

The origin, fate and dispersion of toxicants in the Lower Yarra River: a review

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Summary

This document identifies, summarizes and evaluates issues relating to the current state of knowledge of the origin, fate and dispersion of toxicants in the lower Yarra River, compares the toxicant status of the Yarra with similar urban estuaries, and discusses methods for assessing commonly occurring toxicants in estuarine environments.

The main toxicants of concern in the lower Yarra are metals and a range of organic contaminants. There is far more information available on metals, with copper, lead, zinc, cadmium and mercury all elevated in the estuarine sediments. Of the organics petroleum hydrocarbons, PAHs PCBs and some chlorinated hydrocarbon pesticides have all been recorded in some sediment samples.

The main source of toxicants is probably urban runoff entering directly or via creeks which flow directly into the estuary, with water from the upper Yarra catchment of much less concern. However that assessment is based on concentrations of contaminants recorded in runoff and urban streams, not on contaminant loads which assess the total amount of contaminant entering the lower Yarra, and which are based on both the concentration and the volume of the contaminant.

Within the lower Yarra most of the contaminant material is deposited within the sediment as the freshwater and salt water mix. Predicting the major locations for sediment deposition is not possible in the absence of an adequate understanding of the hydrodynamics of the estuary, however a study currently underway at Monash University is building a hydrodynamic model which should be able to predict areas of sediment deposition in the Yarra estuary.

The main pathway by which toxic materials leave the estuary is presumably in dredge spoil, although very large floods could also wash out considerable volumes of sediment and associated contaminants. Some of the toxic contaminants deposited in the sediments will remain over the long-term.

As the largest and busiest port in Victoria, the lower Yarra is the State's most contaminated estuary, but it is comparable with similar systems elsewhere. Australia has four extremely contaminated estuaries, the Derwent and Macquarie Harbour in Tasmania, Spencer Gulf in South Australia and Cockle Creek in New South Wales. Less contaminated than these four are Port Jackson, the Georges River and Port Hunter in New South Wales. The Yarra seems to rank at the third level, with contamination levels similar to Port Adelaide, Brisbane, Port Hacking and the Hawkesbury, although the extent of contamination in the latter is quite limited.

Compared with international urban estuaries the maximum levels of metal contaminants in the Yarra appear slightly higher than, but comparable to, levels measured elsewhere, including Boston and San Francisco in the US and the Mersey, Clyde and Thames in the UK.

Contaminant assessment needs to focus on sampling of water and suspended particulate material to assess the impact of spillages or floods and for constructing inflow and outflow budgets, but on bottom sediment for long term monitoring. Toxic contaminants are normally present only in very low concentrations so sampling procedures and equipment need to be appropriate to ensure contamination is avoided. Simple parameters such as electrical conductivity and turbidity, which can be measured in the field, may be useful in guiding selection of sample locations for water and suspended particulate material.

For conventional sampling, sample storage and analysis procedures vary depending on the contaminant of interest. Standard analytical methods are available for all metals and most organic contaminants and NATA accredited laboratories should always be used for sample analysis, particularly for assessment against specific guidelines.

Fluorometric methods developed to assess some organic contaminants in water in situ will probably not be useful in the short term for monitoring in the lower Yarra. While fluorometric methods appear to work successfully in off-shore marine waters, in inland waters where the concentrations of natural organics (which include some PAHs) are far higher and turbidity levels are also high they appear to be of limited value. Fluorometric techniques can be usefully used to assess algal biomass and abundance of higher level algal taxa under most natural turbidity conditions. Continuous bioassay techniques can also be used for non-specific detection of toxic materials, but the methods are expensive to establish.

A risk assessment for toxic contaminants in the Lower Yarra should be conducted. The assessment should not be conducted until the hydrodynamic model currently being developed by Monash University is available, and has been adapted for toxicant studies. The model should then be used to help in the design of an appropriate toxic contaminant survey of the lower Yarra that would provide the basic data for the risk analysis.

1. Introduction

1.1 Background

Much of the runoff from the land reaches the sea via estuaries. As the interface between rivers, the land and the sea, estuaries are physically and ecologically complex systems. Environmentally they are also one of the locations in the landscape where human influences are most apparent, since they may be impacted by local changes and by changes occurring far upstream in the river system and its catchment.

Estuaries have often been favoured places for human settlements. They often provide extensive areas of flat fertile land suitable for agriculture, abundant water from the river and access to trade routes via the sea. Consequently many estuaries are densely populated, often supporting large cities. Bangkok, Saigon, Alexandria, New York, New Orleans, Buenos Aires and San Francisco are all large cities located on estuaries while the Netherlands and Bangladesh are two countries almost entirely contained within estuarine environments.

Within Australia most of the capital cities are located on estuaries. Perth, Brisbane, Hobart and Melbourne are all located on estuaries, and the growth of Sydney depended on the estuaries of the Parramatta, Georges and Hawkesbury rivers.

Melbourne became the first successful large settlement in Victoria because of its location on the Yarra River estuary. The settlement was located at the point on the river where a rocky reef restricted the upstream movement of saline water, thus providing a source of freshwater for domestic, agricultural, and later industrial use, as well as a safe harbour with access to the sea for trade.

The growth of Melbourne has resulted in major changes to the Yarra estuary. The river channel has been dramatically altered with bends cut off at Herring Island and past the present Botanic Gardens and by the construction of the Coode Canal in the 1880s downstream of the present Bolte bridge. A natural pool used as a ship turning bay below the present Queen Street bridge was partly filled to create a carpark in the 1950s and then re-excavated in 1996. The Victoria Dock was excavated in the early 1900s and marshes surrounding the river were filled over time. Rock bars at Queens Street and Princes Bridges were removed permitting saline water to extend upstream, possibly as far as Dights Falls at times. With the use of the lower Yarra as a port and for navigation the river was widened and deepened by dredging, snags were removed and the banks stabilized with rock beaching and piles (Otto 2005).

As Melbourne has grown the lower Yarra has been the receiving water for a range of toxicants. Some of these are historical and have long since ceased. Examples include toxic materials released from gold mining in the river and the catchment, and from industries historically located along the river, such as tanning, rendering and brewing. Some toxic materials from these historical activities may still be present within the Yarra system. However, as the city of greater Melbourne has expanded, the amount of urban runoff has increased with its own associated toxicant load. Concurrently the flow of clean water from the upper catchment has decreased as water has been diverted within the catchment, which would tend to increase the concentrations of toxicants, and some, such as zinc, have increased (Pettigrove and Hoffmann 2002), but in other cases improved catchment management and other factors have led to a decrease, as discussed below for lead. The potential for cumulative effects of toxic discharges from small and illegal discharges to urban drains discharging to the river has also grown.

Over recent decades discharges to the river from sewage and septic tanks have decreased as the metropolitan area has increasingly been sewered. Most effluents are now piped to the Western and Eastern Treatment Plants outside the Yarra catchment. Only a relatively small amount of wastewater

from sewage treatment plants still discharges into the Yarra, via Olinda Creek, Brushy Creek and Merri Creek.

The quality of storm runoff reaching the river may also be improving. The change from leaded to unleaded petrol has decreased lead in road runoff (Pettigrove and Hoffmann 2002), and the installation of flood retarding basins has incidentally provided settling basins for sediments and their associated contaminants during major floods.

1.2 Objectives

The purpose of this paper is to review the current knowledge of the origins, fate and dispersion of toxicants in estuarine systems with particular reference to the lower Yarra River, which is identified as that part of the river extending from Dights Falls to Hobsons Bay. The literature review identifies, summarizes and evaluates issues relating to:

- ▶ The current state of knowledge of origins, fate and dispersion of toxicants in the lower Yarra area;
- ▶ Benchmarking of this knowledge to similar urban estuarine environments; and,
- ▶ Methods for assessing commonly occurring toxicants in estuarine environments.

2. Estuarine Environments

Estuaries are complex physical environments (Abbott, Dawson et al. 1971; Reid and Wood 1976). The unidirectional flow of the stream water interacts with the oscillating tidal currents. The fresh water from the inflowing stream is less dense than the sea water which may result in the stream water flowing over the top of the sea water forming a “salt wedge”, a layer of marine water, sometimes sharply defined, below the surface freshwater (Figure 1). Whether, and to what extent, a salt wedge forms depends on a number of factors including the morphology of the estuary, and the amount and velocity of the freshwater flow. The freshwater flow varies with time – seasonally between dry and wet seasons, and irregularly in response to periods of rainfall.

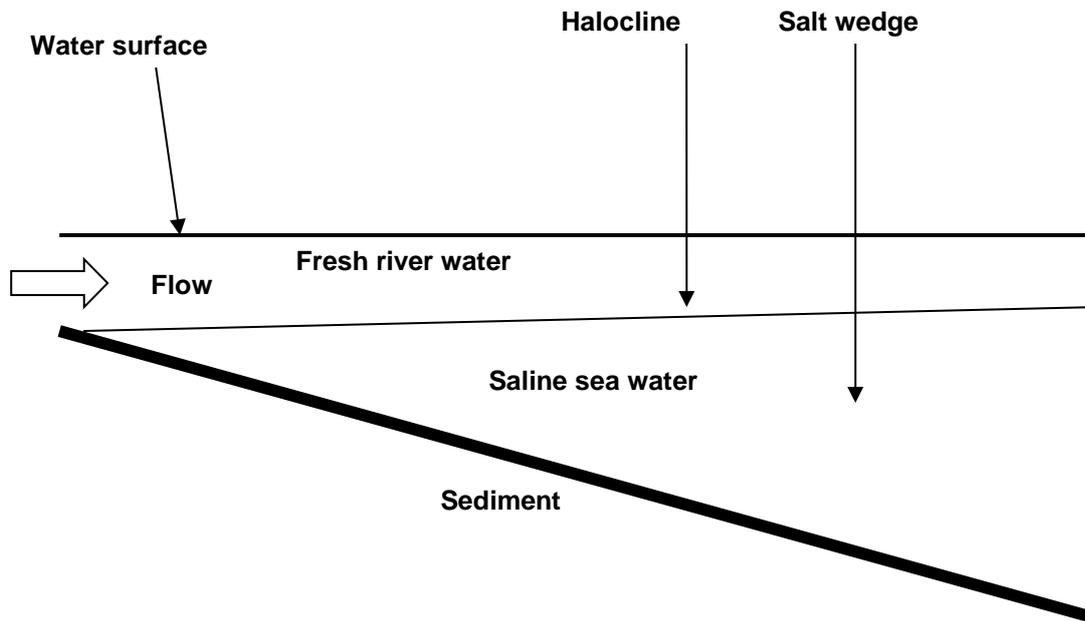


Figure 1 Diagrammatic illustration of an estuary

Indicating the pattern of flow of the freshwater from the river flowing over the top of the saline marine water creating a halocline – a layer where the salinity of the water changes rapidly from fresh to salty.

In the case of the lower Yarra, Beckett and co-workers (Beckett, Easton et al. 1978; Beckett, Easton et al. 1982) identified a well defined salt wedge within the Yarra channel but not within the Maribyrnong arm of the estuary. The location of the upstream tip of the wedge varied depending on the tidal cycle and freshwater flows: under low river flows the wedge extended to above Bridge Road, during medium flows to above Punt Road, and during high river flows only to King Street. They used a simple compartmentalized model to estimate residence times for the fresh and salt water components under a range of flows.

The model produced by Beckett et al. in 1978 has not yet been updated. More recent investigations by SKM (SKM 2005) used the earlier studies by Beckett et al. as their major source of data, but also referred to salinity profile data collected by McGuckin (McGuckin 2003). However, a project currently underway at the Water Studies Centre at Monash University, supported by Melbourne Water and the EPA, is developing a hydraulic model of the estuary which is due to be completed later in 2010. The model is being developed as part of a study of nutrient pathways within the estuary, but will be

sufficiently generalized that it could also be used to support toxicant studies (Perrin Cook pers. comm.).

The changing water chemistry, as the freshwater mixes with the saltier marine water, influences the physicochemical characteristics of solutes and suspended materials in the water. Through hydrodynamic factors and physical, chemical and biological processes, estuaries act as efficient traps for suspended particulate material (Beckett 1988). Efficient scavenging mechanisms such as adsorption, complexation, co-precipitation and biological uptake scrubs the water phase of many elements (Beckett 1988). The high ionic strength of the saline water contributes to coagulation, flocculation and thus to the settling of suspended particulate material and contaminants attached to it. Some metals (e.g. cadmium and zinc) can be remobilized from suspended particulate material in water of higher ionic strength, such as the saline bottom water in estuaries (Hart and Davies 1981).

Whether the settled material with the associated contaminants remains in the estuarine sediments, and for how long, depends on estuarine hydrodynamics, hydrology and chemistry. Material may be resuspended during high flow events and either relocated within the estuary or flushed through to the sea. Dredging activities will remove some sediment, but also resuspend and redistribute it in the estuary or flushed through. Some of the material may remain in the sediment permanently.

The development of the salt wedge may also contribute to de-oxygenation within the estuary. The development of the halocline – the often quite sharp boundary between the upper layer of freshwater and the lower layer of sea water, sharply reduces the vertical movement of solutes, including oxygen (Figure 1). Thus the lower layers of water may become deoxygenated, especially where there are large amounts of organic material being deposited that is aerobically decomposed by microorganisms using up oxygen from solution.

Reduced oxygen concentrations may have direct and indirect impacts on the biota, as well as causing chemical changes to toxic contaminants. If oxygen concentrations are low enough for long enough fish and other animals may be killed. Non-lethal reduced oxygen concentrations reduce the tolerance of fish and invertebrates to toxic stressors, so that chronic or even acute toxicity may occur.

Under anoxic conditions some toxicants bound to particulates are desorbed and pass more readily into solution. In solution they are more readily bioavailable, and thus more effectively toxic (Allan 1986). For example iron hydroxides, which bind many metals, dissolve under anaerobic conditions, and release adsorbed metals such as lead at low pH (Florence 1986). The salt wedge in the Yarra is known to become anoxic periodically (P. Cook pers. comm.).

Estuaries also frequently have complex interactions with terrestrial or semi-terrestrial systems such as salt marshes. This was once the case with the lower Yarra (Otto 2005), but the marshes and most of the other components of the natural riparian environment of the lower Yarra have long since disappeared under urban development (Arundel and Barton 2007). Some of the particulate material transported by rivers is deposited in the fringing salt marshes of estuaries during high river flows and/or high tides, but this process no longer occurs within the Yarra because these fringing systems are no longer present, having been filled and replaced by rock beaching and wharves.

3. Toxicants

3.1 Categorization of Toxicants

Toxicants can be categorized in a range of ways depending on the purpose. One categorization distinguishes inorganic (mainly metals and metalloids) and organic materials. Both tend to be relatively insoluble in water and are mainly transported associated with suspended particulate material.

Some toxicants are soluble in water and will enter and leave the lower Yarra mainly in solution. In general there are relatively few such compounds and they tend to be of less long-term concern. They may be present in the sediments, but if the concentration in the overlying water falls, then the material will diffuse out of the sediment and be flushed out of the system (Durum 1971). Soluble compounds tend to be diluted during high river flows so their concentrations frequently drop during flood hydrographs unless there is a constant source or spillage.

Toxic materials which are insoluble in water are primarily transported adsorbed on to particulate matter suspended in the water column. These materials tend to increase in concentration at the beginning of a flood hydrograph, and a time series plot of concentration forms a hysteresis curve (Chapman 1996). Toxicants attached to particulates may settle out in the sediments of the lower Yarra where they may remain until either they are flushed out in to Port Phillip Bay by a large flood event, removed by dredging or they breakdown. Metals are elements and therefore never break down, and some organic materials are very refractile (i.e they are stable and don't decompose readily), so both may remain in the estuary for a very long time.

Another useful categorization of toxicants is by persistence, generally measured as half life, the time taken for half of the initial amount of material to break down. Some toxic materials break down relatively quickly in the environment. Included in this group are a number of pesticides and some pharmaceuticals which may have half lives of days to weeks. Other toxicants, including many of the chlorinated hydrocarbons break down far more slowly, with half lives of years to decades. The final group are toxicants such as metals such as mercury or cadmium which never break down. They may be bound in relatively less toxic forms, but they always have the potential to be remobilized.

3.2 Water Soluble Toxicants

Water soluble toxicants are generally not persistent, particularly in river systems. They include materials such as ammonia, chlorine, sulphides, surfactants and some dyes.

Within the Yarra River key dissolved potential toxicants, in the broadest sense, include ammonia, oxygen (or the lack thereof), and salt, which may be toxic to the freshwater biota (Hart, Bailey et al. 1991). Most metals are more toxic in their dissolved, free ionic form than in other chemical forms (Daly, Campbell et al. 1990), but it is the other forms that are more abundant under the most common environmental conditions encountered in estuaries (Ellaway 1980).

In general water soluble toxicants and toxicants in suspension, are only likely to be responsible for short term acute water quality events in the lower Yarra. Such events would occur following storm flows, discharges or spillages. After a spill or a storm the water flushes through the system and disperses the toxicants unless there is a continuing source of material.

3.3 Particle-bound Toxicants

Many contaminants, including many toxic materials, are primarily transported in rivers attached to suspended particulates. These include phosphorus, metals, chlorinated pesticides, PAHs, PCBs, dioxins and furans (Ongley 1996). Ongley, (1966) noted that 65% of the 128 priority pollutants listed by the United States Environmental Protection Agency are found mainly, or exclusively, in association with sediment and biota. Much of that material, on reaching an estuary, is deposited in the estuarine sediment.

Once contaminants become bound to particle surfaces, or sorbed into the interior matrix, they are less likely to be biotransformed and desorption is usually very slow (Burton and Landrum 2003). As a result sorbed contaminants will remain in the sediment for a long time. If the contaminant in the sediment is causing acute toxic episodes, there is usually sufficient toxicant in the associated water to also cause toxicity, but chronic ecological or toxicological consequences, including bioaccumulation impacts may occur due to sediment contamination even if concentrations of toxic material in the water are very low.

3.3.1 Metals

A variety of metals are toxic to aquatic organisms (ANZECC 2000). Those that have been considered of concern in the lower Yarra include cadmium, copper, chromium, lead, mercury, nickel, silver and zinc. Particular metals may be of potential concern because they are especially toxic (e.g. cadmium (USEPA 1976)), or because they are common contaminants of aquatic systems(Lewin 1997). Copper, lead and zinc are, or were, commonly used in urban and industrial environments(Pettigrove and Hoffmann 2002). Copper and lead were used in pipes and plumbing, and zinc as a protective coating on galvanized building materials. As a result of their widespread usage there is great potential for them to have leached or eroded and washed into waterways. Lead was also an additive in petrol until recently, so atmospheric deposition of lead was also a major source in urban environments, and lead wash off from roads and other surfaces would have entered streams. Notably lead levels in stream sediments around Melbourne have decreased since the 1980s when lead in petrol was phased out. Iron is even more common, but is far less toxic so of far less concern. Cadmium, mercury and silver are, or were, all used fairly widely in industrial processes. For example cadmium has been used in electroplating, pigments and textile processing (USEPA 1976), mercury was used as a fungicide and also for the production of chlorine and silver was used in photographic processes and as a catalyst in a number of chemical processes(USEPA 1976). Consequently all are likely to have been present in liquid waste discharges historically, and in landfills and waste dumps now, and are all relatively toxic(Hart 1982).

High levels of metals have been recorded in urban runoff and in urban streams within the Yarra catchment (Weeks 1981; Pettigrove and Hoffmann 2002; Pettigrove and Hoffmann 2003; Pettigrove 2003). That is not surprising since it is well known that urban runoff is contaminated particularly by metals and organic contaminants (Field and Turkeltaub 1981; Pitt, Field et al. 1995). Contaminants in the tributary streams, if they are chemically stable, eventually find their way into the main stream and most of the metals in the tributaries have also been recorded from either the Yarra mainstream or the estuary(Pettigrove 1998; Pettigrove and Hoffmann 2002; Coleman and Tiller 2006).

3.3.2 Organics

Many organic toxicants are hydrophobic (water hating) and preferentially bind to suspended particles or sediment rather than remaining in the water column. There are a broad range of groups of organic chemicals recognized as having strongly toxic effects and that are known or likely to occur within the lower Yarra. They include:

- ▶ Petroleum hydrocarbons (TPHs) derived mainly from fuels, oils and their by-products and breakdown products;
- ▶ Polycyclic Aromatic Hydrocarbons (PAHs) derived from a variety of sources including the burning of fossil fuels and petrochemicals (Bagg, Smith et al. 1981);
- ▶ Polychlorinated Biphenyls (PCBs) were initially developed as cooling and insulation fluid for industrial transformers and capacitors but have also been used for a variety of other purposes including as stabilizers in flexible PVC (polyvinyl chloride) and in adhesives and waterproofing compounds;
- ▶ Organochlorine compounds (OCs) are a broad group of compounds which received a great deal of publicity in an environmental context because it contained a number of very stable pesticides such as DDT and dieldrin, but also includes materials such as PVC and solvents such as chloroform and dichloromethane; and,
- ▶ Organophosphorus compounds (OPs) are degradable compounds primarily developed as replacement pesticides for the far more stable organochlorine pesticides. They include compounds such as malathion.

As with metals, organic toxicants are widely encountered in urban runoff throughout the world (Pitt, Field et al. 1995). PAHs, because they may be volatilized, may also be dispersed aerially, via precipitation (Smith and Maher 1984).

4. Toxicants in the Lower Yarra

The discussion of sources and fates of toxic materials in the lower Yarra is based on a conceptual model identifying major sources and sinks (Figure 2).

4.1 Toxicant Sources

4.1.1 Toxicants from Waterways and Runoff

Toxicants may enter the lower Yarra from a variety of sources. Stream flow passing over Dights Falls from the Yarra River upstream drains a forested and agricultural catchment, but also urban areas of the suburbs of Melbourne. The Maribyrnong River, the other major tributary stream, also has rural agricultural headwaters before flowing through urban areas. The smaller streams which drain directly into the lower Yarra include Merri Creek, Gardiners Creek and Moonee Ponds Creek. They are all essentially urban streams with all or most of their catchments developed for residential, commercial and industrial activities. In addition to these small streams there are a number of storm water drains, many of which were small creeks prior to the urbanization of Melbourne, which drain directly into the estuarine section of the river. These include drains under Elizabeth Street, Fitzroy Gardens and South Yarra.

The small urban streams have some baseflow fed from groundwater, but they gain their higher flows from stormwater runoff. Consequently their chemical water quality is usually poor during high flow periods. Weeks (Weeks 1982) reported metal concentrations from a number of urban streams and drains in Melbourne, including several tributaries of the lower Yarra and lead, zinc, copper and chromium were all high in several streams.

More recently Pettigrove (Pettigrove 1998; Pettigrove and Hoffmann 2002; Pettigrove and Hoffmann 2003; Pettigrove 2003) surveyed metal concentrations from 171 sites in 64 streams in the greater Melbourne area. He noted that only 10% of sites in urban streams in the Yarra valley upstream of Dights Falls had one or more metals exceeding the Interim Sediment Quality Guidelines recommended by ANZECC (ANZECC 2000), whilst 79% of sites within Gardiners Creek and 78% of sites in the northern and western suburbs had at least one metal which exceeded the guidelines. Zinc, cadmium, lead and nickel were the metals most frequently elevated, and levels seemed to be higher with lower urbanization levels in areas on basaltic rather than sedimentary soils. That is not a surprising result since the clay soils more common in sedimentary areas will tend to bind metals.

Overall Pettigrove's results suggest that most metals entering the lower Yarra are arising from urban runoff and entering 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.

There is less information available on organic contaminants in streams in the Yarra catchment. O'Connor and Moore (O'Connor and Moore 2001) report a range of organic contaminants including PAHs, PCBs and pesticides. The pesticides recorded included chlorpyrifos, dieldrin, lindane, endrin and DDT, and they were more often detected in urban rather than in rural locations.

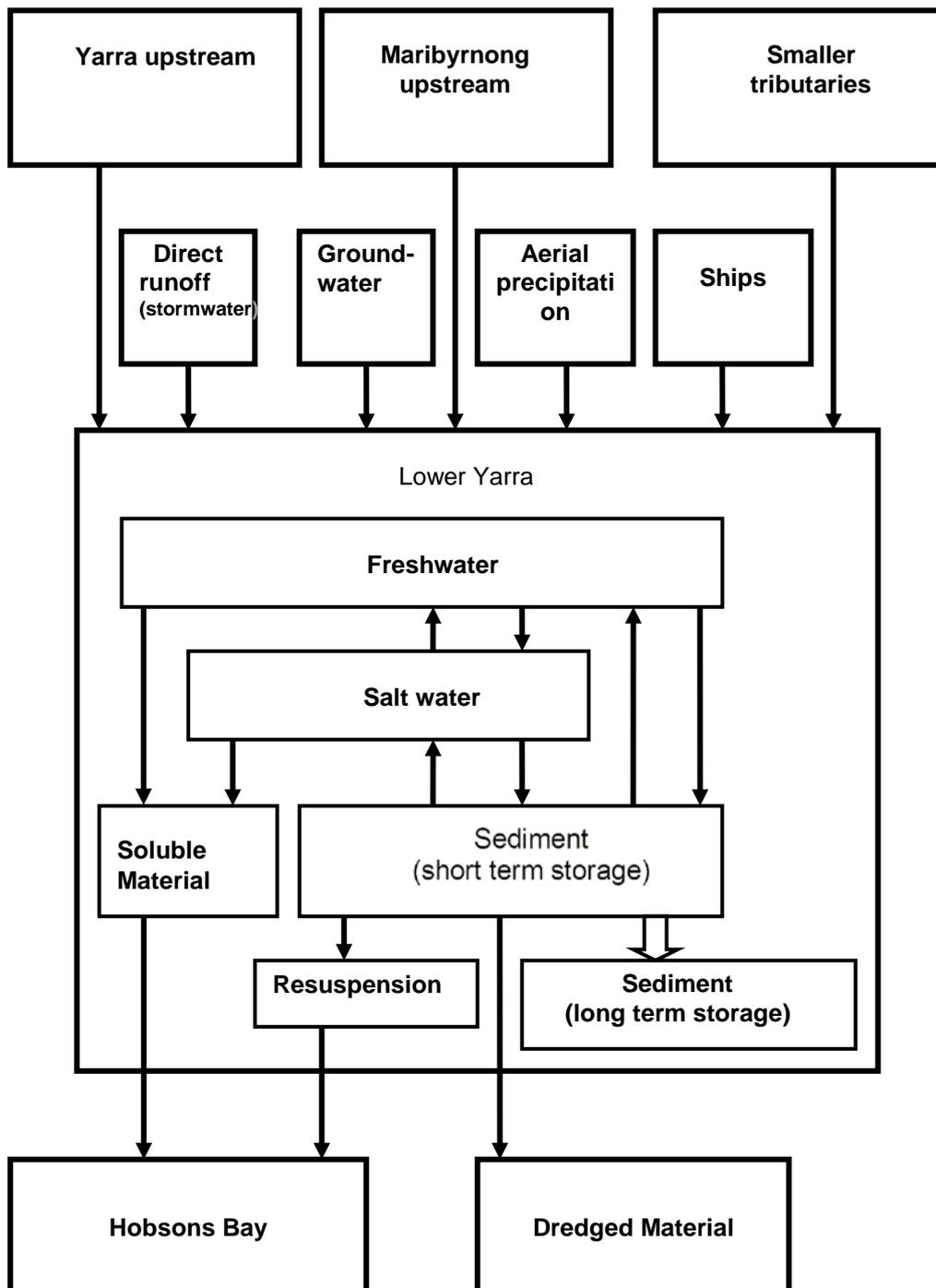


Figure 2 A Conceptual Model of Toxicant Pathways within the Lower Yarra

The extent to which contaminants in tributary streams pose a risk to the Lower Yarra depends on more than their concentrations in the tributary sediments or suspended particulate matter, although that is usually the only parameter reported. Obviously the volume of contaminated sediment present is also critical in determining the total amount of sediment that may be delivered to the estuary. How much is delivered, and over what time period, then depends on the hydrology of the tributary, the size and frequency of floods which may deliver the material, and the morphology of the stream channel. Concrete drains such as the lower sections of Moonee Ponds and Gardiners Creeks will retain effectively no sediment during a high flow period, while complex channels with connected floodplain

areas may retain quite a lot of material for long periods of time. With long retention periods some toxic organic materials may break down before reaching the estuary, but that is not the case for trace metals.

4.1.2 Toxicants in Groundwater

In addition to surface flows toxic materials may be transported by groundwater. The Port Phillip Bay study suggested that only 2-12% of groundwater flows pass directly to the bay, with the rest entering streams (Harris, Batley et al. 1996). The extent of groundwater flows into the lower Yarra is not known, but much of the port and industrial area has been built on former wetlands where groundwater levels must have been quite high. With urbanization and the current drought that may no longer be the case. Contaminants identified as present in, or likely to be present in, groundwater include a range of metals (Iron, chromium, copper, nickel, lead, zinc, arsenic, and cadmium) while a review conducted for the Port Phillip Bay investigation identified phenols as the organic contaminant of most concern (Harris, Batley et al. 1996).

A recent audit of the Whitehall Street Yarraville precinct (GHD 2009) identified risks to the environment from a number of toxicants in groundwater. A high level of risk was identified from hydrocarbons, a medium risk from toxicants including arsenic, copper, zinc and ammonia and a medium risk from nutrients all via groundwater leaching from contaminated sites, although there appeared to be a paucity of data on movement of groundwater or its contaminant levels.

4.1.3 Toxicants from Ships

Within the port area of the estuary toxic contaminants from ships are of potential concern. The potential sources include leachates from ship surfaces which include anti-fouling agents such as tributyl tin (TBT) and metal ions, leakage and discharges from ships which can include petroleum hydrocarbons such as oils, grease and fuel as well as wastewater, and finally accidental spillages which can include cargo materials. Accidental spillages can result in large volumes of material entering the waterway, but are rare events, while the other sources contribute small volumes of material from any individual vessel, but impacts can arise from the large number of vessels over a long period of time. The Port Phillip Bay study found that levels of TBT, lead and zinc were marginally higher in the Melbourne port than elsewhere in the bay (Harris, Batley et al. 1996).

4.1.4 Toxicants from Aerial Precipitation

Finally toxic material may be deposited directly by dust and rainfall. A literature review conducted for the Port Phillip Bay study concluded that there is insufficient data to support credible estimates of the atmospheric inputs of toxicants to Port Phillip Bay (Beer, Carnovale et al. 1992). The review noted that atmospheric inputs had been shown to be major contributors to toxicant loads in the Great Lakes and some marine systems (Bidleman 1988; Beer, Carnovale et al. 1992). In the case of the lower Yarra the elongated shape means that it has a relatively high ratio of edge to surface area, and much of the dust from urban and industrial areas adjacent to the river could be expected to contain relatively high levels of toxic contaminants so airborne particulates may not be a negligible source of contamination.

4.2 Toxicant Sources for the Lower Yarra

To be confident that major toxicant sources for the lower Yarra were identified would require development of a budget taking account of loads of material coming from various sources. Loads are calculated from the concentrations of toxicants in the water (or precipitation) and the volume of water. Based on existing information it appears likely that urban runoff and urban streams such as Gardiners Creek and the Maribyrnong River are the major sources of metals and probably also organic contaminants. That assessment is based solely on recorded high levels of contaminants in those systems. No information on toxicant loads transported by the streams is currently available.

Development of a toxicant input budget for the lower Yarra would be difficult and expensive. The concentrations of toxic contaminants in streams and urban drains change dramatically with discharge, so an effective monitoring program needs to use sampling equipment which collects samples through flood hydrographs. In the case of the Yarra estuary there are also a large number of inflowing creeks, drains and other sources (Figure 2) that would need to be considered and potentially included in an assessment.

Whether such a complex and potentially expensive sampling project is justified depends on the level of risk currently perceived in the estuary. In view of the large number of toxic materials present, and occasional high concentrations recorded, a preliminary risk analysis would seem advisable.

5. Toxicant Fates

5.1 Water Soluble Toxicants

Within the lower Yarra deoxygenation has been reported several times, and may be a cause or a contributing factor in occasional fish kills. Deoxygenation results when organic material is sufficiently abundant and the hydrodynamics result in low reaeration rates. Other potential soluble toxicants are also strongly affected by the hydrodynamics, being either flushed through into the marine environment or breaking down through physico-chemical or biological processes. Because rivers, including the lower Yarra, are essentially flow through systems soluble materials of any kind do not accumulate but move with the water. Materials such as ammonia may also be lost to the system through bacterial conversion to nitrite or through volatilization, but the nature of biogeochemical cycles within the lower Yarra is not known. A study led by the Water Studies Centre at Monash University is underway focussing on the influence of hydrodynamic processes in the lower Yarra on deoxygenation and nitrogen cycling.

Fire retarding chemicals have recently become a concern as they are more extensively applied both to bushfires and in urban and industrial locations. Several of these that are applied to forest fires break down into ammonia and ammonia-based compounds (Chandler et al 1983), but while they may contribute to nutrient enrichment it is difficult to see them creating toxic problems in lower Yarra unless they were to be applied to a fire in Studley Park or a similar nearby locality.

5.2 Particle-Bound Toxicants

Many of the most toxic chemicals that occur in aquatic systems are either hydrophobic or preferentially adsorbed on to particles, particularly fine particles < 20 µm and clay. Both toxic metals and organic contaminants are often closely associated with suspended particulate material in the water column or bottom sediments (Allan 1988).

Suspended particulate material tends to flocculate and sediment out when fresh river water mixes with sea water in estuaries (Beckett 1988). However these processes may be complex, variable and influenced by flow. Iron, copper, cadmium, zinc lead and tin have been identified as metals removed from the Yarra water column by natural sedimentation processes when the fresh and sea waters mix (Hart and Davies 1981; Harris, Batley et al. 1996; Fabris.G.J 1999). Sedimentation has been identified as one of the processes responsible for an inverse relationship between salinity and suspended particulate material and filterable iron in the Yarra estuary (Ellaway 1980; Beckett 1988).

As a consequence of these sedimentation processes estuarine and inshore sediments often contain relatively high levels of metals and organic contaminants (Allan 1988).

5.2.1 Metals in the Lower Yarra Sediments

Within the lower Yarra sediments high levels a number of metals have been recorded. High levels of copper, lead and zinc were noted by the Port Phillip Bay study (Harris, Batley et al. 1996) based on EPA data from 1976. High levels of cadmium, copper, lead and zinc were recorded by Ellaway and co-workers near the head of the estuarine section of the river (Ellaway, Hart et al. 1982), which they attributed to coagulation and sedimentation of trace-metal-enriched iron and manganese oxides in the estuarine region.

Coleman and Tiller (Coleman and Tiller 2006) reported metals levels in sediments from 11 sites between Herring Island and Fairview park. Zinc was present at levels presenting high risk to ecosystem health based on the ANZECC guidelines (ANZECC 2000) in all samples, and lead was present at a high risk level in one sample and at a moderate risk level in the other 10 samples. Mercury was present at a moderate risk in all eleven samples as was nickel in 9 of 11 samples. Both

copper and cadmium were present at moderate risk levels in a single sample each. Chromium and arsenic were present at levels below the moderate risk level in all samples.

Twenty-two fish of five species from the lower Yarra and the Maribyrnong were analyzed for arsenic, copper, mercury, selenium and zinc (Coleman and Tiller 2006) but none had levels of any metal which exceeded the Australia and New Zealand Food Standards Maximum Residue Limit.

More recently analysis of sediments in the vicinity of the crossing site for the Melbourne Main Sewer, near Grimes Bridge identified that more than half the sixteen samples tested exceeded the EPA Publication 691 maximum and minimum sediment screening levels for lead, nickel silver and zinc (GHD 2008).

Precipitation and sedimentation processes ensure that sediment levels of toxic contaminants are not uniform. For example the levels of metals within the estuarine section of the river are higher than the levels in either the freshwater or marine sections (Ellaway, Hart et al. 1982). However the study by Ellaway et al. (Ellaway, Hart et al. 1982) appears to be the only systematic investigation of the longitudinal distribution of metals within the estuarine sediment, and that study did not investigate patterns in other reaches of the estuary, such as the Maribyrnong.

5.2.2 Toxic Organics in the Lower Yarra Sediments

Elevated levels of a range of organic toxicants have also been recorded from the lower Yarra. Bagg et al. (Bagg, Smith et al. 1981) reported the first analyses of PAHs from any Australian estuary or river recording high levels of benzo[a] pyrene, a known carcinogen, and perylene in sediments in the mainstream as well as in sediments from Moonee Ponds Creek and Stony Creek. Smith and Maher (Smith and Maher 1984) sampled locations in Port Phillip Bay, Corio Bay and the Yarra estuary for aromatic hydrocarbons, which are indicators of fuel oil contamination. The highest concentrations they recorded occurred in the Yarra downstream of the confluence with Moonee Ponds Creek, at a location where high levels of PAHs had previously been recorded. The samples at this locality emitted fluorescence spectra consistent with the presence of some crude oil, whereas all other samples spectra were consistent with refined oil products.

Good and Gibbs (Good and Gibbs 1995) conducted the first comprehensive survey of organic contaminants across Port Phillip Bay, including parts of the Yarra estuary (Harris, Batley et al. 1996). The contaminants surveyed included petroleum hydrocarbons, polynuclear aromatic hydrocarbons, organochlorine and organophosphorus insecticides, chlorinated phenols and triazine pesticides. The highest concentrations of petroleum hydrocarbons (810 mg/kg) were recorded in the Yarra estuary (Harris, Batley et al. 1996). The Yarra mouth and Hobsons Bay were also the only localities where significant DDT concentrations were found, and the levels of PCBs in those localities appeared unchanged since the 1970s (Harris, Batley et al. 1996).

Coleman and Tiller (Coleman and Tiller 2006) sampled sediment from 11 sites along the estuary between South Yarra and Hawthorn. They detected Arochlors 1260, a PCB in one sample, and traces of the same PCB and Arochlor 1254 in all samples. One eel, caught at Herring Island in the same study also contained Arochlor 1254 at a level of 1.5 mg/kg in muscle tissue.

More recently analysis of sediments from a site near Grimes Bridge revealed a large number of organic toxicants at elevated concentrations (GHD 2008). Of fifteen samples analyzed, 14 exceeded the EPA Publication 691 minimum screening level for dieldrin, 11 exceeded the level for 4,4'-DDD, 12 exceeded the level for 4,4'-DDE and 13 exceeded the minimum screening level for total PAHs. A number of individual constituents also exceeded EPA criteria of either the EPA Publication 691 minimum screening level or the twice background level.

5.2.3 Fate of Particle Bound Contaminants

Some of the sediment deposited in the Yarra estuary may be flushed through into the marine environment during high flow events, some may be removed by dredging and some may remain for very long periods. Because suspended particulates usually flocculate out in saline water no significant amount of the material would be transported upstream by tidal movement.. In the case of the lower Yarra there is a continuing maintenance dredging program to maintain adequate depth for ship movements, and there have also been a number of large one-off dredging operations associated with port development such as the recent Port of Melbourne channel deepening project (Lee 2009). The dredging presumably prevents a continuous accumulation of sediment, although sediment may build up in quiet backwaters

Organic toxicants bound to sediments will be broken down over time. For example PAHs may be broken down through photooxidation or metabolized by aerobic or anaerobic bacteria. The half life depends on the particular compound, and the conditions. Photooxidation requires light, oxygen, and aerobic bacteria, which metabolize the material more quickly than anaerobic bacteria. However known half-lives range from weeks to many years (Nagpal 1993).

6. Comparison with Other Estuaries

6.1 Introduction

This comparison between the Yarra and other estuaries is conducted on several scales: other estuaries within Victoria, other estuaries within Australia and other estuaries globally. Most investigations of toxic contaminants within estuaries have been conducted either because of an existing or perceived problem, or because the estuary was identified as likely to be uncontaminated and thus a good basis for comparison with potentially contaminated sites. So the data set is biased towards the very good and the very bad.

In comparing toxic contamination in estuaries there are several factors to be considered. One is the level or concentration of the contaminants. Thus an estuary such as the Derwent in Tasmania with 42,000 $\mu\text{g g}^{-1}$ of lead (Birch 2000) would be considered more contaminated than the Yarra estuary where levels recorded have been only 240 $\mu\text{g g}^{-1}$ (Coleman and Tiller 2006). However a second consideration is the area of contamination within an estuary. That could be considered as the total area of contaminated sediment – an estuary with 500 ha of contaminated sediment may be considered in worse condition than one with only 100 ha of contaminated sediment for example. However it could also be considered in terms of the proportion of the estuary impacted. Mordialloc Creek is far smaller than the Yarra estuary, so that 100ha of contaminated sediment in Mordialloc Creek would be a far greater proportion of the total estuary area than 100ha of contaminated sediment on the Yarra. Finally the volume of sediment may be an important consideration, especially in the context of possible remediation if sediment removal is being considered.

6.2 Comparisons with Victorian Estuaries

Within Victoria the Lower Yarra and estuary appears to be one of the most contaminated. The Port Phillip Bay study identified higher levels of metals in estuaries on the eastern side of Port Phillip Bay, such as Mordialloc Creek than in the Yarra Estuary (Harris, Batley et al. 1996), and (Good and Gibbs 1995) found higher concentrations of some organic contaminants in Corio Bay than in the Yarra Estuary. But Birch (Birch 2000) noted higher metal levels in Port Phillip Bay, and the Yarra estuary than in Corio Bay, and the metal levels reported by Coleman and Tiller (Coleman and Tiller 2006) from the lower River exceed those of Corio Bay, whilst organic contaminant levels in the Yarra estuary exceeded those in Mordialloc Creek and Patterson River in samples taken for the Port Phillip Bay study (Harris, Batley et al. 1996).

Melbourne Water are currently conducting an assessment using the Index of Estuarine Condition under development by the Department of Sustainability and Environment (Sophie Bourgues pers, comm.). The work is being carried out by Deakin University, who have previously reviewed information on the general ecological information on estuaries in Victoria (Arundal and Barton 2007), and is intended to allow a comparison of the overall health of Victorian estuaries, as well as tracking trends in estuarine health over time. The Victorian EPA has also recently released draft water quality guidelines for Victorian riverine estuaries excluding the Yarra estuary (EPA 2009)

6.3 Comparison with Australian Estuaries

Birch (Birch 2000) has compared metals pollution in 20 Australian estuaries and harbours for which data was available. He compared between estuaries and also levels in estuaries with those on the continental shelf. Birch (2000) distinguished four highly contaminated estuaries, all associated with particular industrial sites or clusters of industrial sites: the Derwent in eastern Tasmania, upper Spencer Gulf in South Australia, Cockle Creek in Lake Macquarie in central NSW and Macquarie Harbour in southwestern Tasmania.

After the four highly contaminated estuaries, Birch (Birch 2000) evaluated 15 other contaminated estuaries for which he had data. These include a number of estuaries associated with large urban areas including those around Sydney (Port Jackson, Georges River, Hawkesbury River) Newcastle (Hunter River, Port Hunter), Adelaide (Port Adelaide), and Brisbane (Brisbane River). Birch (2000) had relatively little metals data for the Swan River at Perth, although more is now available (Trust 2009).

Table 1 Maximum published values for metals in sediments (expressed as $\mu\text{g g}^{-1}$) from several studies on the Yarra estuary and data from some other Australian estuaries reported by Birch (2000).

| Author | Cu | Pb | Zn | Cd | Cr | Ni | Hg |
|-----------------------------------|------|------|------|-----|-----|----|------|
| Yarra | | | | | | | |
| Ellaway et al. 1982 | 197 | 587 | 1034 | 5.5 | - | - | |
| Coleman and Tiller 2006 | 67 | 240 | 850 | 1.8 | 41 | 30 | 0.36 |
| GHD 2008 | 92 | 274 | 601 | 2 | - | 35 | 0.4 |
| Harris et al. 2006 | 62 | 113 | 640 | 1 | 94 | 42 | 0.5 |
| Other Australian Estuaries | | | | | | | |
| Port Hacking | 140 | 291 | 367 | <1 | 72 | 76 | - |
| Hawkesbury River | 203 | 174 | 272 | - | - | - | - |
| Hunter River | 193 | 777 | 1638 | - | 78 | 94 | - |
| Port Jackson | 1078 | 1319 | 2246 | 10 | 118 | 38 | - |
| Brisbane River | 30 | 82 | 144 | 2 | 54 | - | - |
| Port Adelaide | 293 | 329 | 403 | 3.4 | | | 2.0 |

Birch (Birch, Shotton et al. 1998) assessed Port Jackson in Sydney as the most contaminated Australian estuary for all heavy metals followed by the Georges River/Botany Bay, and Port Hunter at Newcastle. He considered that Port Hacking, the Hawkesbury River, Port Adelaide and Port Phillip Bay were all ranked similarly and were difficult to distinguish based on metals concentrations alone (Birch 2000). The Birch ranking rates Port Phillip Bay as a total system rather than the lower Yarra and estuary upstream of Hobsons Bay, which is the area of concern for this review, and which is more contaminated than the bay as a whole (Harris, Batley et al. 1996).

Comparing data on metals in sediments from the Yarra estuary with the data from other Australian estuaries compiled by Birch suggests that the Yarra estuary is comparable to other urban estuarine ports (Table 1). Maximum published concentrations of metals in sediments in the Yarra estuary have been tabulated together with maximum values from other studies. Port Jackson is clearly more contaminated with metals than any other site. Excluding Port Jackson, the Yarra has the highest levels of cadmium and chromium, but at least one other estuary exceeds it for each of the other

metals. Brisbane appears to be in the best condition, but it is also the system for which there is least data, and the levels of metals in estuarine sediments are highly spatially variable (e.g. (Ellaway 1980; Ellaway, Hart et al. 1982), so it is not possible on the data available to be confident that Brisbane is accurately represented.

There is far less data available to assess the relative condition of the Yarra estuary with regard to organic toxicants. There does not appear to be any comprehensive studies, and for most estuaries there is no data. Connell (Connell 1995) provides some data for PAHs and other hydrocarbons from sediments in the Brisbane River, Western Port, the Parramatta River, the Yarra River estuary and Mallacoota Inlet, however since there is a mix of parameters (PAH, total hydrocarbons and grease) it is not possible to make sensible comparisons.

Table 2 Maximum concentrations of selected trace metals in sediments from a range of estuaries serving as ports for large cities in the US, UK and South Africa. All measurements in $\mu\text{g g}^{-1}$. International data from (Birch 2000).

| Estuary | Cu | Pb | Zn | Cd | Cr | Ni | Hg |
|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Yarra | 197 | 587 | 1034 | 5.5 | 94 | 42 | 0.5 |
| Other Estuaries | | | | | | | |
| Boston Harbour (USA) | 148 | 124 | 292 | 1.6 | 224 | - | 1.1 |
| Chesapeake Bay (USA) | 5 | 5 | 9 | 0.2 | 24 | - | <0.1 |
| San Francisco Bay (USA) | 161 | 67 | 501 | 0.5 | 1467 | - | 0.3 |
| Mersey Estuary (UK) | 84 | 124 | 379 | 1.2 | 84 | 29 | 3 |
| Severn Estuary (UK) | 38 | 89 | 259 | 0.6 | 55 | 33 | 0.5 |
| Clyde Estuary (UK) | 172 | 215 | 590 | 9 | - | - | - |
| Thames Estuary (UK) | 123 | 465 | 401 | 3 | 87 | 55 | - |
| Port Elizabeth (Sth Africa) | 32 | 34 | 111 | <0.1 | 11 | 8 | 0.1 |
| Durban (Sth Africa) | 56 | 84 | 184 | 0.1 | 60 | 19 | 0.2 |

6.4 Comparison with International Estuaries

For metals it is possible to compare the Yarra with some estuary/port systems in other countries. Based on data on maximum metals concentrations measured in sediments for selected estuaries in the US, UK and South Africa extracted from (Birch 2000) (Table 2) the Yarra would appear to be somewhat higher in copper, lead and zinc than most other systems, but lower in cadmium, nickel and mercury. In general the Yarra does not appear to stand out either as being much more, or much less, contaminated than other estuaries which serve as ports for large cities.

7. Toxicant Sampling

The design of toxicant sampling programs, and the equipment necessary depend on the purpose of the sampling program. Two obvious potential sampling program purposes would be monitoring to provide a long-term data set which can be used to assess progress in environmental management, and secondly to investigate a short term issue which may arise quite suddenly. Such an issue could be a spillage, a fish kill or an algal bloom.

Long term monitoring of the Yarra estuary would need to be based on sediment monitoring. It is in the sediments that most of the toxicants of concern primarily accumulate, potentially causing long term chronic toxicity issues. Toxic materials in the sediment may become bioavailable through changes in the water chemistry or through the activities of benthic organisms which live and feed in the sediment, and in turn may be eaten by pelagic fish and/or birds.

Monitoring of toxic incidents is likely to require sampling of water and suspended particulate material. Toxic incidents, such as fish kills are likely to occur either when:

- ▶ toxic material in solution or suspension enters the system either flushed in by rainfall or stormwater flows,
- ▶ Spilled on land and accidentally flushed in the river during the emergency response or cleanup operation,
- ▶ spilled directly into the water
- ▶ physico-chemical changes in the estuary cause toxic material normally bound to the sediment to be released into the water. Such a release could occur if the bottom waters adjacent to the sediment became deoxygenated for some reason.

Sediment sampling programs addressing long-term change can be planned, designed and budgeted well in advance. It is possible to prepare for water and suspended sediment sampling for acute events, in terms of having protocols and equipment in place and available, but it is not possible to plan in any detail, especially for spillages which happen without warning.

Post event sediment sampling can be conducted to establish the area over which toxic materials have settled, and the concentrations remaining. These types of sampling programs need to be informed by an understanding of the hydrodynamics of the estuary at the time of the contamination event – tidal direction, strength of freshwater flows, possibly wind direction, since these will have a major influence on the areas where contaminants may settle.

7.1 Sampling for Laboratory Analysis

There are two critical issues to be kept in mind in sampling for toxicants in rivers and estuaries. The first is that toxicants are usually present in, and toxic at, very low concentrations. As a result great care must be taken not to contaminate samples and to ensure that the sample on arrival at the laboratory still contains the contaminant at the same concentration as it did when collected. Secondly there needs to be awareness that both metals and organic contaminants are mostly associated with suspended particulate material in the water column or bottom sediments. Thus analyzing only filtered water samples is of very little value in assessing the presence and levels of these sorts of contaminants in rivers and estuaries.

In sampling for suspended material in rivers, if loads are to be calculated, the sampling will need to take account of the distribution of the sediment particles in the water column. There are numerous

detailed prescriptions for appropriate sampling techniques for sediment (and thus toxicant) loads (e.g. (Ongley 1996). In the case of stratified estuaries, such as the Yarra, the upper freshwater layers and the lower saline layers need to be sampled separately, since they may even be moving in opposite directions at times.

Detailed discussions of sampling issues and techniques are presented in (Chapman 1996). In sampling of metals it is important to avoid using metal sampling apparatus if possible. Sampling equipment should be plastic, plastic coated or glass. If a metal grab is used to sample sediment a subsample of the material that has not been in contact with the metal should be used for analysis (Ongley 1996). For samples collected for organic toxicants plastic equipment should be avoided. All sampling equipment should be acid cleaned and thoroughly rinsed with double-distilled water.

Core sampling may be employed to identify historic and recent contamination events. There are a number of texts that review sediment sampling methods (e.g. (Forstner 2002), encompassing both grab samples for bulk sediments and cores which enable time series to be established. If cores are collected and sectioned anthropogenic chemicals present in the sediments can be used to date the sediment sections, and historic time series of contamination may be established.

7.2 Laboratory Analysis Methods

There is an extensive published literature on analytical techniques for metals and organic contaminants in water and sediments, so this review will not deal with the topic intensively. Standard methods are available for all metals and many of the organic fractions (APHA 1995; Apte, Batley et al. 2002; Revill 2002) and are followed by NATA accredited laboratories. One issue, particularly for organic contaminants, may be appropriate levels of detection. In some cases, for example with some dioxins, the best practicable levels of detection in laboratory analyses may still be above the No Observed Ecologically Adverse Effect Level (NOEL), which is mathematically derived from toxicity data. In these cases a “no detect” result does not guarantee that the contaminant is not present at a sufficient concentration to have some chronic sublethal effect.

7.3 *In situ* Assessment Methods

There are limited means of assessing the presence of toxicants using in-situ techniques that are capable of giving rapid indications of toxicant presence. There are three potential approaches: the use of surrogates, the use of fluorimetric methods and the use of continuous or portable bioassays.

A problem with direct measurement of both metals and organic contaminants is that they are usually present, and toxic, at very low concentrations. As a consequence measurement is difficult and it is easy for samples to be contaminated or for interference with measurements by non-target materials. One possible solution is to use surrogate measures, such as turbidity or conductivity to track plumes associated with spillages (Mckelvie 2002), floods or unexpected events, and to supplement those measures with conventional samples which can be analysed at a later time. This approach has been advocated even for some fluorimetric techniques used for tracking oil plumes (Henry 1999). The disadvantage of the approach is that it does not provide a direct real time indication of toxicant concentrations, but it does have the advantage of being able to be implemented with existing relatively inexpensive equipment.

Submersible field fluorometers are being increasingly widely used to allow rapid assessment of a variety of environmental parameters. Essentially they work by exposing a water sample to a pulse of bright light of a known wavelength which may be absorbed by materials within the water and then re-emitted at a different wavelength. Different materials in the water will absorb different wavelengths,

and also emit the absorbed light at a slightly different wavelength. These responses can be used to measure the amounts of various materials.

The technique has been usefully applied to measuring algal abundance. Various forms of chlorophyll present in algae respond strongly, and because different forms of algae contain different mixtures of the various forms of chlorophyll data can be collected both on the total amount of algae present and the relative proportions of different algal groups present – such a green algae or cyanobacterial (blue-green algae).

Fluorimetry has been more recently applied to measuring presence of organic chemicals in water. The main application appears to have been monitoring marine oil spills (Hundahl and Højerslev 1988; Henry 1999) but the techniques are being evaluated in coastal waters and inland waters (Tedetti, Guigue et al. in press). The difficulties in contaminated waters are that there is an extensive range of potential confounding materials, often present in high concentrations. Tedetti (Tedetti, Guigue et al. in press) found that attempts to measure PAHs with a commercial instrument were confounded in sites contaminated with sewage where tryptophan-like and humic materials interfered with the instrument readings.

A major obstacle to use of fluorometric techniques in rivers is the high level of turbidity often encountered. All optical methods rely on passing a light beam through the water, and if the turbidity is too high there is insufficient light passed through to obtain a reading. This was a difficulty in the Fly River in PNG which made it difficult to measure algal biomass, and is a greater difficulty when trying to measure compounds such as PAHs which are often present in low concentrations. It is a particular issue because turbidity in rivers is usually greatest during floods, which is also the time when most organic contaminants are likely to be transported.

The final potential suite of techniques for in situ assessment of toxicity is a series of techniques based on conventional toxicity testing. There are a number of continuous rapid toxicity detection methods available. They have the advantage of being non-specific – so they will detect any toxic material present. But that is also a disadvantage since they will not indicate what the material is – whether it is a metal or organic, whether a PCB or a pesticide. They are very expensive to establish and operate, but have been successfully employed as early warning systems in the US, South Africa and Europe (Morgan 1977; Westlake and Schalie 1977). River water is pumped continuously through a series of aquaria containing fish or other test organisms. The behaviour of the fish is monitored electronically, and any sudden change in behaviour triggers an alarm. River water can then be sampled by conventional chemical techniques to ascertain whether there are toxicity issues.

8. Knowledge Gaps

It is clear that in the Yarra, as with other estuarine systems, the main collection of toxicants lies within the bottom sediment and not in the water. However knowledge of the distribution and levels of toxicants within the lower Yarra sediments is patchy and fragmented. The distribution of toxicants is a product of both the locations of the sources and the physico-chemical processes within the estuary. This influences where particulates to which most toxicants are bound settle out. The locations of greatest concentration are not necessarily the same for all toxicants.

There has been no comprehensive hydrodynamic study of the estuary since that of Beckett and co-workers (Beckett, Easton et al. 1978; Beckett, Easton et al. 1982) over thirty years ago. In view of the long drought, or climatic step change, Melbourne is currently experiencing (Howe, Jones et al. 2005; O'Neill 2009) it is necessary to update understanding of the Yarra hydrodynamics. The reduced freshwater inflows will, at the very least, have altered the position of the salt wedge. The potential alteration in tidal conditions following the channel deepening project may also have influenced the estuary to some extent. The hydrodynamics, including the presence and location of the salt wedge in the main channel, and whether a wedge is also occurring in the Maribyrnong, is fundamental to understanding the likely locations of sediment and toxicant deposition.

The study presently being carried out by the Water Studies Centre at Monash University and collaborators including the EPA should start to fill this gap. It will provide a hydrodynamic model which includes freshwater inflows, tidal movement of saline water, nutrients and oxygen. Since much of the nutrient is particulate bound the model should be adaptable for contaminant transport modelling, and the intention is to produce a model with potential applications beyond the present nitrogen cycling study (P. Cook pers. Comm.).

Another substantial knowledge gap is the absence of sufficient data to determine the current toxicant status of the estuary. Present data is fragmentary, much of it based on a small number of sampling locations, often because it was intended to address issues other than the status of the Yarra estuary. Collection of a more comprehensive data set would serve two purposes, it would act as a baseline against which future change can be assessed, and it would provide a necessary input to a risk assessment that can be used to provide a transparent process to identify whether further investigations are warranted. Such a study could usefully be established within the current EPA risk assessment protocol (EPA 2009).

There is sufficient data already available to identify broadly the sources of most metal and organic toxicants occurring in the estuary. There is also sufficient information on possible management strategies that may be used to ameliorate and reduce toxicant input. Measuring actual toxicant loads entering the estuary would be a major undertaking that could only be justified were it to be identified as necessary to manage a high and unacceptable risk.

9. Recommendations In Relation to Origin, Fate, Dispersion and Knowledge

Elevated levels of both metals and organic contaminants have been detected in the lower Yarra, sometimes at levels of concern. However the movement and deposition of these contaminants, most of which are bound to particulates, is strongly influenced by the hydrodynamics of the estuary. The most urgent need for understanding the potential risks of these contaminants is to develop a model which can predict where they will accumulate within the system.

The hydrodynamic model currently being developed through the study led by the Water Studies Centre at Monash University should be able to do this, although it may need to be adapted for the purpose. Consequently the EPA should maintain contact with the Monash group and obtain access to the model when it is functional later in 2010.

Once the model is functional, and has been adapted to model metals, organics and even bacteria, it should be used to develop a survey design to establish, more comprehensively than at present, the distribution and levels of metals and organic contaminants within the lower Yarra.

The model and the survey results should then be utilized as an input to a preliminary risk assessment, following the standard EPA risk assessment procedure. An initial semi-quantitative assessment should be conducted as a basis for deciding whether a full quantitative assessment, and the studies that would be necessary for such as assessment, would be warranted.

10. References

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