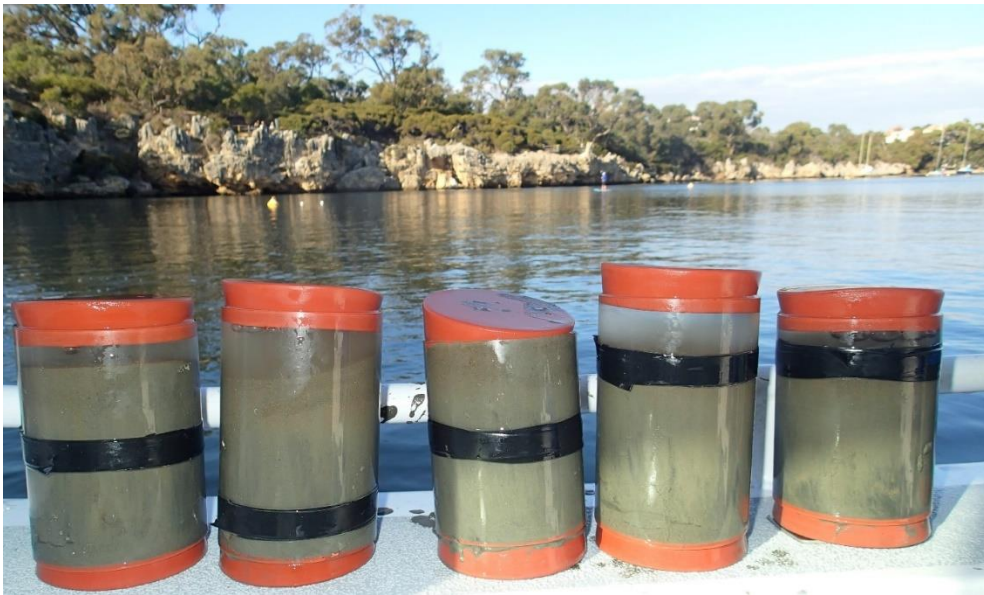




**Biodiversity and
Conservation Science**

An assessment of contaminants in the sediments of the Swan Canning Estuary



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Rivers and Estuaries Science Program

November 2022



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Summary

This report provides a snapshot of sediment contamination in the Swan Canning Estuary eight years after the initial baseline survey was completed by the Department of Water and Environmental Regulation (previously Department of Water) in 2007, as part of the Swan River Trust's Non-Nutrient Contaminant program. In doing so, this study fulfills a recommendation of the earlier work to undertake ongoing sampling of sediments in the estuary to monitor any significant changes in sediment contamination.

To facilitate a comparison of sediment contamination between the two studies, the current study replicated the sampling methods of the baseline survey by sampling surficial (top 3 cm) sediments at the same 20 sites throughout the estuary. It expanded on the baseline by sampling deeper in the sediment profile (3-10 cm depth) to determine if contaminant concentrations varied with depth, and also added polychlorinated biphenyls (PCBs) and glyphosate to the analyte suite. The addition of the PCBs to the suite constitutes the first comprehensive study of PCBs within sediments of the estuary and will greatly contribute to our understanding of the distribution of this contaminant group within the system.

At an estuary wide scale, the contamination status of the Swan Canning Estuary hasn't changed markedly since the baseline study was conducted in 2007 (Nice 2009). Concentrations of contaminants remained highest in the Middle Swan Estuary between sites 9-12 and there was little change in the contaminant concentrations in this region between the two studies. Contaminant concentrations in sediments have generally remained low since the baseline survey, however there were exceedances of ANZG values for five contaminants, the metals zinc, copper and lead, the organochlorine pesticide DDE, and PCBs. Across the estuary, the number of contaminants that exceeded the ANZG values decreased since the baseline survey as mercury was not detected in the estuary in current study, however overall, the number of exceedances increased marginally with additional exceedances of the ANZG high guideline for zinc. Exceedances of the ANZG values were generally observed in the Middle Swan Estuary, Canning Estuary and Lower Canning River. The addition of polychlorinated biphenyls into the suite of analytes revealed concentrations of Aroclor 2054 at the CBD site exceeded the ANZG default value.

The analysis of subsurface sediments showed inconsistent patterns in the distribution of contaminants compared with surficial sediments. This result suggests surficial sediment sampling is not adequate to characterise sediments and that prior to any future sediment disturbance works, baseline sampling should investigate sediments at depth. The characterisation of the sites in a method consistent with Nice 2009, should continue to facilitate appropriate management decisions based on sufficient and contemporary data that allows for the changes in sediment condition to be monitored over time.

1 Introduction

1.1 Contaminants in estuarine environments

Urban estuaries, situated within major metropolitan regions, are exposed to run off from industrial, commercial and residential land uses that often contain a range of anthropogenic compounds, some of which can be harmful to aquatic life. These contaminants include, among others, heavy metals, pesticides, hydrocarbons (including petroleum hydrocarbons and polycyclic aromatic hydrocarbons) and polychlorinated biphenyls (PCBs). Once released to the aquatic environment, a portion of these substances, bind to sediment particles and organic matter. These substances may accumulate in sediments over time may, depending on land uses, water and sediment type and quality, accumulate in the sediment at concentrations that may cause toxic effects in aquatic life and impact ecological processes within the estuary.

Harmful effects to aquatic life may occur when organisms burrow into the sediment, ingest sediment, and when sediment is disturbed and suspended in the water column. Many species of aquatic biota have an ability to regulate the concentration of various contaminants in their body tissues. In particular, many metals are essential elements of biochemical processes within certain species, for instance, copper is a major component of hemocyanin, the oxygen carrying component of crustacean blood (Rainbow 2002). Aquatic species however lack the ability to regulate, to the same extent, non-essential metals, such as lead and mercury. Toxic effects will generally manifest when concentration exceed the species ability to regulate the metals within its body (Rainbow 2002). The toxic effects from exposure to high concentrations of heavy metals may differ depending on the metal, but generally will result in damage to the gills (reducing the surface area for gas exchange), growth and osmoregulatory disturbance (e.g. Grosell et al. 2007). Additionally, a number of metals, such as mercury, can biomagnify through aquatic food webs, placing higher order consumers, including humans, at risk of toxic effects (e.g. Bisi et al. 2012).

The accumulation of organic contaminants, such as organochlorine pesticides (OCP) and PCBs, within the environment poses potential risk to biota and human consumers. In recognition of their environmental persistence and bio accumulative properties, their use has been heavily restricted or banned under the Stockholm Convention, an international agreement of which Australia is a signatory. These compounds bind to lipids in biota, they biomagnify within the food web and can result in endocrine disrupting effects. Despite the ban, import restrictions on PCBs since 1975 and restrictions on the use of OCPs since the 1980s and their eventual phase out by 1997, they have been shown to continue to persist in the environment. Past studies on contaminants in the Swan Canning Estuary have detected these substances (OCPs – Nice (2009), PCBs – Nice (2013) at multiple sites throughout the estuary indicating legacy effects remain.

Given both legacy and contemporary contaminant issues in many urban estuaries, and the ongoing addition of novel substances, there remains potential for

environmental harm. Thus, there is a strong need to understand the concentration and types of contaminants within the sediments of urban estuaries, such as the Swan Canning Estuary, to determine potential sources and inform appropriate control measures for development within such systems, which may result in the disturbance of estuarine sediments.

1.2 Background

Previous investigations into the presence of anthropogenic contaminants in the Swan Canning Estuary have identified a range of metal and organic compounds of potential concern in the sediments of the estuary and its tributaries. These contaminants are likely the result of historic and present day industrial, agricultural and urban activities and are typically conveyed to the estuary through drains, tributaries or groundwater (Nice et al. 2009). Additionally, some of these contaminants have accumulated in regions of the estuary to the extent that sediments are toxic to a range of aquatic organisms (Nice 2011, Nice and Fisher 2011).

Recent investigations into contaminant concentrations in black bream (Hoeksema 2015) and western school prawns (manuscript in development) in the Swan Canning Estuary determined that a number of metal and organic contaminants, including PCBs, are present at low levels within these two important recreational fishing species. It should be noted however, that these trace levels of contaminants did not restrict consumption of these species by recreational fishers.

The current investigation has replicated and expanded the methods used in Nice (2009) to ensure that ongoing management of contaminant issues in the estuary is based on current and appropriate information. It also informs the management of sediment disturbance by development activities within the estuary by addressing the current knowledge gap of sub-surface sediment contamination and provides the first detailed assessment of PCBs in sediments throughout the Swan Canning Estuary.

1.3 Aims

The main aims of this study were to:

- Examine metal and organic contaminants in surface and subsurface sediments at 20 sites throughout the Swan Canning Estuary.
- Compare current surface sediment data with baseline data collected in the 2007 investigation *A baseline study of contaminants in the sediments of the Swan and Canning estuaries* (Nice, 2009).
- Examine PCBs (both Aroclor mixtures and PCB congeners) in surface and subsurface sediments at 30 sites throughout the Swan Canning Estuary, with a particular focus on the historic industrialised area in the Middle Swan Estuary.
- Revise, if required, the characterisation of sites established by Nice (2009).

2 Methods

This study sought to assess contaminant concentrations in sediments throughout the estuary focusing on the 20 sites sampled in 2007 and presented in Nice (2009) (Figure 1). Ten additional sites were included to examine PCB concentrations, that focused around the historic industrialised East Perth area in the Middle Swan Estuary (Figure 2). Site details including site number, name, co-ordinates and estuary ecological management zone are included in Table 1. Samples were collected from the 26-29 May 2015. The 2015 study modified the Nice (2009) experimental design slightly so that at each site, five samples were collected by diver: four replicate samples for chemical analysis and one sample for particle size distribution. Each sample was a composite of five cores collected from each corner and the centre of a 1 m x 1 m quadrat (Nice 2009). Replicate sample at a site were taken from within a single 10 m x 10 m area. To determine if there was any change in the contaminant concentrations through the sediment profile, samples were collected at two depths within each core (surface sample- 0-3 cm depth and bottom sample- 3-10 cm depth).

Sampling at each site was completed by inserting a pre-washed (washed with Decon 90™, rinsed with site water, then methanol and finally distilled water) 9.5 cm internal diameter transparent Perspex core into the sediment to a depth of at least 12 cm depth or until refusal. A rubber bung was pushed into the top of the core to create suction pressure. The core was then slowly removed from the sediment and a second rubber bung inserted to the bottom of the core. Once at the surface, the top 3 cm of the core was removed using a plastic spoon and placed into a clean glass jar (with PTFE lid). Sediment was then removed to a core depth of 10 cm (3-10 cm) and placed into a separate glass jar. Each of the five composite cores for each replicate sample were placed in the same sample jar and stored on ice in an esky. Samples were transported to the laboratory on the day of collection, where they were homogenised prior to analysis. Sediment samples were sent to two NATA accredited laboratories for analysis, one provided chemical analysis and the other sediment particle size distribution.

At each site water column redox potential, dissolved oxygen, pH and temperature were measured using a YSI ProDSS multiple probe 20 cm from the sediment surface, and sediment redox potential was measured using a TPS ORP probe.

2.1 Analyte selection

The analytes selected for investigation in this study were based on those used in Nice (2009). Details of the suite of analytes, limit of reporting and analytical method applied by the laboratory are contained in Table 2. In addition, PCBs and glyphosate were added to the suite. PCBs were not analysed by Nice (2009) due to the lack of appropriate laboratory limits of reporting. The number of sites analysed for the PCB suite was increased to focus on the now remediated historical industrialised area in the Middle Swan Estuary. Glyphosate has become a contaminant of emerging interest and questions remain as to its environmental persistence, thus it was also

added to the analyte list. The study explored glyphosate prevalence in surface sediments at 10 sites throughout the estuary. This constituted a pilot study to test its potential distribution throughout the estuary sediment and build the capacity of the analytical laboratory. A single sample was analysed for glyphosate at each of the 10 sites. At the time of sampling per- and poly-fluoro alkyl substances (PFAS) had not been identified as a contaminant of concern and therefore was not included in the analytical suite.

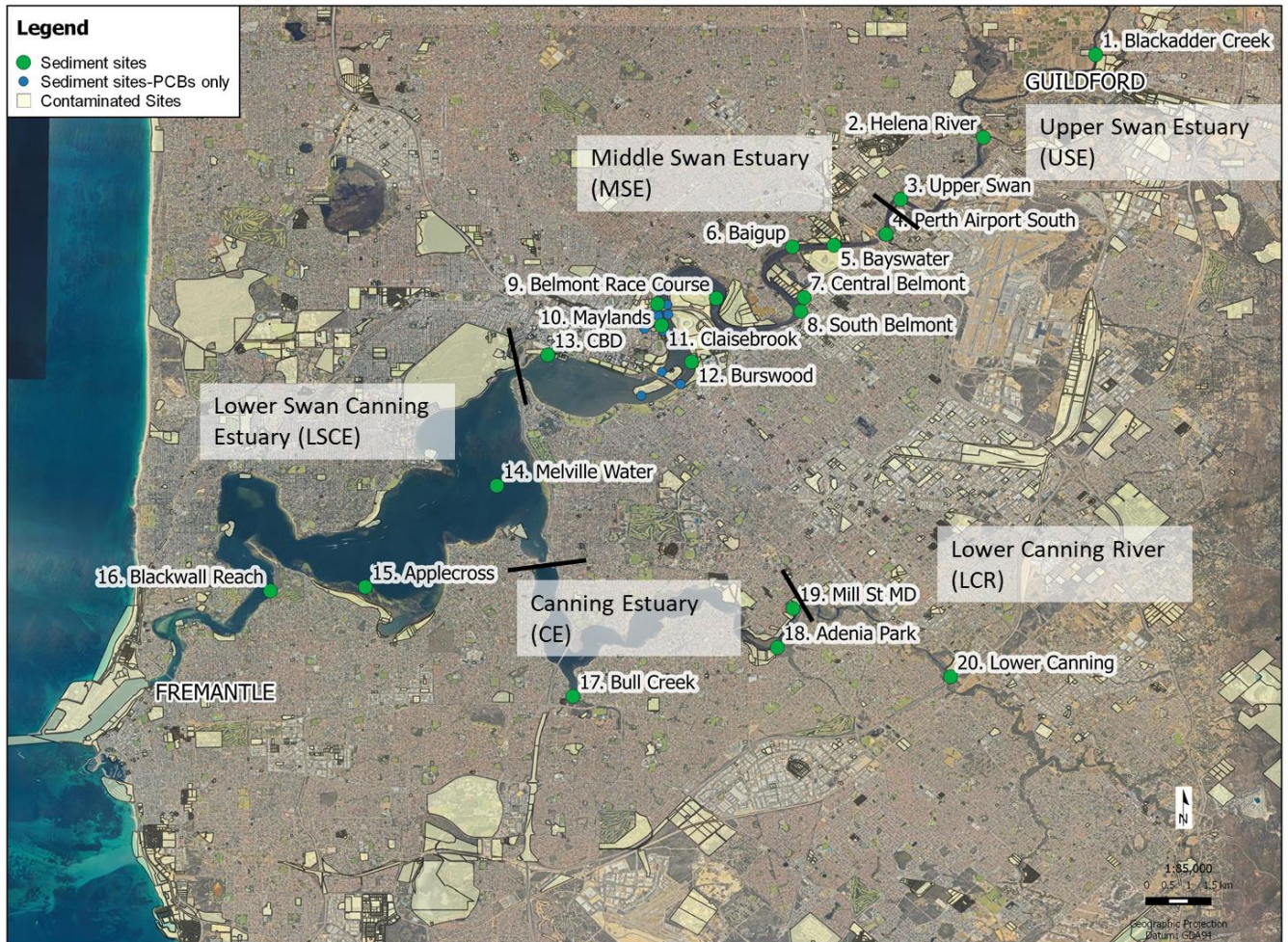


Figure 1. Map of study area showing sites sampled and ecological management zones. The 20 sites consistent with Nice (2009) are highlighted as large green icons and labeled. Current registered contaminated sites are shown on the figure as light shaded areas.

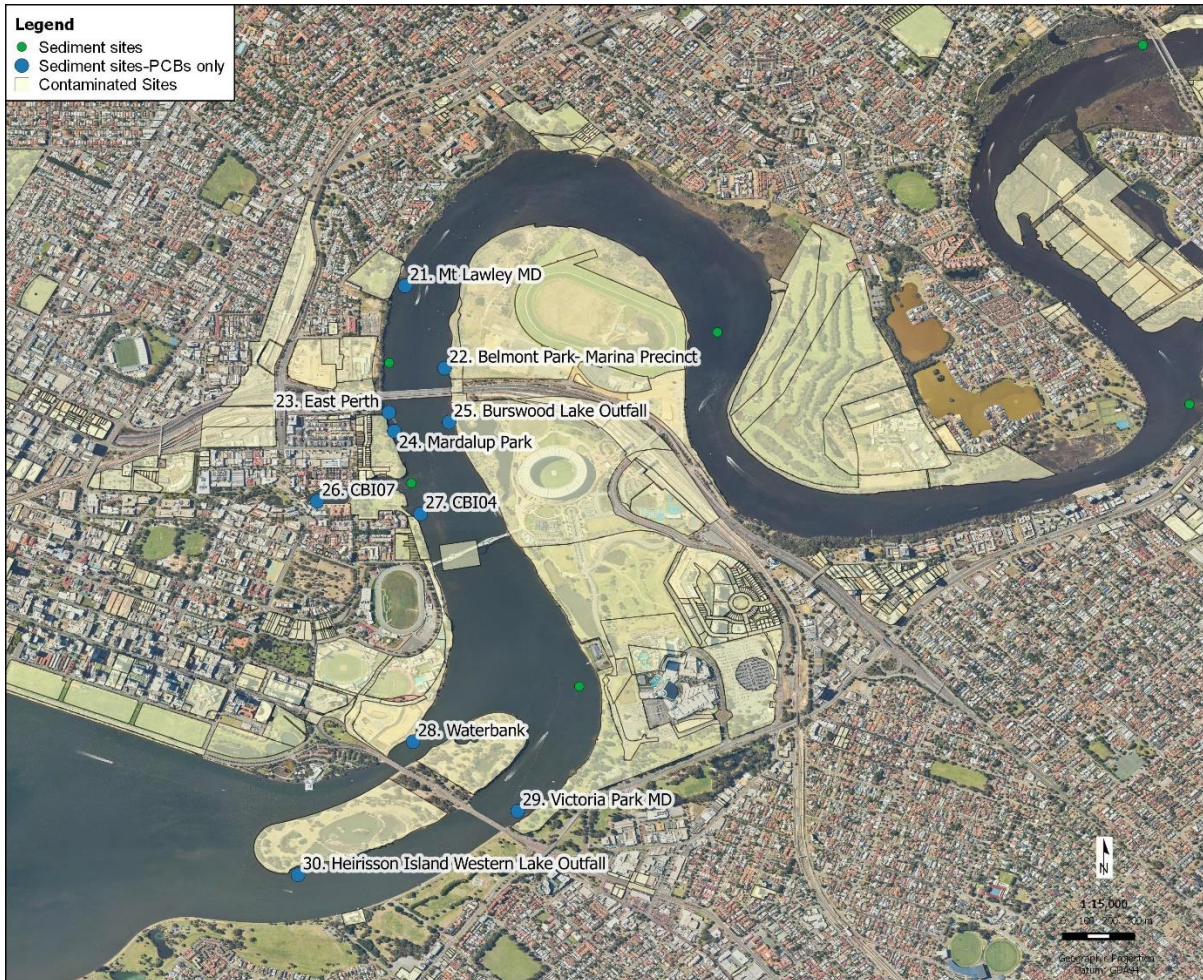


Figure 2. Map of study area showing the ten new sites added in the East Perth, Burswood region of the Middle Swan Estuary, which were sampled for PCBs only. The light shaded area shows the current registered contaminated sites in the region

Table 1. Sampling site details. The shaded sites were the additional sites sampled for PCB's only.

Site Code	Site Name	EMZ	Easting	Northing
01	Blackadder Creek	Upper Swan Estuary	404596	6471992
02	Helena River	Upper Swan Estuary	401961	6469676
03	Upper Swan	Upper Swan Estuary	400020.38	6467932.8
04	Perth Airport South	Middle Swan Estuary	399689	6466972
05	Bayswater	Middle Swan Estuary	398454	6466648
06	Baigup	Middle Swan Estuary	397477	6466595
07	Central Belmont	Middle Swan Estuary	397772.91	6465189.7
08	South Belmont	Middle Swan Estuary	397690	6464811
09	Belmont Racecourse	Middle Swan Estuary	395704.52	6465146.5
10	Maylands	Middle Swan Estuary	394299.01	6464984.5
11	Claisebrook	Middle Swan Estuary	394400	6464385
12	Burswood	Middle Swan Estuary	395122	6463380.7
13	CBD	Middle Swan Estuary	391849	6463531
14	Melville Water	Lower Swan Canning Estuary	390562.26	6459902.2
15	Applecross	Lower Swan Canning Estuary	387484.25	6457058.5
16	Blackwall Reach	Lower Swan Canning Estuary	385236.26	6456927.3
17	Bull Creek	Canning Estuary	392414.25	6454079
18	Adenia Park	Canning Estuary	397312.26	6455636.3
19	Mill St Main Drain	Canning Estuary	397615.95	6456582
20	Lower Canning	Lower Canning River	401321.66	6454682.2
21	Mt Lawley Main Drain	Middle Swan Estuary	394369.61	6465418.29
22	Belmont Park- Marina Precinct	Middle Swan Estuary	394539.15	6464960.40
23	East Perth- Unidentified Drain	Middle Swan Estuary	394285.89	6464740.43
24	Mardalup Park- Zone of Interest	Middle Swan Estuary	394323.44	6464647.24
25	Burswood Lake Outfall	Middle Swan Estuary	394562.51	6464694.90
26	CBI07	Middle Swan Estuary	393959.06	6464309.08
27	CBI04	Middle Swan Estuary	394422.94	6464221.77
28	Waterbank	Middle Swan Estuary	394425.20	6463109
29	Vic Park Main Drain	Middle Swan Estuary	394858.70	6462775.43
30	Heirisson Island Western Lake Outfall	Middle Swan Estuary	393966.62	6462408.89

Table 2. Suite of analytes to be tested in sediment samples collected from the Swan Canning Estuary and the associated Limits of Reporting (mg/kg) for each analyte. * Limits of reporting are also provided for the comparative samples collected in 2007(Nice 2009).

Contaminant group	Analyte	Analysis method	Limit of reporting (mg/kg)	
			2015	2007*
Physical variables	- Moisture content	Dried at 105°C for 24 hours	0.10%	
	- Total organic carbon	Difference between total carbon (combusted at 1400°C) and inorganic carbon (combusted at 500°C)	0.05%	
	- Particle size distribution – ANZECC	Sieving following by laser diffraction (Mudroch et al 1997)	N/A	
Bioavailable metals	- Redox potential	In-situ measurements taken with probe		
	- Mercury (Hg)	Samples are treated with 1M hydrochloric acid on a 1:50 ratio and tumbled for one hour, then filtered and analysed by ICP-OES/MS. ANZECC (2000	0.02	0.2
	- Silver (Ag), cadmium (Cd), total chromium (Cr), molybdenum (Mo), antimony (Sb) and selenium (Se)		0.1	0.5
	- Cobalt (Co), copper (Cu), nickel (Ni)		0.2	0.5
	- Total arsenic (As) and manganese (Mn)		0.4	0.5
	- Lead (Pb)		1.0	0.5
	- Iron (Fe), zinc (Zn)		10	10
- Aluminium (Al)		20	20	
Polycyclic aromatic hydrocarbons (PAH)	Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(e)pyrene, Benzo(b)&(k)fluoranthene, Benzo(ghi)perylene, Chrysene, Dibenzo(ah)anthracene, Fluorene, Fluoranthene, Indeno(1,2,3-cd)pyrene, Naphthalene, Perylene, Phenanthrene, Pyrene	DCM/methanol extraction, followed by chemical drying with sodium sulfate and reduction to approximately 1 mL using a rotary evaporator, and nitrogen blow down. The solvent extract is then transferred to a pre-conditioned flash chromatography column containing approximately 3 g of activated silica gel. The compounds are eluted with 3 mL of pentane/DCM (2:1), and the extracts reduced to 2 mL by nitrogen blowdown Extract analysed using GC-MS	0.01	0.01
Organochlorine pesticides	a-BHC, a-Endosulfan, Aldrin, b-BHC, b-Endosulfan, d-BHC, DDD, DDE, DDT, Dieldrin, Endosulfan Sulfate, Endrin, Heptachlor, Heptachlor Epoxide, Hexachlorobenzene, Lindane, Methoxychlor, Oxychlordane, a-Chlordane, g-Chlordane	Extraction methods as above. Extract analysed by GC-MS-MS	0.001	0.001 0.01
Organophosphate pesticides	Bromophos Ethyl, Chlorfenvinphos E, Chlorfenvinphos Z, Chlorpyrifos Methyl, Chlorpyrifos, Diazinon, Ethion, Fenchlorphos, Fenitrothion, Malathion, Methidathion, Mevinphos, Parathion Methyl, Parathion, Tetrachlorvinphos	Extraction methods as above. Extract analysed by GC-MS-MS	0.01	N/A
	Glyphosate		2	
Polychlorinated biphenyls (PCB)	Mixtures: Aroclor 1016, Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260	Extraction methods as above. Extract analysed using GC-MS using large volume injection and selected ion monitoring mode	0.01	N/A
	Congeners: PCB77, PCB81, PCB105, PCB114, PCB118, PCB123, PCB126, PCB156, PCB157, PCB167, PCB169, PCB189, PCB28, PCB52, PCB101, PCB138, PCB153, PCB180		0.001	

2.2 Data analysis

Following the methods in Nice (2009), the site-by-site results for each contaminant are presented as a box plot, including the:

- The median, 20th and 80th percentile, minimum and maximum for bioavailable metals
- The median, 40th and 60th percentile, minimum and maximum for OC and organophosphate (OP) pesticides, PCBs and PAHs.

To avoid artificially inflating the distribution of contaminants, those that were not detected above the limits of reporting were assigned the value of zero. Those contaminants that were not detected at any site were not included in the analyses. In accordance with the ANZG recommendation the concentration data for the organic contaminants (OC pesticides, PCBs and PAHs) were normalised to 1% total organic carbon (TOC) prior to analysis (ANZG, 2018).

To determine if the sediment contaminants in each core differed between the top 3 cm (surficial sediment) and the bottom 3-10 cm (subsurface sediment) the sediment core was separated into these portions as it was extruded from the corer. Due to different partitioning and sediment binding properties the contaminants were divided into four groups consisting of bioavailable metals, PAHs, pesticides and PCBs, prior to analysis. A multivariate approach was used in the statistical package PRIMER (Version 7, PRIMER-E, Plymouth). To lessen the influence of uncommon very high values, the data were square root transformed before a Euclidean Distance matrix was constructed. To determine any site, depth or interaction effects a two-way PERMANOVA was conducted. The estimates of components of variation are presented as a percentage of the total variation in the statistical model and determine the factor or combination of factors accounting for the greatest variation in the analysis.

2.3 Comparison with 2007 data (Nice, 2009)

A key aim of this study was to determine if the sediment contamination concentration and composition had changed between 2007 and 2015. The Nice (2009) study analysed the surface sediments (<3 cm) only, thus comparisons with the current study are based only on surficial sediments. The samples collected in the Nice (2009) study were collected in 2007 thus data from this study is referred to as 2007 data

The limits of reporting for the contaminants analysed in 2007 were often higher than those available in 2015 (Table 2). To ensure comparability between the studies, if any value in 2015 was lower than the 2007 limit of reporting, it was changed to zero. If any future comparative analyses are conducted, it is recommended that these analyses employ the lower of limits of reporting available in the current study. The directly comparable analytes included in this analysis are shown in Table 3.

Table 3. Analytes used in the comparison between the Nice (2009) study and the current study.

Contaminant group	Analytes
Bioavailable metals	Zn, Hg, Pb, Cu, As, Cd, Ni, Cr, Se, Mn, Al, Co, Fe and Sb
Polycyclic aromatic hydrocarbons	<p>Low molecular weight PAHs</p> <ul style="list-style-type: none"> Acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene, <p>High molecular weight PAHs</p> <ul style="list-style-type: none"> Benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene. <p>Total PAH – this is for comparison to the new SQG</p>
Organochlorine Pesticides	Aldrin, DDD-p,p, DDE-p,p, DDT, Dieldrin, Hexachlorobenzene, Lindane, Chlordane

To determine the differences in contaminant concentrations between the two studies, sites or if there was an interaction between these two effects, a two-way PERMANOVA was used. Prior to the analysis the data were square root transformed and a Euclidean Distance matrix was constructed. The contaminants were divided into groups of like contaminants; bioavailable metals, PAHs, PCBs and pesticides and analysed separately. Eight analytes; mercury, Chlordane, DDT, DDD, Aldrin, Hexachlorobenzene, Acenaphthalene, and Fluorene had very few reported detections and where the contaminant was detected the result was very close to the limit of reporting. The impact on the analysis from this data was disproportionate to their likely ecological impacts (at the concentrations reported) and thus they were removed. The estimates of components of variation are presented as a percentage of the total variation in the statistical model and determine the factor or combination of factors accounting for the greatest variation in the analysis.

Where analytes exceeded the Australian and New Zealand Guidelines for Fresh and Marine Water Quality – Toxicant default guideline value (DGV) or the high guideline value (GV-high) for sediment quality (ANZG 2018) in either 2007 or 2015, a detailed comparison of the changes in contaminant concentration between the two studies on a site by site basis was conducted. Mercury was not included in further analysis despite its detection at three sites in 2007 but not detected at any site in 2015 despite much lower limits of reporting. Two analytes of broader interest, but did not exceed guideline values, including the OC pesticide dieldrin and PAHs were also

selected for the comparison. The primary objective was to determine if the concentration of each contaminant at each site differed between studies. To do this, the data were firstly log transformed to remove the influence of any very high values. A Euclidean distance matrix was then constructed for each contaminant prior to analysis using a two-way (study and site) PERMANOVA. To determine if the concentration of each contaminant, at each site was different between 2007 and 2015, pairwise tests were then conducted.

The particle size distribution in the current study was partitioned according to the international standard (Mudroch et al. 1997) recommended by ANZG (2018), while the Wentworth scale was employed by Nice (2009) which was then the recommendation by ANZECC & ARMCANZ 2000 (Table 4). It should be noted that the partitioning of the smaller fractions differs slightly between the two approaches.

Table 4. The different sediment particle size analytical scales employed by the two studies.

	International standard (Mudroch et al 1997)	Wentworth scale
Clay	<2 µm	<4 µm
Silt	2-63 µm	4-62 µm
Fine sand	63-250 µm	62-250 µm
Medium sand	250-500 µm	250-500 µm
Coarse sand	500-2000 µm	500-2,000 µm
Gravel	>2000 µm	2,000-10,000 µm

2.4 Relevant guidelines

ANZG Australian and New Zealand Guidelines for Fresh and Marine Water Quality – Toxicant default guideline values for sediment quality (ANZG 2018)

For comparability to the work by Nice (2009), data were also compared to the ANZECC *Interim Sediment Quality Guidelines* (ANZECC and ARMCANZ 2000).

3 Results

3.1 Metals

The concentrations and composition of bioavailable metals within the estuary differed between sites and between the surface and bottom sediments. However, the trend was not consistent across sites or depths resulting in a significant interaction effect (Pseudo $F_{19, 159} = 5.4704$, $P < 0.001$). The interaction effect was evident, for example, at sites 19 and 20 where the median concentration of each metal was higher in subsurface sediments at site 19, where, conversely at site 20 the median concentration of each metal was higher in the surficial profile. The site effect accounted for the greatest variation in the model (94% of the estimated total variation), whereas profile accounted for very little (<1%). Metal concentrations were generally more elevated in the Middle Swan Estuary (site 9-12) and the Canning Estuary and Lower Canning River (sites 17-20) (Figure 3).

The bioavailable concentration of three metals, copper, lead and zinc exceeded the ANZG DGV and concentrations of zinc exceeded the GV-high in both the surficial and subsurface sediments. In surficial sediments, the DGV for copper was exceeded at three sites (sites 10, 11, 17), for lead it was exceeded at eight sites (sites 9, 10, 11, 12, 16, 17, 18, 20) and for zinc it was exceeded at nine sites (sites 4, 9, 10, 11, 12, 17, 18, 19, 20). The GV-high was exceeded for zinc at three sites (sites 11, 17, 20).

In the subsurface sediments, the number of exceedances and the sites where the exceedances were recorded were consistent with the surficial sediments, with the following exceptions. The copper DGV was exceeded only at site 17, the lead DGV was exceeded at nine sites, with the inclusion of Site 4 (to the list of surface exceedances above), and the zinc GV-high was exceeded only at site 19 (Figure 3).

Most of the exceedances of the DGV and GV-high occurred in the sites within the Middle Swan Estuary, particularly the region between Burswood to Belmont Racecourse (Sites 9-12) (Figure 3). One sites in the Canning Estuary also recorded an exceedance of the DGV, site 17 as did a site in the Lower Canning River (site 20). Site 16 in the Lower Swan Canning Estuary also recorded an exceedance of the DGV for zinc.

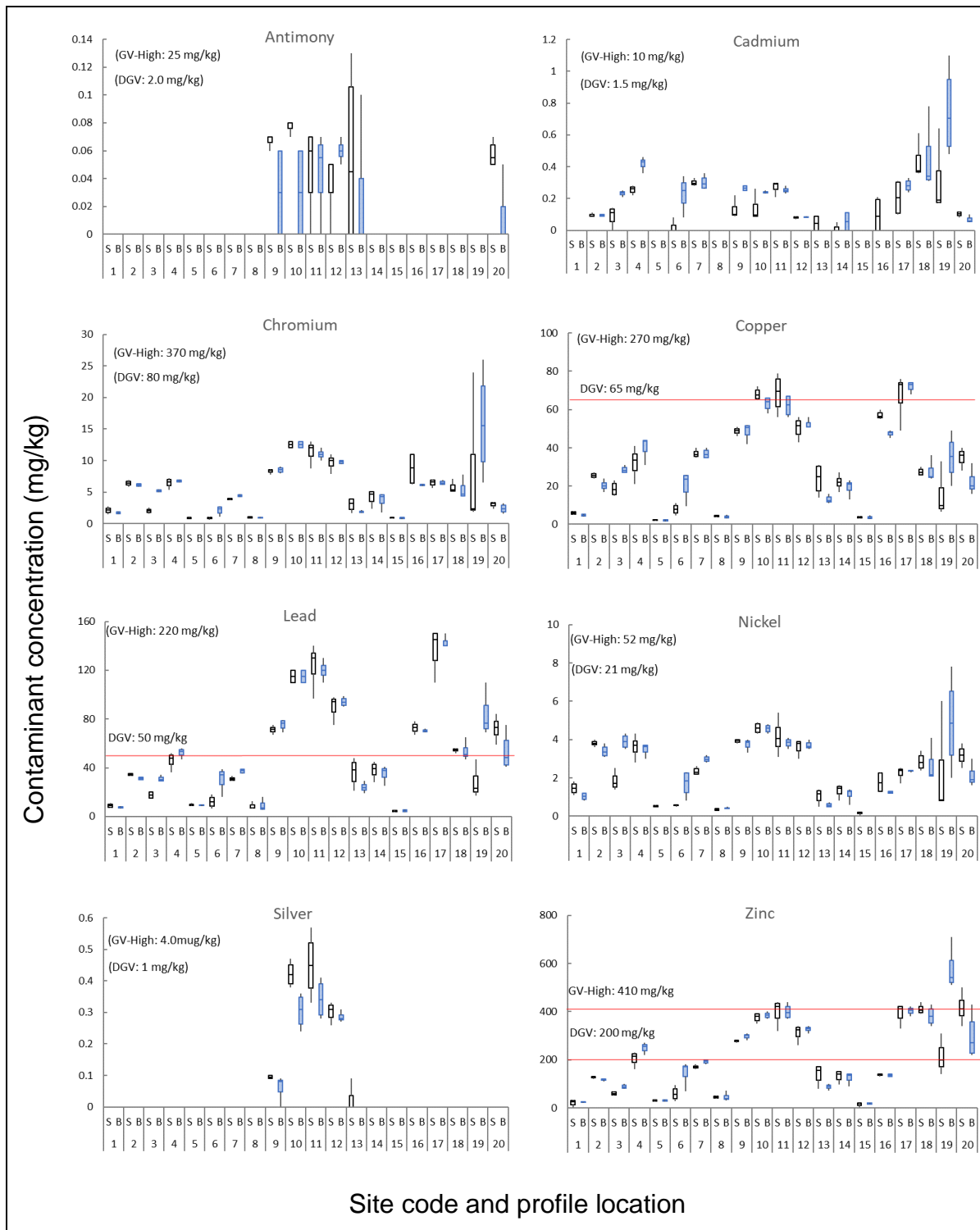


Figure 3. Bioavailable metals in both the surficial (white bars) and bottom (blue bars) sediments. The centreline in the box shows the median, the box represents the 20th and 80th percentile and the whiskers show the minimum and maximum.

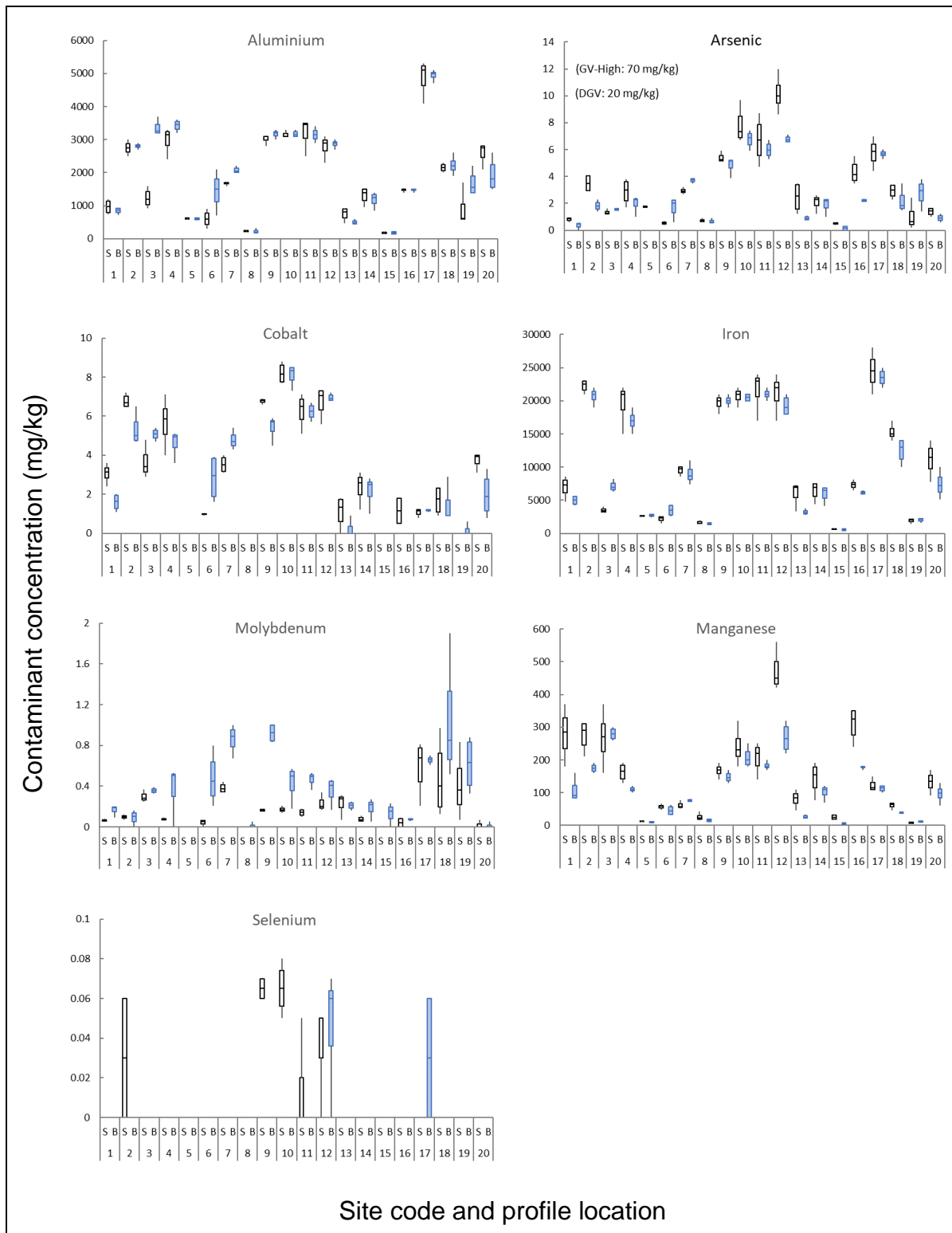


Figure 3. continued

3.2 Polycyclic aromatic hydrocarbons

The concentrations of polycyclic aromatic hydrocarbons (PAHs) in the estuary varied significantly between sites (Pseudo $F_{19,159} = 55.424$, $P < 0.001$), but not with depth and there was not interaction between these effects (Pseudo $F_{1,159} = 1.057$, $P = 0.330$ and Pseudo $F_{19,159} = 1.228$, $P = 0.102$, respectively) (Figure 4). The Middle Swan Estuary, particularly between Sites 9 to 12 and the Lower Swan Canning Estuary at site 16 (Blackwall Reach) had the highest PAH concentrations (Figure 4). The highest median concentration (1429 $\mu\text{g}/\text{kg}$) of PAHs was recorded at Claisebrook (site 11). The guideline value for Total PAHs however, was not exceeded at any site.

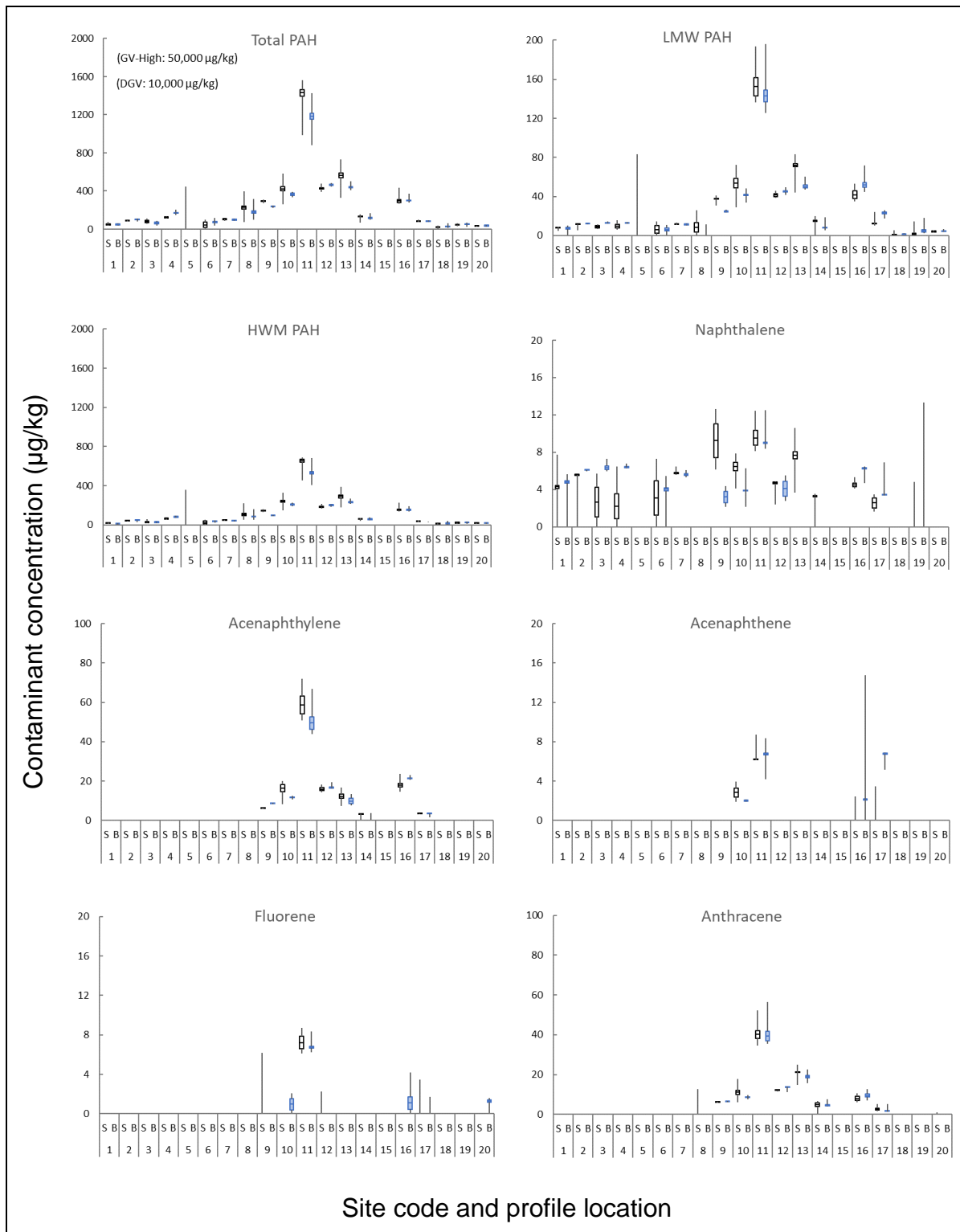


Figure 4. Polycyclic aromatic hydrocarbons in both the surficial (white bars) and bottom (blue bars) sediments. The centreline in the box shows the median, the box represents the 40th and 60th percentile and the whiskers show the minimum and maximum.

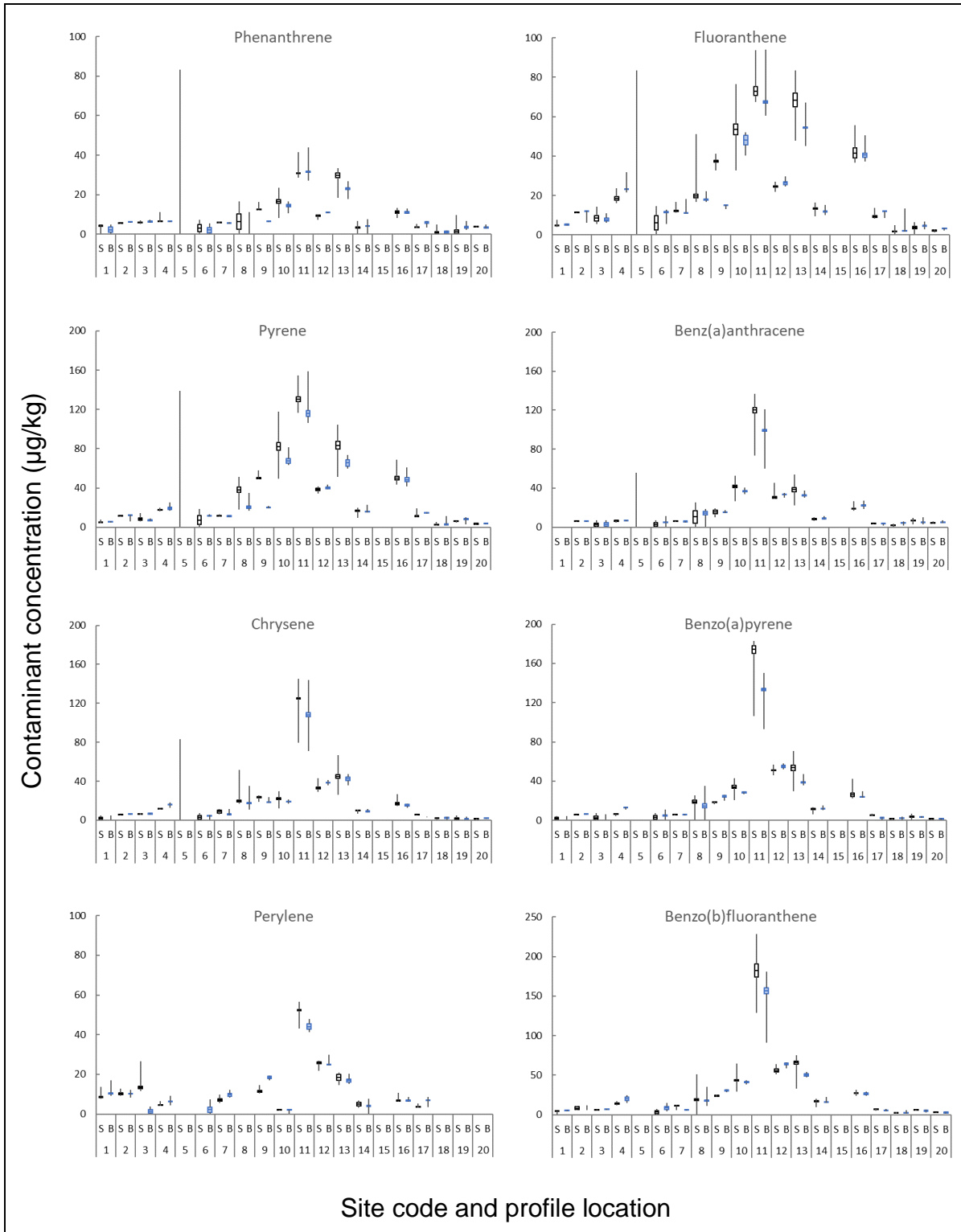


Figure 4. Continued.

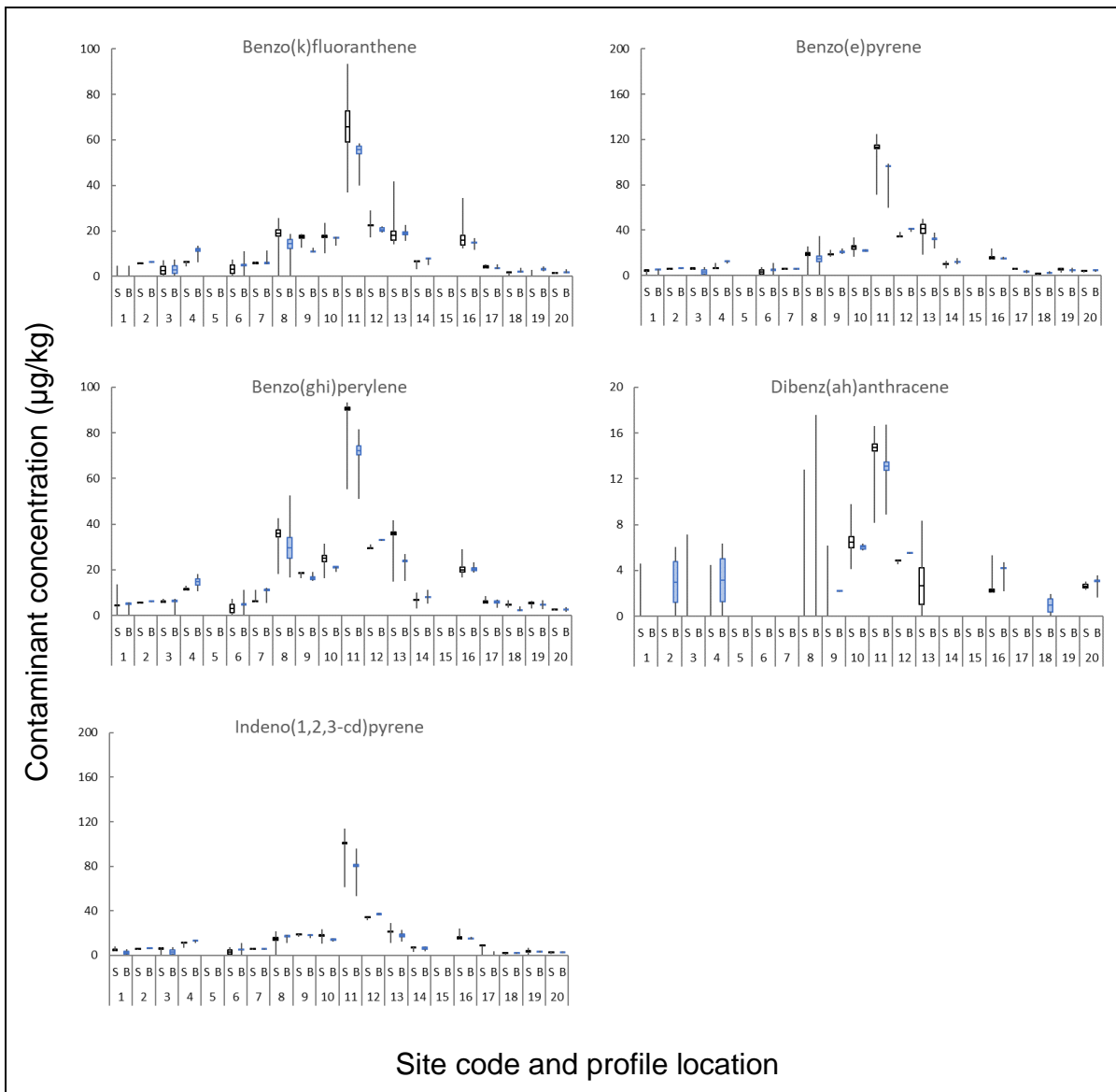


Figure 4. Continued

3.3 Organochlorine pesticides

Six organochlorine pesticides were detected in this study, dieldrin, DDT, DDE, DDD, aldrin and chlordane (Figure 5). The sediment concentration of the pesticides varied significantly across both site and depth and there was a significant interaction between the two effects (interaction effect - Pseudo $F_{19,159} = 2.186$, $P < 0.001$). The greatest source of variation in the model was attributed to the site effect, which accounted for 64% of the estimated variation, while depth accounted for the least variation in the model, i.e., 4%. The concentrations of DDE were most elevated in the Middle Swan Estuary, aldrin and dieldrin were in the Middle and Upper Swan Estuary (Figure 5). In a pattern consistent with the bioavailable metals, the concentrations in the different profiles varied according to the specific contaminant and the site (Figure 5).

Dieldrin was the most commonly detected organochlorine pesticide, detected in surface or subsurface sediments at 14 sites. The highest median concentration (2.35 $\mu\text{g}/\text{kg}$) was in the surface sample at South Belmont (site 8). Generally, dieldrin was highest at sites 8-13 (Middle Swan Estuary). Dieldrin was not detected in the Lower Swan Canning Estuary or Canning Estuary but was detected at the only site in the Lower Canning River (site 20). While DDT was only detected at a single site, its breakdown product DDE was detected at 13 of the 20 sites sampled. The highest concentrations of DDE were recorded within the Middle Swan Estuary from sites 9-13, particularly sites 10 and 11. The DGV for DDE was only exceeded in the surficial sediments at Claisebrook and Maylands (sites 10 and 11, respectively) (Figure 5). and in the subsurface sediments at Maylands (site 11). DDD was detected infrequently and at low concentrations in the Estuary.

3.4 Organophosphorus pesticides

None of the standard suite of organophosphate pesticides were detected at any of the sites surveyed in this study.

Glyphosate, however, was detected at one of the 10 sites analysed. A concentration of 0.3 mg/kg was detected in the Lower Canning (site 20), located in the freshwater reach of the Lower Canning River.

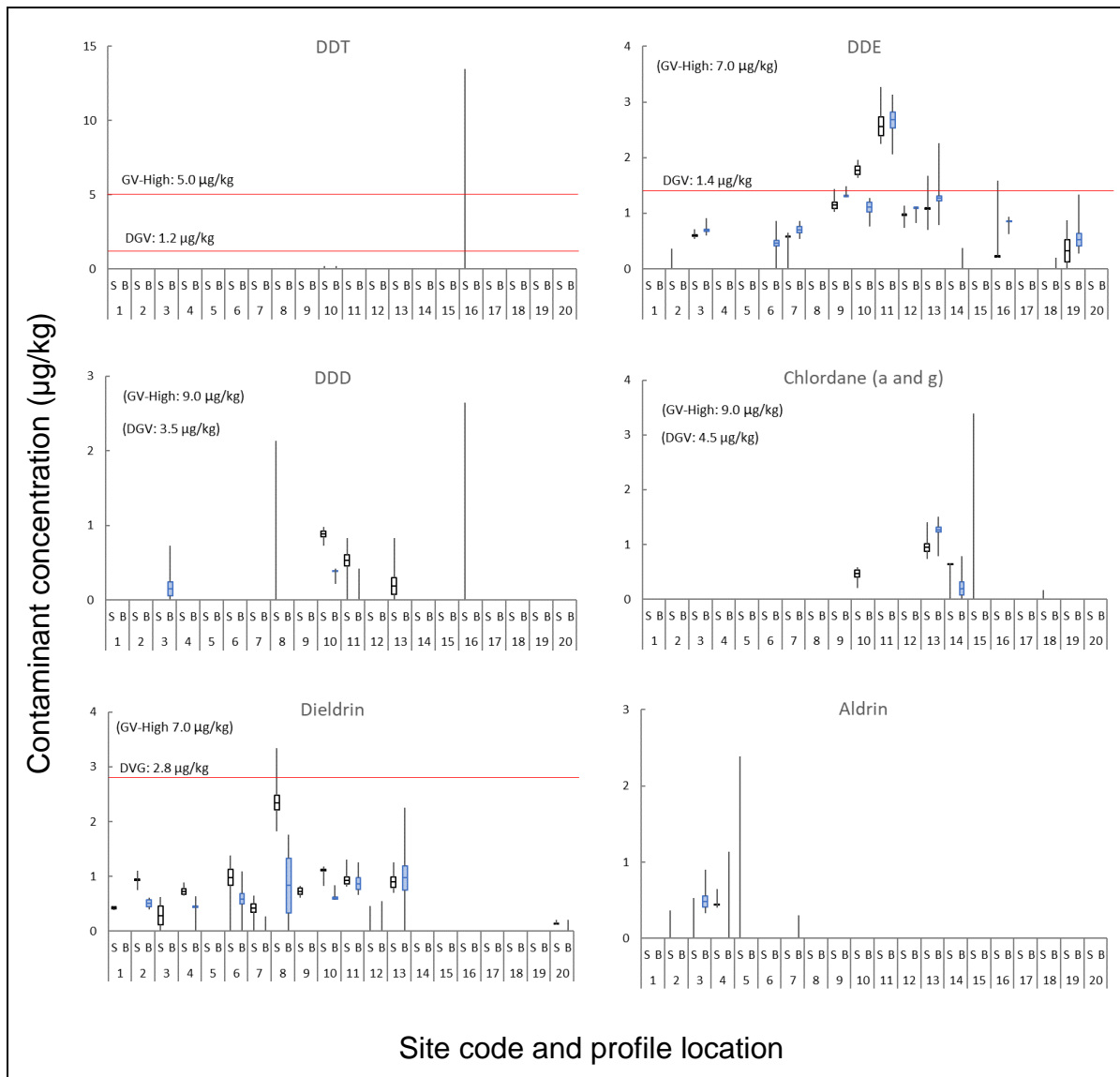


Figure 5. Organochlorine pesticides in both the surficial (white bars) and bottom (blue bars) sediments. The centreline in the box shows the median, the box represents the 40th and 60th percentile and the whiskers show the minimum and maximum.

3.5 Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) were detected widely throughout the estuary, with Aroclor 1254 reported at 25 of the 30 sites (surficial and bottom sediments) and the congener PCB138 detected at 23 sites (Figure 6). Of the seven PCB mixtures tested, only Aroclor 1254 was detected, and 11 of the 18 congeners tested were detected in the estuary. Thus, in line with the ANZG (2018), Aroclor 1254 concentrations were used to assess against the Total PCB DGV, which was exceeded at the CBD site (site 13) (Figure 6). The CBD site had the highest median concentration of Aroclor 1254, which was approximately six times higher than all other sites. Furthermore, PCB concentrations recorded at sites located around the Maylands and East Perth area were more elevated compared to sites elsewhere in the system (Figure 6). There was no clear pattern in PCB concentrations in surficial or subsurface sediments between sites (interaction effect - Pseudo $F_{19,159} = 2.148$, $P < 0.001$). The factor site was dominant in the model and accounted 84% of the estimated variation, while profile accounted for less than 1%.

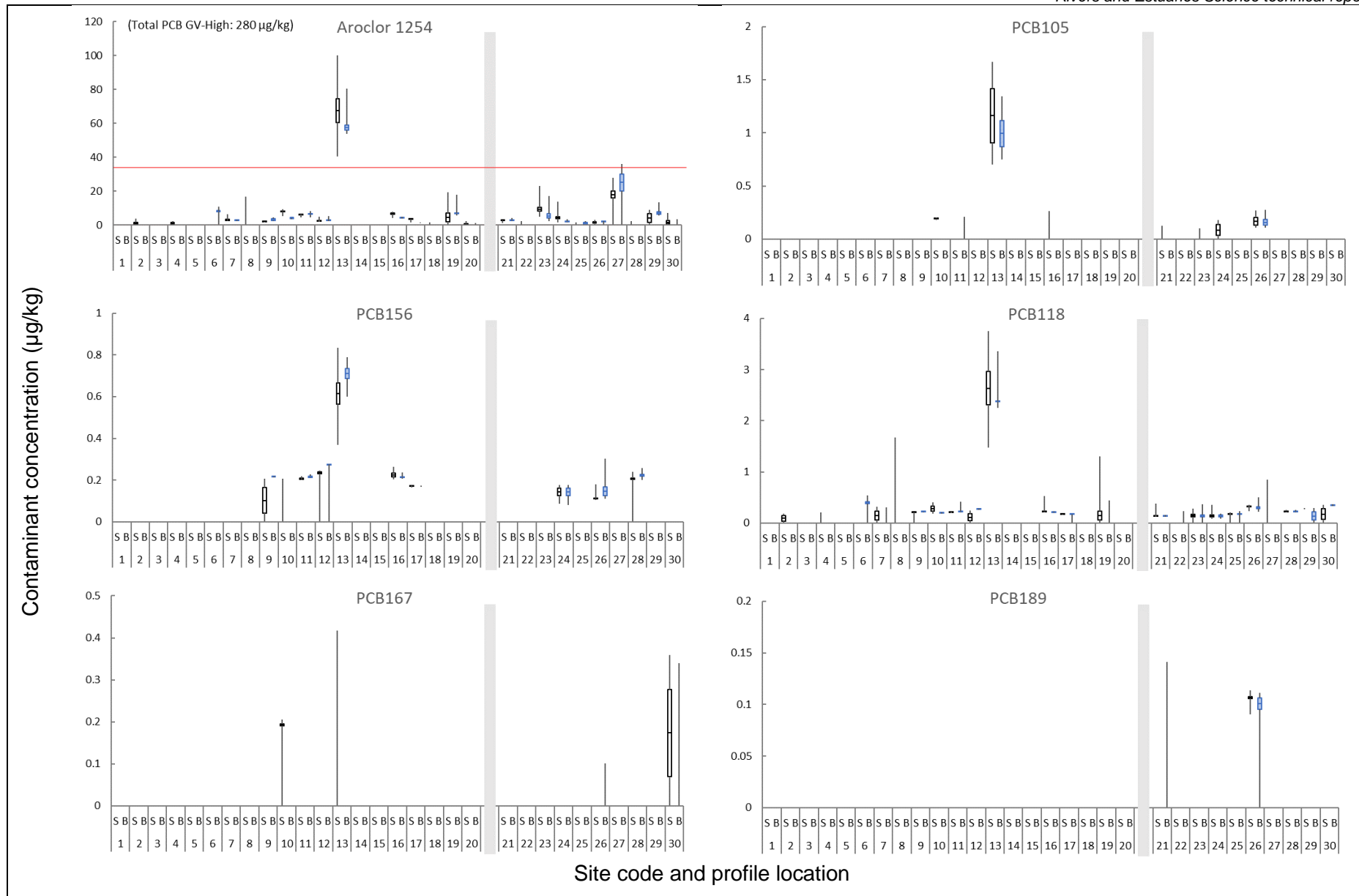


Figure 6. Polychlorinated biphenyls in both the surficial (white bars) and bottom (blue bars) sediments. The centreline in the box shows the median, the box represents the 40th and 60th percentile and the whiskers show the minimum and maximum.

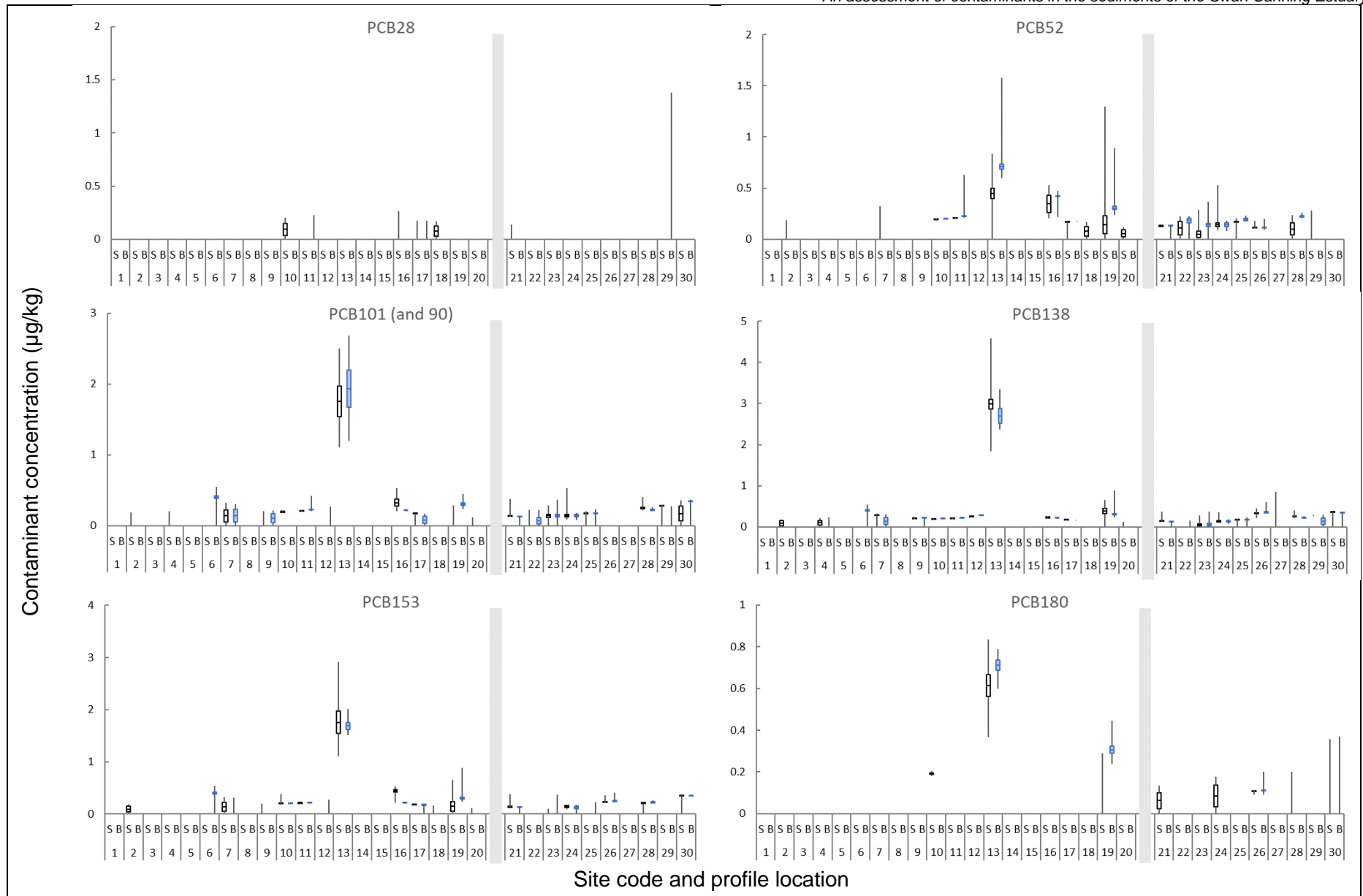


Figure 6. Continued.

3.6 Comparison to 2007 data (Nice 2009)

Contaminant concentrations in surficial sediments varied between sites and studies, however the difference between sites was not uniform between the studies. Consequently, there was a significant interaction between these effects (Pseudo $F_{19, 179} = 8.835$, $p < 0.001$). The estimated components of variation suggested that the majority of variation was explained by site for all analytes (metals = 70%, PAH = 67% and pesticides = 61%). The factor “study” only explained a minor fraction of the model variation (3%, 4% and 1% for metals, PAH and pesticides, respectively). In 2015, 44% of metal contaminants were higher at each site than they were in 2007, 20% were the same and 36% were lower. Furthermore, 38% of organic contaminants were higher in 2015 at each site than they were in 2007, 41% stayed the same and 21% were lower.

There was little difference in the number of exceedances of the toxicant default guidelines (DGV) between the two studies (Table 5). Across both metals and organic contaminants, the DGV was exceeded 22 times in both 2007 and 2015. The GV-high was exceeded three times in 2015 and two times in 2007. Largely, the contaminants that exceeded the guidelines were consistent across the studies, with exceedances in copper, zinc, lead and DDE occurring in both studies. Mercury however, exceeded the DGV in 2007, but was not detected at any site in 2015. Additionally, selenium which was identified as exceeding an adopted international guideline in 2007, was rarely detected in 2015 and where it was detected the concentration was well below the adopted guideline (2 mg/kg).

The analytes that exceeded guideline values in either 2007 or 2015 were selected for detailed comparison of variation in contaminant concentration between the studies. Analytes of broader interest, but did not exceed guideline values, including the OC pesticide dieldrin and PAHs were also selected for the comparison. The total suite of analytes was copper, zinc, lead, DDE, dieldrin, and total PAHs.

Table 5. A comparison of the exceedances of current ANZG (ANZECC guidelines) of comparable contaminants in Nice (2009) and the current study.

	Current study								Nice (2009)			
	Surface 3 cm				Bottom 3-10 cm				Surface 3 cm			
	ISQG		ANZG		ISQG		ANZG		ISQG		ANZG	
	Low	High	Default	High	Low	High	Default	High	Low	High	Default	High
As	0	0	0	0	0	0	0	0	0	0	0	0
Cd	0	0	0	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0	0	0	0
Cu	3	0	3	0	1	0	1	0	1	0	1	0
Hg	0	0	0	0	0	0	0	0	2	0	2	0
Ni	0	0	0	0	0	0	0	0	0	0	0	0
Pb	8	0	8	0	9	0	9	0	9	0	9	0
Zn	9	3	9	3	9	1	9	1	8	2	8	2
Metal exceedances	20	3	20	3	19	1	19	1	20	2	20	2
Naphthalene	0	0			0	0			0	0		
Acenaphthylene	1	0			1	0			0	0		
Acenaphthene	0	0			0	0			0	0		
Fluorene	0	0			0	0			0	0		
Phenanthrene	0	0			0	0			0	0		
Anthracene	0	0			0	0			0	0		
Fluoranthene	0	0			0	0			0	0		
Pyrene	0	0			0	0			0	0		
Benz(a)anthracene	0	0			0	0			0	0		
Chrysene	0	0			0	0			0	0		
Benzo(a)pyrene	0	0			0	0			0	0		
Dibenz(ah)anthracene	0	0			0	0			0	0		
T-PAH	0	0	0	0	0	0	0	0	0	0	0	0
LMW	0	0			0	0			0	0		
HMW	0	0			0	0			0	0		
DDD	0	0	0	0	0	0	0	0	0	0	0	0
DDE	1	0	2	0	1	0	1	0	1	0	2	0
DDT	0	0	0	0	0	0	0	0	0	0	0	0
Dieldrin	12	0	0	0	7	0	0	0	6	0	0	0
Lindane	0	0	0	0	0	0	0	0	0	0	0	0
Chlordane	2	0	0	0	1	0	0	0	0	0	0	0
Organics exceedances	16	0	2	0	10	0	1	0	7	0	2	0
Total exceedances	36	3	22	3	29	1	20	1	27	2	22	2

3.6.1 Metals

For each of the three metals analysed (copper, lead and zinc), a significant interaction effect between site and study was observed (Cu - Pseudo $F_{19,179} = 6.462$, $P = <0.001$, Pb - Pseudo $F_{19,179} = 8.290$, $P = <0.001$, Zn - Pseudo $F_{19,179} = 5.542$, $P = <0.001$). The pairwise comparisons of the copper concentration between the two studies at each site identified 14 sites where concentrations were significantly ($P < 0.05$) higher in the 2015 study (Figure 7a). Of particular note, was the significantly higher concentration in 2015 at sites 10 and 17 which resulted in an exceedance of the DGV. Lead concentrations were significantly higher in 2015 at eight sites (sites 1-5, 8, 14, and 18) and lower at one site (site 15, $p = 0.007$) (Figure 7b). Of the eight sites that were significantly higher in 2015, one recorded an exceedance of the DGV at site 18. Zinc concentrations were significantly higher at six sites in 2015 (sites 2, 4, 5, 14, 18, and 20) and lower at two sites (sites 12 and 15) (Figure 7c). Two occasions resulted in an exceedance of the guidelines, with the DGV exceeded at site 4 and the GV-high at site 18. At site 20, the DGV was exceeded in 2007 and in 2015, the significantly higher median concentration, exceeded the GV-high. Mercury, while detected higher than the DGV at two sites in 2007 was not measured above the detection limit at any site in 2015.

3.6.2 Polycyclic aromatic hydrocarbons

The sediment concentrations of total PAHs were significantly different between sites (Pseudo $F_{19,179} = 25.943$, $P = 0.03$) and studies (Pseudo $F_{1,179} = 4.298$, $P = <0.001$), however there was no interaction effect (Pseudo $F_{19,179} = 0.545$, $P = 0.94$). The pairwise comparisons of the PAH concentration between the two studies at each site determined that concentrations at sites 1-4 and 9 were significantly higher ($P > 0.05$) in 2015 than 2007. The concentration at site 14 was significantly lower in 2015 than 2007 (Figure 8a). There were no exceedances of the DGV at any site in 2007 or 2015.

3.6.3 Organochlorine pesticides

The concentration of DDE varied significantly with site (Pseudo $F_{19,179} = 23.523$, $P < 0.001$). However, there was no significant study effect, nor a significant interaction effect (Pseudo $F_{19,179} = 1.148$, $P = 0.305$). There were no significant ($p > 0.05$) pairwise test results (Figure 8b). Dieldrin however, did vary significantly across study and site (interaction effect – Pseudo $F_{19,179} = 2.0154$, $P = 0.008$). There were two significant ($p > 0.05$) pairwise test results, at site 9 and 11, on both cases the sediment concentration of dieldrin was significantly lower in 2015, than 2007 (Figure 8c). In the 2015 study, there were four detections of DDE (sites 2, 3, 13 and 16) and five of dieldrin (sites 1, 3, 4, 13, and 20), that were not observed in 2007.

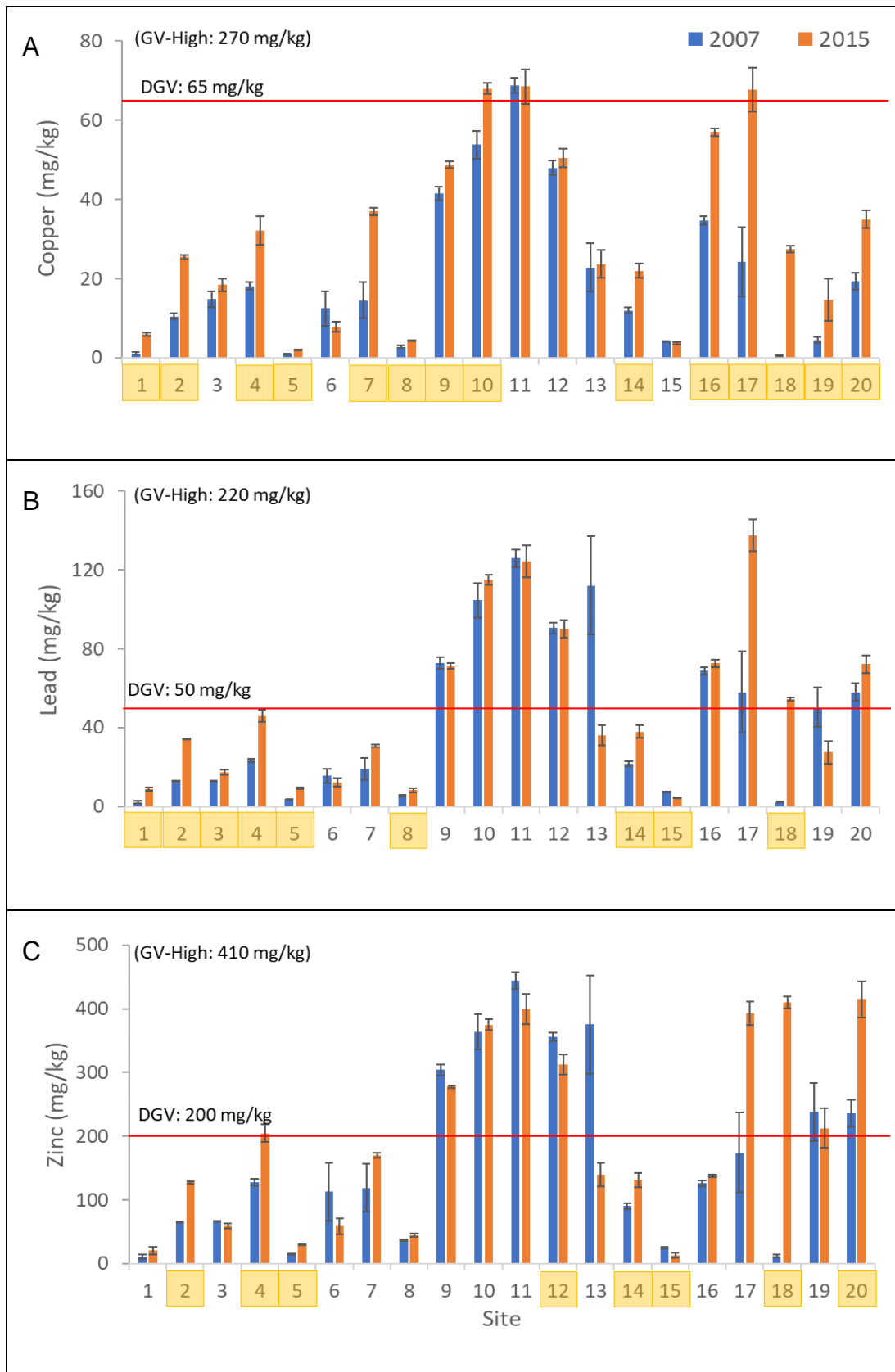


Figure 7. Comparison of mean (SE error bars) 2007 and 2015 contaminant concentrations at each site where exceedances of ANZG guidelines were detected. Where significant differences between years were observed, the site number has been highlighted. Mercury has not been included in this figure as it was not detected in 2015.

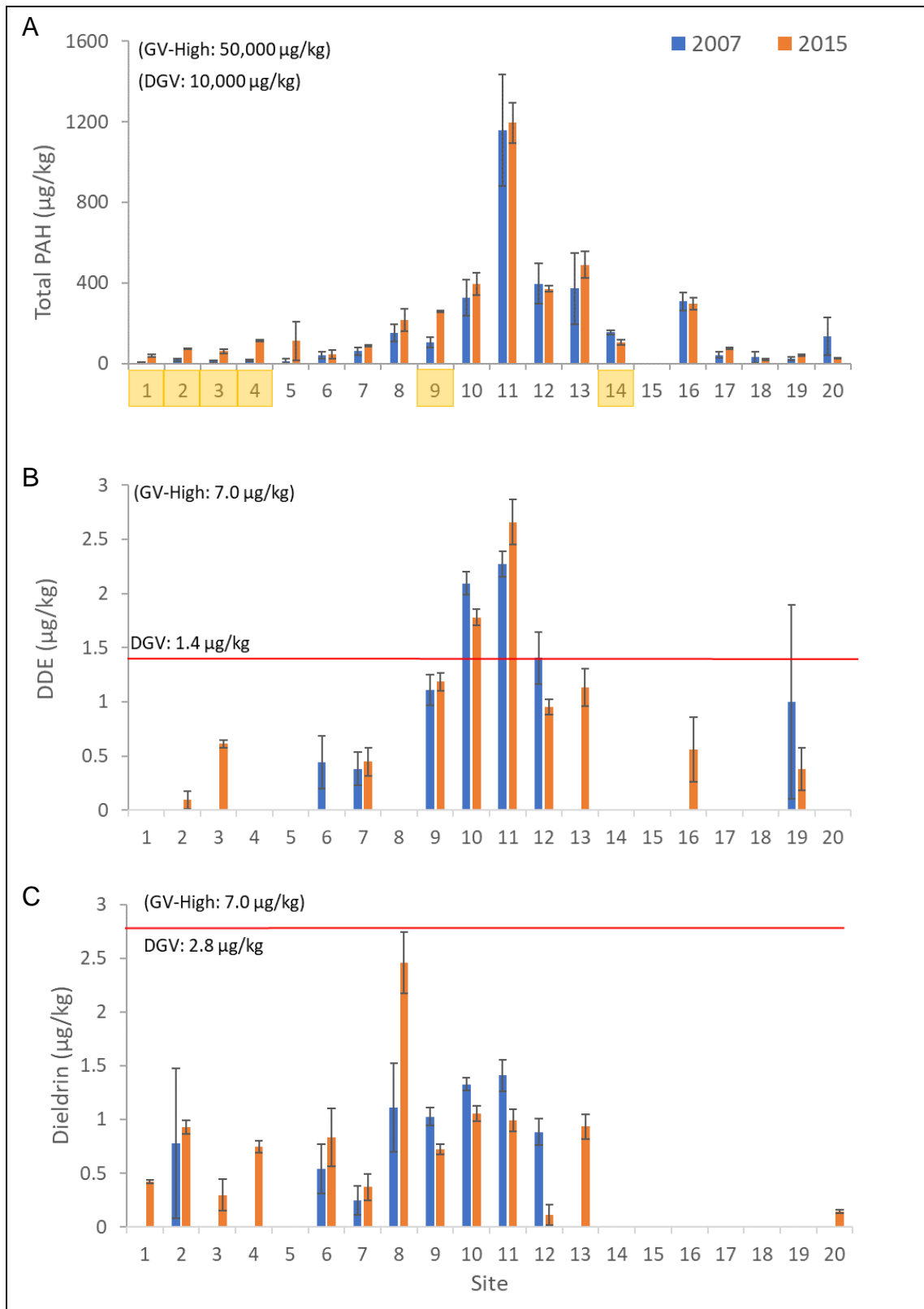


Figure 8. Comparison of mean (SE error bars) 2007 and 2015 contaminant concentrations at each site where exceedances of ANZG guidelines were detected. Dieldrin and PAHs have also been included. Where significant differences between years were observed, the site number has been highlighted. More detects of dieldrin and DDE were recovered in 2015 due to finer limits of reporting available.

3.7 Particle size distribution and redox

3.7.1 Particle size distribution

The dominant sediment fraction in the surficial sediments at 14 of the 20 sites (sites 2-4, 7, 9-14, 16-18, and 20) was silt (<2-63 µm) (Table 6). The sediment particle size at the remaining sites was dominated by the sand fractions (63-2,000 µm). The subsurface sediments were very similar to the surficial sediments with silt dominating at 15 of the 20 sites (with the inclusion of site 19 to the list above), sand was the dominant fraction at the remainder of sites (Table 7).

3.7.2 Redox potential

Redox potentials in the water column generally varied from 5.1 mV at site 26 to 243 mV at site 16. Excluding site 26 water redox potential remained above 100 mV. Sediment surficial and subsurface redox potential was highly variable ranging from -307 to 105 mV. Redox potential was higher in the surficial sediments than the subsurface sediments at 27 of the 30 sites, but this was not observed at sites 2, 7 and 25.

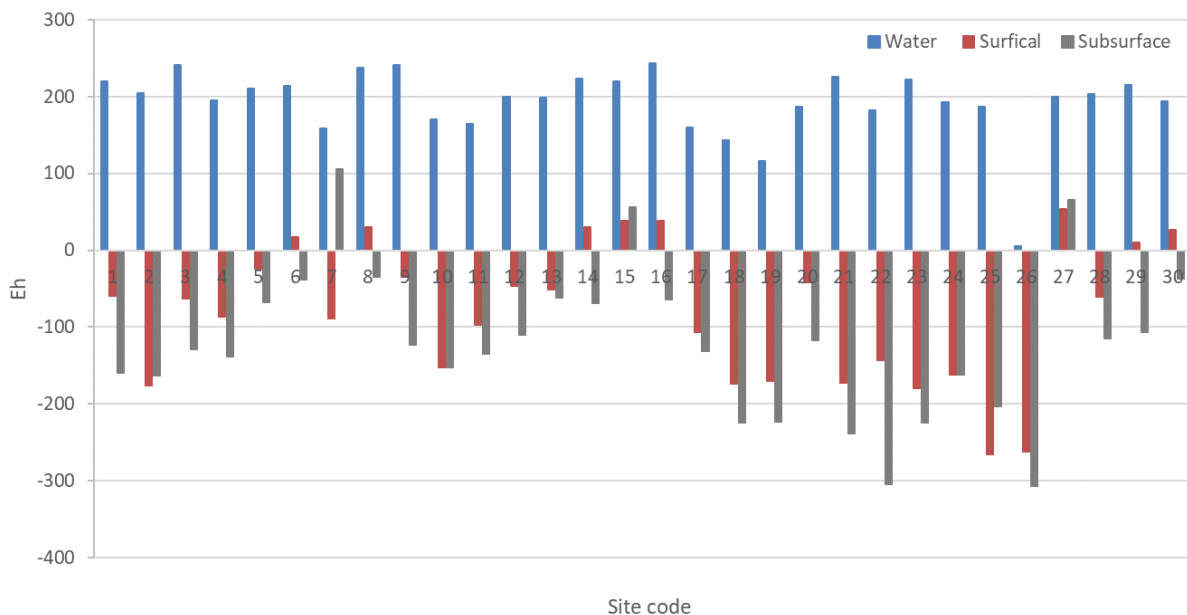


Figure 9. Sediment and water column redox potential (mV) at 30 sites within the Swan Canning Estuary. Eh = measured redox potential relative to hydrogen.

Table 6. Particle size distribution for the surficial sediment profile. Bolded values indicate the dominant particle size fraction at that site. Sites 1-20 were consistent with Nice (2009).

Site	Clay (<2 μm)	Silt (2-63 μm)	Fine sand (63-250 μm)	Medium sand (250- 500 μm)	Coarse sand (500- 2000 μm)	Coarse material (>2000 μm)
1	2.85	28.81	10.13	4.39	47.50	6.32
2	6.89	75.49	12.45	2.47	1.35	1.35
3	9.08	49.39	25.43	9.40	6.36	0.35
4	6.25	69.38	14.88	4.23	3.73	1.53
5	2.17	14.16	21.65	31.96	29.98	0.08
6	2.23	21.16	20.96	9.19	38.09	8.36
7	5.38	66.96	21.77	3.89	0.54	1.46
8	2.19	14.34	24.40	34.01	25.03	0.02
9	9.18	83.33	6.72	0.64	0.13	0.00
10	10.94	74.43	11.94	1.84	0.35	0.49
11	12.51	76.26	8.41	0.80	1.90	0.12
12	13.32	82.11	4.00	0.17	0.19	0.21
13	5.29	45.25	17.32	10.59	14.40	7.15
14	6.52	41.22	15.10	7.17	16.33	13.65
15	1.52	22.17	42.56	30.91	2.40	0.43
16	5.13	76.79	15.82	1.93	0.26	0.06
17	3.98	70.37	18.24	7.05	0.38	0.00
18	1.61	59.55	24.65	7.91	5.87	0.42
19	0.96	30.27	12.59	5.67	48.91	1.60
20	2.93	66.52	23.63	4.30	1.63	0.99
21	5.80	58.06	26.04	5.89	3.53	0.68
22	2.45	20.47	44.92	16.52	9.64	5.99
23	4.65	30.96	17.19	20.14	26.84	0.21
24	9.65	71.96	14.89	2.01	0.96	0.53
25	3.93	35.46	37.89	8.09	9.49	5.12
26	4.00	55.04	20.66	5.15	6.02	9.13
27	4.71	32.53	21.91	15.08	25.71	0.06
28	8.54	67.78	19.03	3.56	0.42	0.67
29	6.36	50.16	12.18	1.93	1.28	28.08
30	7.05	66.38	25.15	1.27	0.15	0.00

Table 7. Particle size distribution for the subsurface sediments. Bolded values indicate the dominant particle size fraction at that site.

Site	Clay (<2 µm)	Silt (2-63 µm)	Fine sand (63-250 µm)	Medium sand (250-500 µm)	Coarse sand (500-2000 µm)	Coarse material (>2000 µm)
1	2.21	22.94	11.39	9.88	44.97	8.61
2	7.07	78.19	11.53	2.18	0.56	0.46
3	13.08	69.31	12.50	3.09	1.86	0.15
4	6.77	75.07	12.05	2.86	1.02	2.22
5	1.43	8.76	15.80	41.42	32.38	0.21
6	3.02	27.04	29.50	11.28	24.49	4.66
7	6.56	69.65	17.06	2.44	0.62	3.67
8	1.97	13.46	24.87	34.48	25.16	0.06
9	9.72	84.42	5.38	0.38	0.06	0.04
10	10.89	72.67	10.20	1.35	0.57	4.32
11	12.62	78.00	8.06	0.89	0.28	0.15
12	13.73	81.12	3.39	0.00	0.18	1.59
13	5.59	43.88	20.01	12.52	16.82	1.17
14	7.58	43.47	18.06	9.66	12.97	8.26
15	0.96	12.03	46.66	37.16	2.77	0.41
16	4.94	76.17	17.05	1.66	0.16	0.02
17	3.58	66.95	19.64	8.38	1.03	0.44
18	1.71	59.85	24.49	7.67	5.64	0.64
19	1.84	41.06	16.99	5.67	31.24	3.20
20	2.71	58.38	24.00	4.74	4.22	5.94
21	5.63	55.21	26.26	5.70	3.59	3.61
22	4.81	32.09	30.56	11.98	7.61	12.96
23	4.13	26.09	18.25	22.76	28.10	0.67
24	10.59	69.54	13.85	2.20	2.35	1.46
25	4.06	35.89	39.78	7.99	7.96	4.32
26	3.87	55.55	23.27	6.21	6.25	4.85
27	3.51	21.71	22.20	24.38	28.20	0.00
28	8.20	66.92	18.94	3.79	1.09	1.06
29	7.11	55.35	14.93	2.96	4.17	15.48
30	6.92	62.38	26.92	1.91	0.32	1.55

4 Discussion

At an estuary wide scale, the contamination status of the Swam Canning Estuary hasn't changed markedly since the baseline study was conducted in 2007 (Nice 2009). Concentrations of contaminants remained highest in the Middle Swan Estuary between sites 9-12 and there was little change in the contaminant concentration in this region between the two studies. Contaminant concentrations in the sediment largely remained low, however there were exceedance of guidelines by five contaminants, primarily the metals zinc, copper and lead, with additional exceedances of the default guideline for the organochlorine pesticide DDE and PCBs. Across the estuary, the number of contaminants compatible with the 2007 study exceeding the guidelines decreased as mercury was not detected in the estuary in 2015, but the number of exceedances increased marginally and included an additional exceedance of the high guideline for zinc. The addition of polychlorinated biphenyls into the analyte suite revealed that the concentration of Aroclor 2054 at the CBD site exceeded the default guideline. Exceedances of the ANZG default guidelines were generally focused on the Middle Swan Estuary region, exceedance were also observed within the Canning Estuary and Lower Canning River with multiple exceedances of the default guideline value (DGV) and the high guideline value (DV-high) for zinc.

4.1 Site categorisation

Sites were characterised into three categories according to the method developed by Nice (2009) and compared to results from that study (Table 8). It should be noted that the guidelines used in this analysis were the revised ANZG - Toxicant default guideline values for sediment quality (ANZG 2018) and not the Interim Sediment Quality Guidelines employed by Nice (2009). The key difference between the guidelines is a large adjustment of the values for dieldrin, with the ISQG- Low being adjusted from 0.02 ug/kg to the DVG of 2.8 ug/kg, resulting in no exceedances of the DGV in the current study. The remaining trigger levels for contaminants of concern did not change markedly in the revision.

The site categories employed in the current study and Nice (2009) were:

- Category 1 sites: ≥ 3 contaminants exceeded the DGV and/or any number of contaminants exceeded the GV High
- Category 2 sites: 1-2 contaminants exceeded the DGV. No contaminants exceeded the GV High
- Category 3 sites: Contaminants present but at levels below DGV.

Four of the five Category 1 sites in the current study were consistent with those reported in Nice (2009), however Mill Street main drain (site 19) was elevated in the current categorisation to a Category 1 site due to an exceedance of the zinc GV-High and the CBD site (Site 13) was lowered to Category 3 due to no exceedances of either zinc (GV-High) or lead DGV. Additionally, the Belmont Racecourse and Burswood sites were lowered from Category 1 to Category 2 sites, based primarily on the changes in the guideline value for dieldrin. The ISQG for dieldrin was below

the available limit of reporting in Nice (2009), thus all detects in that study resulted in an exceedance and inclusion as a Category 2 site. The change in the guideline value for dieldrin also impacted the number of sites listed as Category 2 and 3. In particular, South Belmont and Baigup, did not exceed the revised DGV for dieldrin and were therefore lowered to Category 3. Other changes included the elevation of Adenia Park and Perth Airport South from Category 3 to Category 2 sites based on exceedances of the lead and zinc DGV.

Table 8. Characterisation of sites. If the criteria were met for either surficial or subsurface sediments then the highest value was applied. * indicates sites that exceed both the DGV and GV-High in the surficial sediment. ss indicates the exceedance was for contaminants in the subsurface profile.

Priority	Site code	Site name	Contaminants of concern			
1	10	Maylands	Cu	Pb	Zn	DDE
1	11	Claisebrook	Cu	Pb	Zn*	DDE
1	17	Bull Creek	Cu	Pb	Zn*	
1	19	Mills Street MD	Zn* ^{ss}	Pb ^{ss}		
1	20	Lower Canning	Pb	Zn*		
2	4	Perth Airport South	Zn	Pb ^{ss}		
2	9	Belmont Race Course	Pb	Zn		
2	12	Burswood	Pb	Zn		
2	13	CBD	PCB			
2	16	Blackwall Reach	Pb			
2	18	Adenia Park	Pb	Zn		
3	1	Blackadder creek				
3	2	Helena River				
3	3	Upper Swan				
3	5	Bayswater MD				
3	6	Baigup				
3	7	Central Belmont				
3	8	South Belmont				
3	14	Melville Waters				
3	15	Applecross Foreshore				

4.3 Metal contaminants

Zinc, copper and lead were shown to exceed the DGV in this study. Additionally, zinc exceeded the GV-High. Exceedances of these guideline values indicate a level where toxic effects may occur (DGV), or toxic effects are likely to occur (GV-High). Whilst many metals are essential elements for many physiological processes in fish and crustaceans, many of which have the ability to regulate the concentration of these metals within their body tissues, toxic effects can occur if the concentration exceeds the ability to store or remove these substances. For metals that are non-essential, such as lead, many invertebrate species do not have a strong ability to regulate, store and/or depurate these contaminants and thus toxic effects may be experienced at much lower concentrations (e.g. Rainbow 2002, Cresswell et al. 2015). The exceedance of the DGV for these metals indicate that toxic effects may be experienced by invertebrates exposed to these sediments.

The data indicate an increase in copper, zinc and lead concentrations at many sites between 2007 and 2015. Stormwater networks and urban drains can be a major source of these metals (e.g. Snowdon and Birch 2004), as such catchment inputs should be evaluated where possible. A review of the surface water and sediment metal data collected within the Canning Estuary catchment since 2007 showed multiple exceedances of surface water guidelines for copper, zinc and less frequently lead (SERCUL 2017a, b, 2019). The sites sampled were situated on multiple drainages which drained either directly or indirectly to the Canning Estuary in the vicinity of sites 17, 18 and 19. Sediment samples also revealed some exceedances of the relevant guidelines. However, no increasing trend in metal concentration in the surface water or sediment was evident (SERCUL 2017a, b, 2019). It is worth noting that the sampling is only completed during the winter months and may not detect any large pulses of contaminated material during infrequent summer rainfall events or ground water discharge during the drier months.

The proportion of fine sediment at many sites within the estuary appear to have increased. The accumulation of fine sediment in the estuary is likely a reflection of a lack of scouring events through these estuary sites, fine sediment and detritus production within the estuary and an ongoing and potentially increasing contribution from the catchment. Generally, smaller sediment particle size and resultant increase in surface area may facilitate increased capacity of the sediment to bind contaminants resulting in a higher concentration in these sediments. Thus, at many sites in the Swan Canning Estuary where the sediment particle size decreased, a higher concentration of a contaminants may be observed (ANZG 2018). For example, at Adenia Park (site 18), a very large increase in sediment concentrations of copper, lead and zinc was observed. At this site, the dominant sediment fraction changed from coarse sand in the 2007 study (500-2000 µm in diameter) to silt (4-62 µm diameter) in the current study.

The use of both zinc and copper in antifouling paints used on vessels within the estuary may be contributing to the observed increase in sediment concentrations. Since the use of tributyl tin based antifouling paints was banned in 1991, zinc and copper paints have become widely used, thus spills, sloughing and diffusing of these

metals could be resulting in release of these metals to the estuary. Additionally, zinc is commonly used as a sacrificial anode for boat motors, marinas and pylons to prevent corrosion.

Lead is a metal that has commonly been used in a wide range of applications, from paints (including marine paints), fuel and exhausts, fishing, batteries, cable sheathing, older TV sets and many others (ANZG 2018). Some sources of lead to environment have been reduced, for example, lead based paints are no longer used in both marine and domestic applications and lead has not been added to fuel since 2002. In relation to the Swan Canning Estuary, the East Perth Power Station which operated from 1916-1981 and the East Perth Gasworks which operated from 1922-1971, may have, prior to their decommissioning, been a significant contributor to lead emissions in the area. Thus, the increase in lead concentrations observed in this study may be a result of the accumulation of lead in sediments from ongoing urban and semi-industrial activities within the catchment and the decreasing sediment particle size throughout the estuary may be contributing to its capture.

4.4 Polycyclic aromatic hydrocarbons

Consistent with the baseline investigation, concentrations of PAHs were highest in the Middle Swan Estuary, between sites 9-13. In comparison to the 2007 study concentrations were largely consistent at most sites, however in the current study concentrations were significantly higher at five sites. The higher concentrations may have been a result of the finer sediment recorded at many sites. Additionally, natural sources, such as fire, or anthropogenic sources, such as the burning of fossil fuels, may contribute to the slight increase in PAHs. The current concentrations of PAHs in the estuary are well below the ANZG default values and are unlikely to be a concern at the sites surveyed. However, the elevated concentrations of PAH at sites 10, 11 and 12 and knowledge of historical contamination issues in the region (Nice, 2013), suggest a high level of caution should be applied when considering any new development likely to cause sediment disturbance.

4.5 Organochlorine pesticides

The organochlorine pesticides DDT, DDE, DDD, dieldrin, aldrin and chlordane continue to be detected in the estuary at low levels. DDE was once again detected at concentrations above the ANZG default value at sites 10 and 11. However, there has been little change in the sediment concentrations of these compounds between the two studies. Only concentrations of dieldrin were significantly different between 2007 and 2015, with concentrations being lower in the current study. The detection of these substances highlights their persistence in the environment and provides further evidence that these compounds may continue to impact the environment for many years after they were banned. Emphasising their persistence these compounds were detected in black bream (Hoeksema, 2014) and western school prawns (Novak and Hoeksema, in press).

4.6 Organophosphorus pesticides

The lack of detection of organophosphorus pesticides in this study, except the single detection of glyphosate at Lower Canning (site 20), is consistent with the study by Nice et al. (2009) which investigated a suite of organophosphorus compounds in surface waters and sediments in the catchment and drainage network of the Swan Canning Estuary and did not detect any of these compounds. Organophosphorus pesticides are highly water soluble, but some, such as glyphosate, do bind to soils (e.g. Peruzzo et al. 2008). Additionally, they can breakdown readily in the environment, for example, the half-life of glyphosate in freshwater was found to be approximately 4.2 days (Vera et al. 2010), while in marine water the half-life has been found to vary enormously (47-315 days) dependant on light and temperature (Mercurio et al. 2014). The single detection of glyphosate at the only freshwater site in the study may indicate recent use of the pesticide near the water way.

4.7 Polychlorinated biphenyls

Polychlorinated biphenyls are persistent organic contaminants that were widely used in the past as electrical transformer fluids, industrial coolants and lubricants. Due to significant environmental human impact they were listed in Annex A of the Stockholm Convention. In the original catchment wide study of contaminants (Nice et al., 2009), PCBs were included in the analyte suite but they were not detected at any sites, presumably as a result of the coarse limits of reporting available at the time, which were higher than the ANZECC Interim Sediment Quality Guidelines. They were not included as an analyte in the subsequent estuary sediment contamination study (Nice, 2009). PCBs were however, detected in the sediment in a subsequent sediment study (Nice 2013) and surface water during trials of passive sampler devices (Fisher 2013).

In the current study, the PCB mixture Aroclor 1254 was detected widely throughout the estuary sediments. In a review of the toxicity of Aroclor mixtures to benthic invertebrates, Finkelstein et al. (2016) determined that Aroclor 1254, along with 1248 and 1260, were the most toxic Aroclor mixtures. In addition to the Aroclor mixture 1254, multiple PCB congeners were detected, of which the most prevalent were the mid-level chlorinated compounds (4-6 Cl atoms) consistent with the Aroclor 1254 mixture detection (Frame et al. 1996). Additionally, two of these congeners, PCB118 and PCB138 have been recognised as the highest concern based on toxicity, frequency of occurrence and abundance (McFarland and Clarke 1989). However, the likelihood of these contaminants causing adverse effect in the Swan Canning Estuary is low given the concentration of total PCBs (here using Aroclor 1254) was considerably less than the ANZG value at all sites, except the CBD site (site 13), where the ANZG default guideline was exceeded. It was expected that PCBs would be most elevated at sites around the East Perth Power station, given the predominant use of PCBs has been in electrical capacitors and transformers. Thus, the exceedance of the guideline value at site 13 is of interest. There is a drain outfall nearby the sampling site and a review of the Department of Water and Environmental Regulation contaminated sites database revealed many listed contaminated sites in the catchment but none where PCBs were the cause of the

listing. However, work by Fisher (2013) using passive sampler devices, detected PCBs in the CBD main drain of which the outfall is in close proximity to site sampled in the current study, suggesting a potential source of PCBs in this catchment. Alternatively, excavation works at the recently commenced Elizabeth Quay development may have inadvertently disturbed contaminated sediment. Further monitoring may establish if elevated PCB concentrations at this site are a persistent issue.

Similar to organochlorine pesticides, the detection of these substances long after bans have been in place highlights their persistence in the environment and provides further evidence that these compounds may continue to impact the environment for many years after they were banned. These compounds were detected in black bream (Hoeksema 2015) and western school prawns (Novak and Hoeksema- in press).

4.8 Redox potential

Redox potential in the surface water was generally high suggesting an oxygenated state. However, at site 26 redox was very low indicative of anoxic conditions. Across the estuary sediment redox potential was above -150 mV a threshold below which sulphate reducing condition may occur (Simpson et al. 2005). Below -300 mV methanogenesis is likely to occur (Pepper and Gentry 2015), a result observed in the subsurface samples from site 22 and 26. The redox results in this study vary considerably from the result observed in Nice (2009) where redox was above -150 mV at all sites. While this may reflect a deterioration of sediment quality at these sites, or the increase in finer sediments at many sites within the estuary, it may also reflect recent antecedent environmental conditions which may have included a period of anoxia, which commonly occurs in the estuary (Baker and Cosgrove 2021).

4.9 Surface and subsurface sediment contamination

The highly variable nature of the surface and subsurface results suggest that sediment contamination was highly heterogenous throughout the top 10 cm of the sediment profile.

Further inspection of the data for the six focal contaminants (i.e. those where there were significant differences between the 2007 and 2015 data) indicated three general but inconsistent patterns:

- 1- There were many occasions where a significantly higher concentration was observed in 2015, but there was no difference between the profiles. The consistency of concentration throughout the profile suggests that there has been a change throughout the profile of potentially long-term exposure to higher contaminant concentrations and/or changes in sediment particle size. This was the most commonly observed pattern between the studies and profiles (Table 9).
- 2- A significantly higher concentration in 2015 and a higher concentration in surface sediment which may indicate more recent contamination has occurred

at the site. This occurred at site 2 (copper, lead and zinc), 10 (copper), and site 16 (copper) (Table 9).

- 3- Significantly higher concentrations in 2015 and a lower concentration the surface profile. This may suggest that a site has been exposed to contaminants early in the intervening period, but that through bioturbation and/or resuspension and transportation of fine contaminant bound material, the contaminant concentration has declined in the upper profile. This was observed at site 4 for copper, lead, zinc and PAHs (Table 9).

The results generally suggest that the surface concentration of contaminants is not a good indicator of subsurface contamination. Therefore, while surface contaminants are useful for comparative monitoring overtime, ascertaining biota exposure in-situ, and the identification of hotspots, they may not be appropriate for guiding risk determination where sediment disturbance is planned. Thus, more detailed profiling should occur to provide baselines to guide those works.

Table 9. Focal contaminants showing sites where a significant difference in concentration between 2007 and 2015 data was observed (S↑ = significantly higher in 2015, S↓ = significantly lower in 2015, nsd = no difference, and blank = not detected). The corresponding difference in the concentration between the surface and subsurface profile in 2015 is shown (↑ = higher in surface profile, ↓ = lower in surface profile, and — = no difference between profiles) Note there was no significant difference for DDE recorded between the two studies. (* denotes contaminants that exceeded the sediment quality guideline.)

Site	Copper*		Lead*		Zinc*		ΣPAH		DDE*		Dieldrin	
	Study	Profile	Study	Profile	Study	Profile	Study	Profile	Study	Profile	Study	Profile
1	S↑	—	S↑	—	nsd		S↑	—			nsd	
2	S↑	↑	S↑	↑	S↑	↑	S↑	—	nsd		nsd	
3	nsd		S↑		nsd		S↑	↑	nsd		nsd	
4	S↑	↓	S↑	↓	S↑	↓	S↑	↓			nsd	
5	S↑	—	S↑	—	S↑	—	nsd					
6	nsd		nsd		nsd		nsd		nsd		nsd	
7	S↑	—	nsd		nsd		nsd					
8	S↑	—	S↑	—	nsd		nsd					
9	S↑	—	nsd		nsd		S↑	↑	nsd		S↓	↑
10	S↑	↑	nsd		nsd		nsd		nsd		nsd	
11	nsd		nsd		nsd		nsd		nsd		S↓	—
12	nsd		nsd		S↓	—	nsd		nsd		nsd	
13	nsd		nsd		nsd		nsd		nsd		nsd	
14	S↑	—	S↑	—	S↑	—	S↓	—				
15	nsd		S↓	—	S↓	—	nsd					
16	S↑	↑	nsd		nsd		nsd		nsd			
17	S↑	—	nsd		nsd		nsd					
18	S↑	—	S↑	—	S↑	—	nsd					
19	S↑	↓	nsd		nsd		nsd		nsd			
20	S↑	↑	nsd		S↑	↓	nsd				nsd	

4.10 Recommendations

The following recommendations are made based on the findings of this study:

- Develop a database of GIS layer to enable information on sediment contamination to be easily accessible and incorporated into planning decisions so that regions where contaminants exceed guidelines, and toxic effects have been determined are not disturbed in the future, or appropriate mitigation measures are implemented.
- To provide contemporary information for management, surficial sediment contamination sampling should be conducted periodically with a maximum 10-year interval. This could be accompanied by a surface water sampling program to provide a comparative assessment. Emergent contaminants (e.g. PFAS) should be incorporated into the analyte suite where analytical capacity at commercial laboratories exists.
- Where development involving sediment disturbance is planned, baseline contaminant information should be collected from multiple depths from a core which ideally should be the depth of the sediment disturbance.

References

- ANZECC, and ARMCANZ. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra:1-103.
- ANZG. 2018. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. *in* A. a. N. Z. G. a. A. s. a. t. governments, editor., Canberra ACT, Australia
- Baker, J. D., and J. J. Cosgrove. 2021. Annual Swan Canning Estuarine data report., Department of Biodiversity, Conservation and Attractions Perth.
- Bisi, T. L., G. Lepoint, A. d. F. Azevedo, P. R. Dorneles, L. Flach, K. Das, O. Malm, and J. Lailson-Brito. 2012. Trophic relationships and mercury biomagnification in Brazilian tropical coastal food webs. *Ecological Indicators* **18**:291-302.
- Cresswell, T., S. L. Simpson, D. Mazumder, P. D. Callaghan, and A. P. Nguyen. 2015. Bioaccumulation kinetics and organ distribution of cadmium and zinc in the freshwater decapod crustacean *Macrobrachium australiense*. *Environmental Science & Technology* **49**:1182-1189.
- Finkelstein, K., T. M. Dillon, and N. Beckvar. 2016. PCB dose-response benthic injury models using equilibrium partitioning.
- Fisher, S. J. 2013. Investigations of polychlorinated biphenyls and other organic contaminants in the waters of the Swan Canning Estuary using passive sampling technology. Department of Water Technical Report prepared for the Swan River Trust, Western Australia.
- Frame, G. M., J. W. Cochran, and S. S. Bøwadt. 1996. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *Journal of High Resolution Chromatography* **19**:657-668.
- Grosell, M., J. Blanchard, K. V. Brix, and R. Gerdes. 2007. Physiology is pivotal for interactions between salinity and acute copper toxicity to fish and invertebrates. *Aquatic Toxicology* **84**:162-172.
- Hoeksema, S. D. 2015. A method for providing consumption guidance for recreational fishing species in the Swan Canning estuary: A pilot study examining Black Bream *Acanthopagrus butcheri*. Department of Parks and Wildlife Western Australia
- McFarland, V. A., and J. U. Clarke. 1989. Environmental occurrence, abundance, and potential toxicity of polychlorinated biphenyl congeners: considerations for a congener-specific analysis. *Environmental Health Perspectives* **81**:225-239.
- Mercurio, P., F. Flores, J. F. Mueller, S. Carter, and A. P. Negri. 2014. Glyphosate persistence in seawater. *Marine Pollution Bulletin* **85**:385-390.
- Mudroch, A., J. M. Azcue, and P. Mudroch. 1997. Physico-chemical analysis of aquatic sediments. Lewis publishers Boca Raton, New York, London, Tokyo.
- Nice, H. E. 2009. A baseline study of contaminants in the sediments of the Swan and Canning estuaries. Department of Water, Western Australia

- Nice, H. E. 2011. preliminary ecotoxicological investigation of Bull Creek. Department of Water, Western Australia.
- Nice, H. E. 2013. Benthic macroinvertebrate survey in the Swan Estuary at Claisebrook. Department of Water Western Australia.
- Nice, H. E., and S. J. Fisher. 2011. Ecotoxicological and bioaccumulation investigations of the Swan Estuary in the vicinity of Claisebrook. Department of Water Western Australia.
- Nice, H. E., M. Grassi, G. Foulsham, B. Morgan, S. J. Evans, and M. Robb. 2009. A baseline study of contaminants in the Swan and Canning catchment drainage system. Department of Water, Western Australia
- Pepper, I. L., and T. J. Gentry. 2015. Chapter 4 - Earth Environments. Pages 59-88 in I. L. Pepper, C. P. Gerba, and T. J. Gentry, editors. Environmental Microbiology (Third Edition). Academic Press, San Diego.
- Peruzzo, P. J., A. A. Porta, and A. E. Ronco. 2008. Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in north pampasic region of Argentina. *Environmental Pollution* **156**:61-66.
- Rainbow, P. S. 2002. Trace metal concentrations in aquatic invertebrates: why and so what? *Environmental Pollution* **120**:497-507.
- SERCUL. 2017a. Water and sediment quality in the City of Canning Bull Creek East Catchment - Winter - Spring 2016. SERCUL, Beckenham.
- SERCUL. 2017b. Water quality in the Bannister Creek Catchment. SERCUL, Beckenham.
- SERCUL. 2019. Water and sediment quality in the Bull Creek catchment and City of Melville lakes 2018. SERCUL, Beckenham, Western Australia
- Simpson, S. L., G. E. Batley, A. A. Chariton, J. L. Stauber, C. K. King, J. C. Chapman, R. V. Hyne, S. A. Gale, A. C. Roach, and W. A. Maher. 2005. Handbook for sediment quality assessment. Centre for Environmental Contaminants Research Bangor, NSW.
- Snowdon, R., and G. F. Birch. 2004. The nature and distribution of copper, lead, and zinc in soils of a highly urbanised sub-catchment (Iron Cove) of Port Jackson, Sydney. *Soil Research* **42**:329-338.
- Vera, M. S., L. Lagomarsino, M. Sylvester, G. L. Pérez, P. Rodríguez, H. Mugni, R. Sinistro, M. Ferraro, C. Bonetto, and H. Zagarese. 2010. New evidences of Roundup®(glyphosate formulation) impact on the periphyton community and the water quality of freshwater ecosystems. *Ecotoxicology* **19**:710-721.