below the Maribyrnong River confluence. However, under high flow conditions, the freshwater layer extends down the entire estuary. Similarly, low flow and high tide conditions can extend the lower saline layer along the entire estuary (to just below Dights Falls). However, during high flow conditions (flow of > 9000 ML/day) the saline layer extends only as far upstream as just beyond the Moonee Ponds Creek confluence (Beckett et al. 1978).



## Figure 3: Salt wedge formation in the Yarra Estuary (adapted from Beckett et al. 1982 and Lawson and Treloar 2004).

Residence times vary under different flow conditions and in surface and bottom layers, and were estimated by Beckett et al. (1982). During periods of high flow, water in both layers is likely to be exchanged within a couple of days. Under medium flow conditions, the surface layer has a residence time of less than a day, but the bottom layer may take up to two weeks to be exchanged. Under low flow conditions (which occurred for much of the last decade) residence times are likely to be in the order of several weeks for both layers.

Position in the estuary also affects residence times, with the upstream sections of the estuary (above Gardiners Creek) experiencing longer residence times than downstream sections under more tidal influences. As a consequence, residence times of bottom waters in these upstream sections, under low flow conditions, are likely to be in the order of weeks or

months (Mike Grace, Monash University, personal communication, May 2012).

Residence time affects other water quality parameters, most notably dissolved oxygen. Under high flow conditions, water is rapidly exchanged and oxygen levels remain high throughout the water column. However, under prolonged conditions of low flow, when residence time is long, bottom waters do not get regularly replenished with oxygenated water and anoxic conditions can prevail (Bruce et al. 2011). This can have an effect on the fate of toxicants within the estuary and this is discussed further in section 5.

### 3. Toxicants in the Yarra Estuary

Evidence for toxicants within the Yarra Estuary comes from the sampling of three mediums: the sediment, water column and biota. Toxicants can move between the sediment, water column and biota, but this is considered in section 5 (Fate of toxicants).

### 3.1 Sediment

There have been a large number of investigations that have assessed toxicants in the sediments of the Yarra Estuary. This includes early work by Milne (1975), Smith and Milne (1979), Bagg et al. (1981) and Ellaway et al. (1982) in the 1970s; investigations during the Port Phillip Bay (PPB) Environmental Study in the early and mid-1990s (Fabris et al. 1995; Good and Gibbs 1995) and a large body of work commissioned by the Port of Melbourne for maintenance dredging campaigns and the Channel Deepening Project (CDP) (Kowarsky 2001; Kowarsky and Associates 2002; SKM 2004; Kowarsky 2005; URS 2007).

Despite the breadth of sampling, there is insufficient data to statistically assess trends or patterns (spatial or temporal) as most studies collected a small number of samples without replicates. The only exception to this is the CDP sampling (SKM 2004; URS 2007), which included a very large number of samples and replicates (135 sample locations with separate analysis of depth profiles), but over a relatively small spatial area (all downstream of Spencer Street Bridge within the port area) and time frame (2003 to 2006). In addition, comparisons between studies are hampered by differences in sampling and analytical techniques. For example, Ellaway et al. (1982) separated sediments into grain size fractions by sifting, then analysing each of the fractions separately, making the results incomparable to those of whole sediment analyses. ANZECC and ARMCANZ (2000) guideline values for organic toxicants have been normalised to 1% organic carbon content and since the release of the guidelines, reporting of these chemicals has been corrected for variations in organic carbon. However, samples collected prior to 2000 are mostly reported without the correction, again making comparisons between studies difficult. Due to these difficulties a more descriptive approach has been adopted and descriptive statistics and comparisons with the ANZECC and ARMCANZ (2000) interim sediment quality guidelines (ISQG) are provided for metals and organic toxicants from a selection of studies for which data could be sourced (Table 1 and Table 2). The ISQG-Low values indicate that there is a low to medium level of risk at these values, whereas the ISQG-High values indicate there is a high level of risk if sediments are at or above these values.

Guideline (trigger) values have been exceeded on at least one occasion for each of the metals presented in Table 1. Mean values for sediment concentrations are above guideline values for lead, mercury, nickel and zinc in both the port area and in the upper sections of the estuary. Maximum concentrations have also been recorded that are above the ISQG-High values for these metals, which indicates a potential risk to the aquatic ecosystem. However, it should be noted that there is a wide range in concentrations of all metals across all studies and that the levels in many samples were low or below detectable limits.

Non-metal, inorganic toxicants such as cyanide, sulphide and ammonia were measured during CDP sampling (SKM 2004; URS 2007). There are no sediment guidelines for these toxicants as the vast majority of total ammonia, total sulphide and total cyanide in marine waters and sediments exist in non-toxic forms. For example, at 15 degrees Celsius and a pH of 7.8, 98 % of the total cyanide is in un-ionised, non-toxic form (ANZECC and ARMCANZ 2000). Mean concentrations of total cyanide in the lower estuary were 0.5 mg/kg and maximum concentrations were approximately 5 mg/kg. Total ammonia had a mean concentration of around 40 mg/kg and a maximum of 230 mg/kg (URS 2007). Total sulphide had a mean concentration of around 3 mg/kg and a maximum of 160 mg/kg (SKM 2004).

Table 1: Descriptive statistics for concentrations of metals (mg/kg) within sediments in the Yarra Estuary. Yellow shading indicates the concentration is above the ISQG-Low values and red shading indicates the concentration is above the ISQG-High values (ANZECC and ARMCANZ 2000).

Toxicant	Date	Min	Max	Mean	Location
Arsenic	2003³	2	20	16	Downstream of Spencer St Bridge
	2005 <sup>4</sup>	7	12	9	Upstream of Melbourne City Centre
	<b>2006</b> ⁵	0.3	22	7.2	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	2006⁵	0.1	150	6.8	Downstream of Spencer St Bridge (consolidated clay - deep)
Cadmium	1995²	0.05	1.45	0.55	Downstream of Spencer St Bridge (Port Area)
	2003³	< 0.05	0.84	0.36	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>4</sup>	0.5	<mark>1.8</mark>	0.7	Upstream of Melbourne City Centre
	2006⁵	< 0.05	1.2	0.3	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	<b>2006</b> ⁵	< 0.05	0.6	0.1	Downstream of Spencer St Bridge (consolidated clay - deep)
Chromium	1995²	24	51	34	Downstream of Spencer St Bridge (Port Area)
	2003 <sup>3</sup>	11	110	63	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>4</sup>	23	41	31	Upstream of Melbourne City Centre
	2006⁵	7	94	35	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	<b>2006</b> ⁵	9	280	29	Downstream of Spencer St Bridge (consolidated clay - deep)
Copper	1979 <sup>1</sup>	5	12	7.2	Downstream of Spencer St Bridge (Port Area)
	1995²	22	78	47	Downstream of Spencer St Bridge (Port Area)
	2003 <sup>3</sup>	12	89	49	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>₄</sup>	48	67	58	Upstream of Melbourne City Centre
	<b>2006</b> ⁵	1	63	27	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	<b>2006</b> ⁵	0.5	25	13	Downstream of Spencer St Bridge (consolidated clay - deep)
Lead	1979 <sup>1</sup>	36	<mark>179</mark>	87	Downstream of Spencer St Bridge (Port Area)
	1995²	13	187	87	Downstream of Spencer St Bridge (Port Area)
	2003 <sup>3</sup>	6	150	55	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>₄</sup>	92	240	128	Upstream of Melbourne City Centre
	<b>2006</b> ⁵	3	98	40	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	<b>2006</b> ⁵	4	20	10	Downstream of Spencer St Bridge (consolidated clay - deep)

Mercury	1995²	0.11	2.23	0.45	Downstream of Spencer St Bridge (Port Area)
	2003³	<0.01	<mark>0.28</mark>	0.19	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>4</sup>	0.12	<mark>0.36</mark>	0.17	Upstream of Melbourne City Centre
	2006⁵	0.01	1.00	0.15	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	2006⁵	0.01	0.07	0.01	Downstream of Spencer St Bridge (consolidated clay - deep)
Nickel	1995²	19	58	28	Downstream of Spencer St Bridge (Port Area)
	2003 <sup>3</sup>	6	68	24	Downstream of Spencer St Bridge (Port Area)
	2005 <sup>₄</sup>	19	30	24	Upstream of Melbourne City Centre
	2006⁵	2	120	25	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	2006⁵	1	97	26	Downstream of Spencer St Bridge (consolidated clay - deep)
Zinc	1979 <sup>1</sup>	44	347	152	Downstream of Spencer St Bridge (Port Area)
	1995²	73	516	239	Downstream of Spencer St Bridge (Port Area)
	2003 <sup>3</sup>	8	430	182	Downstream of Spencer St Bridge (Port Area)
	2005⁴	640	850	704	Upstream of Melbourne City Centre
	2006⁵	4	250	78	Downstream of Spencer St Bridge (unconsolidated silt - surface)
	2006⁵	2	<mark>360</mark>	34	Downstream of Spencer St Bridge (consolidated clay - deep)

<sup>1</sup>Smith and Milne (1979); <sup>2</sup>Fabris et al. (1995); <sup>3</sup>SKM (2004); <sup>4</sup>Melbourne Water (2005); <sup>5</sup>URS (2007).

There are also incidents of guideline exceedence for organic toxicants in the sediments (Table 2). Of particular note is the high concentrations of DDT in sediments within the port area of the estuary both in the 1990s and recently. There is some evidence that other organic chemicals such as PCBs, TBT and TPHs have declined in concentration over the last decade. This is particularly evident for PCBs, which were recorded in high concentrations in the 1980s and during the PPB Environmental Study, but were largely below the limits of reporting in 2003 and 2006 (SKM 2004; URS 2007) and only in very low concentrations in 2009 (O'Brien 2009 as cited by van Gelderen and Pettigrove 2011). Similarly, two types of PAH, benzo(a)pyrene and perylene, were measured in sediments along the Yarra Estuary in 1976 in relatively high concentrations (maximum over 3000  $\mu$ g/kg for each, Bagg et al. 1981, see Figure 4 below). However, samples of surficial sediments collected in 2003 and 2006 were predominantly below the limit of reporting for these two toxicants and maximum concentrations were 650 and 300  $\mu$ g/kg, respectively (SKM 2004; URS 2007) representing a significant decline. This decline is probably best explained by the ban on PCB use in Australia since 1979.

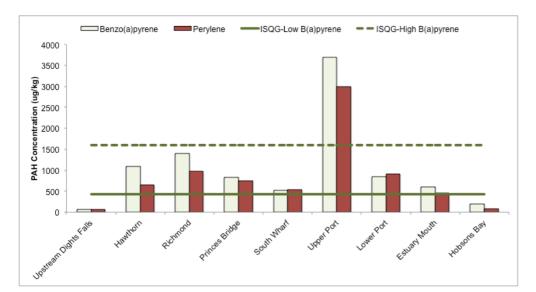
Table 2: Descriptive statistics for concentrations of organic toxicants (mg/kg except where specified) within sediments in the Yarra Estuary. Yellow shading indicates the concentration is above the ISQG-Low values and red shading indicates the concentration is above the ISQG-High values (ANZECC and ARMCANZ 2000). Note there are no guideline values for TPH, and the majority of the data pre-2000 have not been corrected for organic carbon content. LOR = Limit of reporting.

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<sup>1</sup>van Gelderen and Pettigrove (2011); <sup>2</sup>Harris et al. (1995); <sup>3</sup>SKM (2004); <sup>4</sup>Melbourne Water (2006); <sup>5</sup>URS (2007).

Despite the limited number of samples in the mid and upper estuary, many researchers have noted a gradient in toxicants

within the sediments of the Yarra Estuary. In general toxicants are lower in the upper reaches (above the Gardiners Creek confluence), higher in the vicinity of the city and the port area, and lower again as the estuary enters the wider Bay (Bagg et al. 1981; Ellaway et al. 1982; Harris et al. 1996; O'Brien 2009 as cited by van Gelderen and Pettigrove 2011). This is illustrated by the concentration of two PAHs in the sediments collected in 1976 (Bagg et al. 1981; Figure 4), which also illustrates the higher concentrations of toxicants in the estuary as compared to the river above Dights Falls, and the more marine areas of Hobsons Bay.



## Figure 4: Concentrations of two PAHs; benzo(a)pyrene and perylene, in sediments along the Yarra Estuary in 1976 (Bagg et al. 1981). Note that there are no ISQG values for perylene.

Most samples collected have been from surficial sediments, variously described as fine silt or unconsolidated sediments. However, in the Port of Melbourne area, deep cores were collected at a number of sites with unconsolidated sediments analysed separately to deeper, stiff clays. In general, the deeper sediments contained lower concentrations of toxicants, with the exception of isolated samples. Mean concentrations of both metal and organic toxicants in the surficial, unconsolidated sediments above guideline values lead to the description of these sediments within the port area as 'moderately contaminated' (SKM 2004), consistent with the findings of Fabris et al. (1995) in the PPB Environmental Study.

Of note is that the most recent sediment investigations within the port area were undertaken prior to the CDP project. During 2008 and 2009, over five million m<sup>3</sup> of sediment was removed from the lower Yarra Estuary by the CDP and transported to a dredge material ground in Port Phillip Bay. This program removed the vast majority of the unconsolidated "moderately contaminated" sediments as well as variable amounts of the underlying stiff clays, which were mostly lower in toxicant concentrations. It remains unknown if the sediments within the Yarra Estuary remain "moderately contaminated" or if the CDP project removed the majority of the toxicant load stored in the sediments of the port area to the dredge spoil ground.

Although there are less data for sediment toxicant levels in areas of the Yarra Estuary outside the port, results from the 2003 investigation upstream of the city centre around the Gardiners Creek confluence, indicate sediments had mean concentrations of lead, mercury and nickel above ISQG-Low and zinc above ISQG-High values (Melbourne Water 2005). In addition, this study found the presence of PCBs (at levels below ISQG-Low values) and concentrations of TPH comparable to those within the port area. This data would suggest that sediments in the upper and middle sections of the estuary could also be considered contaminated.

### 3.2 Water column

Measurements of toxicants in the water column within the Yarra Estuary have been less than that for sediments, both in terms of sample numbers as well as the toxicants tested. Early work by Hart and Davies (1981) included a small number of metals at a single site in the mid estuary, and Butler and Smith measured arsenic at three sites in the early 1980s. The Port Phillip Bay Environmental Study included a single site in the Yarra port area for metals and organic toxicants (Fabris and Monahan 1995; Good and Gibbs 1995). In more recent times, the Port of Melbourne Corporation commissioned water quality monitoring in the port area as part of the CDP with organic toxicants measured in 2005 and metals from 2005 to 2011 (Enesar 2005; PIRVic 2007; EPA unpublished). Melbourne Water (unpublished) measured metal concentrations in the mid estuary (at Southbank) from 2000 to 2011.

As for sediments, the data for toxicants in water is not suitable for determining statistical trends spatially or over time, so descriptive statistics and comparisons with SEPP (Waters of Victoria) objectives have been made. Note that there are two SEPP (Waters of Victoria) objectives that apply to the Yarra Estuary. Schedule F7 Waters of the Yarra Catchment applies to

the upstream portion of the estuary, upstream of a point roughly equivalent to the confluence with Moonee Ponds Creek (the Bolte Bridge); and F6 Waters of Port Phillip Bay applies downstream of this point. Comparisons with SEPP have applied the relevant objectives dependent on the location of sampling sites.

Summary statistics for metal concentrations indicate values above SEPP objectives recorded on at least one occasion for all metals in Table 3. For toxicants such as arsenic, cadmium, chromium, mercury and nickel, the higher concentrations represent isolated samples. Also, average conditions are generally below guideline levels and often below the limits of reporting.

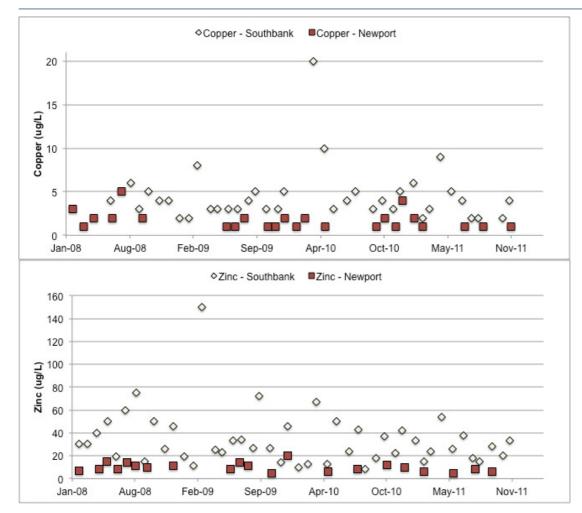
# Table 3: Descriptive statistics for concentrations of metals ( $\mu$ g/L) within the water column of the Yarra Estuary. Yellow shading indicates the concentration is above the SEPP objective. LOR = Limit of reporting.

Toxicant	Date	Total		Disso	lved	Location
		Max	Mean	Max	Mean	
Arsenic	1980 <sup>1</sup>	1.1	0.7			Three sites, surface water
	1995²		0.4		0.2	Single site in port following rain event
	2000-11 <sup>3</sup>	20	3.5			Single site at Southbank
	20064	3.1	2.3			57 samples in the port and lower estuary
	2008-11⁵	3.4	2.3	3.4	2.2	Single site downstream of Westgate Bridge
Cadmium	1976 <sup>6</sup>	0.50	0.37	0.37	0.27	Single site upstream of city centre
	1995²		0.05		0.02	Single site in port following rain event
	2000-11 <sup>3</sup>	4	<lor< td=""><td></td><td></td><td>Single site at Southbank</td></lor<>			Single site at Southbank
	20064	<lor< td=""><td></td><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>				57 samples in the port and lower estuary
	2008-11⁵	<lor< td=""><td></td><td></td><td></td><td>Single site downstream of Westgate Bridge</td></lor<>				Single site downstream of Westgate Bridge
Chromium	1995²		0.4		0.2	Single site in port following rain event
	2000-11 <sup>3</sup>	21	3.8			Single site at Southbank
	2006⁴	5	<lor< td=""><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>			57 samples in the port and lower estuary
	2008-11⁵	3.3	<lor< td=""><td><lor< td=""><td></td><td>Single site downstream of Westgate Bridge</td></lor<></td></lor<>	<lor< td=""><td></td><td>Single site downstream of Westgate Bridge</td></lor<>		Single site downstream of Westgate Bridge
Copper	1976 <sup>6</sup>	7.2	5.2	5.6	4.1	Single site upstream of city centre
	1995²		2.7		1.7	Single site in port following rain event
	2000-11 <sup>3</sup>	30	6.8			Single site at Southbank
	2006⁴	3	<lor< td=""><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>			57 samples in the port and lower estuary
	2008-11 <sup>5</sup>	4	<lor< td=""><td>3</td><td><lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<></td></lor<>	3	<lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<>	Single site downstream of Westgate Bridge

Lead	1976 <sup>6</sup>	22	19	11	6	Single site upstream of city centre
	1995²		4.6		1.1	Single site in port following rain event
2000-11 <sup>3</sup>		25	5			Single site at Southbank
	2006 <sup>4</sup>	2.7	<lor< td=""><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>			57 samples in the port and lower estuary
	2008-11 <sup>5</sup>	1.4	0.5	0.6	<lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<>	Single site downstream of Westgate Bridge
Mercury	1995²		0.007		0.004	Single site in port following rain event
	2005 <sup>7</sup>	0.13	<lor< td=""><td><lor< td=""><td></td><td>Three sites in the port area</td></lor<></td></lor<>	<lor< td=""><td></td><td>Three sites in the port area</td></lor<>		Three sites in the port area
	20064	<lor< td=""><td></td><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>				57 samples in the port and lower estuary
	2008-11 <sup>5</sup>	0.1	<lor< td=""><td>0.1</td><td><lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<></td></lor<>	0.1	<lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<>	Single site downstream of Westgate Bridge
Nickel	1995²		3.2		1.8	Single site in port following rain event
	2000-11 <sup>3</sup>	32	6.5			Single site at Southbank
	2006⁴	<lor< td=""><td></td><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>				57 samples in the port and lower estuary
	2008-11 <sup>5</sup>	29	8.4	3.7	1.2	Single site downstream of Westgate Bridge
Zinc	19766	89	61	55	38	Single site upstream of city centre
	1995²		24		4	Single site in port following rain event
	2000-11 <sup>3</sup>	200	38			Single site at Southbank
	2006⁴	13	<lor< td=""><td></td><td></td><td>57 samples in the port and lower estuary</td></lor<>			57 samples in the port and lower estuary
	2008-11 <sup>5</sup>	20	6	17	<lor< td=""><td>Single site downstream of Westgate Bridge</td></lor<>	Single site downstream of Westgate Bridge

<sup>1</sup>Butler and Smith (1985); <sup>2</sup>Fabris and Monahan (1995); <sup>3</sup>Melbourne Water (unpublished); <sup>4</sup>Hale (2006) <sup>5</sup>EPA (unpublished); <sup>6</sup>Hart and Davies (1981); <sup>7</sup>Enesar (2005).

Concentrations of metals such as copper and zinc appear to be considerably higher in the mid and upper sections of the estuary than in the port area. This is evidenced by consistently higher concentrations recorded by sampling conducted by Melbourne Water (unpublished) in the area adjacent to the city centre, than in the samples collected by EPA (unpublished) and in the port area (Figure 5). This is supported by the early work of Hart and Davies (1981), who recorded relatively high concentrations of copper, lead and zinc in the upper estuary area in the 1970s. The elevated concentrations of copper and lead in the Yarra Estuary, although above SEPP objectives, are below the National Health and Medical Research Council's screening levels for chemicals in recreational water, both for aesthetics and public health measurements (Yarra and Maribyrnong Rivers Steering Committee 2005).



## Figure 5: Comparison of total metal concentrations (copper and zinc) in waters of the Yarra Estuary (2008 to 2011) from the mid section (Southbank) and the lower section (port area).

There is little information on non-metal inorganic toxicants in the Yarra Estuary. Total ammonia, of which a small fraction (< 10%) would be present as the toxic ammonia (NH<sub>3</sub>) as opposed to the non-toxic ammonium (NH<sub>4</sub><sup>+</sup>), is consistently an order of magnitude below ANZECC/ARMCANZ (2000) guideline values for toxicants (EPA unpublished).

There is insufficient data to provide a quantitative description of organic toxicants in the waters of the estuary as is provided for metals above. However, it is likely that concentrations of these toxicants are low. The PPB Environmental Study did not record any concentrations of organic toxicants above guideline levels at any site, including the Yarra Estuary (Harris et al. 1996). Results of over 50 samples from within the lower estuary and port area in 2006 indicated that all reported results for organo-chlorine pesticides, PAHs and TBT were below reporting limits (Hale 2006). Similarly, results from monthly sampling of three sites within the lower estuary/port area from 2004/5 for organo-chlorine pesticides found that all results (except for heptachlor at one site on one occasion) were below the limits of reporting. This lead Enesar (2005) to conclude that organo-chlorine pesticides were below SEPP objectives within estuary waters.

Concentrations of TBT in the water column have been measured in waters of the port area from 2005 to 2011 (Enesar 20056, PIRVic 2007; EPA unpublished) with the vast majority of samples being below the limit of reporting (and SEPP objectives). There is a single record for TBT equalling the SEPP objective (0.006 µg/L) in 2006 (PIRVic 2007).

#### 3.3 Biota

Aquatic biota provide an integrated record of toxicant concentrations, especially for chemicals that bioaccumulate within organisms (Harris et al. 1996). They provide a record of the presence of toxicants that may have been below detectable limits in the water column or passing through the system periodically, that may be undetected in snap-shot water sampling.

Although there is significant data on toxicant concentrations in aquatic biota from Port Phillip Bay (Phillips 1976; Walker 1982; Walker 1988; Nicholson et al. 1990; Fabris et al. 1991; Fabris 1995; Nicholson 1994; the ongoing Victorian Shellfish Quality Assurance Program; Gagnon and Holdway 2002; among others) there are few studies from within the Yarra Estuary itself. However, there has been a series of investigations undertaken by Melbourne Water (2006) and EPA (2007 and 2009) into toxicants in fish within the Yarra Estuary.

In 2005, fish from seven species were collected from sites in the upper estuary around the Gardiners Creek confluence. Metal results were within food safety guidelines (Australian and New Zealand food standards Maximum Residue Limit (MRL); see Table 4) and concentrations of PAHs and all pesticides and insecticides were below the limits of reporting (Melbourne Water 2005). A single eel was reported with a PCB congener concentration of 1.5 mg/kg above the MRL of 0.5 mg/kg. This resulted in additional sampling of eels and another specimen was found to be marginally over the MRL (total PCB 0.558 mg/kg). However, there is debate about the method in which the total PCB concentration was calculated and it is likely that the result was just below the MRL (Gelderen and Pettigrove 2011).

Investigations conducted in 2006 and 2009 (EPA 2007 and 2009) sampled fish at two locations from the lower estuary; one upstream and one downstream of the Westgate Bridge. Results were mostly similar to the earlier survey with low levels of toxicants in the flesh of the fish sampled. Metals were low and within guideline levels (Table 4) and there were no PAHs or organo-phosphate pesticides above the reporting limits in either survey (EPA 2009). Low levels of DDT were found in both surveys, but these were well below USEPA (2000) screening levels. The results for PCBs were mostly below the limits of reporting and all results were well below the MRL of 0.5 mg/kg (maximum values of < 0.1 mg/kg total PCB). The 2009 survey did not include eels, but in 2006 eels had higher levels of PCBs than other fish species, confirming the results of the 2005 survey (EPA 2007).

## Table 4: Descriptive statistics for concentrations of metals (mg/kg) within fish in the Yarra Estuary. LOR = Limit of reporting.

Toxicant	2005		2006		2009	
	Мах	Mean	Мах	Mean	Max	Mean
Arsenic (total)	2.0	0.65	3.1	1.5	2.4	1.6
Arsenic inorganic	< LOR	< LOR	< LOR	< LOR	< LOR	< LOR
Cadmium			< LOR	< LOR	< LOR	< LOR
Copper	0.25	0.17	0.63	0.27	0.19	0.17
Lead			0.03	< LOR	< LOR	< LOR
Mercury	0.26	0.12	0.18	0.09	0.11	0.09
Nickel					< LOR	< LOR
Zinc	8.7	5.0	12	7.7	4.6	4.0
Tributyltin			0.0024	0.0019	0.0075	0.0031

The Department of Human Services issued the following health advice for people who catch fish in the lower Yarra and Maribyrnong Rivers (OEM 2009):

- While it is safe to eat fish from the Lower Yarra and Maribyrnong Rivers, it is recommended that people limit themselves to four serves of fish a month and one serve of eel a month.
- Women of childbearing age and children should limit their fish consumption to one serve a month and should not eat eels from the Lower Yarra and Maribyrnong Rivers.

## 4. Origins of toxicants

The Yarra Estuary is situated adjacent to the City of Melbourne, which has a resident population of nearly one million people, and the estuary catchment encompasses the broader metropolitan area that supports a total of over four million people. It could therefore be assumed that urban and industrial inputs would contribute significantly to toxicants within the Yarra Estuary (Fabris et al. 1999). A historical site assessment compiled a summary of past industrial activities (1860s to 2000) and the chemicals associated with these activities. They identified a very large list of industries from petroleum refineries and gunpowder factories, to abattoirs and tanneries, and a total of 284 chemicals (Golder 2006). This supports the suggestions of Phillips et al. (1992) that the Bay (and lower Yarra River) have received atmospheric and water-borne industrial and urban toxicants for over 100 years. Although there is little information to quantify different sources of toxicants, a description can be provided of the likely pathways. The broad toxicant pathways and sources include:

- surface water inflows rivers, creeks, drains and stormwater
- direct inputs from shipping within the estuary
- groundwater discharges
- atmospheric deposition.

### 4.1 Surface water inflows

Urban stormwater has been identified as the current main source of heavy metals and petroleum hydrocarbons in the Yarra River (Yarra and Maribyrnong Rivers Steering Committee 2005), although historically there were large direct inputs from industries. The toxicants originate from a variety of sources such as vehicles, road run-off, industrial sites, galvanised rooves (which are a source of zinc), lead flashing and agricultural chemicals (Yarra and Maribyrnong Rivers Steering Committee 2005).

Land use is important in determining both the type and quantity of toxicants entering the system via stormwater drains and overland flow. Solokov and Black (1999) indicated that concentrations of copper, lead and zinc in the predominantly urbanised catchment of Gardiners Creek were significantly higher than those in the Yarra River. This lead to comparable loads from both sources, despite the lower volume of water entering from the creek system. This is supported by Pettigrove (2003) who noted that only 10 % of sites in urban streams in the Yarra Valley upstream of Dights Falls had one or more metals exceeding the ISQG values (ANZECC and ARMCANZ 2000), whilst 79 % of sites within Gardiners Creek had at least one metal that exceeded the guidelines. Overall, the work of Solokov and Black (1999) and Pettigrove (2003) suggests that most metals entering the lower Yarra arise from urban run-off and enter via the smaller direct streams (such as Gardiners and Merri Creeks) and presumably via stormwater drains, rather than via the Yarra as it flows over Dights Falls.

Local catchment geology can also have an effect as water bodies located in the basaltic northern and western regions of Melbourne are prone to have higher levels of heavy metal pollution than those in more clay based catchments with similar levels of urbanisation (Pettigrove and Hoffman 2003). The study did not identify the reasons for these differences, but indicated that background levels of copper, chromium and nickel were higher in basalt soils. Even allowing for these differences, concentrations of zinc, lead, copper and cadmium increased more in basalt than sedimentary soils due to urbanisation. They suggested it might be due to differences in pH, turbidity and the adsorbing capacity of sediments from the different underlying geologies.

There is less information available on organic contaminants as opposed to metals in streams in the Yarra catchment. O'Connor and Moore (2001) reported a range of organic contaminants including PAHs, PCBs and pesticides, which were also more often detected in urban rather than rural locations. In addition, there are EPA licences for industrial stormwater discharges directly into the Yarra Estuary that pose controls on organic toxicants such as phenols, TPH and PAHs. It would be expected that the need for such controls is based on the risk of these toxicants being in stormwater discharges from particular industries. The presence of organic toxicants from stormwater discharges is supported by Bagg et al. (1981) who found very high levels of PAHs in the sediment of Moonee Ponds Creek, and decreasing concentrations with distance from stormwater drains. This lead to the conclusion that these drains and waterways were significant sources of organic toxicants in the Yarra Estuary.

Further evidence for the potential influences of industrial stormwater directly inflowing to the estuary comes from samples collected in stormwater drains upstream of the Westgate Bridge, in an area referred to as the 'Whitehall Street Yarraville Precinct' (GHD 2006). Sediment samples from within drains and down gradient contained mean metal concentrations above ISQG-Low and maximum values above ISQG-High (GHD 2006):

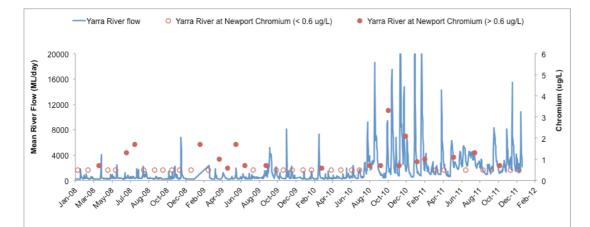
- arsenic maximum 93 mg/kg (ISQG-High = 70 mg/kg)
- lead maximum 1500 mg/kg (ISQG-High = 220 mg/kg)
- mercury maximum 3 mg/kg (ISQG-High = 1 mg/kg).

There is also evidence of the long-term nature of toxicants from stormwater and industrial discharges. An area called the Stony Creek Backwash is located at the confluence of Stony Creek and the Yarra River immediately upstream of the Westgate Bride. It was historically an area of industrial discharge and waste disposal. The sediments contain very high

concentrations of heavy metals (arsenic, cadmium, copper, mercury, nickel, lead and zinc above ISQG-High) and extreme concentrations of TPH (over 20,000 mg/kg). It is suggested that the source of these toxicants is historical industrial activities such as smelting and tanneries in the Stony Creek catchment, rather than current industries in the area (GHD 2006).

Contaminants in both the particulate-bound and the dissolved phase can be transported into the Yarra River via stormwater. The influx of contaminants in stormwater varies both with the pollutant and with the frequency and intensity of storms. The first flush concentrations of contaminants have been shown to be high and it is generally accepted from the outcomes of many studies (e.g. Line et al. 1997; Bertrand-Krajewski et al. 1998; Solokov and Black 1999) that the first flush of stormwater and stream flow contains high concentrations of heavy metals and organic compounds, especially following an extended dry period between significant rainfall events. Fabris and Monahan (1995) estimated that during storm events, between 8 and 25 times the load of metal is carried into (and out of) the Yarra Estuary than under base flow conditions.

The importance of storms and high flows in transporting toxicants is supported by the evidence from water quality monitoring in the lower Yarra River and Port Phillip Bay (EPA 2012), where increased concentrations of heavy metals coincided with storm events and high rainfall in late 2009, after what had been a decade long drought and low flows. There was some evidence linking total chromium concentrations above SEPP objectives with peaks in flow (Figure 6).



# Figure 6: Flows in the Yarra River (ML/day) and chromium concentrations ( $\mu$ g/L) in a site located downstream of the Westgate Bridge (adapted from EPA 2012).

A recent investigation assessing loads of toxicants in stormwater in the Yarra River catchment in urban and industrial areas, found highly variable results under both dry weather and wet weather conditions (McCarthy et al. 2009). The report suggested that to adequately model and determine loads would require further investigation. They found that both industrial and urban catchments contributed heavy metals (copper, nickel and zinc) but only one site was found to contain TPHs in stormwater (McCarthy et al. 2009).

Evidence for agricultural sources of toxicants to the Yarra Estuary comes from investigations of sediments and water in the upper catchment for pesticides and herbicides (Schafer et al. 2011). The study of 24 sites found detectable levels of 48 compounds in grab water samples, 27 in sediments and 34 in integrated passive samplers. Results indicated that many pesticides were above ISQG and water quality guideline levels. For example, maximum concentrations of DDT, chloropyrifos and simazine were above ANZECC and ARMCANZ (2000) water quality guideline levels, and sediment concentrations of pesticides such as DDT and dieldren exceeded ISQG values (Schafer et al. 2011).

Two toxicants that consistently occur in elevated concentrations within the Yarra Estuary are arsenic and nickel (URS 2007). There are a number of factors that support the hypothesis that these toxicants are derived from natural rather anthropogenic contributions. URS (2007) pointed out that nickel concentrations were similar in recently deposited, unconsolidated sediments and deep core samples, indicating that the deposition of nickel is not a recent event. There is a stronger argument to be made for the natural origin of elevated arsenic levels in the Yarra Estuary. Harris et al. (1996) concluded that the excessive arsenic load in the Bay is related to the natural sediment mineralogy, with biogeochemical processes in the sediments resulting in the release of arsenic into the water column. This conclusion was based on the fact that concentrations of arsenic entering into the Bay that could account for the Bay-wide elevation in arsenic concentrations. However, Pettigrove and Hoffman (2003) concluded that arsenic was sourced from the catchment, particularly from areas where previous gold mining activities had occurred and tailings were present. They found the highest concentrations of arsenic in their study of the Yarra catchment in streams in rural and forested regions where there had been past gold mining activities. Given that gold mining in Victoria peaked in the 1850s and 1860s, this may also explain the higher concentrations in deeper, older sediments in Port Phillip Bay that could have been deposited 150 years ago.

### 4.2 Shipping

The Port of Melbourne is a major shipping port and important shipping channels are maintained in the Yarra Estuary. A large number of vessels enter the port each year and historically discharged bilge water, released anti-fouling paint toxins from their hulls, and contributed oil and other hydrocarbons to the water column (Batley 1992). However, there are a number of controls in place, including pilots that accompany ships into the Yarra Estuary, and 'no discharge' policies that prevent the deliberate leakage of potentially contaminated bilge waters and other effluents from any vessels (URS 2007).

Sediments in some sections of the Port of Melbourne and the Yarra River (i.e. berths, main channel and silt traps) contain elevated concentrations of metals (cadmium, copper, nickel, lead, zinc and mercury) (Ellaway et al. 1982) and petroleum hydrocarbons (SKM 2003) compared to sediments upstream or further out in Hobsons Bay. Historically there were concerns for the release of tributyltin (TBT) from anti-fouling paints. The use of TBT for anti-fouling was regulated from 1989 and is banned from use on small vessels (i.e. less than 25 m in length), and is being phased out on larger and international vessels (URS 2007).

### 4.3 Groundwater

In addition to surface flows, toxic materials may be transported by groundwater. The extent of groundwater flows into the lower Yarra is not known but toxicants that have been identified as potentially entering the area through groundwater include lead, mercury, PCBs, PAHs, phenols and oils (Otto 1992). The Port Phillip Bay Environmental Study estimated loads from surface water versus groundwater sources for the Bay, with groundwater accounting for between 2 and 10 % of total toxicant inputs (Fabris et al. 1999). Given the location of the Yarra Estuary with respect to industries and known groundwater pollution sources, it is suspected that groundwater could contribute at least this proportion of toxicants to the estuary.

Groundwater sampling from industrial sites in the lower estuary found very high levels of toxicants with maximum values for arsenic, copper, zinc and ammonia three orders of magnitude greater than the SEPP objectives for the Yarra port (GHD 2006). These results were assessed, together with predicted flow and dilution factors, to assess the potential risk to the river and estuary. A high level of risk was identified from hydrocarbons, and a medium risk from arsenic, copper, zinc and ammonia; all via groundwater leaching from contaminated sites directly into the waters of the estuary (Table 5).

## Table 5: Summary of risk associated with groundwater discharges to the Yarra Estuary from the Whitehall Street Yarraville Precinct (GHD 2006).

Key contaminants	Key receptors	Description	Risk to environment
Petroleum hydrocarbons	Ecosystems associated with the Stony Creek Backwash sediments	The sediments are highly contaminated with petroleum hydrocarbons and metals. This may have arisen from contaminated groundwater from the Mobil site, although it appears most likely to have been caused by historic discharges upstream in Stony Creek or direct to the backwash. It appears that the public does not access the backwash.	High
	Ecosystems associated with the river	There is a plume of free-phase hydrocarbons in the vicinity of Holden Dock. The source for this has not been identified.	Medium
Arsenic, copper, zinc, ammonia	Ecosystems associated with the river bank and sediments	Concentrations of these in groundwater are very high and can be expected to adversely affect ecosystems associated with the river bank.	Medium
	Ecosystems associated with the river water	Concentrations of these contaminants in groundwater are very high but it appears that after dilution, the concentrations in the river water will not exceed the guidelines for protection of the river ecosystems.	Low

### 4.4 Atmosphere

Toxins may be deposited into the Yarra Estuary from the atmosphere, falling as dust or being transported from the air by rainfall. A previous inventory of emissions to air for Port Phillip Bay estimated that on an annual basis 170,000 tonnes of

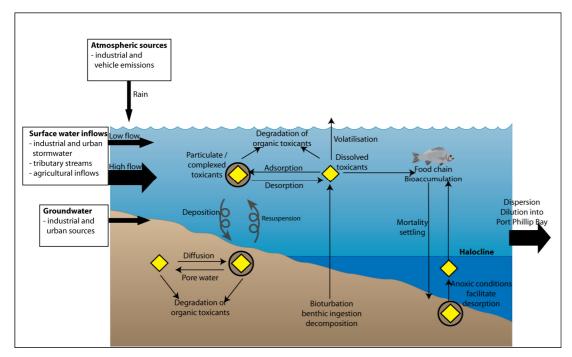
volatile organic compounds, 500 tonnes of lead and 27,000 tonnes of particulates were emitted in 1990 (Carnovale et al. 1991; Carnovale et al. 1992). In the early 1990s, over 90% of the lead was estimated to originate from motor vehicle emission, although the introduction of unleaded petrol will have substantially reduced the atmospheric output in recent years (URS 2007). While there are no estimates of atmospheric inputs of toxicants to the Yarra Estuary, its position within an industrial area may indicate that this is an important pathway. Many of the industries that line the channel of the estuary have discharge licences for toxicants into the air (mercury, sulphur dioxide and particulates).

In addition, the atmospheric deposition of heavy metals (cadmium, cobalt, copper, lead, nickel, manganese and zinc) as well as PAHs and petroleum hydrocarbons, have shown to be present adjacent to industrialised metropolitan areas elsewhere (Carnovale et al. 1992). It is therefore likely that atmospheric contributions of these contaminants may also be present in sediments in the Yarra Estuary.

### 5. Fate of toxicants

The fate of toxicants in an estuarine system is largely determined by the physical, chemical and biological characteristics of both the compound and the water body (Mackay et al. 1997). Different toxicants have various solubilities, volatilisation rates, degradation rates, bioavailability and biological effects.

A generalised conceptual model of the fate of toxicants in the Yarra Estuary is presented in Figure 7. This does not cover the entire myriad of complexities and pathways associated with toxicants in estuarine environments, but provides an overview of the main linkages. The sources as illustrated in the model are described in the previous section, and the processes describing the fate of toxicants once they enter the estuary are described briefly below.

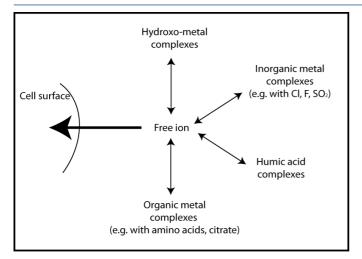


# Figure 7: Conceptual model of the main sources and fate of toxicants within the Yarra Estuary (symbols from the Integration and Application Network, University of Maryland Center for Environmental Science http://ian.umces.edu/imagelibrary/).

### 5.1 Dissolved and particulate states (adsorption and desorption)

Toxicants occur in different forms in aquatic systems and can be in dissolved form, attached to sediment particles (particulate form) or in complexes with other compounds (Goossens and Zwolsman 1996). In terms of metals, the free (dissolved) mode of occurrence is the ionic form. In this free mode, metals are easily taken up by organisms and exert their highest toxicity. Complexed molecules are those where the metal is combined with other molecules (e.g. carbonate, chloride or dissolved organic matter) and while still in the dissolved state, toxicity is greatly reduced. In the particulate state, metals may be precipitated through the formation of an insoluble salt or adsorbed to the surface of particles (such as fine sediment). In the particulate state (both adsorbed and precipitate) the metals cannot be taken up directly by organisms and toxicity is reduced (Goossens and Zwolsman 1996). This is the basis of the Free Ion Activity Model (FIAM) developed by Morel (1983) which illustrates the interaction between different forms of metals and the uptake by cells (Figure 8).

Metals within the Yarra Estuary are predominantly in particulate form, adsorbed to sediment particles. This is clear in data from 2008 to 2011 (EPA unpublished) in which the dissolved fraction of metals were generally less than detection limits. The exception to this was arsenic, where on average 92% of the total arsenic in water samples was in dissolved form, and nickel where on average 80 % of the total concentration was dissolved. There are also isolated occurrences of high proportions of copper and zinc in dissolved state (EPA unpublished). However, whether these metals were in the form of free ions or attached to fine particles (small enough to past through filters) remains unknown. Given the pH, salinity and other chemical conditions in the lower Yarra Estuary, it is more likely that they were in complexes and not bioavailable (Mike Grace, Monash University, personal communication, May 2012).



# Figure 8: Free Ion Activity Model (FIAM) illustrating the interactions between different forms of metal in water and uptake through cell walls (adapted from Campbell 1995).

The chemistry of organic toxicants is more complex, with solubility in both water and fats being a consideration. The binding of organic chemicals to suspended matter is measured in terms of the 'octanol-water partition coefficient' of the chemical ( $K_{ow}$ ). Typically chemicals with high  $K_{ow}$  values (> 3) are considered to have the potential to bind to suspended matter sufficiently to reduce their bioavailability (Chapman et al. 2001). Conversely, these are the compounds that are highly fat-soluble and will adsorb to lipids in biota, and are therefore likely to bioaccumulate (Connell 1990). The majority of organic toxicants found in the Yarra Estuary have relatively high  $K_{ow}$ . However, there is little data on dissolved versus particulate organic toxicants from within the Yarra River as almost all results provide for 'total' concentrations only, that is, combined dissolved and particulate.

A change in state from particulate to dissolved forms of toxicants can occur in the sediment or water column and is dependent on a number of factors such as temperature, light and oxygen concentration. Of particular interest for the Yarra Estuary is the role of the halocline (salinity stratification) and the effect on dissolved oxygen concentrations in bottom waters. A number of toxicants transition from particulate to ionised, dissolved states under low oxygen conditions. This includes a number of metals such as arsenic, cadmium, copper and zinc (Whitehead et al. 2010). In the Yarra Estuary, higher concentrations of arsenic have been recorded below the halocline in low dissolved oxygen waters, as compared to the oxygenated waters above (Butler and Smith 1985). However, similar evidence of the release of dissolved fraction metals from the sediment, below the halocline, has not been recorded in recent water quality monitoring programs in the estuary. Monitoring from 2008 to 2011 included separate sampling of bottom and surface waters if there was a pronounced halocline present. However, heavy metal concentrations in bottom waters were not higher than those in surface waters (EPA unpublished).

### 5.2 Sediment as a sink and source (deposition and resuspension)

The fate of toxicants that arrive into the Yarra Estuary is dependent on their state (dissolved or particulate) and a wide range of environmental variables within the system. Particulate toxicants can deposit to the sediment, which becomes a sink or store. The high concentration of many toxicants within the sediments of the Yarra Estuary (see section 3.1 above) is testament to the role of the sediment as a sink and the importance of deposition as a process.

Ellaway et al. (1982) noted that the fine fraction of the sediment (< 0.63 µm) had the greatest concentrations of metals and suggested that the estuary was an area of deposition for toxicants from the broader catchment. Similarly, the investigations of sediments for the CDP (SKM 2004; URS 2007) found that there were thick layers of unconsolidated fine sediment in the edges (silt traps) of the lower estuary and that these sediments had the greatest concentrations of toxicants (as opposed to deeper stiff clays).

Disturbance of the sediment by natural means or human activities such as dredging, can lead to the resuspension of sediments and toxicants into the water column. The majority of toxicants stored within the sediments are in particulate form. Resuspension of these particulate toxicants can result in transport downstream and out of the system, or a return to the sediments through deposition. However, a portion of the toxicants within the sediments exists in the interstitial waters (pore waters) and these may be in dissolved or particulate states, and disturbance of the sediments may lead to the release of toxicants in dissolved, bioavailable forms (Fabris et al. 1995).

Within the Yarra Estuary, there have been investigations into the fate of disturbed sediments with respect to toxicants. Hale (2006) monitored water quality within dredge plumes within the lower Yarra Estuary. This BACI (Before-After-Control-Impact) study did not detect any release of toxicants into the water column from dredge plumes associated with maintenance dredging.

Elutriate tests of sediment samples were undertaken as part of the CDP (SKM 2004; URS 2007). This involves the mixing of

sediments with water (collected from the estuary) and analysis of the dissolved fraction to determine if dissolved, potentially bioavailable toxicants are released in the process of disturbing the sediments. The vast majority of results from the over 100 samples were below the limits of reporting, and all organic and metal compounds were below ANZECC/ARMCANZ (2000) water quality guideline values (URS 2007).

The results of this investigation suggest that toxicants stored within the sediments of the port area in the lower Yarra Estuary are unlikely to be released into the water column following resuspension. This is supported by the water quality sampling that was conducted during dredging that did not find a correlation between water column toxicant concentrations and dredging activity (EPA 2012). However, there are significant concentrations of toxicants in the sediments upstream (see Table 1), where sediment characteristics may be different, and it remains unknown if there could be release of toxicants into the water column if these were to be disturbed.

### 5.3 Losses (volatilisation, degradation, dispersion)

A portion of the toxicant load that enters the Yarra Estuary leaves the system by a number of means. The most significant (in terms of total load) is loss to Port Phillip Bay as waters and suspended sediments flow through the system and out into the Bay. The Yarra River is recognised as a significant contributor of toxicant loads to Port Phillip Bay (Fabris et al. 1995; EPA 2012) indicating that the proportion of toxicants that pass through the system, rather than remaining in the estuary, may be significant.

Certain toxicants also either degrade or volatilise (turn into gas form and disperse into the atmosphere). The removal of toxicants by these means is dependent on a wide range of factors, including temperature, pH, oxygen concentrations, light and the nature of the compound. Organic compounds in particular degrade into non-toxic forms and this is often measured in 'half-life'. For example the half-life of butyltins by light is estimated at between 18 and 89 days depending on conditions, while phenol is < 12 hours and atrazine is more than a year (ANZECC and ARMCANZ 2000). However, this pathway of photo-degradation requires UV light to reach the compounds, and light is probably insufficient even for surface sediments in the turbid Yarra Estuary.

### 5.4 Biological effects

The biological effects of toxicants can be direct (that is affecting organisms through contact with the skin, gills or ingestion) or through bioaccumulation and biomagnification. The first of these can be assessed through toxicity testing of waters or sediments. Exposing organisms to whole sediments (or pore waters), allows for an assessment of the cumulative or synergistic effects of the suite of toxicants present within a sample of biota.

As part of the CDP program, toxicity testing was undertaken on the 'moderately contaminated' sediments of the lower Yarra Estuary. Toxicity tests included sub-acute and chronic testing on a suite of species designed to represent the range of biota and biotic sensitivities (URS 2007). Over 50 % of the samples tested from the Yarra Estuary were considered toxic in at least one test. This included 12 samples that tested positive for sea urchin larval development toxicity, 24 samples for algal cell viability and 21 samples for oyster larval development (URS 2007). However, as many samples exceeded guideline values of more than one toxicant, it is unknown if a single toxicant was responsible for the biological effects or the cumulative effects of multiple toxicants.

The toxicity of organic toxicants on biota is more difficult to assess, as many of these compounds can biomagnify through the food chain and bioaccumulate in individuals. Assessment of the concentrations of toxicants in fish in the mid estuary (Melbourne Water 2006; EPA 2007; EPA 2009) found that for the vast majority of fish sampled, toxicants were below detection limits and/or guideline values. The exception to this was the presence of PCBs in a small number of eels. PCBs are known to bioaccumulate, and as short-finned eels are a relatively long-lived species, it is possible that these toxicants accumulated over time. It is also unknown whether the individuals accumulated the toxicants from within the estuary or elsewhere. Short-finned eels are a diadromous species, spending most of their adult lives in freshwater environments (Native Fish Australia). As such it is likely that the toxicants accumulated in the upstream reaches of the catchment.

## 6. Yarra Estuary in the context of other estuarine systems

To place the state of the Yarra Estuary with respect to toxicants in context, comparisons with other estuaries in Australia and globally have been made. As sediments are an integrator of conditions over time and less susceptible to the high variability associated with 'snap-shot' water column sampling, this comparison has been made based on sediments. However, it should be noted that there are still a number of limitations in making such comparisons including:

- the objective of the study for which data was collected (samples may have been biased towards very good or very poor sites)
- the methods used to collect and analyse samples vary
- the sediment types (in terms of composition and grain size) vary between estuaries
- the limits of reporting (LOR) differs between studies
- the number of samples collected is highly variable.

Metal concentrations in sediments both in Australia and globally vary by up to two orders of magnitude (Table 6). Maximum concentrations in the Yarra Estuary were neither highest nor lowest for any of the metals. In the Australian context, sediments in the Yarra Estuary contain higher concentrations of most metals than Darwin Harbour (NT), but are significantly lower than those in the Derwent Estuary (Tasmania) and Port Jackson (NSW). Internationally, maximum mercury and arsenic concentrations in the Yarra Estuary are at the upper end of the spectrum reported globally, while concentrations of other metals are within the ranges reported elsewhere.

## Table 6: Maximum metal concentrations (mg/kg) in sediments from industrial and urban estuaries worldwide.

Site	As	Cd	Cu	Cr	Pb	Hg	Ni	Zn
Yarra Estuary <sup>1</sup>	150	1.8	89	280	240	2.2	120	850
Brisbane River (QLD) <sup>2</sup>	41	3.3	67	57	104	0.5	40	246
Darwin River (NT) <sup>3</sup>	103	7	13		48	0.05	21	66
Derwent River (Hobart, TAS) <sup>2</sup>	1400	477	1490	122	8120	130	197	59000
Swan River (Perth, WA)⁵	0.86	<lor< td=""><td>680</td><td>1.6</td><td>17</td><td>0.01</td><td>1.7</td><td>330</td></lor<>	680	1.6	17	0.01	1.7	330
Port Jackson (Sydney, NSW) <sup>6</sup>		24	1078	1472	3604		245	7622
Thames River (UK) <sup>7</sup>	45	10	348	240	1634	5.7	157	1050
Chesapeake Bay to Cape Cod (USA) <sup>8</sup>	36	7	680	348	323	2	136	797
Guadalquivir Estuary (Spain) <sup>9</sup>	9	1.3	44		87		J	273
San Francisco Bay (USA) <sup>10</sup>		0.5	161	1467	67	1.1		
Tokyo Bay (Japan) <sup>11</sup>		1.4	80	126	58		44	405
South Africa (multiple locations) <sup>12</sup>		0.6	102	114	86		28	184
Venice Lagoon (Italy) <sup>13</sup>		2	32	106	306		20	306
Restronguet Estuary (USA) <sup>14</sup>	1740	1.5	2398		341	0.46		2821
Mersey Estuary (UK) <sup>14</sup>	42	1.1	84	84	124	3.0		379

<sup>1</sup>This report; <sup>2</sup>Cox and Preda 2005; <sup>3</sup>Padovan 2003; <sup>4</sup>Whitehead et al. 2010; <sup>5</sup>Swan River Trust 2001, <sup>6</sup>Birch and Taylor 1999; <sup>7</sup>Attrill and Thomes 1995; <sup>8</sup>Paul et al. 2002; <sup>9</sup>Riba et al. 2004; <sup>10</sup>Birch 2000; <sup>11</sup>Fukushima et al. 1992; <sup>12</sup>Henry et al. 1989; <sup>13</sup>Sfriso et al. 1995; <sup>14</sup>Bryan and Langston 1992.

In terms of tributyltin concentrations in surface sediments, the Yarra Estuary maximum concentration is lower than many other harbours and estuaries (Table 7), especially given that the site includes an active port.

### Table 7: Maximum tributyltin concentrations ( $\mu$ g/kg) in sediments from estuaries worldwide.

Site	Tributyltin
Yarra Estuary <sup>1</sup>	64
Port River Estuary (Adelaide, SA) <sup>2</sup>	101
Darwin River (NT) <sup>3</sup>	63
Swan River (Perth, WA) <sup>4</sup>	255
Suva Harbour (Fiji)⁵	360000
Chesapeake Bay to Cape Cod (USA)⁵	570
Arcachon Bay (France)⁵	5000
San Diego Harbour (USA)⁵	143
Sado Estuary (Portugal)⁵	213
Poole Harbour (UK)⁵	213
Great Bay Estuary (USA)⁵	20
Kaipara Harbour (NZ)⁵	759

<sup>1</sup>This report; <sup>2</sup>EPA (SA) 1996; <sup>3</sup>KBR 2001; <sup>4</sup>Swan River Trust 2007, <sup>5</sup>Maata and Koshy 2001.

In terms of organic toxicants such as PAHs, TPHs, PCBs and pesticides, there is a very large disparity in reporting and analysis methods worldwide, requiring caution when making comparisons. However, both DDT and PCBs have been recorded in the Yarra sediments above guideline levels and a comparison with data from elsewhere is provided in Table 8.

This comparison indicates that concentrations of DDT in sediments in the Yarra River may be very high on global scales, with the maximum concentration from the port area significantly higher than most comparable estuaries and bays globally. It is worth noting that the 80<sup>th</sup> percentile of available DDT data from the port area (20.6  $\mu$ g/kg, URS 2007) is significantly lower than the maximum, although this is still relatively high. On a global scale, PCB concentrations are generally lower than other estuarine systems. This is consistent with the finding from a review on PCBs in the Yarra and Maribyrnong Rivers that indicated concentrations in the Yarra Estuary were very small compared to comparable sites globally (Gelderen and Pettigrove 2011). PCBs are no longer actively used in Australia and recent concentrations within the estuary sediments (< 10  $\mu$ g/kg) are orders of magnitude lower than recent results published for Chesapeake Bay in the United States (maximum > 2400  $\mu$ g/kg) and the Mersey Estuary in the United Kingdom (maximum > 1400  $\mu$ g/kg) (Gelderen and Pettigrove 2011). Table 8: Maximum total DDT and PCB concentrations ( $\mu$ g/kg) in sediments from estuaries worldwide.

Site	Total DDT	Total PCB
Yarra Estuary <sup>1</sup>	1100	64
Parramatta River (NSW)	26	160
Swan River (WA)	2.1	35
Daliaohe Estuary (China)	0.3	2.3
Luanhe Estuary (China)		1.4
Haihe Estuary (China)	10.5	3.2
Huanghe Estuary (China)		1.3
Changjiang Estuary (China)	0.2	7.1
Huangpujiang Estuary (China)	1.3	19.9
Qingtangjiang Estuary (China)	0.1	12.8
Jiulongjiang Estuary (China)	5.2	0.8
Zhujiang Estuary (China)	11.1	
Mandovi River Estuary (India)	73	170
Ciliwung River (Indonesia)	13	79
Mataniko River (Solomon Islands)	750	5
Osaka Bay (Japan)	2.5	63
Keelong River (Taiwan)	10	230
Scheldt Estuary (Netherlands)		257
South Carolina Estuary (USA)	17.2	622
The San Francisco Estuary (USA)	2.1	164

<sup>1</sup>This report; all others - Wu et al. 1999.

A comparison of total PAHs from Australia (Table 9) and globally indicates that the Yarra Estuary is comparable to other sites in Australia and some in Europe, much lower than known polluted sites in the USA such as Chesapeake Bay and Boston Harbour, and higher than sites in China and the Middle East.

### Table 9: Maximum total PAH concentrations ( $\mu$ g/kg) in sediments from estuaries worldwide.

Site	Total PAHs
Yarra Estuary <sup>1</sup>	11000
Brisbane River (QLD) <sup>2</sup>	16100
Townsville Harbour (QLD) <sup>2</sup>	13400
Swan (Perth, WA) <sup>3</sup>	240620
Tamar Estuary (UK) <sup>2</sup>	14070
Chesapeake Bay (USA)²	178000
Casco Bay (USA) <sup>2</sup>	14425
Boston Harbour (USA) <sup>2</sup>	718364
Shatt Al-Arab River (Persian Gulf) <sup>2</sup>	68
Yalujiang Estuary (China) <sup>3</sup>	1500
Yangtze Estuary (China) <sup>4</sup>	670
Huangpu Estuary (China) <sup>4</sup>	2100

<sup>1</sup>This report; <sup>2</sup>Brown and Maher 1992; <sup>3</sup>Wu et al. 2003; <sup>4</sup>Liu et al. 2008.

### 7. Key issues and recommendations

### 7.1 Potential issues and knowledge gaps

Toxicants within the Yarra Estuary exceed guideline values for a large number of compounds in both the water column and the sediment. While there is some evidence that concentrations of a few toxicants (PCBs, TPHs, TBT) may have decreased in recent times, concentrations of other compounds remain high. Recent sediment samples indicate that arsenic, lead, mercury, nickel, zinc and DDT exceeded ISQG-High values. With respect to DDT, concentrations in the Yarra sediments were also comparatively high on a global scale.

However, the majority of the high toxicant concentrations were recorded from the port area in the lower estuary in the surficial unconsolidated sediments. Most of these sediments were removed during the CDP during 2008 and 2009. The current status of sediments in this area is unknown, but given the lower toxicant concentrations in the underlying stiff clays and the short period of time for deposition of new unconsolidated material, it is likely that toxicant concentrations in this area are lower.

While the limited data available for biota in the estuary indicates that concentrations of metals within fish flesh are below guideline levels, there is no data available for other species. In addition, samples of eel flesh have exceeded guideline values for PCBs, although, the organic toxicants may have accumulated over a long period of time and from areas outside the estuary. There is little evidence of widespread ecosystem decline or dysfunction in the estuary or the bay, but toxicity tests from sediment data indicate that unconsolidated sediments that were within the port area prior to the CDP were toxic to marine biota. However, most of these sediments were removed during the CDP and it is unknown if current sediments have the same degree of toxicity.

The information base for toxicants within the estuary is highly biased spatially with the vast majority of water and sediment sampling occurring in the lower estuary within the Port of Melbourne. The limited data for upstream sections indicates that these areas may contain high concentrations of toxicants, the biological effects of which remains unknown. Evidence from across the estuary indicates that the highest loads of toxicants are within surficial, fine sediments. Unlike the sediments within the port area, which are removed during large scale dredging (such as the CDP) and maintenance dredging campaigns, fine, surficial sediment in the mid and upper estuary sections may have accumulated over a long period of time, and be a significant sink of toxicants in the system.

There are multiple lines of evidence supporting the importance of urban and industrial stormwater (direct and catchment based) as a source of toxicants to the Yarra Estuary. The greatest loads enter the system during storm events and high river flows. This type of diffuse source of pollution is difficult to manage. What is not known is if there are 'hot-spots' or potential direct sources of toxicants in the estuary or the catchment, which could be targeted to manage toxicant loads to the system.

The CDP provided a large volume of data on the presence and behaviour of toxicants within the lower Yarra Estuary. The results of monitoring during maintenance and capital dredging indicated that toxicants bound in the sediment are unlikely to be released into bioavailable forms in the water column when the sediments are disturbed (by natural means or human activities). This is supported by the small amount of data on levels of toxicants within biota. Fish sampled did not contain detectable levels of pesticides and contained low levels of metals, despite the high concentrations of these toxicants in the sediments of the estuary. What is unknown is the effect of these high concentrations on benthic biota or filter feeding organisms such as mussels.

While knowledge on the toxicants within the Yarra Estuary is far from complete, there is a substantial amount of data and information available. Current monitoring programs conducted by EPA and Melbourne Water provide information on metal concentrations in the water column. Although these do not capture organic toxicants, historical monitoring of water in the port area for these compounds produced results consistently below detection or reporting limits, indicating that repeating this in the future is not warranted and may constitute a poor use of resources.

The majority of the knowledge gaps relate to areas in the mid and upper estuary, where data is limited. While it could be assumed that the toxicants within sediments in these areas behave similarly to those in the lower estuary, where toxicants mostly remain in the particulate state and do not become bioavailable even following disturbance, this is unknown. There is also a level of uncertainty with regard to the status of toxicants within the port area after the CDP. However, it is likely that sediments are lower in toxicants than that during the 2006 sediment sampling. Therefore, recommendations for repeated sampling in this area would be to satisfy scientific curiosity rather than to address risks to the ecology of the Yarra Estuary.

#### 7.2 Recommendations

Despite many toxicants exceeding guideline values, most remain bound to particles and are unavailable for uptake in biota. They therefore pose a low risk to people collecting fish from the area. With this fact in mind and given the large amount of data available for the system, recommendations for future monitoring and investigation are limited. While there is not a complete understanding of all aspects of toxicant presence and behaviours within the system, recommendations for extensive scientific studies to fully model loads or processes are not warranted. Following the discussion of knowledge gaps and issues above, recommendations related to the state of knowledge of toxicants within the Yarra Estuary are to:

investigate the status and likelihood of the release of toxicants in the upper and mid estuary

• continue periodic assessments of toxicants within the Yarra Estuary, adopting a multiple lines and levels of evidence approach. Methods to be considered in the design of such a monitoring program include deployed mussels, fish, sediment, pore water, groundwater and water column measures.

### 8. Conclusions

Toxicants within the Yarra Estuary have been studied for over three decades. Although there is some spatial bias in the sampling, the following conclusions can be made:

- Concentrations of arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc, PAH, PCB, TBT and DDT in sediments have each exceeded ANZECC ISQG-Low levels on occasion.
- Concentrations of arsenic, lead, mercury, nickel, zinc and DDT in sediments have exceeded ISQG-High levels in the last decade.
- Concentrations of some metals (arsenic, cadmium, chromium, lead, mercury nickel and zinc) in the water column
  have exceeded SEPP objectives on at least one occasion in the last decade. However, on average they are generally
  within SEPP objectives.
- The majority of metals in the water column are in particulate form, with the exception of arsenic and nickel, which are mostly in dissolved forms.
- Concentrations of organic toxicants in the water column are below detection or reporting limits.
- Concentrations of metals within fish are within guideline levels.
- Concentrations of organic toxicants in fish are mostly within guideline levels, with the exception of a few shortfinned eels sampled that exceeded guideline values for PCBs.
- Compared to other estuaries nationally and globally, the Yarra Estuary contains comparable concentrations of most toxicants. However, compared to results reported for estuaries worldwide, the Yarra contains higher concentrations of arsenic and nickel, and higher concentrations of DDT in the sediments.
- Urban and industrial stormwater entering the estuary from the city and the catchment is the dominant source of toxicants. Most of the toxicants enter during high flow events following heavy rainfall.
- Natural sources are likely for arsenic (and possibly nickel) rather than human activities in the catchment.
- The sediment is the major sink of toxicants in the estuary with the greatest concentrations in the surficial fine, unconsolidated sediments. Evidence from the lower estuary indicates that disturbance of the sediment does not result in the release of high concentrations of bioavailable toxicants into the water column.
- Results of toxicity testing indicate that surficial sediments (in the lower estuary) are toxic to marine biota. However most of the sediments that were tested were removed from the estuary during the Channel Deepening Project (CDP).

### 9. References

ANZECC & ARMCANZ 2000, Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Australian and New Zealand Environment Conservation Council.

Attrill MJ & Thomes RM 1995, Heavy metal concentrations in sediment from the Thames Estuary, UK, *Marine Pollution Bulletin*, vol. 30(11), pp. 742-744.

Bagg J, Smith D & Maher W 1981, 'Distribution of polycyclic aromatic hydrocarbons in sediments from estuaries of southeastern Australia', Australian Journal of Marine and Freshwater Research, vol. 32, pp. 65 – 73.

Batley G 1992, 'Toxicants', In: Hall D (ed), *Port Phillip Bay Environmental Study: Status Review*, pp. 80-111, Technical Report No. 9, CSIRO Port Phillip Bay Environmental Study, Melbourne.

Beckett R, Easton A, Hart BT, Ho T & McKelvie I 1978, A study of the hydrodynamics of the Yarra and Maribyrnong estuaries, Report prepared by the Water Studies Centre of the Caulfield Institute of Technology for EPA Victoria.

Beckett R, Easton AK, Hart BT & McKelvie ID 1982, 'Water movement and salinity in the Yarra and Maribyrnong Estuaries', *Australian Journal of Marine and Freshwater Research*, vol. 33, pp. 401-415.

Bertrand-Krajewski J, Chebbo G & Saget A 1998, 'Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon', *Water Research*, vol. 32, pp. 2341-2356.

Birch G 2000, 'Marine pollution in Australia, with special emphasis on central New South Wales estuaries and adjacent continental margin', *International Journal of Environment and Pollution*, vol. 13, pp. 573-607.

Brown G & Maher W 1992, 'The occurrence, distribution and sources of polycyclic aromatic hydrocarbons in the sediments of the Georges River Estuary, Australia', *Organic Geochemistry*, vol. 18(5), pp. 657-668.

Bruce LC, Cook PLM & Hipsey MR 2011, 'Using a 3D hydrodynamic-biogeochemical model to compare estuarine nitrogen assimilation efficiency under anoxic and oxic conditions', 19th International Congress on Modelling and Simulation, Perth.

Bryan G & Langston W 1992, 'Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review', *Environmental Pollution*, vol. 76, pp. 89-131.

Butler E & Smith J 1985, 'lodine and arsenic redox species in oxygen-deficient estuarine waters', Australian Journal of Marine and Freshwater Research, vol. 36, pp. 301-309.

Campbell PGC 1995, 'Interactions between trace metals and aquatic organisms'. In: Tessier A & Turner DR (eds.), *Metal Speciation and Bioavailability in Aquatic Systems*.

John Wiley & Sons, New York, NY, USA, pp. 45-102.

Carnovale F, Alviano P, Carvalho C, Deitch G, Jiang S, Macaulay D & Summers M 1991, *Air Emissions Inventory Port Phillip Control Region: Planning for the Future*, EPA Victoria, SRS 91/001.

Carnovale F, Carvalho C & Cope M 1992, *Literature Review of Aeolian and Atmospheric Inputs of Nutrients to Port Phillip Bay*, Port Phillip Bay Environment Study, Technical Report No. 5, CSIRO.

Carty R & Pierotti S 2010, *Yarra River Application Project: Source Catchments Hydrology Calibration Report*, Water Cooperative Research Centre, Canberra.

Cox ME & Preda M 2005, 'Trace metal distribution within marine and estuarine sediments of Western Moreton Bay, Queensland, Australia: Relation to land use and setting', *Geographical Research*, vol. 43(2), pp. 173-193.

DSE (Department of Environment and Sustainability) 2011, Victorian Water Resources Data Warehouse <u>http://www.vicwaterdata.net/vicwaterdata/MeasureByMeasure/MbyMDetailForm.aspx?SiteID=15364&MDefID=213&MDefDes</u> <u>c=FLOW&ObsCount=209</u> accessed 2 April 2012.

Ellaway M, Hart BT & Beckett R 1982, 'Trace metals in sediments from the Yarra River', Australian Journal of Marine and Freshwater Research, vol. 33 pp. 761-778.

Enesar 2005, Monthly Progress Report, Channel Deepening Project, Report No. 1159\_6, Enesar Consulting, Melbourne.

EPA 2007, Yarra and Maribyrnong Estuaries: Investigation of Contamination in Fish. Publication 1094, EPA Victoria, Melbourne.

EPA 2009, Lower Yarra River Fish Study: Investigation of Contaminants in Fish, Publication 1283, EPA Victoria, Melbourne.

EPA 2012, *Water Quality Monitoring Program - Milestone Report No.* 9, Channel Deepening Baywide Monitoring Programs, EPA Victoria, Melbourne.

EPA (South Australia) 1996, Sediment Quality Monitoring of the Port River Estuary, Report No.1, EPA South Australia, Adelaide.

Fabris GJ 1995, *Toxicants in Aquatic Biota from Port Phillip Bay: Data Analysis*, Port Phillip Bay Environmental Study Technical Report No. 22, CSIRO.

Fabris G & Monahan CA 1995, *Characterisation of Toxicants in Waters from Port Phillip Bay*, Port Phillip Bay Environmental Study Technical Report No. 18, CSIRO.

Fabris GJ, Monahan C, Nicholson GJ & Walker TI 1992, 'Total mercury concentrations in sand flathead, *Platycephalus bassensis* Cuvier & Valenciennes, and yank flathead, *Platycephalus speculator* Klunzinger, from Port Phillip Bay, Victoria'. *Australian Journal of Marine and Freshwater Research*, vol. 43, 1393-1402

Fabris G, Monahan C & Batley G 1999, 'Heavy metals in waters and sediments of Port Phillip Bay, Australia', Marine and Freshwater Research, vol. 50(6), pp. 503-153.

Fabris G, Monahan CA, Werner GF & Theodoropoulos T 1995, *Impact of Shipping and Dredging on Toxicants in Port Phillip Bay*, Port Phillip Bay Environmental Study Technical Report No. 20, CSIRO.

Fukushima K, Saino T & Kodama Y 1992, 'Trace metal contamination in Tokyo Bay, Japan', *Science of the Total Environment*, vol. 125, pp. 373-389.

Gagnon MM & Holdway DA 2002, 'EROD activity, serum SDH and PAH biliary metabolites in sand flathead (*Platycephalus bassensis*) collected in Port Phillip Bay, Australia', *Marine Pollution Bulletin*, vol. 44, pp. 230-237.

GHD 2006, Report for Whitehall Street, Yarraville Precinct: Environmental Audit Report, EPA Victoria, Melbourne.

Golder Associates 2006, Historical review and chemical screening assessment to identify chemicals of potential concern in the Lower Yarra River and Port Phillip Bay sediments. Draft Report.

Good J & Gibbs C 1995, Port Phillip Bay Environmental Study, Task T7 - Organic Toxicants in Sediments, EPA Victoria, Melbourne.

Goossens H & Zwolsman J 1996, 'An Evaluation of the Behaviour of Pollutants During Dredging Activities', *Terra et Aqua*, vol. 62, pp. 20-28.

Hale J 2006, *Minor Maintenance Dredging Campaign Water Quality Monitoring in the Dredge and Disposal Plumes*, Report to Port of Melbourne Corporation, Melbourne.

Hart B & Davies S 1981, 'Trace metal speciation in the fresh-water and estuarine regions of the Yarra River, Victoria, Australia', *Estuarine Coastal and Shelf Science*, vol. 12(4), pp. 353-374.

Harris G, Batley G, Fox G, Hall D, Jernakoff P, Molloy R, Murray A, Newell B, Parslow J, Skyring G & Walker S 1996, Port Phillip Bay Environmental Study Final Report, CSIRO, Canberra.

Henry JL, McGibbon S, Davis G, Mackay RM & Moldan AGS 1989, *Heavy metals, carbon and hydrocarbons in the sediments of Table Bay Harbour*. Sea Fisheries Research Institute, Dept. of Environmental Affairs, Republic of South Africa, Special Report.

John Kowarsky and Associates 2002, *Evaluating Potential Environmental Impacts from Major Maintenance Dredging Works, Sediment Quality Assessment*, Port of Melbourne Channels, John Kowarsky and Associates, South Yarra, Victoria.

KBR 2001, Marine Sediment Monitoring, 18 June 2001: Results. A consultancy report for Department of Defence. Halliburton KBR Pty Ltd, Darwin.

Kowarsky J 2001, Sediment Sampling and Analysis Melbourne Lower Port Waters, John Kowarsky and Associates, South Yarra, Victoria.

Kowarsky J 2005, Review of Recent Sediment Quality Data Port Melbourne 2005

Minor Dredging Campaign, John Kowarsky and Associates, South Yarra, Victoria.

Lawson and Treloar Pty Ltd 2004, PoMC Channel Deepening Hydrodynamics, Sediment Transport and Water Quality Modelling, Report Rm2054/J5372, Lawson and Treloar Pty Ltd, Notting Hill, Victoria.

Line D, Wu J, Arnold J, Jennings G & Rubin A 1997, 'Water quality of first flush run-off from 20 industrial sites', *Water Environment Research*, vol. 69, pp. 305-310.

Lui Y, Chen L, Jianfu Z, Qinghui H, Zhiliang Z & Hongwen G 2008, 'Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China', *Environmental Pollution*, vol. 154, pp. 298-305.

Maata M & Koshy K 2001, 'A study on tributyltin contamination of marine sediments in the major ports of Fiji', South Pacific Journal of Natural Science, vol. 19, pp. 1–4.

Mackay D, Shiu W & Ma K 1997, Illustrated Handbook of Physical-chemical Properties and Environmental Fate of Organic Chemicals, CRC Press.

McCarty D, Bratieres K & Lewis J 2009, Effective monitoring and assessment of contaminants impacting the mid to lower Yarra catchments: a temporal scale assessment.

Melbourne Water 2006, Yarra and Maribyrnong Estuaries: Preliminary Investigation of Contaminants within Fish, Melbourne Water and EPA Victoria, Melbourne.

Milne PJ 1975, Some aspects of the behaviour of trace metals in estuarine conditions, B.Sc. (Hons.) thesis, University of Melbourne.

Morel FMM 1983, Principles of aquatic chemistry, John Wiley and Sons, New York, USA.

Native Fish Australia, http://www.nativefish.asn.au/ accessed 10 April 2012.

Nicholson GJ, Theodoropoulos T & Fabris GJ 1991, Petroleum and chlorinated hydrocarbons in the axial muscle tissue and liver of sand flathead (Platycephalus bassensis Cuvier & Valenciennes) from Port Phillip Bay. Internal Report No. 197, Marine Science Laboratories, Fisheries Division, Department of Conservation and Environment, Victoria.

O'Brien M 2009, *Polychlorinated Biphenyl (PCB) Sediment Monitoring Program in the Greater Melbourne Area*, Centre for Environmental Stress and Adaptation Research, Victoria.

O'Connor N & Moore S 2001, 'Sediment contaminants in urban streams: their effect on stream health'. *Journal of the Australian Water Association*, September 2001, pp. 60-62.

OEM (Office of the Environmental Monitor) 2009, *Lower Yarra River Fish Study*, <u>http://www.oem.vic.gov.au/2009LowerYarraRiverFishStudy</u> accessed 5 April 2012.

Padovan A 2003, 'Darwin Harbour water and sediment quality', *Proceedings of the Darwin Harbour Public Presentations*, February 2003.

Paul JF, Comeleo R & Copeland J 2002, 'Landscape Metrics and Estuarine Sediment Contamination in the Mid-Atlantic and Southern New England Regions', *Journal of Environmental Quality*, vol. 31(3), pp. 836-845.

Pettigrove V 2003, 'Impact of urbanisation on heavy metal contamination in urban stream'. Australasian Journal of *Ecotoxicology*, vol. 9, pp. 119-128.

Pettigrove V & Hoffmann A 2003, *Major sources of heavy metal pollution during base flows from sewered urban catchments in the City of Melbourne*. 3rd South Pacific conference on stormwater and Aquatic resource Protection combined with 10th Annual conference of the Australasian chapter of the Internationals Erosion control Association, Auckland, New Zealand, New Zealand water & wastes Association, 14-16 May 2003.

Phillips DJH 1976, 'The common mussel *Mytilus edulis* as an indicator of pollution by zinc, cadmium, lead and copper: Effects of environmental variables on uptake of metals', *Marine Biology*, vol. 38, pp. 59-69.

PIRVic 2007, Port of Melbourne Corporation Channel Deepening Project Baseline Water Quality Monitoring 2006-2007, Primary Industries Research Victoria.

PoMC (Port of Melbourne Corporation) 2007, Supplementary Environmental Effects Statement Channel Deepening Project, PoMC, Melbourne.

PoMC (Port of Melbourne Corporation) 2009, Quarterly Project Report No. 7 - December 2009, PoMC, Melbourne.

PoMC 2011, *History of the Port*, <u>http://www.portofmelbourne.com/community/maritimeheritage/porthistory.aspx</u> accessed 2 April 2012.

Poore GCB and Kudenov JD 1978, 'Benthos of the Port of Melbourne: The Yarra River and Hobsons Bay, Victoria', Australian Journal of Marine and Freshwater Research, vol. 29, pp. 141-155.

Riba I, Conradi M, Forja M & DelValls T 2004, 'Sediment quality in the Guadalquivir estuary: lethal effects associated with the Aznalcóllar mining spill', *Marine Pollution Bulletin*, vol. 48(1-2), pp. 144-152.

Schafer RB, Pettigrove V, Rose G, Allinson G, Wightwick A, von der Ohe P, Shimeta J, Kuhne R & Kefford BJ 2011, 'Effects of pesticides monitored with three sampling methods in 24 sites on macroinvertebrates and microorganisms', *Environmental Science and Technology*, vol. 45, pp. 1665-1672.

Sfriso A, Marcomini A & Zanette M 1995, 'Heavy metals in sediments, SPM and phytozoobenthos of the Lagoon of Venice', *Marine Pollution Bulletin*, vol. 30, pp. 116-124.

SKM 2003, Channel Deepening Environmental Effects Statement Specialist Studies, Report on Sediment Chemistry - Volume 1, Environmental Surveys, Sinclair Knight Merz, Melbourne.

SKM 2004, Stage 2 Additional Environmental Survey Work, Port of Melbourne Channel Deepening Project, Sinclair Knight Merz, Melbourne.

SKM 2005, Determination of the Minimum Environmental Water Requirement for the Yarra River, Sinclair Knight Merz, Victoria.

Smith DJ & Milne PJ 1979, 'Determination of iron in suspended matter and sediments of the Yarra River Estuary, and the distribution of copper, lead, zinc and manganese in the sediments', *Australian Journal of Marine and Freshwater Research*, vol. 30, pp. 731 - 739.

Sokolov S & Black KP 1999, 'Long-term prediction of water quality for three types of catchments', *Marine and Freshwater Research*, vol. 50, pp. 493-501.

Spencer KL & MacLeod CL 2002, 'Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards', *Hydrology and Earth System Sciences*, vol. 6(6), pp. 989-998.

Swan River Trust 2007, Tributyltin and Heavy Metal Survey in the Swan River: Swan Yacht Club Sediment and Mussel Tissue Quality, Oceanica Consulting, Perth.

URS 2007, Northern Channels Sediment Investigation, Port Phillip Bay Supplementary Environmental Effects Statement, URS Australia.

USEPA 2000, *Guidance for Assessing Chemical Contaminant Data for Use In Fish Advisories*. Volume 1: Fish Sampling and Analysis – Third Edition. Web: <u>http://www.epa.gov/ost/fishadvice/volume1/</u> accessed 2010

van Gelderen R & Pettigrove V 2011, Polychlorinated Biphenyls (PCBs) within the Yarra / Maribyrnong Rivers and Port Phillip Bay, Victoria, Australia, CAPIM, Publication No. 4.

Walker TI 1982, 'Effects of length and locality on the mercury content of blacklip abalone, *Notohaliotis ruber* (Leach), blue mussel, *Myrilus edulis planulatus* (Lamarck), sand flathead, *Platycephalus bassensis* Cuvier & Valenciennes, and long-nosed flathead, *Platycephalus caeruleopunctatus* (McCulloch), from Port Phillip Bay, Victoria', *Australian Journal of Marine and Freshwater Research*, vol. 33, pp. 553-60.

Walker TI, Glover JW & Powell DGM 1982, 'Effects of length, locality and tissue type on mercury and cadmium content of the commercial scallop, *Pecten alba* Tate, from Port Phillip Bay, Victoria', *Australian Journal of Marine and Freshwater Research*, vol. 33, pp. 547-52.

Walker TI 1988, 'Mercury concentrations in edible tissues of elasmobranchs, teleosts, crustaceans and molluscs from Southeastern Australian waters', *Australian Journal of Marine and Freshwater Research*, vol. 39, pp. 39-49.

Whitehead J, Coughanowr C, Agius J, Chrispijn J, Taylor U & Wells F 2010, State of the Derwent Estuary 2009: a review of pollution sources, loads and environmental quality data from 2003 – 2009. Derwent Estuary Program, DPIPWE, Tasmania.

Wu Y, Zhang J & Zhou Q 1999, 'Persistent organochlorine residues in sediments from Chinese River/Estuary systems', *Environmental Pollution*, vol. 105, pp. 143-150.

Wu Y, Zhang J & Zhu Z 2003, 'Polycyclic aromatic hydrocarbons in the sediments of the Yalujiang Estuary, North China', *Marine Pollution Bulletin*, vol. 46, pp. 619–625.

Yarra and Maribyrnong Rivers Steering Committee 2005, *Strengthening the Management of the Yarra and Maribyrnong Rivers: A Background Report for Future Water Quality Management*, Victorian Government Department of Sustainability and Environment, Melbourne.