An assessment of sediment toxicants in Western Port and major tributaries

Simon Sharp

Jackie Myers

Vincent Pettigrove

July 2013

CAPIM Technical Report No 27

Executive Summary

Western Port is a remarkable marine environment, supporting a diversity of plants, animals and ecosystems, including several unique and threatened species, four marine national parks, large tracts of mangroves and seagrasses and, in addition it is listed as a RAMSAR site of international significance. The Better Bays and Waterways plan (2009) defines the environmental values, threats and management approaches to improve and sustain water quality of the rivers, creeks, and marine environments of Western Port.

Based on the recommendations of a recent knowledge review for the Western Port environment (Keough et al 2011), a preliminary survey of toxicants in sediments collected from multiple sites throughout Western Port was undertaken to determine whether they pose a risk to the health of marine organisms. A total of 42 sites were surveyed within the four major dynamic zones of Western Port as well as inflowing streams and estuaries, including measurements of heavy metals, petroleum hydrocarbons, pesticides and organotins.

Results indicated that, in general, toxicants in Western Port sediments are not at levels likely to be causing effects to resident fauna and flora. However, in some areas several metals including arsenic, nickel, mercury and organotins, were detected at levels exceeding sediment quality guidelines and pose a moderate risk to ecosystem health. Current toxicant concentrations in sediments were compared with those reported from previous studies conducted over the past 35 years. The different techniques used in these studies prevented a robust statistical comparison between these studies. However, arsenic concentrations tended to be higher and nickel concentrations lower in 2012 than in earlier studies. Hydrocarbon concentrations have generally remained constant. Organotin concentrations (tributyltin and metabolites) were much lower in 2012 than those reported in 1988 and 1997 and were below guideline concentrations, with the exception of one site in Hastings. Therefore organotins are becoming less of a concern for Western Port.

A total of 17 pesticides were detected in sediments from eight of the 22 sites surveyed. Several herbicides, particularly diuron and prometryn, and the fungicide boscalid, were detected at concentrations that may impact the health of estuarine and marine organisms. These pesticides were predominantly present in estuarine sediments near inflowing streams, and absent in bay sediments. Currently there are few guidelines for pesticides in sediments. The incidence of elevated pesticide concentrations highlights the need for further assessment into this group of toxicants to determine if the ecosystems of Western Port are at risk. Subsequent investigations should determine thresholds for aquatic flora (in particular seagrass, mangroves and phytoplankton) to the pesticides of main concern, (diuron, prometryn and boscalid) and involve

spatial and temporal monitoring of these toxicants to understand potential exposure concentrations and patterns of occurrence. The highest priority for further research involves monitoring herbicides in Sawtells Creek, the Western Contour drain, Watsons Creek and the areas just beyond their estuary. This research will allow an indication of the overall level of risk and the development of sound management protocols to ensure the long term protection of this valuable natural resource.

Priority recommendations for further research from this study are:

1. Identify the major sources of key pesticides entering Western Port
2. Determine whether the common herbicides entering Western Port pose a threat to mangroves, seagrasses and phytoplankton.
3. Continue monitoring pesticides in key inflows to the bay.

Contents

FIGURES

TABLES

APPENDICES

Introduction

Western Port is a unique marine environment of international significance (RAMSAR listed) that contains a diversity of habitats including open water, rocky reefs, extensive seagrass beds, mangroves, salt marsh and intertidal mud flats (Keough et al., 2011). It is of fundamental importance as a natural asset that provides habitat for fish, invertebrates, marine mammals, birds, plants and other marine life. The bay has an area of around 680 km^2, of which approximately 40% comprises intertidal mud flats, and a total catchment area of around 3,443 km^2 (Keough et al., 2011).

Western Port is a popular destination for recreational activities, including boating, fishing, swimming, snorkelling, diving and surfing. Commercial fishing has decreased over the last 30 years, while recreational fishing has seen significant growth with the primary catch species including King George whiting, elephant fish, snapper, black bream, gummy shark, Australian salmon, estuary perch, sea garfish, yellow eye mullet, flathead and southern calamari (Jenkins, 2011). The western and lower arms support many container shipments each year that dock at the Hastings Point shipyard. A large aquaculture facility located off Flinders in the Western Arm was established in 1985 for farming shellfish, primarily blue mussels (*Mytilus edulis*) (Arnott et al., 2000).

Western Port's catchment is mostly rural, with agriculture being the major land-use including dairy, irrigation and horticulture. Parts of Western Port's catchment have experienced major urban growth over the last 15 years (128 – 172 % between 1996 and 2010 (ABS, 2011)), with further expansion likely to continue particularly in the City of Casey and Cardinia Shire. This raises concerns regarding pollution from rural and urban run-off and regional expansion and its potential to threaten some of the natural values of Western Port in the future.

Toxicants are chemical contaminants that may have toxic effects on biota, and those of greatest concern typically include metals, petroleum hydrocarbons and pesticides (ANZECC and ARMCANZ, 2000). The toxicants that are considered likely to be of most concern for Western Port based on recently collected data (CAPIM, unpublished data 2010-2011), as well as knowledge of catchment use and impacts are pesticides, heavy metals and petroleum hydrocarbons from agricultural and industrial run-off, endocrine disrupting chemicals (EDCs), pharmaceuticals and other personal care products (i.e. detergents) from sewage effluents and septic tanks, and veterinary pharmaceuticals and oestrogens from dairying (McKinlay et al., 2008, Fisher and Scott, 2008).

Sediments are a major sink for toxicants, which can accumulate in intertidal and subtidal areas. Sediment-bound toxicants create an exposure risk for benthic organisms that can bioaccumulate through ingestion of sediment-dwelling taxa by predators, direct exposure to dissolved and particular forms in pore and surface waters and uptake by plants and algae (Roberts et al., 2006).

Study Context

Melbourne Water, the Department of Sustainability and Environment and the Port Phillip and Western Port Catchment Management Authority recently commissioned a comprehensive review of the state-of-the-science of Western Port (Keough et al., 2011). This review focused on updating and consolidating the current understanding of Western Port to help inform:

- natural resource management,
- environment protection,
- policy and planning,
- on-ground works, and,
- future research needs/recommendations.

The report raised the issue of toxicants within Western Port, and noted the lack of information on toxicant levels in the bay and considerable uncertainty regarding potential risks posed to the ecosystems (Keough et al., 2011). A screening of toxicants in the bay was identified as one of the 13 priority tasks to receive funding in the first round of the study.

A number of legislative tools afford the protection of ecosystem health within Western Port. For example, the State Environment Protection Policy (SEPP) Waters of Victoria (WoV) (Schedule 8 – Waters of Western Port and Catchment) requires catchment managers and protection agencies to identify key sources of sediment load inputs and associated toxicants, with particular regards to improvements to the East arm segment (i.e. Corinella and the eastern half of the North Upper Arm (Clause 19) (Victorian Government, 2001).

With increasing pressure from rapid urban development and broad scale agriculture within the catchment, there is a risk of adverse impacts to waterways and aquatic ecosystems from toxicants. A key strategy for tackling the issues around water quality in Western Port has been addressed in the Better Bays and Waterways Water Quality Improvement Plan for Western Port (EPA Victoria and Melbourne Water, 2009).

To determine the potential threat of toxicants within Western Port, an assessment of the concentrations of major toxicants within the bay was conducted, focusing on intertidal and subtidal areas of deposition, such as mud flats, estuary mouths and deeper channels as well as major rivers.

Sedimentation processes

Sediment distribution in Western Port is influenced by several major factors including bathymetry, hydrodynamics, zones of sediment input, and seagrass density (Wallbrink and Hancock, 2003). The greatest input of sediment into the bay in terms of total loads comes from the Bunyip Main Drain, Lang Lang River, Bass River and Cardinia and Yallock Creeks, respectively (Hughes et al., 2003), all of which, with the exception of Bass River, drain into the north eastern side of the bay (Figure 1).

The Western Entrance receives the major flows of marine waters and highest degree of coastal flushing, and contains more coarse and sandy sediments compared to other areas of the bay, (Hancock et al., 2001) which all contribute to this area being considered as a low risk area for toxicant deposition (Figure 1).

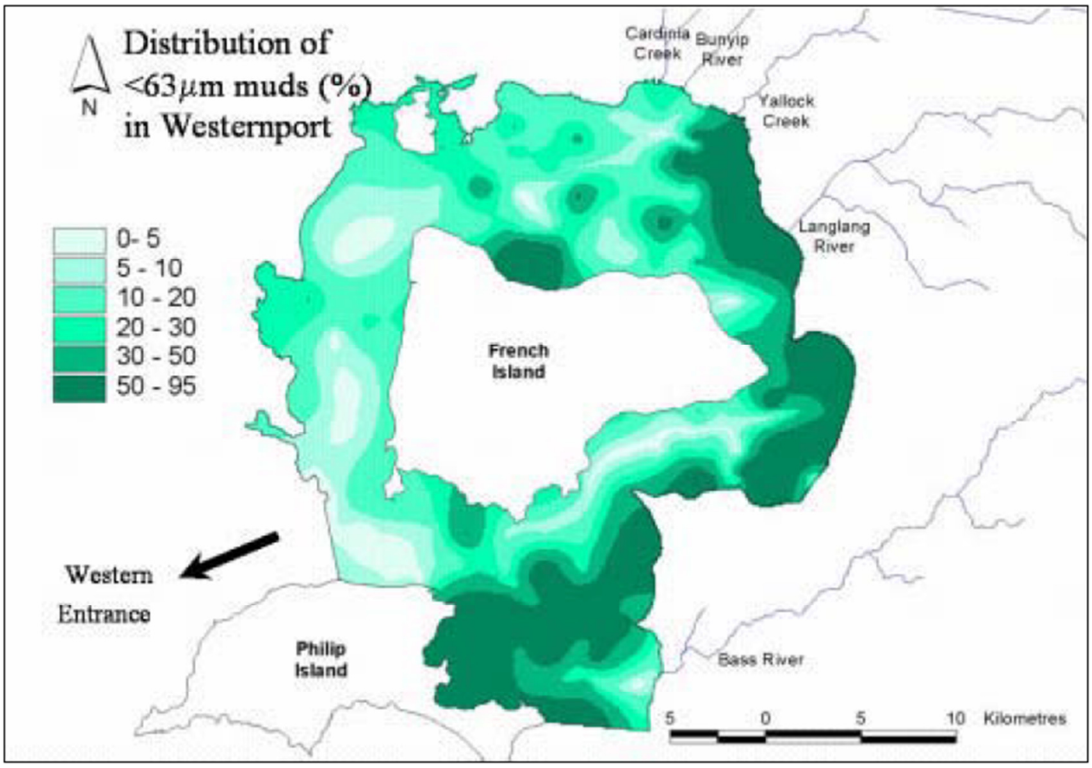

Figure 1 - Particle size distribution (%) of surface sediment between 4 and 63 µm (Hancock et al 2001).

Historical sediment quality issues

Heavy metals

Previous sediment monitoring programs have recorded elevated concentrations of heavy metals in sediments from Western Port and its waterways, primarily arsenic, mercury and nickel. For example, Rees et al. (1998) recorded arsenic concentrations in Cardinia Creek sediments that exceeded the low interim sediment quality guideline (ISQG-low) (ANZECC and ARMCANZ, 2000). Hardwick (1998) found chromium and nickel in Merricks and Coolart Creeks and lead in sediment from Warringine Creek that exceeded the ISQG-low. Concentrations above the ISQG-low indicating that sediments may be potentially toxic and further investigations are required to determine this risk. On occasions, these elevated concentrations are due to the presence of naturally high levels of metals in catchments. The basalts that are present in the southern part of the Mornington Peninsula and Phillip Island have elevated concentrations of chromium, copper and nickel (Pettigrove & Hoffman, 2003) and arsenic is commonly found throughout many parts of Victoria including gold mining and coastal areas (Fabris et al, 1999).

Within bay sediments, EPA fixed site monitoring undertaken between 1988 and 1994 on one occasion detected total mercury concentrations at levels exceeding the ISQG-low in the Corinella arm (0.49 mg/kg; median 0.03 mg/kg, N=15) and dilute extractable cadmium exceeded the ISQG-low at Barralliar Island in the Upper North Arm (1.8 mg/kg, median 0.15 mg/kg, N=13) (EPA Victoria, unpublished data 1988 - 1994).

Hydrocarbons

Previous assessments of total petroleum hydrocarbons in bay sediments were made by Burns and Smith (1977) and Rees and colleagues (1998). In 1997, the highest recorded concentrations of total petroleum hydrocarbons (TPHs) in the bay were 50 mg/kg at Cardinia Creek estuary mouth and 48 mg/kg in the French Island Marine National Park (Rees et al., 1998). Since 2010 Melbourne Water has established a sediment quality monitoring program that includes measures of TPH concentrations in two freshwater and six estuarine sites around Western Port (Melbourne Water unpublished data, 2010 - 2011). The highest concentrations of hydrocarbons were found in freshwaters at Cardinia Creek at Ballarto Road (240 - 1270 mg/kg) and Deep Creek at Ballarto Road (120 - 330 mg/kg). The highest hydrocarbon concentrations in estuarine sediments were recorded at Merricks Creek estuary (110 - 520 mg/kg), Watsons Creek estuary (150 - 340 mg/kg) and on one occasion from the Bunyip River estuary (320 mg/kg in 2011). While more recent studies did not differentiate between biogenic (naturally occurring) and anthropogenic sources of TPHs, concentrations in waterways are higher than those previously reported and hence there is a need to remeasure concentrations in the bay.

Pesticides

A number of studies have detected pesticides in several of the rivers and creeks that flow into Western Port. For instance, Melbourne Water sediment quality data from 2008 – 2009 indicated that pesticides were entering the bay via Watsons Creek, which flows into Yaringa Marine Park in the Lower North Arm, flagging this section of the bay as a crucial area for follow up monitoring. This study also detected pesticides in Cardinia Creek sediments including low concentrations of simazine and metabolites of DDT. Earlier reports detected various organochlorine pesticides (including metabolites of DDT, lindane, endosulfan and chlorpyrifos) in freshwaters including Watsons Creek, Warringine Creek and Lang Lang River among other waterways entering the bay (Hardwick, 1998, Coleman and Pettigrove, 2001). In 1997, the concentration of pesticides measured at 10 sites were all below the limits of detection including atrazine (50 µg/kg), organochlorines (<5 µg/kg) and organophosphates (<50 µg/kg) (Rees et al., 1998), with concentrations also below detection limits at four sites measured for 2,4-D (<50 µg/kg). It should be noted that the limits of detection used by Rees et al (1998) were significantly higher than those used in the studies undertaken by Hardwick (1998) and Coleman and Pettigrove (2001) which may explain why there were no pesticides detected. Beyond preliminary data of waterways, the full extent of pesticide contamination in Western Port has yet to be determined.

Antifoulant paints

Internationally, the use of tributyltin (TBT) on small vessels (<25m in length) has been banned in many countries, including Australia, since the early 1990s (Clark, 1988; Pitt, 1995). In 2001, the International Maritime Organisation (IMO) adopted the International Convention on the *Control of Harmful Anti-fouling Systems on Ships (the HAFS Convention)* and this entered into force internationally on 17th September 2008 (IMO, 2001). In January 2007, Australia became a party to the HAFS Convention, which has been implemented in Australian domestic legislation by the *Protection of the Sea (Harmful Anti-fouling Systems) Act 2006* which commenced in September 2008 to coincide with the implementation of the HAFS Convention. From 2008, TBT was no longer allowed to be present on ships in Australian ports, unless sealed to prevent it leaching into the environment (Australian Government, Department of Infrastructure and Transport, Control of Harmful Anti-fouling Systems on Ships, Available online: http://www.infrastructure.gov.au/maritime/environment/anti_fouling.aspx, updated 27th Feb 2013).

Previous studies found elevated concentrations of organotins near marinas and high use boating sites within Western Port (Daly and Fabris, 1993, Rees et al., 1998), and since organotins are highly persistent in sediments, existing concentrations may still pose an ecological risk (Rees et al., 1998, NHT, 2004). Since the ban was introduced on the use of TBT antifouling paints in 1989 for small vessels (<25m), only large vessels entering the bay would represent a potential new source of TBT up until 2008, however thereafter there should be no further input of TBT to the bay from antifouling activities.

Objectives

The Western Port knowledge review identified an important knowledge gap regarding the extent to which toxicants entering Western Port pose a threat to the marine environment (Table 1). The present study was conducted to provide an initial estimate of the risk from toxicants beyond waterway discharge points (Task 36; Keough et al., 2011).

The key objectives were to identify which toxicants occur in Western Port sediments, examine potential pathways for their dispersion in Western Port and the surrounding catchment area, and to determine if they may pose any threats to the diverse array of organisms and ecosystems within the bay.

Table 1 – Key knowledge gaps regarding toxicants in Western Port identified in the Western Port knowledge review (Keough et al., 2011).

Theme	No.	Priority	Brief Description	Details	Justification/Benefit	Chapters
Toxicants	36	1	Initial estimate of risk from toxicants	Measure levels of toxicants away from discharge points.	First cut at indicating whether toxicant are likely to be a threat across wide areas of Western Port	7 – 14
	37	2-3	Impacts of toxicants on vegetation	Understand effects of toxicants on habitat-forming species, including seagrasses (Priority 2) mangroves, (Priority 2), saltmarshes (Priority 2) and algae (Priority 3).	Input to refinement of water quality targets. Conditional on outcome for R36.	8, 9, 10
	38	2	Investigate the climate change and toxicant effects on fish	Investigate the tolerances of fish species, particularly more vulnerable eggs and larvae, to reduced water quality in north of bay, and increased temperature associated with climate change. Concurrent with laboratory studies to determine vulnerability of eggs and larvae to varying levels of water quality parameters including suspended sediments, toxicants, temperature, salinity and UVB.	The early life stages are the key to sustaining healthy fish populations but are also the most vulnerable to changes in water quality through climate change or toxicant input. Understanding the tolerance of eggs and larvae of key species to water quality changes would help in setting water quality targets.	11

This project forms part of the strategic knowledge review and aims to provide management agencies, industry, local communities and environmental groups with a greater understanding of sediment quality to help identify clear goals for catchment management and further research needs.

The main objectives of this study were to:

1) Assess if concentrations of toxicants throughout Western Port and its associated waterways exceed guidelines and/or background levels,

2) Determine if there are spatial patterns and/or common sources for certain toxicants,
3) Compare current toxicant concentrations in sediments with previous studies to determine any temporal changes.

Methods

Study Area

The Western Port catchment comprises an area of approximately 3,433 km^2, including around 2,232 km of rivers and creeks (Keough et al., 2011). Land use in the catchment in 2003 was predominately rural, with less than 5% comprising urban areas (Keough et al., 2011). Between 1996 and 2010 the population increased in the local municipalities of Cardinia, Casey, Bass Coast and Mornington by 172, 172, 144 and 128%, respectively, while the total Victorian increase in population was 122% (ABS, 2011). The average annual rainfall ranges from 750 mm along the coastline to 1200 mm in the northern reaches (Lee, 2011). Prior to extensive agricultural clearing, the lower catchment areas of Westernport contained the Koo Wee Rup Swamp, covering around 400 km^2. The swamp was drained for agricultural use in the late 1800’s and many of the waterways in the lower catchment are now extensively modified and exist as channelised drains (OCE, 1998).

Marsden (1979) divided Western Port into five key segments on the basis of hydrodynamics and bathymetry (Figure 2). Based on hydrodynamic modelling undertaken by the Victorian EPA (2011), concentrations of toxicants are predicted to be highest in the north-east of Western Port, with contaminant levels in this area closely linked to catchment inputs along the northern shores of the bay. The models predict that toxicants from other catchment inputs are likely to be well flushed from the bay by strong currents within channels and the entrance to Western Port. In the Victorian EPA’s SEPP (WoV) policy impact statement it was identified that significant knowledge gaps exist around toxicants in Northern and South Eastern Peninsula Arms and around French Island and Phillip Island (EPA Victoria, 2001).

This study therefore focused on the two north (lower and upper) and south eastern segments (Rhyll and Corinella) of the bay and included freshwater and estuarine areas as separate sections (Figure 3). The Western Entrance segment of the bay was not sampled in this study as modelling data indicates a low risk for the accumulation of heavy metals and/or other toxicants in sediments (EPA Victoria, 2011). Further, the very low organic carbon levels in sediments, negligible amounts of clay and silt (Statham, 1977), and the significant tidal exchange in this region is expected to greatly reduce toxicant binding and accumulation (EPA Victoria, 2011).

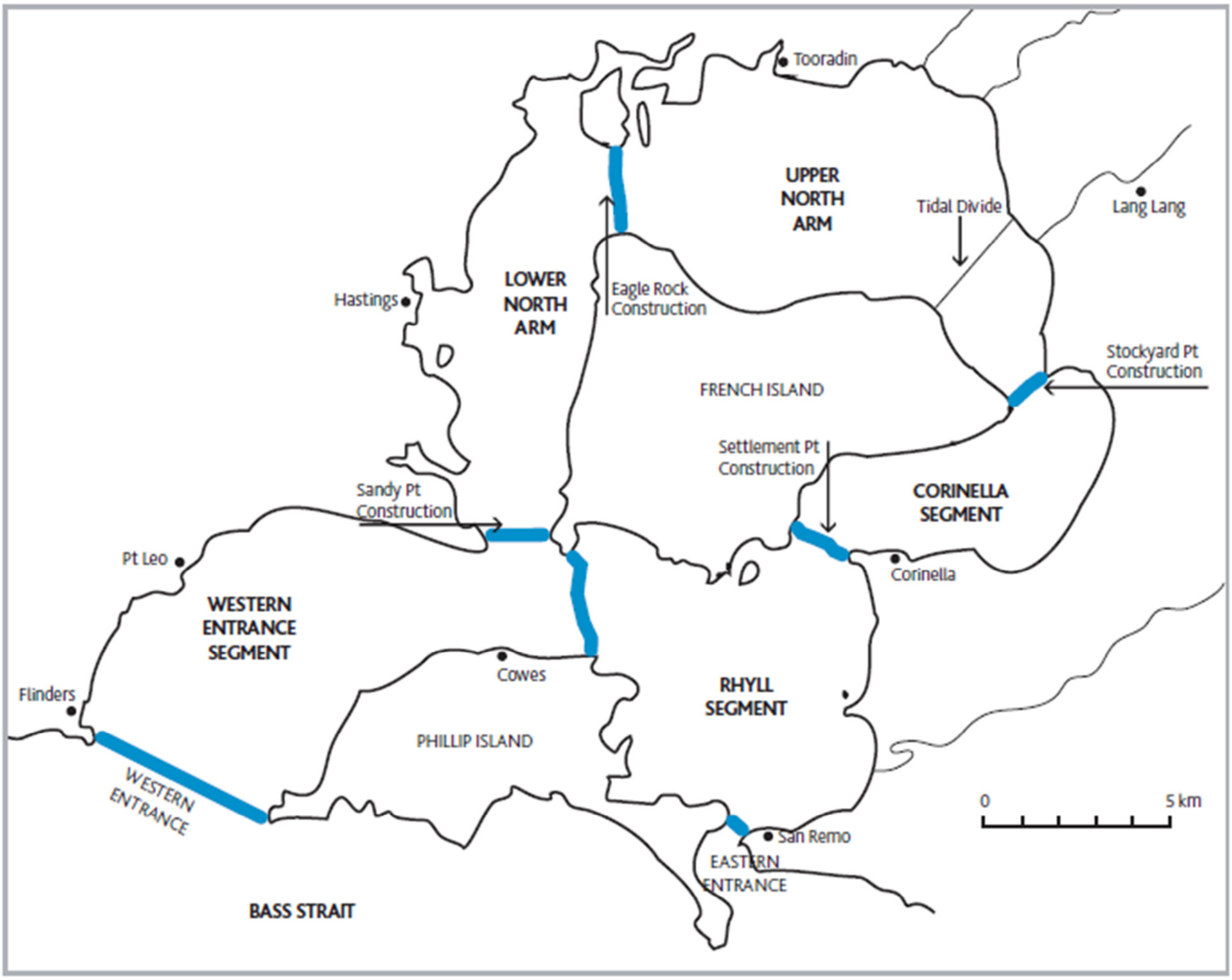

Figure 2 – Segments of Western Port (After: (Marsden et al., 1979); Source: (Keough et al., 2011)

Sample collection

Sediment samples were collected from 42 sites within Western Port and surrounding estuaries, rivers and creeks between March and July 2012 (Table 2; Figure 3). A total of 22 sites were located within the bay, 16 in estuaries and 4 in freshwaters. An additional 7 sites were sampled for TBT near marinas and boat ramps. Sampling site locations were located using Global Position System (GPS) and Table 2 lists all the sampling site co-ordinates.

Sites were selected based on a number of factors, including: previous studies by Statham (1977), Rees et al 1998 and Coleman and Pettigrove (2001), existing use in Melbourne Water sediment quality monitoring, proximity to known or suspected inputs.

Sediment samples were collected in shallow sites using a shovel and in deeper sites using a Birge-Ekman Grab Sampler from a boat. Sediment samples were lifted to the surface ensuring minimal disturbance of top sediment layers. A sample of the oxidised upper 0 - 2 cm sediment layer was collected using a plastic spatula and transferred into pre-washed 250 ml glass jars with a Teflon coated lid (Simpson et al., 2005) (see appendix 1 for details). This is in future referred to as a whole sediment sample. Filtered sediment samples were then taken by sieving the upper 0 – 2 cm sediment layer through a 63 µm nylon mesh net and transferring the collected sediment into 250 ml prewashed glass jars. Sediments were transported on ice to the laboratory where they were kept below 4˚C until analysis. At each site samples were taken in duplicate. Sample blanks, consisting of acid rinsed sand, were filtered and rinsed with distilled deionised water during field sampling and thereafter processed as per all other samples.

Pore waters were collected (as a pilot investigation) at two freshwater sites (UN15 and UN16) and two estuarine sites (UN17 and LN9) which have previously shown higher concentrations of certain metals in sediments (based on CAPIM unpublished data, 2010 – 2011). Sediments were collected in 50 mL polyethylene tubes, transported on ice to the laboratory where they were centrifuged (4500 rpm) for 10 minutes at 4˚C. In a nitrogen chamber, water was decanted into 10 mL plastic syringes, filtered through 0.45 µm membrane filters into 60 mL plastic containers and preserved with nitric acid (HNO_3) then refrigerated (4˚C) until analysis. All equipment was soaked in nitric acid and triple rinsed with reverse osmosis water. Samples were analysed for total dissolved metals by inductively coupled plasma mass spectrometry (ICP-MS). Detailed method descriptions are provided in Appendix 1.

Table 2 - Sampling locations and geographical reference points. Datum GDA94. Area codes are: CR (Corinella); LN (Lower North); RY (Rhyll); UN (Upper North); ES (Estuary); FW (Freshwater).

Site	Area	Date	Latitude	Longitude	Location
CR1	CR	27/03/2012	-38.3947	145.433	Guys Channel mudflats
CR2	CR	27/03/2012	-38.3904	145.4463	Corinella Arm Northeast (2 km) of Guys Channel
CR3	CR	27/03/2012	-38.3832	145.5384	Corinella mudflats Northeast (2.5 km) Grantville
CR4	CR	27/03/2012	-38.3512	145.5201	South (1 km) of Stockyard Point
CR6	CR	19/07/2012	-38.3277	145.5054	South East (1 km) Bluff Point
LN2	LN	22/03/2012	-38.2891	145.2283	North of Steel Wharves Lower North arm
LN3	ES	1/06/2012	-38.2273	145.2576	Watsons Creek Estuary
LN4	ES	12/03/2012	-38.231	145.2643	Yaringa MNP
LN6	LN	22/03/2012	-38.3604	145.2202	South (1 km) of South Crib Point
LN7	LN	22/03/2012	-38.3075	145.2764	Middle Spit North channel marker
LN9	ES	8/06/2012	-38.3239	145.194	Warringine Creek Estuary
RY1	ES	30/05/2012	-38.4955	145.4432	Bass River Estuary
RY2	RY	4/04/2012	-38.4715	145.3404	North Churchill Island (2.5 km) Rhyll arm
RY3	RY	4/04/2012	-38.4993	145.4203	West (1 km) of Bass River mouth
RY4	RY	4/04/2012	-38.4814	145.4124	Bass River silt jetties South (1 km) of Reef Island
RY5	RY	4/04/2012	-38.4936	145.3159	Churchill Island MNP
UN1	UN	19/07/2012	-38.2742	145.4696	Boulton Channel mudflats
UN3	UN	3/04/2012	-38.2509	145.4232	Lyalls Channel mudflats
UN4	UN	19/03/2012	-38.2297	145.3536	Blind Bight Channel
UN5	UN	14/03/2012	-38.2512	145.3323	Gentle Annie Channel north muds
UN6	ES	19/03/2012	-38.2206	145.3098	Rutherford Inlet west of Chinaman Island
UN8	ES	21/03/2012	-38.2158	145.3769	Sawtells Inlet
UN9	ES	21/03/2012	-38.2034	145.3865	Sawtells Creek at Hopetown Road
UN10	UN	30/03/2012	-38.2843	145.3404	French Island MNP
UN11	UN	19/07/2012	-38.2823	145.5188	Lang Lang River Estuary Mouth
UN13	FW	8/03/2012	-38.2173	145.5053	Yallock Cut at Sth Gippsland Highway
UN15	FW	8/06/2012	-38.1494	145.4487	Deep Creek at Ballarto Road
UN16	FW	7/06/2012	-38.147	145.4323	Cardinia Creek at Ballarto Road
UN17	ES	8/06/2012	-38.2109	145.4367	Cardinia River Estuary at Sth Gippsland H'way
UN18	ES	8/06/2012	-38.2132	145.4584	Bunyip River Estuary at Sth Gippsland H'way
UN20	UN	17/06/2012	-38.2488	145.3544	Gentle Annie Channel south
UN22	UN	30/03/2012	-38.2804	145.3249	Chicory Lane east (2.2 km) of Scrub Point
UN24	UN	14/03/2012	-38.2517	145.3167	Adams Inlet China Bay east of Chinaman Island
UN25	FW	8/03/2012	-38.2558	145.5491	Lang Lang River at South Gippsland Hway
UN27	UN	13/03/2012	-38.2476	145.3082	Rutherford Inlet West of Chinaman Island
UN26	ES	8/03/2012	-38.1943	145.3523	Western Contour Drain US South Gippsland Hway
UN28	ES	19/03/2012	-38.2165	145.35	Western Contour Drain Estuary Mouth Blind Bight
UN29	ES	3/04/2012	-38.2207	145.4518	Bunyip River Estuary Mouth
UN30	ES	3/04/2012	-38.2197	145.4414	Deep Creek Estuary Mouth
UN31	ES	3/04/2012	-38.2165	145.4393	Deep Creek Estuary 100 m upstream of mouth
UN32	ES	3/04/2012	-38.218	145.4343	Cardinia Creek Estuary Mouth
WS2	ES	1/06/2012	-38.3894	145.1243	Merricks River Estuary at Beach Road

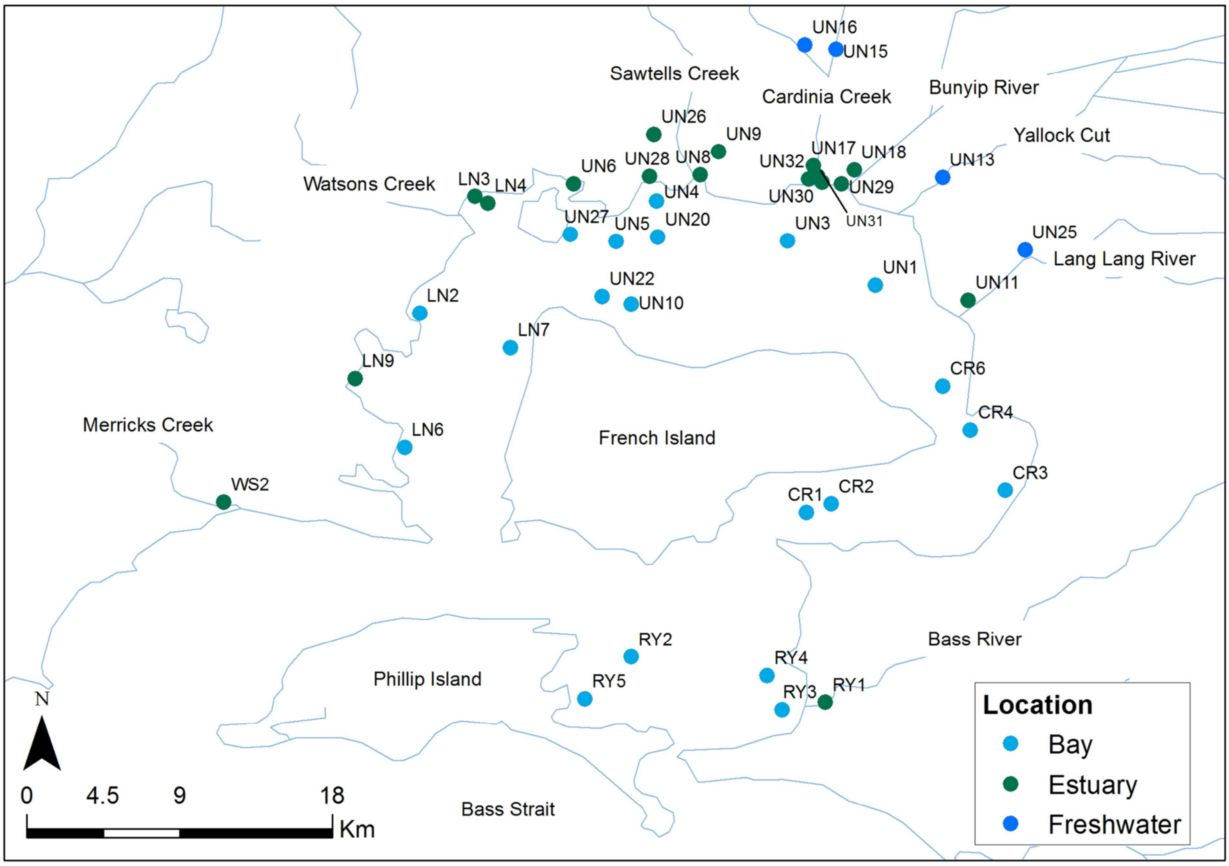

Figure 3 - Estuarine, freshwater and bay sites sampled during this study. See Table 1 for location names and geographical references.

Sample analyses

Sediment samples (whole and/or filtered) were analysed for some or all of the following components: particle size, total metals, dilute acid metals, total organic carbon (TOC), total petroleum hydrocarbons (TPHs), pesticides, organotins and pore water metal concentrations. All metals, grain size and hydrocarbons analyses were processed on duplicate samples to assess for within site variation. Table 3 details the parameters analysed, the number of locations sampled, the sediment sample type processed for each particular analysis, the limits of detection and analytical methods reference (see Appendix 2 and 3 for LORs for each toxicant analysed).

Table 3 - Sediment quality parameters sampled during this study. See Appendix 2 & 3 for Limits of Reporting (LOR) and Coefficients of Variation for each parameter.

Parameter	Number of locations sampled	Sediment type analysed	Method Reference
Particle size analysis	41 sites	Whole sediment	Method adapted from (Woolfe et al., 2000, Sperazza et al., 2004)
Total heavy metals Aluminium, arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel and zinc	All 42 sites	42 sites filtered sediments 18 sites whole sediments	(NEPM, 1999)
Dilute acid metals Aluminium, cadmium, chromium, copper, iron, lead, manganese, nickel and zinc	41 sites	41 sites filtered sediments 22 sites whole sediments (including 7 heavy boat use and marina sites as for TBT analysis)	(NEPM, 1999)
Total mercury	All 42 sites	42 sites filtered sediments 9 sites whole sediments	(NEPM, 1999)
Total petroleum hydrocarbons (TPH) C10 - C36	6 Bay, 6 Estuarine and 2 Freshwater	14 sites filtered sediment 7 sites whole sediments	(NEPM, 1999)
Total Organic Carbon (TOC)	40 sites	40 sites filtered sediments	(NEPM, 1999)
Pesticides OC and OP pesticides , Synthetic Pyrethroids, NPD Triazine herbicides, Fipronil & metabolites, LC-MSMS screen	8 bay, 10 estuarine and 4 freshwater	Filtered sediments	Methods reported in (Schäfer et al., 2011)
Organotins Tributyltin, Dibutyltin, Monobutyltin	7 heavy boat use and marina sites	Whole sediments	Method based on (USEPA, 2007).
Pore water Aluminium, arsenic, cadmium, chromium, cobalt, copper, lead, nickel and zinc	2 freshwater and 2 estuarine	Whole sediments	Method based on Simpson (2000)

Interim sediment quality guideline (ISQG) low trigger values were used as concentration thresholds for assessing the risk of toxicants. ISQGs are largely derived from empirical analyses of field and laboratory data in whole sediments from various estuaries, bays and freshwaters in America and represent a concentration threshold above which adverse effects are possible (low trigger value) or probable (high trigger value) (ANZECC and ARMCANZ, 2000). Guidelines are not based on experimental evidence where causality was established for each toxicant and should be used as a screening tool to highlight where further investigations of toxicity are needed (Long and MacDonald, 1998).

While total metals are used in the current interim sediment quality guidelines (ANZECC and ARMCANZ, 2000), it has been shown that dilute acid-extractable metal concentrations are better predictors of bioavailable metals (Batley and Simpson, 2008). Both these parameters were measured to assess the potential toxicity according to ISQGs and for comparison with historical studies (Rees et al., 1998).

Particle size analysis was conducted at the Melbourne School of Land and Environment (MSLE). Dilute acid metals were analysed by the Surface and Chemical Analysis Network (SCAN), School of Chemistry, University of Melbourne. Total metals, TOC, TPHs and organotins were analysed by Australian Laboratory Services (ALS). Pesticides were analysed by DPI Victoria, Future Farming Systems Research (FFSR) Macleod, Victoria. A full list of pesticides and limits of reporting are detailed in Appendix 2.

Quality Control

A minimum of one laboratory control spike, extraction blank, post-digestion spike and matrix spike were made every 20 samples and one duplicate was included in every 10 samples for all chemical analyses. Particle size analysis included a background measurement, rinse and realignment every sample and a duplicate was measured in every 10 samples. Recoveries for spike concentrations of total metals were between 70 and 130% for arsenic, cobalt, manganese and total organic carbon. Cadmium ranged 83.3 to 111%, chromium 89.2 to 117%, copper 90.1 to 114%, lead 85.2 to 111%, nickel 88.3 to 116% and zinc ranged 88.9 to 112%. Recovery of total mercury ranged 74 to 126%. Recovery of tributyltin ranged 45 to 134% with slightly better recovery for other organotins. Pesticide recoveries ranged for OCs 46-103 %, OPs (57 – 86 %), SPs (61 – 75 %), NPD (49 – 111 %), Triazines (35 – 86 %), Fipronil (77 – 122 %) and LC-MSMS (28 – 87 %). Recoveries include multiple repeats at several spiking levels and include an estimate of both accuracy and precision.

Data Analysis

Individual site concentrations of key toxicants were superimposed on a map of Western Port using ArcGIS (version 10). Boxplots were used in initial assessment for each toxicant following the method of Goudey (2007). Boxplots display the median (centre line) and inter-quartile range (25th and 75th percentiles). Whiskers show the highest and lowest concentrations, excluding outliers (circles) (exceeding 1.5 box-lengths) and extreme values (stars) that exceed 3 box lengths. Sediment toxicant concentrations were compared to ANZECC and ARMCANZ (2000) interim sediment quality guidelines (ISQG) to determine risk to aquatic organisms. Concentrations exceeding the ISQG-low and ISQG-high indicate that these sediments have a moderate and high probability of being toxic to aquatic life, respectively.

Results

Metals

Mean total metal concentrations for sediments from the six areas are shown in Table 4, while dilute acid extractable metal concentrations are shown in Table 5. A number of metal concentrations, including cadmium, copper, iron, lead, manganese, mercury and zinc were highest in estuarine and freshwater areas, while concentrations of aluminium, arsenic, chromium and nickel were highest in bay and estuarine areas and lowest in the freshwater area (Figures 4 and 5; Table 4; see Appendix 4 and 5 for site specific concentrations). The freshwater area was the only area to have no metal concentrations exceeding ISQG-low guidelines (Figure 4 and Figure 5).

Total arsenic concentrations exceeded the ISQG-low of 20 mg/kg at 22 sites, suggesting a potential for adverse impacts of arsenic on aquatic faunal assemblages at these sites (Figure 6). The highest concentrations were measured in the bay at 30 mg/kg at Rutherford Inlet West of Chinaman Island (UN27) and in Yaringa Marine National Park (LN4) (see Appendix 4 for site specific concentrations). Further investigation of dilute acid extractable arsenic concentrations however, were well below ISQG-low suggesting the bioavailable fraction of arsenic is not at concentrations likely to have adverse impacts on aquatic faunal assemblages at any of the sites (Table 5).

The concentrations of total aluminium, chromium, copper, lead, iron, manganese and zinc at all sites in the bay, estuary and freshwater areas were below the ISQG-low values (Figures 7-9, 12; Table 4; Appendix 4 for site specific concentrations). Total cadmium concentrations were below detection limits (1 mg/kg) at all sites, therefore dilute acid extractable cadmium was compared to the ISQG-low, which all sites were below (Figure 4b; Table 4 and 5; see Appendix 4 and 5 for site specific concentrations). This suggests that these metals are unlikely to be having a detrimental effect on the aquatic fauna at sites sampled.

Two sites, in the estuarine area, had concentrations of mercury that exceeded the ISQG-low of 0.15 mg/kg suggesting a moderate risk of mercury on aquatic faunal assemblages at these sites (Figure 10; see Appendix 4 for site specific concentrations). The highest mean concentration of mercury was 0.17 mg/kg detected in Deep Creek estuary (UN32) followed by 0.16 mg/kg in Warringine Creek estuary (LN9). Replicate measurements for mercury at these sites were highly variable (replicate measurements of 0.01, 0.3 and <0.01, 0.3 for sites UN32 and LN9 respectively). Mercury concentrations did not exceed the ISQG-low at any sites in the bay or freshwater areas, mean area concentrations ranging <0.01 to 0.04 mg/kg, respectively (Table 4; Figure 5b).

Total nickel concentrations were highest in the estuaries, with concentrations at several sites including Sawtells Creek estuary (UN9) and Merricks Creek estuary (WS2) exceeding the ISQG-low suggesting a potential moderate impact of nickel on aquatic faunal assemblages at these sites (Figure 11). In the Western Contour Drain (UN26) nickel concentrations equalled the ISQG-low of 21 mg/kg. Further investigation of dilute acid extractable nickel concentrations showed that for sites UN9, WS2 and UN26 concentrations were below the ISQG-low, suggesting that the bioavailable fraction of nickel presents a low risk to aquatic fauna at these sites (Table 5). Within the bay and freshwater areas all sites were below the ISQG-low guideline, mean area concentrations ranging 10.1 to 16.5 mg/kg (Table 4; Figure 5c; see Appendix 4 and 5 for site specific concentrations).

Table 4 - Concentrations of total metals (± SD) in filtered sediments from areas of Western Port. Units are mg/kg for metals, % Total Organic Content (TOC) and % sediment <63 µm.

Parameter	Corinella	Lower North	Rhyll	Upper North	Estuarine	Freshwater	ISQG-Low
	n=5	n= 4	n=4	n=10	n=15	n=4	(mg/Kg)
Aluminium	15240 ±726	15417 ±944	13900 ±2316	18397 ±4406	22107 ±5435	16121 ±2551	-
Arsenic	17 ±3	23 ±2	19 ±5	22 ±5	21 ±7	8 ±7	20
Cadmium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.5
Chromium	25.4 ±3.1	38.2 ±2.0	26.4 ±6.0	32.0 ±8.0	37.4 ±9.4	25.2 ±5.3	80
Copper	8.7 ±1.0	9.0 ±0.9	9.1 ±1.1	9.0 ±1.3	12.7 ±3.5	18.1 ±6.6	65
Iron	18870±1316	19833±553	18875 ±2571	19491 ±2094	24945 ±5822	22708 ±1928	-
Lead	11.6 ±1.1	11.3 ±0.3	10.1 ±1.9	12.1 ±1.8	15.5 ±3.0	17.7 ±3.5	50
Manganese	85.5 ±22.4	58.3 ±3.2	65.5 ±8.6	65.4 ±26.9	98.4 ±50.8	365.8 ±214.3	-
Mercury	0.02 ±0.01	0.01 ±0.01	0.02 ±0.01	0.01 ±0.01	0.04 ±0.05	0.03 ±0.02	0.15
Nickel	10.1 ±1.4	16.5 ±2.2	12.0 ±0.9	12.4 ±2.9	16.4 ±6.5	11.6 ±2.1	21
Zinc	23 ±3	30 ±4	26 ±2	24 ±5	38 ±9	61 ±32	200
TOC	1.52 ±0.16	2.33 ±0.13	1.85 ±0.35	2.38 ±0.38	2.74 ±0.96	2.11 ±0.10	-
<63 µm	40.4 ±29.6	31.6 ±16.0	45.7 ±29.1	42.4 ±20.8	56.3 ±22.2	64.6 ±10.6	-

Table 5 - Concentrations of dilute acid extractable metals (± SD) in filtered sediments from areas of Western Port. Units are mg/kg.

Parameter	Corinella	Lower North	Rhyll	Upper North	Estuary	Freshwater	ISQG - Low
	n = 5	n = 4	n = 4	n = 8	n = 16	n = 4	(mg/Kg)
Aluminium	505± 153	624 ± 77	557 ± 188	611 ± 110	629 ± 130	657 ± 150	-
Arsenic	0.76 ± 0.2	1.46 ± 0.41	0.95 ± 0.45	1.34 ± 0.35	1.19 ± 0.47	0.94 ± 0.36	20
Cadmium	0.03 ± 0.01	0.05 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.06 ± 0.02	0.09 ± 0.01	1.5
Chromium	1.17 ± 0.31	1.92 ± 0.3	1.29 ± 0.21	1.55 ± 0.34	1.22 ± 0.43	0.85 ± 0.15	80
Copper	0.37 ± 0.12	0.67 ± 0.3	0.5 ± 0.47	0.55 ± 0.09	0.89 ± 0.49	2.43 ± 1.22	65
Iron	916 ± 148	1169 ± 219	894 ± 269	1163 ± 174	1397 ± 324	1743 ± 126	-
Lead	2.15 ± 0.42	2.6 ± 0.5	2 ± 0.41	2.78 ± 0.4	3.31 ± 0.82	3.85 ± 0.76	50
Manganese	12.67 ± 2.82	6.58 ± 1.97	6.68 ± 1.94	8.87 ± 3.14	20.2 ± 21.4	75.9 ± 41.8	-
Nickel	0.94 ± 0.21	1.38 ± 0.25	1.06 ± 0.36	1.27 ± 0.14	1.3 ± 0.65	1.47 ± 0.25	0.15
Zinc	1.79 ± 0.23	3.89 ± 1.35	2.36 ± 1.09	2.6 ± 0.47	4.94 ± 2.72	11.78 ± 8.19	200

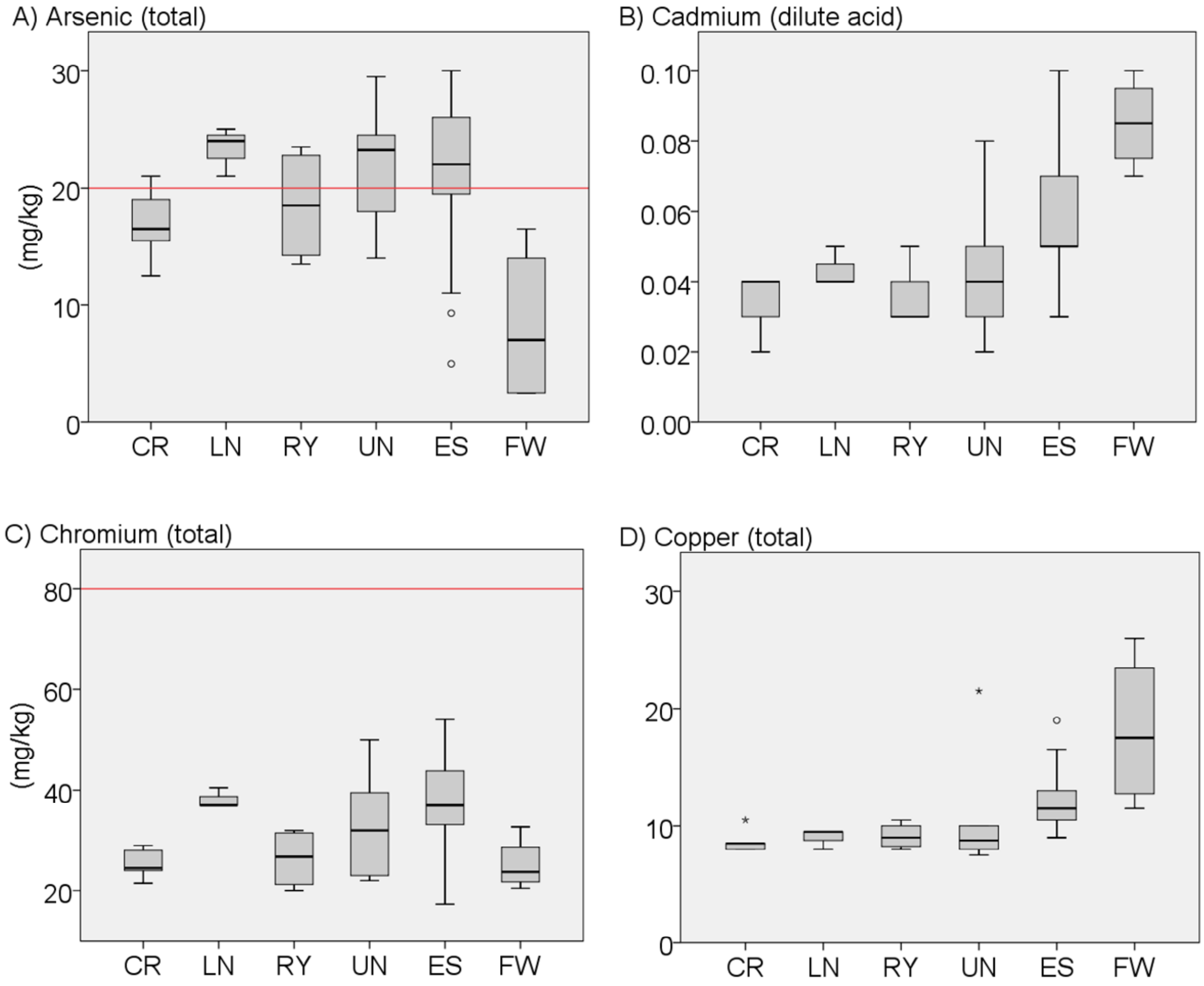

Figure 4 - Concentrations of metals in sediments from bay segments, estuaries and freshwater reaches (see Table 2 for definitions) of Western Port (red reference line indicates ISQG-low trigger value). ISQG-low trigger values are 1.5 mg/kg for cadmium and 65 mg/kg for copper.

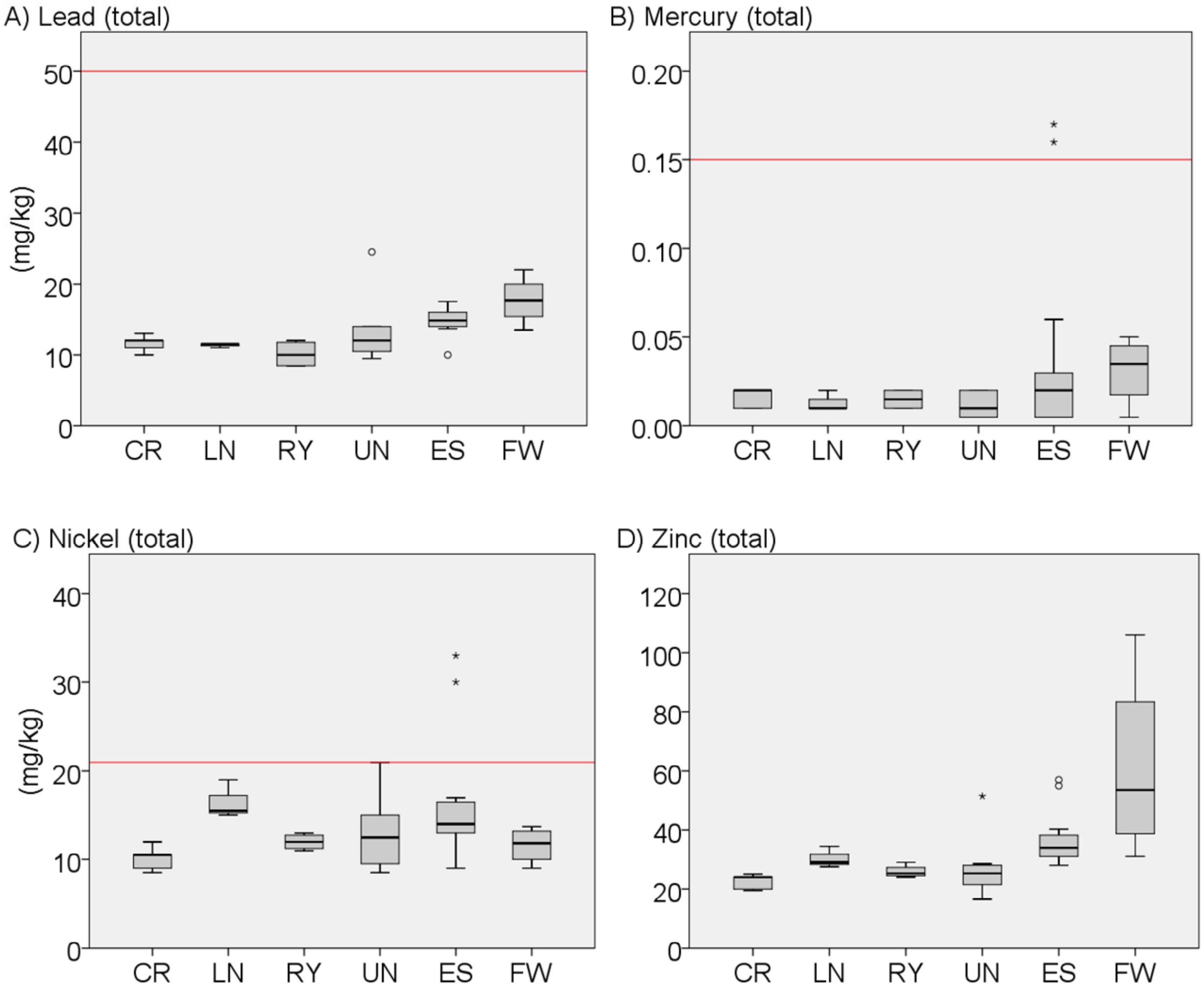

Figure 5 - Concentrations of metals in sediments from bay segments, estuaries and freshwater reaches (see Table 2 for definitions) of Western Port (red reference line indicates ISQG-low trigger value). ISQG-low trigger value is 200 mg/kg for zinc.

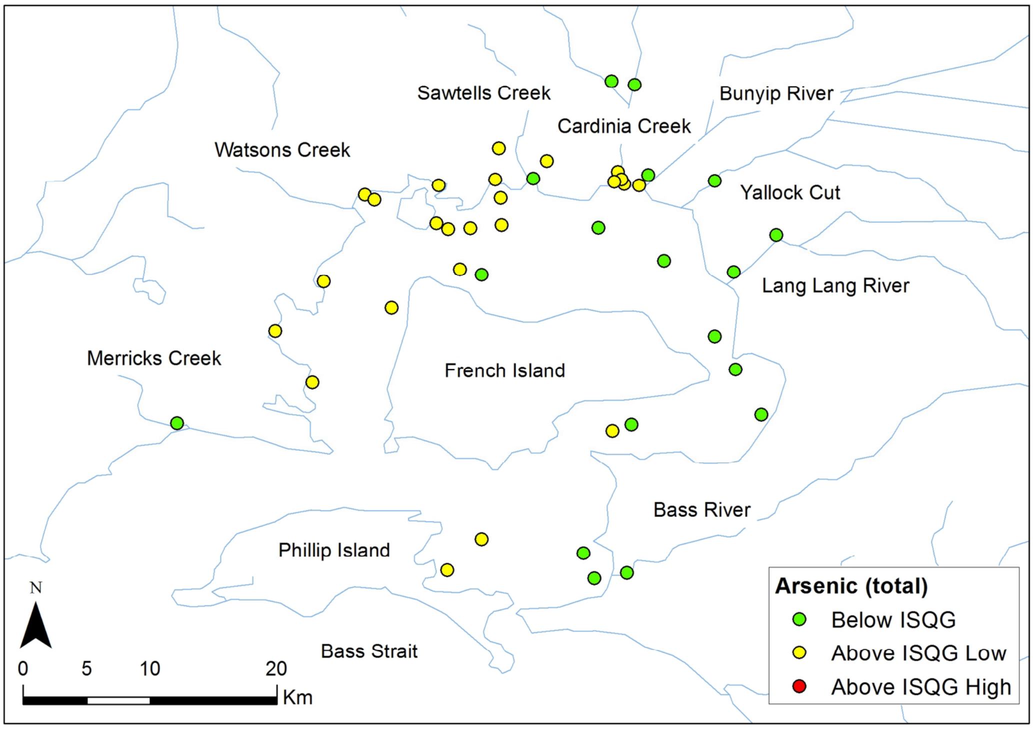

Figure 6 - Total arsenic concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 20 mg/Kg, ISQG-high = 70 mg/Kg.

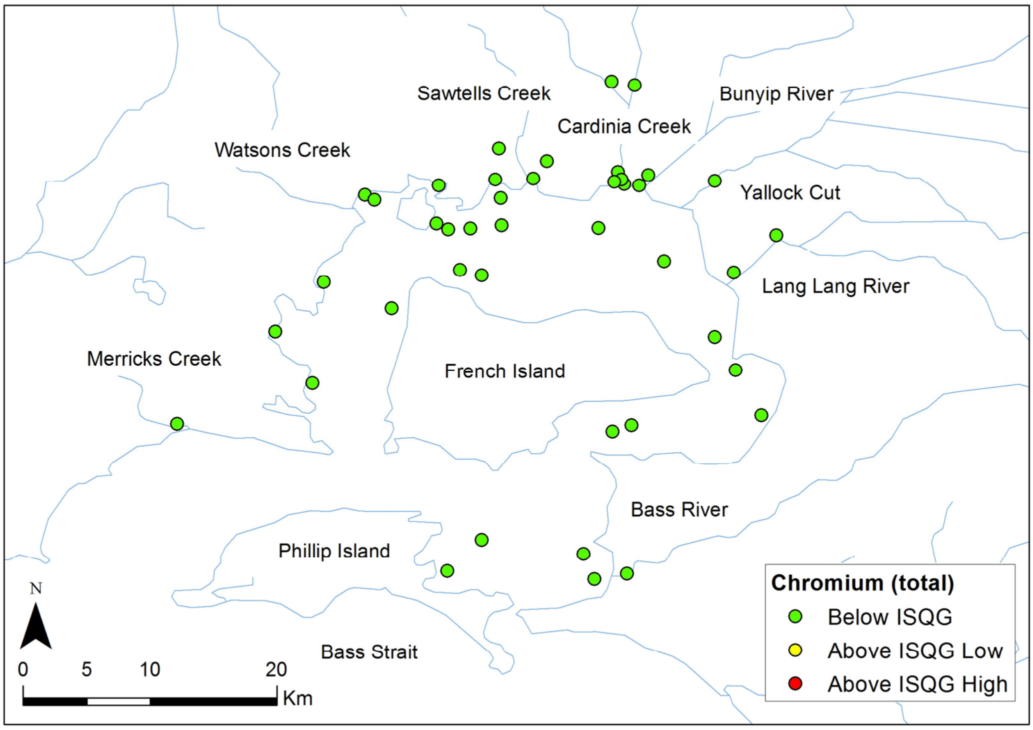

Figure 7 - Total chromium concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 80 mg/Kg, ISQG – high = 370 mg/Kg.

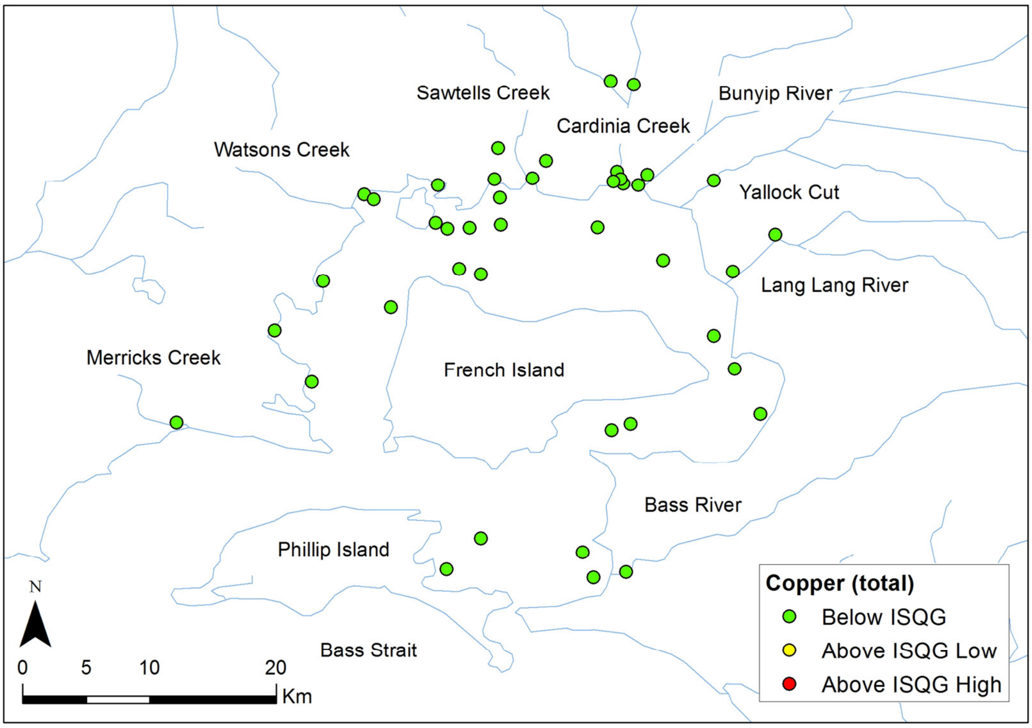

Figure 8 - Total copper concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 65 mg/Kg, ISQG-high = 270 mg/Kg.

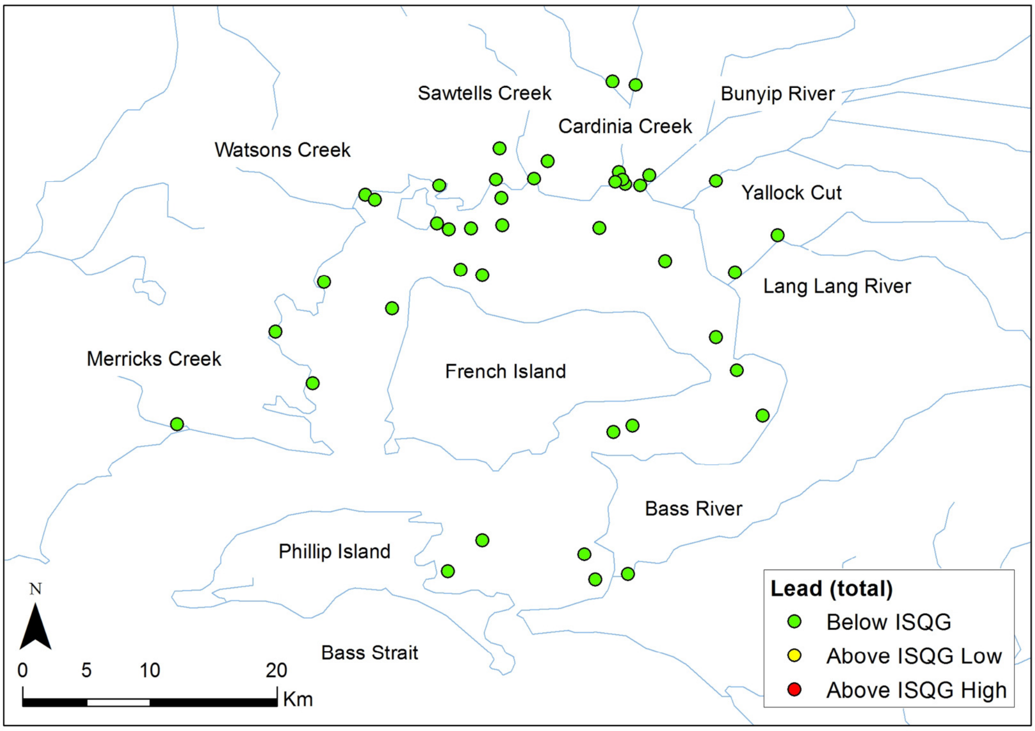

Figure 9 - Total lead concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 50 mg/Kg, ISQG-high = 220 mg/Kg.

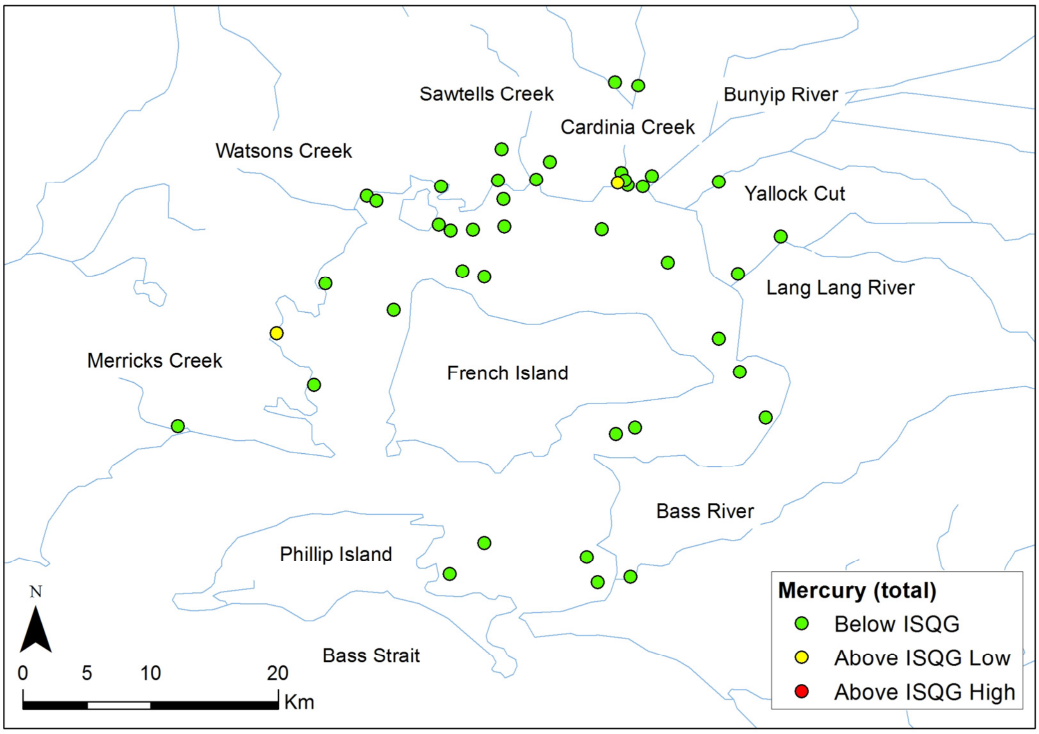

Figure 10 - Total mercury concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 0.15 mg/Kg, ISQG-high = 1.0 mg/Kg.

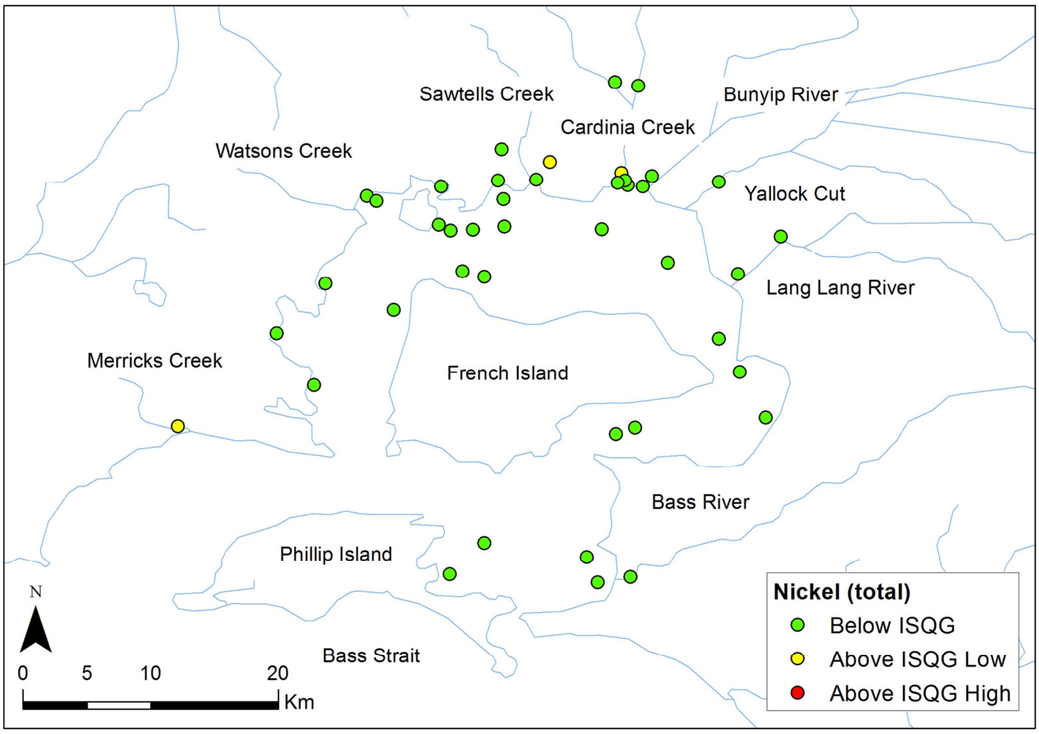

Figure 11 - Total nickel concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 21 mg/Kg, ISQG – high = 52 mg/Kg.

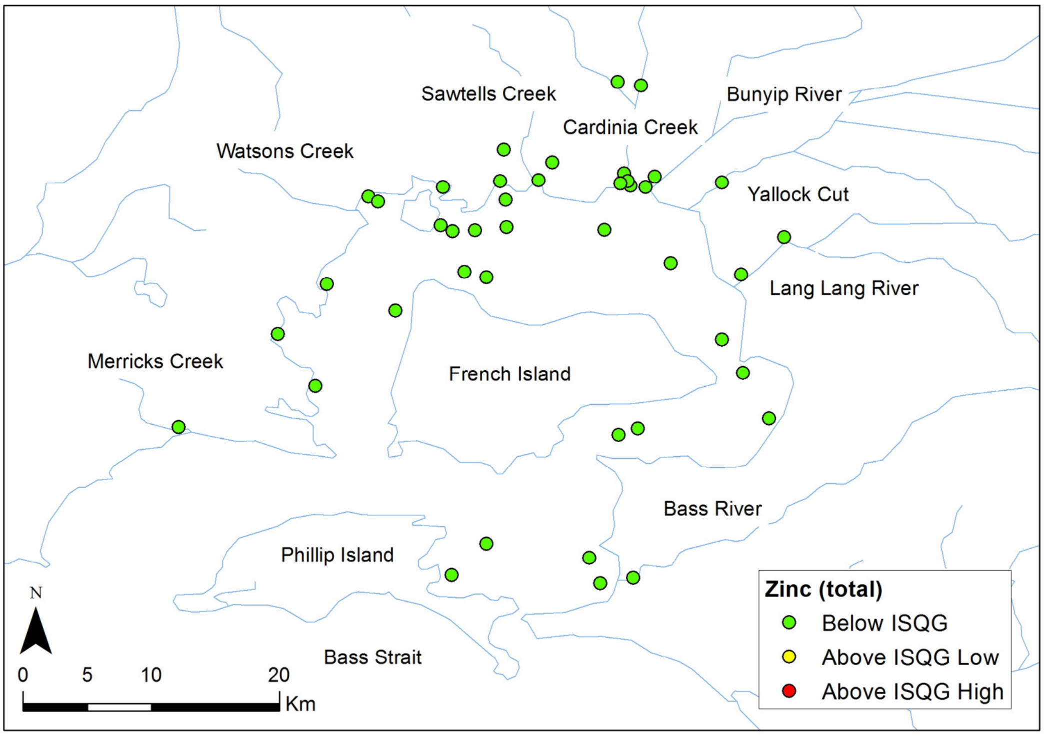

Figure 12 - Total zinc concentrations within Western Port as defined by Interim sediment quality guidelines. ISQG-low = 200 mg/Kg, ISQG-high = 410 mg/Kg.

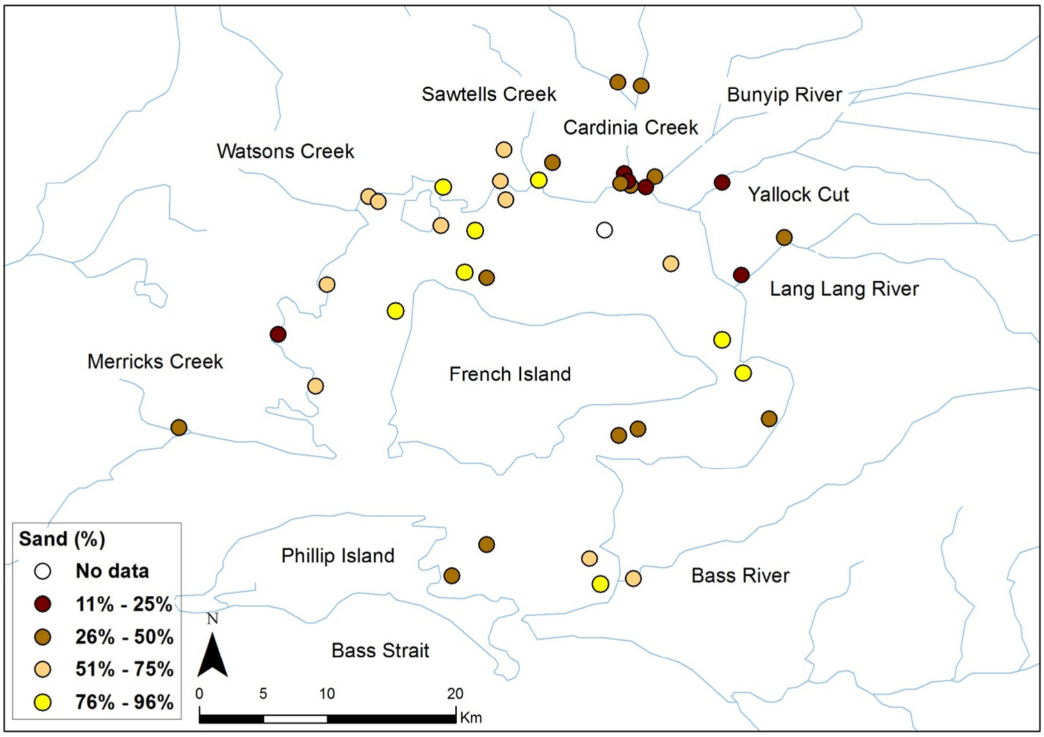

Figure 13 - Percentage of sand at sites within Western Port. Grain size data was not available for one site in the Upper North arm (UN3).

Pore water metals

Metal concentrations in pore waters for the sites sampled are shown in Table 6 and were compared to SEPP (WoV) surface water objectives. A number of metals exceeded the SEPP (WoV) objective values, including aluminium, arsenic, chromium, cobalt, copper, manganese, mercury, nickel and zinc at one or more of the sites sampled. However, the variation in replicate samples for the metals aluminium, arsenic, chromium, copper, manganese, and mercury was very high and additional sampling would be required to confirm if objectives were actually exceeded (Table 6). Cobalt concentrations at the two marine sites sampled, Warringine (LN9) and Cardinia (UN17) estuaries, nickel and zinc concentrations at site UN17, and aluminium concentrations at the freshwater site UN15 were above the SEPP (WoV) objectives thus indicating moderate potential for toxic effects in aquatic biota at these sites (Table 6).

Table 6 - Metal concentrations in pore waters (mean ± S.D.) (N=2) and SEPP (WoV) environmental quality surface water objectives for Western Port (Victorian Government, 2001). All units are µg/L.

	Freshwater			Marine			
Metal	**UN15**	**UN16**	**SEPP (WoV)**	**LN9**	**SEPP (WoV) North Arm**	**UN17**	**SEPP (WoV) East Arm**
Aluminium	**485 ± 106**	**490 ± 523**	55	29 ± 5	NV	26 ± 1	NV
Arsenic	11 ± 1	3 ± 4	13[a], 24[b]	3.6 ± 0.9	**3**	2.4 ± 0.2	**5**
Cadmium	<0.1	<0.1	0.2	<0.2	**0.05**	<0.2	**0.05**
Chromium	1.0	1.3 ± 1.1	NV[c],1[d]	3 ± 1	4.4[c],27.4[d]	1 ± 0	4.4[c],27.4[d]
Cobalt	6.1 ± 2.1	13.1 ± 16.1	NV	3 ± 0	1	11 ± 1	1
Copper	1.1 ± 1.1	1.1 ± 0.1	1.4	4 ± 5	**1**	2 ± 1	**2**
Lead	1.1 ± 0.1	1.1 ± 0.1	3.4	0.6 ± 0.7	**1**	<0.2	**2**
Mercury	0.05 ± 0.00	0.28 ± 0.32	0.06	-	**0.005**	-	**0.01**
Nickel	5.1 ± 1.1	5.1 ± 7.1	11	40.0 ± 45.7	**1**	7.3 ± 0.3	**3**
Zinc	<5	<5	8	68.5 ± 72.8	**2**	14.5 ± 3.5	**5**

a-Arsenic (AsIII); b-Arsenic (AsV); c –Chromium (CrIII); d-Chromium (CrVI)

NV – no trigger value exists

🟦	SEPP objective lower than laboratory limit of reporting
🟩	Monitoring results less than the laboratory limit of reporting
🟨	Given uncertainty monitoring results require additional data to be assessed against SEPP
🟥	Monitoring results exceeding SEPP

N.B. Metal concentrations in pore waters from freshwater sites were not corrected for hardness due to insufficient volumes extracted. Insufficient volumes of pore water were available for mercury analyses from marine sites.

Total Organic Carbon

The mean total organic carbon (TOC) for the six areas of Western Port ranged between 1.5 to 2.5% (Table 4). The mean TOC was highest in estuaries and Lower North arm bay sediments (2.5% in each), while Corinella Arm had the lowest amount of organic carbon (1.5%; Table 4). The highest TOC was 5.35 % at Merricks Creek estuary (WS2) and the lowest was 1.31 % approximately 1 km south of Stockyard Point in the Corinella arm (CR4) (see Appendix 4 for site specific concentrations).

Sediment grain size

Fine grained sediment (<63 µm) was found predominantly within the freshwater and estuarine sites (64% and 58% respectively; Figure 13; Table 4). Within the bay, sites in the Corinella arm had the highest percentage of fine sediments followed by sediment with the Rhyll arm (52% and 47% respectively; Table 4). Sites in the Lower North arm had the lowest percentage of fine sediments (32%; Table 4) (see Appendix 6 for site specific grain size data).

Total Petroleum Hydrocarbons (TPH)

Hydrocarbon concentrations were highest in the freshwater and the Upper North bay areas (Figure 14). Mean TPH concentrations in estuarine sediments were generally below 55 mg/kg, with the exception of 133 mg/kg measured at Sawtells Inlet (UN8). In the three bay segments (Corinella, Lower North Arm and Rhyll), TPH concentrations were all below 81 mg/kg (see Appendix 2 for site specific concentrations). Overall, no TPH concentrations in this study exceeded the proposed TPH guideline of 275 mg/kg (Simpson et al., 2010).

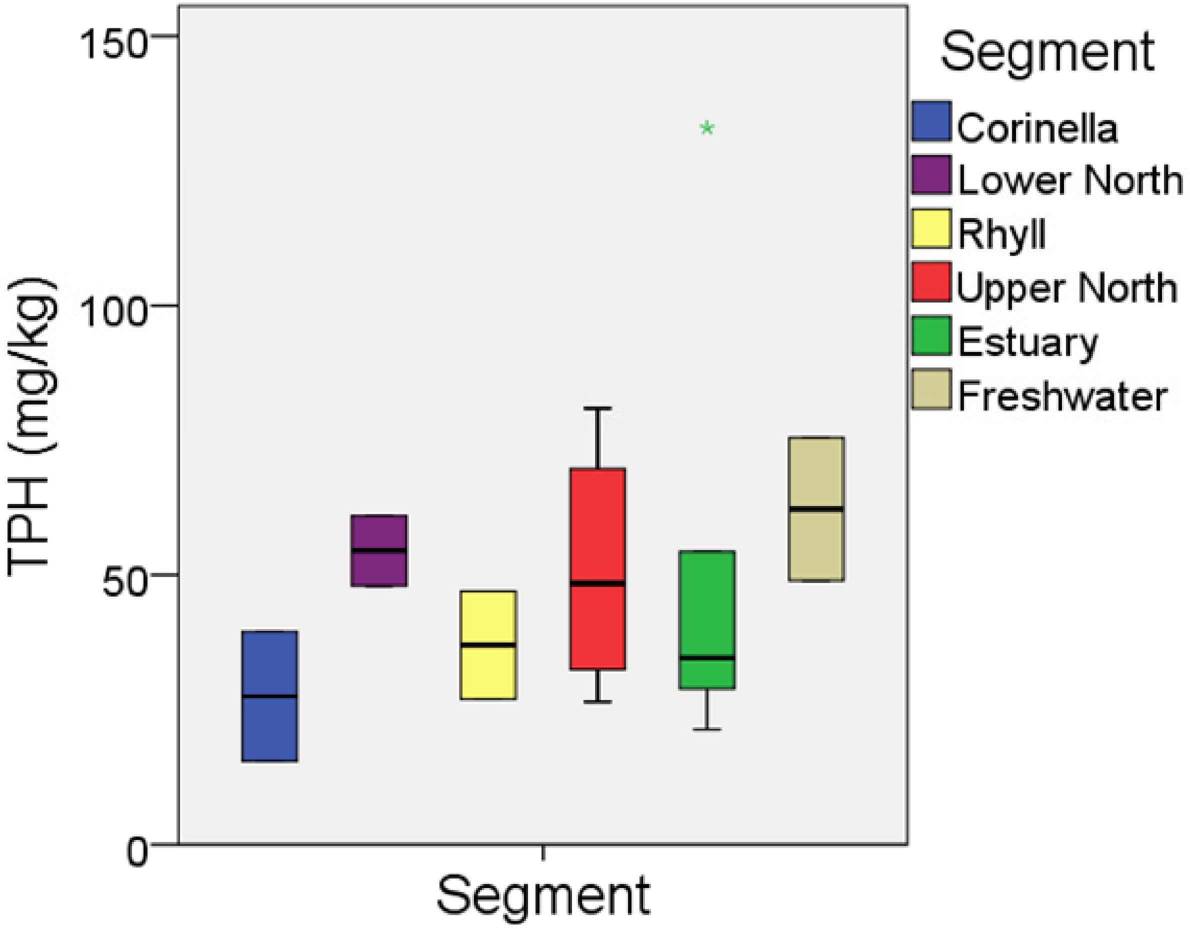

Figure 14 - Total Petroleum hydrocarbon (TPH) concentrations in Western Port in filtered sediments in 2012. Proposed TPH threshold of 275 mg/kg (Simpson et al., 2010).

Pesticides

Of the 22 sites sampled for pesticides in sediments, eight sites had detections (Table 7; Figure 15). A total of 17 pesticides were detected, with up to nine different pesticides occurring at Western Contour Drain (UN26) which included four herbicides (simazine, metolachlor, prometryn and linuron), four fungicides (oxadixyl, azoxystrobin, boscalid and cyprodinil) and the insecticide fenamiphos (Table 7). The highest concentrations detected for the triazine herbicide prometryn and fungicide boscalid (15 and 22 µg/kg respectively) occurred in the Western Contour Drain (UN26). Watsons Creek estuary had the second highest number of detections (8) being a source of four insecticides (two organochlorines (pp-DDE and pp-DDT; pirimicarb and fenamiphos), three triazine herbicides (metolachlor, prometryn, and linuron) and the fungicide boscalid at 8 µg/kg. At Yallock Cut and Deep Creek a total of four and five different pesticides were detected respectively. At Deep Creek the organochlorine derivatives, pp-DDE and pp-DDT were above the ISQG-low suggesting a potential moderate impact to aquatic faunal assemblages. The other pesticides detected at both of these sites were below 2 µg/Kg, however no guidelines exist for any of the other pesticides detected. At Sawtells Creek three pesticides were detected. The organochlorine derivative pp-DDE was detected at a concentration of 0.73 µg/kg which was below the ISQG-low suggesting it is unlikely to be having a detrimental effect on aquatic fauna at this site. The synthetic pyrethroid insecticide bifenthrin was detected at 5 µg/Kg and the herbicide diuron at 28 µg/kg. There are no ISQG values for these pesticides. The other three sites (Western Contour estuary, Lang Lang River and Bass River estuary) had only one pesticide detected, concentrations ranging between trace and 1 µg/kg, with the exception of boscalid in Western Contour estuary at 6 µg/kg (Table 7). No pesticides were detected at any of the six sites in Western Port or in sediments from Warringine Creek (LN9), Cardinia Creek (UN17, UN32), Bunyip River (UN29), Deep Creek (UN30, UN31), Merricks Creek (WS2) and Sawtells Inlet (UN8).

The most commonly detected pesticides were the organochlorine derivatives pp-DDE and pp-DDT (four and three sites respectively), followed by the triazine herbicide simazine and the fungicides azoxystrobin and boscalid (three sites each). The herbicide diruon was only detected at one site, however was the highest concentration detected across all detections, 28 µg/kg, this was followed by the fungicide boscalid at 22 µg/Kg and triazine herbicide prometryn at 15 µg/kg (Table 7). It should be noted that there are currently no ISQG guidelines for any of the pesticides other than the organochlorines detected in this study.

Table 7 – Sites with detectable levels of pesticides in sediments from Western Port. N = 1. Units are µg/kg for pesticide and % total organic carbon (%TOC). ND = Non Detect, T = Trace (between detection and reporting limits). ISQG low and high from (ANZECC and ARMCANZ, 2000).

Mode of Action			Insecticide					Herbicide					Insecticide		Fungicide						
Group			OC				SP	Triazine				Urea	LC-MSMS Screen (various groups)								
Name	Site	Total Organic Carbon (%)	p,p'-DDE	P,p”-DDE normalised*	p,p'-DDT	p,p'-DDT normalised*	Bifenthrin	Simazine	Metolachlor	Prometryn	Linuron	Diuron	Pirimicarb	Fenamiphos	Oxadixyl	Azoxystrobin	Pyrimethanil	Boscalid	Myclobutanil	Triadimenol	Cyprodinil
Yallock Cut	UN13	1.98	T	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	T	ND	2	ND	ND
Sawtells Creek	UN9	4.50	3.3	0.73	ND	ND	5	T	ND	ND	ND	28	ND	ND	ND	ND	ND	ND	ND	ND	ND
W.C.D.	UN26	2.63	ND	ND	ND	ND	ND	T	T	15	T	ND	ND	T	5	1	ND	22	ND	ND	T
W.C.E.	UN28	2.30	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6	ND	ND	ND
Lang Lang River	UN25	2.14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	ND	ND	ND	ND	ND
Deep Creek	UN15	2.21	5	2.26	6	2.7	ND	T	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND	T	ND
Bass River	RY1	1.67	ND	ND	T	T	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Watsons Creek	LN3	3.33	T	T	T	T	ND	ND	T	T	T	ND	1	T	ND	ND	ND	8	ND	ND	ND
LOR		0.1%	3	3	5	5	5	5	10	5	2	20	1	5	1	1	3	3	2	2	5
ISQG-low		-	-	2.2	-	1.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ISQG-high		-	-	27		46	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Pesticide Groups: OC – Organochlorine, SP – Synthetic Pyrethroids, LC-MSMS – Liquid Chromatography – Tandem Mass Spectrometry. No guideline exists for pesticides marked with a dash. WCD = Western Contour Drain, WCE = Western Contour Estuary. * normalised to carbon

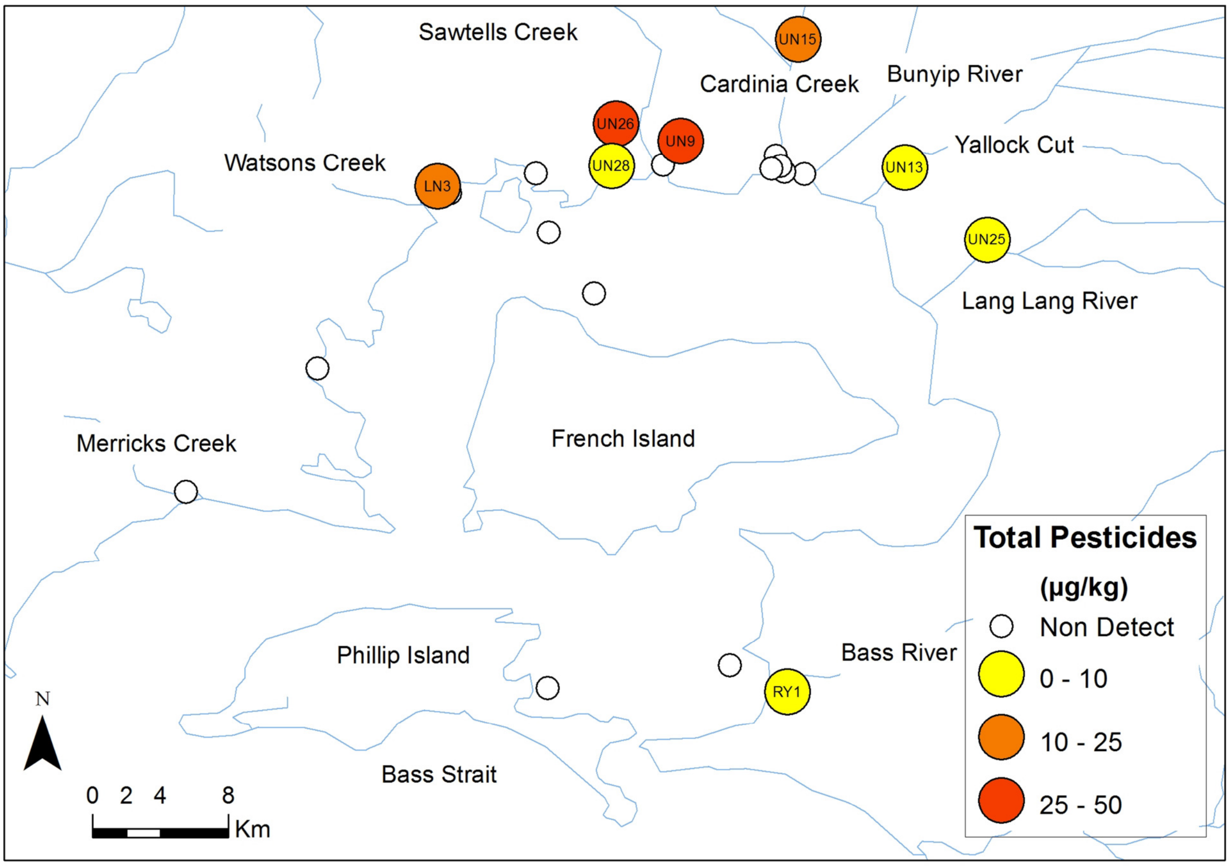

Figure 15 - Total pesticide concentrations within filtered sediments throughout Western Port.

Temporal trends in sediment toxicant concentrations

Temporal changes in metals

Concentrations of metals (cadmium, chromium, copper, nickel, lead, zinc, arsenic and mercury) in whole sediments from bay and inputs (estuaries and freshwaters) of Western Port from 1977, 1997 and 2012 were compared and are presented in Table 8.

Concentrations of arsenic within bay and inputs of western port measured in 2012 (range 2.5 to 33.5 mg/Kg) where higher than those measured in 1997 (range 1 – 23.9 mg/Kg) (Table 8). While concentrations of cadmium, nickel and lead measured in bay and input sediments in 2012 have decreased compared to concentrations measured in 1977 and/or 1997 (Table 8). In bay sediments concentrations of chromium have also decreased from 1977 (mean range 3.1 to 8.5 mg/Kg) to 2012 (mean range 0.08 to 2.2 mg/Kg). In input sediments concentrations of copper have decreased from 1997 (range <0.5 to 15.3 mg/Kg) to 2012 (range 0.14 to 3.1 mg/Kg) (Table 8), while concentrations of copper in the bay appear unchanged since 1997 (Table 8). Zinc concentrations have decreased in the bay since 1977 (mean 12.1±10.7 mg/Kg), although appear stable between 1997 and 2012 (mean 5±4 and 4±4.1, respectively; Table 8). In the inputs zinc concentrations also remain unchanged from 1997 (mean 13.9±8.9 mg/Kg) to 2012 (mean 10.6±8.6 mg/Kg) (Table 8). Mercury concentrations have remained unchanged between 1997 and 2012 in both bay and input sediments (Table 8).

Concentrations of metals (arsenic, chromium, copper, lead, nickel, zinc) in filtered sediments from major waterways of Western Port from 1994-1997 (Hardwick, 1998; Coleman and Pettigrove, 2001; Lewin, 1997) and 2010-2012 (CAPIM sediment quality monitoring program) were compared and are presented in Figures 16-22.

Concentrations of arsenic in sediments of major waterways of Western Port have tended to increase between 1994-98 and 2010-12 (Figure 16). Arsenic concentrations in sediments collected in 1994-98 were all below ISQG-low of 20 mg/Kg, with the exception of one sample (22 mg/kg) from Lang Lang River in 1997 (Coleman and Pettigrove, 2001). In 2012, Watsons Creek, Warrangine Creek and Cardinia Creek arsenic concentrations exceeded the ISQG-low guideline (Figure 16).

In general, chromium concentrations appear similar for the major waterways between 1994-98 and 2010-12 (Figure 17). The Bass River and Warrangine Creek had higher chromium concentrations, while Deep Creek was slightly lower in 2010-12 compared to 1994-98 (Figure 17). Concentrations of chromium were mostly below the ISQG-low of 80 mg/Kg. The one exception was Merricks Creek in 1994-98 where chromium concentrations exceeded the ISQG-low.

Copper concentrations in major waterways of Bass River, Cardinia Creek and Deep Creek were similar across years (Figure 18). Concentrations of copper in Warringine Creek were substantially higher in 1994-97 than current. For Watsons Creek, Merricks Creek and Lang Lang River copper concentrations were greater in the current sampling (2012) compared to 1994-1997. Watsons Creek differences may be due to differences in the sites sampled. In 2012 the estuary was sampled, while in 1994-1997 an upstream freshwater site was sampled. No sites had concentrations exceeding ISQG-low values (Figure 18).

In general, lead concentrations appear similar between years for most of the major waterways (Figure 19). There were several instances of higher concentrations of lead in Cardinia Creek during 2010 – 2012. The one sample taken at Warringine Creek between 1994 and 1998 was higher and exceeded the ISQG-low, while concentrations in 2010 – 2012 were well below guidelines. Concentrations in Watsons Creek also appear lower in 2010 – 2012 than previously.

Nickel concentrations in Bass River were similar across years. In Lang Lang River, Deep Creek and Watsons Creek nickel concentrations were lower in 2010 – 2012 (Figure 20). While concentrations of nickel in Cardinia Creek, Merricks Creek and Warrangine Creek were higher in 2010-2012, and several concentrations in Cardinia and Merricks Creeks exceeded the ISQG-low.

Comparisons of zinc concentrations in Western Port's major waterways show that concentrations of zinc may have increased in some waterways while in others concentrations have likely decreased (Figure 21). Bass River, Warringine and Watsons Creek zinc concentrations have decreased, however current monitoring sites are located within estuarine waters and are subjected to marine intrusions and flushing. While in Deep Creek, Cardinia Creek, Lang Lang River and Merricks Creek zinc concentrations appear to have increased since 1994 - 1998. All concentrations were below ISQG-low guidelines in both years (Figure 21).

Table 8 – Summary of current and historical metal concentrations in Western Port. Mean, Standard Deviation (SD), minimum and maximum dilute extractable metal concentrations in whole sediments from Bay areas and Inputs (estuaries and freshwaters) from 1977, 1997 and 2012. *Arsenic and Mercury are total metal concentrations. Units are mg/Kg. (n = sample size, '-' = no data available).

	BAY														
	1977					1997					2012				
Metal	n	Mean	S.D.	Min	Max	n	Mean	S.D.	Min	Max	n	Mean	S.D.	Min	Max
Cd	11	0.12	0.10	0.04	0.36	28	0.06	0.05	<0.05	0.19	13	0.03	0.02	0.01	0.05
Cr	12	5.3	1.7	3.1	8.5	-	-	-	-	-	13	0.86	0.68	0.08	2.2
Cu	7	3.6	0.48	3.2	4.3	28	1.7	1.1	<0.5	4.1	13	1.1	1.7	0.05	5.1
Ni	16	5.7	5.3	0.5	14.6	28	1.7	1.0	<0.5	4.2	13	0.8	0.5	0.29	1.9
Pb	15	7.6	5.1	1.0	14.6	28	2.9	1.5	<0.3	6.0	13	1.5	1.1	0.13	3.9
Zn	17	12.1	10.7	1.9	41.3	28	5.0	4.0	<0.5	19.6	13	4.0	4.1	0.25	11.5
As*	-	-	-	-	-	28	8.9	4.5	1.90	18.2	9	11.4	7.0	2.5	28.0
Hg*	-	-	-	-	-	28	0.02	0.02	<0.01	0.06	5	0.01	0.01	0.01	0.02

	INPUTS														
	1977					1997					2012				
Metal	n	Mean	S.D.	Min	Max	n	Mean	S.D.	Min	Max	n	Mean	S.D.	Min	Max
Cd	-	-	-	-	-	15	0.19	0.09	<0.05	0.36	9	0.06	0.04	0.01	0.12
Cr	-	-	-	-	-	-	-	-	-	-	9	0.96	0.62	0.37	2.0
Cu	-	-	-	-	-	15	4.5	3.5	<0.5	15.3	9	1.4	1.1	0.14	3.1
Ni	-	-	-	-	-	15	2.4	1.6	<0.5	5.5	9	1.2	0.57	0.38	1.8
Pb	-	-	-	-	-	15	6.2	3.7	2.5	12.1	9	2.8	1.5	0.9	5.2
Zn	-	-	-	-	-	15	13.9	8.9	3.2	32.8	9	10.6	8.6	1.3	27.8
As*	-	-	-	-	-	15	7.7	7.7	1.0	23.9	9	15.6	9.4	2.5	33.5
Hg*	-	-	-	-	-	15	0.02	0.02	<0.01	0.09	4	0.03	0.01	0.02	0.03

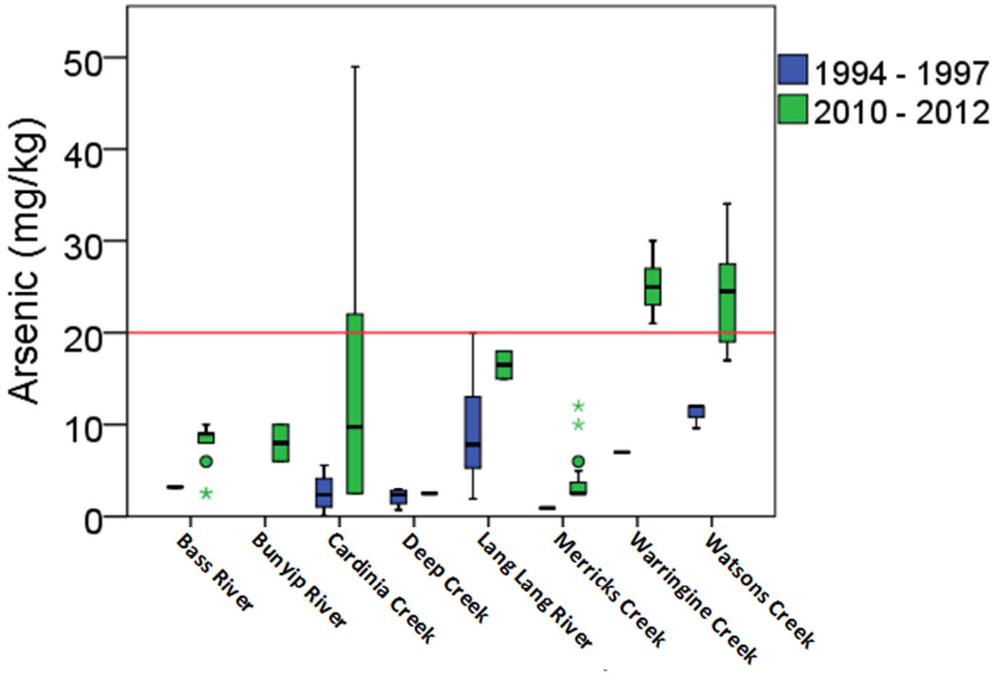

Figure 16 - Concentrations of arsenic (total) in filtered sediments from 1994 - 1998 and 2010 - 2012. Red line indicates ISQG-low.

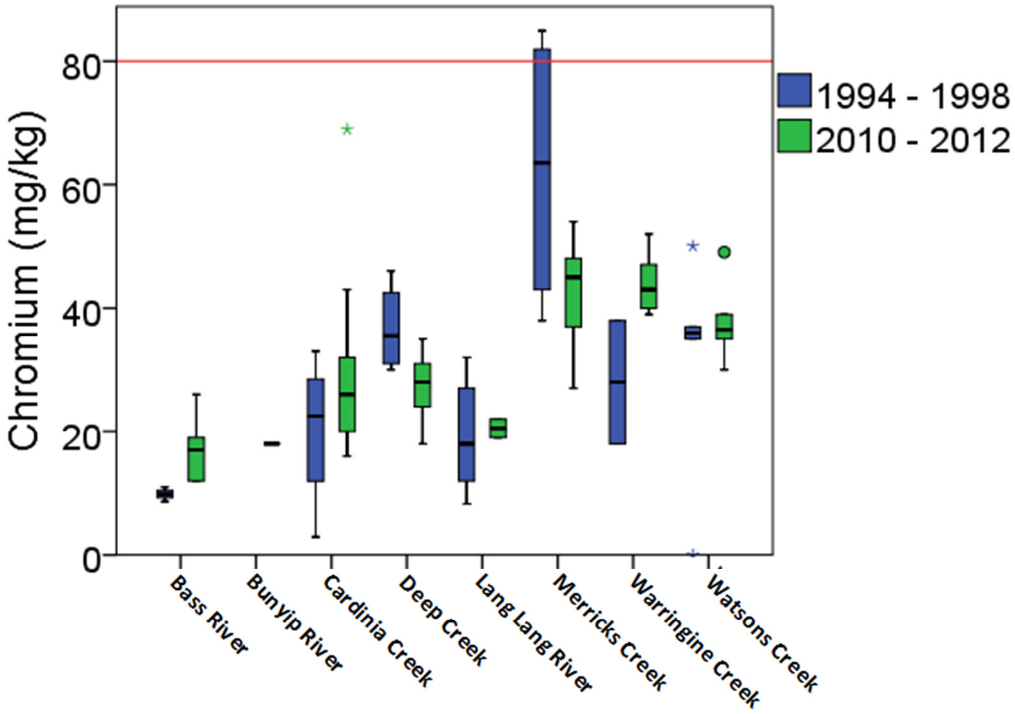

Figure 17 - Concentrations of chromium (total) in filtered sediments from 1994 - 1998 and 2010 - 2012. Red line indicates ISQG-low.

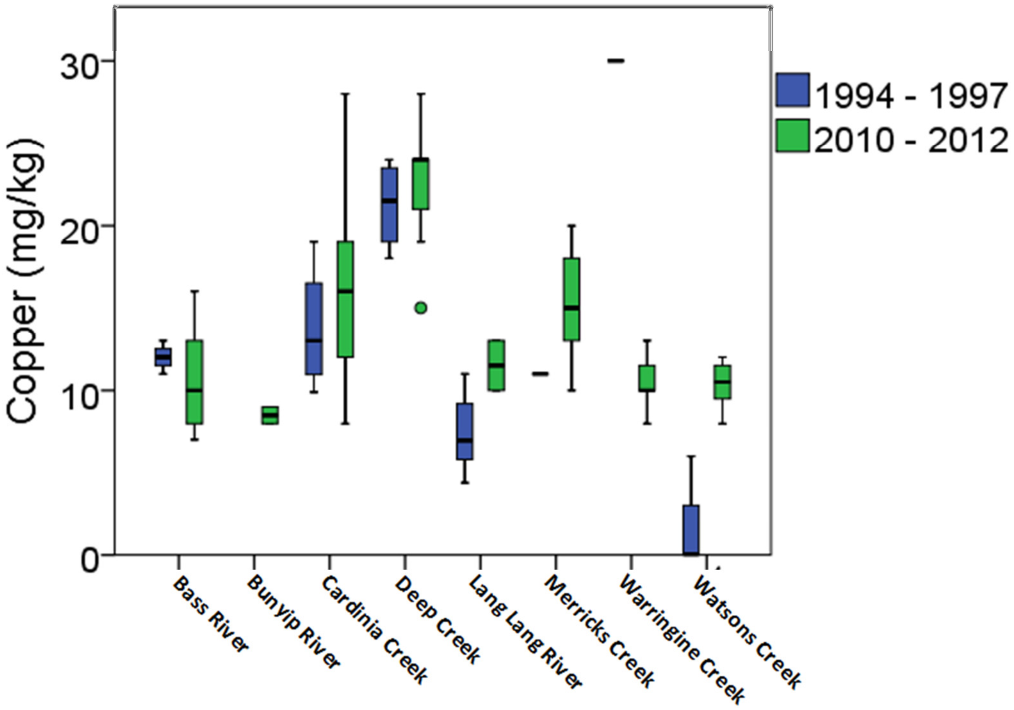

Figure 18 –Copper concentrations (total) in filtered sediments 1994 – 1997 and 2010 – 2012. ISQG-low is 65 mg/kg.

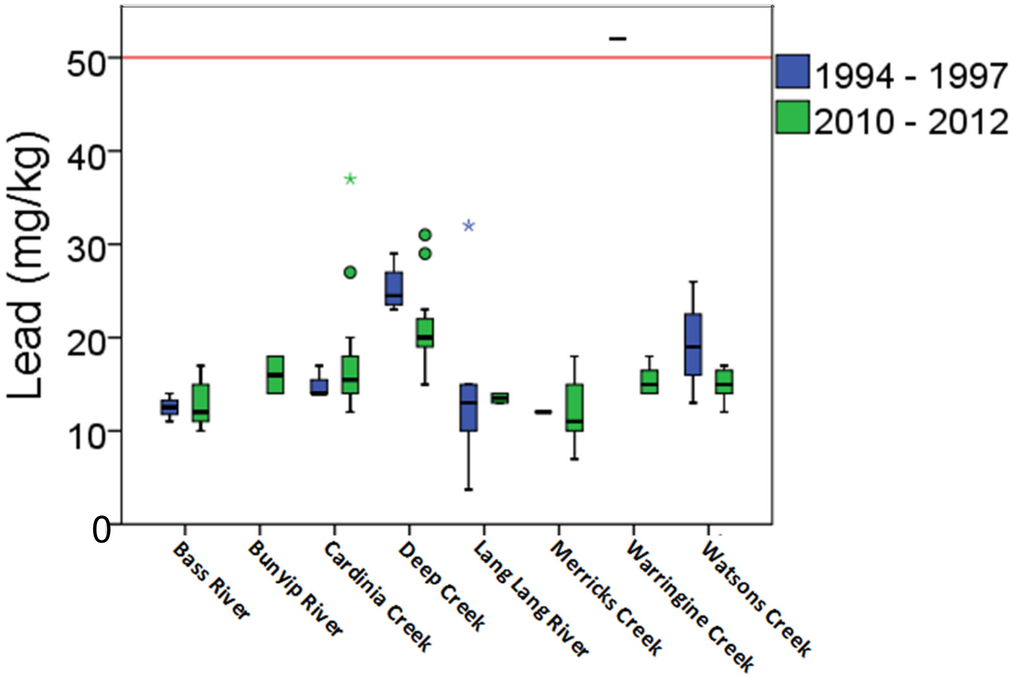

Figure 19 -Concentrations of lead (total) in filtered sediments from 1994 – 1997 and 2010 – 2012. Red line indicates ISQG-low.

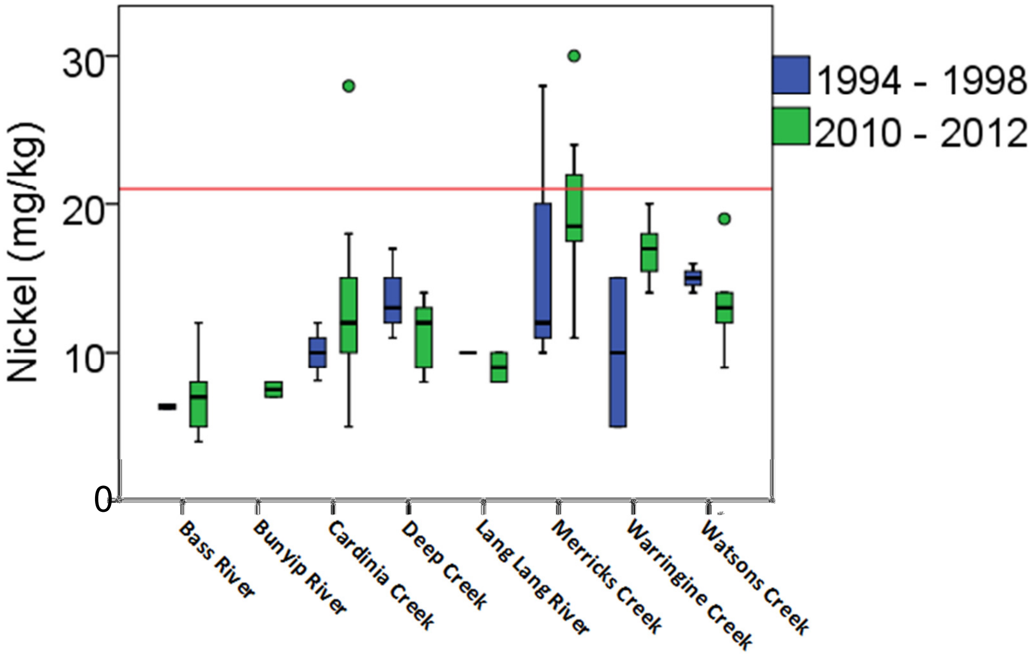

Figure 20 - Nickel concentrations (total) in filtered sediments from 1994 - 1997 and 2010 - 2012. Red line indicates ISQG-low.

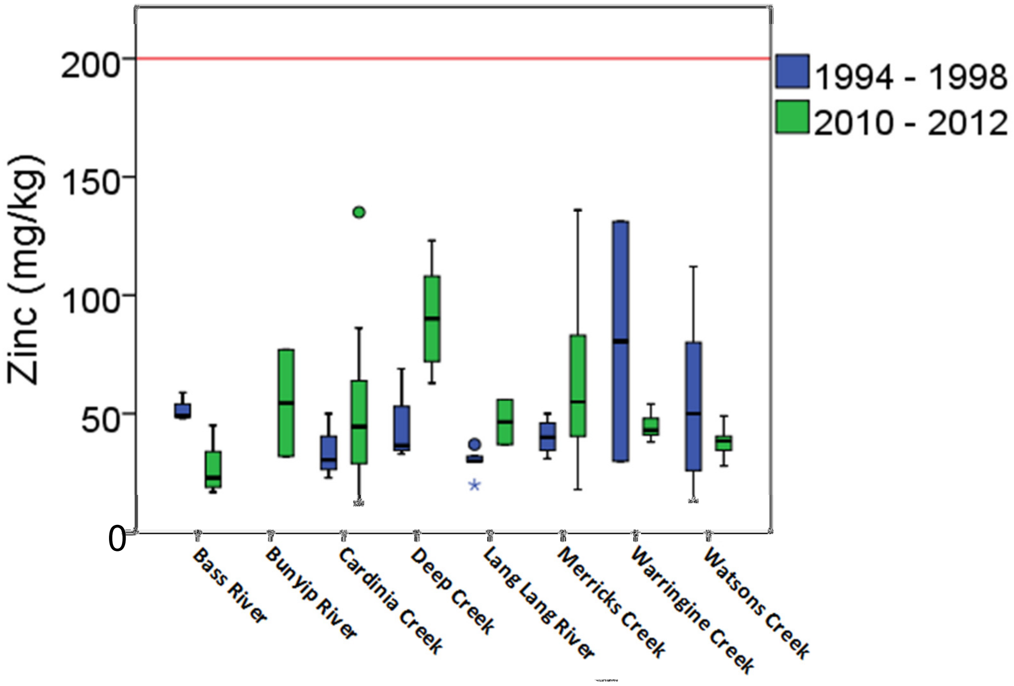

Figure 21 - Concentrations of zinc (total) in filtered sediments from 1994 - 1998 and 2010 - 2012. Red line indicates ISQG-low.

Temporal changes in hydrocarbons

Concentrations of hydrocarbons in Western Port from years 1974-6, 1997 and 2012 are presented in Table 9. Whole sediments from bay and estuarine areas sampled in 1974-6 and 1997 showed similar concentrations of TPHs. Similarly TPH concentrations in whole sediments from 2012 in the bay areas of Corinella, Lower North and the Estuary did not change. However, whole sediments sampled in 2012 showed higher TPH concentrations in the upper North and freshwater areas compared to 1974-76 and 1997 data.

Table 9: Mean (± S.D.) total petroleum hydrocarbon concentrations in sediments from Western Port in 1974-6, 1997 and 2012 whole sediments. Units are mg/kg.

		1974-1976		1997		2012	
Sections	Area	Mean	S.D.	Mean	S.D.	Mean	S.D.
Corinella	CR	7.8	3.5	-	-	3	0
Estuary	ES	36.2	-	24	22.5	30.7	3.2
Freshwater	FW	-	-	17.5	3.5	67.5	21.9
Lower North	LN	29.5	24.5	9.8	9.2	29	18.2
Rhyll	RY	3.2	0.6	12.5	3.5	-	-
Upper North	UN	2.5	0.3	12.7	15.6	73	26.9

Temporal changes in Pesticides

Review of the available literature on pesticide types and concentrations in Western Port are detailed in Table 10. Rees et al. (1998) analysed for herbicides and organochlorine and organophosphate pesticides in sediments of Western Port in 1997, however no pesticides were detected. This is likely to be due to poor detection limits reported in Rees et al. (1998) compared with this recent study. This current study of 2012 did not detect any pesticides in bay sediments.

Melbourne Water's sediment quality monitoring program detected the synthetic pyrethroid esfenvalerate, fungicides boscalid and azoxystrobin, and insecticide fenamiphos in the Watsons Creek estuary in 2010-11 (CAPIM, unpublished data). These fungicides were also detected in the current study at similar concentrations (Table 7). At a freshwater site in Watsons Creek during 1998, elevated concentrations of organophosphate and organochlorine insecticides were detected. In particular dieldrin (20 µg/kg) and p,p'-DDE (30 µg/kg) were detected at concentrations of 20 and 30 µg/kg respectively. p,p'-DDE was also detected in this study in 2012 at Watsons Creek , at trace levels (less than LOR 3 and 5 µg/kg for pp-DDE and pp-DDT respectively). Although they are significantly lower concentrations, they are still above ISQG-low values (Table 10). Monitoring undertaken by Melbourne Water (unpublished data, 2008) in the upstream sections of Watsons Creek detected elevated levels of triazine herbicides simazine and prometryn and the fungicide boscalid in sediments. The same study also detected simazine and prometryn in water samples (Table 10).

In 1998, the organochlorine dieldrin was detected in Warringine Creek (freshwater) (Table 10). However this was not detected in the current 2012 study. As in this study, no pesticides were detected in Merricks Creek at Flinders – Hastings Road in 1998 (Hardwick, 1998) or in Merricks Creek estuary at Balnarring Road in 2010 – 2011 (CAPIM, unpublished data, 2010 – 2011). Current and previous analyses have not detected any pesticides in sediments within Bunyip River estuary (CAPIM 2010 – 2011, unpublished data).

Whole sediments from the Lang Lang River catchment were analysed for organochlorine pesticides between 1996 and 1997 (Coleman and Pettigrove, 2001). Dieldrin and p,p'-DDE were above detection limits (5 µg/kg) at two sites (Table). In the present 2012 study, only 1 µg/kg of azoxystrobin was detected at Lang Lang River (UN25).

Table 10 - Concentrations and pesticides detected in sediments from previous studies of Western Port sites.

Site	Date	Chemicals detected	Reference
Watson Creek estuary	2010 - 2011	Esfenvalerate, boscalid, fenamiphos, azoxystrobin	Melbourne Water Sediment Quality Monitoring, CAPIM 2010-2011, unpublished data
Wastons Creek (freshwater site)	1998	Chlorpyrifos (40 µg/kg), endosulfan 1 (40 µg/kg), endosulfan 11 (80 µg/kg), endosulfan sulphate (40 µg/kg), dieldrin (20 µg/kg) and p,p'-DDE (30 µg/kg)	Hardwick , 1998
Watsons Creek	2008	Sediments: simazine (8 - 230 µg/kg), prometryn (20 – 374 µg/kg), boscalid (10 – 48 µg/kg Waters: simazine (0.14 – 15 ug/L) and prometryn (1.3 – 21 ug/L)	Melbourne Water, unpublished data 2008
Warrigine Creek (freshwater)	1998	20 µg/kg of dieldrin	Hardwick, 1998
Lang Lang River catchment (4 sites)	1996 - 1997	Dieldrin 0.7 µg/kg to 5 µg/kg (normalized to 1% OC), p,p'-DDE 0.5 µg/kg to 1.2 µg/kg (normalized to 1% OC)	Coleman, 2001
Western Port sediments	1997	No pesticides detected	Rees et al 1998
Merricks Creek	1998	No pesticides detected	Hardwick 1998
Merricks Creek estuary	2010 - 2011	No pesticides detected	Melbourne Water Sediment Quality Monitoring, CAPIM 2010-2011, unpublished data

Temporal changes in organotins

Concentrations of organotins from Western Port measured in 1988, 1997 and 2012 are presented in Table 11. Six of the seven sites surveyed during May - June 2012 had detectable concentrations of organotin compounds. Tributyltin (TBT) concentrations in 2012 ranged between <0.5 and 7 µg Sn/kg. The highest recorded level was detected at Hastings boat ramp. Sediment at Warneet slipway also had elevated concentrations of TBT with a concentration of 5 µg Sn/kg. The concentration of TBT was below the detection limit at one site, located south of Hastings boat ramp and to the north of the Westhaven marina, with no TBT detected at this site in 1997 (Table 10). Levels of TBT detected during the 1988 ranged <1 to 83 µg Sn/Kg and in 1997 from <0.3 to 69 µg Sn/Kg which were generally much greater than those detected in the current study (Table 11).

Dibutyltin (DBT) concentrations ranged from <1 to 6 µg Sn/kg, with the highest concentration recorded off the end of the boat ramp and floating pier at Hastings (Table 11). Concentrations for DBT were below detection limits at two sites. Concentrations of monobutyltin were all below the detection limit (<1 µg Sn/kg), with the exception of one site located off the end of the boat ramp and floating pier at Hastings with a concentration of 1 µg Sn/kg. These concentrations are significantly lower than those found in 1988 and 1997 (DBT <0.3 – 249 µg Sn/kg and MBT 37 – 430 µg Sn/kg) and are all below ISQG-low concentrations for TBT with the exception of one site in Hastings (DBT and MBT estimated to be 10 – 100 times less toxic).

Table 11 - Concentrations of organotins from sites located close to marina and boat ramps in Westernport from 1988 (Daly & Fabris 1993), 1997 (Rees et al 1998) and 2012 (this study). Units are reported in µg Sn/kg. Values in bold are in excess of the ISQG low.

Site	Location	Date	Tributyltin	Dibutyltin	Monobutyltin
ISQG	**low**		**5**	**-**	**-**
	high		**70**	**-**	**-**
17	Hastings (South of Hastings boat ramp north-side of Westhaven marina)	1997	<0.3	23	240
TBT2		2012	<0.5	<1	<1
17	Hastings (Outside Westhaven marina)	1988	<1	<1	138
17A	Hastings (Outside Westhaven marina south-side)	1997	**26**	<0.3	430
TBT3		2012	2.6	2	<1
18	Hastings (mooring, marina)	1988	**83**	249	310
18	Hastings (Off end of marina pier)	1997	<0.3	<0.3	73
TBT4		2012	3.7	3	<1
19	Hastings (slipway, marina)	1988	**60**	232	245
19	Hastings (Off end of boat ramp floating pier)	1997	**69**	28	95
TBT5		2012	**7**	6	1
20	Warneet (Warneet south pier near mooring and slipway)	1988	<1	29	<1
20		1997	<0.3	<0.3	69
TBT6		2012	**5.1**	4	<1
21	Newhaven (moorings marina)	1988	**61**	<1	<1
21		1997	**200**	64	77
TBT7		2012	1.6	<1	<1
TBT8	Yaringa (moorings marina)	2012	2.4	1	<1

Discussion

The results of this study indicate that in general toxicants in Western Port are below sediment quality guideline values and therefore are likely to be a low risk to ecosystem health. However, the results do highlight some localised areas in the Western Port catchment where toxicants are at levels of concern. Generally, contamination is confined to areas that receive flows from catchment tributaries and is low in the majority of the bay. In particular, sediment chemical analysis indicated moderate levels of several heavy metals (arsenic, nickel, mercury), a total of 17 pesticides, including herbicides, fungicides and organochlorine insecticides, and elevated levels of TPHs are occurring at sites, predominantly in estuaries, followed by the bay and freshwater areas of Western Port. In this study there were seven key areas identified as having toxicants present at levels exceeding guideline values and/or the occurrence of multiple toxicants potentially presenting a risk to ecosystem health. These areas include:

- Western Contour Drain – Pesticides including triazine herbicides (simazine, prometryn, linuron and metolachlor) and fungicides (boscalid, oxadixyl, azoxystrobin, cyprodinil).
- Watsons Creek Estuary – Triazine herbicides (prometryn, metolachlor, linuron) and fungicides (boscalid). Organochlorine pesticides at trace levels. Low levels of insecticides (pirimicarb, fenamiphos).
- Sawtells Creek estuary –TPHs. Synthetic pyrethroid insecticide (bifenthrin), phenyl urea herbicide (diuron), organochlorines (pp-DDE) and trace levels of triazines (simazine).
- Cardinia creek estuary and Warringine Creek –mercury. In pore waters cobalt and in Cardinia nickel and zinc.
- Deep Creek estuary – heavy metal aluminum (pore waters). Organochlorine insecticides (pp-DDE and pp-DDT), trace amounts of triazine herbicide (simazine), insecticide (pirimicarb), and fungicide (triadimenol).
- Heavy boat use sites – organotins (tributyltin and dibutyltin).

The key types of toxicants, their concentrations and spatial and temporal trends are discussed in more detail below.

Metals

The primary anthropogenic sources of heavy metals in marine environments typically include urban run-off, industrial effluents, mining operations, atmospheric deposition and agricultural activity (Haynes and Johnson, 2000). In this study all heavy metals analysed for were detected in sediments from all areas of Western Port investigated. The metals cadmium, copper, iron, lead, manganese, mercury and zinc were predominantly highest in the urban freshwater and estuarine areas compared to the bay. However the metals arsenic, aluminium, chromium and nickel were in higher concentrations in bay and estuarine areas, particularly around the lower and upper north arms in the waterways and inlets around Watsons, Warneet and Sawtells Inlets and in the estuarine reaches of Cardinia and Deep Creek.

Twenty-four out of 42 sites exceeded or equalled the ISQG-low for one or more metals, the majority of these being for arsenic. Nickel and mercury were the only other two metals, of the 11 metals measured, that occurred in concentrations exceeding the ISQG-low sediment value, and no metals were detected above the ISQG-high values (ANZECC and ARMCANZ, 2000).

Arsenic concentrations exceeding or equalling the ISQG-low of 21mg/kg were predominantly detected in sediments from the estuarine area (12 sites), however this seemed to persist into the bay sediments in the upper north arm (7 sites) and lower north arm (2 sites). Two bay sites in the Rhyll arm and one in the Corinella arm also had arsenic concentrations exceeding the ISQG-low. Assessment of the bioavailable fraction of arsenic (dilute acid extractable portion), however, showed that these concentrations were below ISQG-low and therefore present a low risk to ecosystem health. Arsenic naturally occurs throughout the Mornington Peninsula region with concentrations as high as 500 mg/kg arsenic being reported along the shores of Port Phillip Bay ((Fabris et al., 1999) ; Melbourne Water unpublished data) and on the Mornington peninsula (CAPIM unpublished data, 2010-2012; Melbourne Water, unpublished data). As the case appears with Port Phillip Bay, it is probable that most of the arsenic in the top of Western Port is derived from natural geological sources, a theory that has also been proposed by (Fabris and Longmore, 2005) as stated by Lee (2011). Temporal analysis of arsenic from 1997 to 2012 shows that there has been an increase in the concentrations in bay and input areas of Western Port, arsenic concentrations in 2012 in major waterways exceeding ISQG-low (ANZECC & ARMCANZ 2000) at a number of sites.

Nickel was detected at concentrations exceeding the ISQG-low guideline of 21 mg/kg at two of the estuarine sites, namely Merricks Creek estuary (WS2) and Sawtells Creek (UN9). In the Western Contour Drain (UN26) nickel concentration equalled but did not exceed the ISQG-low value. Assessment of the bioavailable fraction of nickel (dilute acid extractable portion) did show that these concentrations were below ISQG-low and therefore present a low risk. Similarly to arsenic, naturally high concentrations of nickel occur in basalt soils and are therefore often reported to exceed ISQG-low (Pettigrove & Hoffmann, 2003). Underlying basalt is found towards the south-west of Western Port between Balnarring and Flinders (Pettigrove & Hoffmann, 2003) which may account for the occurrence of the high nickel in Merricks Creek estuary. Temporal analysis of nickel concentrations from the bay and a number of major creeks and rivers entering Western Port show that there has been a general decrease in concentrations from 1994 to 2012.

Mercury was detected at concentrations exceeding the ISQG-low at two sites in this study, namely Cardinia Creek estuary (UN32) and Warringine Creek estuary (LN9). Similar concentrations of mercury have been reported in sediment quality monitoring studies at Deep Creek, Cardinia Creek and its estuary, Watsons Creek and Bunyip River (Melbourne Water, 2010 – 2012 unpublished data), Hastings fixed site (EPA Victoria unpublished data 1988 – 1993) and Lang Lang River (Coleman and Pettigrove, 2001). Mercury has potential for bioaccumulation and is extremely toxic at low concentrations and can persist in the tissues of organisms for long periods after exposure (Boening, 2000). The occurrence of mercury at levels exceeding ISQG-low values is of concern for potential low to moderate impacts to aquatic fauna at these particular sites; however the results of this study indicate that there is no evidence of any consistent mercury pollution in Western Port. Long-term monitoring, currently underway, will give greater insight to any potential risks from mercury and any need for further investigation.

Pore waters are often sampled to give an indication of the bioavailability of metals in sediments. During this study a limited number of freshwater and estuarine sites were sampled for pore waters and the results indicated that all sites had metals occurring at concentrations exceeding SEPP (WoV) surface water objectives. In the freshwater sites, Deep and Cardinia Creeks, aluminium was the only metal exceeding the SEPP (WoV) environmental quality objectives, while in marine sites cobalt exceeded the SEPP (WoV) objective for the north arm at Warringine estuary (LN9), and at Cardinia estuary (UN17) cobalt, nickel and zinc concentrations exceeded the SEPP (WoV) objective for the East Arm of Western Port. The occurrence of these elevated levels indicates a moderate potential for toxicity to benthic organisms living in these sites.

Concentrations of metals in pore water can be highly variable and influenced by various chemical and physical processes such as oxidation state and sediment properties, particularly grain size and organic carbon (Simpson, 2005). Metal toxicity will depend on both physico-chemical sediment properties and organism physiology and feeding behaviour (Simpson, 2005). The pore water samples taken during the current study provide a ‘snapshot’ of metal concentrations at the point of sampling. To provide greater assurance in determining risk from pore water metal exposure time-integrated samples where assessment of metals in water is done by comparing the median of multiple samples over time against the guideline trigger values (ANZECC and ARMCANZ, 2000) may be more useful. Metal toxicity has been shown to be strongly related to dissolved metal flux in pore waters, which can be measured using diffusive gradients in thin films (DGTs) (Amato et al., 2012, Simpson et al., 2012). For future pore water assessment, DGTs may offer a cheaper, more reliable and practical assessment of time integrated sampling with more power to detect differences in bioavailable metals between contaminated and uncontaminated sites (Webb and Keough, 2002, Simpson et al., 2012).

Pesticides

Pesticides can enter aquatic systems through spray drift, in runoff, groundwater (Kookana et al., 1998). In the current study a number of pesticides were detected in sediments from estuarine and freshwater areas, while there were no detections in sediments from bay areas. Prior to this study, there had been no reports of pesticides occurring in sediments of Western Port, however numerous reports of detections in estuarine and freshwater areas of the catchment (CAPIM, unpublished data; Rees et al 1998; Coleman et al 2001; Hardwick 1998; Schafer et al 2011). To date there are limited to no sediment quality guidelines for the majority of pesticides in use (ANZECC and ARMCANZ 2000). A limited number of pesticides have trigger values derived for water concentrations; however the organochlorine pesticides are the only pesticides to have sediment guideline values (ANZECC and ARMCANZ 2000).

In the current study the organochlorine insecticides were the most commonly detected pesticide. Organochlorine insecticides were widely used in Australia to control pests around homes and in agriculture from the 1950’s to the early 1970’s. Most organochlorine pesticides were deregistered and banned for agricultural use by 1981 and pest control use phased out by 1995 (Kellar et al., 2011). More recently in 2010, endosulfan was banned after a review which concluded its persistence and potential for bioaccumulation pose it as a high risk to aquatic and human health (APVMA, 2010). There occurrence in the environment is therefore it likely to be due to due past use and their persistent nature. Organochlorine pesticides have been a major concern in the aquatic environment as they are known to accumulate in fauna and biomagnify up the food chain, they are also known to be highly toxic to invertebrates and fish (Muir, 1988). In the current study p,p’-DDE and p,p’-DDT were the two organochlorine insecticides detected at up to 5 sites (Yallock Creek, Sawtells Creek, Deep Creek, Bass River estuary and Watsons Creek estuary). Concentrations were generally below ISQG-low value at these sites, with the exception of Deep Creek (UN15) where concentrations exceeded ISQG-low for both pp-DDE and pp-DDT suggesting that these concentrations have a moderate probability of adversely affecting the aquatic fauna in Deep Creek. The organochlorines dieldrin, endosulfan and endosulfan sulphate were detected in Watsons Creek sediments during 2010-11 at concentrations up to 20, 11 and 80 µg/kg respectively (CAPIM 2010-11, unpublished data). Dieldrin was also been detected in sediments of Warringine Creek in 1998 (Hardwick, 1998) and Lang Lang River in 1996-97 (Coleman & Pettigrove, 2001) at concentrations of 20 and 5 µg/kg respectively. The levels detected in the current study are lower than those reported in these earlier studies.

The herbicides were the second most detected group of pesticides during the current investigations. The triazine herbicides simazine, prometryn, metolachlor and linuron and phenyl urea herbicide diuron were detected at four sites (Sawtells Creek, Western Contour Drain, Deep Creek and Watsons Creek estuary). Herbicides are produced in the largest quantities of any of the pesticide products (Radcliffe, 2002). Triazine and phenylurea herbicides are commonly used in general weed control in urban and agricultural areas (Macinnis-Ng and Ralph, 2003). These herbicides act by inhibiting different processes involved in photosynthesis and are non species-specific. Recently the APVMA finalised a detailed review on the registration and use of diuron, following concerns regarding environmental fate and human health. A key issue was the potential for contamination of waterways from agricultural runoff. As a result of this review, APVMA have issued new restrictions on the use of diuron with the objective of reducing the occurrence of diuron in aquatic systems (APVMA, 2012). As there are no formal guidelines for herbicides in sediments, it is difficult to determine what they pose for the environment. It is likely that they pose the highest threat to floral communities as they are designed and applied to be active against plants.

Studies in a variety of seagrass species have shown photosynthesis is inhibited within hours by exposure to water concentrations of 10 µg/L of the herbicides diuron, atrazine and simazine (Haynes et al., 2000a, Macinnis-Ng and Ralph, 2003, APVMA, 2012). Smaller species such as *Halophila ovalis* seem to be impacted by water concentrations as low as 0.1 ug/L of diuron (Haynes et al., 2000b). No reports were found for the effects of prometryn to marine plants; however freshwater macrophytes have been affected in the range 11.8 - 85 µg/L water concentrations and microalgae in the range 1-46 µg/L (Kegley et al., 2011). The concentrations of prometryn (15 µg/kg at Western Contour Drain) and diuron (28 µg/kg at Sawtells Creek) that were detected in the current study and levels of simazine (230 µg/kg) and prometryn (20-374 µg/kg) detected in Watsons Creek in (2008) study by Melbourne Water, are significantly greater than the levels shown to effect seagrass and some freshwater macrophytes and microalgae described above. Accordingly, these chemicals may present a risk to seagrass beds and other significant flora such as mangroves that are situated at the entrance to the estuaries where these concentrations were detected. Investigation of spatial and temporal concentrations of herbicides and understanding of threshold concentrations to key flora species would allow understanding of risks to these environments.

The fungicides boscalid and azoxystrobin were detected at three sites each during this study. Both boscalid and azoxystrobin are predominantly used in agriculture for food crops such as grapes, eggplant, potatoes, pumpkin and tomatoes to control rot and fungi. Their main source into Western Port would most likely be through runoff. Boscalid was present in sediments in the Western Contour Drain and estuary and the Watson Creek estuary. Azoxystrobin was detected in the Western Contour Drain, Yallock Cut and Lang Lang River. Currently there are no sediment quality guidelines for these fungicides and limited toxicological data exist, the US EPA reporting that the absence of data on acute and chronic toxicity of spiked sediments results in high uncertainty regarding sensitivity of benthic organisms (USEPA, 2010). There is a need to understand the toxicity of boscalid to local aquatic fauna and flora to provide details of risks posed.

There were four key areas of concern in regards to the occurrence of pesticides, identified during this study and from review of data from past studies. Western Contour Drain, Watsons

Creek estuary, Sawtells Creek and Deep Creek all had either significantly elevated pesticide concentrations in sediments and/or mixtures of up to 9 different pesticides occurring. The lack of information regarding the toxicity of these to fauna and flora communities is a key issue to determining suitable environmental protection thresholds.

Hydrocarbons

Total petroleum hydrocarbons are common pollutants in water and sediments of urbanized water bodies. Hydrocarbon inputs in Western Port include effluent discharge, industry, oil spills, boating activities, urban runoff and biogenic hydrocarbons produced naturally by marine organisms (Burns and Smith, 1977). Generally TPHs are degraded under microbial action very slowly and are therefore considered to be moderately persistent, particularly in sediments with high organic content and in the absence of oxygen (Foulsham et al., 2009).

There are no current Australian guidelines for TPHs in marine or freshwater sediments. The earliest comprehensive TPH study in Western Port by Burns and Smith (1977) used a threshold of 72 mg/kg TPHs for marine sediments based on correlations in subtidal sediments that corresponded to an absence of a sensitive marine amphipod (Family: Ampeliscidae) (Sanders et al., 1972) following the West Falmouth oil spill (Blumer and Sass, 1972). More recent studies of hydrocarbon toxicity to marine organisms suggest sub-lethal effects may occur in the concentration range of 30-400 mg/kg. For instance Long and co-workers reported an aversion to sediments with concentrations greater than 37.5 mg/kg crude oil by the blue mussel *Mytilus edulus planulatus* (Sara Long, pers. comm., 2012). Further research on low concentrations of TPH in sub-tidal sediments (below 50 mg/kg) show no change in macrofaunal communities, with an opportunistic polychaete species increasing with elevated TPH concentrations between 100 – 1,000 mg/kg (Glémarec and Hussenot, 1982).

In freshwater sediments, Pettigrove & Hoffmann (2005) derived a threshold concentration of 860 mg/kg based on field microcosm experiments using freshwater invertebrates and synthetic motor oils (C>16). They found that hydrocarbon concentrations of 860 mg/kg dry weight hydrocarbons altered community structure and chironomid abundances, while concentrations above 1,858 mg/kg significantly impaired taxa richness and abundance (Pettigrove & Hoffmann, 2005). The most recent review of sediment quality guidelines by Simpson et al. (2010) proposed a TPH threshold concentration low of 275 mg/kg and high of 960 mg/kg based on the available literature and these have been adopted for this study.

TPH concentrations detected in bay and estuarine sites during the current study ranged 16 to 133 mg/kg, in general were below a concentration of 81 mg/kg. All TPH concentrations in the bay were below the proposed threshold of 275 mg/kg and therefore present a low risk to aquatic biota. The highest concentration was in Sawtells Inlet (UN8) in the estuarine area where a TPH concentration of 133 mg/kg was recorded, however it is still well below the lower threshold suggested by Simpson et al. (2010) and in the range of no observed effect concentrations for macro fauna described above. The level at this site should be evaluated in ongoing monitoring programs and if elevated concentrations persist may warrant toxicological investigation to confirm risk.

Similarly, TPH concentrations in freshwater sediments collected during this study were below 150 mg/kg and did not exceed the proposed threshold value of 275 mg/kg proposed by Simpson et al (2010). Results from freshwater sites sampled during the current study suggest there is low risk of effects from TPHs to aquatic fauna at freshwater sites. Earlier monitoring in Cardinia Creek (UN15) detected one instance where TPH concentrations were above the proposed high threshold of 960 mg/kg (CAPIM, unpublished data, 2010). It is possible that hydrocarbons could have been washed down from upstream urban areas or local roads. No subsequent concentrations have exceeded the high threshold, and ongoing monitoring will confirm if TPHs are of any further concern.

Hydrocarbons can also occur naturally from decaying organic matter. Volkman et al. (1992) suggested that concentrations of total hydrocarbons from biogenic sources may exceed those from pollutant sources where the concentration is less than 50 mg/kg. While no differentiation was made in this study between anthropogenic petroleum and biogenic sources of total hydrocarbons, Burns and Smith (1982) reported an average biogenic hydrocarbon concentration of 25 mg/kg for Western Port based on samples taken from a mix of seagrasses, macroalgae and other organics.

Total petroleum hydrocarbon concentrations in sediments do not appear to have changed significantly between 1977, 1997 and 2012 for most areas of Western Port. The exception to this is the freshwater areas of Western Port were there appears to have been an increase in TPH concentrations between 1997 (mean 17.5±3.5 mg/Kg) and 2012 (mean 67.5±21.9 mg/Kg) and in the Upper North area where TPH concentrations have also appeared to have increased from 2.5±0.3 mg/Kg in 1977 to 73±26.9 mg/Kg in 2012. Analytical methods used in this study are similar to those of Rees et al. (1998) with TPH concentrations reported having not been corrected for any biogenic contributions as done by (Burns and Smith, 1977). Freshwater sediments sampled during the current 2012 study ranged from 26.5 to 60.8 mg/kg and were much lower than concentrations previously detected as part of on-going monitoring (CAPIM, unpublished data 2010 - 2011).

Organotins

Tributyltin (TBTs) and other organotin metabolites from antifouling paints have previously been identified as a risk to marine fauna in Western Port (Daly and Fabris, 1993, Rees et al., 1998). The longevity of TBT in the environment is of concern for localised species, as the degradation processes of TBT in sediments are extremely slow (Meador, 2000). Degradation of TBT is significantly influenced by the amount of oxidation of sediments and a number of biogenic factors including benthic activity, grain size and organic carbon (Daly and Fabris, 1993). An estimation of degradation rates of organotin compounds (assuming a constant rate of decrease since concentrations in 1997) in Western Port appear to be relatively slow, with an estimated half-life ranging between two and seven years in sediments. TBT is progressively debutylated via a process of photolysis and microbial action into the degradation products dibutyltin, monobytyltin and other inorganic forms of tin that are decreasingly toxic (Clark et al., 1988). Bioaccumulation in tissues, reduced growth and imposex (a condition where females develop male sexual characteristics) are key issues associated with TBT exposure (Rees et al., 2001). Based on field and laboratory studies, there is evidence to suggest that imposex may be induced in gastropod molluscs at concentrations around 1 -2 ng Sn/L (Gibbs et al., 1991) .

In the current study there were several incidences of elevated tributyltin in sediments from the seven sites sampled, concentrations exceeding the ISQG low trigger value (5 µg Sn/kg) at two sites including Hastings boat ramp (TBT5) and at Warneet slipway (TBT6). Concentrations of degradation product dibutyltin were also slightly elevated at these sites, although there are no ISQG values for degradation products they are considered to be less toxic that the parent compound TBT (Thompson et al., 1985). Changes in concentrations are likely to be due to dilution and/or dispersion from movement of sediments and reduced inputs. These results indicate that there may be a slight risk of toxicity from TBT to organisms, in particular molluscs at Hastings and Warneet.

Temporal analysis from 1988 to 2012 of TBT and its degradation products show a general decrease in concentrations in Western Port. The exceptions are Hastings marina pier (TBT4) and Warneet slipway (TBT6) where concentrations of TBT appeared to increase (potentially explained by sampling site differences).

Since the ban on use of TBT several other products have been introduced to the market including a number of herbicides such as diuron and irgarol 1051. These may be a direct source of herbicides in the marine environment for instance diuron and irgarol 1051 have commonly been detected in water and sediments near coastal areas in the United Kingdom (Thomas et al., 2000). These products warrant further investigation in areas of high boating activity in Western Port.

Conclusions

At present, sediments in the Western Port marine environment (open bay areas) have low toxicant concentrations, with no pesticides being detected in these sediments. In contrast to the bay, Western Port estuarine sediments contained elevated concentrations of a range of toxicants. A key concern is the presence of herbicides prometryn, simazine and diuron and the fungicide boscalid in sediments that may be impacting biota. No sediment guidelines currently exist for these pesticides, and further research is required to detail what impacts they are having on the environment. Some legacy residues of previously used pesticides such as DDT were detected, although in lower concentrations than earlier studies.

Other risks to the Western Port environment from toxicants appear comparatively small. Mercury was slightly elevated at two estuarine sites when compared with interim sediment quality guideline low thresholds. However concentrations do not appear to have changed in bay and input areas since 1997. Similarly organotins exceeded sediment guidelines at two sites close to high boating activity. The levels at these sites may pose a moderate risk to aquatic fauna health, although there appears to be low risk in other sections of the bay, estuaries and freshwater areas.

The results from this study have provided insight into the types of toxicants, concentrations and areas of occurrence in Western Port. While toxicant concentrations in the bay in general appear to be below guideline values a number of toxicants have been identified in some areas that warrant further investigation. Future monitoring and assessment programs should incorporate toxicological assessments to determine if toxicants are causing ecological effects. Furthermore, if they are linked with catchment management works they could inform of how any changes have improved ecological conditions, or reduced inputs to Western Port.

Further research and recommendations

Based on the findings of this study, it is recommended that further research is completed to investigate the potential effects of toxicants in key areas on resident fauna and flora. The following recommendations are based on understanding risks posed by elevated concentrations of toxicants and maintaining and improving aquatic health in Western Port. The recommended priority investigations include:

(1) Investigate the levels of herbicides and fungicides in estuaries and mudflats of Western Port to understand risk posed to resident biota. Notably:

- investigate spatial and temporal concentrations of organic toxicants (herbicides and fungicide boscalid) in Western Contour Drain, Watsons Creek and Sawtells Creek estuary and surrounding mud flats to assess the potential risks to estuarine and marine flora and fauna,
- develop concentration thresholds for herbicides and insecticides in Western Port by conducting toxicity tests using local estuarine and marine fauna and flora,
- review our current understanding of toxicants and thresholds for estuarine organisms based on existing laboratory and field toxicity tests,
- Prepare a risk assessment for herbicides (prometryn, simazine, diuron) and fungicide boscalid in Western Port

(2) Maintain monitoring programs in Western Port at key sites to understand changes in toxicant types and concentrations. Notably:

- continue with the existing sediment quality monitoring program at key estuarine sites to monitor toxicants[a] entering the bay,
- determine if sites where elevated concentrations of metals (arsenic, nickel and mercury), organotins and TPHs were detected are having ecological effects,

---

a. Key toxicants include arsenic, mercury, nickel, TBT and metabolites, diuron, bifenthrin, simazine, prometryn, oxadixyl, boscalid and TPHs.

Acknowledgements

We sincerely thank the following people and organisations:

Rhys Coleman (Melbourne Water) for his dedicated guidance, support and assistance with the project including scoping, site selection, field assistance and comments on the report.

Bryant Gagliardi, Kathryn Hassell, Allyson O'Brien, and David Sharley (CAPIM) for their suggestions, comments or reviews of earlier versions of the report. Daniel MacMahon, Katherine Jeppe, Bryant Gagliardi, Cameron Amos and Simon Pahor for field and sampling assistance.

Associate Professor Augustine Doronila and Dr Alex Duan (Melbourne University Chemistry Department) for performing the analyses of dilute acid-extractable metals and analytical advice.

Gavin Rose and Pei Zhang (DPI Victoria) for performing the analyses of pesticides and analytical advice.

ALS environmental sample management and analysis of total metals, organotins, hydrocarbons and total organic carbon.

Funding of this review was provided by Melbourne Water, Victorian Government Department of Sustainability and Environment, and the Port Phillip and Westernport Catchment Management Authority through the Victorian Government's Natural Resources Investment Program (NRIP).

Glossary

ANZECC & ARMCANZ: Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

Anthropogenic: Caused by human activities.

Bay: An open body of water dominated by marine waters and tides, including Western Port and Port Phillip

Benthic: Relating to processes that occur on or within the sediment at the bottom of a water body.

Bioavailable: The proportion of a chemical that an organism is exposed to through water, sediment, soil, suspended particles, organic carbon and/or food

Catchment: the area of land that rain lands in and drains into waterways.

Ecosystem: A community of plants, animals, bacteria and the interrelated chemical and physical environment

Discharge: The release of water or material from a source.

Estuaries and Inlets: Areas where marine waters mix through tidal exchange with freshwater flows, other than Port Phillip Bay, Western Port and the Gippsland Lakes (SEPP (WoV) 2001.

Flushing: The rate at which a waterbody exchanges its water content.

Flux: the flow of material.

Freshwater: Waters that flow through natural or man-made channels where there is no influence from marine water.

Indicator: A measurable variable that can be used to assess the condition or change in a management unit, such as water or sediment quality or ecosystem health.

ISQG: Interim sediment quality guidelines (ANZECC and ARMCANZ, 2000).

Photosynthesis: The process whereby light energy is used to convert carbon dioxide and water to organic molecules and the associated release of oxygen.

RAMSAR Site: A wetland of international importance listed under the Convention on Wetlands.

Sediment: mineral and organic matter that is deposited at the bottom of a water body.

Suspended solids: The total amount of particulate matter in the water column.

Toxicants: A chemical that causes harmful effects to biota, such as heavy metals or synthetic organic compounds.

Toxicity: Where the exposure of a chemical is high enough to induce a toxic effect in biota.

References

ABS. 2011. *3218.0 Regional Population Growth, Australia* [Online]. Australian Bureau of Statistics. Available: http://www.abs.gov.au/ausstats/abs@.nsf/Products/3218.0~2011~Main+Features~Victoria?OpenDocument [Accessed 15 September 2012].

Amato, E., Simpson, S. L. & Jolley, D. 2012. Towards developing a rapid technique for assessing the bioavailability of metals in sediments. *SETAC.* Brisbane.

ANZECC & ARMCANZ 2000. National Water Quality Management Strategy, Australia and New Zealand Guidelines for Fresh and Marine Water Quality. *In:* ZEALAND, A. A. N. Z. E. A. C. C. A. A. R. M. C. O. A. A. N. (ed.). Artarmon, NSW, Australia: Australian Water Association.

APVMA 2003. Cancellations of Registrations and Label Approvals: Tributyltin. *In:* AUSTRALIAN PHARMACEUTICALS VETERINARY MEDICINES AUTHORITY (ed.) *Gazette No. 5, 6 May 2003.*

APVMA. 2010. *Cancellations of Registrations and Label Approvals: Endosulfan* [Online]. Available: http://www.apvma.gov.au/products/review/completed/endosulfan.php [Accessed].

APVMA 2012. Diuron Review - Supplemental Environmental Assessment Report. *Report prepared by for the Australian Pesticides and Vetinary Medicines Authority by the Australian Government Department of Sustainability, Environment, Water, Population and Communities.* Accessed online 10 November 2012 at www.apvma,gov.au/.

Arnott, G. H., S.D., C., G.W., B. & D.J., R. 2000. Victorian Shellfish Quality Assurance Program 8. Sanitary Survey of Flinders Bight Shellfish Growing Area. *In:* FISHERIES, D. O. (ed.). Melbourne.

Batley, G. & Simpson, S. 2008. Advancing Australia's Sediment Quality Guidelines. *Australasian Journal of Ecotoxicology,* 14**,** 11-20.

Blumer, M. & Sass, J. 1972. The West Falmouth oil spill. II. Chemistry. *Technical Report 72-19.* Woods Hole Oceanographic Institution.

Boening, D. W. 2000. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere,* 40**,** 1335-51.

Burns, K. & Smith, J. 1977. Distribution of Petroleum Hydrocarbons in Westernport Bay (Australia): Results of Chronic Low Level Inputs. *In:* WOLFE, D. A. (ed.) *Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems.*: Pergammon Press

Burns, K. A. & Smith, J. L. 1982. Hydrocarbons in Victorian coastal ecosystems (Australia): chronic petroleum inputs to Western Port and Port Phillip Bays. *Archives Of Environmental Contamination And Toxicology,* 11**,** 129-140.

Clark, E. A. 1988. The fate of tributyltin in the aquatic environment. *Environmental science & technology,* 22**,** 600.

Clark, E. A., Sterritt, R. M. & Lester, J. N. 1988. The fate of tributyltin in the aquatic environment. *Environmental Science & Technology,* 22**,** 600-604.

Coleman, R. & Pettigrove, V. 2001. Waterway assessment in the Western Port Catchment: The health of the Lang Lang River. Waterways Group, Melbourne Water Corporation.

Coulter, B. 2011. LS 13 320 Laser Diffraction Particle Size Analyzer: Instructions for use.

Daly, H. & Fabris, G. J. 1993. An environmental study of tributyltin in Victorian waters. *Publication #SRS 90/020.* EPA Victoria.

EPA Victoria 2001. Policy impact assessment Protecting the waters of Western Port and catchment. State Environment Protection Policy (Waters of Victoria) – Schedule F8 Western Port and catchment. *Publication 797.*

EPA Victoria 2011. Port Phillip and Western Port receiving water quality modelling: Lagrangian dispersal.

EPA Victoria & Melbourne Water 2009. Better Bays and Waterways: A Water Quality Improvement Plan for Port Phillip Bay and Western Port. . Melbourne, Australia.

Eshel, G., Levy, G. J., Mingelgrin, U. & Singer, M. J. 2004. Critical Evaluation of the Use of Laser Diffraction for Particle-Size Distribution Analysis. *Soil Sci. Soc. Am. J.,* 68**,** 736-743.

Fabris, G. J. & Longmore, A. R. 2005. An examination of key metals and their speciation and potential ecosystem risk to Victorian bays, inlets and estuaries in relation to the new ANZECC guidelines: arsenic. . Report to the Environment Protection Authority, Victoria.

Fabris, G. J., Monahan, C. A. & Batley, G. E. 1999. Heavy metals in waters and sediments of Port Phillip Bay, Australia. *Marine and Freshwater Research,* 50**,** 503-513.

Fisher, P. M. J. & Scott, R. 2008. Evaluating and controlling pharmaceutical emissions from dairy farms: a critical first step in developing a preventative management approach. . *Journal of Cleaner Production,* 16**,** 1437-1446.

Foulsham, G., Nice, H., Fisher, S., Mueller, J., Bartkow, M. & Komorova, T. 2009. A baseline study of organic contaminants in the Swan and Canning catchment drainage system using passive sampling devices. *Water Science Technical Series Report No. 5. .* Department of Water, Western Australia.

Gibbs, P. E., Pascoe, P. L. & Bryan, G. W. 1991. Tributyltin-induced imposex in stenoglossan gastropods: Pathological effects on the female reproductive system. *Comparative Biochemistry and Physiology Part C: Comparative Pharmacology,* 100**,** 231-235.

Glémarec, M. & Hussenot, E. 1982. A three-year ecological survey in benoit and wrac'h abers following the Amoco Cadiz oil spill. *Netherlands Journal of Sea Research,* 16**,** 483-490.

Hancock, G. J., Olley, J. M. & Wallbrink, P. J. 2001. Sediment transport and accumulation in Westernport. . *Technical report 47/01.* CSIRO Land and Water.

Hardwick, R. 1998. Waterway assessment in the Western Port catchment: The environmental health of Western Port Peninsula Streams. *Report prepared for Waterways and Drainage Group, Melbourne Water.*: Australian Water Technologies (AWT) Pty Ltd.

Haynes, D. & Johnson, J. E. 2000. Organochlorine, Heavy Metal and Polyaromatic Hydrocarbon Pollutant Concentrations in the Great Barrier Reef (Australia) Environment: a Review. *Marine Pollution Bulletin,* 41**,** 267-278.

Haynes, D., Muller, J. & Carter, S. 2000a. Pesticide and herbicide residues in sediments and seagrasses from the Great Barrier Reef World Heritage Area and Queensland coast. *Marine Pollution Bulletin,* 41.

Haynes, D., Ralph, P., Prange, J. & Dennison, B. 2000b. The Impact of the Herbicide Diuron on Photosynthesis in Three Species of Tropical Seagrass. *Marine Pollution Bulletin,* 41**,** 288-293.

Hughes, A. O., Prosser, I. P., Wallbrink, P. J. & Stevenson, J. 2003. Suspended Sediment and Bedload Budgets for the Western Port Bay Basin. *Technical Report 4/03, March 2003.* CSIRO Land and Water, Canberra.

IMO, I. M. O. 2001. International Convention on the Control of Harmful Anti-fouling Systems on Ships. Adoption: 5 October 2001.

Jenkins, G. 2011. Fish (Chapter 11). *In:* AL., K. E. (ed.) *Understanding the Western Port environment: a summary of current knowledge and priorities for future research.* Melbourne Water.

Kegley, S. E., Hill, B. R., S., O. & A.H., C. 2011. *PAN Pesticide Database, Pesticide Action Network* [Online]. North America (San Francisco, CA). Available: http://www.pesticideinfo.org [Accessed].

Kellar, C., Hassell, K., Long, S. M., Myers, J., Golding, L., Kumar, A. & Pettigrove, V. 2011. Identifying the primary factors influencing aquatic ecosystem health in the Upper Dandenong Creek Catchment. . Victorian Centre for Aquatic Pollution and Identification Technical Report 6.

Keough, M. J., Bathgate, R., Lee, R., Jenkins, G., KWalker, D., Quinn, G., Wilson, R., Dittmann, S., Ross, J., Boon, P. I. & Dann, P. 2011. *Understanding the Western Port environment: A summary of current knowledge and priorities for future research.*

Kookana, R. S., Baskaran, S. & Naidu, R. 1998. Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. *Soil Research,* 36**,** 715-764.

Lee, R. 2011. Physical and chemical setting (Chapter 4). *In:* AL., K. E. (ed.) *Understanding the Western Port Environment: A summary of current knowledge and priorities for future research.* Melbourne Water, Victoria.

Lewin, K. 1997. Streamwatch toxicant monitoring program: Annual report 1996.

Long, E. R. & MacDonald, D. D. 1998. Recommended Uses of Empirically Derived, Sediment Quality Guidelines for Marine and Estuarine Ecosystems. *Human and Ecological Risk Assessment,* 4**,** 1019-1039.

Macinnis-Ng, C. M. O. & Ralph, P. J. 2003. Short-term response and recovery of Zostera capricorni photosynthesis after herbicide exposure. *Aquatic Botany,* 76**,** 1-15.

Marsden, M. A. H., Mallett, C. W. & Donaldson, A. K. 1979. Geological and physical setting, sediments and environments, Western Port, Victoria. *Marine Geology,* 30**,** 11-46.

McKinlay, R., Plant, J. A., Bell, J. N. B. & Voulvoulis, N. 2008. Endocrine disrupting pesticides: implications for risk assessment. . *Environment International,* 34**,** 168-183.

Meador, J. P. 2000. Predicting the fate and effects of tributyltin in marine systems. *Reviews of Environmental Contamination and Toxicology,* 166**,** 1-48.

Muir, D. C. G. 1988. Organochlorine contaminants in arctic marine food chains: Accumulation of specific polychlorinated biphenyls and chlordane-related compounds. *Environmental science & technology,* 22**,** 1071.

NEPM 1999. Schedule B(3) Guideline on Laboratory Analysis of Potentially Contaminated Soils. *In:* MEASURE, N. E. P. (ed.). Environment Protection and Heritage Council.

NHT 2004. TBT analysis protocol development and current contamination assessment. . National Heritage Trust Department of the Environment and Heritage.

O'Brien, A. L. & Keough, M. J. in review. Understanding benthic community responses to pollution in estuaries. *Submitted to Environmental Pollution.* .

OCE 1998. Victoria's inland waters: State of the environment report. Office of the Commissioner for the Environment.

Pettigrove, V. 2003. Impact of urbanisation on heavy metal contamination in urban stream sediments: influence of catchment geology. *Australasian journal of ecotoxicology,* 9**,** 119.

Pettigrove, V. & Hoffmann, A. 2005. A field-based microcosm method to assess the effects of polluted urban stream sediments on aquatic macroinvertebrates. *Environmental Toxicology and Chemistry,* 24**,** 170-180.

Pitt, R. E. 1995. Biological effects of urban runoff discharge. *Stormwater runoff and receiving systems: impact, monitoring and assessment.*: CRC, Boca Raton.

Radcliffe, J. C. 2002. *Pesticide use in Australia: a review undertaken by the Australian Academy of Technological Sciences and Engineering*.

Rees, C. M., Brady, B. A. & Fabris, G. J. 2001. Incidence of Imposex in Thais orbita from Port Phillip Bay (Victoria, Australia), Following 10 Years of Regulation on Use of TBT. *Marine Pollution Bulletin,* 42**,** 873-878.

Rees, C. M., Fabris, G. J. & Sporcic, M. I. 1998. Toxicants in Western Port Sediments. Marine and Freshwater Resources Institute (MAFRI).

Roberts, D. A., Poore, A. G. B. & Johnston, E. L. 2006. Ecological consequences of copper contamination in macroalgae: Effects on epifauna and associated herbivores. *Environmental Toxicology and Chemistry,* 25**,** 2470-2479.

Sanders, H. L., Grassle, J. F. & Hampson, G. R. 1972. The West Falmouth oil spill I. Biology W.H.O.I. *Technical Report 72-20.*

Schäfer, R. B., Pettigrove, V., Rose, G., Allinson, G., Wightwick, A., von der Ohe, P. C., Shimeta, J., Kühne, R. & Kefford, B. J. 2011. Effects of Pesticides Monitored with Three Sampling Methods in 24 Sites on Macroinvertebrates and Microorganisms. *Environmental Science & Technology,* 45**,** 1665-1672.

Simpson, S. L. 2005. Exposure-effect model for calculating copper effect concentrations in sediments with varying copper binding properties: a synthesis. *Environ Sci Technol,* 39**,** 7089-96.

Simpson, S. L., Batley, G. E. & Chariton, A. A. 2010. Revision of the ANZECC & ARMCANZ sediment quality guidelines. *Prepared for the Department of the Environment, Water, Heritage and the Arts. .* CSIRO Land and Water Science Report 08/07. .

Simpson, S. L., Batley, G. E., Chariton, A. A., Stauber, J. L., King, C. K., Chapman, J. C., Hyne, R. V., Gale, S. A., Roach, A. C. & Maher, W. A. 2005. Handbook for sediment quality assessment. Bangor, NSW.: CSIRO.

Simpson, S. L., Pettigrove, V. & Batley, G. E. 2000. Pore water analyses and toxicity testing of sediments from urban waterways in Melbourne. *Report No. ET/IR306.* Centre for Advanced Analytical Chemistry Energy Technology, CSIRO.: Report Prepared for Melbourne Water, Australia, June 2000.

Simpson, S. L., Yverneau, H., Cremazy, A., Jarolimek, C. V., Price, H. L. & Jolley, D. F. 2012. DGT-Induced Copper Flux Predicts Bioaccumulation and Toxicity to Bivalves in Sediments with Varying Properties. *Environmental Science & Technology,* 46**,** 9038-9046.

Sperazza, M., Moore, J. N. & Hendrix, M. S. 2004. High-Resolution Particle Size Analysis of Naturally Occurring Very Fine-Grained Sediment Through Laser Diffractometry. *Journal of Sedimentary Research,* 74.

Statham, P. J. 1977. *Trace metals in Western Port sediments : final report, December 1977 / by P.J. Statham*, [Melbourne] : Marine Chemistry Unit, Ministry for Conservation, 1977.

Thomas, K. V., Blake, S. J. & Waldock, M. J. 2000. Antifouling Paint Booster Biocide Contamination in UK Marine Sediments. *Marine Pollution Bulletin,* 40**,** 739-745.

Thompson, J., Sheffer, R. C., Pierce, Y. K., Chau, J. J., Cooney, W. R. C. & J., M. R. 1985. Organotin compounds in the aquatic environment: scientific criteria for assessing their effects on environmental quality. . *NRCC 22.* Ottawa, Canada.: National Research Council Canada.

Udden, J. A. 1914. Mechanical composition of some elastic sediments. *Bull. Geol. Soc. Am.,* 25**,** 655-744.

USEPA 2007. Method 8270D: Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). US Environemntal Protection Agency, Washington DC.

USEPA 2010. Environmental Fate and Ecological Risk Assessment for Boscalid: New uses on Alfalfa and Citrus (Group 10). US Environemntal Protection Agency, Washington DC.

Victorian Government 2001. Variation of State Environment protection policy (Waters of Victoria) - Insertion of Schedule F8. Waters if Western Port and Catchment. Victorian Government Gazette.

Volkman, J. K., Holdsworth, D. G., Neill, G. P. & Bavor Jr, H. J. 1992. Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *Science of The Total Environment,* 112**,** 203-219.

Wallbrink, P. J. & Hancock, G. J. 2003. Western Port sediment study: Review of literature and assessment of knowledge gaps. *Technical report 12/03.* CSIRO Land and Water.

Webb, J. A. & Keough, M. J. 2002. Measurement of environmental trace-metal levels with transplanted mussels and diffusive gradients in thin films (DGT): a comparison of techniques. *Marine Pollution Bulletin,* 44**,** 222-229.

Wentworth, C. K. 1922. A Scale of Grade and Class Terms for Clastic Sediments. *The journal of geology,* 30**,** 377.

Woolfe, K. J., Larcombe, P. & Stewart, L. K. 2000. Shelf sediments adjacent to the Herbert River delta, Great Barrier Reef, Australia*. *Australian Journal of Earth Sciences,* 47**,** 301-308.

Appendix 1 – Detailed description of the analytical methods

Sample Container Preparation

Sample containers were prepared in accordance with AS/NZ 5667.1 (1998) and IWRG701 (EPA Victoria, 2009) guidelines. Jars were soaked in analytical grade detergent (Extran MA03) for 24 hours, triple rinsed with deionised water then soaked in 1M nitric acid for 24 hours and triple rinsed with distilled deionised water prior to air drying.

Moisture content

The moisture contents were determined on separate sub-samples of each sediment sample. A gravimetric procedure based on weight loss over a 12 hour drying period at 103-105˚C was used (NEPM 2010, Schedule B(3)).

Particle Size Analysis

Grain size analysis was measured for each sample to compare relative differences in distribution of sediment particles and allow comparisons with previous studies. As previously discussed, hydrophobic chemicals such as metals have affinity of to become more easily bound to the clay silt fraction, such that samples were filtered to < 63 µm. Whole sediment particles size does not constitute the composition of filtered samples that were analysed for other parameters.

Grain size was measured for each site within the bay by laser diffraction particle size analyser (Beckman Coulter LS1332) using The Mie Theory (Coulter, 2011). This method has been shown to give reasonable agreement with grain size classification made using settling tubes (regression coefficients 0.7, 0.69 and 0.82 for clay, silt and sand respectively) (Eshel et al., 2004). Samples were agitated and homogenised prior to analysis using a sonication bath. Samples were then sieved to less than 2.0 mm. Sonication was used for 60 seconds prior to and during the analysis (60 seconds) to disseminate any bound fine particles (Woolfe et al., 2000, Sperazza et al., 2004). The amount of sample required for analysis was dependant on grain size, and for fine silts and clays requires around 5 – 10 g. Sample was added using a clean dry spoon or spatula. Enough sample was added to give achieve suitable obscuration (approximately 10 %). Detector offsets, alignment and background values were checked between each sample. Duplicates were measured every 10 samples and coefficient of variation calculated with relatively good precision ~5 % (Sperazza et al., 2004).

Laser particle size analysis generated 92 points with sediment fractions clay (0.04 – 4 µm), silt (4 – 62.9 µm), and sand (63 - 2,0000 µm) summarised using the Udden-Wentworth grain size scale

(Udden, 1914, Wentworth, 1922).

Total Metals

For total metal digestion, 1.0g of air dry sediment was digested at 95°C with aqua regia (1:3 HNO3:HCl) for two hours or until the volume was sufficiently reduced. The solution was then cooled and Hydrogen Peroxide was added and samples heated and cooled again before being filtered and bulked to volume for analysis (NEPM (1999) Schedule B(3) (Method 202)).

Total acid extractable digests were measured by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), utilising a highly efficient argon plasma to ionize selected elements. Ions are then passed into a high vacuum mass spectrometer, which separates the analytes based on their distinct atomic emission to charge ratios prior to their measurement by a discrete dynode ion detector (APHA 21st ed., 3125).

This is a different procedure than was previously used for the analysis for total arsenic, where Rees et al (1998) measured total arsenic by dry ashing the sediment with magnesium nitrate, dissolving in 6 M HCl, then reducing arsenate to arsenite by treatment with potassium iodide, followed by analysis with hydride generation AAS. This method was not used as the recovery of standard reference material (Canadian Reference Material BCSS-1) for arsenic was statistically different at 5 %, with the confidence interval for the obtained mean being slightly lower than that for the certified mean (Rees et al 1998).

Total Mercury

Total Mercury in sediments was determined following acid digestion. Total Mercury digests were measured by Flow-injection (SnCl2) Cold Vapour generation Atomic Absorption Spectrometry (FIMS-AAS). A bromate/bromide reagent is used to oxidise any organic mercury compounds in the sample. The ionic mercury is reduced online to atomic mercury vapour by SnCl2 which is then purged into a heated quartz cell. Quantification is by comparing absorbance against a calibration curve (APHA 21st ed. 3112 Hg – B; (NEPM, 1999) Schedule B(3)).

Total Petroleum Hydrocarbons

Total Petroleum Hydrocarbons (TPH C10-C36), consisting only the semi-volatile fractions, were measured by analysing a sample extract by Capillary Gas Chromatography/ Flame Ionisation Detector (GC/FID) and quantification is by comparison against an established 5 point calibration curve of n-Alkanet standards (USEPA SW 846 – 8270B; NEPM 1999 B(3) Method 504). Three fractions were measured which have three fractions (C10-C14, C15-C28, and C29-C36). For the extraction, 20g of soil was extracted with 100 ml of 1: 1 Dichloromethane and Acetone and concentrated the whole volume down to final volume of 1 mL using KD (Kuderna-Danish) apparatus and analyzed using Gas Chromatography – Flame Ionisation Detector (GC-FID).

Total Organic Carbon

Total Organic Carbon (TOC) was analysed using a high temperature combustion technique, which utilises the 183 Boat Sampling Module coupled to the DC-190 TOC analyser. Air dried and pulverised sample was reacted with acid to remove inorganic carbonates, then combusted in a LECO furnace in the presence of strong oxidants and catalysts. The evolved (organic) carbon (as CO2) was automatically measured by infra-red detector.

5 to 20 mg of treated sample is placed into the Boat Sampling Module Furnace at 8000C. Here in the combustion zone, all the carbonaceous matter is oxidised to CO2, which is quantified by the infrared detector in the DC-190 TOC analyser.

Volatile organic compounds may be lost during sample drying. Samples that are high in carbon may ‘overload’ the detector with CO2, thus giving erroneous results. To ensure minimal interferences from volatile organic compounds and high carbon, duplicate samples were measured at different weights. Not all carbonates are determined by this procedure, as some of these may require combustion temperatures above 950°C to decompose.

Dilute Acid Extractable Metals

Dilute acid metals (Al, As, Co, Cd, Cu, Fe, Ni, Pb and Zn) were extracted with 0.5 M hydrochloric acid (HCl) as in previous studies (Statham 1977, Rees et al 1998). Sediments were air dried and approximately 3 g of homogenised sediment was weighed into 50 ml polypropelene tubes. Then 40 ml of 0.5 M HCl was added to the samples and then placed on an orbital shaker at 200 orbits per minute for 16 hours. The solution was then transferred to a polypropelene centrifuge tube with a screw cap and centrifuged for 10 minutes at 2000 rpm. The supernatant solution was decanted to a 50 ml centrifuge tube and made to volume with distilled de-ionised water. Duplicate samples, spike recoveries, reagent and rinse blanks were analysed with the samples.

Dilute acid metals were analysed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES AMSRI - ICP Varian 720 es) with the mean concentration from 5 replicate readings and the available wavelengths taken as the sample value.

The standard solutions were prepared in 0.5 M hydrochloric acid. The calibration standards were prepared with concentrations of 0, 0.5, 1.0, 2.5, 10, 25 and 50 µg/mL using ICP-AM-5 standard solution (100 µg/mL in 5% HCl).

All sediment samples were dried at 60°C prior to the extraction with 0.5 M HCl acid extraction and trace metal analysis by ICP-OES. Drying methods were also compared: 3 samples were dried at 103˚C, 3 samples were dried at 60˚C and 3 samples were freeze dried (see comments in the attachment).

Pesticides

Analysis of pesticides in sediments were determined by DPI Victoria, Future Farming Systems Research (Macleod, Ernest Jones Drive, Macleod, Victoria) GC and LC-MS-MS using in-house 10146 methods. Analytes included Organochlorine (OC), organophosphates (OP), synthetic pyrethroids (SP), triazine herbicides, carbamates and selected insecticides and fungicides. This facility complies with the requirements of ISO/IEC 17025:2005 (NATA accredited).

Sediment samples were dried and ground, and then shaken (5g) for 30min with 30 mL of 35% water/acetone (adjusted to pH <3) on a mechanical shaker. After shaking the mixture was then sonicated for 15 min, and then centrifuged at 2800rpm for 5 min. Thereafter, the supernatant liquid was passed through a glass fibre filter and collected in a 250mL flask. The extraction was repeated with 30 mL and the combined filtered extract was concentrated to around 20mL on a rotary evaporator at 30˚C under 95 kPa vacuum. The concentrated extract was transferred into a 250mL measuring cylinder. The rotary evaporator flask was rinsed with 1mL MeOH and added to the concentrated extract along with sufficient Mill-Q water to make the final volume 240mL. The aqueous extract was split into two parts which were subjected to different SPE clean up procedures.

One aliquot (160mL) was passed through a UCT Enviro Clean® Universal Extraction Cartridge 525 to remove interferences before gas chromatography determination. The Enviro Clean® 525 cartridge was conditioned with 10mL each of ethyl acetate: DCM (1:1, v/v) and MeOH before loading the aqueous extract. Compounds of interest were eluted from the cartridge with first 10mL ethyl acetate, then 2x10mL ethyl acetate: DCM (1:1 v/v). The combined eluates were concentrated using a rotary evaporator at 30˚C under 95 kPa vacuum to about 5mL., The extract was dried with anhydrous sodium sulphate, then transferred into a test tube and evaporated to near dryness under N_2. The residue was reconstituted in 0.2mL acetone and 1.8mL hexane. Sulphur was removed using copper granules.

An aliquot (1mL) of the final extract solution was injected on GC-PFPD and GC-NPD for organophosphates (OP) and fungicides. The other half of the extract was subjected to further clean up using a florisil cartridge to separate organochlorines (OC) and synthetic pyrethroid (SP) compounds. The OC and SP analytes were eluted from the florisil cartridge with 3 mL of DCM: hexane : acetornitrile (50:48:2%). The eluate was evaporated to dryness under N_2 and reconstituted in 1 mL hexane. This hexane solution was directly injected into a GC-ECD for SP analysis. A further one to ten dilution of the extract was performed before injection into GC-ECD for OC analysis.

The second aliquot (80mL) was transferred onto a Bond Elut® PPL 500mg/3 mL SPE cartridge for LC-tandem mass spectrometry. The Bond Elut® PPL was pre-conditioned with 5mL MeOH followed by 5mL Mill-Q water. Then the 80 mL aqueous extract was loaded on the cartridge. Target compounds collected on the cartridge were eluted with 5mL acetonitrile. The eluate was evaporated to dryness under a stream of N_2. The residues were dissolved in 1mL MeOH: H_2O (1:1, v/v). The final extract was filtered through a 0.45µm PTFE syringe filter before analysis by LC-tandem mass spectrometry.

Organotins (Tributyltin, Dibutyltin & Monobutyltin)

20g sample was spiked with surrogate and leached in a methanol:acetic acid:Ultra high purity water mix and vacuum filtered. Reagents and solvents were added to the sample and the mixture tumbled. The butyltin compounds were simultaneously derivatised and extracted. The extract was further extracted with petroleum ether. The resultant extracts were then combined and concentrated for analysis. Prepared sample extracts were analysed by GC/MS coupled with high volume injection and quantified against an established calibration curve (USEPA SW 846 - 8270D).

Pore water extraction and analysis

Pore water extractions were done as a trial to assess concentrations of metals in sediment pore waters. Following the sampling of sediments, four sites were chosen and resampled where metal concentrations were of particular concern for more detailed analysis of the bioavailability of metals within pore waters. Measurements of concentrations within pore waters allow for comparison with SEPP (WoV) environmental quality indicators and objectives (freshwater guidelines are specified in ANZEECC & ARMCANZ (2000) water quality guidelines). Redox measurements were taken *in situ* from each sediment sample using a portable multi-probe analyser (TPS WP-84). As surface sediments were all unoxidised (less than +0 mv), all extractions and filtering were done in a nitrogen atmosphere, using a glove box with plastic bench coatings laid on the work surface. Pore water extractions were done using 50 mL sterilised polyethenele test tube containers which were filled with sediments on site. Test tubes were centrifuged at 4500 rpm for 10 minutes (Beckman Model J2-21) at 4˚C. Samples were completely filled leaving no headspace with lids securely fastened.

Water was decanted into acid washed plastic syringes (10 ml, Terumo) and filtered through 0.45 µm membrane filters (33 mm, Millipore). Blank Milli-Q water sample was included as a control in the analysis. Approximately 10 - 20 mL of filtered pore water was extracted into acid washed containers and preserved with nitric acid ($HNO3$) and refrigerated (4˚C) until analysis.

Samples were analysed for total dissolved metals including arsenic, cadmium, chromium, cobalt, iron, lead, manganese, nickel and zinc using inductively coupled plasma mass spectrometry (ICP-MS) for freshwater sites and by Octopole Reaction Cell (ORC) coupled to ICP-MS. Samples are 0.45 um filtered prior to analysis. The ORC-ICPMS technique removes interfering species through a series of chemical reactions prior to ion detection. Ions are passed into a high vacuum mass spectrometer, which separates the analytes based on their distinct mass to charge ratios prior to measurement by a discrete dynode ion detector (NEPM (1999) Schedule B(3) (Appendix 2), APHA 21st ed., 3125; USEPA SW846 – 6020).

Appendix 2 - Chemical names and respective Limits of Reporting (LOR) of pesticides analysed in sediment samples from this study. Units are µg/kg.

Organochlorines (OC)	
HCB	3
Lindane	3
Aldrin	4
Heptachlor epoxide	2
p,p'-DDE	3
p,p'-DDD	5
p,p'-DDT	5
Dieldrin	4
BHC-alpha	3
BHC-beta	5
BHC-delta	2
Heptachlor	4
Oxychlordane	4
trans-Chlordane	4
cis-Chlordane	4
Endrin	4
Endosulfan-alpha	5
Endosulfan-beta	5
Endosulfan sulfate	7

Organophosphates (OP)	
Dichlorvos	5
Parathion ethyl	4
Parathion methyl	3
Chlorpyrifos	4
Chlorpyrifos methyl	4
Ethion	2
Fenchlorphos	12
Fenitrothion	3
Fenthion	3
Malathion	4
Prothiofos	4

NPD	
Bupirimate	50
Buprofezin	50
Chlorothalonil	500
Iprodione	150
Procymidone	150

Fipronil & metabolites	
Fipronil	2
Fipronil sulfide	2
Fipronil sulfone	2
Fipronil desulfinyl	2

Synthetic Pyreithroids (SP)	
Bifenthrin	5
Cyfluthrin	4
Cyhalothrin	5
Cypermethrin	5
Deltamethrin	4
Esfenvalerate	4
Fenvalerate	4
Permethrin	20

LC-MSMS	
Omethoate	5
Methomyl	2
Imidacloprid	5
Trichlorfon	5
Dimethoate	2
Mevinphos	2
Oxadixyl	1
Carbaryl	2
Pirimicarb	1
Metalaxyl	1
Methidathion	3
Azinphos Methyl	3
Azoxystrobin	1
Pyrimethanil	3
Dimethomorph	4
Methiocarb	2
Boscalid	3
Triadimefon	2
Myclobutanil	2

LC-MSMS (cont.)	
Cyproconazole	5
Azinphos Ethyl	5
Triadimenol	2
Fenarimol	5
Tetraconazole	2
Fenamiphos	5
Tebufenozide	1
Fenoxycarb	1
Cyprodinil	5
Penconazole	2
Diazinon	2
Tebuconazole	4
Propiconazole	4
Pyraclostrobin	1
Difenoconazole	2
Trifloxystrobin	1
Indoxacarb	2
Propargite	4

Triazines	
Desisopropylatrazine	5
Desethylatrazine	5
Metribuzin	5
Simazine	5
Hexazinone	5
Cyanazine	5
Propachlor	10
Atrazine	5
Diuron	20
Propazine	10
Terbuthylazine	10
Metolachlor	10
Prometryn	5
Terbutryn	5
Linuron	2
Pendimethalin	10

Appendix 3 - Chemical names and respective Limits of Reporting (LOR) of grain size, metals, hydrocarbons, total organic content and pesticides in sediment and metals in water samples from this study.

Parameter	Units & MDL		%CV
Particle size analysis	0.4 – 2,000 µm		4.3 %
	63.0 – 2,000 µm		10.9 %
	4.0 – 62.9 µm		3.8 %
	0.4 – 3.9 µm		3.9 %
Total heavy metals	mg/kg		
Aluminium	Al	50	3.6%
Arsenic	As	5	2.5%
Cadmium	Cd	1	n/a
Chromium	Cr	2	3.1%
Copper	Cu	5	4.6%
Iron	Fe	5	2.3%
Lead	Pb	5	2.7%
Manganese	Mn	5	3.9%
Nickel	Ni	2	4.2%
Zinc	Zn	5	2.5%
Dilute acid metals	mg/kg		
Aluminium	Al	2	26 %
Arsenic	As	0.5	26 %
Cadmium	Cd	0.01	21 %
Chromium	Cr	0.1	28 %
Copper	Cu	0.1	22 %
Iron	Fe	2	25 %
Lead	Mn	0.1	21 %
Manganese	Ni	0.2	26 %
Nickel	Pb	0.3	20 %
Zinc	Zn	0.3	19 %

Total mercury	Hg 0.01	23.6%
Total petroleum hydrocarbons (TPH) C10 – C14 C15 – C28 C29 – C36	**mg/kg** C10 -14 3 C15-28 5 C29-36 5	 18.0 % 8.3 % 9.1 %
Total Organic Carbon (TOC)	% TOC 0.1	3.4%
Pesticides and Herbicides Organochlorine pesticides Organophosphate pesticides Synthetic Pyrethroids NPD Triazine herbicides Fipronil & metabolites LC-MSMS screen	µg/kg OCs 2 - 7 OPs 2 - 12 SPs 4 - 20 NPD 50 - 500 Triazines 2 - 20 Fipronil 2 LC-MSMS 1 - 5	Various – see Quality Control
Organotins Tributyltin Dibutyltin Monobutyltin	µg Sn/kg TBT <0.5 DBT <1 MBT <1	 13% 26% -
Pore water Aluminium, arsenic, cadmium, chromium, cobalt, copper, lead, nickel and zinc	Various	Various

Appendix 4 - Concentration of total metals (mg/kg), total petroleum hydrocarbons (TPH; mg/kg) and total organic content (TOC%) in filtered sediments from Western Port bay, estuaries and freshwater rivers. *TPH Proposed threshold (Simpson et al. 2010).

Site	Al	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Zn	TPH*	TOC
ISQG-L	-	20	1	80	65	-	50	-	0.15	21	200	275	-
ISQG-H	-	70	10	370	270	-	220	-	1	50	410	960	-
CR1	15950	21.0	<1	29.0	8.5	20300	12.0	122	0.01	12.0	25.0	40	1.65
CR2	14550	15.5	<1	24.5	10.5	17600	12.0	76	0.02	10.5	24.0	-	1.42
CR3	16100	19.0	<1	28.0	8.5	20050	13.0	64	0.02	10.5	24.0	-	1.54
CR4	14800	16.5	<1	24.0	8.0	17500	11.0	90	0.01	9.0	20.0	-	1.31
CR6	14800	12.5	<1	21.5	8.0	18900	10.0	75.5	0.02	8.5	19.5	16	1.70
LN2	14600	25.0	<1	37.0	9.5	19900	11.0	56	0.01	15.0	34.5	-	2.48
LN3	18650	19.0	<1	37.0	11.0	23300	14.0	36	<0.01	13.0	38.5	37	3.33
LN4	21900	30.0	<1	45.5	11.5	20800	14.5	42	<0.01	16.5	33.5	-	3.04
LN6	15200	21.0	<1	40.5	9.5	20350	11.5	62	0.01	19.0	29.0	-	2.25
LN7	16450	24.0	<1	37.0	8.0	19250	11.5	57	0.02	15.5	27.5	-	2.27
LN9	17400	26.0	<1	42.7	9.0	24867	14.7	50	0.16	16.0	40.3	21	2.80
RY1	12600	9.3	<1	17.3	13.0	21800	13.7	198	0.04	9.0	38.0	54	1.67
RY2	16550	23.5	<1	31.0	8.0	21000	11.5	78	0.01	12.5	25.0	-	1.77
RY3	12300	15.0	<1	20.0	10.5	16600	8.5	61	0.02	11.0	29.0	-	2.36
RY4	11650	13.5	<1	22.5	8.5	16700	8.5	64	0.02	11.5	25.5	-	1.63
RY5	15100	22.0	<1	32.0	9.5	21200	12.0	59	0.01	13.0	24.0	47	1.62
UN1	16900	18.0	<1	22.5	8.5	18950	10	62	0.02	9.5	17.0	-	2.82
UN3	23400	20.0	<1	34.0	10.0	20300	14.0	136	<0.01	13.0	28.0	-	2.04
UN4	21600	24.0	<1	39.5	10.0	20950	14.0	50	0.01	15.0	28.5	-	2.29
UN5	16150	24.5	<1	29.5	7.5	19650	11.0	63	0.02	11.0	22.0	-	2.28
UN6	17900	28.0	<1	35.0	14.0	23800	16.0	66	0.02	13.5	36.0	-	2.74
UN8	16550	20.0	<1	28.0	10.0	18600	14.0	58	0.02	12.0	28.5	133	2.12
UN9	32450	21.5	<1	24.5	16.5	41650	14.0	35	0.02	33.0	55.0	-	4.50
UN10	11370	18.0	<1	23.0	7.5	14705	9.5	32	<0.01	9.0	16.5	59	2.62
UN11	16650	14.0	<1	22.0	8.0	19200	10.5	65	0.02	8.5	21.5	39	1.70
UN13	16550	11.5	<1	24.5	14.0	23000	18.0	287	0.04	11.0	31.0	76	1.98
UN15	19533	<5.0	<1	32.7	26.0	25233	22.0	147	<0.01	13.7	106.0	49	2.21
UN16	14600	<5.0	<1	23.0	21.0	20700	17.3	374	0.05	12.7	60.7	-	2.10
UN17	27200	26.0	<1	41.0	13.0	26200	17.5	153	0.06	15.5	34.5	33	2.36
UN18	20867	11.0	<1	31.3	9.7	22800	16.7	161	0.02	12.0	37.7	29	2.47
UN20	13700	23.0	<1	30.0	8.0	18000	12.0	53.0	<0.01	12.0	25.0	81	-
UN22	23300	23.5	<1	40.0	9.5	19450	12.0	67	<0.01	15.5	25.5	-	-
UN24	16900	29.5	<1	34.5	9.0	21800	13.5	64	0.01	13.0	26.0	-	2.56
UN25	13800	16.5	<1	20.5	11.5	21900	13.5	655	0.03	9.0	46.5	-	2.14
UN26	29850	25.5	<1	50.0	21.5	33750	24.5	93	0.01	21.0	51.5	-	2.63
UN27	24000	30.0	<1	45.0	11.5	21900	14.0	62	<0.01	17.0	31.5	-	2.75
UN28	26750	26.0	<1	45.5	11.5	23600	16.0	68	0.01	16.5	32.5	-	2.30
UN29	24650	22.0	<1	37.0	11.0	23300	16.5	122	0.01	14.0	31.5	-	2.19
UN30	22800	22.0	<1	35.0	11.0	21000	15.0	145	<0.01	13.0	28.0	-	2.15
UN31	24550	23.5	<1	37.5	11.5	22150	16.0	92	<0.01	14.0	30.5	-	2.14
UN32	23700	21.0	<1	36.5	10.0	21000	15.0	115	0.17	14.0	28.5	-	2.02
WS2	15900	5.0	<1	54.0	19.0	30500	10.0	141	0.02	30.0	57.0	-	5.35

Appendix 5 -Concentration of dilute acid extractable metals (mg/kg) in filtered sediments from Western Port bay, estuaries and freshwater rivers.

Site	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CR1	641.83	0.97	0.04	1.56	0.31	1050.64	16.8	1.17	2.5	2.1
CR2	585.6	0.76	0.04	1.26	0.6	920.96	14.62	1.07	2.3	1.81
CR3	612.89	0.89	0.04	1.36	0.27	1057.45	9.17	1.08	2.58	1.96
CR4	457	0.8	0.03	1.02	0.28	904.38	12.64	0.76	1.9	1.46
CR6	225.54	0.4	0.02	0.65	0.39	648.14	10.1	0.64	1.45	1.64
LN2	696.67	1.75	0.05	2.31	0.94	1393.42	9.35	1.7	2.82	5.71
LN3	790.53	1.58	0.05	1.57	1.08	1457.46	6.25	0.98	3.22	4.93
LN4	683.81	1.88	0.06	1.93	0.9	1320.45	4.67	1.23	3.2	4.04
LN6	569.14	1.11	0.04	1.88	0.52	985.72	6.24	1.46	2.22	3.19
LN7	546.3	1.13	0.04	1.57	0.31	977.07	6.07	1.15	2.14	2.6
LN9	745.37	1.59	0.06	2.23	0.95	1611.07	7.16	1.39	3.63	6.55
RY1	580.19	0.6	0.05	0.56	1.33	1327.39	25.37	0.82	2.73	4.16
RY2	492.54	0.8	0.03	1.27	0.25	912.91	8.19	0.89	2.05	1.83
RY3	836.8	1.61	0.05	1.59	1.2	1239.2	8.52	1.58	2.55	3.95
RY4	463.91	0.73	0.03	1.11	0.31	587.62	5.05	0.98	1.59	2.11
RY5	434.77	0.64	0.03	1.2	0.23	837.38	4.97	0.78	1.8	1.54
UN1	367.35	0.99	0.02	0.85	0.54	1024.26	8.84	1.24	2.04	1.76
UN4	629.34	1.02	0.04	1.43	0.6	1117.65	13.26	1.1	2.88	2.73
UN5	675.03	1.27	0.04	1.74	0.52	1196.14	9.6	1.3	2.84	2.64
UN6	586.29	1.39	0.05	1.53	0.78	1281.57	8.19	1.11	3.38	4.28
UN8	739.97	1.56	0.05	1.55	0.79	1284.02	11.56	1.4	3.72	4.11
UN9	775.31	2.11	0.1	0.63	0.85	1555.15	4.79	3.56	4.26	8.1
UN10	645.23	1.53	0.05	1.6	0.58	1124.98	5.01	1.43	2.87	2.45
UN11	333.13	0.56	0.02	0.75	0.43	914.51	9.12	0.86	2	2.19
UN13	616.9	1.27	0.09	0.98	1.63	1782.37	62.14	1.66	3.89	4.76
UN15	839.01	0.71	0.1	0.96	3.97	1835.11	29.94	1.52	4.79	23.14
UN16	692.61	0.56	0.07	0.66	2.82	1797.67	81.84	1.58	3.78	12.19
UN17	744.87	1.48	0.08	1.59	1.19	1864.62	32.13	1.53	4.02	3.97
UN18	711.75	0.93	0.08	0.83	1.13	2095.55	94.01	1.26	4.06	11.51
UN20	-	-	-	-	-	-	-	-	-	-
UN22	561.59	1.39	0.04	1.43	0.53	1087.03	8.68	1.16	2.54	2.27
UN24	740.23	1.75	0.05	2.02	0.72	1475.67	12.49	1.49	3.41	3.22
UN25	480.32	1.21	0.08	0.79	1.3	1556.75	129.76	1.11	2.93	7.03
UN26	717.84	1.59	0.08	1.31	2.35	1664.64	14.45	1.56	5.12	7.66
UN27	639.89	1.82	0.05	1.78	0.43	1341.8	8.79	1.29	3.08	3.16
UN28	567.76	1.1	0.03	1.32	0.38	925.64	9.76	0.96	2.75	2.65
UN29	605.3	0.97	0.06	1.19	0.8	1365.62	19.56	1.12	3.27	3
UN3	626.67	0.91	0.03	1.57	0.46	934.36	4.26	1.12	2.58	2.58
UN30	650.64	1.21	0.05	1.38	0.77	1393.59	28.48	1.21	3.34	2.9
UN31	513.57	1.02	0.05	1.04	0.67	1129.21	12.37	0.89	2.79	2.54
UN32	432.59	0.91	0.05	0.9	0.49	1005.75	16.19	0.8	2.44	2.14
WS2	561.48	0.35	0.08	1.19	0.24	1470.99	23.96	1.29	2.27	8.29

Appendix 6 - Sediment particle size composition of the whole homogenised fraction from the study sites within Western Port.

Site Code	Area	Clay%	Silt%	Sand%	<63%
CR1	CR	12.1	42.2	45.7	54.3
CR2	CR	21.0	48.0	31.1	68.9
CR3	CR	17.8	56.1	26.2	73.8
CR4	CR	3.3	8.7	88.1	11.9
CR6	CR	1.2	3.9	94.9	5.1
LN2	LN	4.5	22.3	73.1	26.9
LN3	ES	7.6	35.1	57.3	42.7
LN4	ES	9.9	50.0	40.2	59.8
LN6	LN	6.4	45.7	47.9	52.1
LN7	LN	3.8	14.7	81.5	18.6
LN9	ES	12.3	65.9	21.9	78.1
RY1	ES	9.1	35.7	55.2	44.8
RY2	RY	14.8	64.0	21.2	78.8
RY3	RY	0.9	3.4	95.7	4.3
RY4	RY	6.8	41.0	52.2	47.8
RY5	RY	10.9	46.3	42.8	57.2
UN1	UN	7.5	36.2	56.3	43.7
UN3	UN	-	-	-	-
UN4	UN	7.6	28.7	63.7	36.3
UN5	UN	3.1	14.1	82.8	17.2
UN6	ES	5.4	17.2	77.4	22.7
UN8	ES	5.0	17.3	77.7	22.3
UN9	ES	7.0	68.0	25.1	75.0
UN10	UN	9.8	57.8	32.5	67.6
UN11	UN	17.1	58.1	24.9	75.2
UN13	FW	16.7	60.4	23.0	77.1
UN15	FW	9.3	51.0	39.7	60.3
UN16	FW	6.3	46.1	47.6	52.4
UN17	ES	15.9	68.9	15.2	84.8
UN18	ES	11.9	59.5	28.7	71.3
UN20	UN	12	52.8	35.2	64.8
UN22	UN	2.3	11.0	86.7	13.3
UN24	UN	6.3	33.3	60.5	39.6
UN25	FW	11.3	56.7	32.0	68.0
UN26	ES	8.6	30.0	61.4	38.6
UN27	UN	5.5	31.0	63.6	36.5
UN28	ES	9.3	24.5	66.2	33.8
UN29	ES	22.6	63.6	13.9	86.2
UN30	ES	13.6	49.0	37.5	62.6
UN31	ES	17.5	68.8	13.8	86.3
UN32	ES	11.1	42.0	46.9	53.1
WS2	ES	5.0	53.6	41.5	58.6