USING SEDIMENT CORES TO RECONSTRUCT HISTORICAL POLLUTION RECORDS

DIGGING UP THE YARRA'S DIRTY PAST

Anna Mariko Lintern

BA/BEng (Hons.) (Monash University)

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"…everything has a past. Everything – a person, an object, a word, everything. If you don't know the past, you can't understand the present and plan properly for the future."

— Chaim Potok, *Davita's Harp*

"… it is worth remembering that our definitions are abstractions from reality, and reality is much more complicated than our definitions can be, and rather than trying to fit reality into the abstraction, we should adapt the definitions to reality. "

— Yehuda Bauer, *On the Holocaust and Other Genocides*

Abstract

Despite the increasing threat of flooding due to climate change, there is limited understanding of the level of contamination of flood deposits, and their risk to humans and the environment. It is expected that sediment cores can provide a better understanding of the contaminants deposited by floods, because sediment cores can preserve both the pollution and flood histories of aquatic systems. This PhD thesis aims to use sediment cores to identify pollutant levels (heavy metal concentrations) in sediments deposited by past fluvial floods. The Yarra River, which flows through a metropolitan area (Melbourne) in South-East Australia is used as a case study, and contaminant levels within fluvial flood deposits during the 20th century are identified in sediment cores from two floodplain lakes (billabongs).

First, overall pollution trends within the Yarra River billabongs are explored. It is found that current sediment quality trigger values used in Australia do not reflect background heavy metal concentrations in the Yarra River billabongs. This highlights the need to use sediment cores to identify the background conditions of aquatic systems, when developing environmental management targets, instead of relying on generic trigger values. Also, urban stormwater from purely residential catchments appears to result in heavy metal pollution of aquatic systems. Although the installation of a stormwater treatment wetland has coincided with a slight decrease in heavy metal levels within one of the billabongs, background levels have not been restored.

Second, two methods for identifying discrete flood deposits within sediment cores are presented. One method utilises the elemental composition of sediments, a flood proxy not previously sufficiently explored, to identify flood layers. The historical flood records reconstructed using billabong sediment cores can be used to infer that flooding frequency of the Yarra River has decreased through the 20th century. These reconstructed records were checked using measured flow data

An uncertainty framework for using sediment cores to obtain historical pollution records is also presented. The greatest source of uncertainty is the assumption that all metals entering the aquatic system are deposited on the sediment bed. Observations during a 12-month field monitoring period indicate that whilst there may be a discrepancy between the total mass of metal inputs and total mass of metals deposited on the bed sediment, they vary throughout the year in a similar manner. These results suggest that sediment core heavy metal profiles are indicative of historical pollution trends in the aquatic system.

The thesis also demonstrates how high resolution historical pollution and hydrologic trends, both reconstructed using sediment cores, can be used together to determine the pollution sources of aquatic systems. This shows that the main source of pollution in billabongs can vary greatly even if these billabongs are close to each other spatially. Whilst one billabong had higher heavy metal concentrations in flood-deposited sediments, the other had higher concentrations in sediments that were not deposited by floods. Cumulative distribution functions of heavy metal concentrations (lead and zinc) in sediments deposited by Yarra River floods at the two billabongs over the 20th century are also presented. These functions could be used to help predict the contaminant deposition by future floods of the Yarra River at the two billabongs.

The methods presented in this thesis can be applied to other river catchments to better understand their sources of contamination; in particular, the importance of flooding in the deposition of contaminants in floodplains and billabongs. Furthermore, having these data of heavy metal concentrations in flood deposits will better equip us for the future, enabling us to better understand the risks associated with fluvial floods, and the management strategies that are required.

General Declaration (Thesis including published works)

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes 1 original paper published in peer reviewed journals and 4 unpublished publications. The core theme of the thesis is water quality. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the Department of Civil Engineering under the supervision of Dr David McCarthy, Professor Ana Deletic, Dr Paul Leahy (EPA Victoria) and Professor Henk Heijnis (Institute for Environmental Research at the Australian Nuclear Science and Technology Organisation). The contributions of individuals other than my supervisors are detailed in the tables below.

My contribution to the work involved the following:

Thesis chapter	Publication title	Publication status	Nature and extent (%) of students contribution
4	Digging up the dirty past: evidence for stormwater's contribution to pollution of an urban floodplain lake	Published	Student's contribution: 80% Initiation, ideas, experimental work, data analysis, interpretation and write up were conducted by the student. Heavy metals and POPs analyses were outsourced to NATA accredited laboratories (ALS and National Measurement Institute). The manuscript was revised by a professional editor, Alan Crosier (Text minding manager with Mind Your Way). No guidance was given beyond that of English expression.
4	Using sediment cores to establish targets for the remediation of aquatic environments	Accepted with major revisions	Student's contribution: 75% Ideas, data analysis, interpretation and write up were conducted by the student. Marion Anderson is listed as a co-author. She conducted the data collection. Namely, she sampled the cores and analysed samples for heavy metals.

In addition, three publications that are currently under internal review have been included in the thesis.

Thesis chapter	Publication title	Publication status	Nature and extent (%) of students contribution
5	Using sediment cores to identify historical changes in floodplain lake hydrology	Under internal review	Student's contribution: 70% Initiation, ideas, data collection, data analysis, interpretation and write up were conducted by the student. Atun Zawadzki and Geraldine Jacobsen are listed as co-authors. They conducted the calculations for developing the ^{210}Pb and ^{14}C chronologies. Patricia Gadd is also a co-author. She processed the data collected using the ITRAX core scanner. Simon Connor is also a co-author. He assisted in the preparation of pollen slides and the analysis of these slides. Preparation of pollen slides was outsourced to the Palynology Laboratory at Monash University.
6	Uncertainties in pollution data from sedimentary records	Under internal review	Student's contribution: 70% Initiation, ideas, data collection, data analysis, interpretation and write up were conducted by the student. Patricia Gadd is a co-author. She processed the data collected using the ITRAX core scanner.
7	Recreating historical data from sediment cores; to protect aquatic environments	Under internal review	Student's contribution: 70% Initiation, ideas, data collection, data analysis, interpretation and write up were conducted by the student. Atun Zawadzki and Geraldine Jacobsen are co-authors. They conducted the calculations for developing the ^{210}Pb and ^{14}C chronologies. Patricia Gadd is a co-author. She processed the data collected using the ITRAX core scanner.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

I have not renumbered sections, nor have changed the referencing format of submitted or published papers in order to generate a consistent presentation within the thesis.

Student signature: [redacted] **Date:** 19/08/2015

The undersigned hereby certifies that the above declaration correctly reflects the nature and extent of the student and co-authors' contributions to this work.

Main Supervisor signature: [redacted] **Date:** 19/08/2015

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CHAPTER 1
INTRODUCTION

1.1 Introduction

River floods in both urban and rural areas are a threat to society. Traditional flood risk management measures have focused on protecting infrastructure and society from the large volumes of water that are mobilised (Emdad Haque, 2000; Merz *et al.*, 2010; Ockenfeld *et al.*, 2005; Wheater, 2002). However, the poor quality of flood waters, and the pollutants that can be deposited in inundated areas after flood waters recede are also of increasing concern (Ockenfeld *et al.*, 2005). Following the dispersal of pollutants in areas inundated by the 2002 Elbe River flood (Abraham and Wenderoth, 2005; Wölz *et al.*, 2011), researchers and government organizations around the world have begun to consider human health risks from contact with flood water and flood sediment deposits (Hilscherova *et al.*, 2007; Pulkrabová *et al.*, 2008; Schulz *et al.*, 2009; Stuyt *et al.*, 2007; Umlauf *et al.*, 2005; ten Veldhuis *et al.*, 2010). There are conflicting studies however, with some research suggesting that fluvial flood waters have not deposited contaminants in inundated areas (e.g., Maliszewska-Kordybach *et al.*, 2012). Thus, there is still not enough known about the quality of flood waters and the risk of these flood events to both humans and the natural environment from a water quality point of view.

Whilst long term datasets and established prediction methods exist for estimating flood flow rates (including flood frequency analysis, rainfall-runoff models and hydrodynamic models); knowledge of pollutant levels in flood water is limited (Sauer *et al.*, 2007; Wheater, 2002; Zonta *et al.*, 2005). Indeed, Cánovas *et al.* (2008) recognize that more accurate water quality sampling of floods is needed to assess the importance of these events from a risk management perspective. Most water quality datasets are relatively short, spanning 30-50 years (Benito *et al.*, 2004) and large flood events are often not included in these short records. This is not only due to their infrequency (Walling *et al.*, 1996) but also due to the difficulties associated with obtaining safe and accurate measurements during flood flows (Zak *et al.*, 2009; Zonta *et al.*, 2005). Although there are studies that have sampled flood waters (Caetano *et al.*, 2006), or flood-deposited sediments (Albering *et al.*, 1999; Brown and Chanson, 2012), these studies often include only a handful of flood events.

With climate change looming, threatening increased flooding frequency around the globe (Cofalla *et al.*, 2012; Kundzewicz *et al.*, 2008; Whitehead *et al.*, 2009), it is essential that these data and knowledge gaps are filled. Adequate and cost effective mitigation strategies are possible only if the risks associated with the quality of flood waters are adequately characterised and the main factors are understood. While the implementation of long-term monitoring schemes should be encouraged and

are occurring (Zonta *et al.*, 2005), it will take many decades to collect enough data to implement statistical analyses for flood water and sediment quality estimation.

This problem could be overcome by using sediment cores to trace flood and pollution history (Brown *et al.*, 2000; Walling *et al.*, 1996; Wolfe *et al.*, 2006). Sediment cores from the beds of lakes, estuaries and oceans can retain the depositional history of that environment. Cores have therefore been used to piece together the past in a wide range of studies, such as the reconstruction of fire histories (e.g., Whitlock *et al.*, 2010), studies of megafaunal extinction (e.g., Rule *et al.*, 2012; Turney *et al.*, 2008), and historical ecology of aquatic systems (e.g., Leahy *et al.*, 2005). Sediment cores also have the potential to preserve historical flood deposits and in fact, they have already been used to conduct flood frequency analysis for the prediction of flood flow rates (Baker, 2008; Benito *et al.*, 2004; Wolfe *et al.*, 2006). It is therefore hypothesized that information from sediment cores can be used to identify the quality of sediments deposited by fluvial floods, and thereby understand the water quality of flood events.

The main aim of this PhD is to use sediment cores to identify the historical pollutant concentrations within sediments deposited by overbank fluvial floods. The Yarra River (located in Victoria, Australia) is used as a case study. A dataset of the quality of flood deposits is developed using the contaminant levels detected in flood-deposited sediments in sediment cores from two billabongs (also known as oxbow lakes or floodplain lakes) in the Yarra River catchment (Bolin Billabong and Willsmere Billabong, both within metropolitan Melbourne). As such, the main outputs of this project are:

- a demonstration of how pollution mitigation methods can be assessed using these data from sediment cores,
- an uncertainty framework for developing historical pollution trends of aquatic systems using sediment cores,
- a demonstration of how sediment cores can be used to obtain these data of contaminants in flood deposits,
- a better understanding of the importance of fluvial flood deposits in billabong pollution, and
- a dataset of heavy metal concentrations in past flood sediment deposits**.**

1.2 Thesis structure

The thesis consists of eight chapters in total (as depicted in Figure 1.1 and discussed briefly below). The four main chapters of this thesis (Chapters 4 to 7) contain publications that have been published, accepted with major revisions, or are currently under internal review. Where necessary, additional discussions have also been included to supplement these publications (in Chapters 4, 5 and 7). The reference lists provided at the end of Chapters 4, 5 and 7 therefore includes the references from both the publications and from the additional discussions. The supplementary material accompanying these publications are provided in Appendix A. The structure of this thesis reflects the plan of the project.

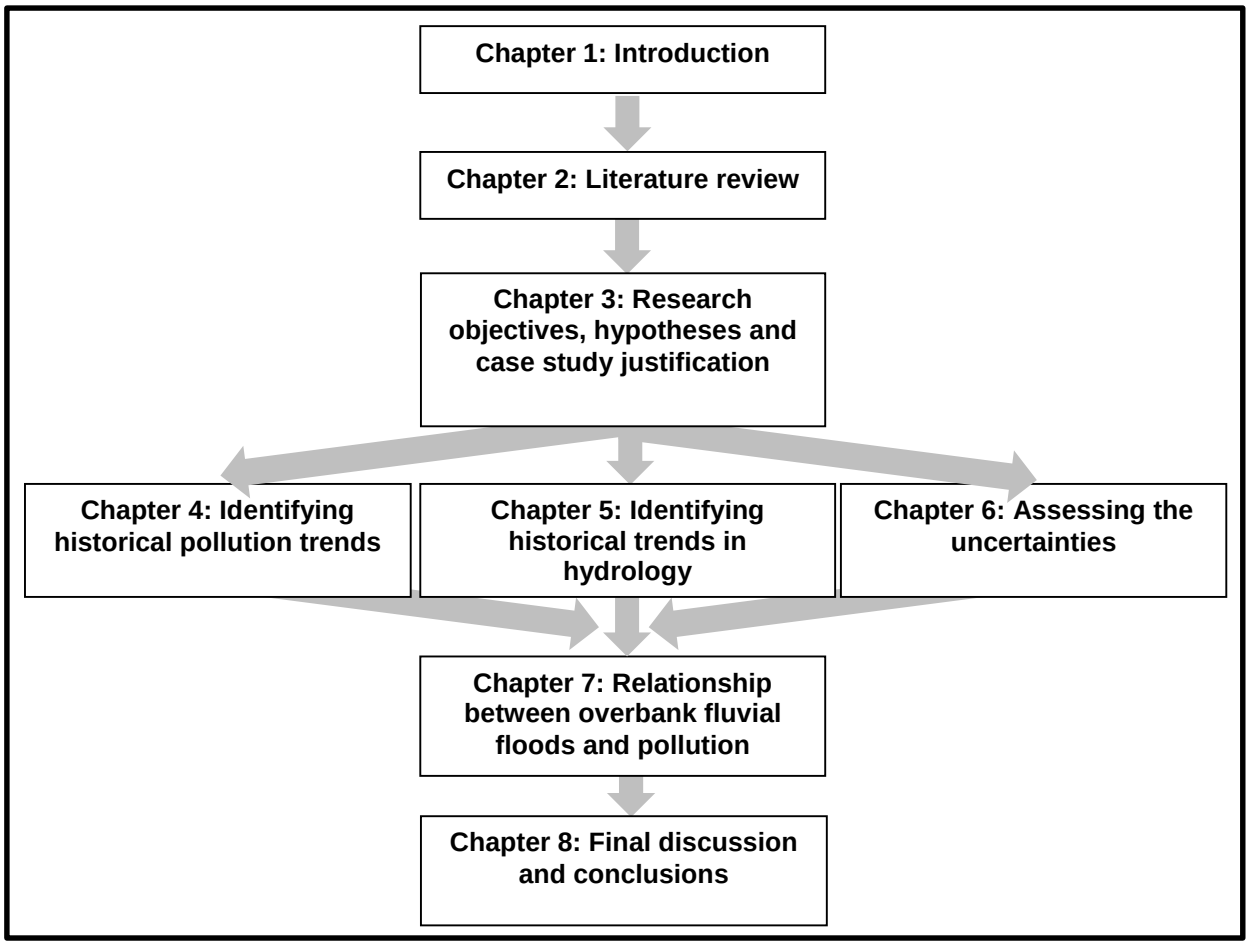

Figure 1.1: Thesis structure

Chapter 1: Introduction

This chapter outlines and justifies the thesis topic by first highlighting the need for more understanding of the contaminants levels deposited by fluvial floods. It then proposes the use of sediment cores from billabongs to gain this understanding. This chapter also provides an outline of the thesis and a discussion of the thesis scope.

Chapter 2: Literature review

This chapter provides an overview of existing methods used to identify pollutant concentrations in flood deposits. It then discusses how sediment cores from aquatic environments are currently used to identify historical trends in pollutant fluxes and flood frequencies, and knowledge gaps in the use of sediment cores for identifying these historical pollution and flood trends.

Chapter 3: Research objectives, hypotheses and case study justification

This chapter presents the four main research objectives for the project alongside their corresponding research questions and hypotheses. Also presented in this chapter is a justification of the use of the Yarra River catchment and its billabongs as a case study.

Chapter 4: Identifying historical pollution trends in the Yarra River billabongs

This chapter discusses the historical pollution trends in the Yarra River billabongs, which have been identified using sediment cores. It consists of two publications: "Using sediment cores to establish targets for the remediation of aquatic environments" (accepted with major revisions to *Water Science and Technology*) and "Digging up the dirty past: evidence for stormwater's contribution to pollution of an urban floodplain lake" (published in *Marine and Freshwater Research*). The paper accepted to *Water Science and Technology* will be cited through the thesis as Lintern *et al.*, (submitted). This chapter also contains a brief discussion that justifies why the Yarra Flats Billabong sedimentary records were not used in this thesis.

Chapter 5: Identifying historical trends in the hydrology of the Yarra River billabongs

This chapter discusses the use of sediment cores to identify the historical trends in hydrology of the Yarra River billabongs. This chapter consists of a publication currently under internal review for submission to *Science of the Total Environment*, titled "Using sediment cores to identify historical changes in floodplain lake hydrology". This publication will be cited throughout the thesis as Lintern *et al.* (in preparation-a). The second half of this chapter discusses the use of sediment mixing models for identifying flood-deposits in sediment cores.

Chapter 6: Assessing the uncertainties

Discussed in this chapter are the uncertainties associated with using sediment cores to understand historical pollution trends of water bodies. This chapter is comprised of a publication currently under internal review for submission to *Quaternary Science Reviews*, titled "Uncertainties in historical pollution data from sedimentary records". This publication is cited as Lintern *et al.* (in preparation-b) in the thesis.

Chapter 7: Identifying the relationship between overbank fluvial floods and heavy metal pollution in billabongs

This chapter builds on the findings of the previous three chapters and discusses how sediment cores were used to determine the contamination levels of flood-deposited sediments. The first part of this chapter is a publication under internal review titled "Recreating historical data from sediment cores; to protect aquatic environments", to be submitted to *Water Research*. This publication is cited as Lintern *et al.* (in preparation-c) throughout the thesis. The second half of this chapter is not a publication. It presents cumulative distribution functions of heavy metal concentrations (lead; Pb and zinc; Zn) in flood-deposited sediments in the Yarra River billabongs. It also presents the relationship between heavy metal concentrations (Pb and Zn) deposited in the Yarra River billabongs and Yarra River flows.

Chapter 8: Final discussion and conclusions

The final chapter of the thesis first identifies strengths and weaknesses in the thesis, and is followed by a summary of the key findings of the thesis. The chapter concludes with suggested areas of further research.

1.3 Thesis scope

This thesis will not be reconstructing historical pollutant concentrations or masses in the water column of aquatic systems. Instead, the 'historical pollution records' in the title of the thesis are presented as pollutant levels in the bed sediments of aquatic systems. The choice of heavy metals as the main focus of this thesis is justified in Chapter 2 and Chapter 4.

Above, it was discussed that a dataset of heavy metal concentrations in past flood deposits will be one of the main outputs of this thesis. This thesis will not provide a list of historical Yarra River flood events, with the pollutants concentration of the sediment deposits of each of these events. Instead an

overview of the distribution and general trends in pollutant levels deposited by floods of the Yarra River is provided. This will enhance understanding of the importance of flood events in contributing pollutants to river floodplains. Furthermore, due to the lack of overbank floods of the Yarra River during the PhD candidature, this dataset (and as such, the methodology used to create this dataset) is not validated using field measurements of pollutant levels in flood-deposited sediments.

Finally, whilst pollutant deposition by fluvial floods is investigated in this thesis, neither flood modelling nor contaminant transport modelling will be conducted. Rather than obtaining data by simulating flood events, this thesis intends to demonstrate how historical data can be collected using sediment cores, and highlight how these historical data can be used in environmental management and flood-risk management.

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CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

As discussed in the previous chapter, there is a pressing need to enhance our understanding of contaminant deposition by fluvial floods, for the protection of both the natural riparian environment and human health. The following literature review has four parts. The first section introduces and summarises methods that are currently available for determining pollutant levels in fluvial flood deposits. The second and third sections discuss the use of sediment cores from aquatic environments to identify historical pollution trends and historical hydrologic trends. These discussions also highlight knowledge gaps in the two areas. Finally, previous studies that have attempted to determine the quality of historical flood deposits using sedimentary records will be evaluated.

2.2 Methods used to estimate the quality of flood-deposited sediments

The quality of flood-deposited sediments can be better understood using measured data of contaminant levels in the sediments deposited by floods. However, as previously highlighted in Chapter 1, measurements of flood-deposited sediments are not available for most sites and the datasets that are available often cover only a relatively short time span such as one flood event (Abraham and Wenderoth, 2005; Pulkrabová *et al.*, 2008; Wölz *et al.*, 2011), or one decade (Hilscherova *et al.*, 2007). More long-term datasets are needed to understand the processes governing contaminant deposition by fluvial floods. Even if monitoring projects are implemented now, due to the infrequency of floods (Walling *et al.*, 1996), it will be many years before a representative sample of flood-deposited sediments can be sampled. Furthermore, long-term monitoring projects can not only be cost-prohibitive, but can also be interrupted when economic climates change (Caughlan and Oakley, 2001).

Although models could also be used to predict the deposition of contaminants in flood-inundated areas, there is a limited availability of models that can meet this objective. Two examples of such predictive models that do exist are Telemac2D (Schulz *et al.*, 2009) and TREX (Velleux *et al.*, 2008). These are both physically-based distributed models that consist of three modules: hydrologic, sediment transport and chemical transport.

Telemac2D was used by Schulz *et al.* (2009) to predict the lead (Pb), mercury (Hg) and arsenic (As) contamination of an area inundated by a hypothetical 200 year Average Recurrence Interval (ARI) flood of the Elbe River in Germany. This model consists of a hydrodynamic (Telemac-2D), sediment transport (Subief-2D) and water quality component (a user defined model). The results of the hydrodynamic module are based on the solution of the Saint-Venant equations. The solution of these

equations feeds into the sediment transport component, which takes into account the deposition and erosion of sediments. However, this model contains a number of parameters that require calibration (e.g., the critical deposition velocity, u_d* or the friction velocity, *u**). Boundary (pollutant concentrations measured in the water column) and initial conditions (pollutant concentrations in the top soil of the studied areas) are also required when applying the model. For the Elbe River study, the boundary and initial conditions were based on pollutant concentrations measured during a flood of the Elbe River in March 2006. Although Telemac2D models the transport and deposition of pollutants in rivers and floodplains, it does not address the problem of pollutant generation within the catchment and the transport of these pollutants to the stream. This is a problem because pollutant loading can be highly variable both temporally and spatially (Ambrose *et al.*, 1993).

In contrast to Telemac2D, TREX (Velleux *et al.*, 2008) simulates the transfer of flow and contaminants between the floodplain and the main river channel. Pollutant load generation is predicted using Universal Soil Loss Equation (USLE) parameters (such as USLE soil management, erodibility and soil cover factors) and parameters representing the association of contaminants to these particulates. In the hydrologic module, overland flow is determined using the two dimensional diffusive wave approximation, and in-stream flow is approximated using the one dimensional diffusive wave approximation. Both overland (2D) and in-stream (1D) physical sediment transport is modelled using advection-dispersion and erosion-deposition processes. The chemical transport component of contaminants is modelled by the processes of chemical partitioning, advection-diffusion, erosion-deposition and infiltration. However, this model still requires boundary and initial conditions. These are flow data, catchment soil and bed sediment pollutant concentrations, and water column pollutant concentrations.

The limitation of both models is that their application requires extensive field data for not only their implementation (initial and boundary conditions), but also for their calibration. Indeed, others have highlighted that there is a lack of data for the development, use and calibration of pollutant deposition models (Letcher *et al.*, 2002; Newham and Drewry, 2006). This problem could be addressed by developing a new method for generating long-term datasets that can be used for initial and boundary conditions as well as calibration/validation datasets in the modelling of contaminants in flood-deposited sediments.

2.3 Using sediment cores to identify historical changes in the contamination of aquatic systems

Previous studies have used sediment cores from aquatic systems such as oceans, lakes, floodplains and estuaries to understand historical water quality changes (e.g., Cundy *et al.*, 1997; Latimer *et al.*, 2003; Moriwaki *et al.*, 2005; Yamashita *et al.*, 2000). These investigations involve the extraction of sediment cores from the beds of lentic environments and the creation of dated vertical contaminant profiles.

2.3.1 Contaminants studied

Heavy metals

Heavy metals are defined as metals having a specific density of more than 5 g/cm^3 in either the particulate or soluble form (Järup, 2003). Heavy metals can accumulate at the beds of aquatic environments due to their association with particulate matter (Bábek *et al.*, 2011; Chon *et al.*, 2012; Förstner and Wittman, 1981; Kolak *et al.*, 1998) and as a result, a significant amount of the heavy metals entering aquatic environments are believed to be retained in the bed sediments. This retention of heavy metals in the bed of aquatic systems is of concern due to the fact that they can remain indefinitely in the bed sediments, and be later resuspended by physical turbulence, or remobilized due to biological and chemical processes within the aquatic system (Hudson-Edwards *et al.*, 1998; Zoumis *et al.*, 2001).

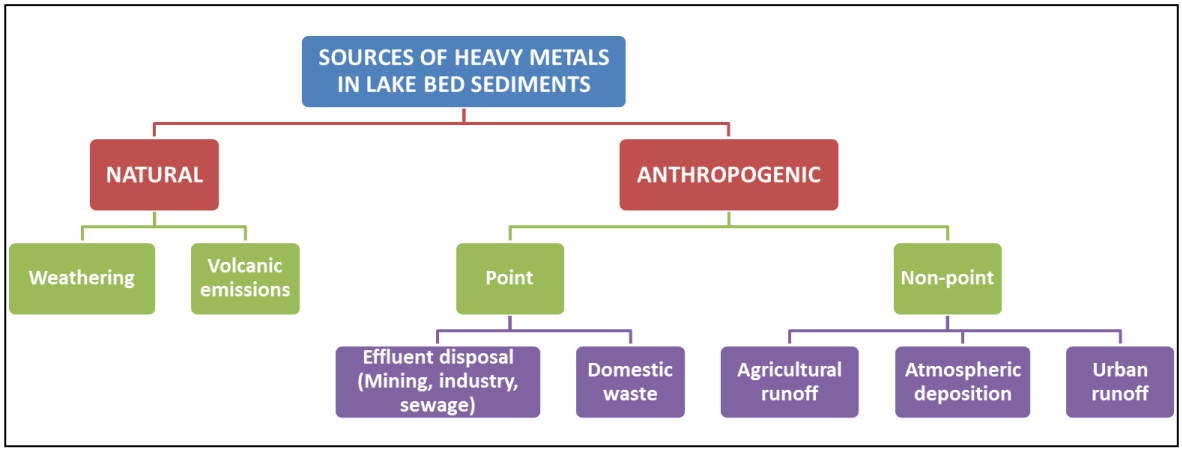

Figure 2.1: Sources of heavy metals in aquatic environments *(*Bradl, 2005; Förstner and Wittman, 1981; Li *et al.*, 2001; Rice, 1999; Ruiz-Fernández, Sanchez-Cabeza, *et al.*, 2012; Swales *et al.*, 2002; Vane *et al.*, 2011).

Heavy metals are also studied in sediment cores due to their relationship with various anthropogenic activities (Figure 2.1). Studies of sediment core heavy metal profiles have therefore been used to identify the main factors affecting the pollution of aquatic systems (Harrison *et al.*, 2003; Swales *et al.*,

2002; Valette-Silver, 1993). For example, Bellucci *et al.* (2012) used dated sediment cores from Augusta Bay in Italy to assess long-term temporal changes in Hg levels in the bay. They found that the Hg levels in the sediment core reached a peak in the 1970s. The decrease in Hg levels after this date has been attributed to controls on mercury emission, such as a demercurization plant and improved waste treatment processes at nearby factories (Bellucci *et al.*, 2012).

Generally, studies rely on prior understanding of the history of catchments to explain the sediment core heavy metal profiles (e.g., Callaway *et al.*, 1998; Meybeck *et al.*, 2007; Santschi *et al.*, 2001). For example, Tang *et al.* (2008) inferred that high heavy metal concentrations (copper; Cu, Pb, zinc; Zn) in sediment cores (dating from the mid-20th century to the end of the 20th century) obtained from Victoria Harbour, Hong Kong were primarily due to urbanisation, namely, the deleterious impact of surface runoff, sewage discharge and industrial inputs into the harbour. These inferences were based on (1) the correlation between the timing of the increase in metals in the sedimentary record to the timing of urbanisation and industrialisation known to have taken place in the region, and (2) the greater concentrations of heavy metals in cores taken closer to the densely urbanised areas compared to cores taken further away.

Sometimes there is limited knowledge about the history of an aquatic system's catchment. This makes it difficult to link pollution profiles to historical catchment changes. In such cases, trends in physical, biological and chemical properties of the sediments within the core can be used to help infer the historical catchment changes, which can then be linked to the pollution profiles. For example, Thevenon *et al.* (2013) identified a correlation between sediment characteristics (elemental composition) in a sedimentary record from three lakes connected to the Aare River in Switzerland, and the construction of reservoirs in the river catchment upstream of the lakes. Changes in elemental composition in the sediment core that were indicative of decreasing streamflow due to reservoir construction, correlated with a decrease in heavy metal concentrations in the sediment core. This was interpreted as evidence that upstream sources are the main source of these heavy metals and river flow is the main transport process of these metals into downstream lakes

Persistent organic pollutants

Persistent organic pollutants (POPs) are defined as toxic organic compounds that have the potential to bioaccumulate, and that can be subjected to long-range atmospheric transportation and deposition (Vallack *et al.*, 1998). Other criteria used to define POPs include a half-life in water greater than two months, and in sediment greater than 6 months (International POPs Elimination Network, 2011). POPs can have both natural and anthropogenic sources, as summarized in Table 2.1. The presence of these

compounds in the environment is of concern because of their detrimental effect on living organisms, particularly the endocrine and reproductive systems (Barakat *et al.*, 2012; Burgess *et al.*, 2003).

Table 2.1: POPs and their sources (Barakat *et al.*, 2012; Gevao *et al.*, 1999; Moon *et al.*, 2009; Piazza *et al.*, 2009; Ravindra *et al.*, 2008; Ruiz-Fernández, Sprovieri, *et al.*, 2012; Taylor *et al.*, 2004; Vallack *et al.*, 1998; Vane *et al.*, 2011; Yamashita *et al.*, 2000; Zennegg *et al.*, 2007).

Contaminant	Source		Year of commercialization
	Natural	**Anthropogenic**	
Polycyclic aromatic hydrocarbons (PAHs)	Deterioration of organic matter in anoxic soils (e.g., Perylene) Combustion of organic matter (forest fires, volcanic eruptions)	Use in pesticides Fuel combustion Waste incineration Industrial processes	
Polychlorinated biphenyls (PCBs)	No known sources	Use in transformers and dielectric capacitors Combustion Coal and wood burning Paints and solvents (ship coating, carbon free copy papers) Softener for plastics and glues	1929
Organochlorine pesticides (OCPs)	No known sources	Insecticides, fungicides	DDT (1939), chlordane (1945), lindane (1942), heptachlor (1951)
Polychlorinated naphthalenes (PCNs)	No known sources	Industrial synthesis (use in transformers, capacitors) Waste combustion Wood and coal combustion Metallurgical Processes	1919
Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)	No known sources	Degradation products of nonylphenol polyethoxylates (used as surfactants) Herbicides Combustion	
Nonylphenols (NPs)	No known sources	Use in detergents, paints and emulsifying agents	

Due to their persistence in bed sediments, many studies have attempted to identify vertical trends in POPs through sediment cores (Blais and Muir, 2001). The substances that have been addressed in such studies include: PAHs, PCBs, TPHs, TAHs, OCPs, PCNs, PCDD/Fs, NPs (Gevao *et al.*, 1997, 1999; Latimer *et al.*, 2003; Mai *et al.*, 2004; Moon *et al.*, 2009; Taylor *et al.*, 2004; Vane *et al.*, 2011; Wei *et al.*, 2008; Yamashita *et al.*, 2000; Zennegg *et al.*, 2007). Studying these pollutants in dated sediment cores allow us to understand the impact of various catchment changes over time (such as urbanization, industrialization or agricultural practices) on the contamination of aquatic environments by POPs, as well as the effectiveness of water quality management strategies (Zennegg *et al.*, 2007).

Although the trends and patterns of POPs found in dated sediment cores vary depending on the specific contaminant and location being studied (Table 2.2), some generalisations can be made about these trends. Most studies find an increase in POPs concentrations in the early to mid-20th century,

corresponding to their introduction and proliferation, followed by decreasing concentrations in the late 20th century. For example, in a study of PCB contamination in Las Matas lagoon in Mexico, Ruiz-Fernandez *et al.* (2012) found that there was an increase in PCB levels after 1940 which was attributed to the increasing use of synthetic PCBs. There were then decreasing levels after 1990, which were linked to the introduction of environmental regulations by the Mexican government in the Las Matas lagoon area from the early 1990s. It must be noted however that there are exceptions to this general pattern. For example, in a study of dated sediments cores from the Pearl River Estuary (China), there was no stabilization or decrease in PCB levels detected at the top of the core and this was hypothesized to be a result of the lack of regulation, or the influx of pre-contaminated eroded soils into the estuary (Mai *et al.*, 2004).

Table 2.2: Vertical trends in POPs levels in sediment cores (Gevao *et al.*, 1999; Hatt *et al.*, 2004; Mai *et al.*, 2004; Moon *et al.*, 2009; Vane *et al.*, 2011; Wei *et al.*, 2008; Yamashita *et al.*, 2000; Zennegg *et al.*, 2007).

Compound	Location cored	Year of increase in pollutant level	Period of peak pollutant level	Reasons identified for increase	Reasons for decrease
PAHs	Tokyo Bay (Japan)	1907	Early 1980s	Fossil fuel combustion	Emissions controls
	Clyde Estuary (Scotland)	1915	1950s	Development of industry at Clyde Estuary (particularly ship-building)	Decline of ship-building industry
PCBs	Clyde Estuary (Scotland)	1950s	1965-1977	Industrial activities (use in transformers, paper production)	Ban on PCB manufacture in 1977
	Espejo de los Lirios (Mexico)	1949	1977, and surface sediment	Introduction and use of PCBs in closed and open systems. Post 1970s industrial development.	Regulation in late 1970s
	Pearl River Delta (China)	1930s-1940s	Surface sediment	Industrial development and import of electrical goods containing PCBs	
OCPs	Homebush (Australia)	1950	1970	Manufacturing of compounds in area.	Regulation of use of OCPs.
	Hong Kong coastal waters	Late 1930s/early 1940s	Late 1960s	Use of OCPs in China and Hong Kong	No significant decrease
NPs	Tokyo Bay (Japan)	Mid-1960s	Mid-1980s	Cleaning products and industrial processing	No significant decrease after peak
	Masan Bay (Korea)	1995	2000	Discharge of wastewater	Upgrade of wastewater treatment plant to include activated sludge treatment
PCDDs/ PCDFs	Greifensee (Switzerland)	1930	1960	Increasing road traffic volume, introduction of municipal waste incineration, use of organochlorine chemicals (e.g., phenols, herbicides)	Municipal waste incineration emission controls, extension of wastewater treatment plants, ban on use of organochlorine chemicals
	Masan Bay (Korea)	1995	2000	Discharge of wastewater	Upgrade of wastewater treatment plant to include activated sludge treatment
PCNs	Esthwaite Water (North West England)	Early 1940s	Late 1950s/early 1960s	Use in insulation and electrical equipment. Present as impurities in PCBs.	Restriction in production and use of PCN in the UK
	Tokyo Bay (Japan)	1960s	1980	Use in PCB mixtures, MSWI, floor finishing mixtures	Emissions controls

2.3.2 Practical application of the historical pollution trends identified using sediment cores

Identifying historical trends of contaminant fluxes into aquatic systems is important because this understanding can aid in the restoration and management of polluted aquatic environments. Firstly, if the sedimentary records contain sediments deposited prior to catchment disturbance, site-specific 'background' levels of metals and POPs can be determined (Bennion *et al.*, 2011; Förstner and Salomons, 1980; Fukue *et al.*, 2006). Current water quality management guidelines in Australia and New Zealand (ANZECC/ARMCANZ, 2000) state that the contamination level of aquatic systems should be assessed by comparing environmental monitoring data with background contaminant levels (Batley and Maher, 2001; Simpson *et al.*, 2005). Recently deposited sediments from pristine lake and rivers generally cannot be used to identify these background contaminant levels, as these sites can be contaminated by global atmospheric deposition (Heyvaert *et al.*, 2000; Ouellet and Jones, 1983).

When site-specific background conditions are not known, the Australian and New Zealand water quality management guidelines recommends the use of default guideline values (ANZECC/ARMCANZ, 2000). Two values are provided, 'low' for low probability of toxic effects and 'high' for medium probability of toxic effects. Current sediment quality default guideline values are based on a database of heavy metal concentrations and their corresponding ecosystem effects from North America (Long *et al.*, 1995). Thus, these guidelines are not based on the ecosystem responses in Australia and New Zealand, and they do not take into account the natural background levels of heavy metals. Metal profiles obtained from sedimentary records can be used to identify site-specific background metal and POPs values for aquatic systems. Batley and Maher (2001) argue that background concentrations should not be used as sediment quality trigger values because they are not necessarily an indication of hazards to organisms within the aquatic system. However if the aim of environmental restoration or management projects is to restore the ecosystem and the aquatic community to its pre-disturbance state rather than merely protect the organisms that currently reside in the aquatic system, it is crucial to recreate the water and sediment quality conditions of that pre-disturbance state (Alve *et al.*, 2009). This is especially true if we do not have a good understanding of the ecosystem of that pre-disturbance state, and hence cannot identify the level of contaminants that would be toxic to the background ecosystem state.

Secondly, sedimentary records can shed light on the main drivers and factors contributing to the contamination of aquatic systems. Understanding the importance of each of these factors enables the design and implementation of suitable mitigation strategies. Several studies have used sediment core heavy metal profiles to assess the success of sewage management improvements, pollution control projects and legislation such as the Clean Water Act (Bellucci *et al.*, 2012; von Gunten *et al.*, 1997;

Huang and Lin, 2003; Santschi *et al.*, 2001) on reducing the pollution of aquatic environments. In particular, sediment cores have the potential to help identify the impact that the expansion of residential land uses has on the health of aquatic systems (Gude *et al.*, 2006). However, there have not been any studies, that we can find, that have studied contaminant profiles of aquatic systems with only residential land uses in its catchment. Furthermore, there have been no situations, to our knowledge, where pollutant records from sediment cores have been used to assist in the restoration of polluted aquatic environments (Saunders and Taffs, 2009).

2.3.3 Uncertainties associated with sediment core historical pollution trends

The assumptions and uncertainties inherent in the use of sedimentary records for the identification of historical pollution trends in aquatic systems, are most likely what hinder the practical application of sediment core pollutant profiles for environmental management. First, it is assumed that the amount of a toxic compound found at a certain depth in the sedimentary record accurately represents the amount of that compound that entered the aquatic system at a particular point in time. However, the association of contaminants to particulate matter, and hence the proportion of contaminants settling on the sediment bed is dependent on a number of factors. For example, particles with larger surface areas (smaller particles), negative charges and high organic matter tend to have greater amounts of heavy metals bound to them (Boyle, 2001a; Foster and Charlesworth, 1996). Additionally, chemical properties of the water column (e.g., pH, dissolved oxygen; DO and salinity) can also affect the adherence of heavy metals to particulate matter (Boyle, 2001a; Foster and Charlesworth, 1996; Hudson-Edwards *et al.*, 1998; Wildi *et al.*, 2004). For example, in anoxic or low pH waters, metals previously bound to sediments can be released and be completely lost to the water column (Foster and Charlesworth, 1996).

Furthermore, contaminants can be mobilized after settlement (Swales *et al.*, 2002) due to physical processes such as resuspension due to wind or benthic organisms (Carper and Bachmann, 1984), biological processes such as uptake by aquatic organisms and plants (Wildi *et al.*, 2004) or the degradation of organic matter (van den Berg *et al.*, 1999). Similarly, Van Metre and Mahler (2004) argue that the levels of POPs found in sediment core samples may underestimate the actual concentration of POPs that were in the water column. Indeed, a study of bed sediments from Lake Superior, Jeremiason *et al.* (1998) found that only 2-5% of the PCBs attached to particulate matter suspended in the water column permanently accumulated in the bottom sediments. This was attributed to the decomposition of organic matter and the release of bound PCBs from surface bed sediments.

Secondly, it has been identified that deposition and burial of pollutants in the bed of aquatic systems may vary spatially within the system. For example, Boyle *et al.* (1998) obtained six sediment cores from Lake Baikal (depth 1620 m and area of approximately 14,000 km^2). These sediment cores were taken at least 30 km apart from each other and visually, these profiles differed profoundly (Boyle *et al.*, 1998). This variability was attributed to the proximity of the cores to different sources of heavy metal contaminants.

Thirdly, the dating of sediment cores can have significant uncertainties. These do not just stem from uncertainties or errors in sampling and laboratory analysis for radio-isotopic activities or radiocarbon dating; there are also errors associated with identifying the age of sediments between the discrete chronological markers (Appleby, 2001; Bjorck and Wohlfarth, 2002; Telford *et al.*, 2004). Using First Order Error Analysis (error propagation) and Monte Carlo Simulation Analysis, Binford (1990) estimated that uncertainties in ^{210}Pb dates can be 1-2 years for 10 year old sediments, 10-20 years for 100 year old sediments and 8-90 years old for 150 year old sediments. Barnekow et al., (1998) have noted an error of approximately 1000 years in the date assigned to bulk sediments that were deposited approximately 9000 years ago.

Despite the existence of these uncertainties, there is currently no uncertainty framework for reconstructing historical pollutant records using sediment cores. As such, it is necessary to undertake a systematic investigation to assess the impact of these uncertainties on the interpretations of sediment core contaminant profiles. This will enable us to interpret these contaminant profiles more accurately, which is critical when applying them to the design of environmental management and restoration strategies.

2.4 Using sediment cores to identify historical changes in hydrology of aquatic systems

A number of studies have used bed sediment cores to identify historical trends in the hydrology of lakes (Arnaud *et al.*, 2005; Moreno *et al.*, 2008), rivers (Bábek *et al.*, 2011; Wolfe *et al.*, 2005, 2006) and estuaries (Malamud-Roam *et al.*, 2006; Zong *et al.*, 2011). The hydrologic changes have been determined by investigating trends in physical, chemical or biological characteristics of the sediments through the sedimentary record (sediment characteristics summarised in Figure 2.2 and discussed in detail below). These sediment characteristics are indicative of the hydrologic state of the aquatic environment, because they are governed by the sources and depositional processes of sediments (e.g., Harrison *et al.*, 2003).

The temporal scales of these investigations have ranged widely. Studies have investigated trends on the scales of several millennia (e.g., Brown *et al.*, 2000; Jones *et al.*, 2012; Nesje *et al.*, 2001), which involve the identification of overall or average trends in sediment characteristics. There have also been studies that have identified historical hydrologic trends at decadal time-scales, or have attempted to identify discrete flood events within the sedimentary records (Czymzik *et al.*, 2010; Dhivert *et al.*, 2015; Provansal *et al.*, 2014; Wolfe *et al.*, 2006). These studies use the same sediment characteristics as those used in the studies at longer temporal scales, however the trends are investigated at a much finer resolution through the sedimentary record.

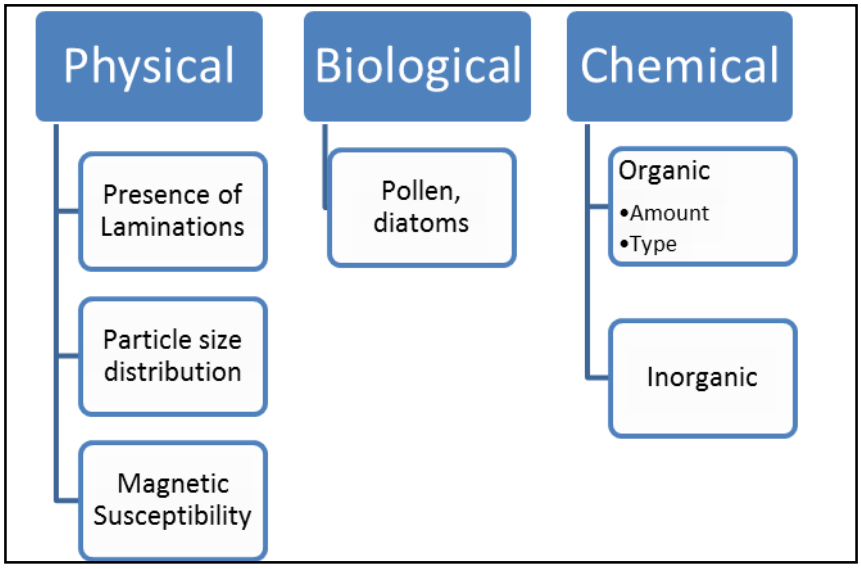

Figure 2.2: Sediment characteristics used to understand changes in hydrology.

2.4.1 Characteristics used to identify changes in hydrology

Physical properties

Presence of laminations

The presence of laminations (or visually distinct layers of sediment), can be used to assist in the identification of changes in hydrology (Bábek *et al.*, 2011; D'Haen *et al.*, 2012; Moreno *et al.*, 2008; Schillereff *et al.*, 2014; Thorndycraft *et al.*, 1998; Wolfe *et al.*, 2006). These laminations can range in thickness from one millimetre (Arnaud *et al.*, 2002; Schiefer *et al.*, 2011) to over several centimetres (Moreno *et al.*, 2008). The colour of these layers in the sediments can be indicative of the source and type of sediment (e.g., Wolfe *et al.*, 2006). A change in the colour of the sediment may be indicative of a shift in origin of the aquatic system both when determining long-term changes in hydrology (e.g., Moreno *et al.*, 2008) and pinpointing individual flood layers in sedimentary records (Bábek *et al.*, 2011; Wolfe *et al.*, 2006).

Particle size distribution

The particle size of sediments is another commonly used tracer of flood-borne sediment deposits (Augustinus *et al.*, 2008; Bábek *et al.*, 2011; Boe *et al.*, 2006; Brown *et al.*, 2000; Daessle *et al.*, 2009). Higher energy flows have the power to pick up and transport larger particles over long distances (Charlton, 2007). Thus, the presence of coarse grains (e.g., sands) in sedimentary records suggest that the sediments were deposited by strong flows (i.e., floods) (Bábek *et al.*, 2011; Brown *et al.*, 2005; Hollins *et al.*, 2011; Schillereff *et al.*, 2014; Vasskog *et al.*, 2011). Particle size distributions within sedimentary deposits can also be more complex, with several sub-layers of different particle sizes (fining upwards) within one layer of flood-deposited sediments (Arnaud *et al.*, 2002; Sandercock and Wyrwoll, 2005). This is believed to be a result of the coarse particles settling out of the water column first, due to its faster settling velocity, and the finer particles settling more slowly. The particle size of sediments has been used and verified using measured flow data as a proxy for high energy fluvial activity (e.g., Winter *et al.*, 2001; Wolfe *et al.*, 2006). For example, in 35-cm long sediment cores obtained from a shallow floodplain lake in the UK, Winter *et al.* (2001) found that there were increases in average particle size at two points in the cores. Daily discharge data for a nearby site showed that there were high discharge events in 1961-1962, and in 1976, which corresponded to the dates assigned the sediment core depths at which the excursions in particle size were detected.

Particle sizes of sediment deposits through a core have traditionally been identified using destructive methods, where the core is sub-sampled by hand, generally with sub-sampling intervals of at least 0.5 cm, and each sample is analysed by sieving and/or laser particle diffraction (Bábek *et al.*, 2011; Wolfe *et al.*, 2006). However, several studies have also proposed that the elemental composition of sediments can be an indication of particle size (e.g., Cuven *et al.*, 2010; Jones *et al.*, 2012; Schillereff *et al.*, 2014). The use of elemental composition enables the identification of particle sizes at finer intervals through the core than would be possible by sub-sampling of the core by hand. This is due to the advent of micro-X-Ray Fluorescence (XRF) core scanning, a non-destructive technique (i.e., not requiring sediment sub-sampling) that enables the detection of the elemental composition of sediment cores at resolutions as fine as 0.1 mm (e.g., Croudace *et al.*, 2006).

Dypvik and Harris (2001) argued that theoretically, the ratio of zirconium to rubidium (Zr/Rb) should correlate positively with grain size due to the fact that zirconium (Zr) is concentrated in coarse-grained materials whilst rubidium (Rb) is concentrated in fine-grained materials. Several other previous studies have attempted to identify a relationship between elements and grain size by comparing the elemental composition of sediments against their particle sizes measured by laser diffraction or sieving. Although Wilhelm *et al.* (2012) identified the ratio of calcium (Ca) to iron (Fe) (Ca/Fe) as a

grain size proxy. However, as both Ca and Fe can have authigenic sources, the grain size obtained from the Ca/Fe ratio should be validated using other methods (Koinig *et al.*, 2003). Cuven *et al.* (2010) found that silicon (Si) and Zr were associated with very coarse silt and sand, potassium (K) and Fe were associated with clay, and titanium (Ti) was associated with silt. Jones *et al.* (2012) found that the Zr/Rb ratio positively correlated with grain size. However, this is an area that needs to be explored further. Both the correlations by Cuven *et al.* (2010) and Jones *et al.* (2012) are based on a limited number of samples (6 and 37, respectively). It is not clear whether the grain size proxies identified in these studies accurately represent short term fluctuations in grain sizes through a sediment core. There is therefore still a need to determine whether an element or elemental ratio can reliably represent the variability in grain size in a sediment core from an aquatic system.

Magnetic susceptibility

Trends in magnetic properties of sediments through sediment cores have also been used to identify historical hydrologic changes, as these characteristics vary depending on the source of the sediments (Arnaud *et al.*, 2005; Bábek *et al.*, 2011; Boe *et al.*, 2006; Brown *et al.*, 2000; Cremer *et al.*, 2010; Dearing, 1999; Foster *et al.*, 1998; Sandgren and Snowball, 2001). Magnetic properties of sediments can be described using several indices such as: magnetic susceptibility, magnetic remanence and magnetic ratios (Foster *et al.*, 1998; Sandgren and Snowball, 2001). However, magnetic susceptibility, which is defined as the magnetization of the material per unit of magnetic field applied, is commonly measured in sedimentary records because it is a non-destructive and quick method for identifying the trend in magnetic properties of a sediment core (Michael and Friedrich, 2003; Sandgren and Snowball, 2001). Sediments with low magnetic susceptibility are usually identified as sands (Cremer *et al.*, 2010; Sandgren and Snowball, 2001) or sediments with high levels of organic matter (Bradshaw and Thompson, 1985). On the other hand, allochthonous clays and silts can have high levels of magnetic susceptibility (Bellucci *et al.*, 2012; Francu *et al.*, 2010; Moreno *et al.*, 2008). If the sediments deposited during high energy flows contain large amounts of sand and low amounts of clays and silts, this may register as a decrease in magnetic susceptibility. Several researchers (e.g., Wolfe *et al.*, 2006) have verified the use of magnetic susceptibility as an indicator of historical trends in hydrology by comparing magnetic susceptibility levels in sediment cores to observed measurements of river levels and flow rates. In this manner, magnetic susceptibility has been used to identify both overall trends in fluvial hydrology (Arnaud *et al.*, 2005; Brown *et al.*, 2000) as well as individual flood layers (Wolfe *et al.*, 2006).

Biological properties

Biological indicators preserved in sediment cores, such as pollen and diatom assemblages, are also used to infer the depositional environment of sediments, and hence can aid in the differentiation between sediments deposited in high and low energy states of aquatic systems (Brock *et al.*, 2010; Kenyon and Rutherfurd, 1999; Moreno *et al.*, 2008). For example, Moreno *et al.* (2008) used the level of preservation of pollen grains buried in the sediments to infer whether the sediments were deposited by floods. It is expected that pollen grains that were deposited in turbulent flows would have suffered a greater extent of degradation than pollen that was deposited in low energy environments.

Diatoms are unicellular eukaryotic organisms that are found in aquatic environments. Because they are sensitive to environmental conditions, the composition of communities can be strongly influenced by lake water depth, pH or nutrient levels (Battarbee *et al.*, 2001; Grundell *et al.*, 2011; Sonneman *et al.*, 2001). Augustinus *et al.* (2008) used the diatom assemblages found within a sediment core from Lake Pupuke in New Zealand to develop a conceptual model of changes to lake levels and catchment hydrology, based on the relative abundance of different species.

Chemical properties

Bulk organic matter

The amount of organic matter found in sedimentary deposits can also be characteristic of the origin of the sediment source. The organic matter content can be represented by total organic carbon, total organic nitrogen content, loss on ignition (LOI), or the ratio of incoherent to coherent scatter (inc/coh) from micro-XRF scan measurements (Croudace and Rothwell, 2015; Guyard *et al.*, 2007; Meyers and Teranes, 2001; Wolfe *et al.*, 2006). Similarly, the density of sediments as inferred from X-Ray radiograph images can be an indication of the organic matter content of sediment deposits, as organic matter has generally low densities and appears as light coloured layers in the radiographic image (Bábek *et al.*, 2011; Gilbert *et al.*, 2006). Sediments deposited under high energy lotic conditions or floods, often contain low amounts of organic matter relative to inorganic matter (Brown *et al.*, 2000; Nesje *et al.*, 2001; Wolfe *et al.*, 2006). This is due to the increased amount of inorganic terrestrial sediments that are carried into aquatic systems or eroded from river beds and banks during these flood events (Rodbell *et al.*, 1999).

Furthermore, the type or origin of organic matter can be inferred using the ratio of carbon to nitrogen (C/N) and isotopic carbon ($\delta^{13}C$) ratios (Meyers and Teranes, 2001). Organic nitrogen is more commonly found in lower plants such as phytoplankton; therefore lower C/N ratios are often

indicative of organic matter produced within the lake environment (Leng *et al.*, 2006). For example, organic matter originating from terrestrial plants have C/N ratios of 20 and greater, whereas organic matter from phytoplankton (i.e., organic matter created within the lake environment) has C/N values commonly between 4 and 10 (Meyers and Teranes, 2001). Similarly it has been suggested that $\delta^{13}C$ will be high during flood events (Brown *et al.*, 2000; Wolfe *et al.*, 2006). The $\delta^{13}C$ of organic matter reflects the carbon source of the plants, which differs between aquatic and terrestrial plants. Terrestrial plants generally have $\delta^{13}C$ values in the range of -25 to -30 ‰ and aquatic plants have more negative values of -29 to -34‰ (Bierman *et al.*, 1997).

Elemental composition of inorganic matter

The amount and composition of inorganic matter within sediment cores can also be used to identify the sources of sediment (de Boer and Crosby, 1995; Cuven *et al.*, 2010; D'Haen *et al.*, 2012; Douglas *et al.*, 2008). Due to its terrestrial (or lithogenic) origins, increased amounts of inorganic matter in sediment deposits can be attributed to greater hydrologic activity of aquatic systems. This is because increased flows will occur when there is greater surface runoff, which can pick up and transport materials from the catchment into the aquatic system (Corella *et al.*, 2014; Kylander *et al.*, 2013). Whilst some lithogenic elements (Si, Zr, Rb, K, Ti) are stable in the environment (Czymzik *et al.*, 2010; Dypvik and Harris, 2001; Kylander *et al.*, 2013), the accumulation of other lithogenic elements such as Ca, manganese (Mn) and Fe in aquatic sediments can be also affected by water quality parameters such as DO (Cuven *et al.*, 2010; Koinig *et al.*, 2003; Kylander *et al.*, 2013).

Some studies have measured the elemental composition of sediments in cores to identify long-term trends in the hydrology of aquatic systems (Corella *et al.*, 2014; Kylander *et al.*, 2013; Moreno *et al.*, 2008). However the use of elemental composition of sediments for identifying discrete flood deposits within sedimentary records has been less explored. Although Schlolaut *et al.* (2014) attempted this, the flood layers identified in the sediment core using maxima in inorganic element composition were not dated and validated using observed flood records. Berner *et al.* (2012) also found flood-deposited sediments in a sediment core by looking for sediments with high levels of calcium oxide (CaO) and strontium, and low levels of potassium oxide (K_2O) and Rb. This assumption about the elements enriched in flood-deposited sediments were based on the elemental composition of suspended sediments in six recent flood events between 1999 and 2002. However the disadvantage of this method is that it is unlikely that the suspended particulate matter in sampled flood events between 1999 and 2002 would be representative of the particulate matter in historical floods. Indeed, there was poor correlation between the identified flood layers in the sediment core and observed flood records.

If the elemental composition of both source sediments throughout the catchment and the inorganic matter within sedimentary records are known, we can identify where in the catchment these sediments in the core originated. This in turn can be used to infer the transport pathway of these sediments. For example, Kujau *et al.* (2010) identified the origin of sediments in a sediment core from the Mississippi River by comparing elemental ratios at certain depths in the sediment core with elemental ratios of surface sediments from various areas within the catchment. Mathematical models have also been used to quantify the contribution of each source to the sediment deposit. One example of a quantitative model is a simple linear mixing model, where a series of linear equations are solved to determine source contributions or the proportions of each end-member (the sediment source) contributing to the sediment sink (the sediment deposit) (Vezzoli *et al.*, 2004a; Weltje, 1997). Bayesian statistical methods have also been implemented to solve such problems (e.g., Fox and Papanicolaou, 2008). This same concept has been applied in microbial source-tracking, which attempts to trace the source of faecal pollution using the composition of microbial communities (the types and amounts of different microorganisms). Indeed, Bayesian models such as SourceTracker (Knights *et al.*, 2011) are available for this microbial source tracking. SourceTracker has been found to outperform other probabilistic methods in determining microbial source proportions (naïve Bayes and random forests; Knights *et al.*, 2011). There is a potential to use SourceTracker, despite its origin as a microbial source apportioning model, to identify the sources of discrete sediment deposits in cores from aquatic systems. Although previous studies have used sediment mixing models to apportion the sources of sediments in sediment cores (e.g., Weltje, 1997) they have not been used for the specific purpose of pinpointing flood-deposited sediments in sediment cores.

2.4.2 The importance of adopting a multi-proxy approach

Trends in the sediment characteristics listed above may not necessarily be a result of changes to the hydrology of the aquatic system or the occurrence of flood events. For example, the presence of laminations in sediment cores could be due to landslides (Moernaut *et al.*, 2007) or land clearing (Enters *et al.*, 2006). Similarly, excursions in particle size within the sediment core can point to a number of different factors such as: an increase in aridity, mass wasting, land clearing, waste disposal, increase in wind strength or the erosion of morphological features (Moreno *et al.*, 2008; Teller and Last, 1990). Particle size can also be affected by land-use (Van Metre and Callender, 1997). Similarly, there can authigenic sources of magnetic particles into aquatic systems, such as (1) bacteria that produce magnetite as part of their metabolic processes; and (2) the formation of magnetic iron sulphides in certain environments (Dearing, 1999; Sandgren and Snowball, 2001).

The abundance of organic and inorganic elements within sedimentary deposits are also not affected by just hydrology and floods. There can be significant spatial variability in sediment deposition in billabongs, particularly during flood events (Bábek *et al.*, 2011). The amount of organic matter detected in the sediments is not only dependent on the amount and type of organic matter that initially entered the aquatic environment, but also on the extent of its degradation and transformation both during transport and after deposition (Meyers and Teranes, 2001). Similarly, since some elements found in sediments, such as Ca, Mn and Fe can have both lithogenic and authigenic sources (Kylander *et al.*, 2013), it is important to identify whether increases in these elements are due to lithogenic processes (e.g., increased hydrologic activity) or authigenic processes (e.g., changes to DO). Furthermore, when comparing inorganic elemental abundances within catchment sediment sources to sediments deposited in aquatic systems, it is important to note that the elemental composition of sediments can change due to weathering during the transport process (D'Haen *et al.*, 2012; Weltje and von Eynatten, 2004).

Thus, given these uncertainties, the use of multiple sediment characteristics is critical when determining the source and depositional environments of sediments within cores (Schillereff *et al.*, 2014). It is also beneficial to have an understanding of the catchment's history, to verify the interpretations of the sedimentary records (Schillereff *et al.*, 2014). In particular, observed measurements of river flow and water level, or anecdotal records of flooding and other significant events within the catchment can be used to verify the reconstructed historical hydrological record reconstructed from multiple proxies (Wolfe *et al.*, 2006).

2.5 Using sediment cores to identify contaminant levels in fluvial flood deposits

As elucidated in the above discussion, sedimentary records can preserve historical fluvial flood deposits and simultaneously record historical contaminant inputs. It is therefore expected that sediment cores can be used to identify the level of contaminants contained in overbank fluvial flood deposits. However, there are few studies that have investigated this, with only a handful of papers using sediment cores from floodplains or floodplain lakes (billabongs) to identify contaminant levels in historical fluvial floods (Bábek *et al.*, 2011; Chen *et al.*, 2015; Daessle *et al.*, 2009; Ferrand *et al.*, 2012; Nguyen *et al.*, 2009). These studies have used proxies such as particle size (Daessle *et al.*, 2009; Ferrand *et al.*, 2012), the presence of laminations in sediment cores (Bábek *et al.*, 2011) and sediment density (Bábek *et al.*, 2011) to identify flood layers in the sediment core. However, few studies have successfully explored the use of sediment elemental composition to identify discrete flood layers in sediment cores. In addition, there are some limitations to these existing studies. Some have not

identified the pollutant levels in discrete flood deposits in sediment cores, but instead have investigated overall (or average) hydrological trends and identified pollution levels in periods of high flood frequency (Chen *et al.*, 2015; Ferrand *et al.*, 2012). Although Bábek *et al.* (2011), Nguyen *et al.* (2009) and Daessle *et al.* (2009) did investigate the pollutant levels in discrete flood layers, there is some uncertainty about their results because the occurrence of the flood layers was not validated using observed flow data.

Furthermore, whilst these studies have attempted to qualitatively understand the importance of fluvial floods in the deposition of toxic compounds in floodplains, they have not linked the contaminant levels in sediment deposits with the characteristics of the flood that deposited the sediments. Ferrand *et al.* (2012) found higher heavy metal concentrations in regions of the sediment core deposited by low to medium discharge flows compared to regions deposited by strong floods. This was inferred from the fact that sediments deposited between 1986 and 1990 and in the early 2000s (when fluvial flows had low to medium average recurrence intervals) had the highest heavy metal concentrations. However, a quantitative link between river flow characteristics and contaminant concentrations in flood-borne deposits is critical to better understand the processes affecting contaminant deposition by floods, and to predict the quality of sediments deposits in future floods.

2.6 Summary and knowledge gaps

There is currently a lack of data and understanding of the contaminant levels in fluvial flood deposits. As such, we must develop alternative methods to identify contaminant levels in fluvial flood deposits. These data could be collected using sedimentary records from aquatic systems and **there is a need to understand how this can be effectively implemented and applied**.

The literature review above highlights that previous studies have identified historical trends in contaminant (heavy metals and POPs) inputs into aquatic systems using bed sediment cores. This technique has been used to determine and explain historical trends in the contamination of aquatic environments. However, several knowledge gaps still remain. Firstly, **the potential for using sediment cores to develop sediment quality guidelines has not yet been explored**. If cores contain sediments deposited in pre-disturbance conditions, background toxicant levels could be identified. Despite the recommendations given by water and sediment quality guidelines in Australia and New Zealand (as well as in other parts of the world) for the use of background or reference conditions for assessing environmental monitoring data, these background conditions have not been identified using sediment

cores. Additionally**, sediment cores have rarely been used to identify the impact of residential land uses on the contamination of aquatic environments**.

Furthermore, whilst metal profiles obtained from sediment cores have been used to evaluate the success of pollution mitigation or control strategies, **the pollution trends have rarely been used to develop mitigation or ecosystem restoration strategies**. The lack of practical application of sediment cores for the development of mitigation strategies, or sediment quality guidelines is most likely due to the fact that there has still been minimal exploration of the uncertainties associated with reconstructing historical water quality records using sediment cores. Namely, there is still a need to check the assumptions that are inherent in the interpretation of contaminant profiles obtained from sedimentary records. In fact, there are many sources of uncertainties that can influence our interpretation of sediment core pollutant profiles. A **global uncertainty framework that could be used to account for these uncertainties would be highly useful** to help interpret these data and aid in better decision making.

Sediment cores can be used to identify changes in the hydrology of aquatic systems at temporal scales ranging from several millennia to individual flood events. These changes can be determined using the physical, chemical or biological characteristics of sediments. There are a large number of proxies or indicators that can be used to reconstruct historical hydrologic trends from sedimentary records. However the high level of uncertainty that exists when using any one of the reviewed proxies means that multiple proxies are always required, and that verification of the identified hydrological trends should be conducted using measured data. Although methods in reconstructing historical hydrologic changes have been widely explored by previous studies, several research gaps in this area still remain. In particular, there is a **need to further explore the use of elemental composition for identifying flood layers within sedimentary records from floodplains.**

Whilst there have been several studies that have attempted to identify the relationship between the occurrence of fluvial flooding and the contamination of floodplain deposits, there are some limitations to these existing studies including: the lack of identification of pollutant levels in discrete flood layers and the lack of validation of identified flood records using observed flow data. As such, **there is a need to use sediment cores to identify pollutant levels in discrete flood deposits that have been validated using observed flood records. Further work should also be done to quantitatively link the characteristics of historical floods with the level of heavy metals contained within flood-deposited**

sediments. The development of these linkages will pave the way for predictive models of fluvial sediment deposit contamination.

2.7 References

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CHAPTER 3
RESEARCH OBJECTIVES, HYPOTHESES AND CASE STUDY JUSTIFICATION

3.1 Research objectives and questions

As discussed in the previous chapters, the main aim of this project is to use sediment cores to identify the pollutant concentrations within sediments deposited by past overbank fluvial floods. The four main research objectives for this study are listed below. Specific research questions, hypotheses and knowledge gaps addressed by these research questions are also discussed.

Research objective 1: To identify the historical contamination trends in the Yarra River billabongs using sedimentary records.

Two specific research questions are associated with this research objective.

1. *What contamination trends can be identified using sedimentary records of the Yarra River billabongs?*

It is hypothesized that variability in pollutant levels in the sedimentary records will correlate with land-use changes, in particular, urbanisation. This research question addresses the gap in knowledge surrounding historical trends in contamination of floodplain lakes in catchments with residential land uses.

2. *To what extent are the existing trigger values provided in guidelines representative of the background state of aquatic environments?*

Current sediment quality trigger values provided in guidelines are not based on an understanding of the pre-disturbed or background state of aquatic systems, let alone site-specific background states. It is hypothesized that there will be a discrepancy between current sediment quality heavy metal trigger values and actual background heavy metal concentrations of aquatic systems. This is due to the fact that the current trigger values are based on the probability of toxic effects (developed using data obtained in North America), rather than site-specific characteristics. Sediment quality trigger values have not previously been evaluated by comparison to background contaminant concentrations obtained from sediment cores.

Research objective 2: To identify discrete fluvial flood deposits in sediment cores from the Yarra River billabongs.

The following research questions will be explored.

3. *What techniques can be used to identify historical hydrologic changes of the Yarra River billabongs, and in particular, identify discrete flood-deposited sediment layers in the Yarra River billabong cores?*

It is hypothesized that changes in hydrology of the Yarra River billabongs would result in shifts in the amount and type of sediment deposited. As such, the characteristics of the sediments within bed sediment cores (i.e., methods outlined in the literature review in Chapter 2) could be used to identify these changes in flow. It is also hypothesized that these inferred changes could be checked using measured flow data.

Another hypothesis is that a multi-proxy approach, using a number of physical and chemical sediment characteristics, could be used to identify discrete flood deposits in the sediment cores. These proxies are hypothesized to be magnetic susceptibility, total inorganic matter content, particle size, the presence of laminations in the core, and elemental composition. As previously outlined in the literature review in Chapter 2, these five sediment characteristics can indicate a change in sediment deposition processes or source. Again, it is envisaged that these flood layers could be verified using measured flow data and anecdotal records of floods. This research question addresses the knowledge gap about whether elemental composition can be used to identify individual flood layers in sedimentary records.

4. *In particular, can sediment mixing models be used to identify discrete flood deposits within sedimentary records?*

Previous studies (as outlined in Chapter 2) have shown that mathematical models can be used to quantitatively apportion the sources contributing to sediment deposits. Two models previously discussed in the literature review (Chapter 2) are simple linear mixing models, and Bayesian models such as SourceTracker (Knights *et al.*, 2011). It is hypothesized that these models could be applied to the sediment cores from the Yarra River billabongs to distinguish the main sources of the sediments at discrete intervals through the sediment core, and that by understanding these sources, it could be determined whether or not they are flood-borne sediments.

Research objective 3: To assess the uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution trends in aquatic systems.

Under this objective, the following research questions will be explored.

5. *What are the uncertainties associated with reconstructing historical heavy metal pollution trends in aquatic systems using bed sediment cores?*

It is hypothesized that an uncertainty framework could be developed, that outlines the uncertainties of reconstructing historical heavy metal pollution of aquatic systems using sediment cores. Specifically, the location from which the core is obtained within the aquatic system, the sub-sampling interval of the cores, and the methods used for heavy metal analysis could impact the reconstruction of historical heavy metal pollution trends.

It is proposed that of these uncertainties, the methods used for heavy metal analysis will have the smallest effect on the reconstruction of historical heavy metal pollution trends. This is because previous studies have found that the analytical methods have minimal effect on the heavy metal pollution trends identified. It is also expected that whilst spatial variability and sub-sampling intervals may affect the interpretation of short term variabilities in heavy metal pollution records, they will not affect the overall trends identified. Whilst it is acknowledged in the literature that there could be uncertainties in the reconstruction of historical pollution trends using sediment cores, the uncertainties have not been quantified, nor has an uncertainty framework been developed.

6. *How does post-depositional transformation or mobilization of contaminants affect the interpretation of sediment core contaminant profiles?*

The literature review (Chapter 2) identified that contaminants such as heavy metals can be susceptible to transformations after deposition and burial. However it is hypothesized that these processes will not have a significant impact on the interpretation of sediment core contaminant profiles. Previous studies have not quantified how post-depositional mobilisation affects the reconstruction of historical heavy metal pollution records.

7. *To what extent does the contaminant level in bed sediments of aquatic systems reflect the pollution state of the aquatic system?*

It is expected that there will be physical (e.g., physical mixing), biological (e.g., biological degradation) and chemical processes (e.g., transformation according to the compound's solubility) within the bed

sediments of aquatic systems, which will impact the extent to which pollution levels in aquatic systems are recorded in bed sediments. Whilst previous studies assume that the pollution states of aquatic systems can be identified from bed sediments, this has not yet been validated using field monitoring.

Research objective 4: To use sediment cores to identify the contaminant levels in flood-deposited sediments in the Yarra River billabongs.

There is one research question associated with the fourth research objective.

8. *What is the level of contaminants contained in fluvial flood deposits and how do they compare to contaminant levels in sediments not deposited by floods within the sediment cores of the Yarra River billabongs?*

It is expected that a dataset of the contaminant concentrations within fluvial flood deposits of the Yarra River could be compiled using the previously identified flood-deposited layers in sediment cores from the river's billabongs (from research question 3). This could be used to assess the importance of overbank fluvial flooding in billabong contamination. However, the accuracy of this is expected to be limited by uncertainties inherent in the reconstruction of historical pollution trends using sediment cores. Although previous studies have qualitatively explored the relationship between pollution and the occurrence of floods using sediment cores, the flood layers in the sediment cores have not been previously compared to observed flow data of the rivers.

3.2 The Yarra River catchment as a case study

3.2.1 Current understanding of the Yarra River catchment

Site Description

The Yarra River, an approximately 240-km long river located in South-Eastern Australia, begins in the Great Dividing Range, and after flowing through the city of Melbourne, discharges into Port Phillip Bay (Leahy, 2007). The catchment itself is approximately 4000 km^2 in area and can be subdivided into three sections: the upper catchment, middle catchment and lower catchment, based on geological and land-use characteristics (Beardsell and Beardsell, 1999; Leahy, 2007) (Figure 3.1). The upper Yarra catchment is mainly forested, whilst the middle and lower catchments are agricultural and urban in land-use (Brizga *et al.*, 1995). There is a wide range of geological deposits within the catchment (Figure 3.2). Also, due to the meandering nature of the Yarra River, there are several billabongs in the catchment.

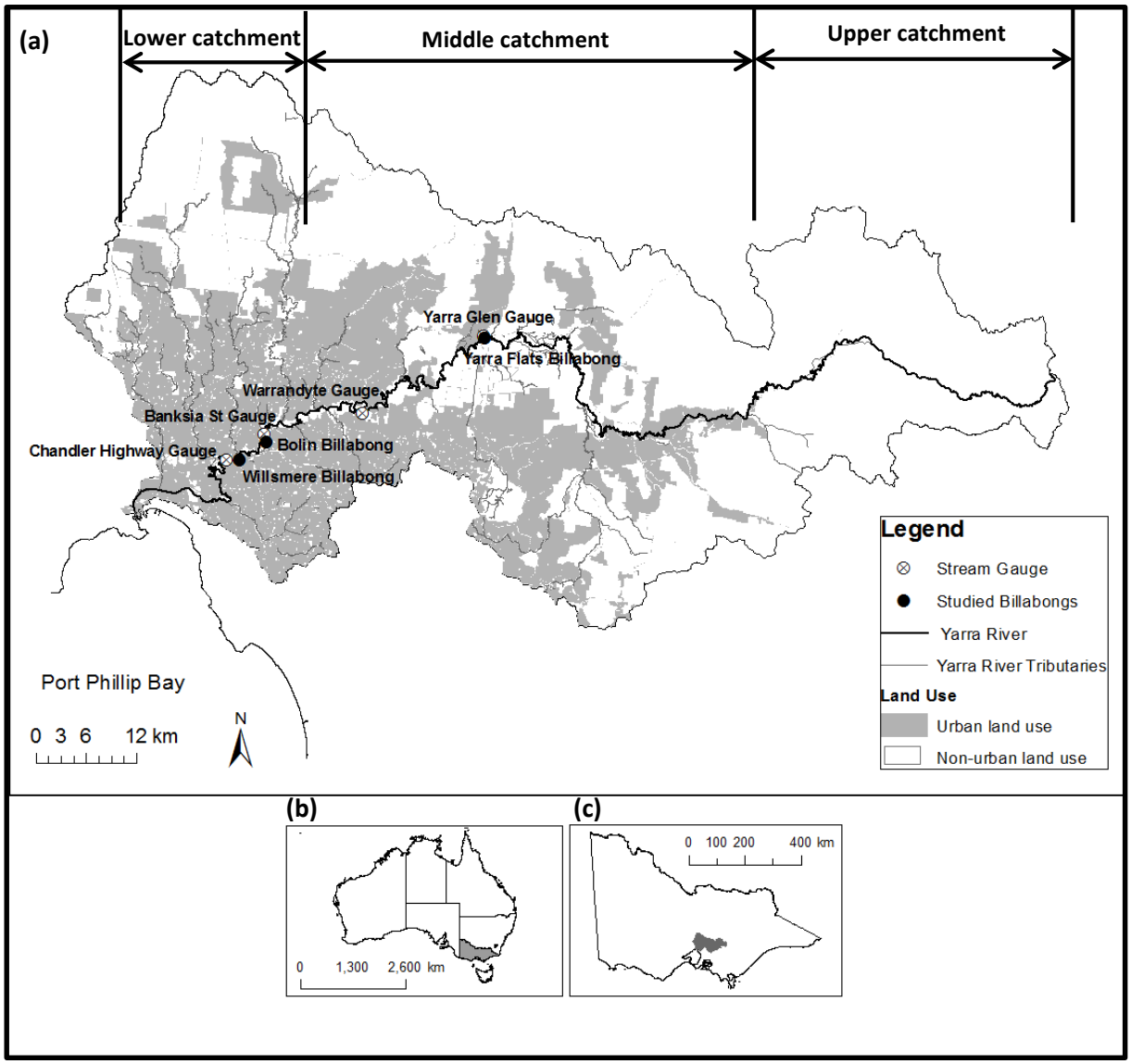

Figure 3.1: The Yarra River catchment, showing land-use and the location of billabongs and stream gauges used in this project (a), location of the state of Victoria in Australia (b), location of the Yarra River catchment in Victoria (c).

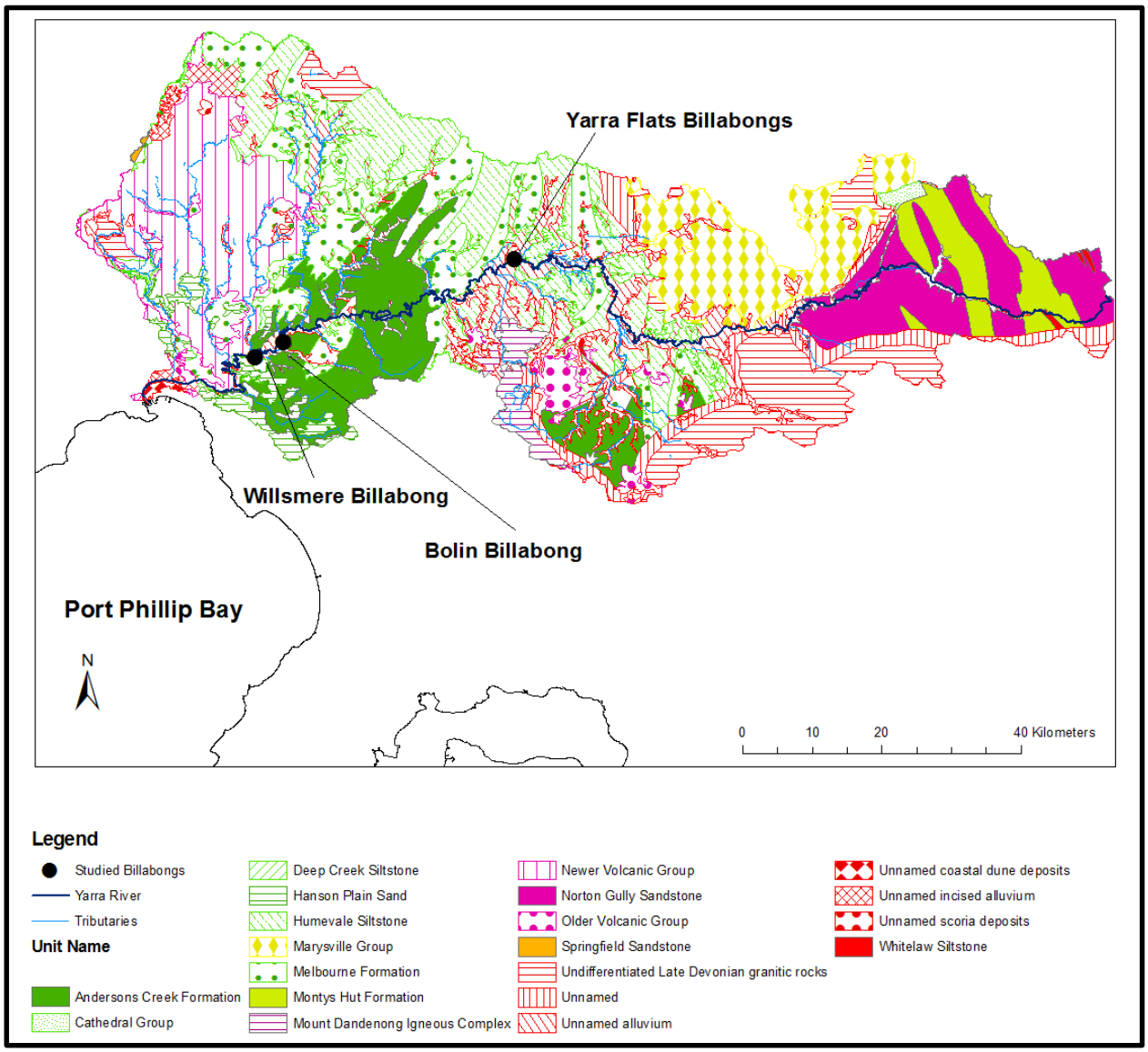

Figure 3.2: Geological deposits in the Yarra River catchment (adapted from State of Victoria, 2015).

Hydrology of the Yarra River

The hydrology of the Yarra River has been studied in detail in previous studies. These studies have focused on the issue of restoring environmental flows for the preservation of downstream ecosystems, whilst balancing human demand for the water from the Yarra River (Brizga *et al.*, 1995; Carty and Pierotti, 2009; Coleman *et al.*, 2011; Sinclair Knight Merz, 2005). It has been estimated that the river discharges between 200 and 1000 GL of water annually to Port Phillip Bay, depending on climatic conditions (Coleman *et al.*, 2011). This discharge is seasonal, with the lowest discharge in the summer months and the highest in late winter and spring (Figure 3.3).

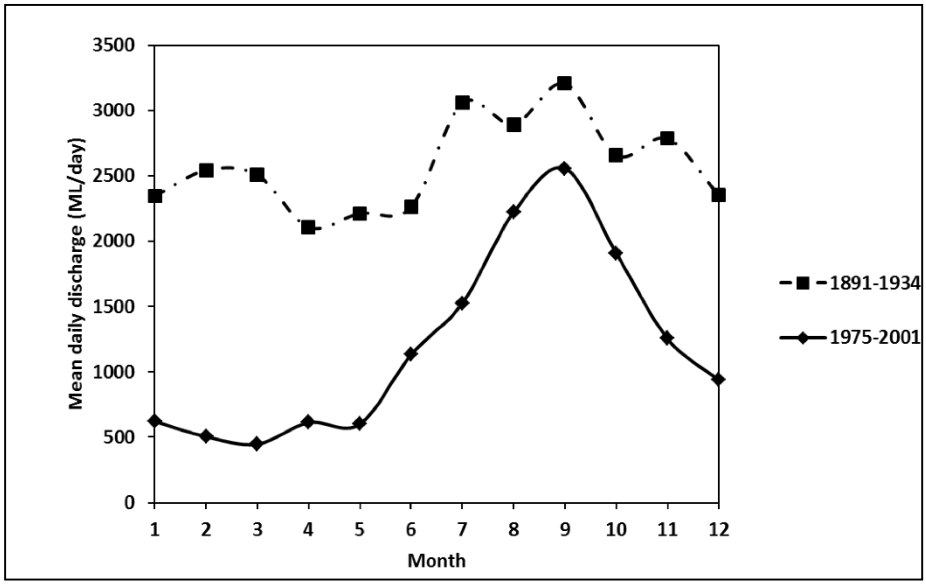

Figure 3.3: Mean daily discharge at the Warrandyte stream gauge in the Yarra River for 1891-1934 and 1975-2001 (Department of Sustainability and Environment, 2013).

The history of river regulation along the Yarra River, summarised in Figure 3.4 indicates that there has been an increase in the amount of water extracted from the river through the 20th century. Figure 3.4 underestimates water extractions as it does not include private diversions or farm dams (Brizga *et al.*, 1995). Previous studies (e.g., Brizga *et al.*, 1995) have pointed out the correlation between this increased water extraction and the decrease in flows recorded at the longest continually operating stream gauge on the Yarra River (the Warrandyte gauge; the location shown in Figure 3.1) over the 20th century. Indeed, Figure 3.3 indicates that the mean monthly flows measured at the Warrandyte stream gauge have decreased considerably over the 20th century, particularly in summer months. A study that modelled the river under both natural and regulated conditions showed that overbank flooding (and therefore, inundation of the Yarra River Billabongs) occurred in the upper and middle reaches of the Yarra River approximately once a year under natural (unregulated) flow conditions, but this has reduced to once every three to four years at present due to water extractions (Sinclair Knight Merz, 2005).

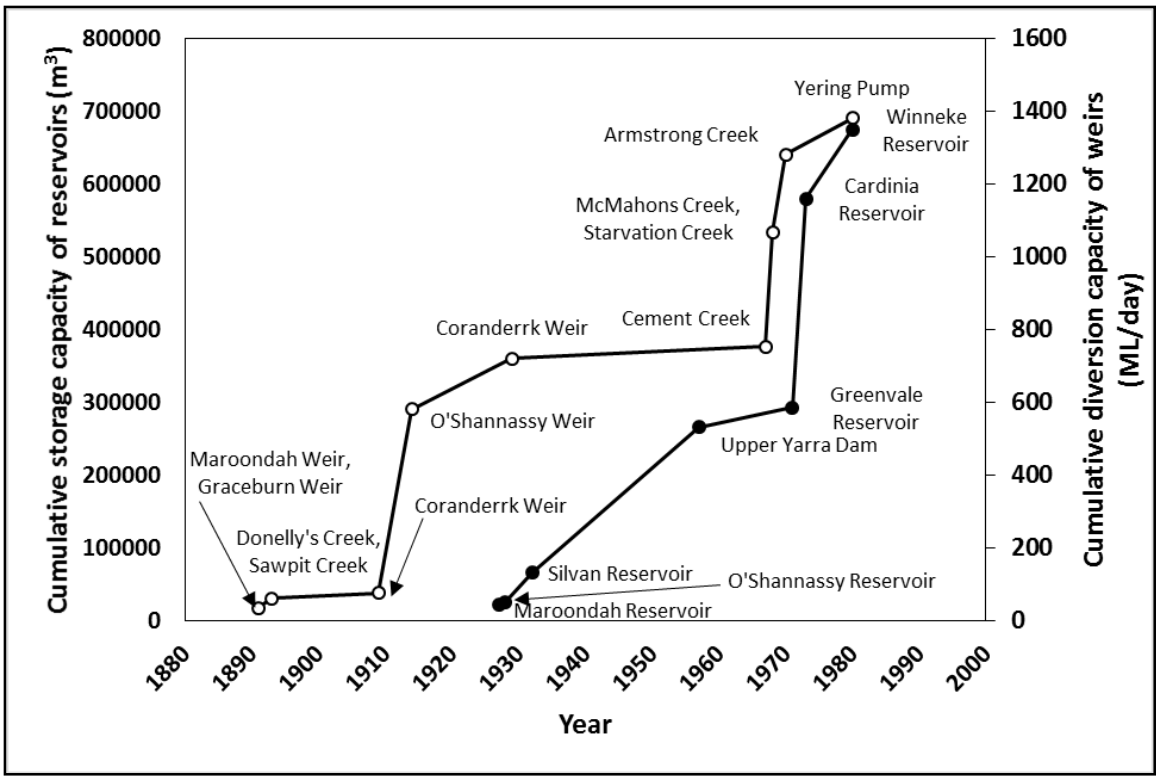

Figure 3.4: Cumulative storage capacity of reservoirs in m^3 (closed circles) and cumulative diversion capacity of weirs in ML/day (open circles) constructed in the Yarra River catchment between 1890 and 1980 (adapted from Brizga *et al.*, 1995).

Water quality of the Yarra River Billabongs

Historical water quality within the Yarra River and its billabongs has previously been studied by Leahy (2007), who used trends in diatom and pollen assemblages in sediment cores from four billabongs (Devon, Henley, Bolin and Willsmere) in the Yarra River catchment to identify the effect of European settlement on the turbidity, pH and nutrient levels in the river and its billabongs. It was found that prior to European arrival, the water in the billabongs was slightly acidic, had low nutrient levels, and had low suspended solids levels. However, the arrival of Europeans in the mid-19th century led to erosion, an increase in nutrient levels, and significant disturbance to the plant community within the catchment.

Previous works have addressed the heavy metal (Ellaway *et al.*, 1982) and persistent organic pollutants (POPs) (Allinson *et al.*, 2014, 2015) contamination currently in the Yarra River. However, there is still limited understanding of the historical level of contaminants such as heavy metals and POPs in the billabongs of the Yarra River.

3.2.2 Justification of the use of the Yarra River catchment as a case study

Under future climate change scenarios, it is expected that rivers in South-East Australia, such as the Yarra River will experience an increased frequency and intensity of extreme events (e.g., flooding) (Turak *et al.*, 2011). The Yarra River is a major river system in Australia that flows through a highly populated region. As such, a large number of people live in close proximity to the Yarra River and may come into contact with flood deposits. There is a need to better understand the relationship between fluvial flooding of the Yarra River and the contamination of its floodplains, to help prepare for this risk. Thus, it is likely that the case study of the Yarra River will not only provide guidance on the contaminant deposition by fluvial floods for other urban river systems around the world. It may also provide an understanding of the risks of fluvial flooding, specific to the Yarra River, which will be of use when managing flood risks in the future.

The Yarra River catchment and its billabongs have experienced influences from a large number of land-uses over approximately the last 150 years of European settlement. The Yarra River catchment currently has both urban and agricultural land-uses, and in the past has had mining occur within the catchment (Brizga *et al.*, 1995). Studying a catchment with a history of diverse land-use enables the exploration of the relationship between land-use and pollutant levels in aquatic systems and their bed sediments.

There are also several resources available that make it ideal to use the Yarra River as a case study for this project. Since European settlement of the Yarra River catchment in the early 19th century, the history of catchment development has been well documented. For example, census data are available for the approximately 150 years of European settlement in the catchment. This includes data on population in specific areas of the catchment, as well as the number of dwellings and the development of key infrastructure. In addition, streamflow of the Yarra River has been monitored over the 20th century, with measured data available from 1891. This long time series of flow data will enable confirmation of hydrologic trends and flood deposits identified by sediment cores from the Yarra River billabongs. Finally, the existence of unopened sediment cores obtained from the Yarra River billabongs during the study by Leahy (2007), which have been in storage for over 10 years at 4^{0}C, can be used to study the effect of post-depositional mobilisation on the sediment core contaminant profiles.

As such, Willsmere and Bolin Billabongs, which are both within urban environments (Figure 3.1) and which were previously studied by Leahy (2007) were selected as study sites. Access to Henley and Devon Billabongs, both billabongs in rural areas studied by Leahy (2007), could not be obtained. So,

the Yarra Flats Billabong, which is outside of the Melbourne metropolitan zone (Figure 3.1), was selected as a study site instead. These three sites are described in further detail in following chapters.

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CHAPTER 4
IDENTIFYING HISTORICAL POLLUTION TRENDS IN THE YARRA RIVER BILLABONGS

Declaration for Thesis Chapter 4

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Initiation, ideas, experimental work, data analysis, interpretation and write up	75 *(Average of contribution to the two publications)*

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Marion Anderson	Collection of heavy metal data.	n/a
Paul Leahy	Sample collection, data interpretation, reviewing of manuscript	n/a
Ana Deletic	Data interpretation, reviewing of manuscript	n/a
David McCarthy	Ideas, data interpretation, reviewing of manuscript	n/a

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	[redacted]	**Date** 19/8/2015
Main Supervisor's Signature		**Date** 19/8/2015

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

4.1 Introduction

The literature review (Chapter 2) indicated that there is great potential for the use of sedimentary records in reconstructing historical trends in contaminant fluxes into aquatic environments. It was identified that understanding these historical trends will allow us to: (1) identify background contaminant levels of the system and use these to develop site-specific sediment quality targets for the system; (2) identify key drivers of pollution and develop strategies to reduce pollutant fluxes into aquatic systems; (3) evaluate pollution reduction measures already in place.

This chapter addresses research objective 1 and its associated research questions 1 to 2, listed below.

Research objective 1: To identify the historical contamination trends in the Yarra River billabongs using sedimentary records.

- *Research question 1: What contamination trends can be identified using sedimentary records of the Yarra River billabongs?*
- *Research question 2: To what extent are the existing trigger values provided in guidelines representative of the background state of aquatic environments?*

The chapter contains two journal papers, each discussing the reconstruction and interpretation of historical water contaminant fluxes into Bolin and Willsmere Billabong (respectively). The results for Bolin Billabong have been accepted with major revisions for publication in *Water Science and Technology.* This paper is cited as Lintern *et al.* (submitted) throughout the thesis. In this publication, both research questions 1 and 2 are addressed. The second paper, which discusses the reconstruction and interpretation of historical water quality records from Willsmere Billabong has already been published in *Marine and Freshwater Research*. Cited as Lintern *et al.* (2015) throughout this thesis, this publication provides a more in-depth discussion of research question 1. The manuscripts for both are provided below. Supplementary material accompanying Lintern *et al.* (submitted) is provided in Appendix A.1 and the supplementary material for Lintern *et al.* (2015) is provided in Appendix A.2.

Although the trends in both heavy metals and POPs are discussed for Willsmere Billabong, the POPs trends are not explored for Bolin Billabong, and will not be addressed in the remainder of this thesis. Due to the fact that there were low detection levels of POPs in both the sedimentary records and the field work, it was decided to not investigate POPs further. Similarly, the historical pollution trends for the Yarra Flats Billabong is not discussed, and the justification of the exclusion of this study site from this chapter and from the remainder of this thesis is discussed at the end of this chapter. This chapter then concludes with a final discussion and conclusions. Additional photographs of Willsmere and Bolin Billabongs and the Yarra Flats Billabong are provided in Appendix B.

4.2 Historical pollution trends of Bolin Billabong

USING SEDIMENT CORES TO ESTABLISH TARGETS FOR THE REMEDIATION OF AQUATIC ENVIRONMENTS

Anna LINTERN[1*], Marion ANDERSON[2], Paul LEAHY[3], Ana DELETIC[1], David MCCARTHY[1]
[1]Monash Water for Liveability, Department of Civil Engineering, Monash University, Clayton 3800, Victoria, Australia
[2]School of Earth, Atmosphere & Environment, Monash University, Clayton 3800, Victoria, Australia
[3]EPA Victoria, Ernest Jones Drive, Macleod, Victoria, 3085, Australia
*Corresponding author email: anna.lintern@monash.edu

ABSTRACT

When assigning site-specific restoration targets for deteriorating aquatic systems, it is necessary to have an understanding of the undisturbed or background state of the system. However, the site-specific characteristics of aquatic systems prior to disturbance are mostly unknown, due to the lack of historical water and sediment quality data. This study aims to introduce a method for filling this gap in our understanding by using dated sediment cores from the beds of aquatic environments. We used Bolin Billabong, a floodplain lake of the Yarra River (South-East Australia) as a case study to demonstrate the application of this method. We identified the concentrations of aluminium, cadmium, chromium, copper, iron, lead, manganese, nickel, tin and zinc at 8 cm intervals through the sediment core. This showed that aluminium, chromium, copper, iron, lead, nickel, tin and zinc concentrations in Bolin Billabong sediments significantly increased after European settlement in the river catchment in the mid-19th century. The differences between current Australian sediment quality guidelines trigger values, and the background metal concentrations in Bolin Billabong sediments underscores the value of using locally relevant background toxicant concentrations when setting water and sediment quality targets.

KEYWORDS

Billabong; contamination; floodplain lake; heavy metals; restoration; sediment core

INTRODUCTION

The contamination of aquatic environments is occurring globally (Kivaisi 2001). A 2011 report found that most aquatic environments in Australia are in a degraded condition (Australian State of the Environment Committee 2011). Elevated levels of heavy metals have been detected in systems such

as the Derwent Estuary in Tasmania (Bloom and Ayling 1977) and the Coxs River in New South Wales (Birch et al. 2001). This contamination poses risks to both humans and the ecosystem.

The Australian and New Zealand water quality management guidelines (ANZECC/ARMCANZ) states that an understanding of the background state, where the background state is defined as the state of the aquatic system before anthropogenic pollution, is critical when assessing environmental monitoring data (Batley and Maher 2001) and when developing remediation strategies to restore polluted environments (ANZECC/ARMCANZ 2000). These background metal concentrations are likely to site-specific due to their dependence on the local geology (Dauvalter 1994). It is not advisable to use recently deposited sediments from pristine lake and rivers to characterise the undisturbed state of aquatic systems. These sediments are compromised for assessing background levels as they can be contaminated by global atmospheric deposition (Heyvaert et al. 2000).

When site-specific background conditions are unknown, ANZECC/ARMCANZ (2000) recommends the use of default guideline values. Two values are provided, 'low' for low probability of toxic effects and 'high' for medium probability of toxic effects. These guidelines are not based on the site-specific context. Therefore, they result in the assessment of environments without taking into account their natural background metal levels.

An understanding of background water and sediment quality can be developed using sediment cores from the beds of aquatic systems (Förstner and Salomons 1980). A large number of studies have used pollutant (e.g., heavy metals) concentrations at discrete depths through a sediment core to infer historical water and sediment quality trends in an aquatic system (Latimer et al. 2003; Morelli et al. 2012). Whilst previous studies have used sediment cores to understand how and why metal levels of aquatic systems have changed historically, they have not been practically applied to the restoration of these environments or to setting environmental quality guidelines (Saunders and Taffs 2009).

The main aim of this study is to identify the heavy metal contamination history of Bolin Billabong (a floodplain lake of the Yarra River in Melbourne, Australia). The specific study objectives are:

- to identify the metal levels in Bolin Billabong prior to European settlement in the area in the mid-19th century (i.e., the background metal concentrations in the bed sediments);
- to compare the background heavy metal levels against generic heavy metal sediment quality trigger levels; and

- to determine and explain the contamination extent of more recent sediments in Bolin Billabong.

METHODS

Site description

The Yarra River is located in South-East Australia (Figure 1). The river flows for approximately 240 km through forested, agricultural and urban areas before discharging into Port Phillip Bay (Brizga et al. 1995). Bolin Billabong ($37^0$46′14”S and $145^0$4′43”E), is a floodplain lake (billabong) of the Yarra River and is located within Melbourne (Leahy et al. 2005). It has a local catchment of 15 ha consisting of mostly parkland and a small residential area, but no stormwater is discharged directly into the lake (Leahy 2007). Hydrologic modelling and measured data show that historically, overbank floods of the Yarra River filled Bolin Billabong once a year. However water harvesting has led to a decrease in inundation frequency to approximately once every three to four years (Sinclair Knight Merz 2005).

Sediment sampling

A 289 cm sediment core was obtained from Bolin Billabong in July 2001 using a light-weight modified hammer-driven piston corer (Neale and Walker 1996) with a 50 mm polyvinyl chloride barrel (Figure 1). The water depth was approximately 3 m. The core was stored at 4^0C for approximately a month before it was opened and sampled at 8-cm intervals for metals analysis. Other analyses conducted on this core (diatom assemblages, pollen) have been discussed in previous works (Leahy 2007; Leahy et al. 2005).

Unsupported ^{210}Pb activities were measured for samples taken at intervals of 1-25 cm in the top 176 cm of the core. Both the Constant Initial Concentration and the Constant Rate of Supply models (Appleby 2001) were applied to identify the ages of the sediments using the unsupported ^{210}Pb activities, but these resulted in different sediment chronologies. As it could not be determined which one of these models were more accurate, independent chronological markers were used instead to date the core. These markers were declining total lead (Pb) concentrations at 16 cm (dated as 1985), a significant increase in Pb concentrations at 108 cm (1932), a peak in magnetic susceptibility at 160 cm attributed to a Yarra River flood (1901), the appearance of *Pinus* pollen at 208-cm depth (1870) and an increase in pollen taxa indicative of land clearing at 265-cm depth (1840). Previous studies have hypothesised that high magnetic susceptibility in sediment cores can be caused by flooding because they deposit high amounts of terrestrial sediments, which are generally rich in magnetic mineral content (Moreno et al. 2008). Other studies have validated this relationship by comparing dated

magnetic susceptibility profiles to measured river flow data (Wolfe et al. 2006). The process of this dating approach is further detailed in Leahy (2007).

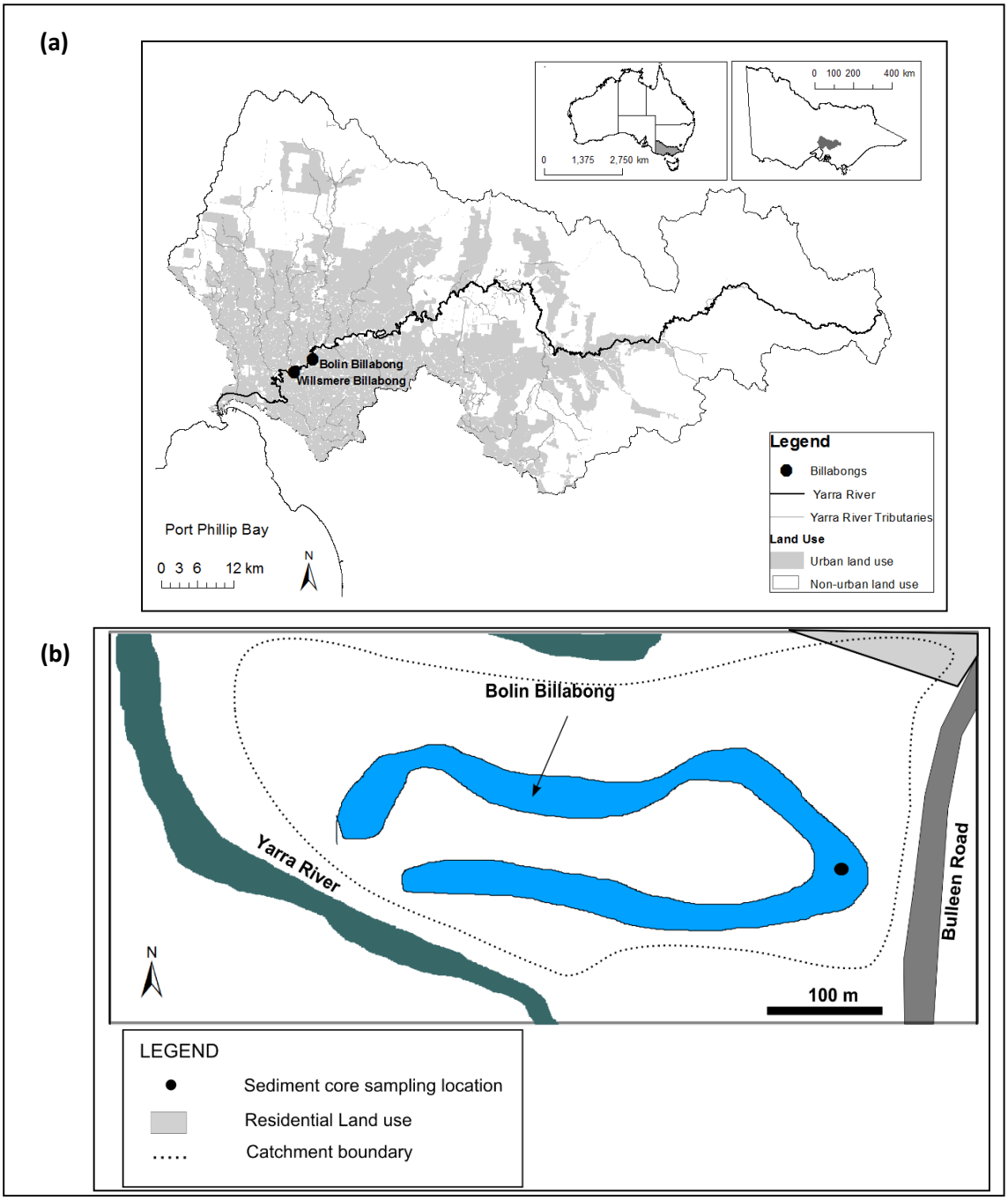

Figure 1. The Yarra River and its catchment showing the location of Bolin Billabong and Willsmere Billabong (a), the local catchment of Bolin Billabong (b).

Sub-samples for heavy metal analysis were dried at 48^{0}C. Nitric acid (HNO_3) partial digestions were conducted at room temperature by adding 1 g of dried sample to 30 mL of 35% HNO_3 as per Pietrzak and McPhail (2004). Metal concentrations were quantified by Inductively Coupled Plasma–Mass

Spectrometry (ICP-MS). Standard quality assurance and control measures were undertaken including the calibration of samples using USGS standards (BHVO-1). Similarly, replicate measurements and blanks were analysed every five to seven analyses. The following analysed metals are discussed: aluminium, Al; cadmium, Cd; chromium, Cr; copper, Cu; iron, Fe; Pb; manganese, Mn; nickel, Ni; tin, Sn; and zinc, Zn.

Data analysis

As the heavy metal concentrations are not distributed normally (according to the Shapiro-Wilk test, $p<0.05$, results in Table S1 in the supplementary material), the heavy metal trends were compared using the Spearman Rank Correlation Coefficients (ρ). It was assumed that sediments deposited in the billabong before 1850 were deposited in undisturbed conditions, as significant development in the Yarra River catchment began in 1851 with the official commencement of gold mining (Brizga et al. 1995). The heavy metal concentrations before 1850 were compared to those deposited after 1850 using the Mann-Whitney U Test ($p<0.05$) to identify if there was a statistically significant difference between the post-disturbance and pre-disturbance heavy metal concentrations. Trends in heavy metals were also compared to trends in population and urban growth using the Spearman Rank Correlation Coefficient (ρ). All statistical tests were conducted using R-studio. Heavy metal concentrations of sediments from the core surface (0 cm) were excluded from the analysis. We believe these data to be suspect due to sediment mixing during sampling. Due to the relatively coarse sub-sampling interval used in this study, overall heavy metals trends rather than short-term variabilities were examined.

The maximum background (pre-1850) heavy metal concentrations from Bolin Billabong were also compared to those obtained from a sediment core taken from the nearby Willsmere Billabong (Figure 1). Background concentrations from both cores were then compared to sediment quality trigger values in ANZECC/ARMCANZ (2000) guidelines. These comparisons were done for Cd, Cr, Cu, Pb, Ni and Zn, because these metals have sediment quality trigger values in ANZECC/ARMCANZ (2000) guidelines.

A separate investigation (Lintern et al. 2015) of heavy metal concentrations in sediment cores from Willsmere Billabong showed relatively stable heavy metal concentrations in sediments deposited between 1700 and 1850 (Figure S1 in the supplementary material). Due to the proximity of these two billabongs (less than 10 km), the background heavy metal concentrations of Bolin Billabong are likely

to be similarly stable. As such, we hypothesise that the background sediments within the studied Bolin Billabong core are representative of long-term background heavy metal concentrations.

RESULTS AND DISCUSSION

Sediment characteristics in the Bolin Billabong sediment core

Sediment characteristics through the Bolin Billabong core have been discussed in previous works (Leahy 2007; Leahy et al. 2005) and are briefly summarized here. Three main lithological units were identified in the core. The top unit (0-132 cm) contained dark grey lake clay with organic matter. The second unit (132-265 cm) contained black, dark grey and dark olive grey clay laminations of 1 to 5-mm thickness. Finally the bottom unit (265-289 cm) contained black organic clay. These changes in the sediments are consistent with those in the nearby Willsmere Billabong (Lintern et al. 2015).

Heavy metal trends in the Bolin Billabong sediment core

Heavy metal trends within the Bolin Billabong sediment core are shown in Figure 2. For some metals (Al, Cr, Cu, Fe, Pb, Ni, Sn and Zn), concentrations are relatively constant in the 19th century, but increase through the 20th century. Mn fluctuates around a central point and Cd also exhibits a slight increasing trend. These patterns are reflected in the Spearman Rank Correlation Coefficients (Table S3 in the supplementary material), which show strong and statistically significant correlations ($\rho>0.75$) between Al, Cr, Cu, Fe, Pb, Ni, Sn and Zn. Thus, the majority of the metals exhibit similar trends, which suggests that their deposition is governed by similar processes. However, the different trends in Cd and Mn suggest that the factors affecting their deposition in Bolin Billabong are different to the other metals.

All elements presented in Figure 2, except Mn, have increased from their background levels over the last 150 years. Thus, if the background condition of the billabong (pre-1850 levels) were taken as target values for sediment quality in Bolin Billabong, we would conclude that reduction in all of these metals is required. In particular, the metals with the greatest increase appear to be Fe, Al, Zn and Pb (Figure S2 in the supplementary material). However, we recognise that four samples were used to identify the background levels. Despite the limited number of samples used, the differences between the pre-1850 and post-1850 sediment metal concentrations were statistically significant for Pb and Zn according to the Mann-Whitney U-test ($p<0.05$; Table S4 in the supplementary material).

The suitability of existing sediment quality trigger values

Table 1 indicates that recommended sediment quality trigger values are generally greater than maximum metal concentrations deposited before 1850 (i.e., background levels). The pre-1850 heavy metal concentrations (maximum) of Willsmere Billabong (Figure 1) are very similar to those of Bolin Billabong (Table 1). In fact, the background levels for the two billabongs are closer to each other than they are to the ANZECC/ARMCANZ sediment quality guidelines. Most metals do not have statistically significant differences ($p>0.05$) between the heavy metal concentrations in pre-1850 sediments in Willsmere and Bolin Billabong (Table S5 in the supplementary material). As such, it appears that these heavy metal levels obtained from the sediment cores are indicative of a background metal concentration relevant to the Yarra River catchment. If the recommended generic trigger values are used to identify the toxicants of concern, only Pb would be identified as being of concern in Bolin Billabong sediments (Table 1 and Figure 2). However, Table 1 indicates that by applying site-specific background levels, a considerably larger number of metals would be regarded as exceeding guidelines. These site-specific background levels in Table 1 are based on four samples for Bolin Billabong and six samples for Willsmere Billabong. When developing site-specific background levels for water quality monitoring using sediment cores, it is recommended to obtain a larger number of pre-disturbance sediment samples. For example, we recommend that the ideal number of samples be determined using power analysis (Zar, 2010). This will ensure greater statistical power when comparing monitoring data to the calculated site-specific trigger values.

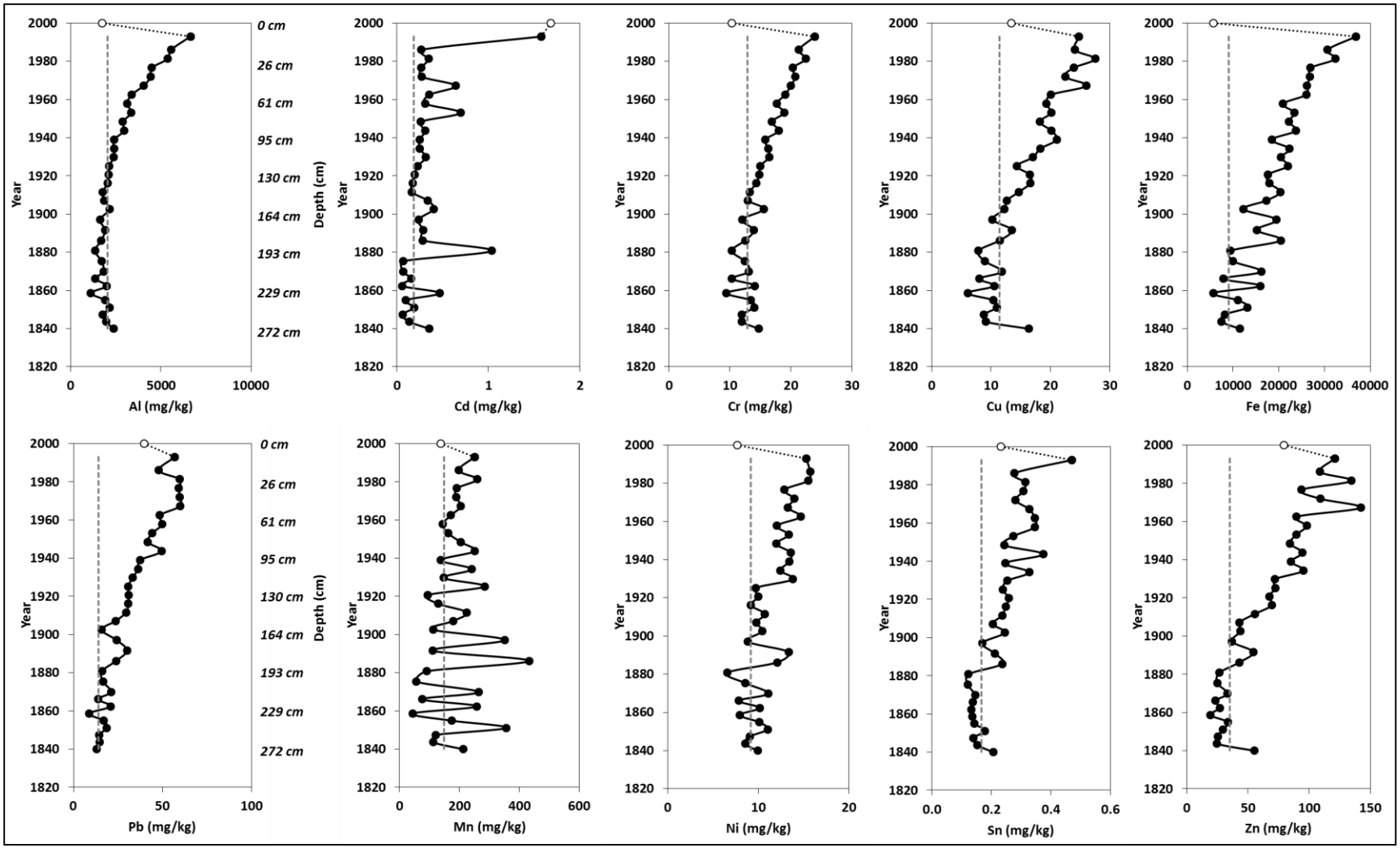

Figure 2: Heavy metal profiles of Bolin Billabong sediment core (core depth shown on secondary Y axis for Al and Pb, open circle with dotted line represents suspect data point at core surface and grey dashed line represents the pre-1850 background concentration of the metal). Metal profiles normalized by the average pre-1850 metal concentration provided in Figure S2 in the supplementary material. Heavy metal concentrations are tabulated in Table S2 in the supplementary material.

Table 1: Trigger values for sediment quality and background concentrations calculated for Bolin (n=4) and Willsmere Billabongs (n=6) using sediment cores.

Metal	Guideline trigger values (mg/kg)[a]		Maximum Bolin Billabong sediment concentration before 1850 (mg/kg)	Maximum Willsmere Billabong sediment concentration before 1850 (mg/kg)
	Low[b]	High[c]		
Cd	1.5	10	0.4	<0.2
Cr	80	370	15	37
Cu	65	270	16	14
Pb	50	220	19	15
Ni	21	52	11	23
Zn	200	410	55	64

[a] (ANZECC/ARMCANZ 2000)
[b] Upper limit of heavy metal concentrations for toxic effects to have a low probability
[c] Lower limit of heavy metal concentrations for toxic effects to have a medium probability

The factors affecting heavy metal contamination in Bolin Billabong

The heavy metal profiles can also be used to infer the main factors affecting historical heavy metal contamination in the lake. Firstly, Al and Fe, which have similar increasing trends with time (ρ=0.81, $p<0.05$; Table S3 in the supplementary material), are likely to have been driven by increased sediment influx into the billabong due to erosion, resulting from urban development and land clearing (indeed, eroded soil is known to contain high concentrations of Fe and Al; Schiff and Weisberg 1999; Schropp et al. 1990). The Al and Fe concentrations trends correlate ($p<0.05$) with increasing population in the municipality in which the billabong is located (Manningham City Council) as well as in the Yarra River catchment upstream of Bolin Billabong (Figure 3 and Table S6 in the supplementary material). A change in sediment texture was also noted at approximately 130 cm (dating to approximately the 1920s), which may be indicative of an increasing flux of these eroded clay materials.

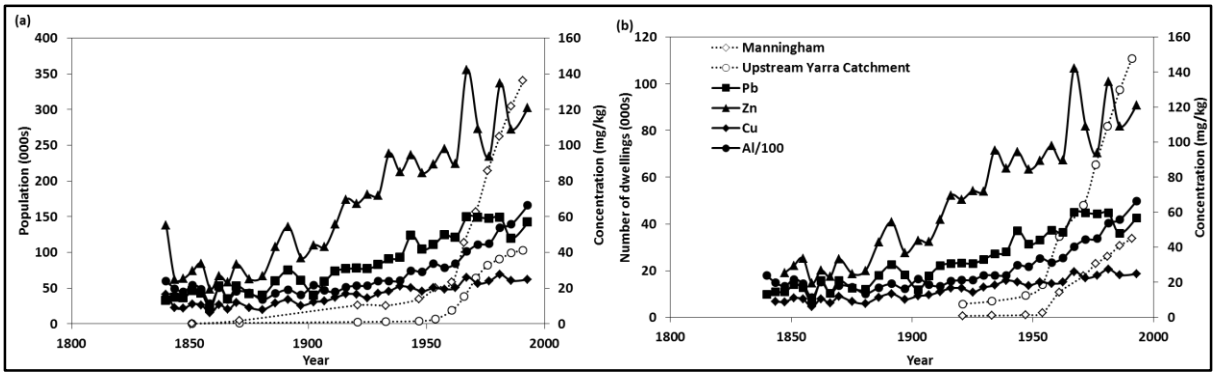

Figure 3. Population in the City of Manningham and the Yarra river catchment upstream of Bolin Billabong, and concentrations of Al, Cu, Pb and Zn (a) and number of dwellings in the City of Manningham and the Yarra river catchment upstream of Bolin Billabong, and concentrations of Al, Cu, Pb and Zn (b).

The increase in Cd, Cr, Cu, Pb, Ni, Sn and Zn in the 20th century could be partly attributed to this sediment influx, as heavy metals are present at trace levels in rocks and soils (Taylor and McLennan 1995). However, the rates of increase in Pb and Zn are greater than that of Al and Fe (Figure 2 and Figure S2 in the supplementary material). Increasing Pb and Zn concentrations could also be driven by motor vehicle emissions, following the introduction of motor vehicles in the early 20th century (Davison 2010). Additionally, Pb and Zn are common building materials (Weeks and Grimmer 1995) and increasing urban development in the Yarra River catchment upstream of the billabong after the 1950s (Figure 3) would have resulted in the leaching of these metals into the Yarra River by urban stormwater (Hart and White 2006). Bolin Billabong would then receive these contaminated flows via overbank flooding of the river. In particular, Zn concentrations increase in the 1970s (Figure 3), which correlates with the introduction of Zinc-Alum roofing (Oppenheim and Sutherland 1978).

Cd deposition in the billabong has also increased slightly since European settlement (ρ=0.46, p<0.05). This may be related to sediments entering the billabong due to urbanization and land clearing, Cd in industrial emissions, or increasing use of fertilisers in the catchment (Fishbein 1981). There are short term fluctuations in the Cd trend (Figure 2) possibly due to Cd input by flooding. However, higher resolution sampling of Cd is required to fully understand the underlying causes of this short term variability.

The relatively stable profile of Mn indicates that Mn deposition is not influenced by the factors discussed above. The lack of a clear upward or downward trend in Mn through the sediment core is most likely due to post-depositional remobilization of Mn by redox processes (Boyle 2001).

The core was sub-sampled at 8 cm intervals. This interval may be equivalent to up to 5 years' worth of sediment accumulation, given the adopted age-depth model has an average sedimentation rate of 1.7 cm/year (Leahy 2007). Although there are uncertainties in the adopted age-depth model, for a better understanding of short term variability in heavy metal contamination of Bolin Billabong (e.g., at an annual time-step), a finer sub-sampling interval would be necessary.

CONCLUSIONS

This study aimed to identify historical heavy metal levels in Bolin Billabong sediments. Comparing the metal concentrations through the sediment core indicate that the billabong bed sediments have experienced increasing concentrations of Al, Cd, Cu, Fe, Ni, Pb, Sn and Zn since 1850. The timing of the heavy metal increases suggest that restoration of metal concentrations to background levels would

require reduction in the transport of fine sediments from the catchment, reduction in metals leached from building materials into the billabong, and the decrease in vehicle emissions.

Comparison between the background heavy metal concentrations in two Yarra River catchment billabongs indicates that the sediment quality trigger values used in Australia may be higher than true background heavy metal concentrations of aquatic sediments. We recognize that if sediment quality trigger values are to be developed using sediment cores, replicate cores from a single aquatic system would be necessary, as would verification that the sediment core is continuous and that it has not been adversely affected by bioturbation, sediment mixing or drought. It is expected that in some continents, such as Europe, which have a long history of industrial and agricultural activity, obtaining site-specific background metal levels may require older sediments than those presented in this investigation due to the longer history of anthropogenic pollution (e.g., due to industrialization, Pb smelting). The key message of this study is that using currently available generic trigger values could lead to the adoption of sediment quality targets that do not sufficiently protect some ecosystems. This study highlights the importance of identifying site-specific background levels of sediments for the protection of aquatic systems and proposes the use of sedimentary records for determining these background levels.

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4.3 Historical pollution trends of Willsmere Billabong

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Digging up the dirty past: evidence for stormwater's contribution to pollution of an urban floodplain lake

Anna Lintern[A,C], *Ana Deletic*[A], *Paul Leahy*[B] *and David McCarthy*[A]

[A]Monash Water for Liveability, Department of Civil Engineering, Monash University, Clayton, Vic. 3800, Australia.
[B]EPA Victoria, Applied Sciences Group, Ernest Jones Drive, Macleod, Vic. 3085, Australia.
[C]Corresponding author. Email: anna.lintern@monash.edu

Abstract. Negative effects of urbanisation on the health of aquatic environments are well recognised; but more data are needed for an accurate assessment of the particular effects of residential development on the health of aquatic systems. This study explores the relationship between residential growth and increasing pollution, by analysing temporal trends of chemical fluxes into Willsmere Billabong – an urban floodplain lake of the Yarra River in South-East Australia. Sediment cores were extracted to reveal depositions over three centuries (~1700–2012). The cores were sub-sampled at high resolution and analysed for heavy metals, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). Pollutant concentrations in the sediments appear to have been significantly affected by residential development in the local catchment. Normalised concentration profiles show these effects to be exacerbated from the mid-20th century, after a stormwater drain was installed in the billabong. The study suggests that urban stormwater management techniques are critical for the protection of aquatic systems incorporated into residential zones.

Additional keywords: floodplain lake, historical reconstruction, residential development, sediments, toxicants, water quality.

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Introduction

Changes in land use affect the health of waterways (Foley *et al.* 2005). Urbanisation brings industrial activities, infrastructure development, more traffic and therefore higher emissions of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and elements that we characterise broadly as heavy metals (Brandenberger *et al.* 2008; Duh *et al.* 2008). The toxicity and bioaccumulation properties of these substances (Ribeiro *et al.* 2005) pose a threat to both humans and the natural environment. The situation is expected to become more serious, with projected global growth in urban areas of 158% from 2000 to 2030 (Seto *et al.* 2012).

Although the effect of industrial development on aquatic environments is well studied (Wu *et al.* 2012), the relationship between residential development and environmental degradation has received less attention. Particularly in developed countries, current and future urban expansion largely comes from the growth of residential zones at the rural–urban fringe (Irwin and Bockstael 2002). Residential developments encroach onto natural and undeveloped catchments, threatening the health of aquatic systems (Gude *et al.* 2006). However, one appeal of extra-urban living is proximity to natural features or in other words, the ideal of a 'water sensitive city' (Brown *et al.* 2005; Wong and Brown 2009), which makes it even more critical to prevent the degradation of these catchments. Understanding the relationship between residential development and water quality is a pressing issue for 21st-century planning (Nuissl *et al.* 2009).

Several research groups have monitored the relationship between water quality and residential growth in American cities over the past 30 years (Interlandi and Crockett 2003; Tu *et al.* 2007); but in general the scarcity of long-term water quality data has held back further investigations. This lack of data has restricted modelling of effects from changes in land use (Bhaduri *et al.* 2000; Wilson and Weng 2011), because simulations demand extensive long-term data for calibration and validation. Some researchers have addressed this problem by comparing several waterways with differing patterns of land use (Jennings *et al.* 2003). However, such comparisons are difficult. Spatial variability in background conditions (such as different elemental compositions in the natural soil of the catchment) can affect the determination of water quality in complex ways. Hence it is important to collect historical data for waterways where the primary land use has been residential, to protect aquatic systems from further residential development.

Undisturbed sediment cores, taken from the beds of aquatic environments, can act as historical records of contamination

from both heavy metals and persistent organic pollutants (POPs). These pollutants accumulate in bed sediments, owing to their post-depositional stability and strong association to particulate matter (Blais and Muir 2001; Boyle 2001). Previous sediment-core studies have focussed on large catchments with mixed land uses, such as residential, commercial, industrial, mining and agriculture (Brandenberger *et al.* 2008; Vane *et al.* 2011). Despite a critical need to understand the particular effects of residential use, these have rarely been investigated using sediment cores.

We therefore focus on a site strongly affected by residential activities but only minimally by industry. Our aim is to acquire a long-term dataset from sediment cores, and use it to isolate the relationship between residential use and water quality. Encompassing 150 years of development within a catchment, our dataset can be used to estimate the effect of future residential development on aquatic environments and to identify strategies to mitigate the effects. The site used for this investigation is Willsmere Billabong, a floodplain lake of the Yarra River in South-East Australia.

Our central hypothesis is that residential growth – as marked by trends in heavy metals (a term that we use inclusively, extending to Arsenic and other metalloid elements), PAHs and OCPs identified in sediment cores – has significant detrimental effects on aquatic environments. This study will stand as a proof of concept – for sediment core studies that yield a better understanding of the environmental effects of residential growth and for a framework that can be applied in practice during residential development.

Materials and methods

Site geography

Willsmere Billabong (37°47′23″S, 145°2′33″E) is a 1.9-ha floodplain lake (Leahy 2007) of the Yarra River located in Kew, an inner suburb of the city of Melbourne in South-East Australia (Fig. 1). The billabong's local catchment has no history of industrial development (Pru Sanderson Design Pty Ltd 1988); but the catchment of the Yarra River, which runs 240 km from the Great Dividing Range to Port Phillip Bay, includes both urbanised areas (industrial, commercial, residential) and non-urbanised areas (agricultural, forested).

The billabong receives water from both the local catchment (15 ha) and the greater Yarra River Catchment (3285 km^2) (Leahy 2007). Stormwater from the local catchment enters by overland runoff and also through a stormwater drain installed in 1940 (David Barclay, City of Boroondara, pers. comm., 2 April 2013). Given rainfall trends in Melbourne, this local input is estimated to occur twice per week on average (Blecken *et al.* 2009). The billabong also receives flow from the main river channel, although only when there is overbank flooding of the river. Sediment cores will therefore reflect the history of both the local catchment and the Yarra River Catchment. Hydrologic modelling has shown that in natural conditions, overbank flooding would occur approximately once per year (Sinclair Knight Merz 2005), but late 20th-century construction of dams in the upper reaches has reduced the frequency to once every 3 or 4 years (Sinclair Knight Merz 2005; Leahy 2007).

Site history

The Yarra River Catchment was continuously inhabited by the Wurundjeri people from *c*. 46 000 years ago (Otto 2005). Since European settlement in 1835, Melbourne has experienced steady and significant urban growth (Fig. 1*d*). Fig. 2 summarises major developments and events in the catchment between 1835 and 2010.

Sediment sampling

Five sediment cores were collected from Willsmere Billabong (Fig. 1) in October 2012. Three cores were taken using a lightweight modified hammer-driven piston corer with a polyvinyl chloride (PVC) barrel of diameter 50 mm (Neale and Walker 1996). Lengths of the cores were 210 cm (W1), 230 cm (W2) and 200 cm (W3). Two additional cores (W4 and W5) were taken with a Livingstone corer of diameter 40 mm (Livingstone 1955). W4 consisted of one drive from the bed surface to depth 96 cm. W5 was taken from a different guide hole with a recovered length of 91 cm. The cores were stored at 4°C.

Magnetic susceptibility was measured on all cores at 1-cm intervals using a Bartington MS Series One meter and core scanning loop (Bartington Instruments, Witney, UK). To account for drift, readings were taken from both top to bottom and bottom to top and then averaged (Leahy *et al.* 2005). The longest intact cores (W1 and W4) were both halved longitudinally. Texture, colour and the presence of macrofossils and laminations were used to identify the main sediment units. One-half of each core was then sub-sampled using unplasticised PVC (uPVC) equipment: at 0.5 cm for W1 and at 1 cm for W4. To avoid contamination or smearing, all sediment in contact with the inner core barrel was removed. Sub-samples were stored at 4°C for ~48 h in glass jars, using lids lined with polytetrafluoroethylene (PTFE), before being composited (over 1 cm for heavy metals and 4 cm for POPs) and then air-dried.

These sub-sampled sediments were analysed for metals, PAHs and OCPs at laboratories accredited by the National Association of Testing Authorities (NATA). Heavy metal analyses of sediments were conducted at ALS (Melbourne) and POPs analyses at the National Measurement Institute (Sydney). For metals, digestion using aqua regia (nitric and hydrochloric acids) was followed by inductively coupled plasma mass spectrometry (ICP-MS) in accordance with USEPA SW846 Rev 2007 (US EPA 2007). Gas chromatography mass spectrometry (GC-MS) was employed for PAHs following US EPA 3540/8270; and gas chromatography with an electron capture detector (GC-ECD) following US EPA 3550/8081 (US EPA 2007) was used for OCPs. Limits of reporting (LORs) are 5 mg kg^{-1} dry weight (DW) for aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), silver (Ag), strontium (Sr), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn); 10 mg kg^{-1} DW for boron (B), iron (Fe); 0.2 mg kg^{-1} DW for cadmium (Cd); 0.05 mg kg^{-1} DW for mercury (Hg); 0.01 mg kg^{-1} DW for PAHs; 0.001 mg kg^{-1} DW for PCBs; and 0.0002 mg kg^{-1} DW for OCPs. Standard quality assurance and control procedures were undertaken, including analyses of blank and duplicate samples and identification of recovery rates using spiked samples.

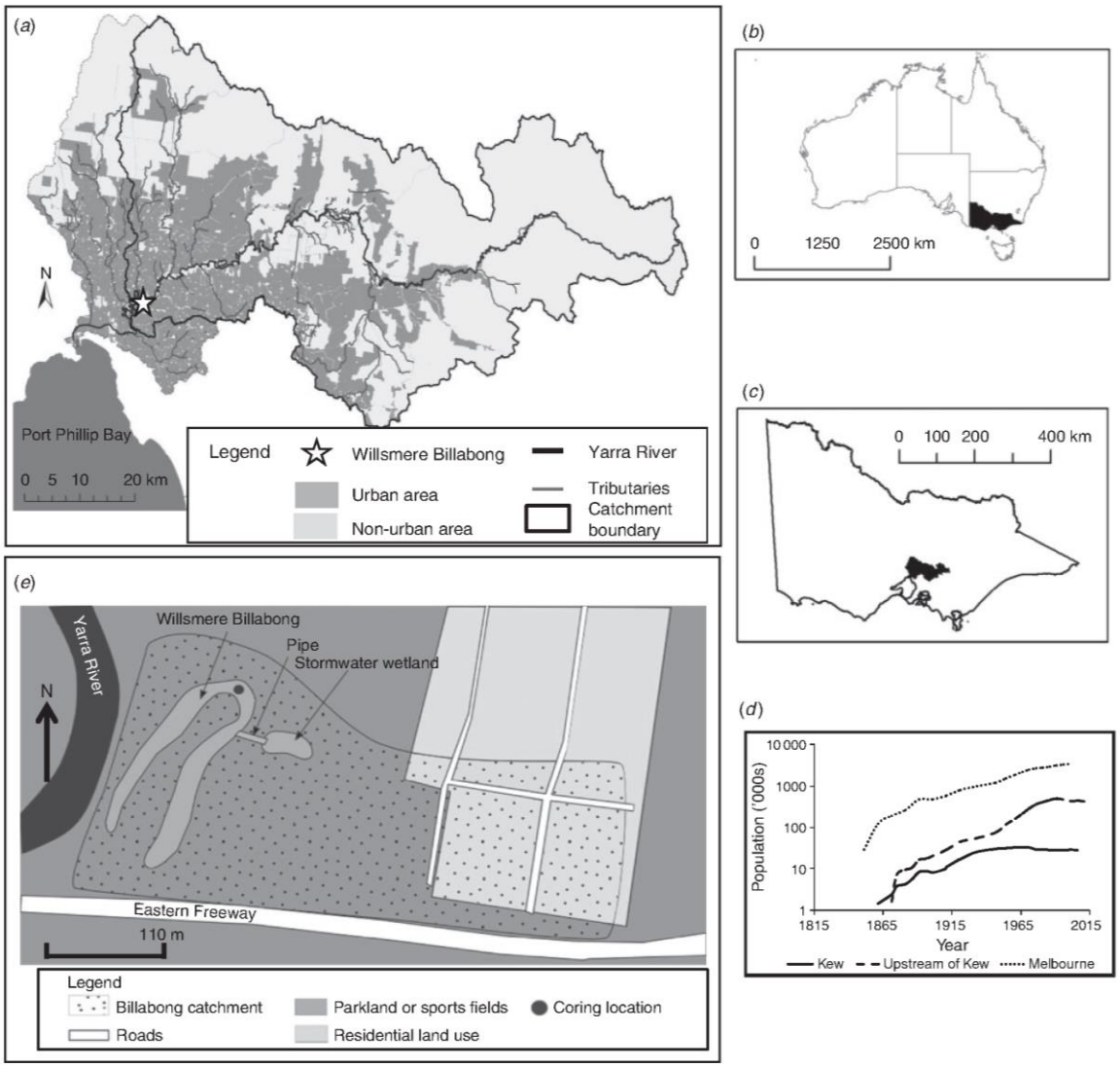

Fig. 1. (*a*) Yarra River Catchment showing Willsmere Billabong, the Yarra Catchment upstream of this billabong, and land use within the catchment; (*b*) Australia, showing location of the state of Victoria; (*c*) Victoria, showing location of Yarra Catchment; (*d*) population growth of Kew, the Yarra Catchment upstream of Kew, and Melbourne (developed using data from the Australian Bureau of Statistics); and (*e*) a map of Willsmere Billabong showing the current local catchment.

For metals, recovery rates were above 82% and relative percentage differences between duplicate samples ranged from 0.2 to 18.5%. For POPs, recovery rates of spiked samples were above 88% and relative percentage differences between duplicate samples ranged from 8.5 to 38%.

Sediment dating

In a previous study, an age–depth model was developed for a 270-cm sediment core taken in 2001 from the same location as W1 and W4 (Leahy 2007). Nine sub-samples from the top 52.5 cm of the 2001 core (intervals of 1–5 cm) were dated using lead isotopes (^{210}Pb). Other chronological markers for this age–depth model included a distinct clay deposit at 33–35-cm depth because of the construction of a nearby freeway (early 1970s), a maximum in magnetic susceptibility at ~85 cm caused by a flood of the Yarra River (1901), appearance of significant amounts of pine pollen at 190 cm (1870), and a wood sample at 260 cm that was deposited in 1535 according to radiocarbon (^{14}C) dating (Leahy 2007). The year 1870 was assigned to the appearance of *Pinus radiata* pollen in the core. This is because the first recorded planting of *P. radiata* in Victoria was ~5 km from Willsmere Billabong in 1859 and it is estimated that *Pinus* species take between 5 and 10 years to produce pollen (McDonald and Laacke 1990). Full details

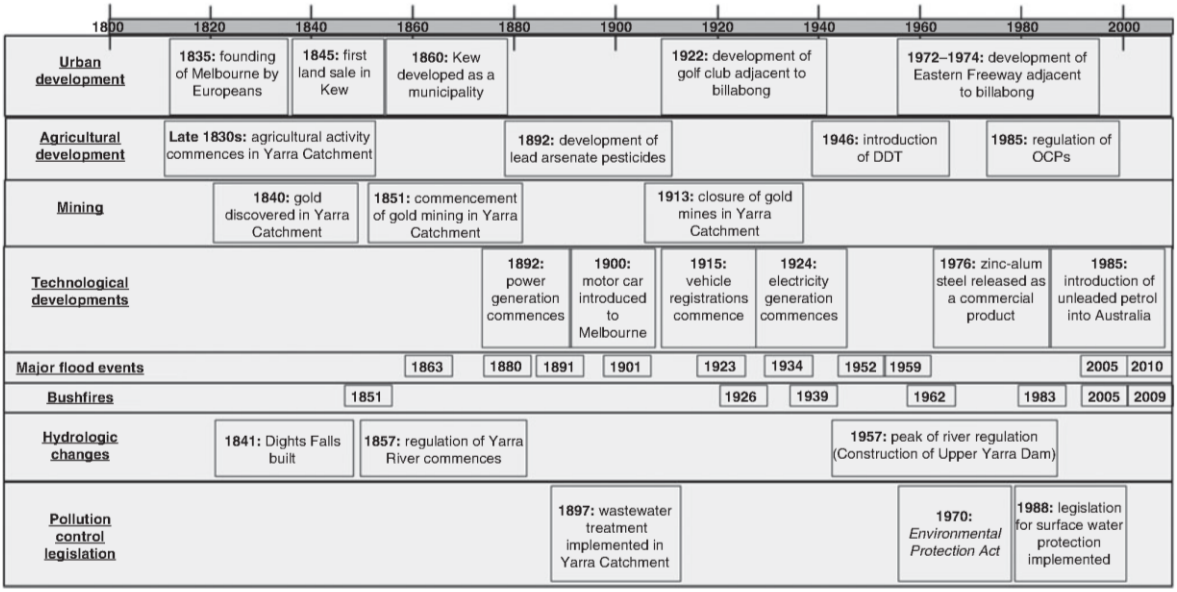

Fig. 2. Timeline of significant events in the Yarra River Catchment.

about the age–depth model for this 2001 core can be found in Leahy (2007).

Age–depth models were developed for the W1 and W4 cores by correlating their magnetic susceptibility profiles to those of the 2001 core (Leahy 2007). Visual features in the sediment cores were also used to determine the ages at which certain sediments were deposited. These features include the leaf layer at the top of W4 (which indicates that the surface sediment was captured), and also a yellow clay layer (45.5–49.3 cm) in W4 that suggests the occurrence of major construction activities (Leahy 2007). In addition, a wood sample obtained at 155 cm was submitted to an accredited laboratory (ISO 17025, laboratory number Beta-351481) for ^{14}C AMS dating. Reference materials with known values were used to verify the laboratory procedures.

Data analysis

Several factors affect the concentrations of metals and POPs in sedimentary deposits. Concentrations reflect not only the amounts deposited, but also the substances' chemical properties (such as affinity to certain types of sediments) and the total sediment fluxes (which may dilute or concentrate metals and POPs in a sedimentary record). Although it would be ideal to determine metal and POP mass fluxes, we were unable to obtain a high-resolution profile of total sediment accumulation because of the low resolution of the age–depth model. Instead, we normalised metal and POP concentrations against reference substances to help in allowing for variability in sediment characteristics and total sediment flux (Förstner 2004). Following the practice of other authors (Townsend and Seen 2012; Ontiveros-Cuadras *et al.* 2014), Al was used as the normalising element for metals. Al is suitable because it is abundant in the earth's crust, there is low possibility of anthropogenic Al pollution in waterways, and Al is strongly correlated with the level of fine-grained clay sediments (the sediment fraction with which metals are generally associated) (Schropp *et al.* 1990; Förstner 2004). However, Hg was normalised to S and not to Al because Hg has a higher association with S (Santschi *et al.* 2001). POP concentrations were normalised to organic matter because of their preferential attachment to it (Bogdal *et al.* 2008). Mo incoherent/coherent ratio (inc/coh) was obtained when the two sediment cores were scanned using the ITRAX micro-X-ray fluorescence (XRF) core scanner (Croudace *et al.* 2006), and this ratio was used as a measure of organic matter. A Mo tube (voltage 30 kV, current 45 mA) was used with a 10-s exposure time, reading at 1-mm intervals. Inc/coh has been used as a measure of organic matter in a sediment core by previous studies (Guyard *et al.* 2007). The XRF core scanner was also used to obtain levels of S through the sediment core. The inc/coh and S profiles are provided and discussed in the Supplementary material (Fig. S1).

The normalised profiles of the metals (data standardised before statistical testing) were partitioned with hierarchical cluster analysis using the Euclidean distance measure and the average linkage method (Danielsson *et al.* 1999). When the concentration of a compound or element fell below its assigned LOR over the whole core, that substance was excluded from the data analysis. When there were readings for an element both above and below the LOR within a single core, the readings below the LOR were adjusted to be half of the LOR.

Results

Sediment core description and magnetic susceptibility

The Willsmere Billabong cores (W1 and W4) consisted of black to pale yellow lake clay (Fig. 3*b*, *c*). Gradual transitions

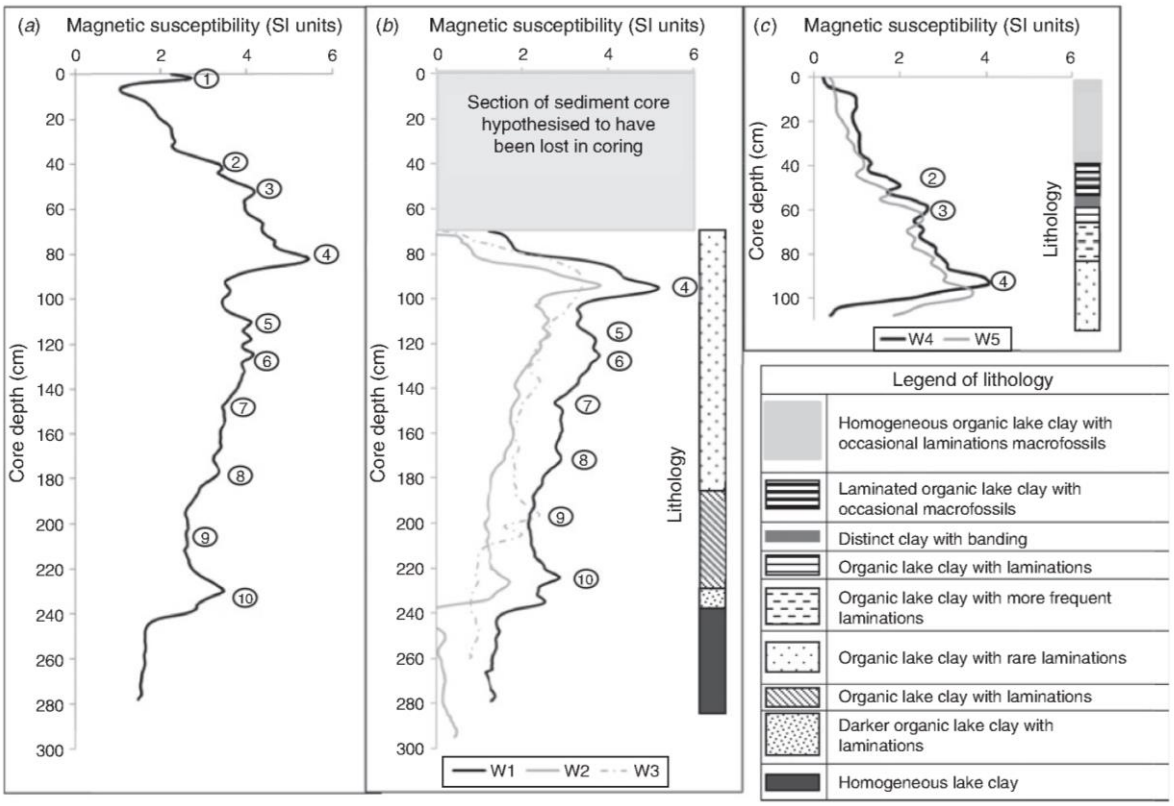

Fig. 3. Magnetic Susceptibility profiles and lithology for: (*a*) Willsmere Billabong core which has a reported age–depth model (in Leahy 2007); (*b*) 2012 Willsmere Billabong cores W1, W2, W3; and (*c*) 2012 Willsmere Billabong cores W4, W5. Numbers represent common peaks in magnetic susceptibility profiles.

suggested negligible erosion between lithological units. Surface sediments were identified by a layer of leaf matter at the core surface; and because this layer was found on W4 but not on W1, it is inferred that W4 included and W1 lacked the more recent sediments. Fig. 3*b* has been shifted downward by 70 cm, because the top 70 cm of the lightweight modified hammer-driven piston cores appear to have been lost during collection (due to stiffness in some sedimentary units). This inference will be justified below.

There is a distinct layer of yellow clay in W4 (Fig. 3*c*), which is again missing from W1 (Fig. 3*b*). Leahy (2007) suggests that this layer was deposited during construction of the Freeway (within the billabong's catchment) in the 1970s. There is a layer of organic matter at 68 cm in W1 and also at 9 cm in W4, and these appear to be the same sedimentary unit. There is also a distinct visual and textural change of the sediment in W1 at 158 cm, marking a transition from black lake clay with very dark grey and pale yellow laminations of thickness 1 to 5 mm to a drier and more compacted homogeneous black lake clay. Leahy (2007) previously found a significantly different mix of pollen species in these two sedimentary units, and inferred that this transition boundary represented the settlement of Europeans in the area. Photographs of the 2012 cores are shown in the Supplementary material (Fig. S2).

W1, W2 and W3 are similar in their magnetic susceptibility profiles, and so are W4 and W5 (Fig. 3). This suggests that the cores contain the same sedimentary units. Measuring the amounts of magnetic minerals, magnetic susceptibility profiles may give evidence that sedimentary deposits have similar origins (Maher 2007). Discrepancies between the profiles of cores from the lightweight modified hammer-driven piston corer (W1, W2 and W3) on the one hand and from the Livingstone corer (W4 and W5) on the other suggest that the top 70 cm of W1, W2 and W3 were lost. From these profiles and also from the lithology of the cores, it seems that those from the lightweight corer represent a continuation of those from the Livingstone corer, with a period of overlap (Fig. 3). Comparison of magnetic susceptibility profiles in these 2012 cores with the core taken in 2001 supports this inference. Indeed, peaks 2 and 3 in magnetic susceptibility (preceding the large peak 4, see Fig. 3) which are identified in the 2001 core, are not present in cores W1, W2 and W3; but they are visible in W4 and W5. In addition to the loss of sediment, visual inspection suggests sediment mixing in the top 15 cm of W1. Believing these data

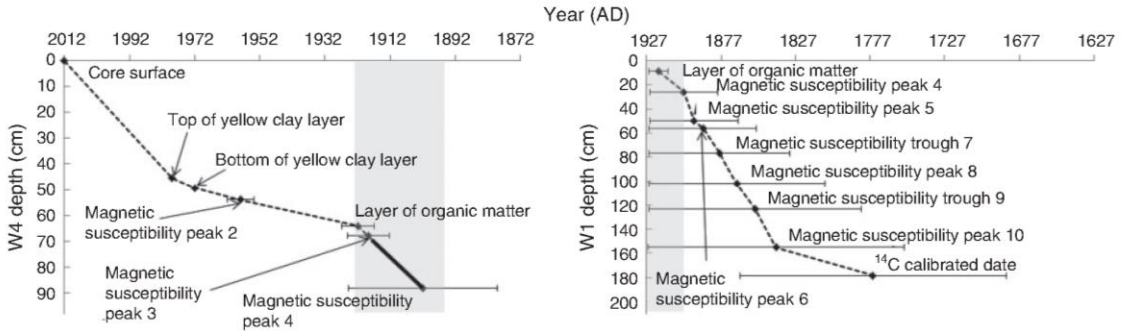

Fig. 4. Age–depth models for W4 (left) and W1 (right) constructed using measurements by Leahy (2007); shaded areas showing the area of overlap between the two cores (thick black lines represent periods where extrapolation occurred).

to be suspect, we have removed them from trend analyses for metal, PAHs and OCPs.

Age–depth model

After correlating the magnetic susceptibility profiles of the 2012 and 2001 cores (Fig. 3), we identified additional chronological markers. These markers include: (1) the leaf matter at the surface of the core (representing 2012); (2) the distinct clay layer at depth 45.5–49.3 cm in W4 (representing deposits from 1972 to 1977); (3) a layer, 2–4 cm thick, of organic matter used to correlate W1 and W4; and (4) a wood sample found at depth 178.5 cm in W1, for which dating with ^{14}C AMS revealed a conventional radiocarbon age of 160 ± 30 years before present and a $^{13}C/^{12}C$ value of -25.7. Using the IntCal09 database, this was calibrated to a date of 1775 ± 55 years AD. The distinct clay layer at 45.5–49.3-cm depth in W4 is thought to have been deposited during construction of a nearby freeway (Leahy 2007), so it was assigned to 1972–1977 (the period of that construction) (Leahy 2007). The age–depth model shown in Fig. 4 was developed assuming constant sediment accumulation rate (SAR).

Age–depth modelling has several sources of error. Laboratory and analytical uncertainty associated with the radioanalysis of ^{210}Pb was quantified in Leahy (2007) as between 5 and 20 years. The uncertainty of the age–depth markers in W1 and W4 was assumed equivalent to those reported for the 2001 core in Leahy (2007). But there are also unquantifiable uncertainties, such as the potential thinning of sediment units in the core due to frictional forces during the coring process (Glew *et al.* 2002). Although this uncertainty could be minimised by using a corer of greater diameter, we believe that the 5-cm corer is adequate for Willsmere Billabong. Leahy (2007) also used a 5-cm corer at the same site, and the age–depth model developed by ^{210}Pb radioanalysis was verified by reference to independent chronological markers.

Metal profiles

Selected profiles of normalised metal concentrations from W1 and W4 are shown in Fig. 5. (See also Supplementary material: for absolute concentrations, Table S1; for profiles of data used for normalisation, Fig. S1.) There were some sections in the cores where metal concentrations were below the LOR. This meant that we could not obtain the complete temporal patterns for all the elements. Regardless, we believe that these profiles were sufficient to identify general trends in the metals. Several elements (Ag, B, Be, Mo, Sb, Sn and Tl) were excluded from the analysis because they were not detected at any point in the core. This may be because they are naturally present in sediments at levels below the LOR we assigned for this study (Taylor 1964; Li *et al.* 2011). These low concentrations also suggest that there has always been only a minimal discharge of these metals into the billabong. Indeed, common sources of these metals are mining (e.g. Sn), sewage disposal and solid waste incineration (Chillrud *et al.* 1999; Müller *et al.* 2000; Paetzel *et al.* 2003), which have not occurred in any part of the billabong catchment.

The normalised concentration profiles in Fig. 5 fall into four groups. The first category includes elements without a significant change in concentration over time (Ba, Sr, V). The second category contains elements with maxima in the early 20th century (As, beginning to increase in 1870 and decreasing after a peak in 1919; and Hg, reaching a peak in 1896). In the third category are elements with consistently increasing concentrations (Cd, Cr, Cu, Fe, Pb, Ni and Zn), though the timing and magnitude of the increases differ slightly for each pollutant. Evidence for increase in Fe begins at the bottom of the core; but the other pollutants were low from 1700, with higher levels emerging quite late: in 1933 (Cd), 1954 (Cr, Ni), 1895 (Cu) and 1870 (Pb, Zn). The fourth category contains only Ti, which appears to have had decreasing concentrations over time.

Cluster analysis produced different clustering patterns for W4 and W1 (Fig. S4 in the Supplementary material). The number of clusters differed between the two cores (8 for W4, 5 for W1) and the elements in each cluster differed. The diversity in these patterns suggests that different factors underlie the pollutant concentrations in W1 (1700–1897) as opposed to W4 (1897–2012). For example, whereas Cd, Cu, Pb and Zn were clustered together in W4, only Cu and Zn were clustered in W1.

The normalised metal concentrations were 1.2–1.4 times greater in W4 than in W1. It can be inferred that there is spatial variability in the association of these elements to Al, possibly due to more Al without associated pollutants being buried in the location of W1. This conjecture (effectively, of more uncontaminated terrestrial sediment input for W1 than for W4) gains support from generally higher magnetic susceptibility in W1

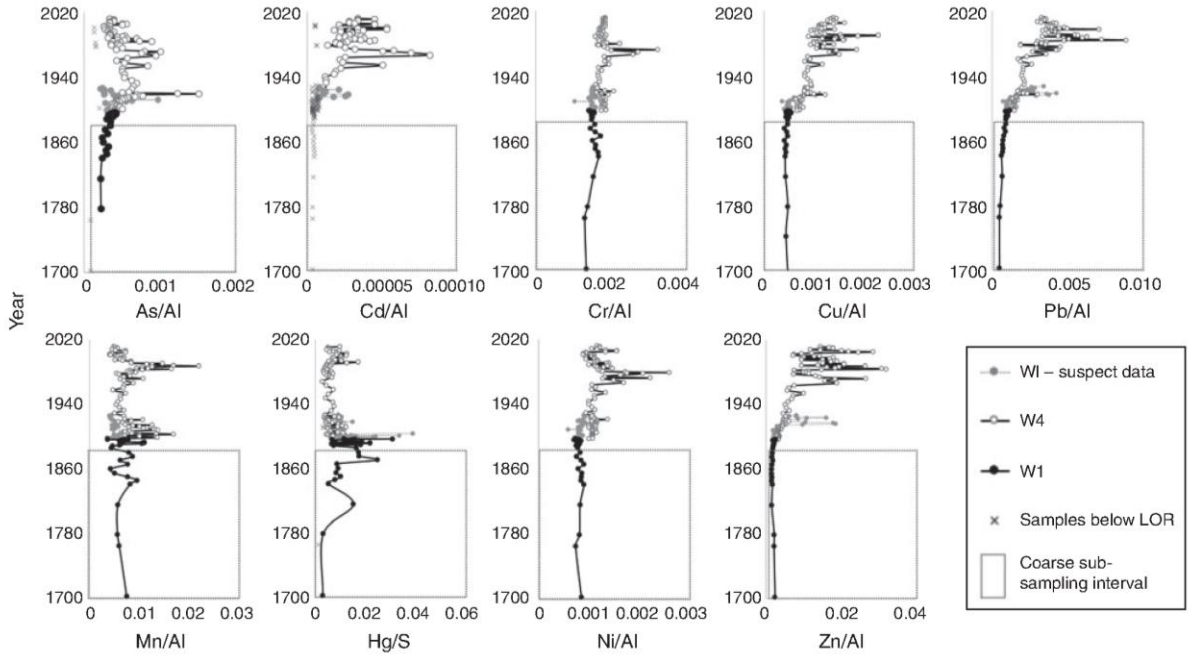

Fig. 5. Selected heavy metal profiles. Profiles of other heavy metals are provided in Fig. S2 in the Supplementary material.

than in W4 (Fig. 3). Spatial variability on a small scale has been reported previously (Bindler *et al.* 2001), so it is not unexpected between our two cores taken ~1.5 m apart (shown in more detail in Fig. S5). Although spatial variability in sediment and pollutant concentrations could be further verified by detailed bathymetric analysis of the billabong bed, we believe that the profiles in their current form are adequate to identify and explain historical trends of chemicals being deposited in Willsmere Billabong.

POPs profiles

In the analysis of PAHs and OCPs, there were several compounds that were below the LOR at certain depths in the sediment core. Owing to this lack of detection and the coarse sub-sampling resolution, only general trends of the POP normalised concentrations could be obtained from the profiles in Fig. 6 (and for absolute POP concentrations see Table S2). Fig. 6 shows POP concentrations normalised to organic matter (where inc/coh is used to represent organic matter content). Fig. 6 shows the profiles for the PAHs napthalene (NA), acenaphthylene (ACL), acenaphthene (AC), fluorene (FL), phenanthrene (PHE), benz[a]anthracene (BaA), anthracene (AN), benzo[ghi] pyrene (BghiP); and the OCPs dieldrin, dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), dichlorodiphenyltrichloroethane (DDT). The remaining profiles are shown in Fig. S6 in the Supplementary material.

NA, ACL and AC in both cores – along with FL in W1 – exhibited no clear increasing or decreasing trend. The rest of the PAHs all increased in concentration with time in W1. In W4, they all showed maxima in the late 19th century, with another period of elevated concentrations in the 20th century. For some pollutants these elevated concentrations occurred only between 1920 and 1950 (BaA, BghiP, ACL, FA, PY, BbkFA, BaP, IP, DBahA and CHR); but for PHE and AN, high levels lasted until 1980.

Of the OCPs, only dieldrin, DDE, DDD and DDT were detected in both W1 and W4. In W4, high OCP concentrations were detected for deposits from 1979 (Fig. 6). Elevated levels of DDE began before the increased levels of DDD and DDT; and in fact, DDE appears in the sediment core before DDT. This is most likely due to the transformation of DDT into its metabolite DDE, in the lower part of the core (Eganhouse *et al.* 2000; Zhang *et al.* 2002). The first detection of DDE actually precedes the documented introduction of OCPs into Australia in 1945; we suspect this discrepancy is accounted for by uncertainty in the age–depth model (especially in this region, where there were no independent chronological markers).

Discussion

Temporal variations in chemical concentrations

With the exception of Cd, all elements actually detected in the cores were present in pre-European sediments (before 1835), consistent with their natural occurrence in the environment: Al, As, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Sr, Ti, V and Zn. (Again, certain elements of interest were *not* detected in our cores: Ag, B, Be, Mo, Sb, Sn and Tl.) Although Cd does in fact occur in natural sediments (such as marine sediments) up to a concentration of 1 mg kg^{-1}, we suspect that in this catchment, pre-European Cd levels were simply too low for detection. Similarly, although most POPs are derived synthetically, some PAHs occur naturally (e.g. BaA, PHE, FL, NA, FA, PY). Concentrations of some PAHs in the pre-European deposits were

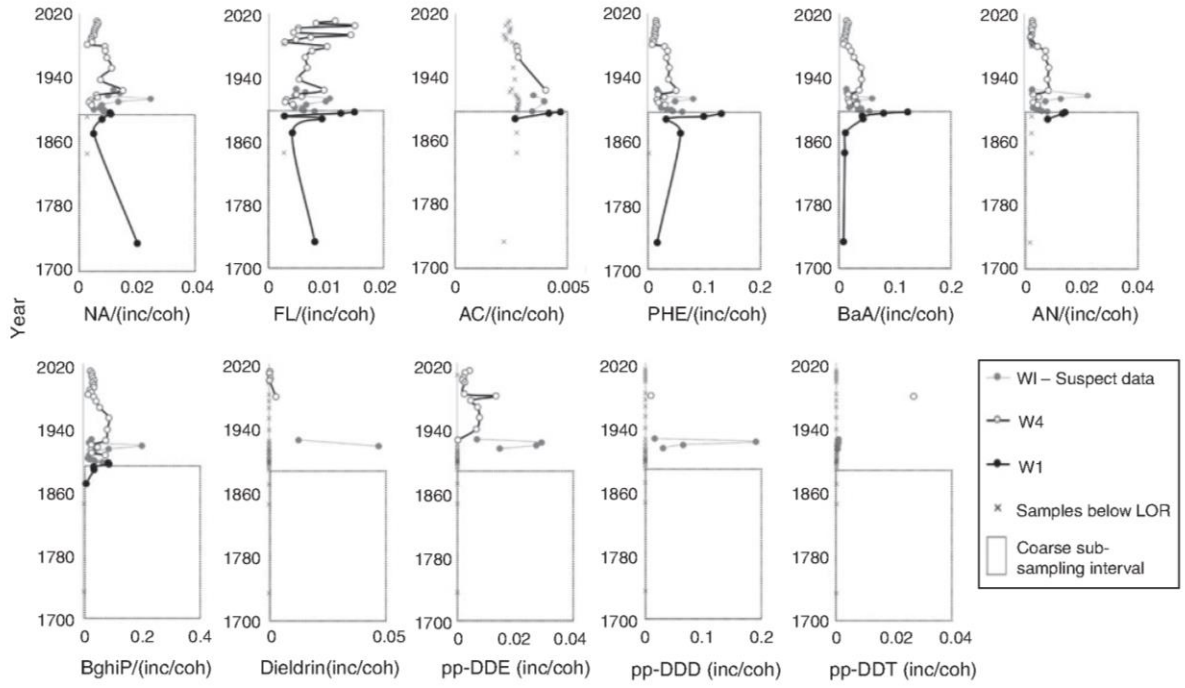

Fig. 6. Selected PAH and OCP profiles. Profiles of other PAHs and OCPs are provided in Fig. S5 in the Supplementary material.

similar to those in the latter half of the 20th century. We note that although NA appears to have been higher in pre-European sediments than in later sediment, NA samples can be easily contaminated in the field or the laboratory (Capdeville and Budzinski 2011), and may therefore not accurately represent the NA trends.

It is beyond the scope of this paper to discuss post-depositional transformations of chemicals within sediment cores; but we note that preservation of metals in a sediment matrix can be affected by environmental factors such as DO, salinity, pH and redox (Foster and Charlesworth 1996). For example, Fe and Mn are more soluble in anoxic conditions; so in the more anoxic deeper layers of the sediment core, Fe and Mn previously bound to sediments can dissociate from particles and be released into porewater (Monteiro *et al.* 2012). Conversely, metals are less likely to form metal-sulfide complexes or bind to particulate matter in oxic conditions (Slotton and Reuter 1995). These redox-controlled processes have been detailed in other studies (e.g. Boyle 2001).

Regardless of uncertainties about the potential mobility of chemicals in the bed sediment, major trends in water quality fluxes are evident in the profiles. For example, recently deposited sediments (2000–2012) show far higher pollutant levels than those deposited before European settlement in the early 19th century, particularly for Cd, Cu, Ni, Pb and Zn. Although there was no clear trend in the POPs profiles, there were elevated PAH and OCP concentrations during certain periods (Fig. 6 and Fig. S6). The metals, PAHs and OCPs could have been brought into the billabong by: (1) stormwater runoff from the local billabong catchment; (2) overbank flows of the Yarra River; or (3) atmospheric deposition. These potential transport pathways will be discussed in more detail below.

Relationship between chemical inputs and local residential growth

There appears to be an association between the concentration of heavy metals and PAHs in the billabong and residential development in its local catchment. On evidence from W1 and W4 (Fig. S1), Al and Fe concentrations increased over the first 75 years of residential development in Kew (1845–1920). Because clay minerals often contain these metals (Ip *et al.* 2004), increase in their levels suggests an increasing flux of weathered terrestrial sediment into the billabong from construction and land clearing. Indeed, maximum SAR was reached in the late 19th century (Fig. S1). Because Ti minerals are generally indicative of silt and Al minerals of clay, a decrease in Ti/Al ratio during this period indicates an increase in clay particles entering the billabong, relative to silt particles (Schropp and Windom 1998; Cuven *et al.* 2010). It appears that the increased catchment erosion was primarily from disturbance of clay; and this erosion probably contributed to observed increases in Cr, Cu, Pb, Ni and Zn concentrations, as these are naturally present in the environment (Ip *et al.* 2004).

Erosion as a result of land clearing and construction processes certainly increases the deposition of metals into receiving waters; but with urban development there is also expansion in impervious surfaces such as pavements and roads. This facilitates the transport of metals released by anthropogenic

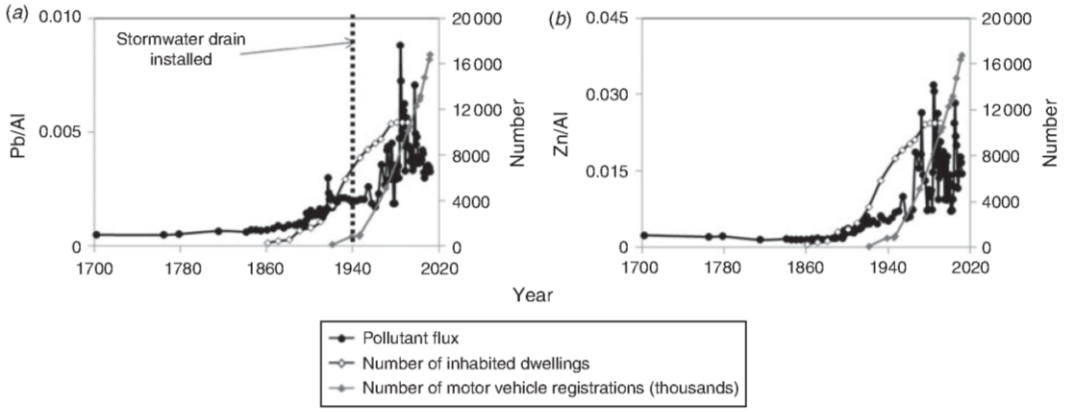

Fig. 7. Number of inhabited dwellings in the suburb of Kew, motor vehicle registrations in Australia, and normalised concentrations of Pb (*a*) and Zn (*b*). Note that the suspect data in W1 have not been included. Developed using data from the Australian Bureau of Statistics.

activities (Hatt *et al.* 2004). There is a positive correlation between proliferation of inhabited residences and Cd, Cr, Cu, Ni, Pb and Zn fluxes in the 19th and 20th centuries (see Pb and Zn fluxes in Fig. 7) – most likely from increased use of chemicals containing those elements, and from increased impervious surface area. Over the relevant period Cu, Pb, Ni and Zn were used in building materials, along with Cd and Cr in paints (Weeks and Grimmer 1995; Hart and White 2006; Berge 2009). Chemicals containing these six elements can leach from buildings to contaminate aquatic systems. There are high normalised PAH concentrations from 1938 to 1979, which could be caused by increased fuel combustion (Sun and Zang 2012).

Metals such as those six are also present in motor vehicle emissions (Hjortenkrans *et al.* 2006). As Fig. 7 shows, trends for Cu, Zn and Pb track expansion in the use of such vehicles since their arrival in Melbourne *c*. 1900 (Davison 2010). This timing coincides with evidence in Fig. 5 for normalised concentrations of Zn, Cu and Pb in the early 20th century. As further confirmation of a causal link, after the 1980s Pb concentrations plateaued and then decreased – in response to Australia's adoption of unleaded petrol, and its exclusive use in subsequent decades (O'Connor *et al.* 1990).

Transition between various sources of energy might have affected the profiles of other metals, and also PAHs. For example, Ni and PAH concentrations in the billabong sediments decreased in the late 20th century, which could be explained by a shift from crude oil and brown coal briquettes to natural gas in local domestic and commercial use (Bush *et al.* 1995; McLennan 1998; Bush *et al.* 1999; DEWHA 2008). Catalytic converters were mandated for new cars in the 1970s (Department of Infrastructure and Transport 2013), which also probably contributed to decreased PAH levels in the billabong.

Fig. 6 shows peaks in the OCP profiles in 1979. Agricultural activities in the area had long ceased; but pesticides such as DDTs were still used by residential gardeners. No OCPs were detected in the sediment core after 1985, the year they were restricted in Australia (APVMA 2012).

Trends in pollutant concentrations and residential growth become more closely correlated in the latter half of the 20th century, most likely due to the installation of a stormwater drain for Willsmere Billabong in 1940 (David Barclay, City of Boroondara, pers. comm., 2 April 2013). Concentrations were also more variable after the drain was installed. Many studies have demonstrated that pollutant levels in stormwater can fluctuate (Vaze and Chiew 2003). The major contribution of residential stormwater can also be inferred from a decrease in some pollutants after 2006, when a wetland for retention and treatment of locally generated stormwater was constructed adjacent to the billabong (Leahy 2007). From 2006 to 2012, normalised concentrations of common stormwater pollutants such as Cu, Pb, Ni and Zn declined by 14, 19, 25 and 49% (Fig. 5).

Willsmere Billabong's response to regional processes

Although there are strong correlations between pollutant concentrations in the Willsmere Billabong sediment cores and residential development of its local catchment, pollutants may also have been deposited through more remote activities. The effect of industrial activities outside of the local catchment is particularly clear in the case of Hg and As before the mid-20th century. These elements were most likely introduced into the Yarra River by mining, far upstream from the billabong. Hg can accumulate from its use to extract gold (Brizga *et al.* 1995); and gold-sulfide ore contains As (Ogola *et al.* 2002). Normalised As and Hg concentrations in our billabong cores increased in the early 1800s and decreased after 1915, reflecting the history of gold mining in the Yarra Catchment (Fig. 8). Fig. 8 also shows a correlation between quantities of gold mined in the catchment and As and Hg fluxes. Although the As concentrations decreased after 1915 they did not return to pre-1840 levels. Arsenic minerals are present in soil deposits in the Yarra Catchment (Pettigrove and Hoffman 2003), and mining activities most likely brought these minerals to the surface, making them more susceptible to transport into the river by runoff.

Hydrologic connectivity between Willsmere Billabong and the Yarra River also appears to have affected billabong PAH concentrations in the late 19th century. For example, Fig. 6 and Fig. S6 (Supplementary material) show significant increases in

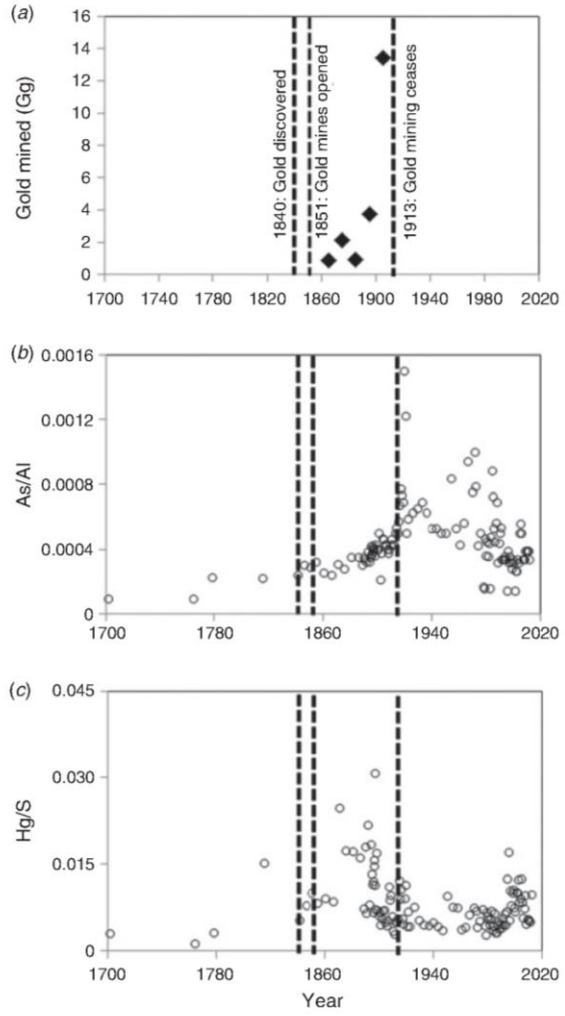

Fig. 8. Gold mined in the Yarra Catchment (adapted from Brizga *et al.* 1995). (*a*) As concentrations normalised to Al; (*b*) Hg concentrations normalised to S; and (*c*) in Willsmere Billabong sediments. Note that the suspect data in W1 have not been included.

concentration in 1895. Major floods are recorded in 1891 and 1901 (Lacey 2004). Elevated PAH concentrations in sediments deposited in 1895 could be related to such events, which would have transported PAHs, deposited in the Upper Yarra Catchment after bushfires (Unknown 1893*a*, 1893*b*, 1895), downstream and into the billabong. Indeed, there is a decrease in the ratio of PAHs of low molecular weight to those of high molecular weight in the 1890s (Fig. S7), indicating the pyrogenic origin of the deposited PAHs (Tobiszewski and Namiesnik 2012).

Finally, some pollutants in the billabong may have arrived by atmospheric deposition. From 1850 to 1875, Pb concentrations increased slightly above background levels – correlating with the emergence of industrial activities outside of the local catchment, downstream of the billabong in the 1850s. Atmospheric emissions from these industries (breweries, flour mills, textiles) might have been deposited directly in the billabong, or through overland runoff after deposition into the local catchment. With the Environment Protection Act implemented in the state of Victoria in 1970, industrial practices changed to reduce emissions of toxic compounds such as PAHs and metals. This probably contributed to the decreasing PAH levels in the late 20th century (O'Connor *et al.* 1990).

Strategies to mitigate the effect of future urban growth on aquatic environments

The historical trends in pollutant deposition discussed above can be used as a case study of how aquatic environments deteriorate with urbanisation. In particular, the correlation between residential development and the pollutant concentrations in the Willsmere Billabong sediment cores (especially after 1940) shows such a link. Data we present above suggest the necessity of measures to protect aquatic systems, by implementing mitigation strategies at the sources of pollution. These would require policies to reduce emissions of metals and PAHs by motor vehicles, and to mandate materials in the built environment that will not leach into urban runoff. We have confirmed that even without industry in the catchment, residential activities pollute local aquatic systems; and Willsmere Billabong underwent a significant increase in pollutant flux following installation of a stormwater drain. These findings can be used to design future urban growth policies to ensure protection of aquatic systems.

Such a significant increase in the billabong's chemical concentrations from a new stormwater drain emphasises the importance of control strategies to treat urban runoff before discharge into urban aquatic systems. Decreasing pollutant concentrations observed after implementation of a stormwater wetland in 2006 are promising; but more interventions may be necessary to restore pollutant concentrations to pre-disturbance levels, including at-source strategies throughout the catchment (e.g. rainwater tanks or swales), or retention systems at the stormwater outlet. As stormwater conveyance will increase with the development of more residential areas and urban sprawl, our case study highlights stormwater management tools such as biofiltration systems and wetlands (Blecken *et al.* 2009; Feng *et al.* 2012), as essential components in future residential development, to ensure the protection of local aquatic systems.

Chemical concentration profiles in Willsmere Billabong between 1700 and 2012 demonstrate that urban development leads to significant increases in heavy metals and POPs in aquatic environments. Over two centuries there has been a connection between increasing levels of Cd, Cr, Cu, Ni, Pb, Zn and PAH and number of dwellings in the vicinity. This correlation grew more evident after the mid-20th century; and the timing coincides with incorporation of the billabong into the local stormwater drainage network. Correlations also indicate, as we have demonstrated, that residential growth itself can have a significant local influence on pollution. Beyond increased stormwater runoff, such growth entails construction and use of buildings and greater traffic volumes, both of which bring products of combustion to the mix – and with these, metals and PAHs that can be transported into the billabong by overland runoff or atmospheric deposition. However, local stormwater and residential development are not the only factors affecting

deposition of pollutants and chemicals in Willsmere Billabong. Especially before installation of the stormwater outlet, there are trends in pollutant concentrations that could be attributed to atmospheric deposition from industrial activities outside the local catchment; and sections of the pollutant profiles can also be attributed to the transport of pollutants from historical mining activities, by overbank flooding of the Yarra River.

Willsmere Billabong's chemical profiles highlight the role of stormwater from residential areas in the degradation of local waterways by effective transport of pollutants. Indeed, it appears that concentrations in billabong sediments decreased after the implementation of stormwater management strategies (i.e. a constructed wetland). This case study supplies the historical evidence that stormwater management and treatment will be essential features in the design of sustainable new residential developments.

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4.4 Justification of exclusion of Yarra Flats Billabong from analysis

4.4.1 Site description

The Yarra Flats Billabong is located in the upper Yarra River catchment (Figure 4.1), outside of Melbourne metropolitan and close to the township of Yarra Glen (Figure 4.2). The system has a bank-full area of approximately 2.4 ha, and a catchment of approximately 18 ha (Figure 4.2). The Yarra Flats Billabong is a system of interconnected billabongs, with the main point of water entry being on the west bank of the billabongs (Figure 4.2). It is estimated that the billabong fills with water when minor flood levels are reached (approximately 4 m Australian Height Datum; AHD at the Yarra Glen stream gauge; Figure 4.2). Measurements taken at this stream gauge are available from 1991 and according to these observed river levels, the billabong has been inundated approximately 1.9 times per year between 1991 and 2013 (Figure 4.3). However, as indicated in Figure 4.3, there are some years where no inundation events occur, particularly in the early 21st century.

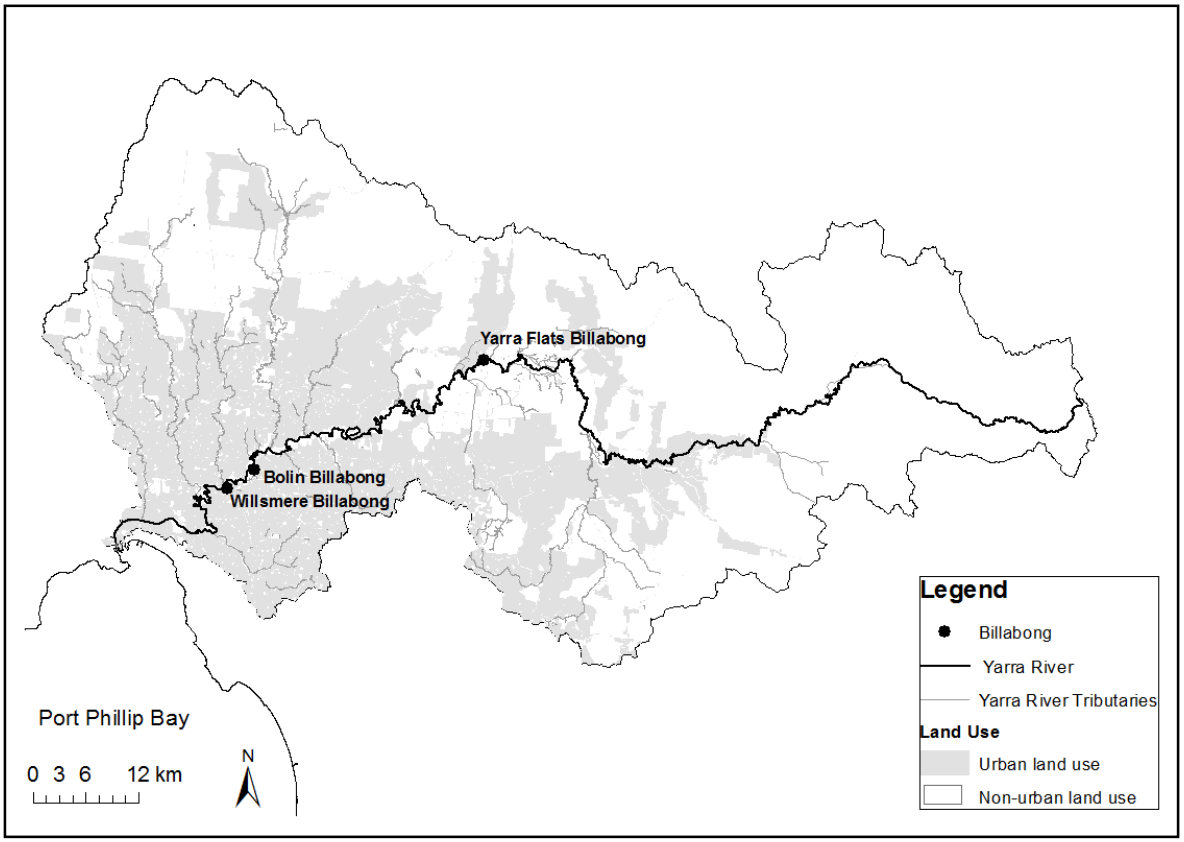

Figure 4.1: Location of the Yarra Flats Billabong within the Yarra River catchment.

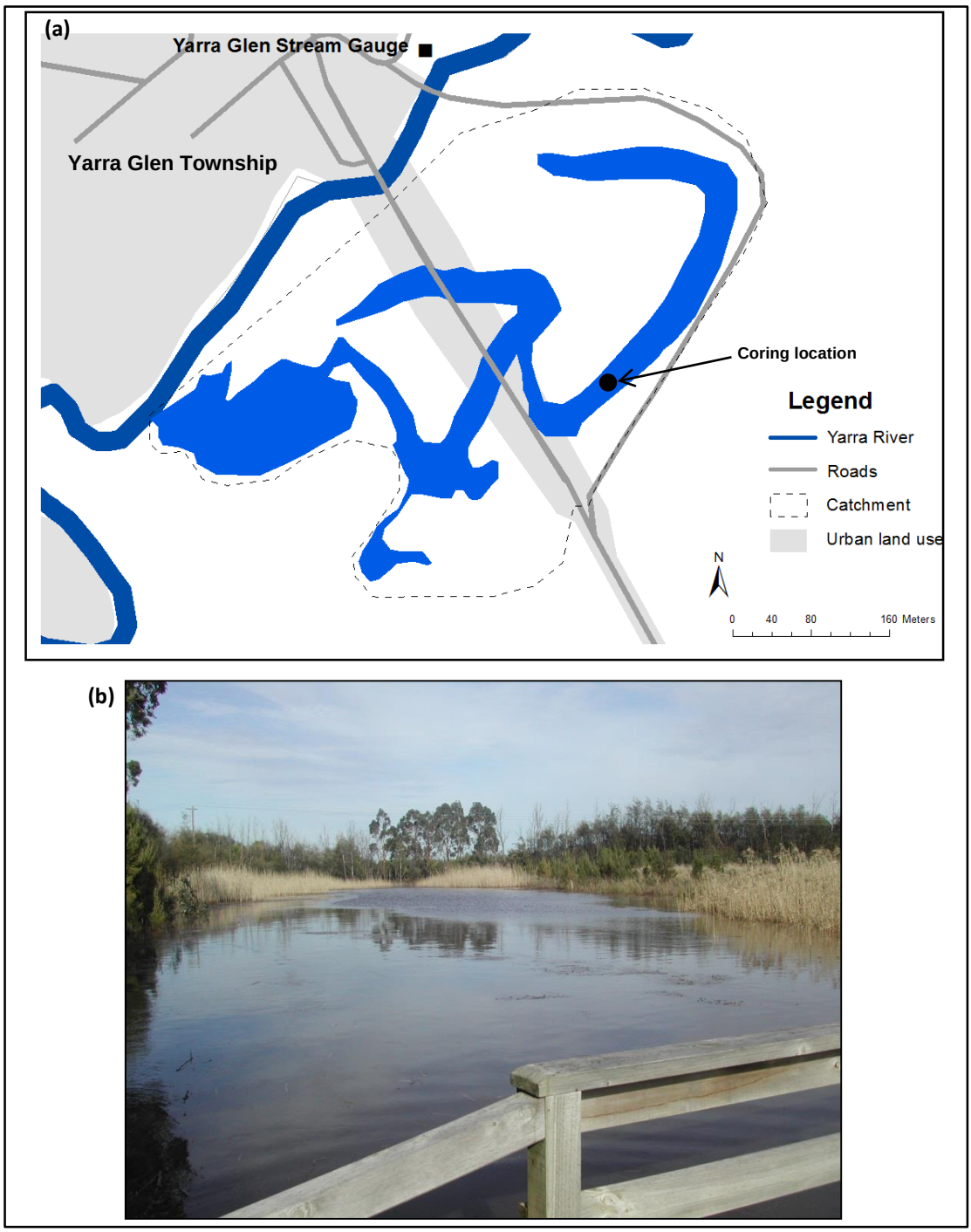

Figure 4.2: Closer view of Yarra Flats Billabong showing the location of the Yarra Glen stream gauge (a) and photograph of the coring site taken August 2013 (b). Additional photographs of the site provided in Appendix B.3.

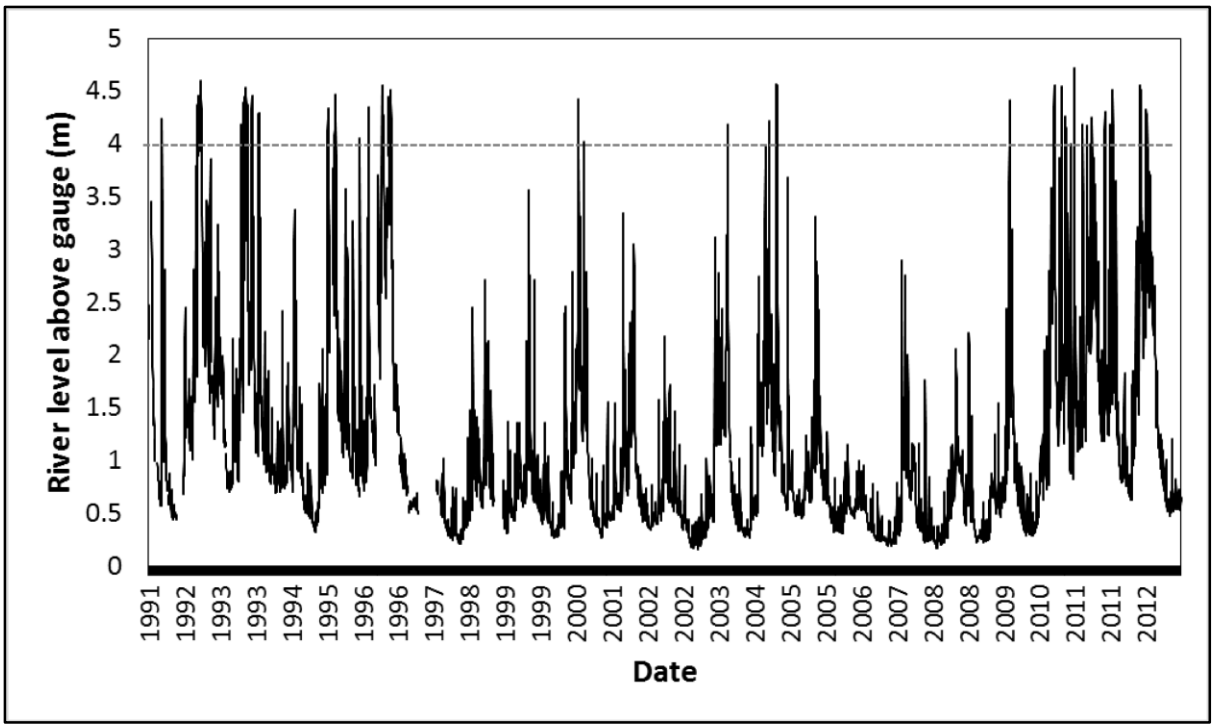

Figure 4.3: River level measured at the Yarra Glen stream gauge (229206A) from September 1991 to May 2013 (Department of Sustainability and Environment, 2013). Horizontal dotted line represents minor flood level (at 4 m AHD).

The presence of aboriginal artefacts in the catchment of the Yarra Flats Billabong suggests that aboriginal tribes were in the region prior to European settlement. The area was first settled by Europeans in 1837 and a township was officially established in 1889 (Blackburn, 1968). Since European settlement, the catchment of the billabong has been used for grazing. This continued until a road was built in the catchment in 1998 (Figure 4.2) and the land to the east of the highway was converted into a natural reserve (Melissa Carmody, Shire of Yarra Ranges, pers. comm., 24 June 2013).

Anecdotal evidence suggests that some alterations have been made to the natural hydrology of the billabongs. One documented change is the construction of a weir in the natural drain between the main river channel and the billabong, to maintain water levels in the billabong for longer periods of time after inundation (Melissa Carmody, Shire of Yarra Ranges, pers. comm., 28 January 2015).

4.4.2 Sample collection and analysis

In August 2013, a sediment core was taken from the location in the Yarra Flats Billabong shown in Figure 4.2. This core was taken in ten drives (bed surface to depth 17 cm; depth 17 cm to depth 46 cm; depth 46 cm to depth 71 cm; depth 71 cm to depth 100 cm; depth 100 cm to depth 131 cm; depth 131 cm to depth 167 cm; depth 167 cm to depth 202.5 cm; depth 202.5 cm to depth 244.5 cm; depth

244.5 cm to depth 298.5 cm; depth 298.5 cm to depth 353.5 cm) using a 40-mm diameter Livingstone corer (Livingstone, 1955). The water level was approximately 2 m at the time of sampling.

All ten drives of the Yarra Flats Billabong core were split longitudinally and half of each core was scanned in the ITRAX micro-X-ray fluorescence (XRF) core scanner (Croudace *et al.*, 2006). A molybdenum tube (voltage of 30 kV, current of 45 mA) was used. There was a 10-s exposure time, with readings at 1-mm intervals. Magnetic susceptibility measurements were taken at 0.5-cm intervals.

The sediment cores were initially dated using unsupported ^{210}Pb activities. 1-cm thick samples were taken at 5-cm intervals in the top 20 cm and at 10-cm intervals from 20 to 50-cm depth. Additional 0.5-cm thick samples were taken at 2-cm, 3.5-cm, 6-cm, 6.5-cm and 7.5-cm depth. The method described in Atahan *et al.* (2015) was used to process the samples at the Australian Nuclear Science and Technology Organisation (ANSTO). As described in Appleby (2001), unsupported ^{210}Pb activities were estimated as the supported ^{210}Pb activity (measured from ^{226}Ra) subtracted from the total ^{210}Pb activity (measured from ^{210}Po). Calendar ages were calculated using the unsupported ^{210}Pb activities and the Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models (Appleby, 2001).

0.5-cm thick sediment samples were obtained for radiocarbon dating at 60-cm (OZS501), 80-cm (OZS502) and 149-cm (OZS503) depth. 2M hydrochloric acid (HCl) (at 60^{0}C) and then multiple sodium hydroxide (NaOH) treatments (at 60^{0}C), with a final 2M HCl treatment (room temperature) were used to remove carbonates and humic acids from these samples. These samples were then dried and combusted to carbon dioxide (CO_2) and reduced to graphite (Hua *et al.*, 2001). ^{14}C dating was done at the Accelerator Mass Spectrometry (AMS) facility at ANSTO (Fink *et al.*, 2004) and the OxCal 4.2 programme (Ramsey, 2009) and the SHCal13 data set (Hogg *et al.*, 2013) was used to calibrate the radiocarbon dates.

Additionally, to distinguish pre-European sediments from post-European sediments, the presence or absence of introduced vegetation pollen grains was used. 1 cm^3 of bulk sediment was taken from 4.5-5-cm, 7-7.5-cm and 8-8.5-cm depth. These samples were treated with 10% sodium pyrophosphate ($Na_2P_2O_7$) and then sieved (210 µm and 7 µm). The fine material was treated using HCl (10%) and then acetolysis. Organic material was removed using heavy liquid separation using sodium polytungstate ($3Na_2WO_4{\cdot}9WO_3$). The organic fraction was then treated with 48% hydrofluoric acid (HF) and 10% HCl. The pollen samples were dehydrated using methanol (C_2H_5OH) and then mounted to slides using glycerol ($C_3H_8O_3$). Slides were examined and compared to the laboratory pollen reference collection.

4.4.3 Chronology

A tentative chronology was developed for the Yarra Flats Billabong sediment core using the ^{210}Pb activities, presence/absence of pollen of introduced vegetation species and ^{14}C dating. The unsupported ^{210}Pb activities are provided in Figure 4.4. Unsupported ^{210}Pb activities were not detected in the samples taken at 3.5 cm, 10 cm, and 15 cm and all samples below 21 cm. This suggests that the limit of sediment dating by ^{210}Pb is reached at 10 cm-depth in the sediment core. Sediment ages were estimated with the CIC model using the unsupported ^{210}Pb activities between 0 and 6.5 cm (mass accumulation rate of 0.34 g/cm^2/yr or 0.47 cm/yr). Sediment ages between 6.5 cm and 8 cm were estimated by linear extrapolation, assuming a constant sediment accumulation rate. Sediment ages were also estimated with the CRS model using the unsupported ^{210}Pb activities between 0 and 8 cm, which gave mass accumulation rates of 0.1 to 0.66 g/cm2/yr. As shown in Figure 4.5, the two dating models lead to varying chronologies.

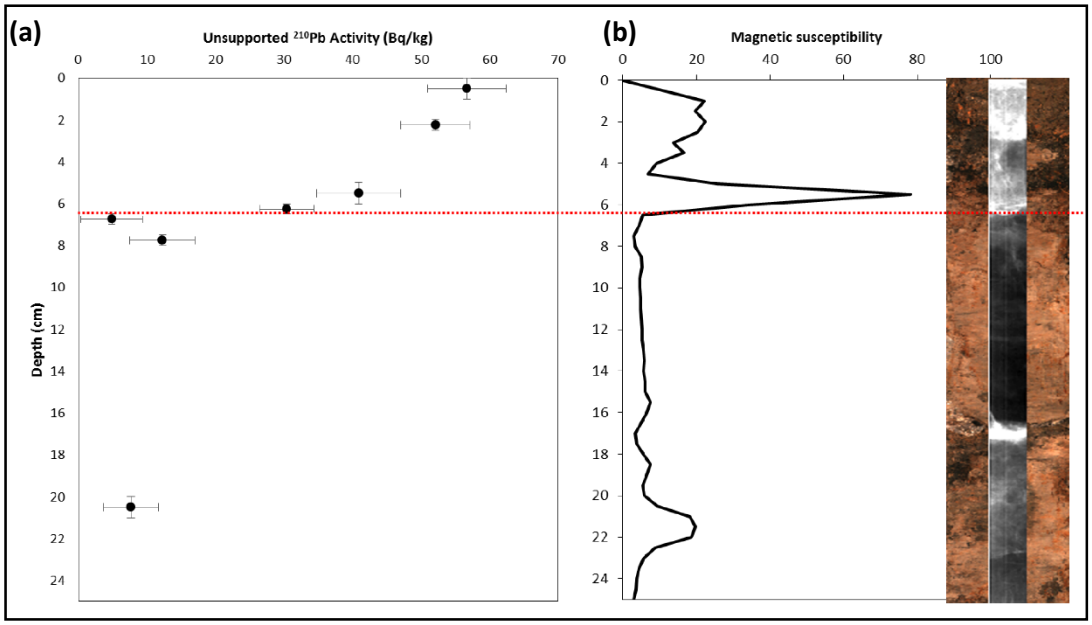

Figure 4.4: Unsupported ^{210}Pb activities of Yarra Flats Billabong sediment core YG1 (a) juxtaposed to magnetic susceptibility profile and optical and radiographic image of core (b). (Dashed red line represents change in stratigraphy).

It is most likely that the CIC model is more representative of the chronology of the sediment core. Construction of a highway occurred adjacent to the Yarra Flats Billabong in 1998, and during this project, sediment from the billabong was removed (Rod Baker, VicRoads, pers. comm., 12 February 2015). This sudden change in the stratigraphy is evident in the optical and radiograph images of the sediment core (Figure 4.4). Thus, it is likely that this boundary of sediment change dates to

approximately 1998, when this construction project and the billabong sediment removal occurred. This helps to validate the CIC model, which dates 8 cm to approximately 1995.

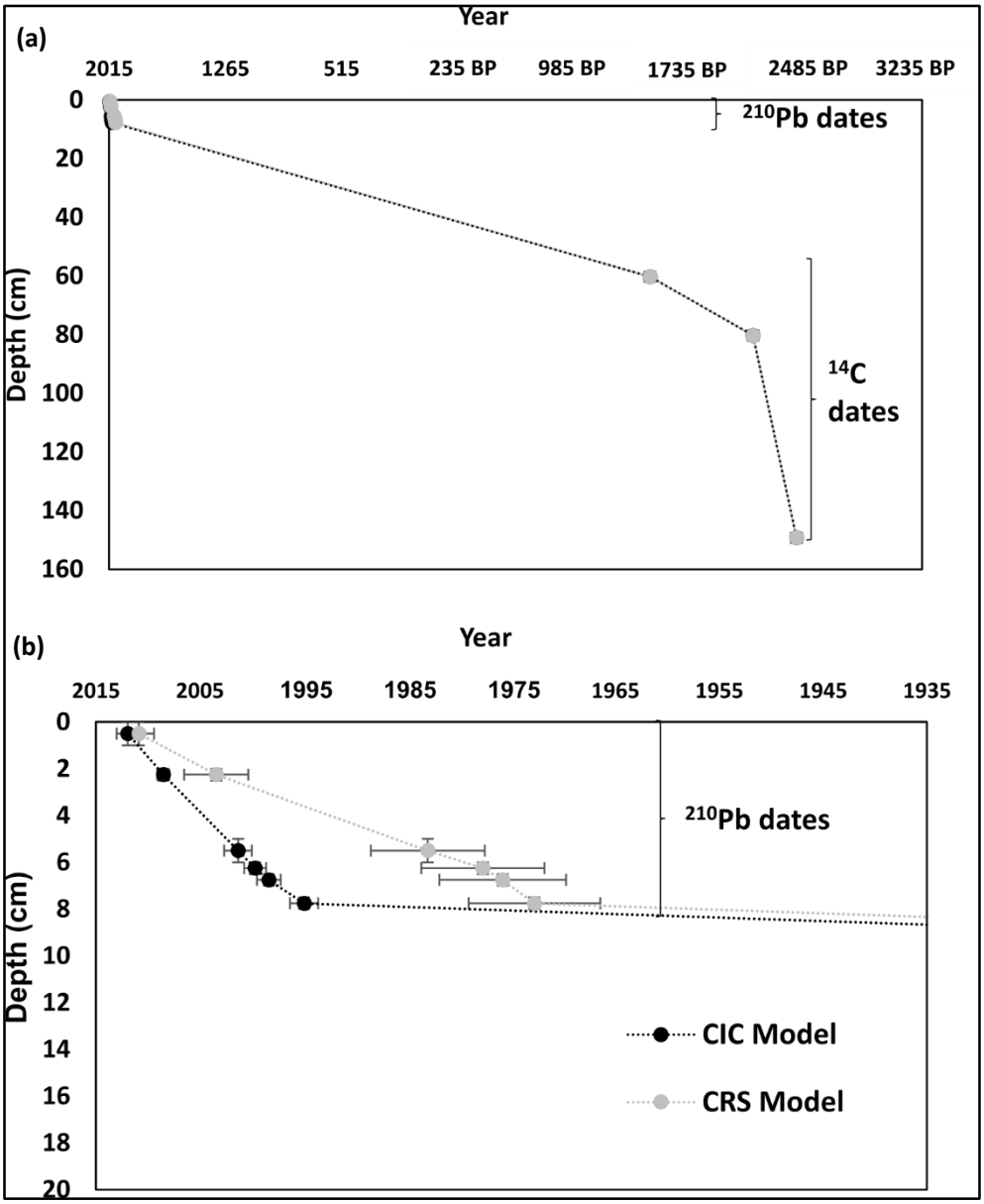

Figure 4.5: Sediment chronologies using CIC and CRS models. Chronology of top 160 cm (a) and chronology of top 20 cm (b).

The age of the sediments between 8 cm and 60 cm (where a ^{14}C date was obtained), is uncertain. The presence of *Pinus* pollen in the sediments at 8-8.5 cm indicates that this region of the sediment core was deposited after European settlement in 1835. 60-cm, 80-cm and 149-cm depth of the Yarra Flats Billabong sediment core YG1 was dated as 1477±35 BP, 2142±35 BP and 2422±35 BP, respectively. However, given that 8-cm depth was deposited after 1835, this leads to a sediment accumulation rate of less than 0.02 cm/yr. This low sediment accumulation rate could be due to either undocumented

dredging of sediment, or an error in the radiocarbon date. It is possible that the deposit itself dates to 1477 BP, but it was not necessarily buried at the site in this year, and that the sediment deposit contained carbon that is older than the year in which the sediments were deposited in the billabong (Dezileau *et al.*, 2014).

Due to the inability to determine the age of the top of the boundary of the sediment dredging, this sediment core was not used for the analysis of historical pollution trends nor historical hydrologic trends.

4.5 Discussion

4.5.1 Main factors affecting pollution in Willsmere Billabong and Bolin Billabong

For both Willsmere Billabong and Bolin Billabong, the main drivers for trends in contaminants (heavy metals and POPs) were identified by comparing the timing of shifts in pollutant levels with events that are recorded to have occurred within the Yarra River catchment. Using this technique, both billabongs were found to have experienced increasing levels of contamination following European settlement in the Yarra River catchment in the mid-19th century. Increasing metal concentrations in Bolin Billabong were attributed to increases in sediment flux due to erosion (Al and Fe), motor vehicle emissions (Pb), and the leaching of Pb and Zn from building materials. Indeed, metal concentrations through the sediment cores (Al, Cu, Pb and Zn) correlated with population growth and the growth in the number of dwellings within the Yarra River catchment upstream of Bolin Billabong.

A more in-depth analysis of the factors affecting contaminant trends (both heavy metals and POPs) was performed for Willsmere Billabong. It was found that trends in As reflected gold mining trends in the upper Yarra River catchment and trends in Pb correlated with industrial growth within the region. PAH trends were found to correlate with both the timing of bushfires, flood events and industrial growth. More important however was the identification of the impact of residential development on the heavy metal and POPs contamination of Willsmere Billabong. This was inferred from the increasing levels of these contaminants within the sedimentary record after 1940, which is when a stormwater drain into Willsmere Billabong was built. It appears that the installation of a stormwater treatment wetland in the local catchment in 2006 has reduced the level of contaminants, particularly heavy metals, settling on the bed of the billabong. However, comparison to background levels indicates that more heavy metal reduction measures, especially those targeting stormwater, are required to return Willsmere Billabong to its background heavy metal conditions.

4.5.2 Comparison between background contaminant concentrations and generic sediment quality trigger values

Current sediment quality guideline trigger values for Australia and New Zealand were found to be higher than background metal levels identified in both Willsmere and Bolin Billabongs. According to current generic sediment quality trigger values (ANZECC/ARMCANZ, 2000), the concentration of heavy metals through the sediment cores of both billabongs do not pose a high risk to organisms that come into contact with the billabongs' sediments. However, it is difficult to imagine that pressures have not been placed on these ecosystems, which have experienced significant increases in metal concentrations above background levels. This work highlights the need to consider site-specific background values, which can be identified using sediment cores, when setting water and sediment quality targets.

4.6 Conclusion

In summary, this chapter has demonstrated:

- why the sedimentary records of the Yarra Flats Billabong have not been used to identify historical pollution and hydrologic trends in this thesis;
- that the concentrations of contaminants in the bed sediments of both Willsmere Billabong and Bolin Billabong have increased since Europeans first settled in the Yarra River catchment; this is most likely due to mining, land clearing, urban growth and the uptake of motor vehicles;
- that site-specific background contaminant concentrations, which can be identified using sediment cores containing sediments prior to catchment disturbance, should be considered when setting water and sediment quality targets for aquatic environments; and
- that dated pollutant profiles from sediment cores can contribute to the assessment of mitigation methods (e.g., stormwater treatment wetlands, pollution reduction legislations).

4.7 References

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CHAPTER 5
IDENTIFYING HISTORICAL TRENDS IN YARRA RIVER HYDROLOGY

Declaration for Thesis Chapter 5

Declaration by candidate

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Initiation, ideas, sample collection, data collection, data analysis, interpretation and preparation of manuscript.	70

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Atun Zawadzki	Data interpretation, reviewing of manuscript	n/a
Geraldine Jacobsen	Data interpretation	n/a
Simon Connor	Sample collection, data collection, data interpretation	n/a
Patricia Gadd	Data collection, data interpretation, reviewing of manuscript	n/a
Henk Heijnis	Data interpretation	n/a
Paul Leahy	Sample collection, data interpretation, reviewing of manuscript	n/a
Ana Deletic	Data interpretation, reviewing of manuscript	n/a
David McCarthy	Ideas, data interpretation, reviewing of manuscript	n/a

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	[redacted]	**Date** 19/8/2015
Main Supervisor's Signature		**Date** 19/8/2015

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

5.1 Introduction

The literature review in Chapter 2 indicated that several sediment characteristics can be used as indicators of historical trends in hydrology. Furthermore, these indicators can be used to identify discrete flood layers in sediment cores. The literature also recommends that multiple indicators (or proxies) be used to reduce uncertainties in the determination of these historical trends.

This chapter addresses research objective 2 and its associated research questions (3 and 4), listed below.

> **Research objective 2: To identify discrete fluvial flood deposits in sediment cores from the Yarra River billabongs.**
>
> - *Research question 3: What techniques can be used to identify historical hydrologic changes of the Yarra River billabongs, and in particular, identify discrete flood-deposited sediment layers in the Yarra River billabong cores?*
> - *Research question 4: In particular, can sediment mixing models be used to identify discrete flood deposits within sedimentary records?*

This chapter is made up of four sections following this introduction. Section 5.2 is a paper currently under internal review for submission to *Science of the Total Environment.* This paper is cited as Lintern *et al.* (in preparation-a) through the rest of the thesis and it addresses research question 3. The supplementary material for this manuscript is provided in Appendix A.3. Section 5.3 addresses research question 4 and is a discussion about the unsuccessful trialling of sediment mixing models for identifying discrete flood deposits in sedimentary records. The third section compares the sediment chronologies developed in Chapter 4 and Chapter 5. The chapter concludes with a summary of the main findings of Chapter 5.

5.2 Using sediment cores to identify historical changes in floodplain lake hydrology

USING SEDIMENT CORES TO IDENTIFY HISTORICAL CHANGES IN FLOODPLAIN LAKE HYDROLOGY

Anna LINTERN[1*], Paul J. LEAHY[2], Atun ZAWADZKI[3], Patricia GADD[3], Henk HEIJNIS[3], Geraldine JACOBSEN[3], Simon CONNOR[4], Ana DELETIC[1,5], David T. MCCARTHY[1,5]

[1]Monash Water for Liveability, Department of Civil Engineering, Monash University, Clayton, 3800, Victoria, Australia
[2]EPA Victoria, Applied Sciences Group, Ernest Jones Drive, Macleod, Victoria, 3085, Australia
[3] Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, New South Wales 2234, Australia
[4] School of Geography, The University of Melbourne, Parkville, 3010, Australia
[5]Environmental and Public Health Microbiology Laboratory (EPHM Lab), Monash University, Clayton, 3800, Australia

**Corresponding author's e-mail: anna.lintern@monash.edu*

ABSTRACT

Anthropogenic activities are contributing to the changing hydrology of rivers, often resulting in their degradation. Understanding the drivers and nature of these changes is critical for the design and implementation of effective mitigation strategies for these systems. However, this can be hindered by gaps in historical measured flow data. This study therefore aims to use sediment cores to identify historical hydrologic changes within a river catchment. Sediment cores from two floodplain lakes (billabongs) in the urbanised Yarra River catchment (South-East Australia) were collected and high resolution images, trends in magnetic susceptibility and trends in elemental composition through the sedimentary records were obtained. These were used to infer historical changes in river hydrology to determine both average trends in hydrology (i.e., coarse temporal resolution) as well as discrete flood layers in the sediment cores (i.e., fine temporal resolution). Through the 20th century, both billabongs became increasingly disconnected from the river, as demonstrated by the decreasing trends in magnetic susceptibility, particle size and inorganic matter in the cores. Additionally the number of discrete flood layers decreased up the cores. These reconstructed trends correlate with measured flow records of the river through the 20th century, which validates the methodology that has been used in this study. Not only does this study provide evidence on how natural catchments can be affected by land-use intensification and urbanisation, but it also introduces a general analytical framework that could be applied to other river systems to assist in the design of hydrologic management strategies.

KEYWORDS

Elemental composition, flood, floodplain lake, hydrology, ITRAX, sediment core

INTRODUCTION

Globally, rivers are experiencing dramatic changes in their hydrology (Gerten *et al.*, 2008). This is partially due to anthropogenic activities within the catchment (Vorosmarty *et al.*, 2010). For example, Ye *et al.* (2003) found that reservoir construction in the 20th century has led to reduced streamflow in the Lena River in the Arctic. During the same century, streamflow has increased in the Comet River (Australia), which has been attributed to land clearing (Siriwardena *et al.*, 2006). Additionally, human induced and natural climate variability has had and will continue to have a significant impact on river hydrology (Vorosmarty *et al.*, 2010). Climate change is expected to lead to an increased frequency of high intensity storms, resulting in more frequent flash flooding, particularly in urban catchments (Cofalla *et al.*, 2012). Modelling has shown that increasing global temperatures will result in decreased streamflows in tropical catchments, but increased spring streamflows in snow-covered catchments (Nijssen *et al.*, 2001). Such transitions in hydrology not only impact river and floodplain ecology but also undermine the safety of human communities within the river catchment (Nilsson and Berggren, 2000; Tharme, 2003).

The design of effective management strategies relies on a clear understanding of the main factors causing changes in river hydrology (Battarbee, 1999). However, the limited availability (both temporally and spatially) of streamflow observations (Benito *et al.*, 2004) undermines our ability to identify site-specific causes of hydrologic shifts. Thus, the design of management strategies is commonly based on generic empirical rules that are not necessarily applicable to all river systems (Arthington *et al.*, 2006). Whilst hindcasting, or modelling of historical flows is an option (Franchini and Pacciani, 1991), these models require: (1) a record of historical rainfall, which is not always available, and (2) a large number of input and calibration parameters that can be difficult to quantify accurately (Delleur *et al.*, 1980; Muleta and Nicklow, 2005). Even a basic model commonly used to estimate streamflow, such as the Rational Method, requires an estimate of the proportion of rainfall converted to runoff (known as the runoff coefficient; C). This parameter varies significantly both spatially and temporally and as such, its accurate determination relies on calibration and verification data (Delleur *et al.*, 1980; Rogger *et al.*, 2012). Alternative methods are therefore required to identify the trends in and main causes of historical change in the hydrology of rivers and their floodplains.

Sediment cores from floodplain lakes (billabongs) can be used to identify historical changes in river hydrology. Sediments that are deposited in billabongs by fluvial floods have specific physical and geochemical properties (Wolfe *et al.*, 2006). By studying trends in these physical and geochemical sediment properties through billabong sediment cores, the historical overbank flooding frequency and trends in river hydrology can be inferred. Indeed, this process has been demonstrated in previous studies at temporal scales ranging from coarse resolutions such as decadal or centennial time-steps (Arnaud *et al.*, 2005; Moreno *et al.*, 2008), to finer resolutions of discrete flood events (Bábek *et al.*, 2011; Berner *et al.*, 2012; Wolfe *et al.*, 2006, 2005). The sediment properties used to reconstruct historical hydrologic trends in these studies are: visual characteristics like sediment colour and texture (D'Haen *et al.*, 2012; Moreno *et al.*, 2008), magnetic susceptibility (Arnaud *et al.*, 2005; Brown *et al.*, 2000), and particle size (Bábek *et al.*, 2011; Harrison *et al.*, 2003).

The elemental composition of sediments has also been used in previous studies to reconstruct historical trends in river hydrology at decadal or centennial time scales (e.g., Kujau *et al.*, 2010; Moreno *et al.*, 2008). However few studies have used the elemental composition of sediments at a finer resolution to pinpoint discrete flood deposits within sedimentary records. Berner et al. (2012) attempted to identify flood deposits within a sedimentary record of the Rhine River using the elemental composition of sediments. The study was based on the assumption that flood layers were enriched in carbonates and low in siliciclastics, a relationship determined from sampling six flood events at the turn of the 21st century. Although this is no doubt a sound assumption for floods deposited in the late 20th century, it is unlikely that the suspended sediments in flood events during this period would have similar elemental abundances as sediments in events earlier in the 20th century.

The aim of this study is to utilize a multi-proxy approach to identify the historical hydrology of the Yarra River. In particular, we have the objective of filling the current gap in knowledge surrounding the use of elemental composition of sediments for the determination of discrete flood deposits in sediment cores. Sediment cores from two billabongs of the urbanised region of the Yarra River catchment (South-East Australia) are used to infer overall changes to the hydrology and flooding frequency of this river over the period of European settlement and urban growth (the last 180 years). We aim to demonstrate a framework that uses multiple flood proxies (in particular, elemental composition) at both coarse and fine temporal resolutions, which can be applied to other river systems, so that an understanding of historical hydrology and trends in flooding can be acquired when designing mitigation strategies to restore river systems to healthier states.

METHODS

Study site

The Yarra River (Victoria, Australia) has a catchment of approximately 4,000 km^2 (Leahy, 2007), containing both developed (urban) and undeveloped (agricultural and forested) areas (Figure 1). Two of the river's billabongs, Bolin Billabong and Willsmere Billabong, both within metropolitan Melbourne, are investigated in this study (Figure 1). Bolin and Willsmere Billabongs have bank-full areas of 3.4 and 1.9 ha respectively. The two lakes receive water from their local catchments of approximately 15 ha. The local billabong catchments are shown in Figure S1 (supplementary material). Although Bolin Billabong receives just overland runoff, Willsmere Billabong receives overland runoff from the park surrounding the billabong in addition to urban stormwater from a 1.8 ha residential catchment through a direct connection to an urban stormwater drainage network. The billabongs also receive flood waters from the greater Yarra River catchment when the Yarra River exceeds bank-full capacity. This occurs at 6 m at the Banksia St stream gauge for Bolin Billabong and at 3 m at the Chandler Highway stream gauge for Willsmere Billabong (Vic SES, 2012a, 2013). The locations of the stream gauges are shown in Figure 1.

Sampling

In 2001, a 204-cm long sediment core was taken from Willsmere Billabong (Figure 1) using a light-weight modified hammer-driven piston corer with a 50-mm diameter polyvinyl chloride (PVC) barrel (Neale and Walker, 1996). This core is referred to as W2001 throughout this study. In 2012, a 212-cm long core was obtained from Willsmere Billabong using the same corer and a 96 cm core was retrieved using a 40-mm diameter Livingstone corer (Livingstone, 1955). These cores are referred to as W1 and W4 respectively. Although W1 is the longest of all three cores from Willsmere Billabong, visual inspection of the sediment core and comparison of magnetic susceptibility profiles between W1, W4 and W2001 suggest that the top 70 cm of W1 was lost in the coring process (as previously discussed in Lintern *et al.*, 2015). Thus, W1 was used only for identifying the ages of the deepest sediments.

In June 2013, a 204-cm long core was taken from Bolin Billabong (Figure 1), again using the light-weight modified hammer-driven piston corer with a 50-mm diameter PVC barrel (Neale and Walker, 1996). A replicate core was taken in two drives (bed surface to depth 65 cm; depth 65 cm to 157 cm) approximately 3 m away from the first core using the 40-mm diameter Livingstone corer (Livingstone, 1955). These cores are called B3 and B5, respectively. The coring locations within each lake are shown in Figure S1 (supplementary material). All cores were stored at 4^0C prior to analysis.

We also obtained rock samples from several locations in the Yarra River catchment to better understand the elemental composition of sediment sources (Figure 1). Each of the six major geological deposits within the Yarra River catchment upstream of Willsmere and Bolin Billabongs were sampled. These major geological deposits are: Early Devonian Sedimentary, Upper Devonian Marysville Igneous Rhyodacite Complex, Silurian Sedimentary (Dargile Formation), Silurian Sedimentary (Anderson Creek Formation), Quaternary Newer Volcanics and Quaternary Alluvium (Leahy, 2007). The specific sampling locations are listed in Table S1 in the supplementary material. Quaternary Alluvium samples were also obtained from the local catchments of Willsmere (from both the parkland and the residential catchment) and Bolin Billabong. The sampling locations from local catchments are shown in Figure S1 of the supplementary material.

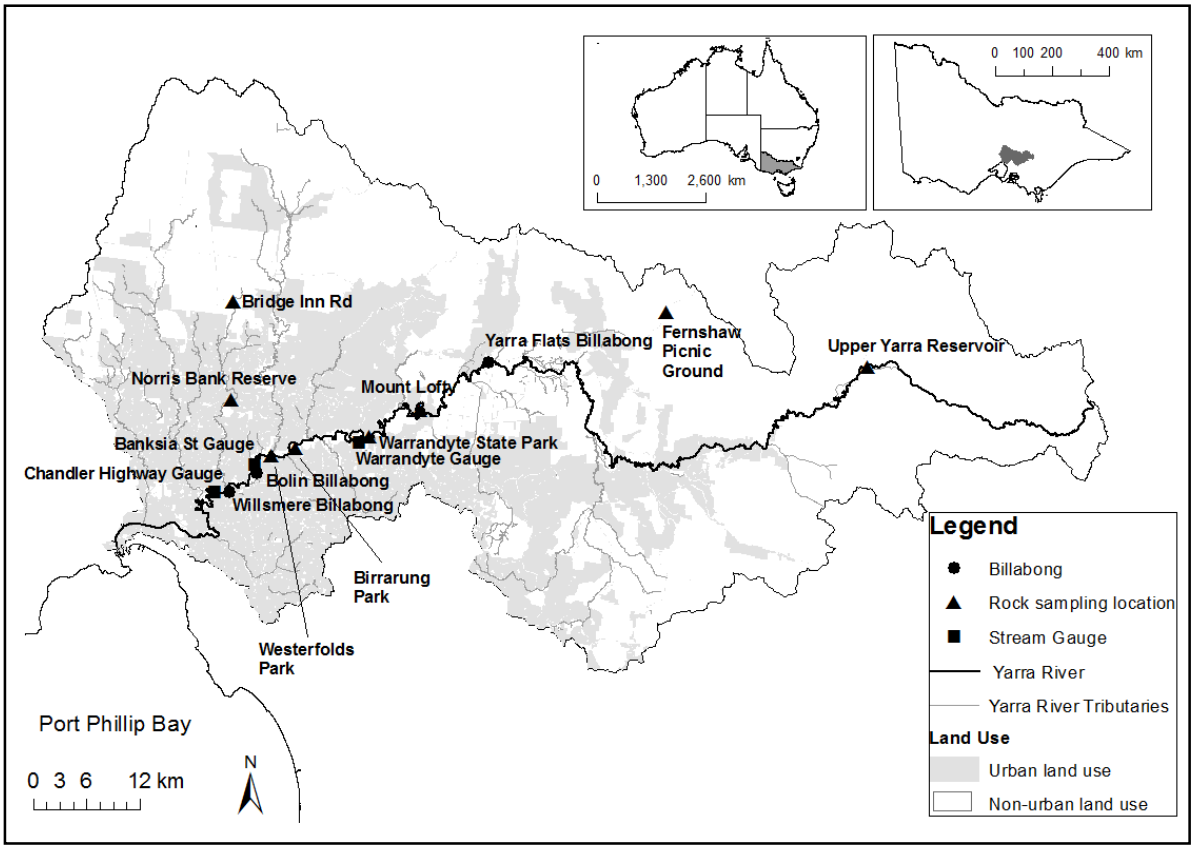

Figure 1: Location of Willsmere Billabong, Bolin Billabongs and stream gauges (Chandler Highway, Banksia St, Warrandyte) in the Yarra River catchment. Other sampling locations shown on the map are described in detail in Table S1 and Discussion S1 in the supplementary material.

Sample analyses

Image and elemental composition analyses

The six sediment cores listed above were split longitudinally and scanned using the ITRAX micro-X-ray fluorescence (XRF) core scanner (Croudace *et al.*, 2006). A molybdenum tube (voltage of 30 kV, current of 45 mA) was used with an exposure time of 10 s, reading at 1-mm intervals. Magnetic susceptibility measurements were taken at 0.5-cm intervals. Although the elemental composition was quantified at 0.1-cm intervals through the core, 0.5-cm averages were taken to match the resolution of the magnetic susceptibility analysis. All element intensities obtained by micro-XRF were normalised to total intensity (kilo-counts per second; kcps) as recommended by Martin *et al.* (2014). The top 13 cm of B3 was not scanned due to its lack of consistency. Catchment rock and soil samples were ground to a fine powder and packed into 3.5-cm diameter petri dishes. These open petri dishes were scanned in the ITRAX micro-XRF core scanner using the same settings as the sediment cores.

Sediment dating

The sediment cores were dated using several methods, including ^{210}Pb and ^{137}Cs radio-isotopic dating. W4 was selected for radio-isotopic analysis as W2001 does not contain the most recent sediment accumulation because it was taken in 2001. Of the two Bolin Billabong sediment cores, B5 was selected for radio-isotopic analysis because the inconsistent and watery nature of the top 13 cm of B3 made it unsuitable for radio-isotopic dating. The age-depth models developed for W4 and B5 using radio-isotope activities were then adapted for W2001 and B3, using the magnetic susceptibility profiles to correlate the two sediment cores from each billabong (i.e., W2001 to W4 and B3 to B5). 1-cm thick samples were taken at intervals of 1-5 cm between 0 and 42-cm depth for W4 and between 0 and 40-cm depth for B5. The difference between total ^{210}Pb activity (measured from ^{210}Po) and supported ^{210}Pb activity (measured from ^{226}Ra), was used to estimate unsupported ^{210}Pb activities (Appleby, 2001). Samples were processed as per Atahan *et al.* (2015). Both the Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models were used to calculate calendar ages from unsupported ^{210}Pb activities (Appleby, 2001). ^{137}Cs activities measured at 5 to 12-cm intervals between 18 and 70-cm depth (W4) and between 17 and 70-cm depth (B5) were used to validate the calendar ages determined using unsupported ^{210}Pb activities (Hollins *et al.*, 2011).

Additionally, the earliest appearance of dichlorodiphenyldichloroethylene (DDE), a metabolite of dichlorodiphenyltrichloroethane (DDT) was used as a chronological marker for 1946. 1946 is the earliest recorded use of DDT in Australia (Olsen *et al.*, 1980). W4 and B3 were both sub-sampled at 1-cm intervals and then composited over 4 cm (W4) and 7 cm (B3). The composited samples were air-

dried for approximately 48 hours before being analysed at a National Association of Testing Authorities (NATA) accredited laboratory (National Measurement Institute, Sydney, Australia). Organochlorine Pesticides (OCPs) were analysed using gas chromatography with an electron capture detector (GC-ECD) in accordance with US EPA 3550/8081 (US EPA, 2007). The limit of reporting was 0.0002 mg/kg (dry weight). Blank and duplicate samples were analysed and recovery rates were identified using spiked samples. Relative percentage differences ranged from 8.5 to 38% and recovery rates were above 88%.

We also used pollen to better understand the chronology of the sedimentary records. We noted the presence or absence of pollen grains of vegetation introduced to Australia by European settlers in the 19th century, such as *Pinus* and *Plantago*, in samples prepared for microscopic analysis. The first recorded planting of *Pinus* in the Yarra River catchment was in 1859 (Leahy, 2007). Given that it takes between 5 and 10 years to produce pollen (McDonald and Laacke, 1990), the earliest appearance of *Pinus* in the sediment core was assumed to represent 1870 (Leahy, 2007). *Plantago* is an introduced weed genus also used as an indicator of European arrival in Australia (Leahy *et al.*, 2005). As such, we assume that the earliest appearance of exotic *Plantago* pollen grains in the core would represent approximately 1870 also. 1-cm thick sediment samples were obtained from 134 to 135-cm depth and 154 to 155-cm depth in B5. 1-cm thick sediment samples were also obtained from B3 at 5-cm intervals between 156 cm and 201 cm and from W1 at 8-cm intervals between 102 cm and 142 cm. 1 cm^3 of bulk sediment from these samples were treated with 10% sodium pyrophosphate ($Na_2P_2O_7$) and sieved at 210 and 7 µm. 10% hydrochloric acid (HCl) and then acetolysis was used to treat the fine material. Heavy liquid separation using sodium polytungstate ($3Na_2WO_4{\cdot}9WO_3$) was conducted twice to remove organic material from the inorganic fraction. 48% hydrofluoric acid (HF) and 10% HCl were used to treat this organic fraction. The pollen samples were mounted to slides using glycerol ($C_3H_8O_3$) after being dehydrated using methanol (C_2H_5OH). The lowest depths in W1 at which pollen grains of *Pinus* or *Plantago* were found were correlated to W2001 using the magnetic susceptibility profiles of the two cores.

In addition, radiocarbon (^{14}C) dates were determined for bulk sediment samples of 1-cm thickness from 169 to 170-cm, 203 to 204-cm depth in W1 (OZS087 and OZS088), and 205 to 206-cm depth in B3 (OZS500). Carbonates and humic acids were removed from these samples by treating the sample with 2M HCl (at 60^{0}C) for carbonate removal, a series of sodium hydroxide (NaOH) treatments (at 60^{0}C) for the removal of humics and a final treatment of 2M HCl (at room temperature). After drying, the samples were combusted to carbon dioxide (CO_2) and reduced to graphite as outlined in Hua *et al.*

(2001). The Accelerator Mass Spectrometry (AMS) facility at the Australian Nuclear Science and Technology Organisation (ANSTO) was used for the ^{14}C dating (Fink *et al.*, 2004). The radiocarbon dates were calibrated with OxCal 4.2 (Ramsey, 2009) using the SHCal13 data set (Hogg *et al.*, 2013). The points in W2001 that correspond to 169 to 170 cm and 203 to 204 cm in W1 was determined by comparing the magnetic susceptibility profiles of the two cores.

Data analyses

First, overall trends in the hydrology of the Yarra River were identified using the Willsmere Billabong core W2001 and the Bolin Billabong core B3. These two cores were selected because they contained the oldest sediments of all five cores (excluding W1). Changes in hydrology were inferred by identifying transitions in sediment sources and depositional processes. These transitions were determined using (1) visual inspection of the high resolution optical and radiographic images of the cores and (2) constrained hierarchical cluster analysis (using the Euclidean distance measure). The variables included in the constrained cluster analysis were: magnetic susceptibility, the ratio of incoherent to coherent scatter (inc/coh) which was used to represent organic matter (Guyard *et al.*, 2007), the ratio of zirconium to rubidium (Zr/Rb) which was used to represent particle size (see Discussion S1 in the supplementary material), and the elemental composition of the sediments, all at 0.5-cm intervals. Only elements with high signal to noise ratios were included in the analysis. These were silicon (Si), potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), iron (Fe), Rb, strontium (Sr), yttrium (Y) and Zr. All data were scaled using the mean and the mean absolute deviation before being used for constrained cluster analysis. These statistical tests were conducted in RStudio version 3.1.0 (Free Software Foundation, Inc. Boston) using the rioja package (Juggins, 2014).

Trends in hydrology were also identified at finer resolutions through the sediment cores by identifying discrete flood layers. Willsmere Billabong core W4 and Bolin Billabong core B5 were selected for these analyses due to the fact that radio-isotopic analysis was performed directly on these two cores and thus there is less uncertainty associated with their chronologies. This greater precision makes it easier to validate the flood frequencies inferred from the cores using historical flow measurements. Flood layers were identified as laminations within the sediment core that have a fining upwards sequence in Zr/Rb (a proxy for grain size, as justified in Discussion S1 of the supplementary material), a dark layer in the radiographic image, a decrease in organic matter (represented by inc/coh) and high magnetic susceptibility. These criteria were inspired by previous studies that have used the presence of high density laminations in the sediment cores, which can be identified by dark layers in radiographic images of the core (Gilbert *et al.*, 2006), high magnetic susceptibility (Arnaud *et al.*, 2005),

low organic matter (Nesje *et al.*, 2001) and fining upwards sequences in grain size (Ambers, 2001) to identify fluvial sediment deposits. This method was called the Traditional Method.

However, due to the heterogeneous nature of flooding, we would not expect all flood-deposited sediments to have the same characteristics. As such, it is possible that the previous approach would overlook some flood deposits. An alternative method is to quantify the likelihood that a certain sediment deposit (e.g., each 0.5-cm sediment interval in a sediment core) is a fluvial flood deposit. For this measure, we have included not only magnetic susceptibility, the organic matter content (inc/coh) and Zr/Rb, as before, but we have also included elements that are expected to be high in flood-borne sediments. Comparison of the elemental composition of local Willsmere and Bolin Billabong catchment soils, and rocks from the Yarra River catchment upstream of these two billabongs, indicated that Si, K, Ti, Zr and terbium (Tb) are more concentrated in rocks and soils in the Yarra River catchment upstream of the two billabongs (Figure S5 in the supplementary material). As such, it is assumed that the flood-borne sediments from the Yarra River would be more enriched in Si, K, Ti, Zr and Tb compared to sediments transported into the billabongs via overland runoff from the local catchments. Each of the eight parameters was scaled to a value between 0 and 1 (profiles of elemental composition through sediment cores W4 and B5 are provided in Figure S6 and Figure S7 in the supplementary material). This scaling process is described in Equation 1, where x is the original value of the parameter at a certain depth in the sediment core, x_{min} is the minimum value of the parameter through the core, x_{max} is the maximum value of the parameter through the core, and x_{scaled} is the scaled value of the parameter at a certain depth in the core. For each discrete 0.5-cm depth interval through W4 and B5, the Flood Signal Strength was calculated as the sum of the eight scaled parameters, divided by the number of parameters (eight). The Flood Signal Strength represents the likelihood that the sediment deposit is of fluvial origin.

$$x_{scaled} = \frac{x - x_{min}}{x_{max} - x_{min}} \qquad \textbf{Equation 1}$$

To verify both techniques for identifying discrete flood deposits in the sedimentary record, flood records developed using both the Traditional Method and the Flood Signal Strength, were compared to flows measured at the Banksia St and Chandler Highway stream gauges (Figure 1), which are the two stream gauges most proximal to Bolin and Willsmere Billabongs, respectively. Daily average flow and river level data is available for these stream gauges from 1975 to 2013. Flow rates at these stream gauges prior to 1975 were modelled. Power functions (Grayson *et al.*, 1996) were used to relate the flow at the two gauges, to the flow measured at an upstream stream gauge at Warrandyte (Figure 1).

This was because a longer dataset was available for the Warrandyte stream gauge (data available for 1891 to 1933, 1959 to 1969 and 1974 to 2001). These power functions are Equation 2 and Equation 3, where Q_B, Q_C and Q_W represent the average daily flows at the Banksia St, Chandler Highway and Warrandyte stream gauges respectively.

$$Q_B = 1.18 Q_W^{0.98} \quad \textbf{Equation 2}$$

$$Q_C = 1.35 Q_W^{0.92} \quad \textbf{Equation 3}$$

Equations 2 and 3, which had Nash-Sutcliffe coefficient of efficiencies (E; Nash and Sutcliffe, 1970) of 0.96 and 0.93 respectively, were used to obtain average daily flow at the Banksia St and Chandler Highway stream gauges for 1891 to 1933 and 1959 to 1969 (the period for which flow data at the Warrandyte stream gauge is available). These modelled flows, along with the rating curves for the Chandler Highway and Banksia St stream gauges (Figure S8 in the supplementary material) were then used to calculate the inundation days per year (the number of days that minor flood levels were exceeded each year) and inundation events per year of Willsmere and Bolin Billabongs, respectively, from 1891-1933 and 1959-1969.

RESULTS AND DISCUSSION

Sediment chronology

The measured ^{210}Pb and ^{137}Cs activities are shown in Figure S9 in the supplementary material. For W4 (the Willsmere Billabong core), the unsupported ^{210}Pb activities exhibited a decreasing profile with depth. The CIC model sediment ages were calculated by assuming a single mass accumulation rate between 0 and 43 cm. Based on the unsupported ^{210}Pb activities, this average mass accumulation rate was estimated to be 0.66 g/cm^2/yr, or 0.94 cm/yr. The CRS model mass accumulation rates were calculated for each depth between 0 and 38-cm depth. The chronology was linearly extrapolated to the bottom of the core (96 cm) from 43 cm (CIC model) and 38 cm (CRS model). There is a close agreement between the CIC and CRS model sediment ages for W4 (Figure S10 in the supplementary material). The ^{137}Cs activity profile for W4 validates both the CIC and CRS models, with a peak in ^{137}Cs activities at 50 cm, corresponding to approximately 1964 (Figure S9 in the supplementary material). In addition, the earliest detection of DDE (1946) in W4 was at 72 cm, which also helps to validate the two models. The sediment ages below 72 cm should be considered as estimates, rather than strict dates, as they are not validated.

For the Bolin Billabong core B5, CIC model ages were calculated using the unsupported ^{210}Pb activities between 0 and 20 cm only. The unsupported ^{210}Pb data between 0 and 20 cm were selected due to the monotonic decreasing trend in unsupported ^{210}Pb activities. This gave an estimated average sediment mass accumulation rate of 0.23 g/cm^2/yr or 0.4 cm/yr. The CRS model was not used to calculate the age of sediments for B5 because independent chronological markers (i.e., ^{137}Cs activities) could not be used to verify whether the non-monotonic decrease in unsupported ^{210}Pb activities below 20 cm is due to varying sedimentation rates, or sediment mixing. The ^{137}Cs activities were too low to adequately validate the chronology. The first appearance of DDE in a core from Bolin Billabong (B3) was at 139.5 cm, which is roughly equivalent to 140.5-cm depth for B5, by correlation using magnetic susceptibility profiles (point 3* in Figure 4 and Figure 5).

In the absence of comprehensive ^{210}Pb and ^{137}Cs chronologies for B5, magnetic susceptibility profiles were used to correlate the cores from Bolin and Willsmere Billabong (i.e., B5 and W4). When visually comparing the magnetic susceptibility profiles of the Willsmere Billabong cores (W4 and W2001) and the Bolin Billabong cores (B3 and B5), it seems likely that the maximum in magnetic susceptibility at 143.5 cm in B3 and at 156 cm in B5, (point 4 in Figure 4 and Figure 5) is the same deposit to that of the maximum in magnetic susceptibility at 76 cm in W2001 and at 84 cm in W4, (point 2 in Figure 2 and Figure 3). Indeed, the presence of *Pinus* pollen at 154-155 cm in B5 indicates that it is likely that this maximum in magnetic susceptibility in B5 (point 4 in Figure 5) was deposited after 1870. As such, these similar deposits were assumed to have been deposited in the same year in the two billabongs, and the age of point 4 in cores B3 and B5 was assumed to be the same as that previously calculated for point 2 in cores W4 and W2001 using linear extrapolation. The above discussion indicates that we conducted only a coarse resolution chronological analysis for Bolin Billabong.

The chronologies for B3 and W2001 were determined by correlating them to B5 and W4 using their magnetic susceptibility profiles. Chronological markers deeper in the core were provided by (1) the presence or absence of pollen of introduced vegetation in the sediment core and (2) radiocarbon dating. For the Willsmere Billabong cores, these older chronological markers were determined for W1 and then the equivalent depth was determined in W2001 by correlating their magnetic susceptibility profiles (Figure S11 in the supplementary material). The first appearance of the pollen of introduced *Plantago* in W1 was at 130.5 cm. As such, this has been assigned the date of 1870. The radiocarbon dates for the bulk sediment samples at 169-170 cm and 203-204 cm in W1 were 1554±77 and 1347±47 years CE. According to the similarities in the magnetic susceptibility profiles between W1 and W2001, 130.5 cm in W1 roughly corresponds to 169 cm in W2001, 169.5 cm in W1 corresponds to

approximately 201 cm in W2001 and 203.5 cm in W1 is older than the sediments in W2001 (Figure S11 in the supplementary material).

In B3, the first appearance of pollen of introduced species (*Pinus*) was at 189.5 cm and thus, this depth was assigned the date of 1870. The radiocarbon date for the sediment sample at 205 cm in B3 had a date of approximately 1610±35 years CE. However, this date for B3 was excluded from the model, because this would mean a sediment accumulation rate of less than 0.04 cm/yr, which seems unlikely given the laminated nature of the sediment core, and previous findings of Leahy *et al.* (2005). The date could be due to the incorporation of old carbon, re-mobilised by flooding into a younger sediment deposit (Dezileau *et al.*, 2014).

The chronologies determined for the four sedimentary records indicates that as hypothesized previously, the longest intact sedimentary records are B3 for Bolin Billabong and W2001 for Willsmere Billabong. The age-depth models of all four cores are provided in Figure S10 in the supplementary material.

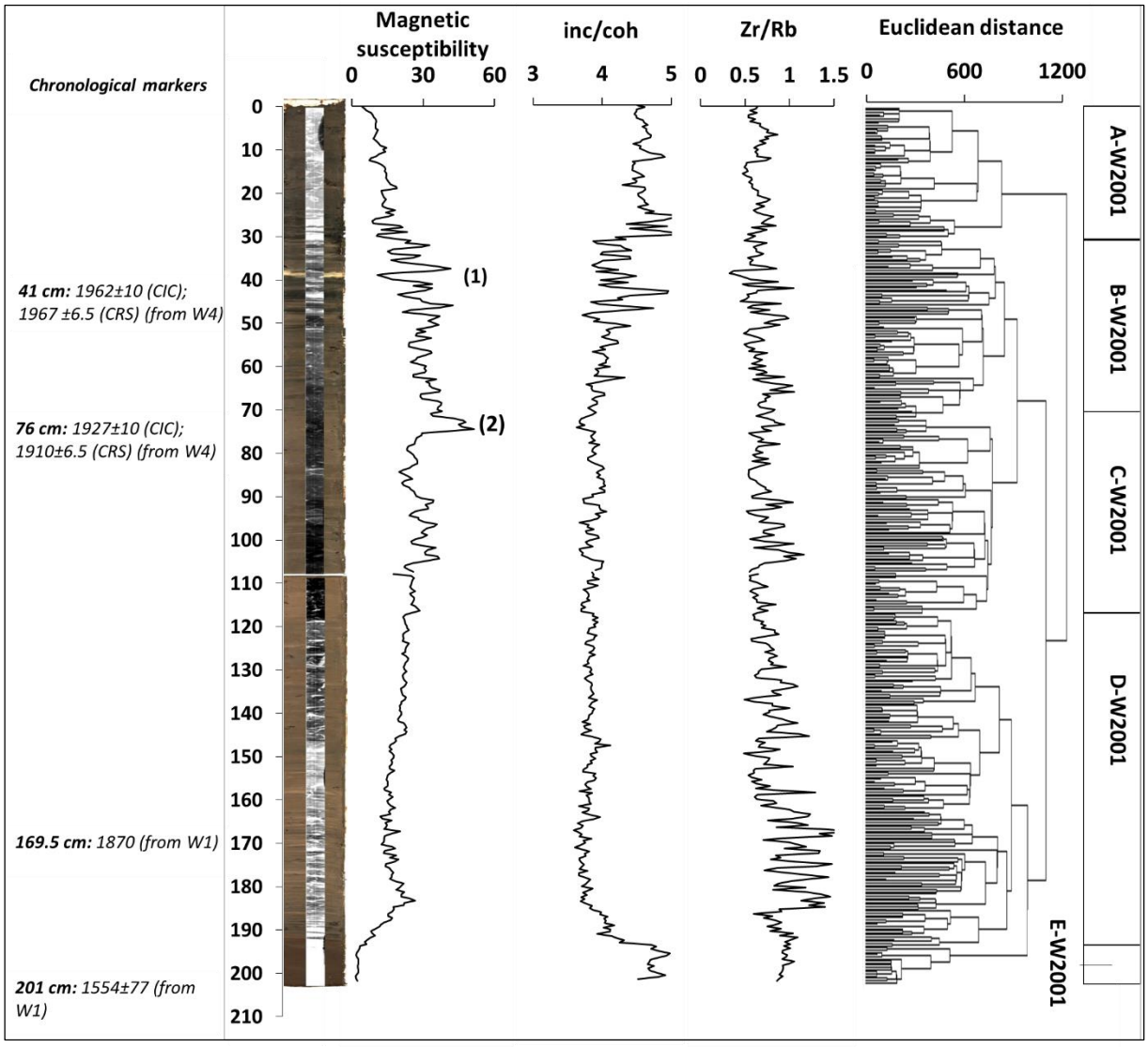

Figure 2: Selected chronological markers and images (optical and radiographic), magnetic susceptibility (in SI units), inc/coh and Zr/Rb trends and the dendrograms obtained from constrained cluster analysis for the Willsmere Billabong core W2001. The trends in elemental composition are provided in the supplementary material, Figure S12. Numbers in magnetic susceptibility profile denote hypothesized core correlation points for Willsmere Billabong cores (magnetic susceptibility profile for W4 is provided in Figure 3 and the profile for W1 is provided in the supplementary material, Figure S11).

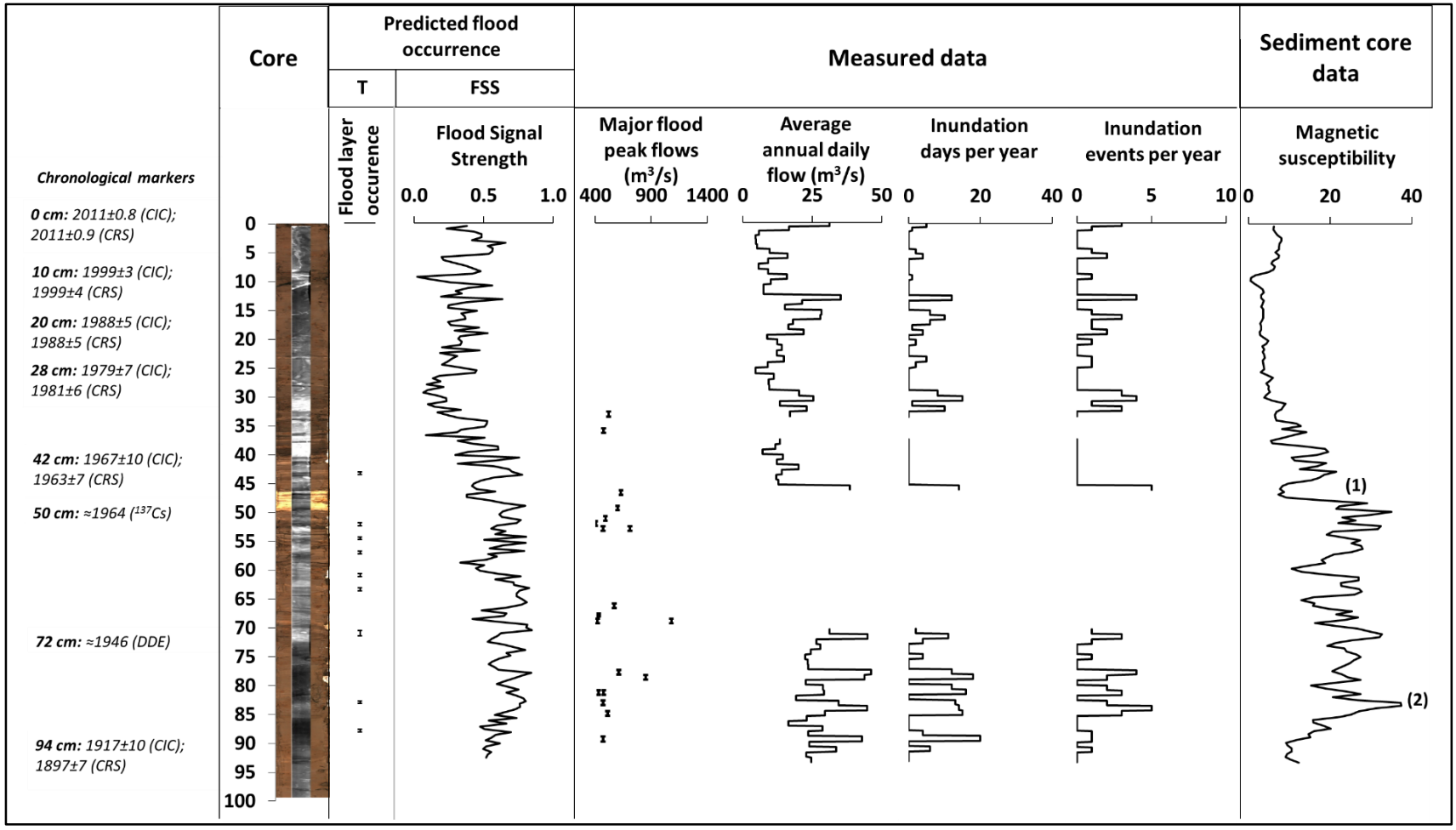

Figure 3: Predicted flood deposits through the Willsmere Billabong core W4. Selected chronological markers and optical and radiographic image of W4 provided on far left. Plot 'T' shows the depths of flood deposits according to the Traditional Method and plot 'FSS' shows the Flood Signal Strength through W4. Measured data plots consist of (from left to right): major flood peak flows adapted from Lacey (2004), average annual daily flows for the Chandler Highway gauge in the Yarra River (modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012), inundation days per year (i.e., number of days which minor flood levels were exceeded at the Chandler Highway gauge in the Yarra River each year; modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012) and events per year (i.e., the number of minor flood events at Willsmere Billabong each year; modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012). Magnetic susceptibility profile (in SI units) with correlations to W2001 (denoted by numbers) provided on far right.

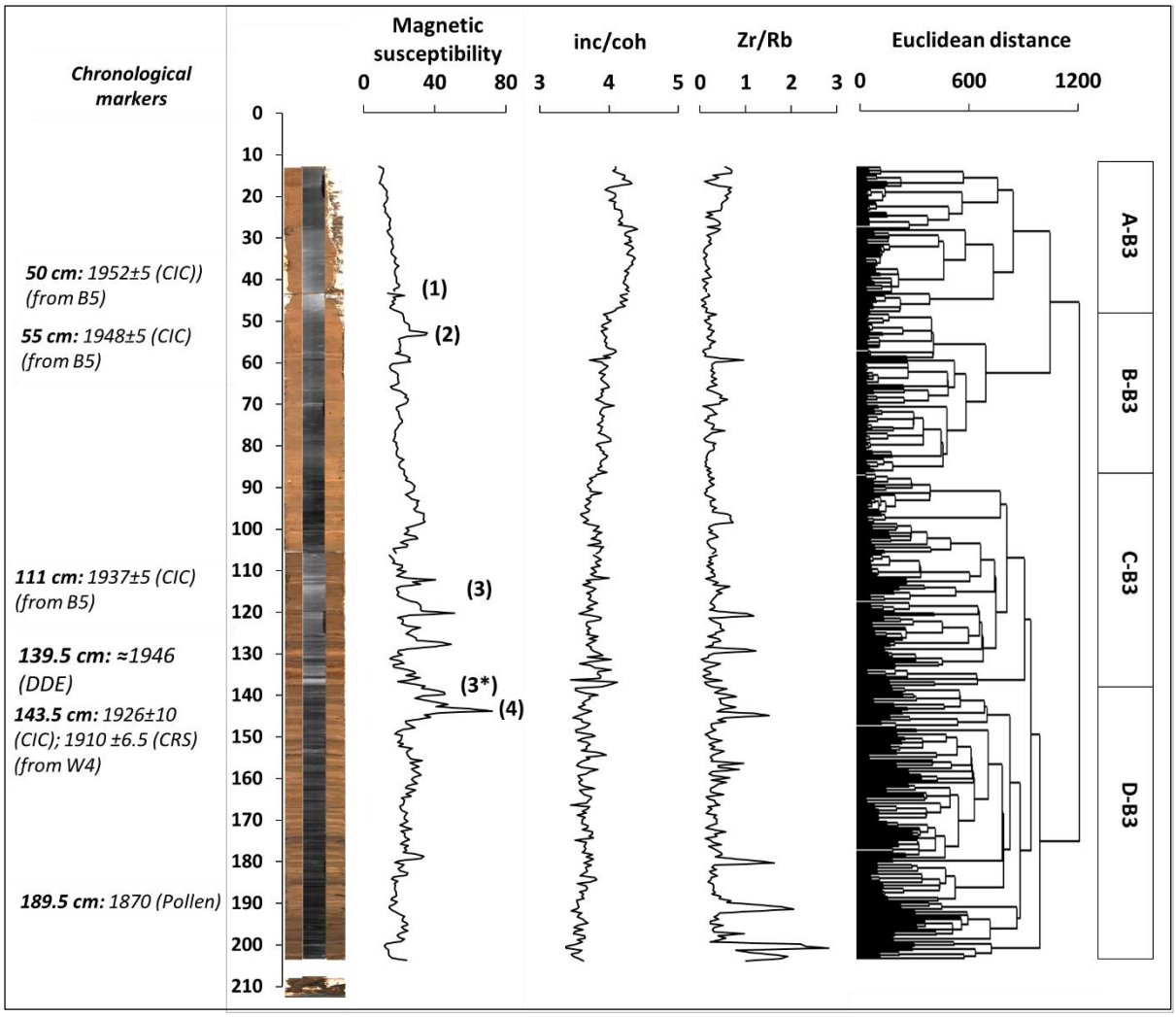

Figure 4: Selected chronological markers and images (optical and radiographic) of the Bolin Billabong core B3, magnetic susceptibility (in SI units), inc/coh and Zr/Rb trends and the dendrograms obtained from constrained cluster analysis. The trends in elemental composition are provided in the supplementary material, Figure S13. Numbers in magnetic susceptibility profile denote hypothesized core correlation points for Bolin Billabong cores (magnetic susceptibility profile for B5 is provided in Figure 5).

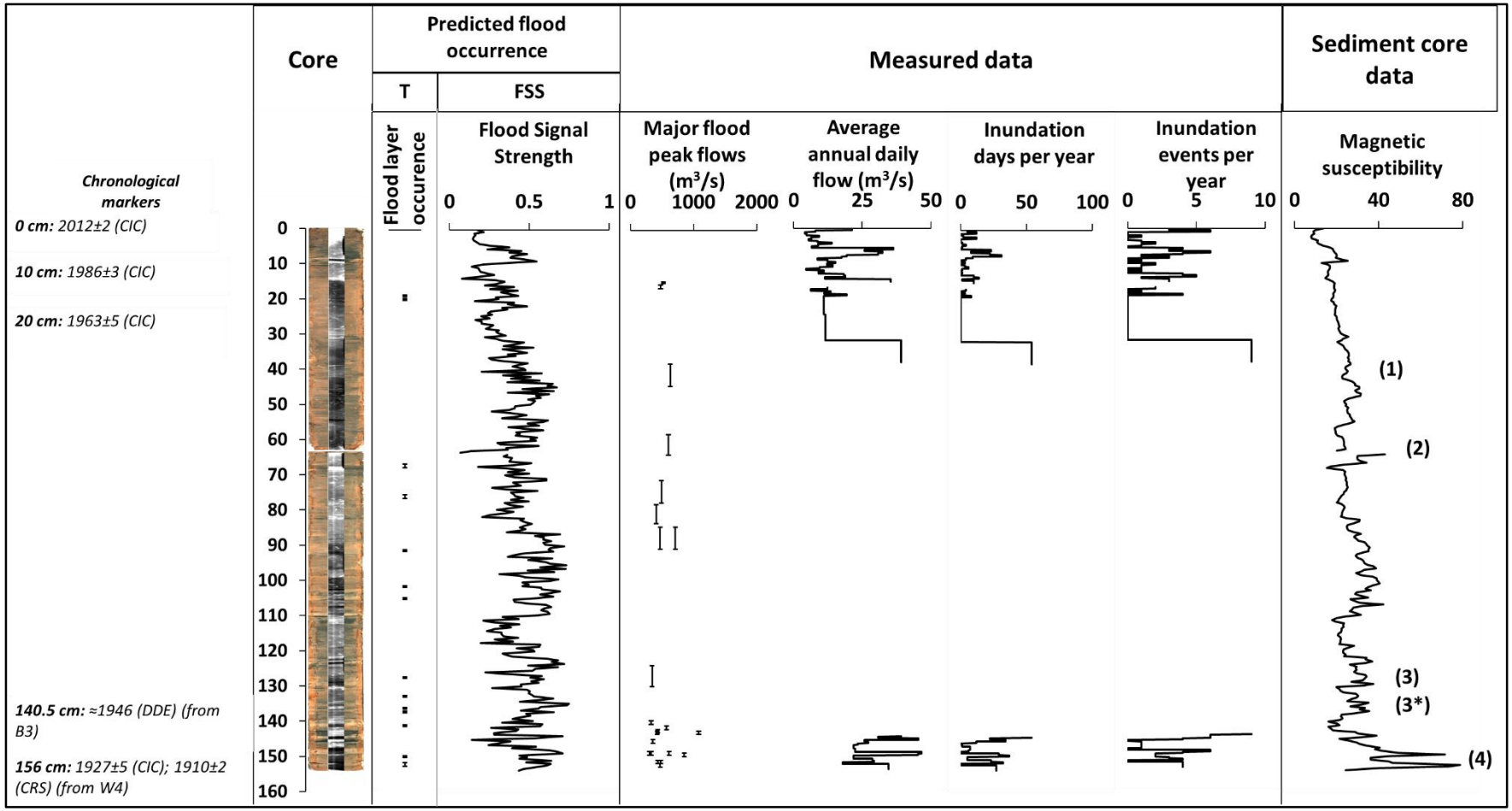

Figure 5: Predicted flood deposits through the Bolin Billabong core B5. Selected chronological markers and optical and radiographic image of B5 provided on far left. Plot 'T' shows the depths of flood deposits according to the Traditional Method and plot 'FSS' shows the Flood Signal Strength through B5. Measured data plots consist of (from left to right): major flood peak flows adapted from Lacey (2004), average annual daily flows for the Banksia St gauge in the Yarra River (modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012), inundation days per year (i.e., number of days which minor flood levels were exceeded at the Banksia St gauge in the Yarra River each year; modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012) and events per year (i.e., the number of minor flood events at Bolin Billabong each year; modelled data from 1892-1932 and 1960-1969 and measured data from 1975-2012). Magnetic susceptibility profile (in SI units) with correlations to B3 (denoted by numbers) provided on far right.

Reconstructing historical river hydrology

The dendrograms from constrained cluster analyses of W2001 and B3 are shown in Figure 2 and Figure 4, respectively. The dendrograms show the similarity between certain regions of the cores based on their sediment characteristics (magnetic susceptibility, inc/coh, Zr/Rb, and elemental composition). As these sediment characteristics are affected by the source and depositional environments of sediments (Arnaud *et al.*, 2005; Bábek *et al.*, 2011; Moreno *et al.*, 2008), the dendrograms can be used to infer time periods (or sediment core regions) with similar sediment sources and transport processes into the billabong and therefore, similar hydrological states. Using the dendrograms, W2001 has been split into five zones, labelled A-W2001 to E-W2001 (Figure 2) and B3 into four zones, labelled A-B3 to D-B3 (Figure 4).

Zone E-W2001 (194.5 cm to the bottom of W2001) was deposited between the late 16th and early 17th century (Figure 2). This region of pre-European sedimentation exhibits high inc/coh levels and relatively low levels of magnetic susceptibility, Zr/Rb and inorganic elements, and these sediment properties are stable through the zone (Figure 2 and Figure S12 in the supplementary material). This suggests that prior to European settlement in the area, sediments deposited in Willsmere Billabong were high in organic matter, and experienced little short term variability in sediment sources or transport processes. A previous study of Willsmere Billabong also identified that pre-European sedimentation was dominated by organic matter (Leahy, 2007).

Zone D-W2001 (117 to 194.5 cm) and Zone C-W2001 (71.5 cm to 117.0 cm), are characterised by inorganic brown lake clay with olive-grey and pale yellow laminations of varying thicknesses (Figure 2). Zone D in the Bolin Billabong core B3 also contain similar inorganic laminated sediments (Figure 4). The age-depth model suggests that Zones D-W2001 and C-W2001 contain sediments deposited between the mid-19th and early 20th century. The age-depth model also suggests that Zone D-B3 was deposited during this period. The presence of frequent laminations suggests that there are rapid fluctuations in depositional processes and sediment sources. As such, we hypothesize that Zones D-W2001, C-W2001 and D-B3 represent a period where there were frequent overbank flooding events and catchment runoff events. Periodic increases in organic matter within these zones (e.g., at 93 cm and 164.5 cm in W2001 and 154 cm and 184 cm in B3) suggest that these overbank floods alternate with periods of organic autochthonous deposition. The overall low inc/coh and high Zr/Rb levels suggest that the zones contain mostly inorganic sediments that were transported into the billabong by strong flows (Figure 2 and Figure 4).The high levels of inorganic sediments deposited during this period by the overbank flood events are hypothesized to be a result of land clearing and urban

development occurring in the late 19th century in the Yarra River catchment and the local catchments of the two billabongs (Leahy, 2007; Lintern *et al.*, 2015). Previous studies have found that erosion and inorganic sediment supply to rivers and lakes increased significantly following European settlement in Australia due to land clearing (Prosser *et al.*, 2001). Indeed, previous palynological studies of sedimentary records from Willsmere Billabong found that there was a shift in pollen taxa deposited in the billabong during the late 19th century, indicative of vegetation removal from the catchment (Leahy, 2007). The sharp change in sediment characteristics between Zones E-W2001 and D-W2001 (i.e., organic sediments to inorganic laminated sediments) is also likely a result of this sudden disturbance of vegetation removal in the catchment.

Zone B-W2001 (31.5 to 71.5 cm) represents the sediments deposited between the early to late 20th century. It has similar sediment characteristics to Zones C-B3 to B-B3 (34 to 125 cm), which contains sediments deposited in the first half of the 20th century. Both Bolin and Willsmere Billabong have lighter coloured radiographs in these zones and increases in inc/coh, which indicate an increase in organic matter content (Giralt *et al.*, 2011). Compared to the previous zones, Zr/Rb and a number of inorganic elements including Si, K, Ti, Rb, Sr, Y and Zr have decreased (Figure 6). The decrease in these properties suggests that the two billabongs have experienced a reduction in inorganic sediment supply. This may be due to soil armouring, or possibly a result of a decline in erosion due to the end of intense catchment disturbance. Indeed, the start (i.e., the bottom) of both Zones B-W2001 and C-B3 in the early 20th century correlates with the end of gold mining in the upper Yarra catchment in 1913 (Brizga *et al.*, 1995).

Zone A-W2001 contains sediments in the top 33 cm of the sediment core, and represents accumulation from the 1970s. There is a further decrease in most indicators of inorganic material in the sediment: magnetic susceptibility, Si, K, Ti, Fe, Rb and Y (Figure 6). Inc/coh increases, suggesting that more organic material is being deposited on the lake bed and the increase in Ca levels (Figure 6) suggests that there are lower water levels. Previous works have shown that decreasing lake levels can result in increasing rates of Ca deposition and precipitation (Haberzettl *et al.*, 2005). Records indicate that There was an outbreak of *Nymphaea capensis* in the late 1980s in Willsmere Billabong (Leahy, 2007), and this may be associated with the increasing organic matter and the decreasing water levels in Willsmere Billabong, that we have inferred from the sedimentary record. It is therefore hypothesized that this zone contains sediments deposited under a more lentic state of the billabong.

Zone A-B3 (the top 34 cm of the sediment core) contains sediments deposited between the 1950s and the end of the 20th century. The lack of laminations within this zone suggests that the billabong has transitioned to a more lentic environment, with less frequent shifts in sediment sources and transport processes. This change to a more lentic environment is also indicated by the greater deposition of organic matter in this system (as shown by the increase in inc/coh; Figure 4). This shift could be linked to the construction of the Upper Yarra Reservoir in 1957. As this dam has a catchment area of 337 km^2 and a capacity of 200,000 ML (Brizga *et al.*, 1995), this would have decreased flow rates in the Yarra River and thereby reduced the frequency of overbank flooding into Bolin Billabong. Indeed, Figure 7 indicates that the flow rates in the Yarra River decreased in the mid-20th century, which is when Bolin Billabong experienced its shift to a lentic environment, according to the sedimentary record. The decreasing flow rates not only indicate a decreasing ability of the river to transport and deposit particulate matter in the billabongs, but it also suggests that the weathering and erosive capabilities of the river would have decreased, thereby resulting in a reduced suspended sediment load.

Despite the overall similarity in the historical hydrologic trends of Willsmere and Bolin Billabongs, the sedimentary records of these two billabongs indicate that there are some differences in the sediment sources and depositional processes experienced by these systems. Between 1870 and the early 20th century there is approximately 60 cm of sediment deposited in Bolin Billabong compared to 100 cm in Willsmere Billabong. This difference in sediment accumulation is most likely due to the fact that at this time, Willsmere Billabong had a local catchment (36 ha) approximately twice the size of Bolin Billabong's catchment (Leahy, 2007). Thus, it would be expected that rainfall events would have brought larger amounts of local catchment sediments into the billabong via overland runoff. The Willsmere Billabong catchment reduced to 15 ha when a freeway was constructed in the catchment in the 1970s (Leahy, 2007).

There is a shift from a lotic to a lentic environment in both billabongs, but this shift appears to have occurred approximately 15 to 20 years earlier in Bolin Billabong compared to Willsmere Billabong (Figure 2 and Figure 4). It is possible that when the Upper Yarra Reservoir was constructed, Willsmere Billabong did not experience a decrease in sediment influx to the same extent as Bolin Billabong because of the presence of a stormwater drain, which transports urban stormwater into the billabong from a local 1.8 ha residential catchment. The urban stormwater from this drain, a relatively regular supply of water and sediments into Willsmere Billabong, most likely buffered the effects of the decreasing flow rates of the Yarra River and kept the water levels from decreasing as much as in Bolin Billabong.

In addition, Ca levels are noticeably lower in the Bolin Billabong core compared to the Willsmere Billabong core (Figure 6). Ca can have both authigenic and lithogenic sources (Koinig *et al.*, 2003). Thus, the higher Ca in Willsmere Billabong may be due to the fact that more organic matter (inc/coh) has been deposited in Willsmere Billabong compared to Bolin Billabong in the 20th century (Figure 2 and Figure 4), thereby enabling higher levels of Ca precipitation and deposition (Haberzettl *et al.*, 2005). On the other hand, Ca is enriched in Quaternary Volcanics deposits in the catchment of Darebin Creek (Figure S5 in the supplementary material), a tributary that meets the Yarra River between the two billabongs (Figure 1), and it is therefore expected that Willsmere Billabong would receive a greater supply of lithogenic Ca compared to Bolin Billabong, which may also be contributing to the higher levels of Ca in Willsmere Billabong in the 19th century.

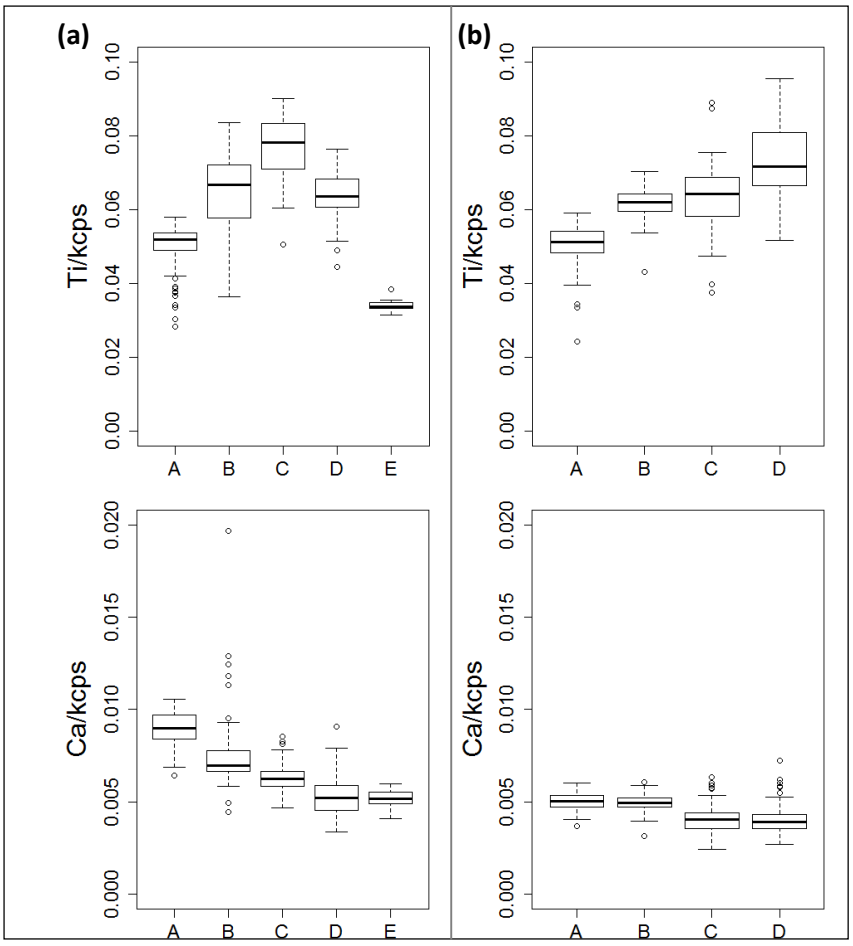

Figure 6: Boxplots showing the distribution of Ti and Ca (normalized to kcps) detected in each zone for W2001 (a) and B3 (b). Remaining elements shown in Figure S14 in the supplementary material.

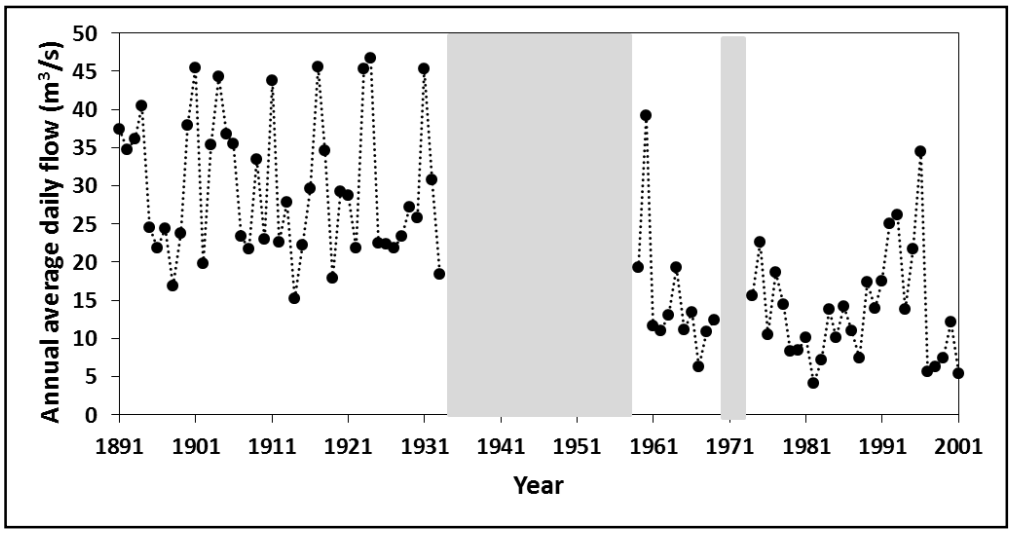

Figure 7: Observed annual average daily flow rates in the Yarra River at the Warrandyte stream gauge (location of gauge shown in Figure 1). Grey boxes indicate missing flow data.

Identifying discrete flood deposited sediment layers

Traditional Method

In both B5 and W4, there are several dark bands in the radiographic image (high density sediment layers) that correlate to local maxima in magnetic susceptibility, Zr/Rb and local minima in inc/coh. Assuming that these represent flood deposits (i.e., the Traditional Method), nine flood deposits were identified in W4 and fourteen in B5 (Figure 3 and Figure 5). These layers appear to correspond to a pale yellow or light brown coloured sediment deposit in the optical image.

The historical flood record determined using the Traditional Method underestimates the number of observed minor flood events of the Yarra River at Willsmere and Bolin Billabongs (Figure 3 and Figure 5). Instead, the flood layers identified in the sediment core using the Traditional Method appear to represent some of the major floods (Lacey, 2004) that have occurred in the Yarra River catchment (Figure 3 and Figure 5). As the chronologies of the sediment cores have an error of five to ten years, only overall trends in the occurrence of flood deposits (according to the Traditional Method) and the major flood events from Lacey (2004) can be assessed. Records indicate that major floods occurred more frequently in the first half of the 20th century compared to later in the century. The approximate timing of the flood deposits identified by the Traditional Method reflects this trend. The most recent flood deposit identified using the traditional method was just below 42 cm for Willsmere Billabong (dated as sometime between 1956 and 1977), and just below 15 cm for Bolin Billabong (dated as sometime between 1971 and 1979). Indeed, the record of major flood events in the Yarra River catchment provided by Lacey (2004) indicates that the most recent major flood event in the Yarra

River was in 1974. Although the Traditional Method has not identified deposits of all of the major flood events, this is most likely due to the high frequency of flooding in some periods. For example, in 1924, there were three floods recorded and the individual flood events would most likely have merged into one agglomerated flood deposit in the sedimentary record.

It is hypothesized that the Traditional Method cannot identify minor flood events because the composition and characteristics of individual flood deposits can have great variability. This has been previously discussed in the literature, and the factors affecting the variability in the characteristics and composition of flood deposits include: the flood strength, the source of the flood, the local catchment erosion activities, land uses at the time and antecedent dry weather period (Fitzjohn *et al.*, 1998; García-Ruiz *et al.*, 2008; Nadal-Romero *et al.*, 2008; Seeger, 2007). We hypothesize that we would expect to see noticeable excursions in all flood deposit indicators only in significant floods, such as those that made an impact to people's lives and therefore recorded in anecdotal records (e.g., Lacey, 2004).

Flood Signal Strength

The Flood Signal Strength for W4 and B5 are presented in Figure 3 and Figure 5. This Flood Signal Strength represents the likelihood that the sediment deposit is flood-borne. For both cores there is a higher Flood Signal Strength in the sediments deposited in the early 20th century, with a decrease in the Flood Signal Strength in the mid- to late 20th century. The Flood Signal Strength was compared to modelled and observed flow rates and river levels of the Yarra River at the stream gauges closest to the two billabongs: Banksia St; and Chandler Highway (gauge locations in Figure 1). Figure 8 shows the Flood Signal Strength averaged over five years against the five year average of daily flow rates and five year average of the number of days of minor flooding each year. Five year averages were selected to take into account uncertainties in the age-depth model. The Flood Signal Strength increases with greater annual average daily flows and minor flooding days per year, which indicates that the Flood Signal Strength is a reasonably reliable indicator of historical flooding history (Figure 8). Furthermore, in both plots, there appears to be a threshold in terms of both the average daily flow and the minor flooding days per year that must be reached before high Flood Signal Strengths are recorded in the sedimentary records. For both W4 and B5, Flood Signal Strength over 0.6 are seen when the annual average daily flows exceed 30 m^3/s and the minor flood days each year exceed 10 days per year.

The trend in the Flood Signal Strength (or the likelihood that the sediments are flood-borne) correlates with the flooding trend detected using the Traditional Method. Many of the layers identified as flood

deposits using the Traditional Method exhibit as local maxima in the Flood Signal Strength. However, the fact that this is not a blanket rule emphasizes the importance of considering the elemental composition of sediments, when determining flood-deposited sediments within cores.

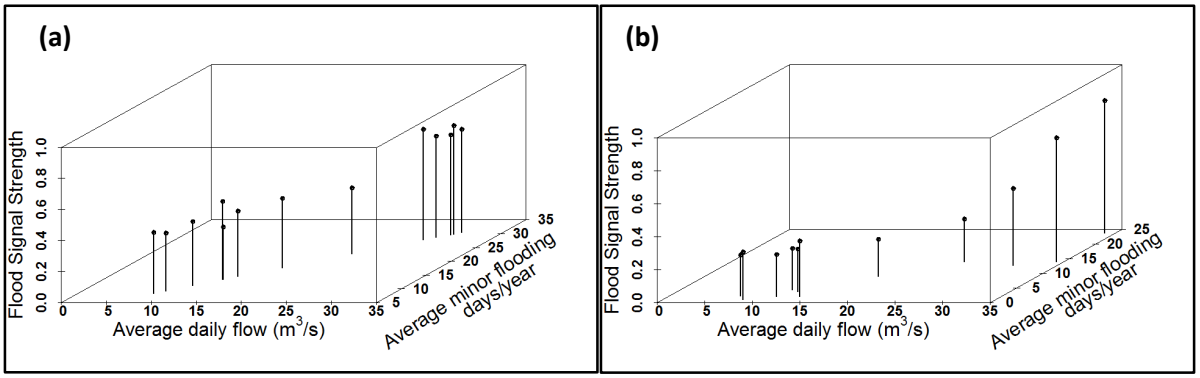

Figure 8: Comparison of five year averages of measured river flows, minor flooding days each year and Flood Signal Strength (i.e., reconstructed flood record) for W4 (a) and B5 (b).

We acknowledge that this approach of using the Flood Signal Strength to identify the likely flood deposits in sedimentary records should be further investigated. There are large periods missing from the streamflow record, particularly during the 1940s and 1950s, which is appears to be when the most significant changes in river flowrates occurred (Figure 7). As such, we recommend that this framework be further verified using river systems with more continuous streamflow monitoring.

CONCLUSIONS

Trends in several sediment characteristics (magnetic susceptibility, organic matter sediment particle size and elemental composition of the sediments) in the sedimentary records from two billabongs of the Yarra River catchment (Willsmere and Bolin Billabongs) indicate that the catchment has experienced significant changes in hydrology and sediment transport since European settlement in the early 19th century. With European settlement, the sediments deposited in Willsmere Billabong became increasingly inorganic, most likely due to the sediments mobilised by land clearing and mining. Both the Willsmere and Bolin Billabong sedimentary records indicate that the level of inorganic sediments in the two billabongs decreased over the 20th century. This is most likely due to both the decrease in catchment disturbance (e.g., the end of mining activities), which would have resulted in lower sediment supply available for transport, and also the increased water extractions from the Yarra River, which would have resulted in less frequent fluvial inundation of the floodplain lakes. Similarly, a decreasing contribution of fluvial sediments to the billabongs was evident using both methods introduced in this study to identify flood-deposited sediments in sediment cores, the Traditional

Method and the Flood Signal Strength. One of these methods used elemental composition of the sediments to identify these flood deposits. Both the reconstructed hydrologic trends over time, as well as the more detailed flood frequency records were verified using anecdotal and measured flow data for the Yarra River in the 19th and 20th centuries. As such, one major output of this work is the demonstration of the use of elemental composition of sediments to identify flood deposits.

A general analytical framework for identifying historical trends in hydrology at both coarse and fine temporal scales was presented. However, further work is required to validate the reliability of the strategies presented in this study for identifying trends in hydrology and historical flood deposited layers. This could be done either by hydrologic modelling to fill the missing regions of the existing flow data for the Yarra River, or by applying these methods to other river catchments with a more continuous record of streamflow. Once these methods have been validated further, they can be used to identify historical hydrologic trends. This understanding that the presented methodology can provide, is critical for the development of environmental flow measures or river restoration strategies. Furthermore, the identification of flood-deposited layers in sedimentary records can be applied to determine the sources of sediment-associated pollutants into these billabongs.

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5.3 Using sediment mixing models to identify flood deposits in sediment cores

5.3.1 Background

Previous studies have used sediment mixing models to identify the origins of sediments deposited in floodplains and lakes (e.g., Vezzoli *et al.*, 2004b; Weltje, 1997). The principles underlying these mixing models have been discussed previously in the literature review (Chapter 2). It was hypothesized that sediment mixing models could be applied to sediment cores to identify sediment deposits composed of mostly flood-borne sediments, and that these flood-borne sediments would be a mixture of sediments eroded from upstream geological deposits. Two sediment mixing models were tested: a linear sediment mixing model, and a Bayesian microbial source apportioning model called SourceTracker (Knights *et al.*, 2011).

5.3.2 Methods

First, a simple linear mixing model (adapted from Weltje, 1997) was used to identify the mixing proportions of the sediment sources contributing to each 0.5-cm thick sediment deposit in W4 and B5. Sediment cores W4 and B5 were selected for this work as they were directly dated and their chronologies are therefore more precise. The linear mixing model that has been adapted from Weltje (1997) is depicted in Equation 1. For each discrete 0.5-cm thick sediment deposit in the core (called *Deposit*), the abundance of *n* elements have been measured. The concentrations of each of these elements in the sediment deposit are labelled as $Deposit_1$ to $Deposit_n$. There are *m* sources (called *Source* in Equation 1) that potentially contribute sediment to each deposit and the concentration of *n* elements is known for the *m* sources (i.e., $Source_{1,1}$ to $Source_{m,n}$ are known). P_1 to P_m represents the proportions of each source *m* contributing sediment to the deposit (*Deposit*), which are the unknowns. The unknowns, P_1 to P_m can be evaluated for each discrete 0.5-cm deposit (*Deposit*), by minimization of squared errors of Equation 1.

$$[Deposit_1 \quad \cdots \quad Deposit_n] = \begin{bmatrix} Source_{1,1} & \cdots & Source_{1,n} \\ \vdots & \ddots & \vdots \\ Source_{m,1} & \cdots & Source_{m,n} \end{bmatrix} \times [P_1 \quad \cdots \quad P_m] \qquad \textbf{Equation 1}$$

$$where \sum_{i=1}^{m} P_i = 1, \sum_{i=1}^{n} Deposit_i = constant, \sum_{i=1}^{n} Source_i = constant$$

The sampling and analysis of elemental compositions of the sources of sediments deposited in Willsmere and Bolin Billabongs (the main geological formations in the Yarra River catchment and the local Willsmere and Bolin Billabong catchments soils) have been discussed previously in Lintern *et al.* (in preparation-a). The sources contributing to sediments deposited in Bolin Billabong were identified as: Early Devonian Sedimentary, Marysville Igneous Rhyodacite Complex, Silurian Sedimentary

(Dargile Formation), Silurian Sedimentary (Anderson Creek Formation) and Quaternary Alluvium both from locations upstream of the billabong and from the local Bolin Billabong catchment. The sediments from all sources except for the local Bolin Billabong catchment could potentially be transported into Bolin Billabong by an overbank flood. The Quaternary Alluvium from the local Bolin Billabong catchment would be transported into the billabong by overland runoff. For Willsmere Billabong, in addition to the sources already listed for Bolin Billabong (excluding local Bolin Billabong catchment Quaternary Alluvium), Quaternary Volcanics and Quaternary Alluvium from the local Willsmere Billabong catchment (both from the park and from the residential area, see Lintern et al., in preparation–a) were considered to be contributing sources. Again, the sediments from all sources but the local Willsmere Billabong catchment could be transported to Willsmere Billabong by overbank flooding.

In summary, there were seven potential sources identified for sediments deposited in Bolin Billabong and nine sources identified for sediments deposited in Willsmere Billabong. The sediments originating from the upstream sources could therefore be thought of as fluvial (or flood-borne) sediments and the sediments from the local Willsmere and Bolin Billabong catchments could be thought of as local catchment runoff sediments.

Analysis of the elemental composition of each 0.5-cm thick deposit in sediment cores W4 and B5 using micro-XRF was also discussed previously in Lintern *et al.* (in preparation-a). Not all elements detected using micro-XRF in the sediment sources and the cores were used in the linear sediment mixing model. The elements selected for the model were Si, K, Ti, Rb, Sr, Y, Zr, cerium (Ce), praseodymium (Pr) and Tb, as these are all stable lithogenic or rare earth elements with high detection levels in the ITRAX micro-XRF core scanner. Each element was normalised by the sum of the ten selected elements. Heavy metals such as Cu, Pb and Zn were excluded so that anthropogenic processes such as urbanisation and technological changes would not influence the geologic signal that we were trying to pinpoint.

The second model applied to identify flood layers in W4 and B5 was SourceTracker (Knights *et al.*, 2011). SourceTracker is a Bayesian source apportioning model initially developed to identify the sources contributing to microbial contamination. The model identifies the most likely contributions of each source, including an unknown source, based on multiple sampling of possible source proportions. The sediment sources used for SourceTracker were the same as the ones used for the linear mixing model. However unlike the linear mixing model, a larger number of elements were used. Stable lithogenic elements with low detections (aluminium; Al, vanadium; V, selenium; Se, gallium; Ga,

bromine; Br, niobium; Nb, palladium; Pd, barium; Ba, lanthanum; La, neodymium; Nd, tantalum; Ta, thulium; Tm, bismuth; Bi) were included in the analysis in addition to Si, K, Ti, Rb, Sr, Y, Zr, Ce, Pr and Tb as 'pseudo-microorganisms'. Elements with low detection were included because the model has an inbuilt rarefaction step, which reduces the influence of the elements with low detections on the final model results. The default rarefaction of 1000 was used when running the model. Like the linear mixing model, the elemental abundances were normalised by the sum of the abundances of all 23 elements used in the model. Due to the way that this model was designed, the element abundances had to be integers (Knights *et al.*, 2011). Thus, to ensure the normalised element abundances were in integer form, they were multiplied by 100,000 and rounded to the nearest integer.

5.3.3 Results and discussion

Linear mixing model

The mixing proportions identified in the linear mixing models for W4 and B5 are provided in Figure 5.1 and Figure 5.2. First, it is promising that the largest contributing sediment source is the same for both the Willsmere and Bolin Billabong sedimentary records (Silurian Sedimentary). This indicates that the sediments deposited in Willsmere and Bolin Billabongs are coming from a similar source, which is expected given that the two systems are only 10 km apart.

However, there are discrepancies between the linear mixing model results and Yarra River streamflow measurements available for the 20th century. Firstly for W4, the largest contribution of local catchment runoff sediments (i.e., Quaternary Alluvium from the local Willsmere Billabong catchment) occurs at the bottom of the core (Figure 5.1). However, given that the highest flows in the Yarra River occurred during this period (Figure 5.3), it is expected that there would have been low levels of local catchment sediments relative to the flood-borne sediments in the early 20th century. Similarly for B5, whilst the proportions of fluvial sediments in the sediment core increase with time (Figure 5.2), observed flows through the Yarra River decrease during the same period.

This lack of correlation between the linear mixing results and the observed annual average daily flows in the Yarra River (Figure 5.3) indicates that the flood deposits for Willsmere and Bolin Billabongs cannot be identified using a linear mixing model. The main problems are probably the assumptions inherent in the linear sediment mixing model: (1) that all potential sediment sources were sampled; (2) that there is minimal variability within the sediment sources (i.e., grab rock and soil samples that were obtained had elemental compositions that were representative of the geological deposit) and (3) that elemental compositions of the source rocks have remained stable throughout the sediment

erosion and transport processes. Indeed previous studies have identified these uncertainties as sources of error in mixing models (Koiter *et al.*, 2013; Pulley *et al.*, 2015b, 2015a).

Another problem with the linear mixing model is that the Quaternary Alluvium samples from the local catchments of Willsmere Billabong (both the residential area and the park) and Bolin Billabong, and from the river catchment upstream of the two billabongs (for sampling locations, see Lintern et al., in preparation-a), are themselves mixtures of eroded sediments from upstream geological deposits. The mixing proportions of upstream geological deposits contributing to Quaternary Alluvium samples from the local Willsmere (both from the park and the residential area) and Bolin Billabong catchments were identified using the linear mixing model. Indeed, for the local Bolin and Willsmere Billabong catchment samples, 90% and 80% (respectively) were attributed to Devonian Sedimentary and the remainder was estimated to originate from Marysville Igneous Rhyodacite Complex. As such, when the model identifies that a large proportion of sediments in the sediment core deposits come from Devonian Sedimentary or Marysville Igneous Rhyodacite, the source of the sediments might actually be the Quaternary Alluvium from the local catchment. This uncertainty may be contributing to the lack of correlation between the proportion of fluvial sediments contributing to W4 and B5 deposits identified using the linear mixing model (Figure 5.1 and Figure 5.2) and the average annual daily flows measured in the Yarra River through the 20th century (Figure 5.3).

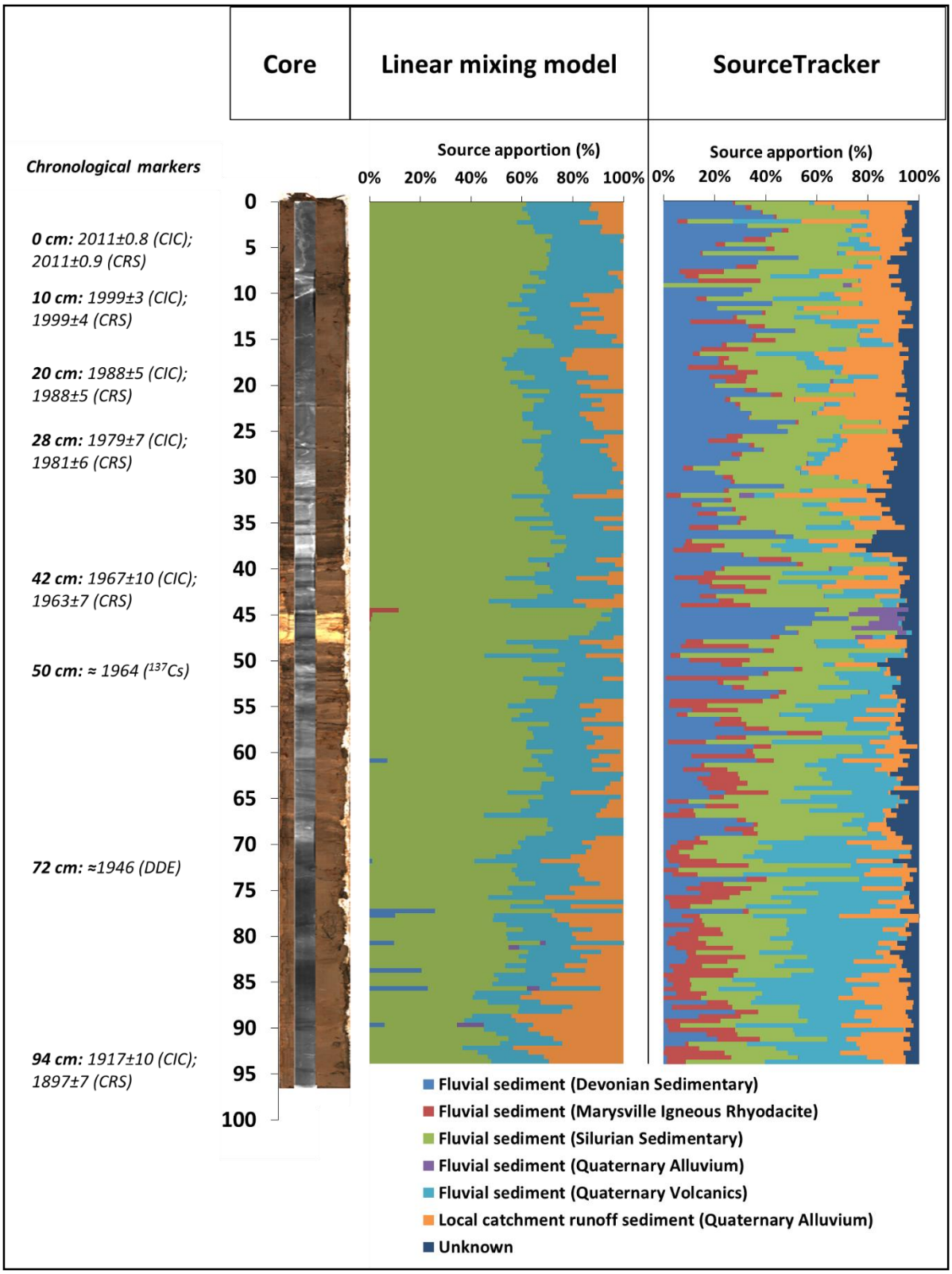

Figure 5.1: Mixing proportions identified in W4 using the linear mixing model and SourceTracker shown next to an image of the sediment core with chronological markers.

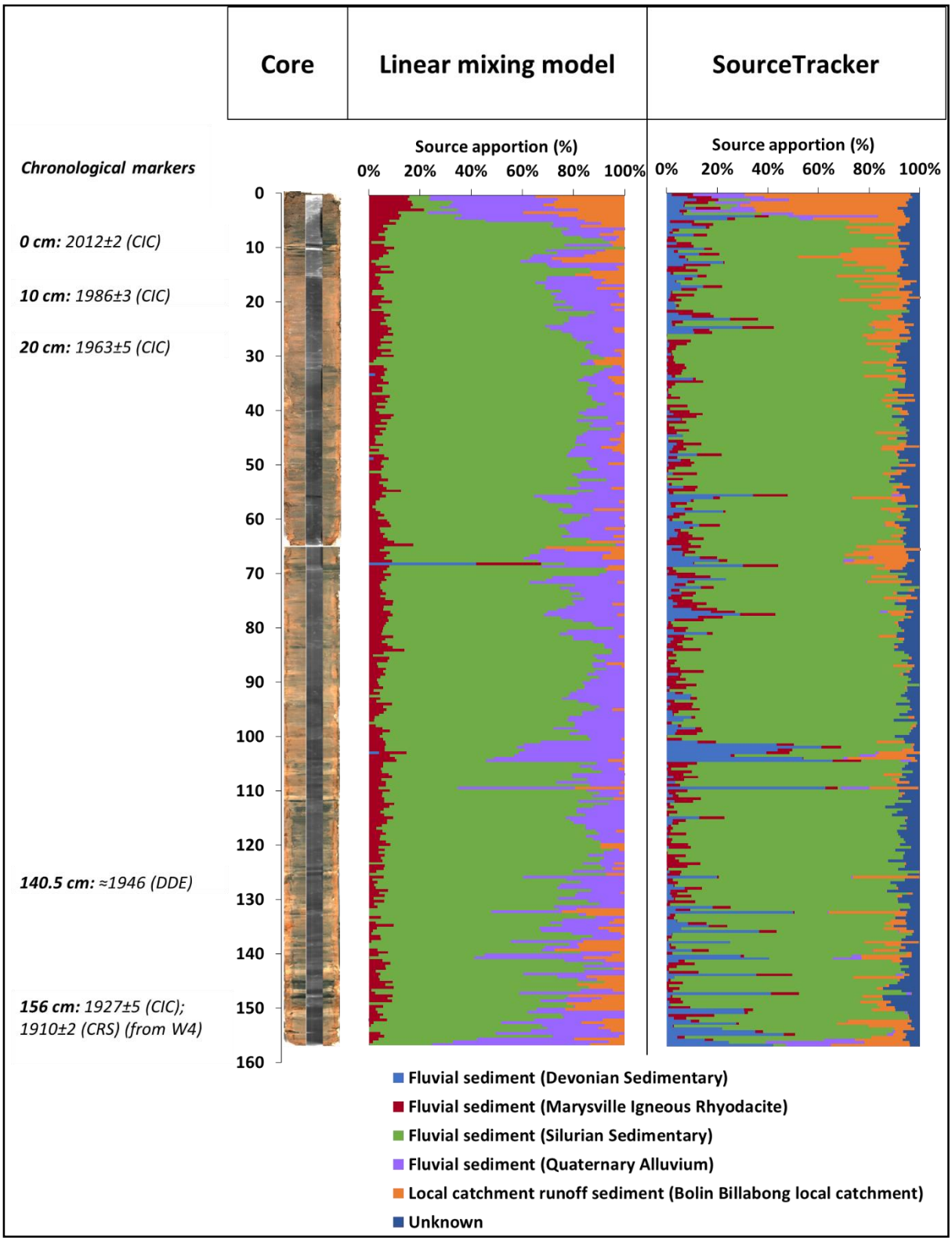

Figure 5.2: Mixing proportions identified in B5 using the linear mixing model and SourceTracker shown next to an image of the sediment core with chronological markers.

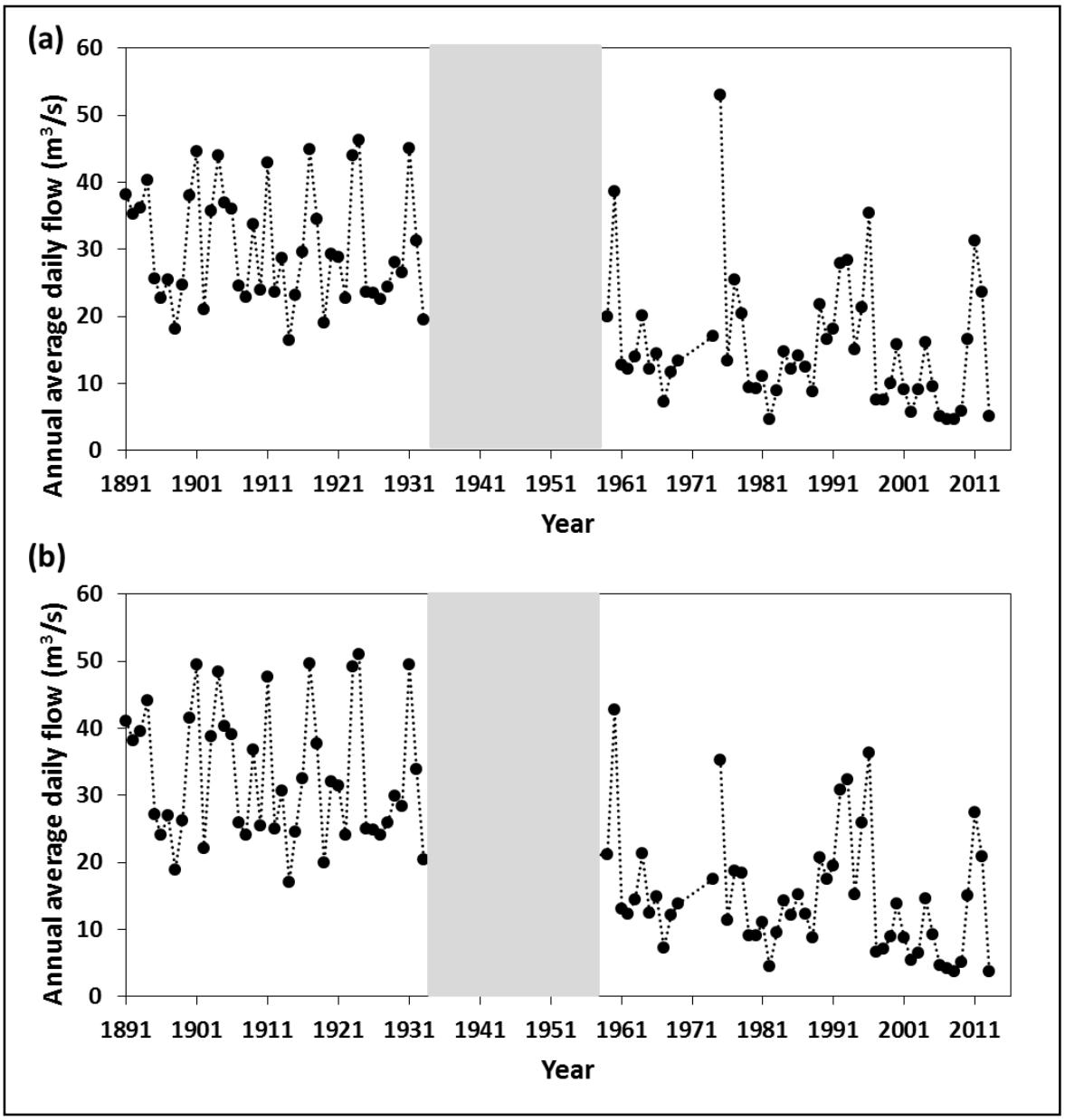

Figure 5.3: Modelled (1891-1971) and observed (1975-2013) average daily flow rates in the Yarra River at the Chandler Highway stream gauge, which is closest to Willsmere Billabong (a) and the Banksia St stream gauge, which is closest to Bolin Billabong (b). Refer to Lintern *et al.* (in preparation-a) for the origin of these data.

SourceTracker

As shown in Figure 5.1 and Figure 5.2, the mixing proportions identified by SourceTracker appear to better represent the historical flooding trends of Willsmere and Bolin Billabongs that are evident in the measured data (Figure 5.3). For W4, the proportion of local overland runoff sediments contained in the sediment deposits is higher in the younger deposits compared to the older deposits, which suggests a decreasing contribution of fluvial sediments to the Willsmere Billabong bed sediment. However, this interpretation is undermined by the fact that the contribution of the sediment source furthest away from the billabong, Devonian Sedimentary, increases in recent sediment deposits also.

As alluded to previously, if there was a decreasing incidence of flooding and reduced flow rates along the Yarra River with time, it would be expected that the contribution of Devonian Sedimentary sediments from the upper Yarra River catchment would decrease up-core.

The increasing proportion of Devonian Sedimentary sediments in recent sediment deposits may be partly influenced by the high proportion of Devonian Sedimentary materials that are contained within the Quaternary Alluvium deposits within the local catchment, as shown in Figure 5.4. As such, it is not clear whether the increase in Devonian Sedimentary sediments in recent deposits in Figure 5.1 should be interpreted as resulting from an increase in the transport of Devonian Sedimentary sediments from the upper Yarra River catchment (i.e., an increasing proportion of fluvial sediments), or whether it is merely indicating an increase in the transport of Quaternary Alluvium from the local Willsmere Billabong catchment, which contains high levels of Devonian Sedimentary sediments (i.e., an increasing proportion of local catchment runoff sediments).

For B5, there are also some similarities between the results of SourceTracker (Figure 5.2) and the observed flows in the Yarra River (Figure 5.3). Firstly, the greatest contribution of Quaternary Alluvium from the local catchment occurs in the top 7 cm of the core. The age-depth model suggests that the top 7 cm was deposited between the early 1990s and 2013. Observed flow data for the Yarra River indicate that this is a period with low flow rates in the river and therefore, low levels of fluvial inputs into the billabong (Figure 5.3). Other than this however, the sediment mixing proportions (i.e., proportion of fluvial sediment contributing to the sediment deposits in the core) generally do not reflect the observed streamflows in the Yarra River in the 20th century. Again, this is most likely due to the fact that the local catchment soils themselves are mixtures of the upstream catchment sediments, as shown in Figure 5.4 (Collins *et al.*, 1998; Meade, 1982).

Thus, it is difficult to use SourceTracker in its current form to identify discrete flood events in sediment cores. It appears that SourceTracker needs to be adapted to enable it to specify whether the sediments originating from the upper regions of the catchment have been transported and deposited directly into the billabongs, or whether they were first deposited as Quaternary Alluvium in the local billabong catchments before being transported and deposited in the billabongs.

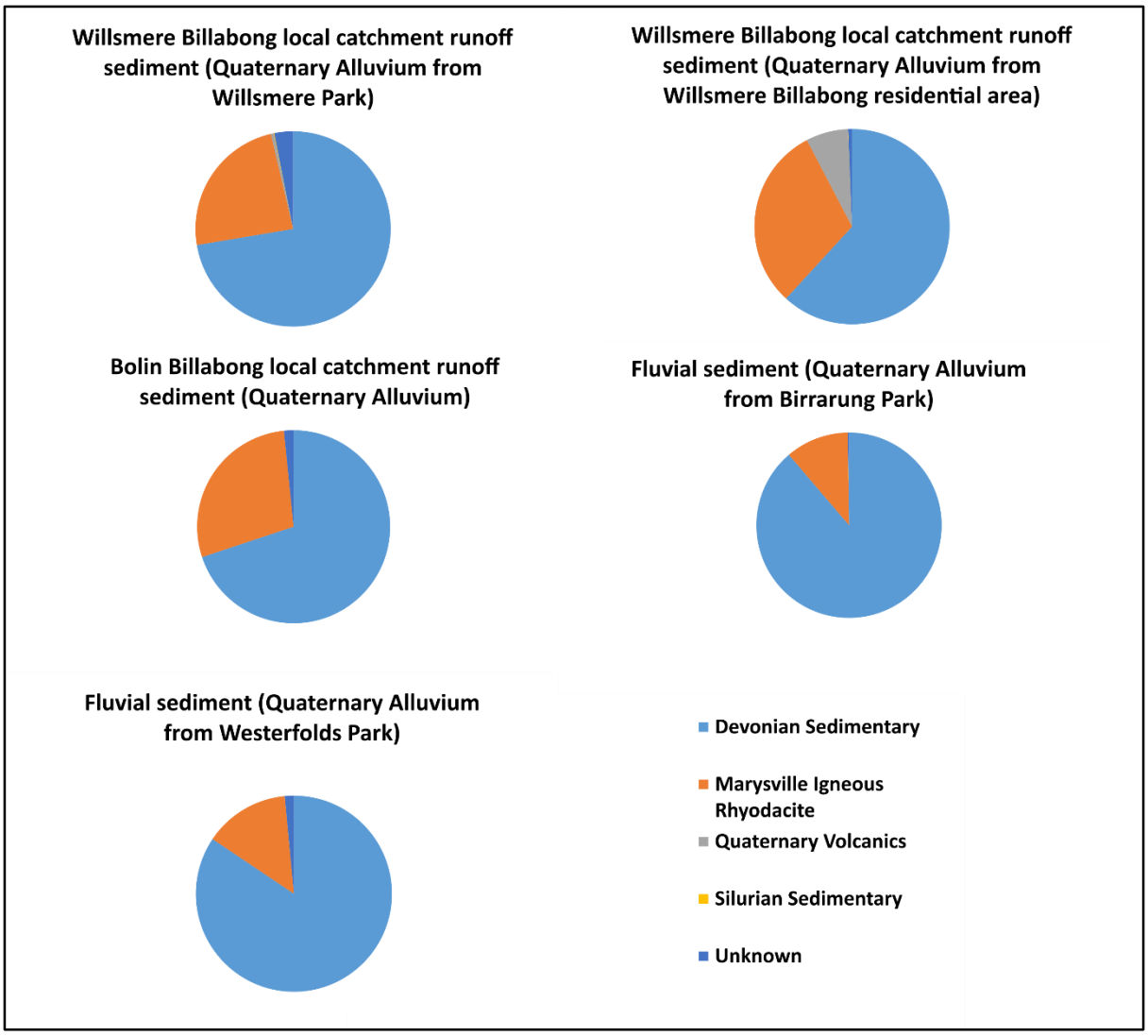

Figure 5.4: Mixing proportions of the upper Yarra catchment geological deposits contributing to local billabong catchment Quaternary Alluvium and Quaternary Alluvium from Westerfolds Park and Birrarung Park, which are both upstream of the two billabongs, identified using SourceTracker.

Both the linear mixing model and SourceTracker appear unable to successfully identify flood deposits within the sediment cores. For the cores from both Willsmere and Bolin Billabong, both sediment mixing models indicated an increase in the contribution of sediments from upstream rock deposits with time. However, it is not known whether this indicates an increase in the contribution of flood-borne sediments to the Willsmere and Bolin Billabong deposits in recent-times, or whether it indicates an increase in the contribution of local billabong catchment sediments (which are themselves sediments that originate from the upstream rock deposits) by overland runoff. Thus, other techniques (i.e., the methods discussed previously in Lintern *et al.*, in preparation-a) are more suited to identifying discrete flood deposits in the sediment cores than the linear mixing models and SourceTracker in their current form.

5.4 Comparison between chronologies developed in Chapter 4 and Chapter 5

A comparison between the age-depth models presented for the Willsmere Billabong cores (W4 and W1) in Chapter 4 and the revised age-depth models (chronologies presented in Section 5.2) is provided in Figure 5.5. Figure 5.5 indicates that there is little difference between the chronologies developed in Chapter 4 and Chapter 5. The similarities between the age-depth models presented in the two chapters, regardless of the different ways in which they were obtained, enables us to have greater confidence in the chronology assigned to the Willsmere Billabong cores. However, due to the more rigorous dating process adopted in Chapter 5, the Chapter 5 chronologies for W4 and W1 will be used through the rest of the thesis.

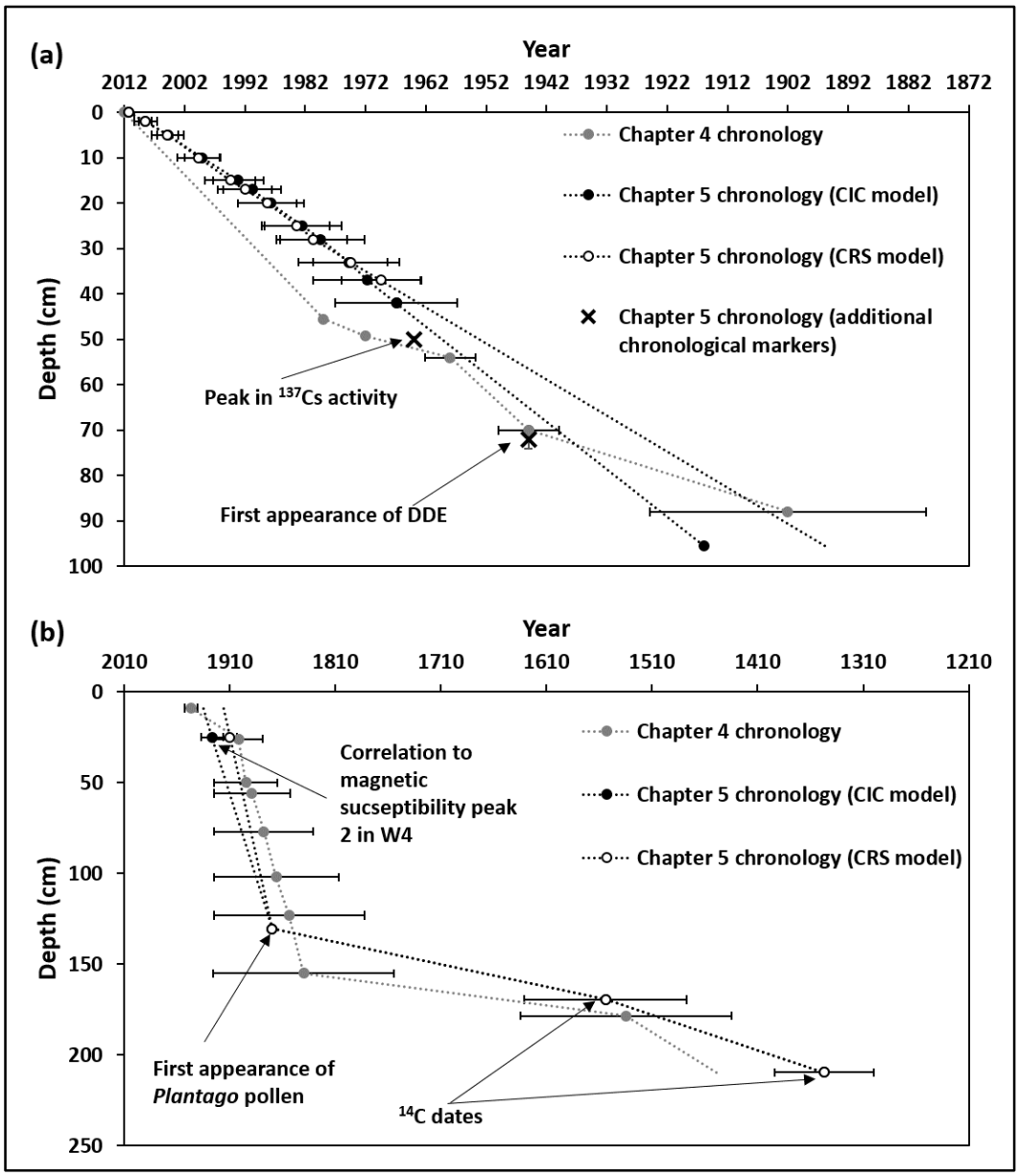

Figure 5.5. Comparison between chronologies of W4 (a) and W1 (b) developed in Chapter 4 and Chapter 5.

5.5 Discussion

5.5.1 Identification of historical hydrologic trends and discrete flood deposits

Historical trends in the hydrology of the Yarra River were reconstructed using the characteristics of sediments in cores from Willsmere and Bolin Billabong. Constrained cluster analysis (using physical and chemical sediment characteristics as variables) identified regions within the sedimentary records where the sediments had similar sources and depositional processes. By comparing the magnetic susceptibility levels, inc/coh (organic matter) levels, Zr/Rb (particle size) and elemental compositions of the sediments within each of these zones, it was inferred that the hydrologic connectivity between the main river channel and Willsmere and Bolin Billabongs has decreased over the 20th century. In other words, it was found that the billabongs shifted from fluvially dominated systems to more lentic systems. These inferred changes in hydrology correlate with observed flow rates available for the Yarra River from 1891 to 2001, which helps to validate both the methods and the results.

The Willsmere Billabong sedimentary record suggests that this billabong shifted to a lentic system approximately 20 years after Bolin Billabong. This may be a result of the presence of a stormwater drain discharging urban stormwater into Willsmere Billabong. Given rainfall patterns in Melbourne, it is likely that Willsmere Billabong would have received stormwater flows through the drain approximately twice a week (Blecken *et al.*, 2009). These relatively consistent inputs of sediment and water would have buffered the changes that had occurred in river hydrology. Whilst this may sound positive, there was a *Nymphaea capensis* outbreak in the 1980s in Willsmere Billabong, and this occurrence coincides with an increase in organic matter (inc/coh) in the sedimentary record. Previous studies have found correlations between the growth of invasive species in wetlands and nutrient enrichment due to stormwater inputs (Lake and Leishman, 2004). As such, it is possible that this outbreak of *Nymphaea capensis* is related to the high nutrient levels in urban stormwater entering the billabong (Walsh, 2000). These findings, along with the findings from Chapter 4 raise questions about the possibility of using stormwater to restore floodplain lakes that are in a degraded state due to reduced river flows, but also the importance of treating this stormwater prior to introducing it into the floodplain lakes.

Two methods were employed for identifying discrete flood layers in the sedimentary record. First, using the traditional proxies for identifying flood layers (magnetic susceptibility, inc/coh, Zr/Rb and high density laminations), flood-deposited sediment layers were identified in B5 and W4. The timing of the floods identified by the Traditional Method correlated better with anecdotally recorded major flood events of the Yarra River, than with the measured flow data; suggesting that the Traditional Method is suited to identifying significant or major flood events. This is most likely due to the

heterogeneous nature of fluvial flood deposits, and it is unlikely that flood-deposited sediments would contain all the identifiers of flood events, unless it was a major flood.

Thus, an alternative method, called the Flood Signal Strength was proposed, which takes into account the heterogeneity of flood deposits. We identified expected characteristics of flood-deposited sediments, including high magnetic susceptibility, low organic matter (represented by inc/coh) and high particle size (represented by Zr/Rb). In addition, elements likely to be enriched in flood-deposited sediments were determined. These elements were selected by comparing the elemental composition of soils from local Willsmere and Bolin Billabong catchments (i.e., sediments entering the billabong via overland runoff) to the greater Yarra River catchment (i.e., sediments entering the billabong via fluvial flooding). As such, this method utilizes elemental composition as a way to identify flood-deposited sediments. Each of these parameters was scaled to a value between 0 and 1. The sum of these scaled parameters normalised by the number of parameters at each depth interval in the sedimentary record was taken as the Flood Signal Strength at that depth interval. The Flood Signal Strength represents the likelihood that the sediment is of fluvial origin. This method appears to identify probable flood layers quite well, with the Flood Signal Strength correlating with measured average flow rates and minor flooding days in the Yarra River from 1911 to 2001.

However, it is acknowledged that further verification of the Flood Signal Strength method is required. There are significant gaps in the available flow data both between 1933 and 1959, and 1969 and 1974. As such we recommend further verification of this method by applying it to a site with continuous long-term streamflow data.

5.5.2 Use of sediment mixing models for identifying discrete flood deposits

Two sediment mixing models were implemented in an attempt to identify discrete flood deposits through the Willsmere and Bolin Billabong sediment cores. These were a linear mixing model adapted from literature (Weltje, 1997), and SourceTracker (Knights *et al.*, 2011), a Bayesian source apportioning model. It was hypothesized that these models would enable the identification of sediment deposits that are largely comprised of sediments sourced from the upper Yarra River catchment (i.e., from the river catchment upstream of the billabongs), which are sediments that are transported into the billabongs by overbank flooding.

However, the results from neither model matched the known flow history of the Yarra River. The proportions of sediments sourced from upstream of the billabongs (flood-borne sediments) increased in recent sediment deposits in both Willsmere and Bolin Billabong. This could be due to uncertainties

and errors in the sampling and analysis of the source rocks (e.g., the assumption that the grab sediment and rock samples have elemental compositions representative of the whole geological deposit). This could also be due to the fact that the models do not take into account that the sediments from the local billabong catchments are themselves mixtures of flood-borne sediments from the upper Yarra River catchment. It is possible that the mixing models cannot distinguish between the sediments from the upstream Yarra River catchment that have been transported directly into the billabongs by floods, and the sediments from the catchment upstream of the billabongs that have been temporarily deposited in the local billabong catchments before being transported into the billabongs by overland runoff. Therefore, further development of these sediment mixing models is required before they can be applied to sediment cores to identify discrete flood deposits.

5.6 Conclusion

The key messages of this chapter can therefore be summarised as the following:

- it was identified that two billabongs in the Yarra River catchment (Willsmere and Bolin Billabong) shifted from fluvially dominated systems to more lentic systems over the 20th century;
- this change was delayed in one of the billabongs (Willsmere Billabong), most likely due to the flow of urban stormwater into the billabong after reduced overbank flooding of the river;
- two methods, the Traditional Method and the Flood Signal Strength were developed and used to identify discrete flood deposits in the Willsmere and Bolin Billabong sediment cores;
- sediment mixing models (the linear mixing model and a Bayesian mixing model) in their current form cannot identify flood-deposited sediments in cores; and
- the methods used in this chapter to identify both the overall trends in hydrology of the billabongs of the Yarra River and the discrete flood layers in the billabong sedimentary records (particularly the application of elemental composition of sediments to identify flood-deposited sediment characteristics), could be applied to other river systems to identify historical trends in hydrology.

5.7 References

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CHAPTER 6
ASSESSING THE UNCERTAINTIES

Declaration for Thesis Chapter 6

Declaration by candidate

In the case of Chapter 6, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Initiation, ideas, sample collection, data collection, data analysis, interpretation and preparation of manuscript.	70

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Patricia Gadd	Data collection, data interpretation, reviewing of manuscript	n/a
Henk Heijnis	Data interpretation, reviewing of manuscript	n/a
Paul Leahy	Sample collection, data interpretation, reviewing of manuscript	n/a
Ana Deletic	Data interpretation	n/a
David McCarthy	Ideas, data interpretation, reviewing of manuscript	n/a

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	[redacted]	**Date** 19/08/2015
Main Supervisor's Signature		**Date** 19/08/2015

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

6.1 Introduction

In the literature review (Chapter 2), we highlighted that there is a need to better understand the uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution trends of aquatic systems. It is generally recognized that there are uncertainties involved when sediment cores from aquatic systems are used to determine historical trends in heavy metal pollution. However, these uncertainties have not been systematically investigated.

This chapter focuses on research objective 3 and its associated research questions 5 to 7, which were first introduced in Chapter 3. These are:

> **Research objective 3: To assess the uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution trends in aquatic systems.**
>
> - *Research question 5: What are the uncertainties associated with reconstructing historical heavy metal pollution trends in aquatic systems using bed sediment cores?*
> - *Research question 6: How does post-depositional transformation or mobilization of contaminants affect the interpretation of sediment core contaminant profiles?*
> - *Research question 7: To what extent does the contaminant level in the bed sediments of aquatic systems reflect the pollution state of the aquatic system?*

The research objective and questions listed above are explored in a paper that is currently under internal review for submission to *Quaternary Science Reviews*. This paper, 'Uncertainties in pollution data from sedimentary records' is cited as Lintern *et al.* (in preparation-b) in other sections of the thesis. The supplementary material accompanying this paper is provided in Appendix A.4.

6.2 Uncertainties in pollution data from sedimentary records

UNCERTAINTIES IN POLLUTION DATA FROM SEDIMENTARY RECORDS

Anna Lintern[A,E], Ana Deletic[A], Paul Leahy[B], Henk Heijnis[C], Patricia Gadd[C], David McCarthy[A,D]

[A] *Monash Water for Liveability, Department of Civil Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia*
[B] *EPA Victoria, Applied Sciences Group, Ernest Jones Drive, Macleod, Victoria 3085, Australia*
[C] *Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, New South Wales 2234, Australia*
[D] *Environmental and Public Health Microbiology Laboratory (EPHM Lab), Monash University, Australia*

[E] Corresponding author, email: anna.lintern@monash.edu

ABSTRACT

Historical pollution records obtained using sediment cores from aquatic environments can provide valuable information about pollution sources. However, before these data can be used to design environmental management strategies, the uncertainties in these records must be understood. The main objective of this study is therefore to identify and quantify the uncertainties associated with reconstructing historical heavy metal pollution records using sediment cores. Willsmere Billabong and Bolin Billabong, floodplain lakes of the Yarra River in South-East Australia, were used to explore these uncertainties. Sediment cores were obtained from these two billabongs and heavy metal concentrations within these cores were identified. In addition, heavy metal deposition onto the sediment bed and heavy metal inputs into Willsmere Billabong were monitored over a 12-month period. In this study we investigate the significance of five sources of uncertainty: (1) uncertainties in analytical methods, (2) uncertainties in spatial variability of sediment core heavy metal profiles, (3) uncertainties due to sub-sampling intervals, (4) uncertainties in the assumption that metal levels in bed sediments reflect the magnitude of metal inputs into the aquatic system, and (5) uncertainties in post-depositional transformation of metals. We found that there are low levels of uncertainty associated with the use of micro-X-Ray Fluorescence for heavy metal analysis when creating the sediment core heavy metal profiles. We also find that spatial variability in heavy metal profiles exists, even between cores taken as close as 30 m. Additionally, when coarse sub-sampling intervals are used to develop heavy metal profiles, the overall heavy metal trends are evident even though short-term fluctuations are lost. We also show that there is an identifiable link between the quantity of heavy metal levels found in billabong bed sediments and the quantity of heavy metals entering the billabong via urban stormwater and atmospheric deposition. Finally, we determine that there is minimal loss or transformation of metals buried in the billabong bed sediment. We envisage that the results from this

study will enable the practical application of sediment core heavy metal profiles in environmental management projects.

KEYWORDS
Heavy metals, historical trends, micro-XRF, sediment cores, uncertainty

INTRODUCTION
Sediment cores from aquatic environments such as lakes, estuaries and oceans can be used to understand historical environmental changes that have occurred within the aquatic system and its catchment (Moy *et al.*, 2002; Turney *et al.*, 2008). In particular, historical trends in the pollution of aquatic systems, for example heavy metal pollution, can be identified using sedimentary records from the beds of these waterbodies. Dated heavy metal depth profiles have great potential to guide the restoration and management of polluted aquatic ecosystems, because they can be used to understand the main factors of pollution (Bindler *et al.*, 2011; Ruiz-Fernandez *et al.*, 2004; Vane *et al.*, 2011). They can also be used to understand the pre-pollution or reference levels of an aquatic system, which can assist in the development of environmental restoration targets (Bennion *et al.*, 2011).

Previous studies (e.g., Boyle, 2001a) have acknowledged that there are uncertainties in reconstructed heavy metal records. However, uncertainties that are inherent in the use of sedimentary records for understanding historical environmental change are still not well understood and generally have not been quantified (Smol *et al.*, 2012). Existing efforts have focused on exploring and quantifying uncertainties in sediment chronologies (Binford, 1990; Blaauw and Heegaard, 2012; Telford *et al.*, 2004; Walker, 2012) and uncertainties in the identification of depth profiles of microfossils (Maher *et al.*, 2012).

Currently there is no uncertainty framework for the reconstruction of historical heavy metal pollution records of aquatic systems using sediment cores. As such, the aim of this work is to propose an uncertainty framework, and to then assess and quantify the sources of uncertainty within this framework. This will be done using sediment cores obtained from two billabongs (floodplain lakes), Willsmere Billabong and Bolin Billabong. These are both floodplain lakes of the Yarra River in South-East Australia). We also use the results of a 12-month monitoring study of Willsmere Billabong. We envisage that this work will facilitate greater confidence in historical heavy metal pollution records developed using sediment cores, which in turn will lead to the implementation of these data in the design of environmental management and restoration strategies.

Uncertainty Framework

Provided below is a literature review of the current understanding of the sources of uncertainties in historical heavy metal pollution records of aquatic systems reconstructed using sediment cores.

Uncertainty in the analytical method. Heavy metal contents of sediment sub-samples from cores can be analysed using techniques such as Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), conventional X-Ray Fluorescence (XRF), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and micro-X-Ray Fluorescence (micro-XRF) core scanning (Boyle, 2001a; Croudace *et al.*, 2006; Haschke, 2006). Whilst the uncertainties associated with metal analysis of sediments using more traditional methods such as ICP-MS, conventional XRF and ICP-AES have been previously explored (e.g., Moor *et al.*, 2001; Pyle *et al.*, 1996), the uncertainties in micro-XRF analyses are still not well understood. Micro-XRF core scanning is an emerging non-destructive technique that provides high resolution (down to 0.2-mm intervals) semi-quantitative data. Although some previous studies have identified the theoretical basis for uncertainties in micro-XRF heavy metal results (Löwemark *et al.*, 2011; Proske *et al.*, 2014; Schillereff *et al.*, 2014; Weltje and Tjallingii, 2008), several studies have identified positive correlations between heavy metal levels quantified using micro-XRF and more conventional methods (Böning *et al.*, 2007; Croudace and Rothwell, 2015; Kido *et al.*, 2006; Miller *et al.*, 2014). These existing works are based on a limited number of samples obtained at coarse resolution through sedimentary records, which means that only overall, average trends in micro-XRF heavy metal abundances through sediment cores have been validated by comparison to the results of more conventional analytical methods. There is a need to verify the accuracy of the heavy metal micro-XRF trends at high resolution, due to the wide-ranging potential applications of these high resolution trends (Croudace *et al.*, 2006). Whilst one study (Poto *et al.*, 2014) has compared fine resolution (1 cm) continuous metal profiles of a peat core from Italy obtained using micro-XRF, to profiles obtained using ICP-MS (a common technique used for heavy metals analysis) the micro-XRF data were manipulated to remove outliers. This most likely led to a better correlation between the two datasets. It would be beneficial to ascertain whether there is a correlation between the high resolution micro-XRF profiles and the heavy metal profiles obtained using ICP-MS even without the removal of outliers.

Spatial variability. When sediment cores are collected from aquatic systems, it is assumed that the region of the sediment bed sampled can reliably represent the deposition occurring in a system that may be as large as several squared kilometres in area. In studies that investigate historical pollution trends in a whole river catchment or watershed, there can be significant differences depending on the site within the catchment that is chosen for sediment coring. These differences appear to be caused

by the presence of local pollution sources, such as stormwater point sources. Indeed, in another study (Lintern *et al.*, in preparation-c) we compared the heavy metal profiles identified in Willsmere and Bolin Billabongs and identified that Willsmere Billabong had maximum Pb and Zn concentrations up to 2.5 and 4 times greater than in the upstream billabong (Bolin). This was attributed to the presence of a direct stormwater connection into the downstream floodplain lake.

There is also the possibility of spatial variability in metal deposition affecting metal profiles obtained within a lake. Although existing studies indicate that there is significant spatial variability in metal profiles obtained from large lakes (e.g., Boyle *et al.*, 1998), the impact of spatial variability in smaller systems (e.g., billabongs) is less understood. Several studies (Bábek *et al.*, 2011; Menounou and Presley, 2003; Winter *et al.*, 2001) have obtained multiple cores from billabongs with areas of 0.03 ha to 40 ha in Europe, the United Kingdom and North America, but the spatial variability between the heavy metal profiles obtained from cores were not investigated quantitatively. There is still a need to understand whether multiple sampling of smaller floodplain lakes is necessary when trying to reconstruct historical pollution trends. It is also necessary to understand the potential errors associated with choosing not to pursue multiple sampling.

Sub-sampling interval uncertainty. The sub-sampling interval must be selected such that the trends in heavy metals (or other sediment characteristics of interest) are easily identifiable. High resolution sampling can improve the precision of the heavy metal profiles. However, at the same time, the costs of analysing a large number of samples can be prohibitive. Although palynologists have done this, there have been no studies, to our knowledge, that have quantified the potential errors associated with selecting coarser resolution sub-sampling to develop pollutant profiles. Better understanding of the errors associated with coarser resolution sub-sampling will allow future studies to select optimal sub-sampling intervals, and thereby, enable more cost-effective analyses.

Sediment chronology uncertainty. Uncertainties in the sediment chronology can result from sub-sampling uncertainties, analytical uncertainties and modelling uncertainties (Appleby, 2001; Bjorck and Wohlfarth, 2002; Telford *et al.*, 2004). The uncertainty due to the sediment core chronology, will not be explored in this work due to the existence of previous studies that have modelled these uncertainties (e.g., Binford, 1990; Telford *et al.*, 2004). For example, using First Order Error Analysis (error propagation) and Monte Carlo Simulation Analysis, Binford (1990) estimated that uncertainties in ^{210}Pb dates can be 1-2 years for 10 year old sediments, 10-20 years for 100 year old sediments and 8-90 years old for 150 year old sediments. This analysis was done for dates obtained for sediment

cores collected from North America (Binford, 1990). Additionally, Barnekow *et al.* (1998) have noted an error of approximately 1000 years in the date assigned to bulk sediments deposited approximately 9000 years ago in a Swedish lake.

Uncertainty due to the assumption that metals in bed sediments reflect metal inputs. It has been hypothesized that the water quality of aquatic systems can affect the extent to which heavy metals bind to particulate matter, which in turn impacts the transfer of the pollution signal from the water column to the bed sediments (Boyle, 2001a; Foster and Charlesworth, 1996). Previous studies have compared historical heavy metal trends reconstructed using sediment cores against known heavy metal emission levels (e.g., Lockhart *et al.*, 2000), and used the correlation between the two to argue that sediment core heavy metal profiles accurately represent historical pollution trends. However, the differences between the heavy metal inputs into an aquatic system and the amount of heavy metals deposited on the bed sediment, have not yet been quantified.

Uncertainty due to post-depositional changes. Several studies have discussed how heavy metals in sediment cores could theoretically transform and move through buried bed sediments (Boyle, 2001b; Foster and Charlesworth, 1996; Hudson-Edwards *et al.*, 1998; Spencer *et al.*, 2003). As outlined in these studies, this can occur due to biological processes such as the up-take of heavy metals by aquatic plants (Wildi *et al.*, 2004) or the degradation of organic matter (van den Berg *et al.*, 1999). Foster and Charlesworth (1996) highlight that chemical processes can have a role also, with the loss of metals from bed sediments under anoxic conditions, or when the water has low pH. The loss of metals from sediments has been monitored in several investigations. Sakata (1985) studied the release of Cu and Pb from freshwater pond sediments in a 38 m deep reservoir in Japan, and found that these metals were generally not released from the bed sediment to the water column. Using seven annually laminated sediment cores from a lake in the North of Sweden, Rydberg *et al.* (2014) compared the concentration of metals on the surface of each of these cores with the concentration of metals in this same layer after burial. Whilst these study found that there was minimal change in heavy metal content of surface sediments as they were buried, they did not assess whether changes in heavy metals affects non-surficial sediments.

Figure 1 is an uncertainty framework that depicts the relationships between the sources of uncertainty listed above. It also describes how these uncertainty sources contribute to the total or overall uncertainty associated with reconstructing historical heavy metal records of aquatic systems using

sediment cores; termed *u(total)* in Figure 1. The relationships between the sources of uncertainty depicted in Figure 1 can be described in the following way:

1. There are firstly uncertainties in the heavy metal depth profiles (*u(metal depth profile)* in Figure 1). This is due to: analytical uncertainties (*u(analytical)*), uncertainty in the representativeness of the coring location, (*u(spatial)*), and uncertainty in the sub-sampling interval of the core (*u(sub-sampling*)). The latter two uncertainties can be grouped together and classified as sampling uncertainties (*u(sampling)*).
2. Uncertainties associated with age-depth modelling; termed *u(chronology)* in Figure 1, have the potential to compound the uncertainties in the heavy metal depth profiles.
3. The assumption that the quality of sediments deposited on the sediment bed is representative of the pollutant levels entering the aquatic system; termed *u(metals in bed sediments reflect metal inputs*) in Figure 1, also contributes to the total uncertainty.
4. Finally contributing to the total uncertainty is the assumption that there is no post-depositional mobilization or loss of heavy metals buried in the bed sediment; represented as *u(post-depositional changes)* in Figure 1.

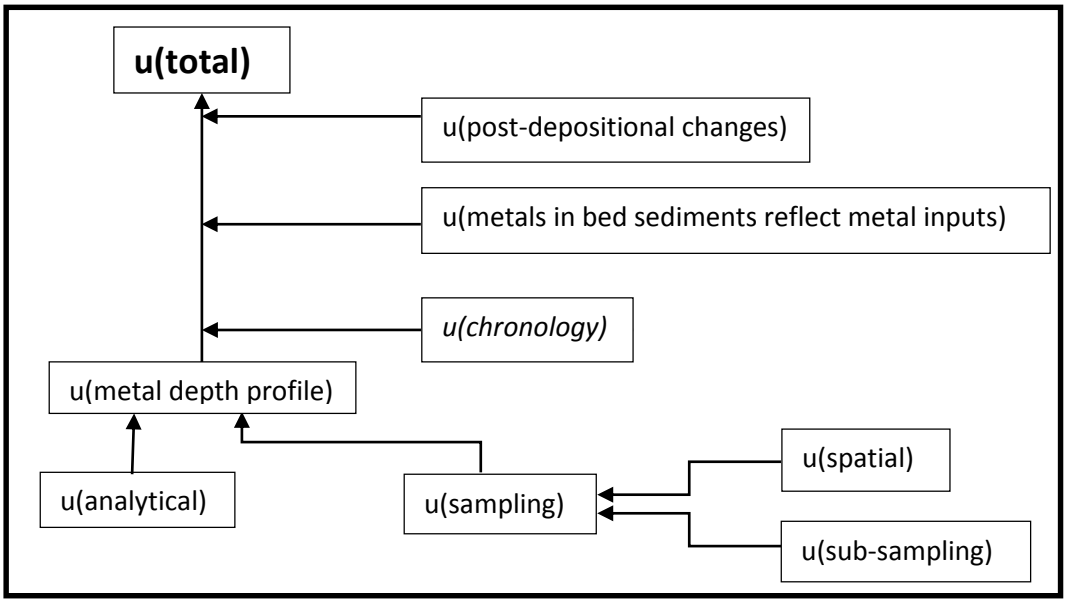


Figure 1: Uncertainty framework of the reconstruction of historical heavy metal records in aquatic systems using sediment cores. *u(chronology)* is not explored in this study, as previously discussed in the text.

MATERIALS AND METHODS

Site geography

Willsmere Billabong (37.79°S, 145.04°E) and Bolin Billabong (37.77°S, 145.08°E) are both located in the Yarra River catchment, in Victoria, Australia (

Figure 2). The bank-full areas are 3.4 ha for Bolin Billabong and 1.9 ha for Willsmere Billabong, and both billabongs have local catchments of approximately 15 ha (Leahy, 2007). Willsmere Billabong receives stormwater from a local residential catchment of 1.8 ha (Figure 3) via a stormwater treatment wetland. Both billabongs also receive overbank flows from the main river channel when the water level exceeds 6 m Australian Height Datum (AHD) at Bolin Billabong (Vic SES, 2012a) and 3 m AHD at Willsmere Billabong (Vic SES, 2013). Historically, these overbank flow events occurred once a year, but in last 60 years, this frequency has reduced to once every 3 to 4 years (Sinclair Knight Merz, 2005).

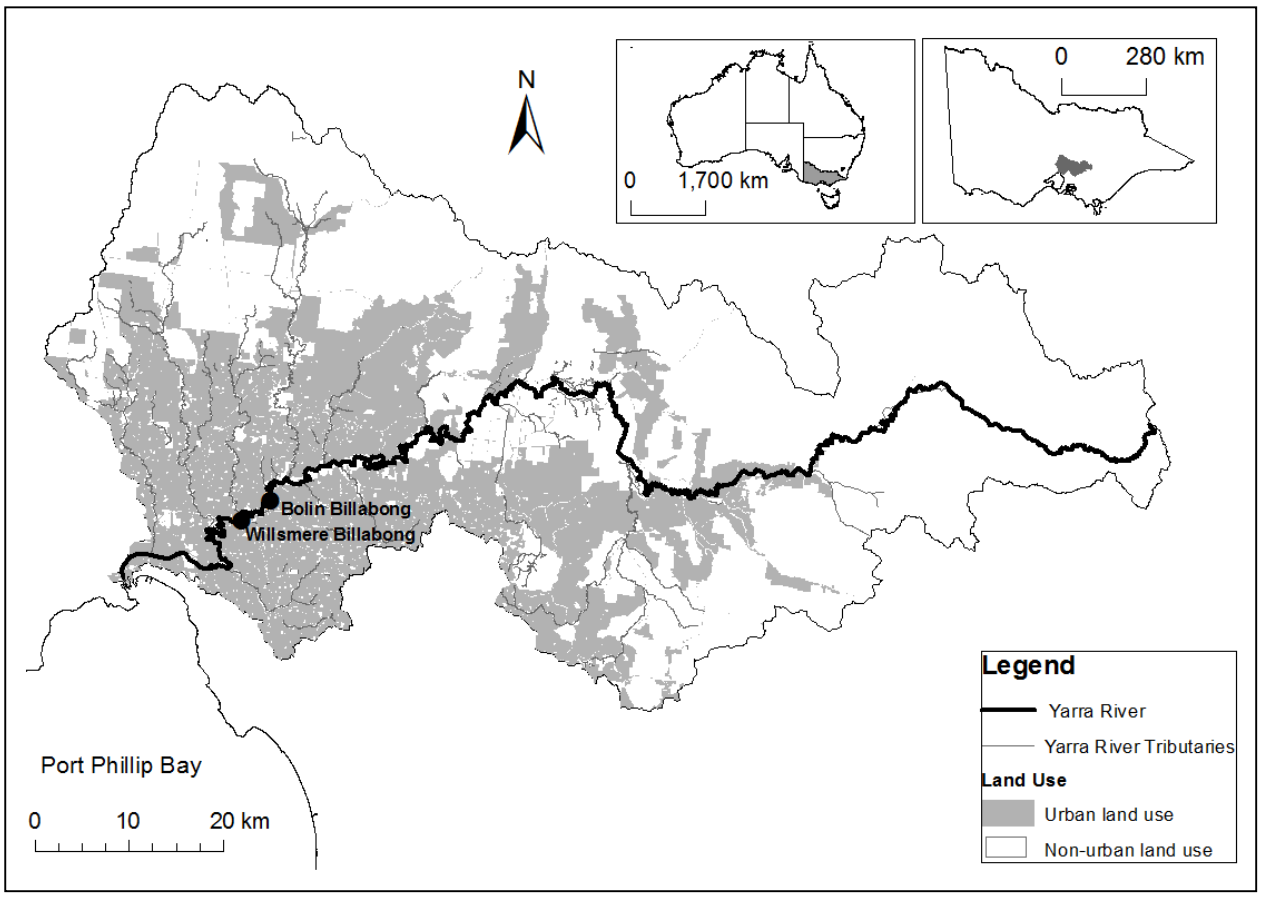


Figure 2: Location of Willsmere and Bolin Billabongs in the Yarra River catchment.

Sediment core sampling and analyses

In October 2012 and September 2013, three sediment cores were obtained from Willsmere Billabong (coring locations shown in Figure 3). These cores were taken using a 40-mm diameter Livingstone corer

(Livingstone, 1955). The lengths were: 81 cm for W1-1 (taken from Location 1 in Figure 3), 96 cm for W4 (taken from Location 2 in Figure 3) and 83 cm for W3-1 (taken from Location 3 in Figure 3). Replicate cores were taken from each of these locations. In June 2013, a 204-cm long core was taken from Bolin Billabong (B3) using the light-weight modified hammer-driven piston corer (Neale and Walker, 1996) with a 50-mm diameter poly-vinyl chloride (PVC) barrel. There cores were stored at 4^0C prior to analysis. There was an additional 204 cm core used for the study, which had previously been taken from Willsmere Billabong in 2001, from Location 2 (Figure 3) using the light-weight modified hammer-driven piston corer (Neale and Walker, 1996) with a 50-mm diameter PVC barrel, and had been in storage at 4^0C for 13 years.

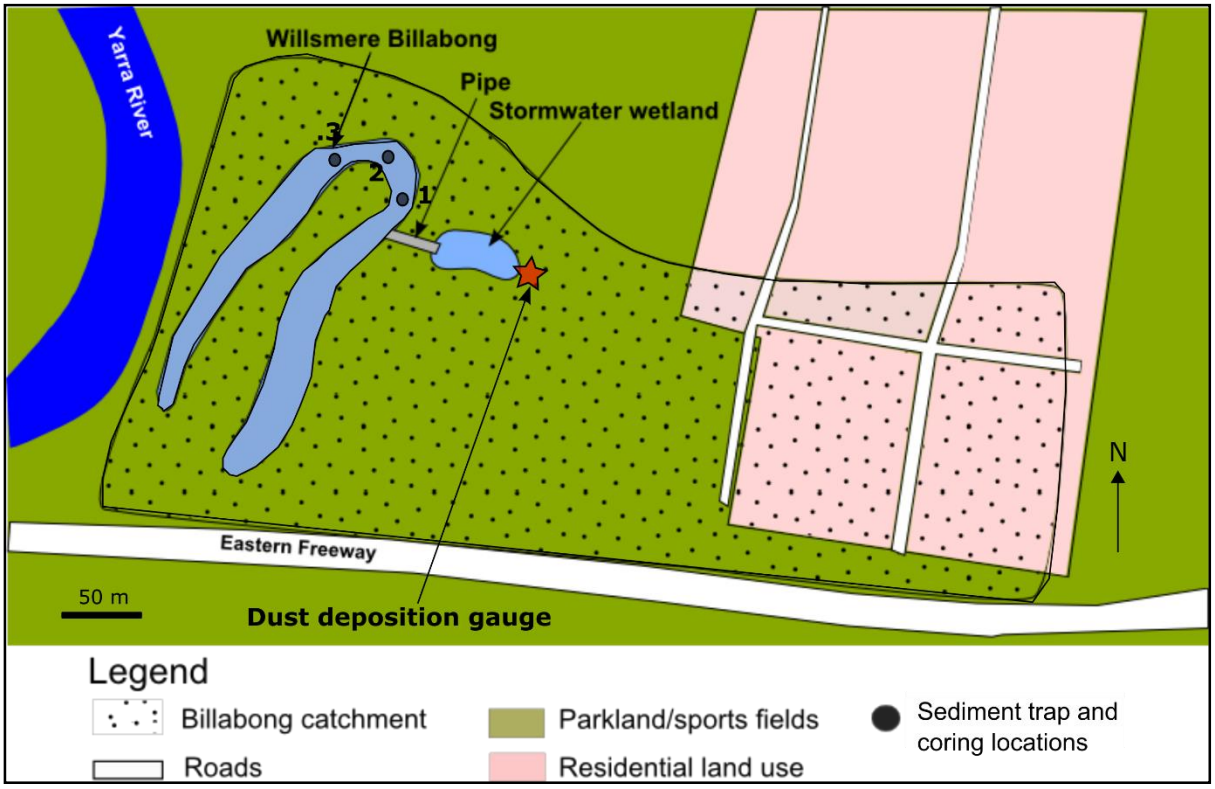


Figure 3: Map of local Willsmere Billabong catchment, showing the three sediment trap installation and sediment coring locations.

Before the cores were opened, magnetic susceptibility was measured at 1-cm intervals using a Bartington MS Series One meter and core scanning loop (Bartington Instruments, Witney, UK). All five sediment cores were then split longitudinally. High resolution optical and radiographic images, and magnetic susceptibility readings at 0.5-cm intervals of the split cores were obtained using the ITRAX micro-XRF core scanner (Croudace *et al.*, 2006) at the Australian Nuclear Science and Technology Organisation (ANSTO). B3 and W2001 were cut into two separate 1.1-m sections, as the ITRAX core scanner can only accommodate a maximum core length of 1.8 m. Micro-XRF data were obtained for

W1-1, W4, W3-1 and B3 using a molybdenum tube (30-kV voltage, 45-mA current) with a 10-s exposure time and readings obtained at 1-mm intervals. It should be noted that arsenic (As) abundances could not be detected using the ITRAX core scanner. As such, micro-XRF data are available for chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn). The counts obtained for each element were normalised to total counts per second as per Martin *et al.* (2014) to enable comparison of heavy metal trends between cores. Micro-XRF data for the top 13 cm of B3 is not available due to the lack of consistency of this unit.

W4, B3 and W2001 were also sub-sampled for heavy metal analyses. W4 was sub-sampled at 1-cm intervals. The top 20 cm of B3 was not sampled due to its watery nature. B3 was instead sampled at 1-cm intervals from 20-170 cm and 5 cm intervals from 170-220 cm. W2001 was sub-sampled at 1-cm intervals from 0-79 cm. All sub-samples were dried, and then sent to a National Association of Testing Authorities (NATA) accredited laboratory for heavy metals analyses. During the drying process, moisture content of the sub-samples was calculated. Metals were analysed using inductively coupled plasma mass spectrometry (ICP-MS) following aqua regia (nitric and hydrochloric acids) digestion (US EPA, 2007). The limits of reporting (LORs) were 5 mg/kg dry weight for As, Cr, Cu, Pb, Ni, and Zn. It should be noted that when heavy metal concentrations were below the LOR, we used the LOR divided by two. Standard quality assurance and control procedures were conducted, including analyses of blank, duplicates and spiked samples.

Field monitoring

Field monitoring of Willsmere Billabong was conducted over the period of one year to assess whether the heavy metal inputs into the aquatic system could be accurately represented by the heavy metal levels in the sediments deposited on the billabong bed. To sample sediments settling on the bed of Willsmere Billabong, sediment traps were installed in September 2013 at the three locations within Willsmere Billabong shown in Figure 3. These sediment traps (Figure 4a) were made up of four PVC tubes (53-mm internal diameter, 300-mm length). These dimensions were selected to ensure an aspect ratio of at least five, as recommended by Bloesch and Burns (1980) for small lakes. The total height of the traps was 1 metre so that the whole device would be submerged under water, to ensure their stability. Historical records of Willsmere Billabong water levels indicated that water levels rarely drop below 1 m (Leahy, 2007). 200 mL jars with 5-cm diameter openings were fixed to the ends of the PVC tubes to collect settling sediment.

Approximately once a month over a 12-month period (from October 2013 until November 2014), the sediment traps from the three locations were brought out of the water and the jars were removed so that the settled sediments could be analysed for heavy metals. Clean jars were then attached and the sediment traps re-deployed. Water depths at each location were also measured at this time. At each collection, water quality parameters (pH and dissolved oxygen; DO) were measured in situ at one location in the billabong using the U-50 Horiba multi-parameter water quality probe (Kyoto, Japan).

An additional sediment trap was installed in September 2013 at Location 2 (Figure 3), which was not recovered once a month. The jars attached to this trap were instead retrieved at the end of the 12-month sampling period in November 2014. As such, this sediment trap collected continuous sediment deposition over 12 months.

The sediments collected in the jars were sent to a NATA accredited laboratory for heavy metals analyses. The suspension was filtered (0.45 µm), and both particulate and dissolved fractions were digested using aqua regia and analysed for As, Cr, Cu, Pb, Ni and Zn contents using ICP-MS (US EPA, 2007). The filtered volume and Total Suspended Solids (TSS) concentration of the suspension were also recorded. The LOR for the particulate fractions are 0.1 µg/sample for As, Cr, Zn and 0.05 µg/sample for Cu, Pb, and Ni. The LOR for the dissolved fractions are 1 µg/L. Triplicate analyses were performed for the sediment suspensions in the 12-month sediment trap.

Each month, prior to retrieving the samples from the sediment traps, we also collected a grab sample of the water column of Willsmere Billabong from just under the water surface. These 200-mL samples were sent to the same NATA accredited laboratory for metals analyses. The same procedures used to analyse metal concentrations (particulate and dissolved) in the sediment trap suspensions were used for these grab samples.

In addition, we monitored the main heavy metal inputs into the billabong. These metal inputs were atmospheric deposition and urban stormwater. To quantify the amount of metals in the urban stormwater entering into Willsmere Billabong, 200-mL grab samples of stormwater were taken from the stormwater drain into the billabong. This was done on nine occasions, following rainfall events of over 1 mm. To quantify the amount of atmospheric deposition contributing to the heavy metal contamination of Willsmere Billabong, a dust deposition gauge (Figure 4b) was deployed approximately 100 m away from the billabong (Figure 3). The gauge was designed in accordance with AS/NZS 3580.10.1:2003 (Standards Australia, 2003). As shown in Figure 4b, this gauge consisted of a

glass funnel (150-mm diameter) attached to a glass jar (250-mL volume) and was attached to a pole approximately 2-m high. The dust deposition samples (combined wet and dry dust deposition) were collected monthly, over a 12-month period, at the same time that samples were collected from the sediment traps. Both the stormwater samples and dust deposition gauge samples were analysed for As, Cr, Cu, Pb, Ni and Zn concentrations (both particulate and dissolved) in the same manner as the sediment trap samples.

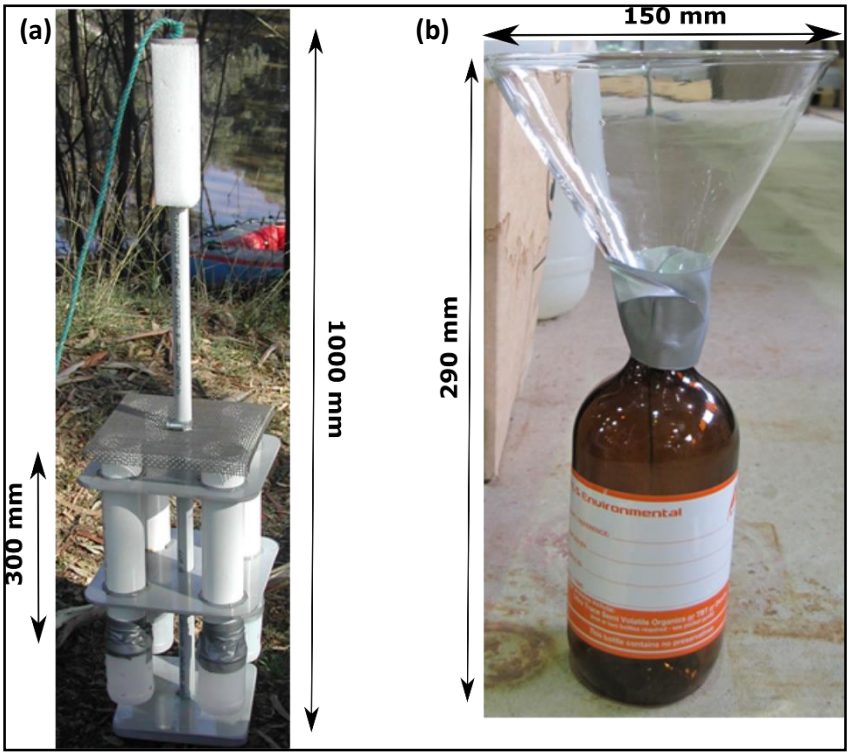


Figure 4: Photographs of the sediment trap (a) and the dust deposition gauge (b).

Data analysis

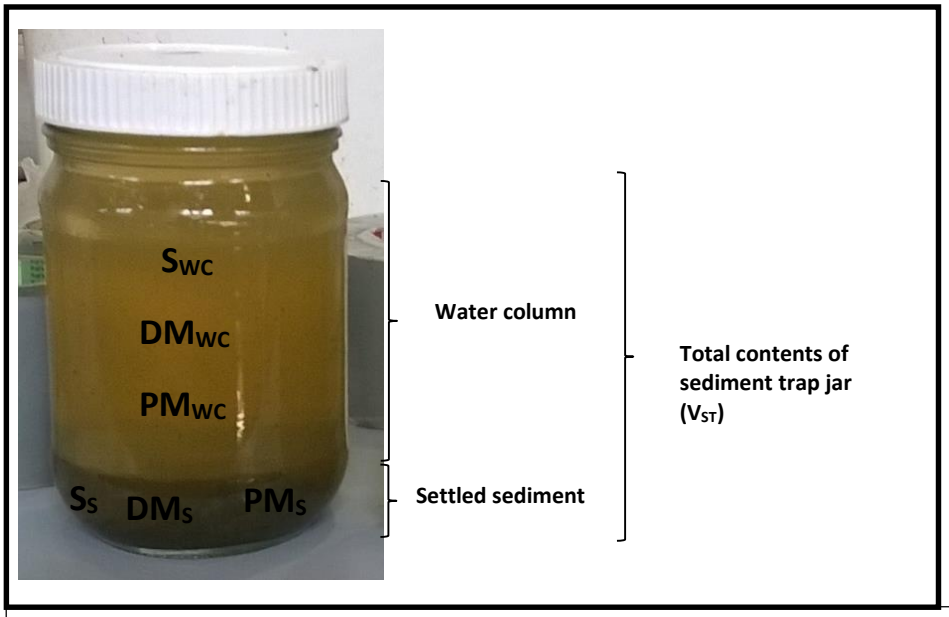
Uncertainty in the analytical method. The micro-XRF data for Cr, Cu, Ni, Pb and Zn were averaged over discrete 1-cm intervals (for W4 and B3 20-169 cm) and 5-cm intervals (for 170-220 cm of B3) to match the sub-sampling interval used for the ICP-MS analysis. We then compared the heavy metal profiles of W4 and B3 obtained using ICP-MS to the heavy metal profiles obtained using micro-XRF, to identify whether there were discrepancies in the profiles based on the analytical method. The Spearman Rank Correlation Coefficient (ρ, $p<0.05$) was used to assess the strength of the similarity between the ICP-MS and the micro-XRF heavy metal profiles. To calculate the uncertainty in the analytical method, both datasets were first scaled by dividing the heavy metal abundances by the range, to account for the different units of the two datasets. The uncertainty was then calculated as the percentage difference between (1) the median of the scaled heavy metal concentrations

quantified using ICP-MS and (2) the median of the scaled concentrations obtained by micro-XRF. We also calculated the percentage difference in the spread (inter-quartile range divided by the median) of the scaled heavy metal concentrations obtained using the two analytical methods. The median and the ratio of the inter-quartile range to the median were used to quantify uncertainty because the heavy metal levels do not have a normal distribution, as identified using the Shapiro-Wilk test ($p<0.05$ for all metals). These uncertainties were calculated for Cr, Cu, Ni, Pb and Zn. Due to the small magnitude of error associated with uncertainty in the analytical methods, subsequent analyses use either ICP-MS or micro-XRF data depending on the availability of these data.

Spatial variability. First, the major sedimentary (or lithological) units contained in the cores were identified using optical and radiographic images obtained for the three cores taken from Willsmere Billabong in 2012 and 2013 (W4, W1-1 and W3-1). Magnetic susceptibility profiles of the three cores were also compared to help identify these units. The heavy metal (Cr, Cu, Ni, Pb, Zn) micro-XRF measurements that were taken at 0.1-cm intervals were averaged over 0.5-cm intervals in order to smooth the profile. The distributions of magnetic susceptibility and heavy metal concentrations contained within each sedimentary unit were compared between the three cores using the Kruskal-Wallis test ($\alpha=0.05$). For each sedimentary unit, the uncertainty due to spatial variability has been quantified as the percentage difference in the central tendency (median) and the spread (the inter-quartile range normalised by the median) of the heavy metal levels across the three cores. For the whole core, the uncertainty due to spatial variability was calculated as the average of the percentage differences in central tendency (medians) and spread (inter-quartile range divided by the median) determined for each of the four sedimentary units. These uncertainties were calculated for each of the heavy metals analysed using micro-XRF (Cr, Cu, Ni, Pb and Zn).

Sub-sampling interval uncertainty. Uncertainties due to coarse sub-sampling intervals were assessed using the ICP-MS 1-cm interval heavy metal profiles (As, Cr, Cu, Ni, Pb, Zn) for W4. The ICP-MS profiles were used so that As could also be included in the analysis. Heavy metal profiles with intervals of 5, 10 and 15 cm were constructed, by selecting every 5^{th}, 10^{th} and 15^{th} sub-sample from the existing ICP-MS dataset and linearly interpolating between these selected points. We assessed the strength of the correlation between the coarse sub-sampling interval heavy metal profiles and the 1-cm resolution sub-sampling heavy metal profile using the Spearman Rank Correlation Coefficient (ρ, $p<0.05$). We then found the percentage difference between the central tendency (represented by the median) and the spread (interquartile range normalised by the median) of the interpolated heavy metal profiles

and the actual heavy metal profile at 1-cm intervals, to assess the accuracy of the heavy metal profiles developed using the coarser resolutions.



Legend

Water column:
S_{WC}: mass of suspended sediments in the water column
DM_{WC}: mass of dissolved metals in the water column
PM_{WC}: mass of particulate metals in the water column

Settled Sediment:
S_S: mass of settled sediments
DM_S: mass of dissolved settled metals
PM_S: mass of particulate settled metals

Total contents of trap:
$S_{ST}=S_{WC}+S_S$: mass of sediments in trap
$DM_{ST}=DM_{WC}+DM_S$: mass of dissolved metals in trap
$PM_{ST}=PM_{WC}+PM_S$: mass of particulate metals in trap
V_{ST}: volume of sediment trap

Figure 5: Contents of the jars retrieved from sediment traps.

Uncertainty due to the assumption that metals in bed sediments reflect metal inputs. This uncertainty was assessed using data from the 12-month monitoring of Willsmere Billabong. The sediment traps retrieved each month contained both settled sediment, and a small portion of the overlying water column (Figure 5). The mass of particulate settled metals collected by the sediment traps (PM_S) were calculated using Equation 1 (the terms are explained in Figure 5). The total mass of particulate metals in the sediment trap (PM_{ST}) and the mass of particulate metals in the water column (PM_{WC}) were calculated using Equations 2 and 3, respectively. In Equation 2, $PM_{ST,conc}$ is the concentration of particulate metals in the sediment trap (in µg/mg), $S_{ST,conc}$ is the concentration of sediments in the sediment trap (in mg/L) and V_{ST} is the volume of the sediment trap (in L). In Equation 3, $PM_{WC,conc}$ is the concentration of particulate metals in the water column of the sediment trap (in µg/mg), $S_{WC,conc}$ is the concentration of sediments in the water column of the sediment trap (in mg/L) and V_{ST} is the volume of the sediment trap (in L). V_{ST} was 250 mL. The suspended sediments (S_{WC}),

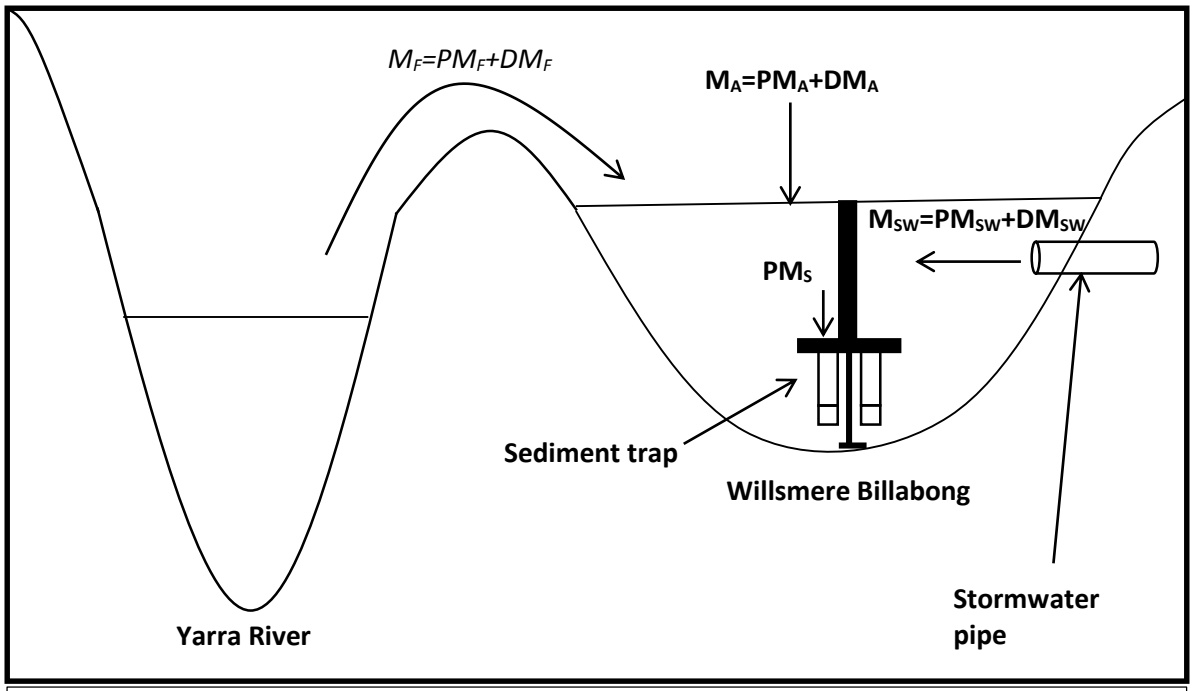
dissolved metal concentrations (DM_{WC}) and particulate metal concentrations (PM_{WC}) in the sediment trap water column were assumed to be equivalent to the suspended sediments, dissolved metals and particulate metal concentrations in the billabong water column (which were measured before each sediment trap retrieval, as previously discussed). It should be noted that when heavy metal concentrations were below the LOR, half of the LOR was adopted.

$$PM_S = PM_{ST} - PM_{WC} \quad \textbf{Equation 1}$$

$$PM_{ST} = (PM_{ST,conc} \times S_{ST,conc}) \times V_{ST} \quad \textbf{Equation 2}$$

$$PM_{WC} = (PM_{WC,conc} \times S_{WC,conc}) \times V_{ST} \quad \textbf{Equation 3}$$

Second, we developed a metals mass balance model of Willsmere Billabong (Figure 6 and Equation 4). This was to identify whether the total mass of metals entering Willsmere Billabong were equivalent to the mass of particulate metals deposited on the bed sediment and subsequently buried there. The total metal inputs into the billabong and the settled particulate metals were expressed in terms of the mass per area (i.e., in mg/m^2). As such, the mass of settled particulate metals (PM_S) was divided by the area of the trap opening (A_J). The diameter of the opening was 5 cm. In the mass balance, we only included the metals deposited on the bed sediment in the particulate form because these are the metals that are analysed when constructing the sediment core heavy metal profile. Furthermore, the mass of dissolved metals in the pore water of settled sediments at the sediment-water interface were found to be negligible when it was included in the mass balance (Figure S1 in the supplementary material). The two main inputs for metals into Willsmere Billabong included in the mass balance are stormwater (M_{SW}) and atmospheric deposition (M_A). Although flooding of Willsmere Billabong by the main river channel (M_F) is also a source of metals into Willsmere Billabong, it was not included in the mass balance because flood events did not occur during the 12-month monitoring period.



Legend

M_F: mass of metals in overbank floods
DM_F: mass of dissolved metals in overbank floods
PM_F: mass of particulate metals in overbank floods

M_A: mass of metals in atmospheric deposition
DM_A: mass of dissolved metals in atmospheric deposition
PM_A: mass of particulate metals in atmospheric deposition

PM_S: mass of particulate metals settled in sediment trap

M_{SW}: mass of metals in stormwater
DM_{SW}: mass of dissolved metals in stormwater
PM_{SW}: mass of particulate metals in stormwater

Figure 6: Visual representation of the metals mass balance model for Willsmere Billabong. Italics denote inputs that were not included in final calculation.

$$M_A + M_{SW} = \frac{PM_S}{A_j}$$ **Equation 4**

$$M_{SW} = \frac{(PM_{SW,conc} \times TSS_{SW,conc} + DM_{SW,conc}) \times V_{SW}}{A_W}$$ **Equation 5**

$$V_{SW} = Rain \times EIA$$ **Equation 6**

$$M_A = \frac{(PM_{A,conc} \times TSS_{A,conc} + DM_{A,conc}) \times V_A}{A_{DDG}}$$ **Equation 7**

We used equation 5 to calculate the mass of metals per squared meters (mg/m^2) entering the billabong through the stormwater drain (M_{SW}) each month. The particulate metal concentrations ($PM_{SW,conc}$), dissolved metal concentrations ($DM_{SW,conc}$) and TSS concentrations ($TSS_{SW,conc}$) in stormwater were estimated by randomly sampling from a log-normal distribution. These log-normal distributions were developed using the mean and standard deviations of log-transformed observed TSS, particulate metal and dissolved metal concentrations in the nine stormwater grab samples obtained. The volume of stormwater discharged into the billabong (V_{SW}) was estimated using equation 6. *Rain* is the total depth of rainfall during the month, calculated using daily rainfall data collected approximately 6 km away from the billabong (Melbourne Regional Office Site; Australian Bureau of Meteorology) and *EIA* is the effective impervious area (or directly connected impervious area) of the urban stormwater catchment. To calculate *EIA*, five individuals were asked to delineate the catchment boundary of the stormwater drain using topographic and stormwater drainage network maps. Then, using satellite photographs, they were asked to measure the areas of directly connected impervious surfaces (roofs, footpaths, roads and driveways) for the stormwater catchment. It was assumed that 50% of the roof area is directly connected to the stormwater drain (based on data about the uptake of rainwater tanks within metropolitan Melbourne; Moglia *et al.*, 2014), and that 90%, 40% and 0% of roads, driveways and footpaths are directly connected, respectively (Roy and Shuster, 2009). The average and standard deviations of the five estimates of the directly connected impervious area were used to develop a normal distribution and random sampling from this distribution was used to estimate the directly connected impervious area (*EIA)*. The aim of this was to take into account measurement errors by the five individuals. The metal mass in stormwater each month was divided by the average wetland surface area (A_W) that month. Surface areas of the billabong were estimated from interpolation of nine satellite images over the 12-month monitoring period from Nearmap (www.nearmap.com).

We then calculated the mass per area of metals entering the billabong by atmospheric deposition (M_A) each month using Equation 7. The particulate metal ($PM_{A,conc}$), total suspended solids ($TSS_{A,conc}$) and dissolved metal concentrations ($DC_{A,conc}$) collected in the dust deposition gauge each month were obtained from sampling the dust deposition gauge. The dust deposition gauge was collected monthly, rather than straight after the gauge was full of rainwater. As such the three parameters ($PM_{A,conc}$, $TSS_{A,conc}$, $DC_{A,conc}$) were calculated by first identifying the mass of metals deposited per day (found by back calculating the number of days that it took to fill the gauge using rainfall records from the Melbourne Regional Office Site; Australian Bureau of Meteorology), which was then multiplied by the total number of days each month, to estimate the total deposition over that month. The volume of

water collected in the dust deposition gauge (V_A) was found using the rainfall records from the Melbourne Regional Office Site (Australian Bureau of Meteorology). The mass of metals deposited in the dust deposition gauge each month was divided by the area of the dust deposition gauge (A_{DDG}) to express the deposited metal mass in terms of mass per area (mg/m^2).

The mass balance model was run 100,000 times to allow parameters to be varied stochastically. The 5th, 25th, 50th, 75th and 95th percentiles of these results were reported. The uncertainty, *u(metals in bed sediments reflect metal inputs)* is quantified as the percentage difference in the central tendency (medians) and the spread (inter-quartile ranges normalized by the median), between (1) the modelled total metal input masses across the 100,000 iterations and (2) the observed 12-month accumulation of particulate metal masses in the sediment traps. The central tendency and spread in the observed settled particulate metal masses were calculated using the metals deposited in the trap left in situ for 12 months (which had three observations due to triplicate analysis) and the sum over the 12 months, of the metals deposited each month in the 1-month traps at the three locations. Thus, the sample size of the observed settled metal masses was six. Statistical significance of the differences in these distributions were assessed using the Kruskal-Wallis test ($p<0.05$).

Uncertainty due to post-depositional changes. We identified the main sedimentary units within cores taken from Willsmere Billabong in 2001 (core W2001) and 2012 (core W4) using the core images (optical and radiographic) and the magnetic susceptibility profiles (as for when uncertainties due to spatial variability were investigated). The heavy metal profiles (As, Cu, Cu, Ni, Pb, Zn) obtained by ICP-MS for W4 and W2001 were compared visually to identify whether there were noticeable differences in the metal profiles due to post-depositional transformation or mobilisation. The Kruskal-Wallis test ($p<0.05$) was also used to identify whether there were significant differences in the distribution of heavy metals in each sedimentary unit between the two cores. We then calculated the percentage difference in the central tendency (the median) of the heavy metal concentration profiles and the spread (the inter-quartile range normalised by the median) in the heavy metal concentration profiles between W4 and W2001 within each sedimentary unit. The overall uncertainty for the whole core was calculated as the average of the percentage differences calculated for each of the four sedimentary units.

RESULTS AND DISCUSSION

Analytical method

We obtained trends in heavy metals for W4 and B3 using two methods: micro-XRF core scanning and ICP-MS (Figure 7). With the exception of Pb and Zn, the correlations between the trends developed by ICP-MS and by micro-XRF scanning are generally weak with low Spearman Rank Correlation Coefficients (Figure 7). It is unlikely that these discrepancies are due to the ICP-MS results, as standard quality assurance and quality control procedures suggest that these results are relatively accurate, with recovery rates of spiked samples exceeding 80.2% and the relative percentage difference between duplicate samples less than 22.6%. The errors expected in the ICP-MS results as identified in these standard quality assurance and quality control procedures are represented by the horizontal error bars in Figure 7. Instead, the discrepancies between the micro-XRF core scan results and the ICP-MS results are most likely related to moisture content of the sediment core. The micro-XRF scan metal intensities represent the element concentration in bulk (or moist) sediments but the ICP-MS results provide element concentrations in dry sediments. As such, if these two data sets are to be compared, one of them needs to be adjusted to account for this difference.

Firstly, the micro-XRF results could be represented in terms of dry sediment instead of bulk sediment, by adjusting the micro-XRF results by the water content of the sediment. Water content of bulk sediments cannot be measured directly by micro-XRF core scanning, but can be approximated by the ratio of incoherent to coherent scatter inc/coh (Jouve *et al.*, 2013) or by the grayscale intensity of the radiograph of the sediment core (Kido *et al.*, 2006). Figure 8 indicates that water content is better represented by inc/coh than the grayscale intensity, and suggests that multiplying the element intensities by inc/coh will provide a representation of the metal concentration in terms of dry weight. Figure 7 shows improvements in the correlation between the metal profiles obtained by micro-XRF and ICP-MS when the inc/coh correction is applied to the micro-XRF profiles.

Another option is to express the ICP-MS heavy metal profiles in terms of concentration of bulk sediment. Figure 7 indicates that there are positive correlations between the micro-XRF and ICP-MS heavy metal profiles when this correction is applied to the ICP-MS data. Thus, if bulk sediment concentrations are required, no correction should to be applied to the micro-XRF element intensities.

Although there is a theoretical basis for possible discrepancies in element trends obtained using micro-XRF and ICP-MS, the comparison of high resolution ICP-MS and micro-XRF data suggests that once the water content is accounted for, there is not a high percentage difference between the central tendencies (medians) and spread (interquartile range divided by the median) in heavy metal profiles

obtained using the two methods (Table 1). In subsequent analyses presented in this paper, micro-XRF data has not been adjusted for water content. The correction was not applied because sediment type (clay and silt content) can significantly affect the moisture content of sediment sub-samples (Last, 1990). Indeed, there was a strong relationship between water content and the type of sediment contained within one of the sediment cores, W4. This relationship is illustrated in Figure S2 in the supplementary material.

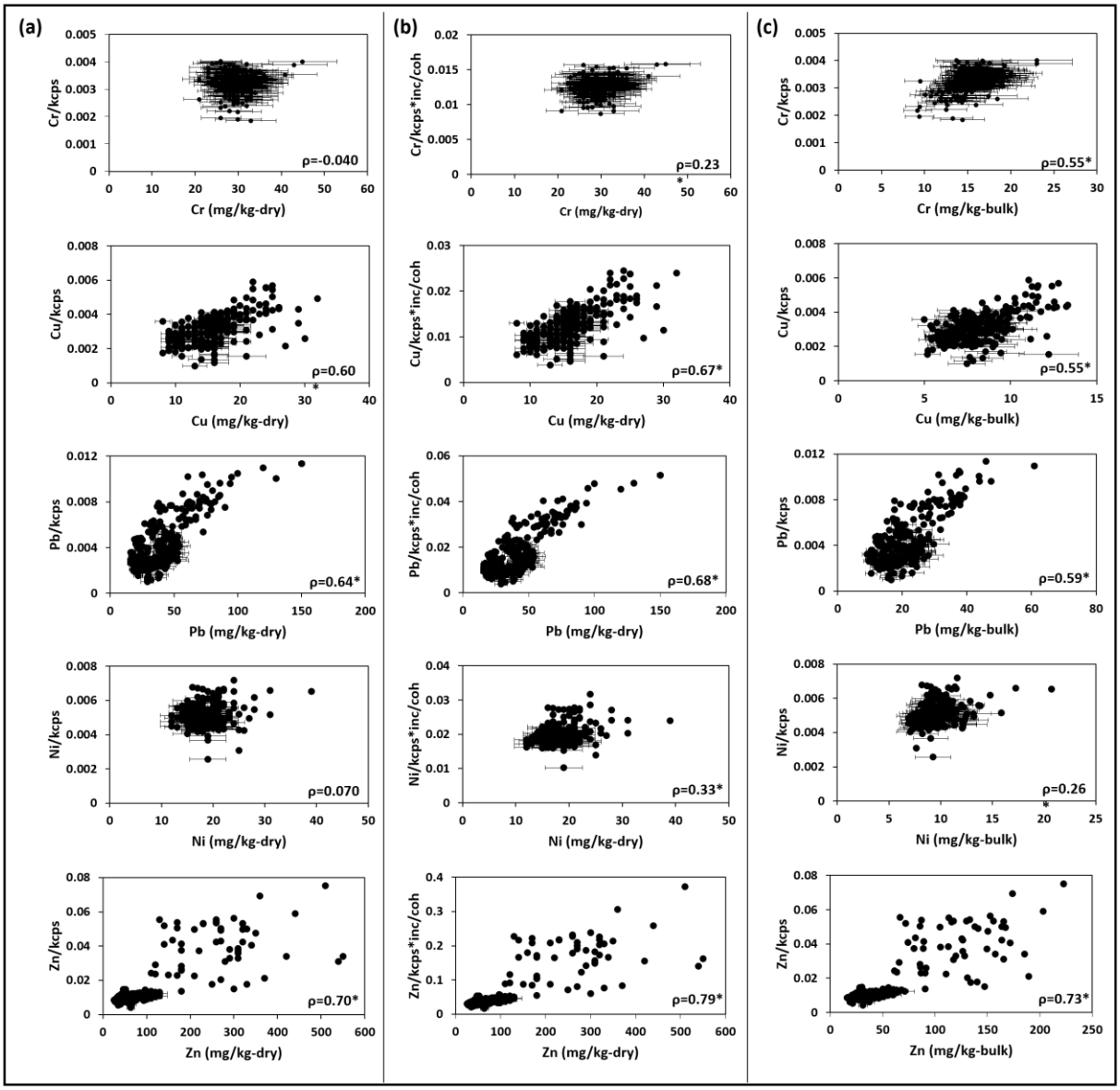


Figure 7: Correlations between heavy metal abundances obtained using micro-XRF and ICP-MS for Cr, Cu, Pb, Ni, Zn in sediment cores W4 and B3. Correlations between sediment concentration (mg/kg dry weight) from ICP-MS and normalized metal abundances from micro-XRF (a), correlations between sediment concentration (mg/kg dry weight) from ICP-MS and normalized metal abundances from micro-XRF corrected for water content using inc/coh (b), and correlations between sediment concentrations (mg/kg bulk weight) from ICP-MS and normalized metal abundances from micro-XRF (c). Asterisk (*) indicates statistically significant ($p<0.05$) Spearman Rank Correlation Coefficients (ρ). Horizontal error bars represent errors expected in ICP-MS results.

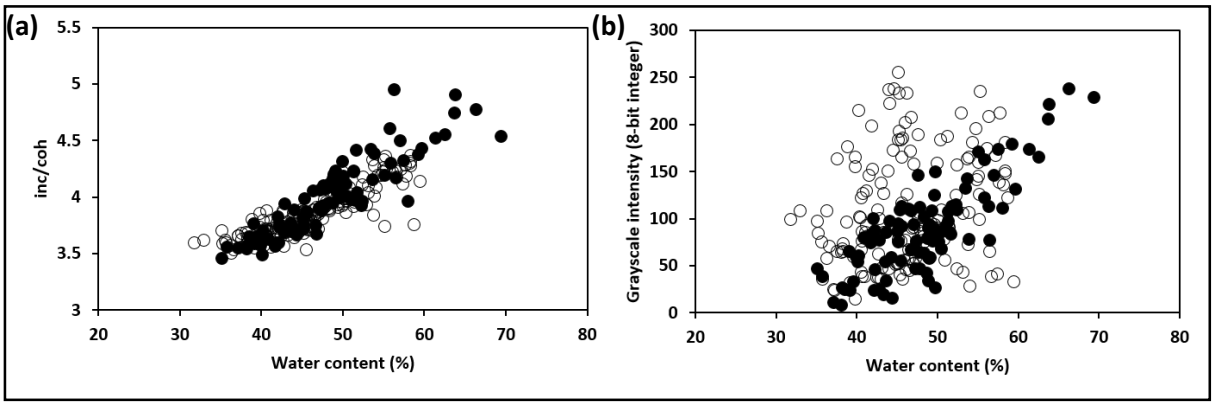


Figure 8: Relationship between inc/coh and measured water content (a) and grayscale intensity and measured water content (b). Filled circles represent 1 cm thick sediment samples from W4 and open circles represent 1 cm thick sediment samples from B3).

Table 1: Quantified uncertainties for As, Cr, Cu, Ni, Pb and Zn. Percentage differences in the central tendency of the heavy metal concentrations (medians) and in the spread of heavy metal concentrations (inter-quartile range divided by the median, in parentheses) provided.

		As	Cr	Cu	Ni	Pb	Zn
u(analytical method)	**Bulk sediment concentration**	-	27% (3.8%)	42% (32%)	47% (19%)[+]	2.3% (33%)	39% (63%)
	Dry sediment concentration	-	35% (39%)[+]	14% (32%)	31% (41%)	10% (31%)	37% (49%)
u(spatial)	**Whole core**	-	11% (45%)	36% (60%)	25% (63%)	40% (59%)	58% (105%)
	Unit A	-	2.1% (26%)	11% (37%) *	13% (32%)*	9% (2.6%) *	16% (54%) *
	Unit B	-	11% (103%)	43% (118%) *	37% (69%) *	47% (87%)*	79% (133%)*
	Unit C	-	24% (37%)*	44% (67%)*	28% (90%)*	68% (82%)*	96% (77%)*
	Unit D	-	6.8% (16%)*	44% (19%)*	23% (59%)*	35% (64%)*	43% (155%)*
u(sub-sampling)	**5 cm**	8.2% (38%)	6.7% (41%)	4.6% (13%)	1.0% (19%)	13% (13%)	18% (20%)
	10 cm	18% (28%) [§]	7.6% (101%) [§]	17% (57%)	15% (37%)	48% (44%)	58% (42%)
	15 cm	38% (74%) [§]	9.0% (95%) [§]	20% (43%)	16% (35%) [§]	47% (39%)	61% (64%)
u(metals in bed sediments reflect metal inputs)		32% (79%)*	74% (97%)*	121% (118%)	73% (148%)	147% (29%)*	32% (94%)*
u(post-depositional changes)	**Whole core**	17% (96%)	4.0% (43%)	6.2% (67%)	7.0% (40%)	10% (31%)	14% (70%)
	Unit A	0.0% (120%)	3.2% (37%) *	4.9% (157%)	11% (113%)	12% (60%) *	17% (164%)
	Unit B	13% (63%)	1.7% (107%)	4.3% (84%)	10% (27%)	19% (6.3%) *	22% (1.0%)
	Unit C	29% (1.9%)*	3.4% (8.5%)	6.1% (15%)	7.6% (21%)	5.6% (21%)	14% (48%)
	Unit D	29% (200%) *	7.7% (21%) *	10% (10%) *	0.0% (0.0%)	4.7% (36%) *	2% (67%)

* Statistically significant differences ($p<0.05$) according to Kruskal-Wallis test.

[+] Weak correlation between ICP-MS heavy metal profiles and micro-XRF heavy metal profile according to Spearman Rank Correlation Coefficient ($\rho<0.5$, $p<0.05$).

§ Weak correlation between linearly interpolated heavy metal profiles and 1 cm resolution (actual) heavy metal profiles according to Spearman Rank Correlation Coefficient ($\rho<0.5$, $p<0.05$).

Spatial variability

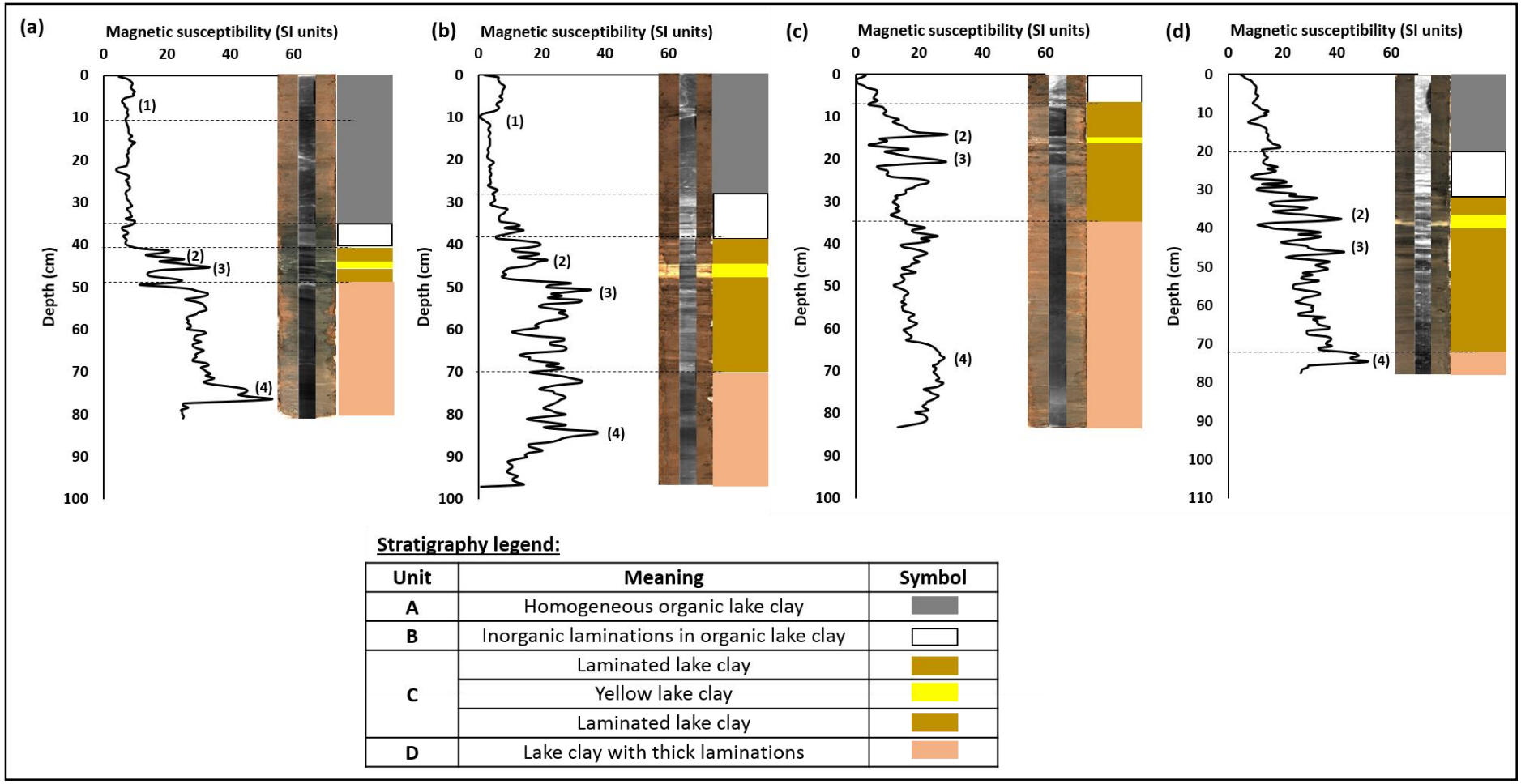
Figure 9 shows the magnetic susceptibility trends and the optical and radiographic images of W1-1, W4 and W3-1 (sediment cores taken from Locations 1 to 3, respectively in Willsmere Billabong; Figure 3). Visual inspection (Figure 9) of the radiographic and optical images of the cores and their magnetic susceptibility profiles indicate that all cores contain the same sedimentary (or lithological) units, which have been labelled A to D. The homogeneous organic lake clay unit at the tops of the cores has been labelled Unit A and the sedimentary unit containing inorganic laminations in organic lake clay has been called Unit B. Unit C consists of laminated lake clay, followed by a distinct yellow clay layer, followed by more laminated lake clay. Unit D is the unit at the bottom of the cores containing lake clay with thick laminations (Figure 9). For the rest of the study, these units will be referred to by their letters A to D. However, the thicknesses of these sedimentary units differ, which suggests that there are different Sediment Accumulation Rates (SARs) and degrees of compaction in the three locations.

For example, a homogeneous lake clay layer (Unit A) is present in the top 28 cm of W4. This unit is thickest in W1-1 (35 cm) and completely absent from W3-1. It is unlikely that this absence is due to the loss of sediment while coring as the coring techniques were kept constant over all three sites. Furthermore, the magnetic susceptibility profile for a replicate core taken at Location 3 suggests that this homogeneous layer was also missing from the top of the replicate core (the magnetic susceptibility profiles of W3-1 and its replicate core is provided in Figure S3 in the supplementary materials). The presence and thickness of the homogeneous lake clay layer may be influenced by the source of this sedimentary unit. The fact that it is thickest in W1-1 and decreases in distance away from the east bank of Willsmere Billabong, suggests that this sediment may be originating from a source on the east bank of the billabong. One possibility is the stormwater drain, which is on the east bank of the billabong (Figure 3).

Visual inspection of the magnetic susceptibility profiles also suggests that whilst the general trends in magnetic susceptibility are similar for all three sediment cores, there are some noticeable differences. For example, in Unit C, although peak 3 is greater than peak 2 in both W4 and W1-1, in W3-1 these two peaks have a similar magnitude. Similarly, W1-1 and W3-1 experience a gradual decrease in magnetic susceptibility from the bottom of the layer of yellow lake clay down to the bottom of the sediment core but W4 remains constant to the bottom of the core. These visual interpretations are supported by statistical tests. The magnetic susceptibility in each sedimentary unit A to D (Figure 9), was found to be statistically significantly different between all three cores according to the Kruskal-Wallis test ($p<0.05$). The Kruskal-Wallis test not only compares the magnitudes of the magnetic susceptibility of the four cores, but also their distributions (Pestman, 2009).

A visual assessment of the distributions in heavy metals contained within each of the sediment units A to D (Figure 10 and Figure in the supplementary material) suggests that the overall heavy metal trends are similar in all three cores. For example, Cr has a decreasing trend up-core and the remaining metals (Cu, Ni, Pb, Zn) have higher levels in the more recent sedimentary deposits in all three cores. However, the short-term fluctuations in these cores appear to differ greatly. Indeed, the Kruskal-Wallis test indicates that the magnitudes and distributions of most metal levels are statistically significantly different ($p<0.05$) across the three sediment cores (Figure 10).

This spatial variability in the heavy metal profiles can enhance our understanding of the factors that may influence the heavy metal levels detected within the sediment core. For example, although W1-1 has lower Zn levels in the sediment Unit A compared to the sediment Unit B, W4 exhibits the opposite pattern. This could be linked to the amount of terrestrial sediments being deposited at each location, as suggested by the different trends in magnetic susceptibility in the two cores (Figure 9). Whilst magnetic susceptibility decreases up-core for W4, for W1-1 there is a slight increase in Unit A. Being a measure of the amount of iron bearing minerals within a sediment deposit, magnetic susceptibility is often used as an indication of the amount of terrestrial or clastic sediments contained within a sediment deposit (Brown *et al.*, 2000; Thompson *et al.*, 1980). As such, the increase in magnetic susceptibility at the top of W1-1 may be indicating that this most recent sediment deposit contains more terrestrial sediments than the most recent deposit in core W4. These clastic sediments may be diluting the Zn concentrations within the most recently deposited sedimentary unit, thereby leading to a lower intensity of Zn in the top sedimentary units of W1-1.



Stratigraphy legend:

Unit	Meaning	Symbol
A	Homogeneous organic lake clay	
B	Inorganic laminations in organic lake clay	
C	Laminated lake clay	
	Yellow lake clay	
	Laminated lake clay	
D	Lake clay with thick laminations	

Figure 9: Magnetic susceptibility profiles, radiographic and optical images of sediment cores taken from four locations in Willsmere Billabong, W1-1 (a), W4 (b), W3-1 (c), W2001 (d). Sediment units A to D indicated alongside sediment core images. Numbers on the magnetic susceptibility profile indicate points in the profile that are common to all four cores.

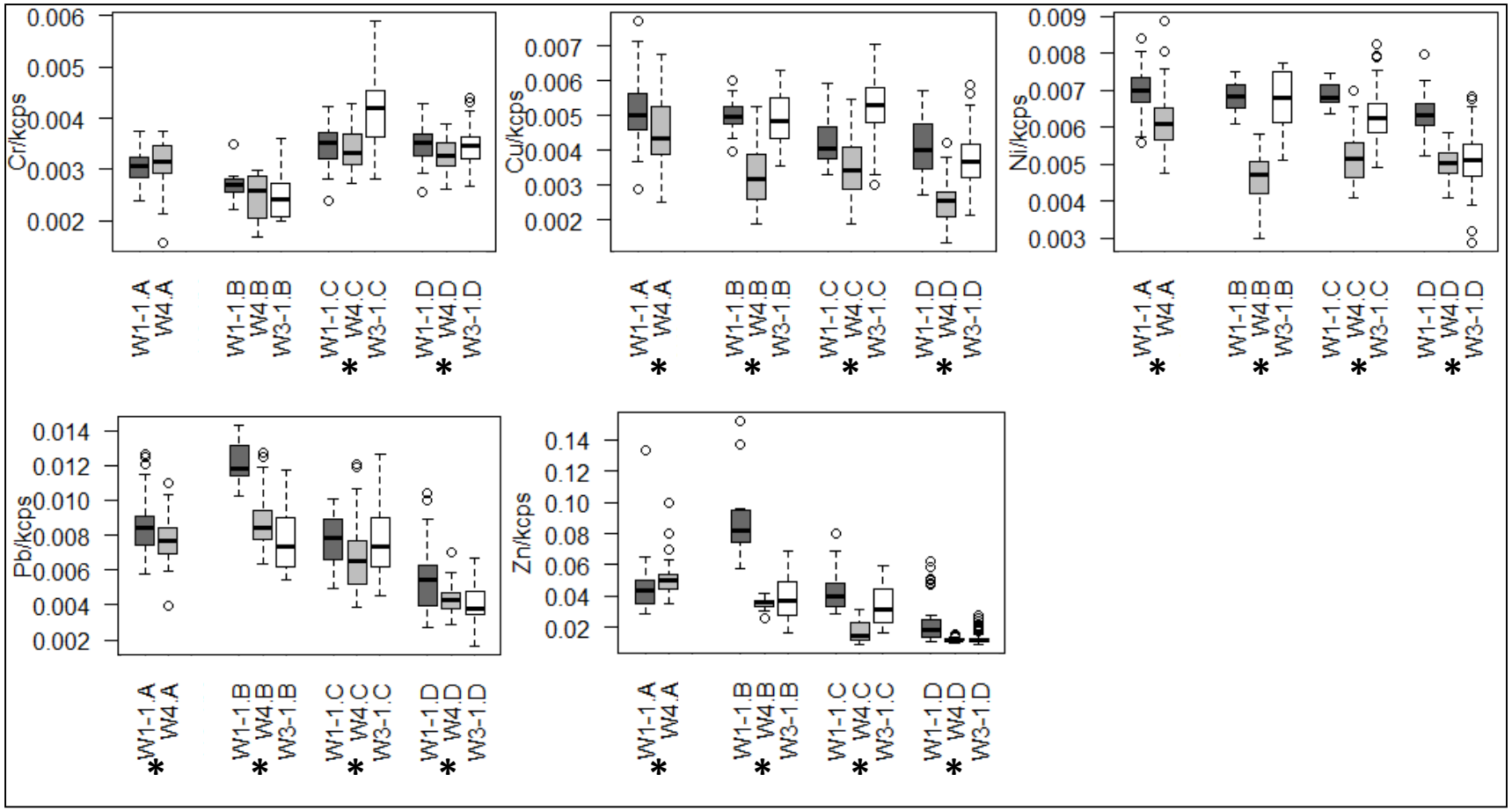


Figure 10: Normalised Cr, Ni, Cu, Pb, Zn distributions in each sedimentary unit for the three cores taken in Willsmere Billabong. Letters A to D on the x axis denotes the sedimentary units described in Figure 9. Unit A: Homogeneous lake clay, Unit B: Organic laminations, Unit C: inorganic laminations and yellow lake clay, Unit D: thick laminations. Asterisks (*) represents sediment units where heavy metals differ statistically significantly ($p<0.05$) between the three cores. Profiles provided in Figure S4 of the supplementary material.

The spatial variability apparent in these sediment cores does not correlate to the spatial variability in metal masses accumulated in the sediment traps installed at these three coring locations over a 12-month period (Figure 11). The main discrepancy is that of the three sediment traps, the greatest amount of sediment deposition occurs at Location 3. However, the absence of Unit A in W3-1 in Figure 9 suggests that the least mass would have accumulated at this location in recent-times. This may be due to sediment movement along the bed (horizontally) away from Location 3 (or sediment focussing), which does not occur if sediments are deposited in the sediment traps. As such, these sediment traps may not be a suitable method of identifying spatial variability in heavy metal accumulation in the bed sediment of Willsmere Billabong.

Table 1 suggests that spatial variability affects the Cu, Pb and Zn profiles the most. The largest percentage differences between medians of heavy metal concentrations observed is 96%, which is the percentage difference observed for Zn in Unit C (Table 1). Both Table 1 and Figure 10 indicate that there is spatial variability in heavy metal accumulation in aquatic environments, even between locations only 30-m apart. This discussion indicates that there are significant benefits to obtaining multiple cores spatially distributed throughout the lake. The comparison between the sedimentary records from different locations within the aquatic system has the potential to enhance our understanding of the factors that may affect metal concentrations detected within sediment cores, as well as possible sources of certain sedimentary deposits and metals.

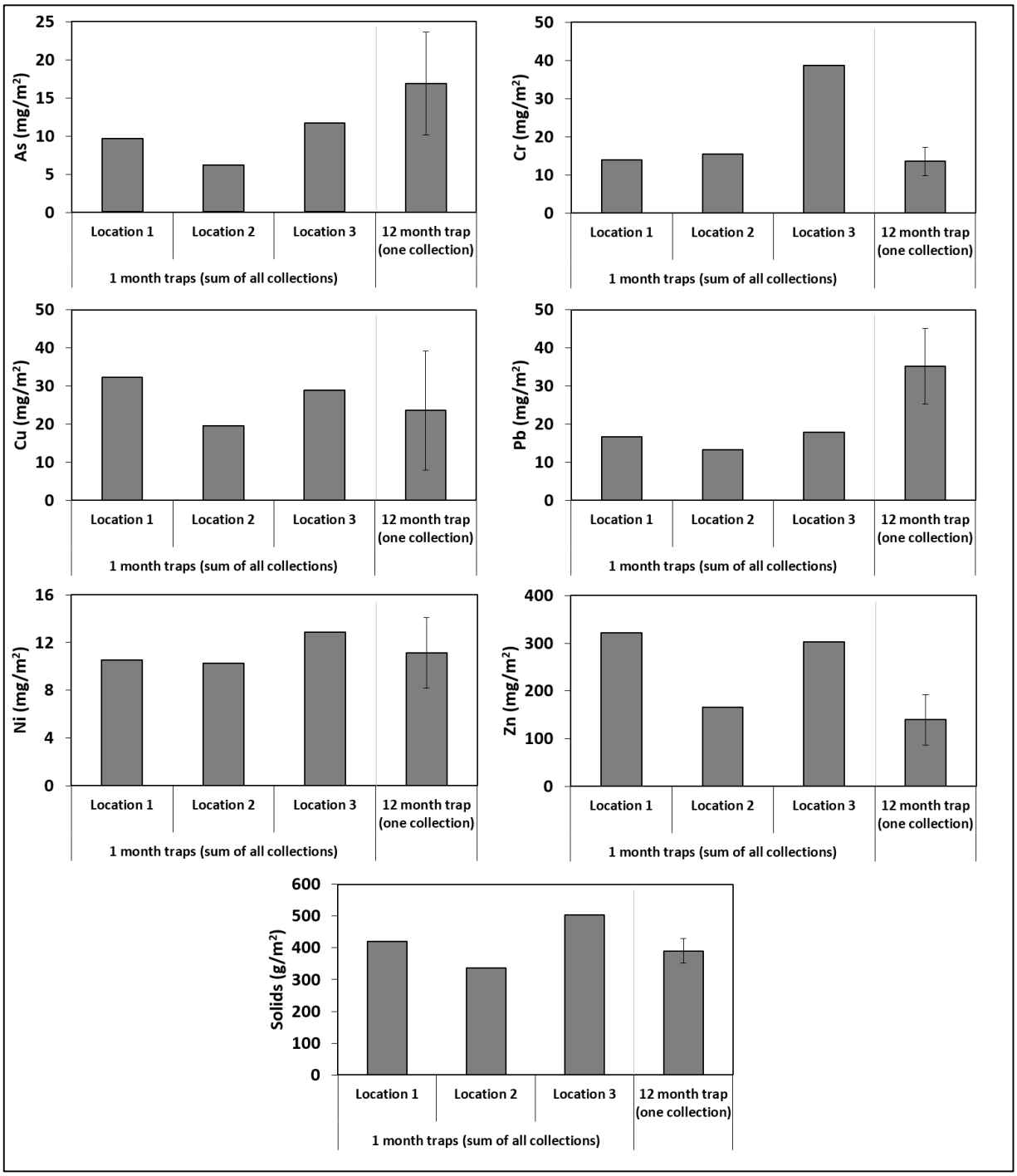


Figure 11: Sum of metal masses from all monthly collections during the 12-month monitoring period and mass from 12-month sediment trap (average of the analysis of triplicate samples) from Willsmere Billabong. Error bars represent the standard deviation of the analysis of triplicate samples of the 12-month sediment trap.

Sub-sampling intervals

Figure 12 indicates that heavy metal profiles can differ significantly based on the sub-sampling intervals. Coarse sampling resolutions are still able to identify general, average trends in the heavy metal profiles. However as the spacing between samples increase, there is a decreasing likelihood that

short term variations or oscillations in the heavy metal profiles will be identified. For example, when coarser sub-sampling intervals of 5, 10 and 15 cm are used, whilst the increase in As concentrations at 50-75 cm are identified, the magnitude of this increase is not shown. Furthermore, the high levels of As detected at 33.5 and 38.5 cm are not detected at all when sub-sampling intervals of 5, 10 and 15 cm are used (Figure 12).

Expected errors for As, Cr, Cu, Ni, Pb and Zn with sub-sampling intervals of 5, 10 and 15 cm are presented in Table 1. The magnitude of error expected for the metal profiles developed using linear interpolation between coarse sub-sampling intervals appears to vary according to the level of variability present in the high resolution (i.e., high precision) heavy metal profile. Where the heavy metal concentrations exhibit low variability, there is generally less error in the coarser resolution profiles. This is not surprising because if there is less short term variability in the sediments, it will be easier to approximate the trends using linear interpolation. Indeed, Spearman Rank Correlation Coefficients indicated weak correlations ($\rho<0.5$) between the measured 1-cm resolution heavy metal profiles and the coarser resolution profiles for As (10-cm and 15-cm interval profiles), Cr (10-cm and 15-cm interval profiles) and Ni (15-cm profile). These three metals exhibit short-term fluctuations in Figure 12.

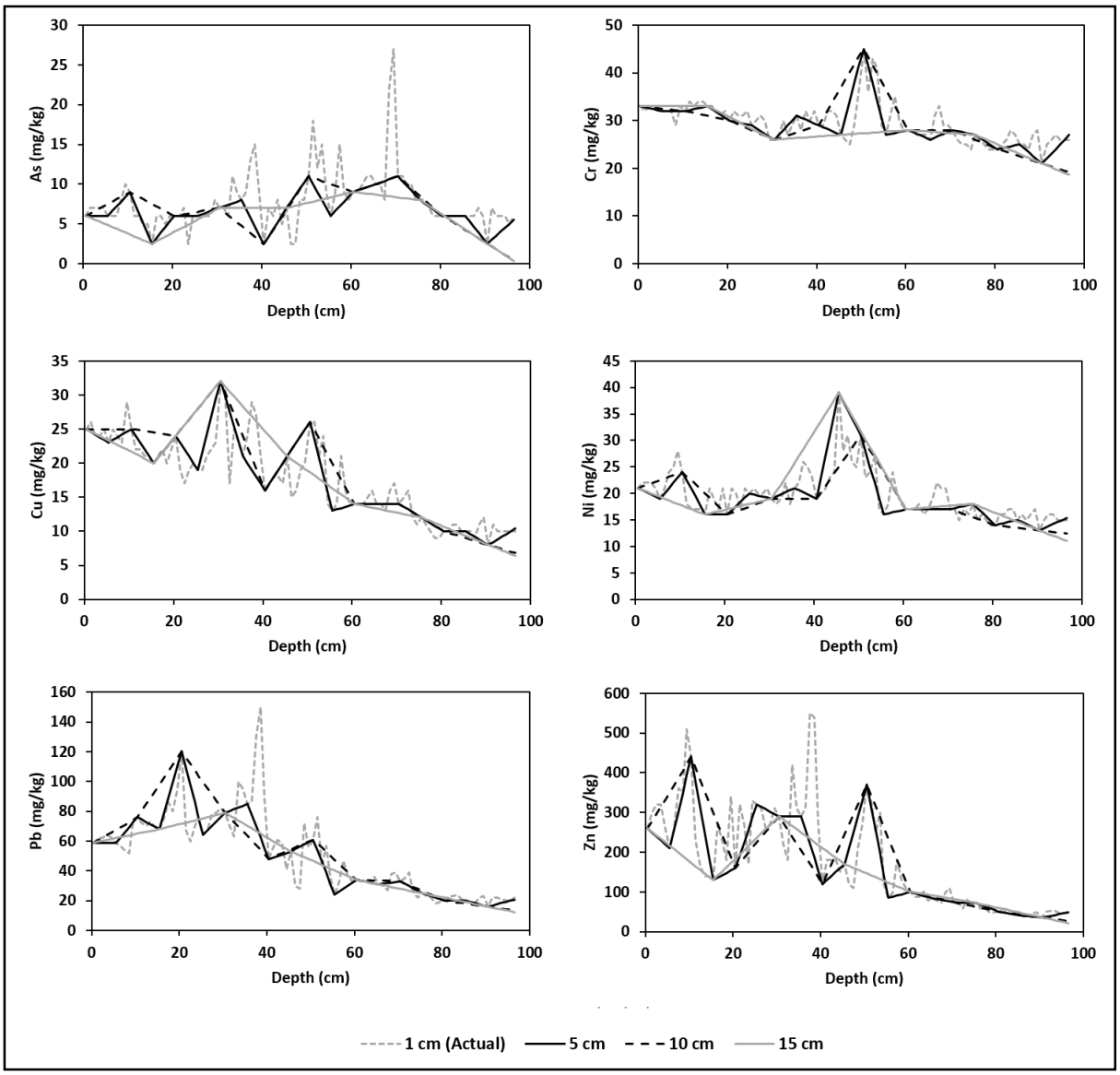


Figure 12: Heavy metal profiles with sub-sampling intervals of 1, 5, 10 and 15 cm for As, Cr, Cu, Pb, Ni, and Zn.

Assumption that metals in bed sediments reflect metal inputs

Figure 13 compares the mass of modelled metal inputs (stormwater and atmospheric deposition) against the mass of metals settling on the sediment bed in particulate form (measured using the sediment traps). For all metals except Pb, the modelled stormwater metal input over 12 months is greater than the modelled metal input by atmospheric deposition (Figure S5 in the supplementary material). The model results also indicate that approximately three times more particulate matter enters the billabong by atmospheric deposition than stormwater. The mass of particulates found to be entering the billabong by atmospheric deposition (56 g/m^2/year) is similar to total particle atmospheric deposition masses calculated for medium traffic density regions in Sydney, Australia (Davis and Birch, 2011). Indeed, Willsmere Billabong is situated less than 300 m from a busy freeway (estimated traffic load of 130,000 vehicles per day; Parris *et al.*, 2009). Stormwater suspended solids concentrations had a mean of 7.5 mg/L and a standard deviation of 2.7 mg/L. Whilst this is less than typical TSS concentrations in stormwater of 150 mg/L (Duncan, 1999), this difference is probably due to the presence of a stormwater treatment wetland. Although the performance of the wetland that treats the stormwater draining into Willsmere Billabong has not been measured, stormwater treatment wetlands can have TSS removal efficiencies of up to 95% (Carleton *et al.*, 2001). The similarity between the modelled data and values from literature helps to validate the assumptions that were used to model metal and sediment inputs by stormwater and atmospheric deposition. Metal concentrations identified in the field monitoring were also similar to values reported in literature, and these values from literature are tabulated in Table S1 and Table S2 in the supplementary material. We recognise however, that despite these similarities between results of the model and values found in literature, there still may have been errors in the sampling strategy and the modelling process. Particularly for stormwater as only nine stormwater grab samples were obtained.

When only the particulate fractions of the metal inputs are considered, the modelled inputs are less than the settled particulate metal masses for most metals (Figure 13). However, when the dissolved metal inputs are considered in addition to the particulate metal inputs, the modelled inputs are more similar to the settled particulate metal masses. This suggests that a considerable amount of the dissolved fraction of the metals coming into billabong may be transforming into the particulate form and settling on the sediment bed. Transformation of metals from the dissolved to the particulate phase within aquatic systems can be affected by several factors such as DO and pH of the water column (Tessier and Campbell, 1987). Indeed, there is a positive correlation between As, Cr, Cu, Pb and Ni settled on the bed sediment each month and average DO (%) measured in the billabong. There is also a correlation between settled Zn particulate masses and average pH measured each month ($\rho>0.5$, Figure S6 in supplementary materials). Although these correlations are not statistically

significant (due to the limited number of data points included in the analysis) similar trends have been observed in other studies (e.g., Linnik and Zubenko, 2000).

The modelled sediment input into the billabong was less than the actual mass of settled sediments. Similarly, the modelled total (particulate and dissolved fractions) input of Pb and Zn into the billabong was less than the actual mass of settled sediments (Figure 13). It is possible that we may have neglected an important source of sediments (and therefore Pb and Zn) in the analysis. One source that has not been quantified in the model is the transport of soils and sediments by overland runoff into the lake (i.e., runoff that does not enter the billabong through the stormwater drain). This may be an important sediment source, particularly given that during the 12-month field monitoring period, several construction projects (playground construction, installation of underground irrigation systems) were observed within the local Willsmere Billabong catchment. These construction activities would have inevitably resulted in the mobilization of local catchment soils and sediments, which could be carried into the billabong by local overland runoff (e.g., Langbein and Schumm, 1958; Wolman and Schick, 1967).

We have also not considered the effects of sediment focussing and resuspension from the billabong bed in the mass balance. Sediments already deposited on the lake bed can be re-suspended by wind and the activity of benthic aquatic species (Carper and Bachmann, 1984; Gulati *et al.*, 2008). Indeed, Verschuren (1999) has previously identified that re-suspension of sediments can affect the accumulation of sediments and climate proxies in lake cores. Sediments re-suspended from other regions of the sediment bed (and therefore not included in stormwater or atmospheric sediment inputs) may have settled in the sediment traps. These sediment traps were designed so that sediments would not be resuspended from the traps (Bloesch and Burns, 1980). Given the short fetch of Willsmere Billabong (less than 140 m for the first 6 months of sampling and less than 60 meters for the last 6 months of sampling), it is unlikely that wind action would have contributed to significant amounts of sediment resuspension (Carper and Bachmann, 1984). However, the presence of wildlife in the billabong may have contributed to sediment re-suspension (Leahy, 2007).

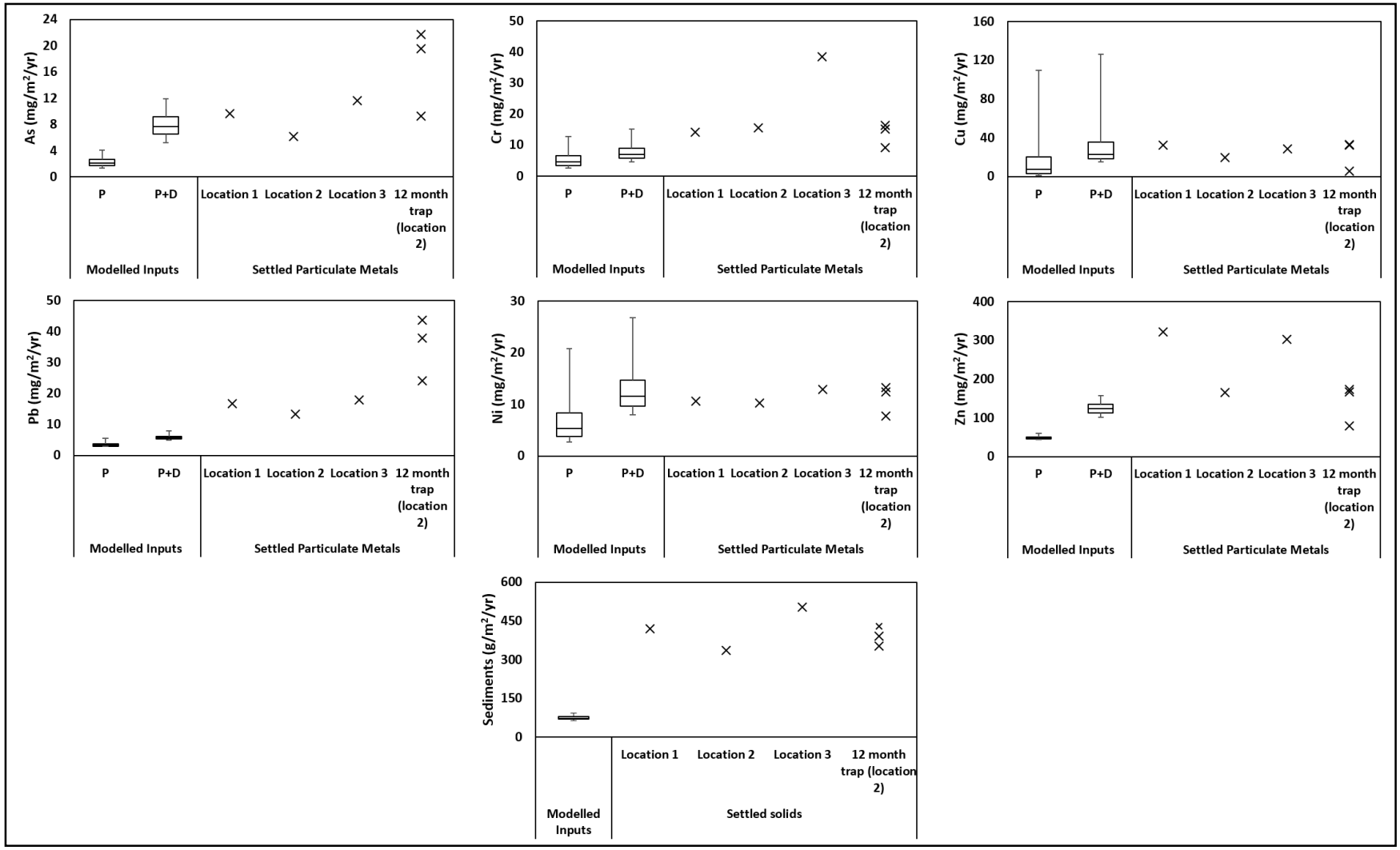


Figure 13: Mass of modelled metal and sediment inputs (stormwater discharge and atmospheric deposition) compared to the mass of settled metals and sediments measured in sediment traps over the 12-month monitoring period. Under modelled inputs, P represents inputs that are only in the particulate form, and P+D represents the total inputs (i.e., sum of particulate and dissolved inputs).

Figure 14 provides the relationship between the deposited mass of particulate metals and the total mass of metals entering the lake by atmospheric deposition and stormwater runoff for each month analysed in the mass balance model. Regardless of the discrepancies between modelled inputs of metals and the settled masses of metals, the trends in the mass of particulate metals deposited on the lake bed generally correlates positively to the trends in the modelled mass of metals entering the system by atmospheric deposition and stormwater each month. There is a strong and statistically significant correlation for Pb according to the Spearman Rank Correlation Coefficient ($\rho=0.71$, $p<0.05$). Spearman Rank Correlation Coefficients for all metals are provided in Figure S7 in the supplementary material. This suggests that a large fraction of the settlement of these metals on the sediment bed is governed by stormwater and atmospheric deposition inputs, even if there are discrepancies in the mass balances (Figure 13). It could therefore be inferred that the heavy metal profiles from Willsmere Billabong reflect the stormwater and atmospheric deposition metal fluxes into the billabong.

Table 1 presents the percentage difference between the bed sediment metal masses (measured by sediment traps) and modelled metal masses entering Willsmere Billabong. Most metals (As, Cr, Pb, Zn) have statistically significant differences between the distributions of modelled metal inputs into the lake and the mass of metals settling on the sediment bed. This may be a statistical artefact due to the large difference in sample sizes used for the Kruskal-Wallis test (6 samples for the settled solids on the sediment bed, 100,000 samples for the modelled inputs). Regardless, it is worth noting that the greatest discrepancy appears to be for Pb, where the difference between medians in the settled masses and the metal inputs into the billabong is greater than 100%. This may be due to high input of Pb via overland runoff from the local catchment where historically accumulated vehicle atmospheric deposits may be present in the local catchment soils. Although, the percentage difference in medians for Cu is also greater than 100%, this is likely a product of the high variability in Cu levels entering the billabong through stormwater (Figure 13).

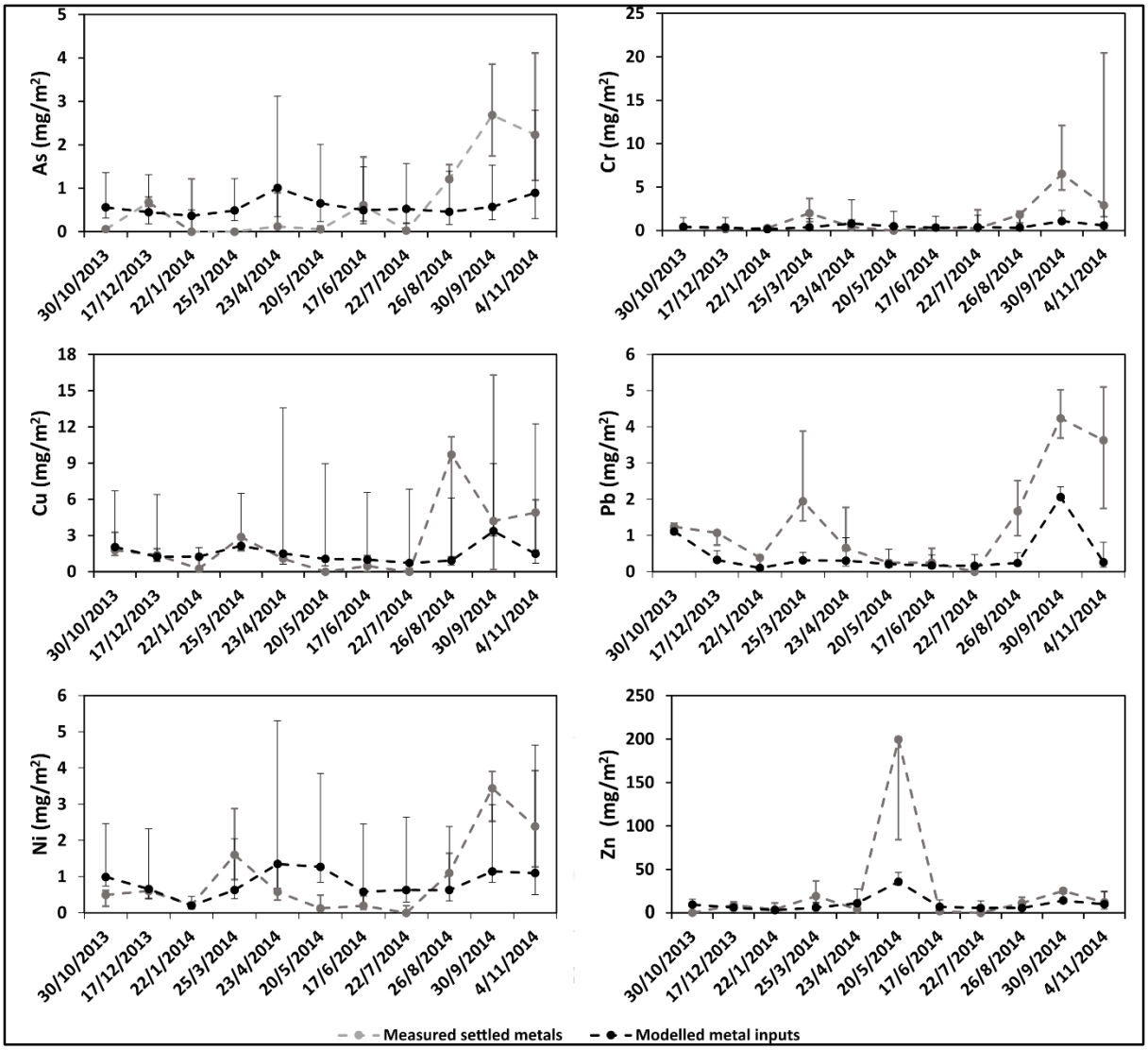


Figure 14: Settled particulate metal mass compared to modelled total metal mass entering Willsmere billabong by atmospheric deposition and stormwater each month. Error bars represent 95% confidence intervals.

Post-depositional mobilisation

The similarities between W2001 and W4 both in terms of their magnetic susceptibility profiles and their images (optical and radiographic) indicate that these two cores contain common sediment units, which have been labelled units A to D as shown in Figure 9. Comparing the images and magnetic susceptibility profiles of the two cores indicates that the top 10 cm of W4 was deposited between 2001 (when W2001 was obtained) and 2012 (when W4 was obtained). Indeed, the age-depth model developed for W4 (Lintern *et al.*, in preparation-a) suggests that 10-11 cm of W4 was deposited in approximately 1999.

The Kruskal-Wallis test was performed to test whether the distribution of heavy metals within each sediment unit were equivalent in the two cores W2001 and W4. These results indicate that whilst

there is a high level of similarity between the heavy metal profiles from the two sediment cores, significant differences were observed for several heavy metals in some of the units (Figure 15). Although these differences were statistically significant, they are within the range of differences resulting from spatial variability in the heavy metal profiles (Table 1). This suggests that the percentage differences between W4 and W2001 heavy metal concentrations may not be a result of post-depositional mobility. This discrepancy instead may be due to spatial variability; because although W4 and W2001 were both taken from the same region in Willsmere Billabong (Location 2 in Figure 3), the two cores were not taken from the exact same point in the billabong. The percentage difference in medians of metal concentrations within Unit A were 3% and 12% for Cr and Pb respectively, and these are in a similar range as the absolute percentage difference in medians that are due to spatial variability (2% for Cr and 9% for Pb; Table 1). Similarly, the percentage difference in the Pb median levels in Unit B in W4 and W2001 is 19%, which is less than the median difference due to spatial variability of 47% (Table 1). Finally, for Unit D, the percentage differences for Cr (7.7%), Cu (10%) and Pb (4.7%) are all less than or similar to that for spatial variability (6.8% for Cr, 44% for Cu and 35% for Pb; Table 1). Indeed, visual inspection of the high resolution metal profiles of W2001 and W4 suggests that the metal trends of the two cores are quite similar (Figure S8 in the supplementary material).

We have also investigated the question of whether there is diagenetic loss of heavy metals from bed surface sediments, using the observations from monitoring of heavy metal deposition in Willsmere Billabong over a 12-month period. Figure 11 shows that the cumulative sum over the 12-month monitoring period of the particulate metals masses collected in the one month traps are similar to the mass of particulate metals continuously deposited in a sediment trap over a 12-month period for most metals. This resemblance suggests that for most metals, there is relatively little diagenetic loss of metals from surface bed sediments over a one year period. However, Pb does not follow this pattern, with the mass of Pb accumulated continuously over a 12-month period being greater than the cumulative sum of Pb masses settled each month. This may be an indication that over time, Pb is being scavenged from the dissolved state and bound to the particulate phase. This process has been identified in other aquatic systems (e.g., Gallon *et al.*, 2004).

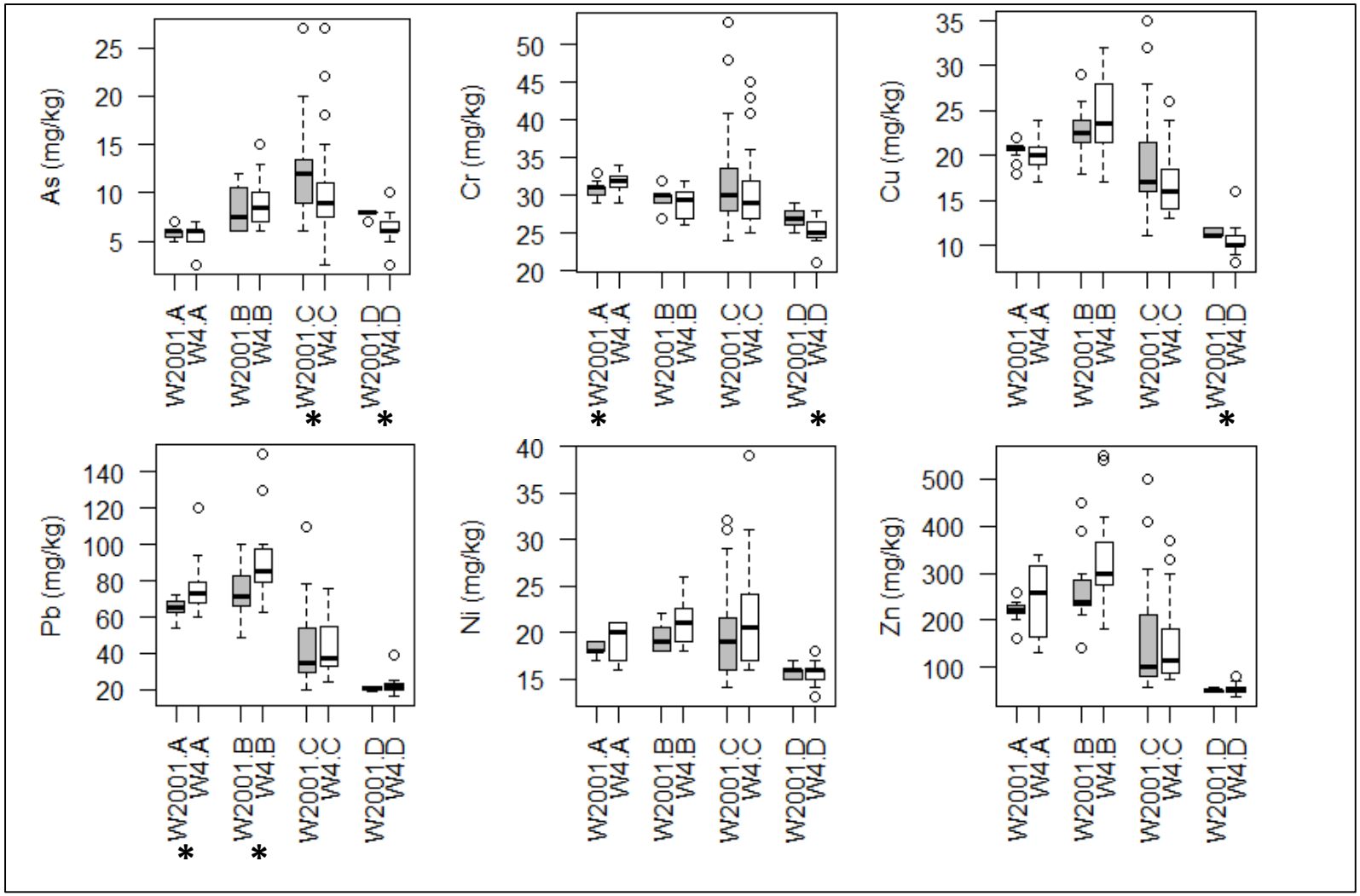


Figure 15: Heavy metal concentrations in sediment units in W2001 and W4. Unit A: Homogeneous lake clay, Unit B: Organic laminations, Unit C: inorganic laminations and yellow lake clay, Unit D: thick laminations. Asterisk (*) denotes units where there is a statistically significant difference ($p<0.05$) between distributions of metals in W2001 and W4 according to the Kruskal-Wallis Test ($p<0.05$).

CONCLUSIONS

We presented a framework that summarizes the uncertainties inherent in reconstructing historical heavy metal pollution trends using sediment cores. First, we have found that micro-XRF core scanning can provide accurate measures of heavy metal concentrations in sediments, and are comparable to ICP-MS results once the appropriate corrections for moisture content are applied to ensure both measurement methods are in consistent units (concentrations in dry weight or in bulk weight). Secondly, whilst general trends in heavy metal profiles may not be affected by spatial variability, statistical tests show that there can be considerable spatial variability in high resolution heavy metal profiles through aquatic systems, even when the sediment cores are taken merely 30 m apart from each other. Thirdly, although short-term fluctuations in the heavy metal profiles are lost, overall trends in heavy metals can still be identified when coarse (e.g., 15 cm) sub-sampling intervals are implemented.

A mass balance model has shown that stormwater and atmospheric metal inputs appear to account for the mass of particulate metals that settle on the bed sediment for As, Cr, Cu and Ni. There is a discrepancy between the inputs and settled masses for Pb and Zn. This may be due to an additional source of Pb and Zn such as overland runoff which was not included in the mass balance model, or possibly due to limitations in sampling and modelling strategies. Regardless of this discrepancy, it was found that the variability in particulate Pb and Zn masses accumulated in the sediment traps generally correlate with modelled Pb and Zn inputs (by stormwater and atmospheric deposition) each month. Finally, there is minimal post-depositional mobilisation and loss of metals occurring in the sediment cores. This was identified by the similarity (both visually and statistically) between two sediment cores taken in the same location 10 years apart, and also using data collected during a 12-month study monitoring study of Willsmere Billabong.

The magnitude of uncertainties and the primary sources of these uncertainties differ depending on the heavy metal. For As, the greatest uncertainty appears to be associated with sub-sampling. However, it should be noted that for As, uncertainties in spatial variability and analytical methods could not be evaluated due to the fact that it could not be detected in the ITRAX micro-XRF core scanner. For Cr, Cu, Ni, Pb and Zn, the greatest uncertainty appears to be the assumption that metal inputs into the billabong are adequately represented by the accumulation of metals in bed sediments. For Pb and Zn, spatial variability of heavy metal profiles can also lead to large uncertainties in Willsmere Billabong. Understanding the main sources of uncertainty of different metals, enables us to better plan sampling and analytical methods in future studies, so as to obtain accurate heavy metal profiles for the heavy metals that are of greatest interest.

Through this investigation, we have demonstrated that despite the many uncertainties and assumptions, sediment cores can provide us with relatively reliable information about historical trends in metal pollution in a small aquatic system. However, we emphasize that the uncertainties quantified in this study are relevant to Willsmere Billabong. We recommend that this uncertainty framework be applied to other aquatic systems with varying characteristics (e.g. climatic conditions, ecologies, catchment characteristics and physico-chemical properties of both the water column and bed sediments), to validate that these findings hold for other aquatic systems. Although there is still further work required in understanding and quantifying the uncertainties, this study indicates that there is great potential for the historical heavy metal pollution records of aquatic systems obtained from sedimentary records to be practically applied in the field of environmental engineering, to guide the design of management and restoration strategies for aquatic environments.

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6.3 Discussion

6.3.1 Uncertainties associated with reconstructing historical heavy metal pollution trends in aquatic systems using bed sediment cores

An uncertainty framework was proposed in this chapter, which summarizes the uncertainties associated with reconstructing historical heavy metal pollution trends using sediment cores. This framework contained four types of uncertainties: (1) uncertainties in creating heavy metal depth profiles using sediment cores (including sampling and analytical uncertainties), (2) uncertainties in dating these heavy metal depth profiles, (3) uncertainties in the assumption that heavy metal inputs are reflected by heavy metals in the bed sediments and (4) uncertainties due to post-depositional changes to metals in sediment cores. The uncertainties associated with building sediment chronologies was not discussed in this chapter.

It was demonstrated that it is important to consider that micro-XRF heavy metal abundances represent heavy metal concentrations in terms of bulk sediment, and that ICP-MS heavy metal concentrations are generally in terms of dry sediment. If either the micro-XRF data or ICP-MS data are adjusted to account for this difference, micro-XRF and ICP-MS heavy metal profiles correlate positively ($\rho>0.3$). As such, these two methods can be used interchangeably when identifying heavy metal abundances in sediment cores. It was also found that heavy metal profiles developed using coarse sub-sampling intervals tend to decrease in accuracy for heavy metals that have short term fluctuations through the sediment core. In fact, this was the greatest source of uncertainty in the development of undated As pollution trends. We also found that there can be quite large uncertainties associated with spatial variability, particularly for Zn, where the percentage difference in median heavy metal concentrations in the profiles is 58% and the percentage difference in the spread of heavy metal concentrations is 105%. The greatest source of uncertainty in the development of Cr, Cu, Ni and Pb pollution trends was the assumption that metal levels deposited on the bed sediments reflect trends in metal inputs.

6.3.2 Effect of post-depositional mobilisation of contaminants on interpretations of sediment core heavy metal profiles

The occurrence of post-depositional mobilisation of heavy metals in sediment cores was assessed using two sediment cores taken approximately 10 years apart in Willsmere Billabong, and also using results obtained from monitoring the heavy metals settling in Willsmere Billabong over a 12 month period. Comparison of the two cores taken 10 years apart (both visually and statistically) indicated that post-depositional mobilisation has a relatively small role to play in the overall uncertainty

framework. Although some metals (e.g., Pb) showed statistically significant differences in heavy metal concentrations between the two cores, this may be due to spatial variability, which generally has larger magnitudes of uncertainty than post-depositional mobilisation. There was also little difference between the cumulative sum of metals settled each month in sediment traps deployed in Willsmere Billabong and the continuous deposition of metals in a sediment trap over a 12-month period. This suggests that post-depositional mobilization of heavy metals in both the bed surface and deeper in bed sediment, has minimal effect on the interpretation of sediment core heavy metal profiles.

6.3.3 Correlation between contaminant levels in the bed sediments of aquatic systems and the pollution state of the aquatic system

To assess whether contaminant levels in bed sediments reflect the pollution state of aquatic systems, the metal masses accumulated on the bed of Willsmere Billabong (measured using sediment traps) were compared to modelled metal inputs (stormwater and atmospheric deposition) of Willsmere Billabong. The results of this mass balance indicate that over a 12-month period, the modelled levels of As, Cr, Cu and Ni entering Willsmere Billabong by stormwater and atmospheric deposition are equivalent to the mass of these metals being deposited on the sediment bed of the billabong. However, it appears that modelled Pb and Zn inputs are less than the masses of these metals deposited on the billabong sediment bed. This may be due to the fact that one or more sources of metals (e.g., overland runoff) were not considered in the mass balance. Regardless of this discrepancy, there was a correlation between the mass of metals coming into the billabong (by stormwater and atmospheric deposition) each month and the mass of metals being deposited on the billabong sediment bed in that same month. This suggests that the heavy metal levels in bed sediments of Willsmere Billabong reflect the pollution of aquatic systems caused by stormwater and atmospheric deposition.

6.4 Conclusion

In summary, this chapter presented:

- a framework that summarises the uncertainties associated with creating historical pollution records from sediment cores;
- that there can be large differences in the heavy metal profiles based on where in the billabong the sediment cores were obtained;
- that there can be errors in the heavy metal profiles if coarser sub-sampling intervals are used particularly when there are short-term fluctuations in the heavy metal profiles;
- that post-depositional mobilisation of heavy metals does not appear to affect the interpretation of sediment core heavy metal profiles; and
- that heavy metal levels in bed sediments appear to vary according to the amount of heavy metals from stormwater and atmospheric deposition entering the aquatic environment.

CHAPTER 7
IDENTIFYING THE RELATIONSHIP BETWEEN OVERBANK FLUVIAL FLOODS AND HEAVY METAL POLLUTION IN BILLABONGS

Declaration for Thesis Chapter 7

Declaration by candidate

In the case of Chapter 7, the nature and extent of my contribution to the work was the following:

Nature of contribution	**Extent of contribution (%)**
Initiation, ideas, sample collection, data collection, data analysis, interpretation and preparation of manuscript.	70

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	**Nature of contribution**	**Extent of contribution (%) for student co-authors only**
Atun Zawadzki	Data interpretation	n/a
Patricia Gadd	Data collection, data interpretation, reviewing of manuscript	n/a
Henk Heijnis	Data interpretation, reviewing of manuscript	n/a
Paul Leahy	Sample collection, data interpretation, reviewing of manuscript	n/a
Ana Deletic	Data interpretation	n/a
David McCarthy	Ideas, data interpretation, reviewing of manuscript	n/a

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work*.

Candidate's Signature	[redacted]	**Date** 19/8/2015
Main Supervisor's Signature		**Date** 19/8/2015

*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

7.1 Introduction

In the literature review (Chapter 2), it was identified that not many studies have used sediment cores to understand how fluvial flooding contributes to the heavy metal pollution of billabongs. Furthermore, the relationship between the concentration of heavy metals deposited in billabongs, and river flow characteristics have not yet been quantified using sediment cores.

This chapter focuses on research objective 4 and its associated research question 8:

> **Research objective 4: To use sediment cores to identify the contaminant levels in flood-deposited sediments in the Yarra River billabongs.**
>
> - *Research question 8: What is the level of contaminants contained in fluvial flood deposits and how do they compare to contaminant levels in sediments not deposited by floods within the sediment cores of the Yarra River billabongs?*

The primary component of this chapter (Section 7.2) is a paper currently under internal review for submission to *Water Research*. This paper, titled "Recreating historical data from sediment cores; to protect aquatic environments" is cited as Lintern *et al.*, (in preparation-c) throughout the thesis. The supplementary material accompanying the paper is provided in Appendix A.5. The paper is followed by the development and presentation of functions that relate river flow characteristics to heavy metal concentrations in billabong sediment deposits (Section 7.3). The chapter finishes with a short discussion and conclusion that summarises the main findings of this chapter (Section 7.4 and 7.5).

7.2 Recreating historical data from sediment cores; to protect aquatic environments

RECREATING HISTORICAL DATA FROM SEDIMENT CORES; TO PROTECT AQUATIC ENVIRONMENTS

Anna LINTERN[1*], Paul J. LEAHY[2], Atun ZAWADZKI[3], Patricia GADD[3], Henk HEIJNIS[3], Ana DELETIC[1,4], David T. MCCARTHY[1,4]

[1]Monash Water for Liveability, Department of Civil Engineering, Monash University, Clayton, 3800, Victoria, Australia
[2] EPA Victoria, Applied Sciences Group, Ernest Jones Drive, Macleod, Victoria, 3085, Australia
[3] Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, New South Wales 2234, Australia
[4]Environmental and Public Health Microbiology Laboratory (EPHM Lab), Monash University, Clayton, 3800, Australia

**Corresponding author's e-mail: anna.lintern@monash.edu*

ABSTRACT

To design mitigation and restoration strategies for aquatic systems affected by heavy metal contamination, we should pinpoint the site-specific sources of these pollutants. In this study, we introduce a methodology that identifies the dominant sources and transport pathways of heavy metal contamination of water-bodies. This is done by comparing sediment core heavy metal profiles (i.e., historical pollution trends) to physical and chemical properties of sediments in these cores (i.e., historical hydrologic trends). This methodology is applied to Willsmere and Bolin Billabongs, two urban floodplain lakes (billabongs) of the Yarra River (South-East Australia). Both billabongs are periodically inundated by flooding of the Yarra River and one billabong (Willsmere Billabong) is connected to an urban stormwater drainage network. 1 to 2-m long sediment cores (containing sediment deposits up to 500 years old) were taken from the billabongs and analysed for heavy metal concentrations (arsenic, chromium, copper, lead, nickel, zinc). In cores from both billabongs, arsenic concentrations are high in the flood-borne sediments, suggesting that historically, arsenic pollution in the billabongs came from the river. The river also appears to be the main source of chromium for both billabongs, possibly due to naturally high chromium levels in soils in the upper regions of the Yarra River catchment. In Bolin Billabong copper, lead and zinc levels tend to be higher in flood-deposited sediments compared to other types of sediment deposits after the 1950s, suggesting that the river is the main source of these metals. In the same period in Willsmere Billabong, copper, lead and zinc levels were generally lower in fluvial flood-borne sediments in the core, suggesting that the main

source of these metals is the local billabong catchment, likely urban stormwater. There was no clear correlation between Ni concentrations in sediments of the two billabongs and the occurrence of fluvial flooding. The methodology presented in this study can be applied to other polluted aquatic systems, to identify the main factors governing contamination of these systems. As a cost effective and less time consuming alternative to extensive field monitoring, our proposed method is an additional tool that can be used by engineers and environmental scientists trying to manage the pollution of aquatic systems.

KEYWORDS

Flood pollutants, heavy metals, micro-XRF, mitigation, stormwater, surface water quality

INTRODUCTION

Heavy metal contamination of aquatic environments is a growing problem (Kivaisi, 2001). Due to the threat to human health and species biodiversity, there is a need for strategies that can prevent and remediate heavy metal pollution in aquatic environments. The development of successful strategies requires: (1) accurate identification of pollutant sources and their magnitudes, thereby allowing efficient and focused mitigation efforts and (2) a sound understanding of the effectiveness of pollution mitigation methods (ANZECC/ARMCANZ, 2000). Accordingly, an understanding of long-term pollution trends is invaluable (Saunders and Taffs, 2009; Seddon *et al.*, 2014). A time series of metal deposition in aquatic environments that spans 50 to 100 years can be used to identify when water quality degradation (or improvement) occurred, and thereby infer the main causes of these fluctuations. Despite the importance of understanding long-term heavy metal contamination trends, water quality data spanning many decades is not available for most aquatic systems (Alexander *et al.*, 1998). On-going field monitoring should also be used to build these datasets but this is a costly and time consuming undertaking.

This paucity in data could be overcome by using sediment cores from the beds of aquatic environments. Indeed, previous works have reconstructed historical pollution records using dated sediment cores (e.g., Ruiz-Fernandez *et al.*, 2002; Townsend and Seen, 2012; Vane *et al.*, 2011). However when investigating the factors governing historical pollution trends in aquatic systems, it is important to also consider concurrent trends in the system's hydrology. These hydrologic trends can reveal the source and transport pathways of contaminants. For example, by comparing contaminant levels in discrete fluvial flood deposits and in discrete local runoff deposits, we can better understand how fluvial floods and local runoff contribute to the contamination of an aquatic system. This understanding will allow us to identify the most critical pollutant sources and thereby focus our

mitigation efforts. It will also enable us to identify the quality of flood-deposited sediments and thereby prepare appropriate risk management strategies.

To our knowledge, five studies (Bábek *et al.*, 2011; Chen *et al.*, 2015; Daessle *et al.*, 2009; Ferrand *et al.*, 2012; Nguyen *et al.*, 2009; Thevenon *et al.*, 2013) have identified pollutant sources in aquatic systems using historical hydrologic trends determined using sediment cores. However, further exploration of this methodology is required. Chen *et al.* (2015), Ferrand *et al.*, (2012) and Thevenon *et al.* (2013) investigate the overall relationship between hydrologic change and pollution levels, rather than identifying pollution levels in discrete sediment layers (e.g., from floods). Bábek *et al.* (2011), Nguyen *et al.* (2009) and Daessle *et al.* (2009) identified discrete flood deposits in floodplain lake sediments and identified the pollutant levels in these deposits. However their findings are somewhat uncertain as the occurrence of these flood layers in the cores were not verified using observed flow data. As such, there is a need to refine this methodology to demonstrate that it can be used for the management of polluted aquatic environments.

The main aim of this study is to demonstrate that we can use sediment cores to help us mitigate the heavy metal contamination of aquatic environments. Two urban floodplain lakes (billabongs), Willsmere and Bolin Billabong, in the Yarra River catchment in South-East Australia are used as case studies. We identify the long-term high resolution heavy metal pollution trends in these billabongs. These are then compared to both overall (or average) historical trends in hydrology and high resolution trends in hydrology (i.e., the occurrence of discrete flood deposits in the cores). These trends and flood deposits were previously identified and verified using flow data in Lintern *et al.* (in preparation-a). The heavy metal profiles from Willsmere and Bolin Billabong have been previously explained in Lintern *et al.* (2015) and Lintern *et al.* (submitted). In this study, some of the findings from these previous works will be verified using an understanding of the hydrologic trends of the billabongs. In addition, the focus will be on comparing the profiles from the two billabongs, to help explain the specific pollution sources and transport pathways. The analysis presented here will not only allow us to identify the sources and transport pathways of the pollutants into the two billabongs but will also further our understanding about the relative importance of fluvial flooding on the heavy metal contamination of these two billabongs. The work also will provide an insight into the contamination levels in overbank flood-borne sediment deposits. We envisage that the methodology used in this study could be applied to other aquatic environments when designing site-specific, water quality management programs.

MATERIALS AND METHODS

Study site

As shown in Figure 1, the Yarra River catchment (Victoria, Australia) is approximately 4000 km^2 in area and contains both urban and non-urban (agricultural and forested) areas. Two billabongs of this river, Bolin Billabong and Willsmere Billabong, are the focus of this study. Both are relatively small systems, with bank-full areas of 3.4 ha for Bolin Billabong, and 1.9 ha for Willsmere Billabong (Leahy, 2007). They receive water from their local catchments (15 ha for both billabongs) by overland runoff and from the greater Yarra River catchment through overbank flows of the Yarra River (Leahy, 2007). Minor flood levels at Bolin Billabong and Willsmere Billabong are approximately 6 m and 3 m Australian Height Datum (AHD) (Vic SES, 2013, 2012a). Although these billabongs historically received water once a year from the Yarra River on average, since the mid-20th century, inundation frequencies have reduced to once every 3 to 4 years (Sinclair Knight Merz, 2005). Willsmere Billabong also receives urban stormwater from a nearby residential area (1.8 ha) through a drain that was installed in the 1940s (David Barclay, City of Boroondara, personal communication, 2nd April 2013). A stormwater treatment wetland was built in 2006, approximately 500 m^2 in surface area, between the residential catchment and Willsmere Billabong, which treats this urban stormwater (Figure 1). Bolin Billabong is not directly connected to the urban drainage network.

Sampling

In October 2012, two cores were obtained from Willsmere Billabong: (1) a 210-cm long core (W1) using a light-weight modified hammer-driven piston corer (Neale and Walker, 1996) with a 50-mm diameter polyvinyl chloride (PVC) barrel and (2) a 96-cm long core (W4) using a 40-mm diameter Livingstone corer (Livingstone, 1955). W1 and W4 have previously been discussed in Lintern *et al.* (2015). In this previous study, it was identified that the top 70 cm of the Willsmere Billabong sedimentary record was lost from W1. W1 therefore is a continuation of W4, with approximately 25 cm of the top of W1 overlapping with the bottom of W4. A 204-cm long sediment core (W2001) that was taken from Willsmere Billabong using the light-weight modified hammer-driven piston corer (Neale and Walker, 1996) in 2001 by Leahy (2007) is also briefly discussed in this study. This core was previously introduced and discussed in detail in Lintern *et al.* (in preparation-a).

A 204-cm long core was taken in June 2013 from Bolin Billabong using the light-weight modified hammer-driven piston corer (Neale and Walker, 1996). This core was named B3. A replicate core was taken in two drives (bed surface to depth 65 cm; depth 65 cm to 157 cm) approximately 3 m away

from the first core using the 40-mm diameter Livingstone corer (Livingstone, 1955) and this core was named B5. Both cores have previously been described in Lintern *et al.* (in preparation-a).

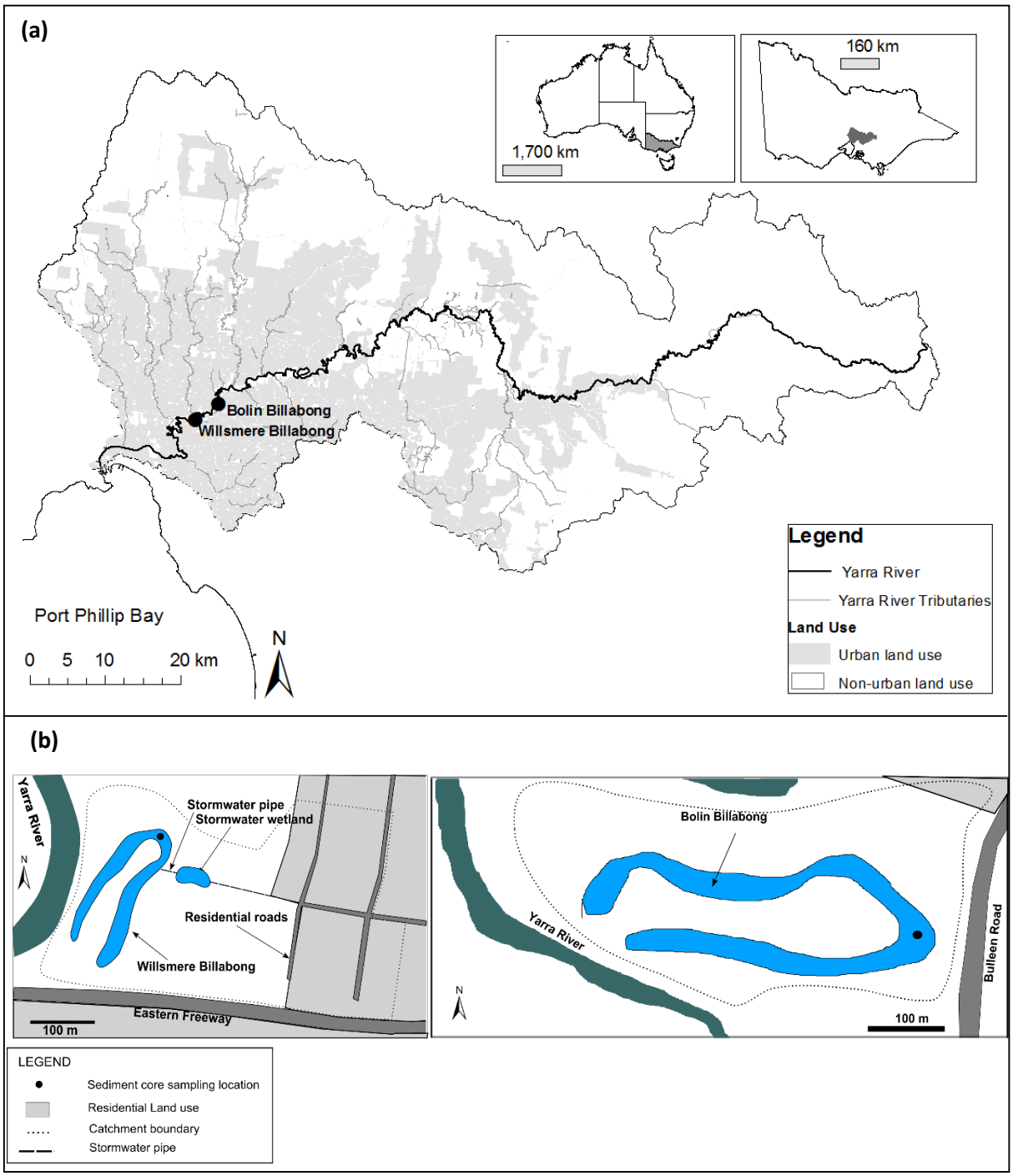

Figure 1: Location of Willsmere Billabong and Bolin Billabong in the Yarra River catchment, with inserts showing the location of the Yarra River catchment in the state of Victoria and the location of the state of Victoria in Australia (a); and the local Willsmere Billabong and Bolin Billabong catchments (b).

Sample analyses

Image and heavy metal analyses

W1, W4, B3 and B5 were split longitudinally and one half of each core was scanned in the ITRAX micro-X-ray fluorescence (XRF) core scanner (Croudace *et al.*, 2006). The top 13 cm of B3 was not scanned due to its watery nature. A molybdenum tube (30-kV voltage, 45-mA current) was used with an exposure time of 10 s and reading at 1-mm intervals. Magnetic susceptibility measurements were also taken at 0.5-cm intervals. All micro-XRF readings were normalised by the total counts per second (kcps) to enable comparisons between the different cores (as per Martin *et al.*, 2014). Due to an error during the micro-XRF scan for W1, micro-XRF readings for W1 were not used in this study. The heavy metals that were analysed using micro-XRF were chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). The levels of other heavy metals were too low for reliable detection. Micro-XRF heavy metal results have been averaged over discrete 0.5-cm depth intervals to match the resolution of the magnetic susceptibility measurements.

Some of the sediment cores (W4, W1 and B3) were also sub-sampled for heavy metal analysis using un-plasticized PVC (uPVC) equipment. The sub-sampling interval was 0.5 cm for W1 and 1 cm for W4 and B3. Samples were stored in glass jars at 4^0C for approximately 48 hours before being composited over 1 cm for W4, and sections of W1 (0-57 cm) and B3 (20-170 cm). The bottom of W1 (57-213 cm) and B3 (170-220) were composited over 10-cm and 5-cm intervals, respectively. The top 20 cm of B3 was not sub-sampled due to its lack of consistency. The composited samples were air-dried and then analysed for heavy metals at a National Association of Testing Authorities (NATA) accredited laboratory (ALS, Melbourne, Australia) using digestion by aqua regia and inductively coupled plasma mass spectrometry (ICP-MS) in accordance with USEPA SW846 Rev 2007 (US EPA, 2007). 24 metals were analysed, of which the following seven metals will be discussed in this study (with Limits of Reporting; LOR provided in parentheses): aluminium; Al (5 mg/kg), arsenic; As (5 mg/kg), Cr (5 mg/kg), Cu (5 mg/kg), Pb (5 mg/kg), Ni (5 mg/kg), Zn (5 mg/kg). Quality assurance and control procedures involved the analysis of blank and duplicate samples and identification of recovery rates using spiked samples. Recovery rates were above 80.6% and relative percentage differences between duplicate samples ranged from 0.2% to 18.5%.

Sediment dating

The sediment cores were dated using radio-isotopic analysis (unsupported ^{210}Pb and ^{137}Cs activities), pollen and radiocarbon (^{14}C). The method used to build the chronologies of these cores has been

discussed in detail in a separate study (Lintern *et al.*, in preparation-a) and is therefore only summarised briefly below.

W4 and B5 were dated using ^{210}Pb and ^{137}Cs. These techniques were not used to date W1 and B3 due to the loss of the top sediment in W1 when coring (Lintern *et al.*, 2015) and the lack of consistency of the top 20 cm of B3. 1-cm thick samples were taken between 0 and 42-cm depth of W4 and between 0 and 40-cm depth of B5, at intervals of 1 to 5 cm. Unsupported ^{210}Pb activities were estimated as the difference between total ^{210}Pb activity (measured from ^{210}Po) and supported ^{210}Pb activity (measured from ^{226}Ra), as described in Appleby (2001). Samples were processed using the method described in Atahan *et al.* (2015). Unsupported ^{210}Pb activities were used to estimate calendar ages using both the Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models for W4 and just the CIC model for B5 (Appleby, 2001). These calendar ages were then validated using ^{137}Cs activities measured for 1-cm thick samples obtained at 5 to 12-cm intervals between 18 and 70-cm depth (W4) and 17 and 34-cm depth (B5). The age-depth models developed for W4 and B5 using radio-isotope activities were then adapted to W1 and B3 by correlating the sediment cores from the same billabongs using magnetic susceptibility profiles obtained in the ITRAX micro-XRF core scanning.

An additional chronological marker for W4 and B3 was the earliest appearance of dichlorodiphenyldichloroethylene (DDE), a metabolite of dichlorodiphenyltrichloroethane (DDT) in the cores. This was given the year of approximately 1946, which is the earliest recorded use of DDT in Australia (Olsen *et al.*, 1992). The 1-cm thick sediment sub-samples were composited over 4 cm for W4 and 7 cm for B3, air-dried and then analysed at a NATA accredited laboratory (National Measurement Institute, Sydney, Australia) using gas chromatography with an electron capture detector (GC-ECD) (US EPA 2007). 0.0002 mg/kg (dry weight) was the limit of reporting. Standard quality assurance and control procedures were implemented (Lintern *et al.*, in preparation-a).

Furthermore, radiocarbon analysis (^{14}C) was performed on two 1-cm thick bulk sediment samples, taken at 169-170-cm depth and 203-204-cm depth in W1 (OZS087 and OZS088). Lastly, sediment samples were taken at 5-cm intervals between 156 and 201 cm in B3, and at 8-cm intervals between 102 and 142 cm in W1 and from 134 to 135-cm depth and 154 to 155-cm depth in B5 for palynological analysis. These were treated as outlined in Lintern *et al.* (in preparation-a) and the pollen slides were used to identify the depth in the cores that pollen grains of non-native vegetation appear (i.e., vegetation introduced into Australia with European settlement in the 19th century). Specifically, we

were looking for *Pinus* and introduced *Plantago* in the pollen slides and the lowest depth at which these pollen appeared in the cores were assigned the date of 1870 (Lintern *et al.*, in preparation-a).

Data analyses

In a previous study (Lintern *et al.*, in preparation-a), sediment cores were used to identify how the hydrologies of Willsmere and Bolin Billabongs have changed over time. The detailed methodology has been previously discussed in Lintern *et al.*, (in preparation-a), and a brief summary is provided below.

Overall trends in hydrology were determined for the Willsmere Billabong core W2001 and the Bolin Billabong core B3. These trends were inferred from shifts in sediment sources and transport processes, which can be identified by changes in sediment characteristics through the cores (D'Haen *et al.*, 2012; Wolfe *et al.*, 2006). Depths in the core where sediment sources and transport processes change were identified using constrained hierarchical cluster analysis with magnetic susceptibility, organic matter (represented by the ratio of incoherent to coherent scatter; inc/coh), particle size (represented by the ratio of zirconium to rubidium; Zr/Rb) and elemental composition as variables. The historical trends in hydrology, inferred from the clusters obtained from the constrained cluster analysis were checked against flow rates measured in the Yarra River between 1891 and 2001.

Discrete flood deposits were also identified in sedimentary records from Willsmere and Bolin Billabong (W4 and B5, respectively) in Lintern *et al.* (in preparation-a). Two methods were developed for identifying these flood deposits. The first, named the Traditional Method, used four common characteristics of flood-deposited sediments to identify discrete flood deposits. These characteristics are: the occurrence of laminations in the core, high magnetic susceptibility, high particle size, and low organic matter. The second method, the Flood Signal Strength method, quantifies the likelihood that a discrete sediment deposit is of fluvial origin, based on the number of flood-borne sediment characteristics that are met and the magnitude of these properties. These flood-borne sediment characteristics are: high levels of magnetic susceptibility, inorganic matter, sediment particle size and elements that are more enriched in the catchment source geological deposits compared to local soils (silicon; Si, potassium; K, titanium; Ti, zirconium; Zr, terbium; Tb). Each of these parameters was scaled to a value between 0 and 1 (Equation 1) and the sum of the scaled parameters at discrete depths through the sediment core was calculated as the Flood Signal Strength. In Equation 1, x is the original unscaled value of the parameter at a certain depth in the core, x_{min} is the minimum value of the parameter through the core, $x_{\max}$ is the maximum value of the parameter through the core, and x_{scaled} is the scaled value of the parameter at a certain depth in the core. Heavy metals (Cr, Cu, Ni, Pb, Zn)

were not included in the Flood Signal Strength. Comparison of observed flood records of the Yarra River to the reconstructed flood histories indicated that whilst the Traditional Method could only identify major floods, the Flood Signal Strength was also able to identify minor floods events.

$$x_{scaled} = \frac{x - x_{min}}{x_{max} - x_{min}} \qquad \textbf{Equation 1}$$

For the work presented here, the previously identified historical hydrological trends were compared to heavy metal profiles developed for the Willsmere and Bolin Billabong sediment cores. Due to the loss of the top 70 cm of W1, heavy metal and sediment characteristic profiles for W4 and W1 have been plotted together, showing W1 as a continuation of W4, with the top of W1 corresponding to 70-cm depth in W4. B3 trends are presented only below 20 cm because the top 20 cm was discarded for ICP-MS. First we compared the overall trends in hydrology for Willsmere and Bolin Billabongs to the heavy metal profiles (As, Cr, Ni, Cu, Pb, Zn) created using ICP-MS heavy metal analyses. These heavy metal profiles were created for B3, W4 and W1, but historical trends in hydrology were not identified directly for W4 and W1 in the previous study (Lintern *et al.*, in preparation-a). As such, we determined historical trends in hydrology for W4 and W1 by correlating both W4 and W1 to W2001 using their magnetic susceptibility profiles (correlations between the cores provided in Figure S1 in the supplementary material).

We then identified the level of heavy metals contained in discrete flood layers in the sediment cores from Willsmere and Bolin Billabong (W4 and B5). The 0.5-cm resolution micro-XRF heavy metal profiles were used to determine the heavy metal concentrations in the flood deposits instead of the ICP-MS heavy metal profiles because of their higher resolution. It should be noted that As trends could not be identified at this higher resolution as the detection limits for As using micro-XRF were too high. The Mann-Whitney test was used to assess whether there were statistically significant differences in heavy metal concentrations in flood-deposited sediments compared with sediments not deposited by floods, identified by the Traditional Method. This statistical test was selected as it is a non-parametric test and it can be used when groups have unequal sample sizes (Mann and Whitney, 1947; Sheskin, 2004). Spearman's Rank Correlation Coefficient (ρ) was used to assess the strength of the relationship between the Flood Signal Strength (i.e., the likelihood that the deposit is flood-borne) and heavy metal concentrations. Plots showing cross-correlations (with Spearman's Rank Correlation Coefficients) between the parameters that make up the Flood Signal Strength (magnetic susceptibility, inc/coh, Zr/Rb, Si, K, Ti, Zr, Tb) and the heavy metals (Cr, Cu, Ni, Pb and Zn) are provided in Figure S2 and Figure S3 in the supplementary material.

RESULTS AND DISCUSSION

Identifying pollutant sources and transport processes

Previously in Lintern *et al.* (in preparation-a), both Willsmere and Bolin Billabong were found to have experienced significant changes in hydrology through the 19th and 20th centuries. These changes can be conceptualised as hydrological zones (Figure 2). The identified hydrological trends were discussed in detail in Lintern *et al.* (in preparation-a), and are summarised only briefly below. Prior to European settlement, mainly organic sediments were deposited on the lake bed (Zone E-Wil). However, after European settlement, from the mid- to late 19th century, inorganic materials entering the billabongs increased, most likely due to increased catchment disturbance (Zone C-Wil and Zone D-Wil and Zone C-Bol and Zone D-Bol). The sediment deposits within these regions of the sedimentary record are characterised by high magnetic susceptibility, high Zr/Rb (i.e., sediment particle size) and inorganic element levels (e.g., Si, K, Ti) (Lintern *et al.*, in preparation-a). In the 20th century, the billabongs are less influenced by fluvial flows, and receive less inorganic sediments (Zone A-Wil, Zone B-Wil, Zone A-Bol and Zone B-Bol). In these regions of the sedimentary record, there are decreasing levels of magnetic susceptibility and Zr/Rb, and increasing levels of inc/coh (i.e., organic matter).

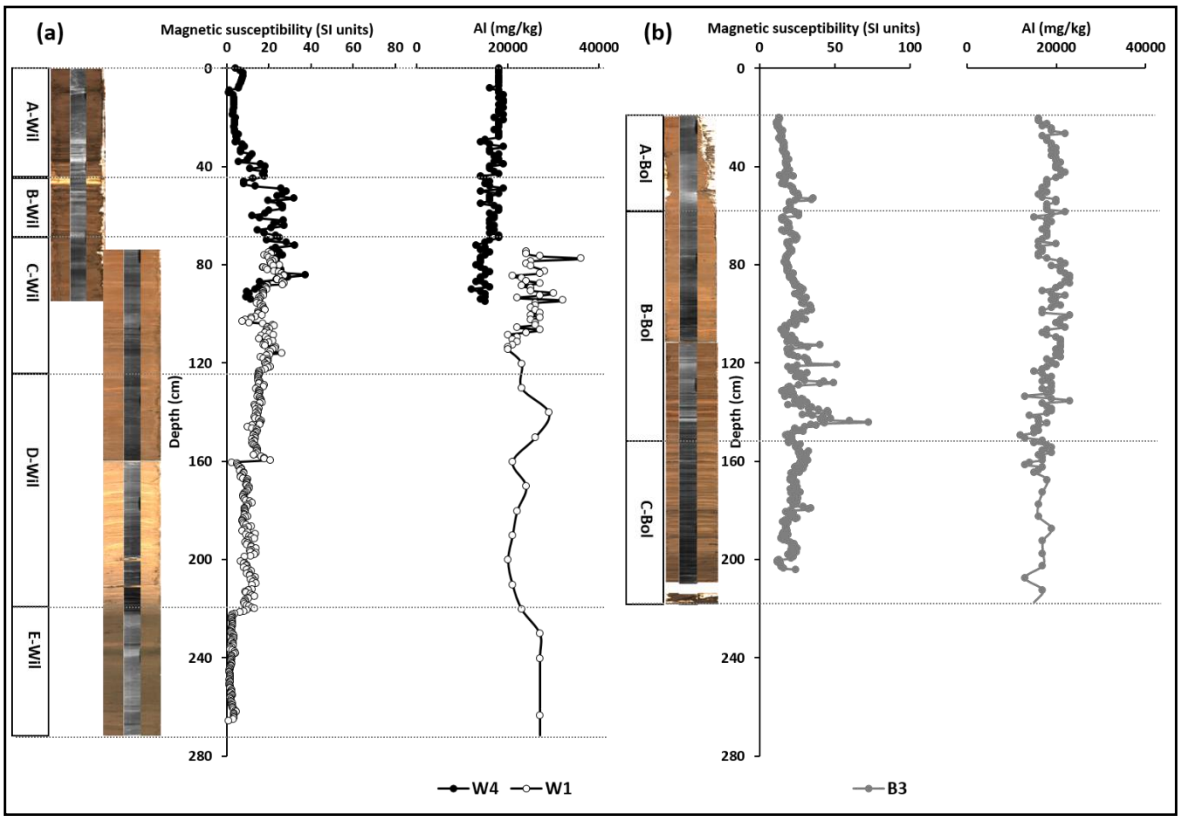

Figure 2: Zones based on sediment deposition processes, optical and radiographic images, magnetic susceptibility and Al (mg/kg) profiles for Willsmere Billabong cores W4 and W1 (a) and Bolin Billabong core B3 (b). Zones adapted from Lintern *et al.*, (in preparation-a). W1 profile has been shifted 70 cm downwards (i.e., core surface is at 70 cm depth).

We compared the As, Cr, Cu, Pb, Ni and Zn profiles (determined using ICP-MS) to the hydrological trends described above (as shown in Figure 3). Absolute concentrations in terms of mg/kg (dry weight) are provided in Figure 3. As noted previously in Lintern *et al.* (2015) there is some discrepancy between the W4 and W1 heavy metal concentrations in the region that these sedimentary records overlap, but this is most likely due to spatial variability within the billabong. We have not corrected for this spatial variability because these differences do not interfere with our interpretations of the heavy metal profiles.

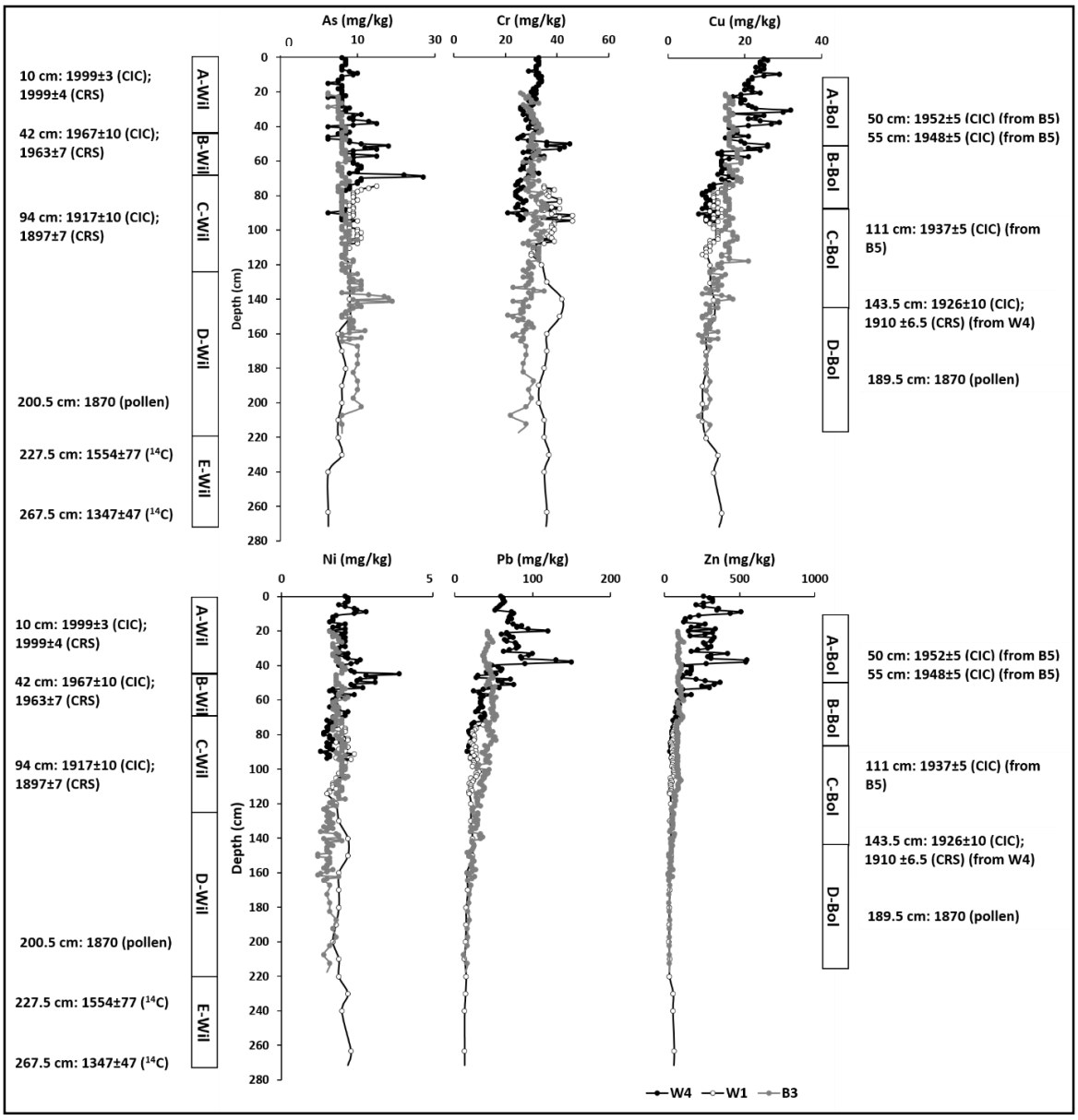

Figure 3: Absolute metal concentrations deposited in the sediments of Willsmere Billabong and Bolin Billabong. W1 profile has been shifted 70 cm downwards (i.e., core surface is at 70 cm depth). Depositional zones and chronological markers for Willsmere Billabong cores on left and those for the Bolin Billabong core is on the right.

For both lakes, absolute As concentrations are low and relatively stable in sediments that were deposited in the 19th century, followed by a maximum in the early 20th century (Figure 3). In a previous study (Lintern *et al.*, 2015), based on the timing of this As maximum, we hypothesized that the As trend in the Willsmere Billabong sedimentary record was being significantly influenced by gold mining activities in the Yarra River Catchment upstream of Willsmere Billabong. Gold mining occurred in the river catchment between 1850 and 1913, with the highest levels of gold extraction occurring in 1905 (Brizga *et al.*, 1995). The heavy metal profile of B3, and an understanding of the hydrology of Willsmere and Bolin Billabongs, helps to strengthen our earlier findings. The fact that As exhibits a similar trend

in a sedimentary record from a separate billabong suggests that the As of both billabongs have common sources. Arsenic mobilized by gold mining in the Yarra River catchment could be transported into both Willsmere and Bolin Billabongs during high flows of the Yarra River. Indeed, the region of the sediment cores with high As concentrations corresponds to regions of the sedimentary records that are characterized by high fluvial activity (Zones C-Wil and C-Bol). The decrease in As coincides not only with the cessation of gold mining, but also with start of Zones B-Wil and B-Bol, which are regions of the sediment core that that contain sediments deposited when the billabong was more disconnected from the main river channel (Lintern *et al.*, in preparation-a).

There is a region of elevated absolute Cr concentrations in W4 but such a region of high Cr is not apparent in B3 (Figure 3). In the region of W4 where high Cr concentrations occur (50-53 cm in W4), there are also elevated levels of magnetic susceptibility and Zr/Rb (representing particle size; Lintern *et al.*, in preparation-a) (Figure S4 in the supplementary material). These are characteristic of flood-borne sediments. There are also elevated levels of calcium (Ca), Ti, iron (Fe) and strontium (Sr). We found in a previous study that these elements are elevated in geological deposits in the Darebin Creek catchment (Figure S5 in the supplementary material), which meets the Yarra River downstream of Bolin Billabong but upstream of Willsmere Billabong (Lintern *et al.*, in preparation-a). Indeed, there may be higher Cr in flood-borne deposits from Darebin Creek due to high Cr levels in the geological deposits in the Darebin Creek catchment (Figure S5 in the supplementary material). Thus it appears the increasing level of Cr in W4 at this region of the core correlates to overbank flooding of the Yarra River, and in particular, flood sediments from the Darebin Creek catchment.

Both billabongs experienced increasing Cu, Pb and Zn concentrations over time. However, Figure 3 shows that concentrations are noticeably higher in the Willsmere Billabong core compared to the Bolin Billabong core. The increasing trend in Cu, Pb and Zn in both billabongs is most likely due to the increase in heavy metal emissions due to urbanisation, the introduction and proliferation of motor vehicles and industrial development through the 20th century, as previously discussed in Lintern *et al*. (2015) and Lintern *et al.* (submitted). The difference in the magnitude of the increase may be due to the fact that Willsmere Billabong is downstream of Bolin Billabong. It is possible that there are heavy metal inputs into the Yarra River between the two billabongs via both tributaries and stormwater inputs that contribute to higher levels of heavy metal pollution at Willsmere Billabong.

Another possible explanation for the discrepancy between the two billabongs is that Willsmere Billabong is connected to the local stormwater drainage network but Bolin Billabong is not. Indeed,

Cu, Pb, and Zn concentrations in Willsmere Billabong begin to overtake Bolin Billabong at 60 cm depth in W4 and 84 cm depth in B3. These sediment core depths date to approximately the 1940s, which is when the stormwater drain was installed in Willsmere Billabong (David Barclay, City of Boroondara, personal communication, 2nd April 2013). Furthermore, in the mid-1970s, a major freeway (estimated to have a vehicle load of 130,000 in 2009; Parris *et al*., 2009) was constructed 300 m away from Willsmere Billabong (the Eastern Freeway; Figure 1). It would be expected that motor vehicle emissions due to the this freeway may contribute considerable amounts of Cu, Pb and Zn (Hjortenkrans *et al.*, 2006) via atmospheric deposition either directly into Willsmere Billabong or into the billabong's local catchment, which can then be transported into the billabong by urban stormwater runoff. Indeed, there are further increases evident in Cu, Pb and Zn levels in W4 sediments from approximately the 1970s (approximately 40-cm depth; Figure 3).

In W4 the highest levels of Cu, Pb and Zn coincide with a period in which Willsmere Billabong was largely disconnected from the main river channel (Zone A-Wil; Figure 3). The fact that the greatest deposition of Cu, Pb and Zn occurs when there is a low amount of flood-borne sediments within the sediment core suggests that fluvial activity is likely not a significant source of heavy metal pollution in Willsmere Billabong. On the other hand, this increase in Cu, Pb and Zn may be due to higher metal concentrations in the deposits of individual flood events, even if there is a fewer number of these flood events. As such, the main cause of the increase in Cu, Pb and Zn concentrations is not clear without identifying the Cu, Pb and Zn levels in discrete flood deposits through the sediment cores.

Determining heavy metal abundances in flood deposits

Heavy metal concentrations in flood deposits identified using the Traditional Method

The flood-deposited sediments identified in the sedimentary records from Willsmere Billabong (W4) and Bolin Billabong (B5) using the Traditional Method were previously presented in Lintern *et al.* (in preparation-a), and these results are provided again in Figure S6 and Figure S7 in the supplementary materials. The heavy metal concentrations in the flood-deposited sediments identified using the Traditional Method are shown in Figure 4, where the heavy metal abundances in flood deposits are also compared to that of sediments that were not deposited by floods.

For Willsmere Billabong, sediments that are not deposited by floods have greater Zn concentrations compared to flood-deposited sediments and this difference is statistically significant ($p<0.05$). Visually, Ni, Cu, Pb appear to also have greater concentrations in non-flood deposits (Figure 4), but these differences are not statistically significant, most likely due to the small sample size of flood-deposits.

This suggests that local catchment inputs, such as the urban stormwater runoff, appear to be contributing to heavy metal contamination of Willsmere Billabong's bed sediments, more so than fluvial floods. The higher concentration of heavy metals in the non-flood deposits in Willsmere Billabong could also be due to the fact that heavy metals preferentially bind to fine-grained or organic sediments (Foster and Charlesworth, 1996; Loring and Rantala, 1992), which are enriched in the non-flood deposits of Willsmere Billabong.

In Bolin Billabong, there are no statistically significant differences between heavy metal concentrations in flood and non-flood deposits. This suggests that the major floods identified by the Traditional Method contribute similar amounts of heavy metals to the billabong as non-flood deposits. However, flood-borne sediments at Bolin Billabong have statistically significantly higher Zn concentrations ($p<0.05$) compared to the flood-borne sediments at Willsmere Billabong. This may result from the larger number of stormwater outlets, which can act as inputs of heavy metals into the Yarra River, close to Bolin Billabong (the nearest drain, which is 600 mm in width being less than 1 km upstream) compared to Willsmere Billabong (where the nearest drain of 300-mm diameter, is 3.4 km upstream). The fact that the other metals have similar concentrations in the flood deposits of the two billabongs suggests that these remaining metals may not be greatly affected by these stormwater outlets near Bolin Billabong.

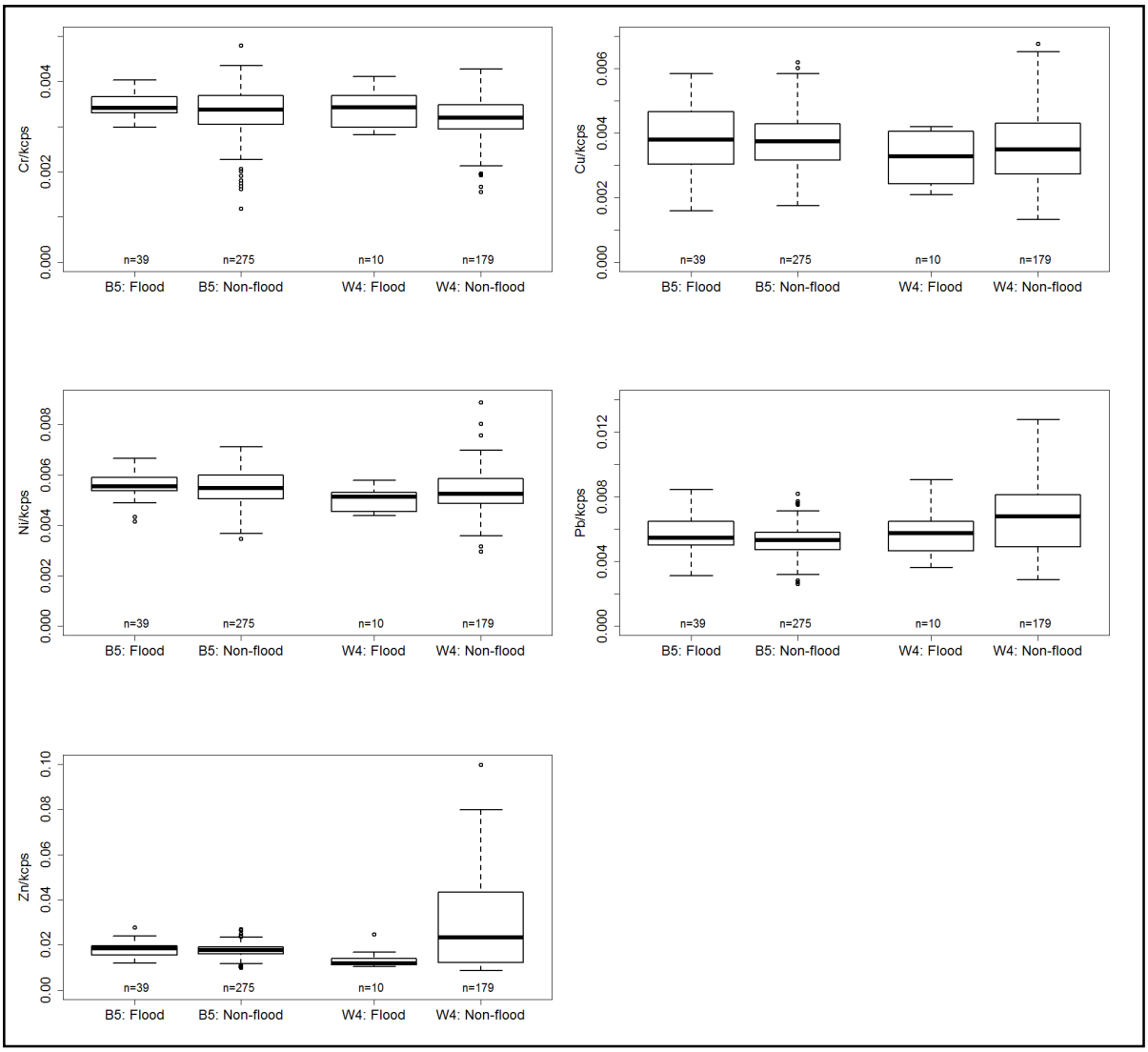

Figure 4: Distribution of Cr, Ni, Cu, Pb and Zn intensities normalised to total counts per second in flood-deposited sediments (Flood) and sediments not deposited by floods (Non-flood) for the Willsmere Billabong core W4 and the Bolin Billabong core B5. Number of samples used to create each boxplot (n) shown in plots.

Heavy metal concentrations in likely flood deposits identified using the Flood Signal Strength

The Flood Signal Strength identified for the Willsmere and Bolin Billabong sedimentary records, W4 and B5 were previously presented and checked in Lintern *et al.* (in preparation-a) and the results are included in Figures S6 and S7 in the supplementary materials. The relationships between the previously evaluated Flood Signal Strengths and heavy metal concentrations at 0.5-cm intervals in W4 and B5 are shown in Figure 5. The relationship between the heavy metal concentrations and the Flood Signal Strength essentially represents the relationship between heavy metal abundances and the extent to which the sediment deposits match characteristics of flood-borne sediments.

Spearman Rank Correlation Coefficients (ρ) indicated that for both W4 and B5, there was a positive relationship between Cr and the Flood Signal Strength (Figure 5). This positive relationship suggests that the main source of Cr into the billabongs is the Yarra River. Although this contrasts with the results of the Traditional Method (Figure 4), it was previously found by comparing the hydrologic trends and the pollution trends that Cr appeared to be entering Willsmere Billabong by fluvial flooding. This difference is most likely due to the fact that the Traditional Method was not able to identify the minor flood deposits in the sedimentary records (Lintern *et al.*, in preparation-a). It is possible that it is these minor flood events that are contributing high amounts of Cr to the floodplain lakes.

For W4, the remaining metals (Ni, Cu, Zn and Pb) do not have a positive relationship to Flood Signal Strength, indicating that the concentrations of these metals in Willsmere Billabong sediment deposits are not correlated to the occurrence of fluvial flooding. In fact, there is a negative relationship ($p<0.05$) between the Flood Signal Strength and Cu, Zn and Pb (Figure 5), again suggesting the importance of local catchment metal inputs in the Cu, Zn and Pb pollution of Willsmere Billabong. This negative relationship may be due to the direct urban stormwater input. Due to high levels of heavy metals in urban stormwater (Duncan, 1999), this drain may be the main source of Cu, Pb and Zn into the billabong and the occurrence of flood events may be diluting this pollutant load. Furthermore, the urban stormwater runoff from the local Willsmere Billabong catchment is expected to be higher in Cu, Pb and Zn also, due to the proximity of the Eastern Freeway (Figure 1). This correlates with the findings (particularly for Zn) that were obtained when the Traditional Method was used to identify flood deposits.

For B5, there is no clear positive or negative relationship between Ni, Cu, Zn and Pb and the Flood Signal Strength (Figure 5). However, if the dataset for Pb is partitioned at 70 cm (a depth that dates to approximately the mid-1950s) there is a positive relationship between Pb and the Flood Signal Strength in the recent deposits and a negative relationship in the older deposits. This could be indicating changing sources of Pb into Bolin Billabong over time. The negative correlation between Flood Signal Strength and Pb in the first half of the 20th century suggests that the primary source of Pb into the billabong may have been overland runoff in the local billabong catchment. Between 1919 and 1934, the local Bolin Billabong catchment was used for agriculture (Leahy, 2007; Leahy *et al.*, 2005). It is therefore likely that Pb-based pesticides would have been used, leading to high Pb levels in local catchment soils, which could be transported into the billabong by overland runoff. However, with the end to agricultural activities in the catchment, the supply of Pb in the local catchment would have decreased. As a result, fluvial flooding may have become a more significant source of Pb into Bolin

Billabong, particularly due to the presence of two stormwater drains into the Yarra River less than 1 km upstream of the billabong. If the Cu and Zn datasets are also partitioned at 70 cm, there is also a slight positive trend between the pollutant levels and the Flood Signal Strengths in the more recent sediments. This suggests that in the second half of the 20th century the occurrence of fluvial floods may be contributing to the Cu, Zn and Pb contamination of sediments deposited in Bolin Billabong. When the Traditional Method was used to identify flood deposits we did not find significant differences in the Cu, Ni, Pb and Zn concentrations in flood and non-flood deposits, but this may be indicating that it is the minor flood events rather than the major floods (that are identified using the Traditional Method), that contribute heavy metals to the billabongs.

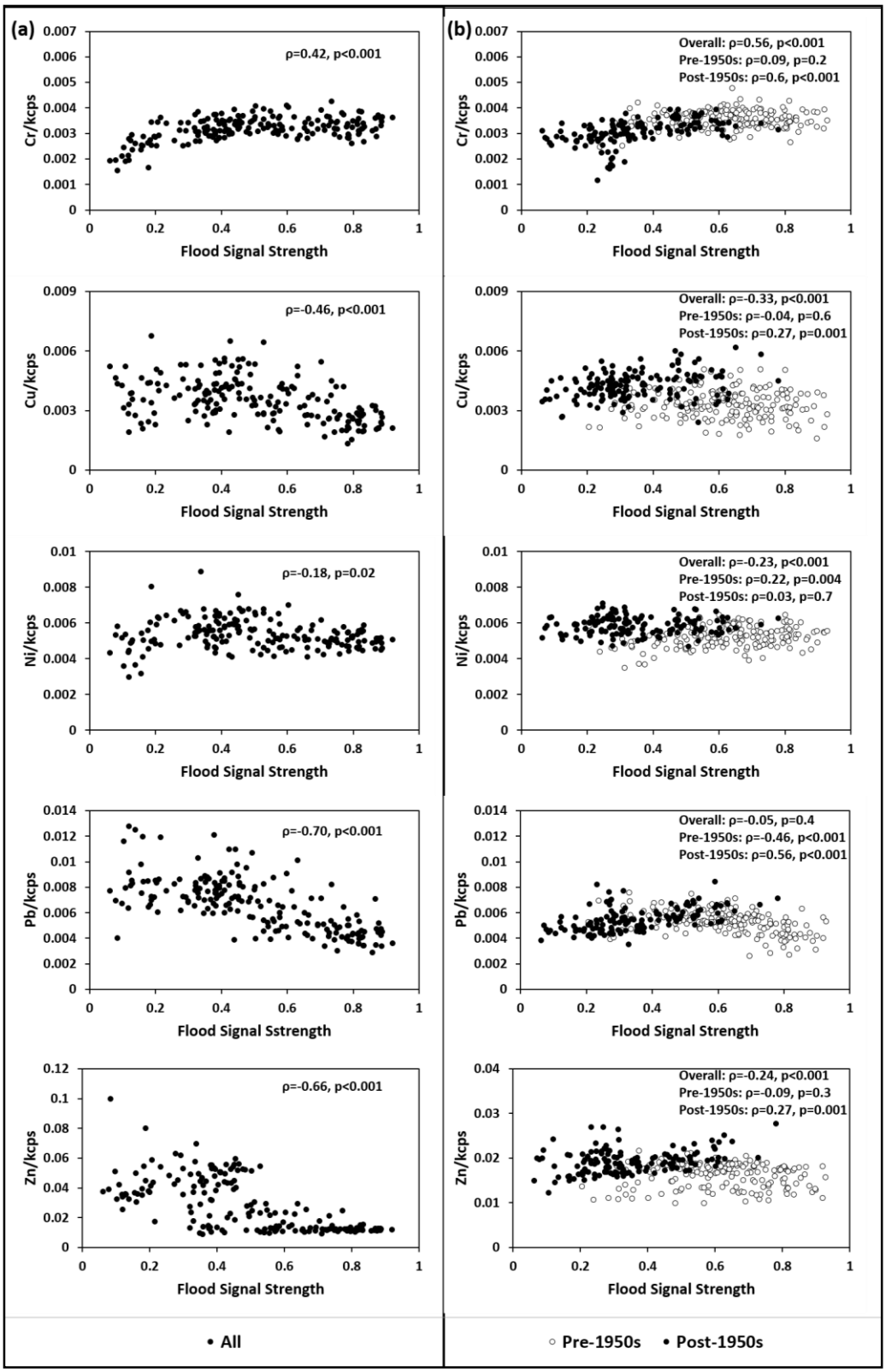

Figure 5: Correlation between heavy metal intensity and Flood Signal Strength for Willsmere Billabong core W4 (a) and Bolin Billabong core B5 (b). Spearman Rank Correlation Coefficients (ρ), p-values are provided.

Using the proposed methodology to develop management strategies

An enhanced understanding of the transport processes and sources of heavy metals into aquatic environments allows us to develop targeted mitigation strategies for polluted systems. For example, we found that there was a negative correlation between the presence of flood deposits and Cu, Pb and Zn contamination in the Willsmere Billabong sediment core. This suggests that the main driver for metal contamination in Willsmere Billabong may be urban stormwater. As such, the findings above indicate that to decrease Cu, Pb and Zn levels in the bed sediments of Willsmere Billabong, stormwater quality improvement strategies in the local catchment would be required. Although there has been a slight decrease in Cu, Pb and Zn levels following the construction of the stormwater treatment wetland in 2006, metal concentrations at the core surface (i.e., in sediments deposited in 2012) are still 2.5 to 5.5 times greater than at the beginning of the sedimentary record in the late-19th century. Therefore, it appears that alternative mitigation strategies, specifically designed for the removal of Cu, Pb and Zn are required to further reduce the amount of heavy metals entering Willsmere Billabong via urban stormwater.

We also found that the heavy metals depositing on the Bolin Billabong bed sediment appear to be influenced by overbank flooding. Thus, although Bolin Billabong has experienced less heavy metal contamination compared to Willsmere Billabong, decreasing the contamination of Bolin Billabong may be more difficult, as instead of a localised point source, the heavy metal pollution of the main river channel will need to be addressed. Without one point source of heavy metals that can be targeted, the restoration of Bolin Billabong may be reliant on reducing the emission of heavy metals at their sources (Charlesworth *et al.*, 2003).

This investigation also demonstrated that conveying urban stormwater, even after treatment, into aquatic systems can result in the heavy metal contamination of bed sediments of aquatic systems. In the early 2010s, there was a proposal to discharge treated stormwater into Bolin Billabong, (Lachlan Johnson, City of Manningham, personal communication, 26th June 2013). It was envisaged that this additional water supply to Bolin Billabong would help keep lake levels high even in the face of decreased hydrologic connectivity to the Yarra River (Lintern *et al.*, in preparation-a). Although this plan never came to fruition, the example of Willsmere Billabong indicates that such plans may have deleterious implications for the health of the billabong in terms of toxicant contamination.

CONCLUSIONS

This investigation demonstrated how an understanding of historical water quality juxtaposed with our understanding of whether the sediments are flood-borne, can be used to infer the origins and transport pathways of pollutants. This understanding can be used to identify the sources that must be targeted for the remediation of aquatic environments. In the case of Willsmere and Bolin Billabongs, it was determined that As appeared to have been transported into the billabongs by overbank flooding from its source in the middle and upper Yarra catchment. Pollutant levels contained in fluvial flood deposits indicates that the occurrence of fluvial flooding appears to be influencing Cr levels in Willsmere and Bolin Billabong sediments. The recent deposits of Cu, Pb and Zn in Bolin Billabong also appear to be governed by the occurrence of flood events. On the other hand, Cu, Pb and Zn concentrations in Willsmere Billabong sediments are lower in flood deposits. This suggests that the main source of Cu, Pb and Zn into Willsmere Billabong is the local catchment (likely the urban stormwater drain). These results highlight that different strategies need to be employed to reduce Cu, Pb and Zn levels in Willsmere and Bolin Billabongs. Whilst local catchment sources (i.e., urban stormwater) should be targeted for Willsmere Billabong, at-source pollution control strategies for reducing the emission of heavy metals into the main river channel are likely to be more successful for Bolin Billabong.

We believe that the approach demonstrated in this study has wide applications. This technique can be used to design effective and targeted mitigation strategies for degraded aquatic environments. For example, the influence of the direct connection to the urban stormwater drainage network on the contamination of Willsmere Billabong sediments was identified using our understanding of the sediment core heavy metal profile and the location of discrete flood deposits through the sediment core. This suggests that treatment of this stormwater would aid in the reduction of these heavy metal concentrations in Willsmere Billabong bed sediments. Similarly, we determined that whilst Bolin Billabong has not experienced such a dramatic increase in Cu, Pb and Zn concentrations, reducing these concentrations to background levels may be more complex due to the diffuse nature of the pollutants.

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7.3 Heavy metal concentrations in fluvial flood deposits

7.3.1 Objectives

This section has the objective of identifying the heavy metal concentrations in units of mg/kg (dry weight) contained in flood-deposited sediments in Willsmere and Bolin Billabongs. The predicted heavy metal concentrations are in mg/kg (dry weight), to enable comparison to current Australian sediment quality guidelines (ANZECC/ARMCANZ, 2000). Previously in Chapter 4 (Lintern *et al.*, submitted), it was argued that current generic sediment quality trigger values provided in ANZECC/ARMCANZ guidelines (ANZECC/ARMCANZ, 2000) may not be appropriate for use as sediment quality trigger values for the Yarra River catchment, due to the discrepancy between these generic values and background conditions. As such, both the generic sediment quality trigger values from ANZECC/ARMCANZ (2000) and the reference conditions discussed in Lintern *et al.* (submitted) will be used for the comparisons. It is envisaged that this dataset of the distribution of heavy metal concentrations in fluvial flood deposits could be used to help predict the concentration of heavy metals deposited by the Yarra River in its floodplains during future overbank floods.

7.3.2 Methodology

Expressing micro-XRF data in terms of mg/kg (dry weight)

Least squares linear regression was used to convert elemental abundances identified using micro X-Ray Fluorescence (micro-XRF) into heavy metal concentrations in terms of mg/kg (dry weight). The (1) micro-XRF heavy metal abundances (adjusted for moisture content using inc/coh) and (2) the heavy metal concentrations found using ICP-MS and expressed in terms of mg/kg (dry weight) for the Willsmere Billabong core W4 and the Bolin Billabong core B3, both at 1-cm intervals were used for the regression. Both of these datasets were introduced and described previously in Chapter 6 in Lintern *et al.* (in preparation-b). The linear functions developed for all metals were forced through the origin, as it would be expected that when the micro-XRF heavy metal abundances are zero, the heavy metal concentrations in terms of mg/kg (dry weight) will also be zero (Weltje and Tjallingii, 2008). The linear functions obtained for chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), are shown in Figure 7.1 with Nash-Sutcliffe Coefficient of Efficiency values (E) (Nash and Sutcliffe, 1970) and 95% confidence intervals. The E values were above 0.5 for only Pb and Zn. Therefore, only these two heavy metals were investigated further. It was previously demonstrated in Lintern *et al.* (in preparation-b) that trends in Cr, Ni and Cu obtained by ICP-MS correlate to those obtained using micro-XRF. The linear functions in Figure 7.1 probably have a poor fit for these three metals because the functions were forced through the origin. As such, it appears that whilst the trends in Cr, Ni and Cu can be represented by trends in micro-XRF heavy metal abundances, simple linear functions cannot be used to convert micro-XRF heavy metal abundances of these three metals into heavy metal concentrations in terms of

mg/kg (dry weight). Further investigations are required to develop functions for converting the micro-XRF heavy metal abundances into sediment concentrations by dry weight for these three metals.

The linear functions provided in Figure 7.1 for Pb and Zn were used to convert the micro-XRF Pb and Zn abundances obtained at 0.5-cm intervals for the Willsmere Billabong core W4 and the Bolin Billabong core B5 into heavy metal concentrations in terms of mg/kg (dry weight).

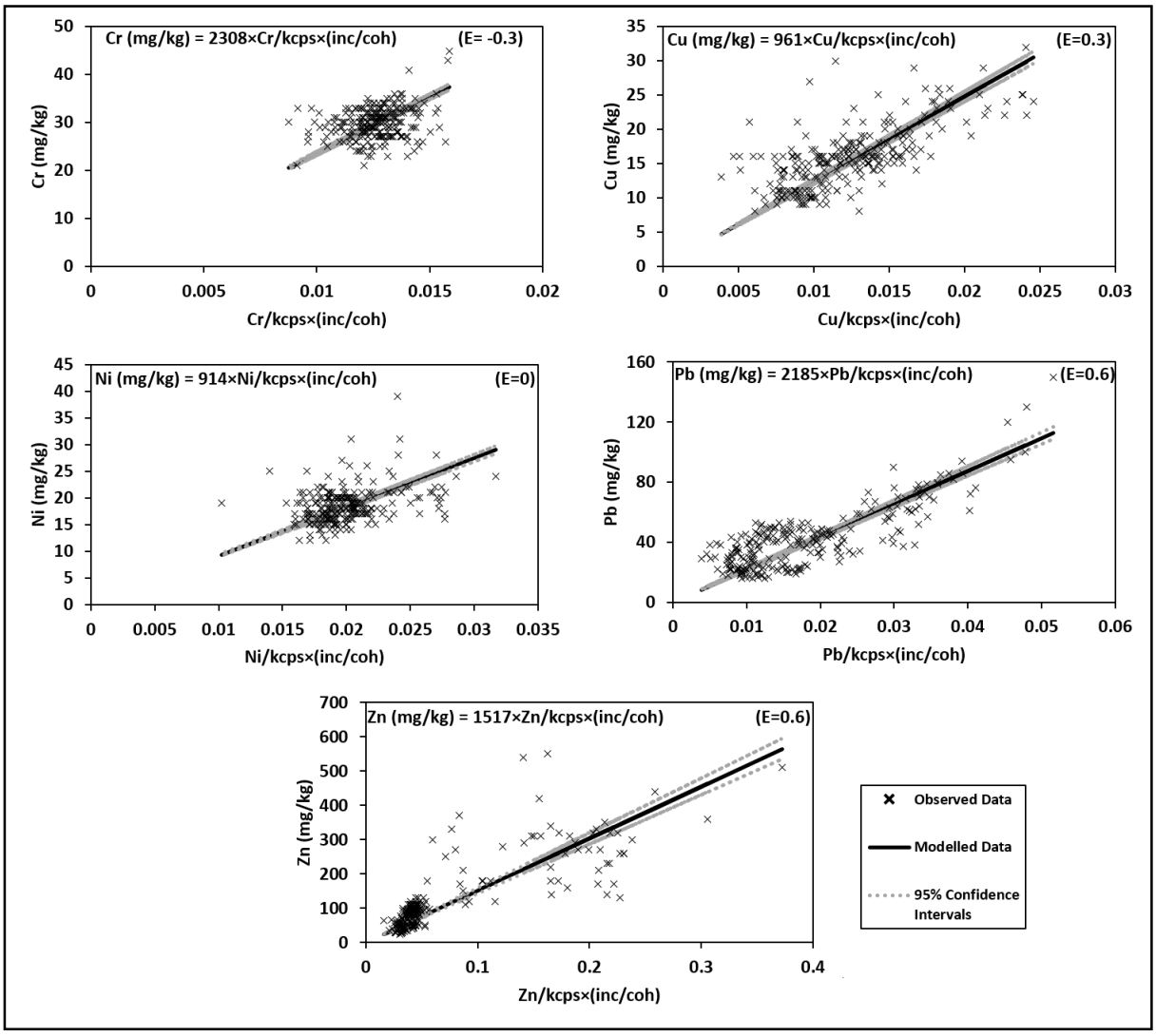

Figure 7.1: Linear functions identified for Cr, Cu, Ni, Pb and Zn that can be used to express micro-XRF heavy metal abundances in terms of mg/kg (dry weight).

Identifying the heavy metal concentrations in flood deposits

In Chapter 5 (Lintern *et al.*, in preparation-a), two methods for identifying flood deposits in sediment cores were introduced. The first was the Traditional Method, which uses flood proxies commonly used in literature to identify flood-deposited sediments in sediment cores. These characteristics are the

occurrence of high density in the sediment core (Gilbert *et al.*, 2006), maxima in magnetic susceptibility (Arnaud *et al.*, 2005), minima in organic matter (Nesje *et al.*, 2001), and fining upwards sequences in particle size (Ambers, 2001). In Section 7.2 (Lintern *et al.*, in preparation-c), boxplots were presented, that depict the distribution of heavy metals abundances (in micro-XRF units) in flood-deposited sediments that were identified using the Traditional Method in W4 and B5. These boxplots were re-created here, where Pb and Zn levels are expressed in terms of mg/kg (dry weight) instead of in micro-XRF units. These data were also used to develop cumulative density functions of Pb and Zn concentrations in fluvial flood deposits in Bolin Billabong and Willsmere Billabong.

The second method used to identify flood deposits in the sedimentary records, the Flood Signal Strength, is a more novel method. The Flood Signal Strength quantifies the likelihood that the sediments were deposited by fluvial flooding. This is done by finding the magnitude of flood-borne sediment characteristics (high magnetic susceptibility, low organic matter, high particle size and high levels of elements that are more enriched in the upstream Yarra River catchment compared to the local Willsmere and Bolin Billabong catchments) at discrete intervals through the sediment core. As previously discussed in Lintern *et al.* (in preparation-a), the elements that were included were silicon (Si), potassium (K), titanium (Ti), zirconium (Zr) and terbium (Tb). Heavy metals (e.g., Pb and Zn) were not included in the calculation of the Flood Signal Strength. In Chapter 5 (Lintern *et al.*, in preparation-a) we showed that the five year averages of the Flood Signal Strength positively correlate to five year averages of the flow characteristics of the Yarra River adjacent to the two billabongs (average daily flow and the number of days each year that the billabong was flooded). We developed a statistical model, using least squares linear regression, to express the Flood Signal Strength in terms of river flow characteristics. As the number of minor flooding days had little effect on the overall linear function (i.e., $p>0.05$), this parameter was removed from the statistical model. The functions that relate the Flood Signal Strength to average daily flow are shown in Figure 7.2. The E values of these functions are above 0.5, suggesting that these statistical models are relatively strong. These functions enabled us to find the average daily flows (m^3/s) at 0.5-cm intervals through W4 and B5, using the Flood Signal Strengths identified in Chapter 5 (Lintern *et al.*, in preparation-a). The average daily flows calculated using these functions represent the average daily flow occurring in the river whilst each discrete 0.5-cm thick sediment layer was deposited in the billabong. These average daily flows corresponding to each 0.5-cm thick sediment deposit were then compared to Pb and Zn heavy metal concentrations (expressed in mg/kg; dry weight) in these 0.5-cm thick sediment deposits (identified using the functions in Figure 7.2).

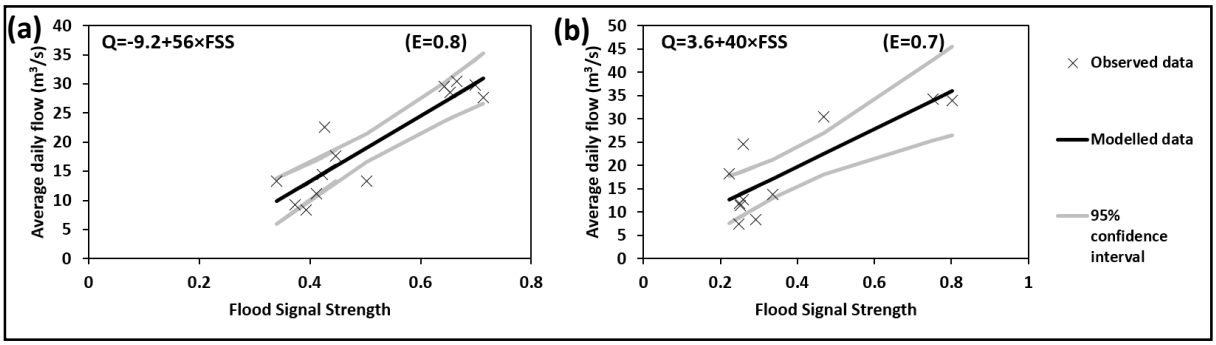

Figure 7.2: Linear functions relating FSS (Flood Signal Strength) to Q (average daily flow m^3/s) at five year averages for Willsmere Billabong core W4 (a) and Bolin Billabong core B5 (b), showing E values.

7.3.3 Results and Discussion

Heavy metal concentrations in flood deposits identified by the Traditional Method

The distribution of Pb and Zn concentrations (mg/kg) in flood-deposited sediments through the 20th century identified using the Traditional Method in Bolin and Willsmere Billabongs are provided in Figure 7.3 and Figure 7.4. The Mann-Whitney U-test indicated that Pb concentrations in flood-deposited sediments were not significantly different to those in sediments not deposited by floods for neither B5 nor W4 ($p>0.05$ for both B5 and W4). However, the lack of statistical significance could be influenced by the small number of flood events detected in W4 using the Traditional Method (10 events). Figure 7.3 suggests visually that Pb levels are greater in flood-deposited sediments compared to sediments that are not deposited by floods in W4.

By expressing the heavy metal levels in concentrations (mg/kg) instead of in micro-XRF units, we can compare the Pb concentrations in flood deposits against the sediment quality guideline trigger values provided by ANZECC/ARMCANZ (2000). Figure 7.3 shows that the 75th percentile Pb concentrations in flood deposits in both Willsmere Billabong and Bolin Billabong are above the trigger values that represent low probability of toxic effects (50 mg/kg). As such, both sediments deposited by floods and those not deposited by floods in Willsmere and Bolin Billabongs have concentrations exceeding recommended sediment quality guideline trigger values. The cumulative density functions in Figure 7.4 indicate that the 90th percentile Pb concentration in flood deposited sediments is approximately 58 mg/kg (above the trigger value of 50 mg/kg for low probability of toxic effects) for both Willsmere Billabong and Bolin Billabong. However, both flood and non-flood Pb concentrations in the two billabongs are consistently above the background concentrations of Pb in Willsmere and Bolin Billabongs obtained in Lintern *et al.* (submitted) from Chapter 4.

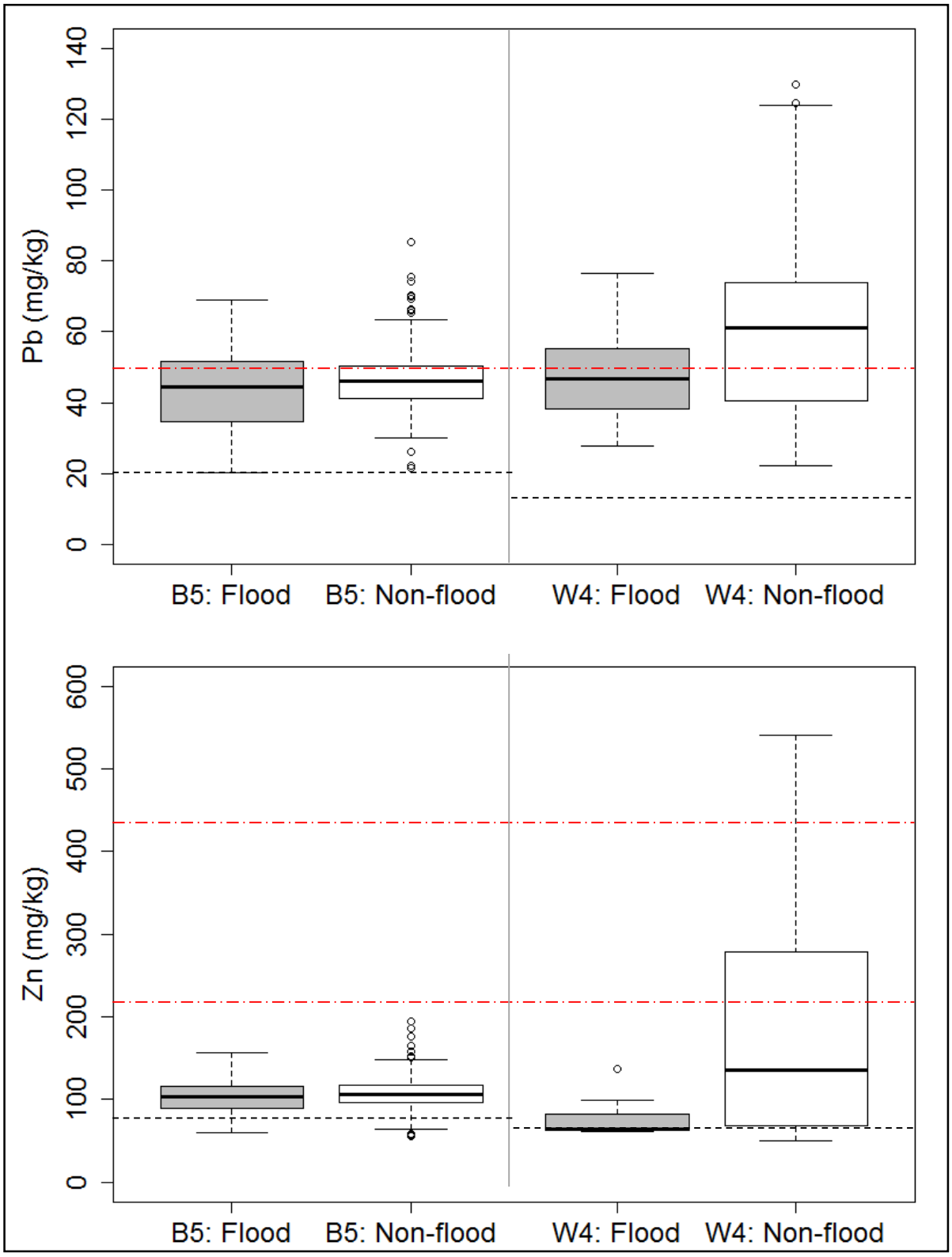

Figure 7.3: Boxplots showing distribution of Pb and Zn concentrations expected in sediments deposited by floods (as identified by the Traditional Method) in the middle Yarra River catchment at Bolin Billabong (B5) and Willsmere Billabong (W4). Dot-dash lines in red represent the guideline trigger values for low and high probability of toxic effects provided in the ANZECC/ARMCANZ sediment quality guidelines (2000). Dashed lines in black represent the background Pb and Zn concentrations for Bolin and Willsmere Billabongs identified in Lintern *et al.* (submitted) from Chapter 4. One outlier in W4, non-flood deposits for Zn at 800 mg/kg is not shown.

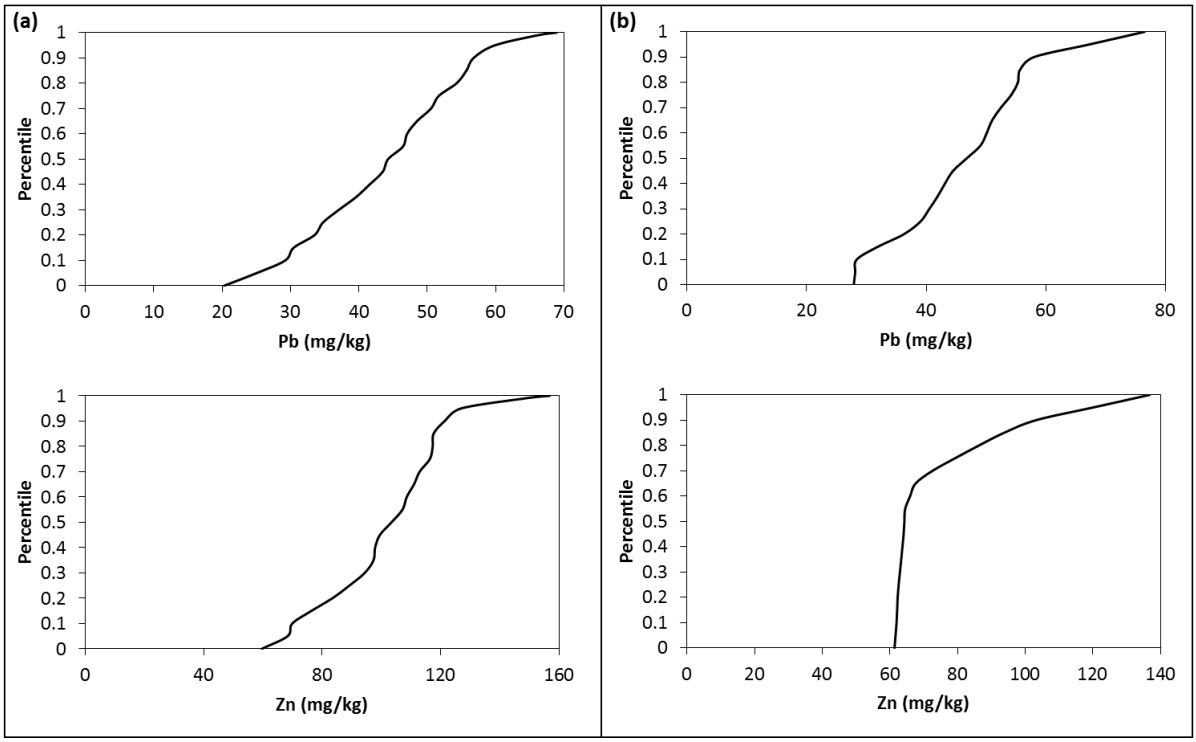

Figure 7.4: Cumulative density functions of Pb and Zn concentrations in fluvial flood-deposited sediments (identified using the Traditional Method) in Bolin Billabong (a) and Willsmere Billabong (b).

Zn concentrations in flood deposits are significantly less than in non-flood deposits for W4 ($p<0.05$) but are not significantly different in B5 ($p=0.29$). This also corresponds with the findings of Section 7.2, suggesting that major floods do not contribute Zn pollution to either billabong and in fact major floods appear to reduce Zn pollution in Willsmere Billabong. Figure 7.3 shows that Zn concentrations in the flood deposits in both Willsmere Billabong and Bolin Billabong are below the guideline trigger values provided by ANZECC/ARMCANZ (2000). The cumulative density functions of Zn concentrations in fluvial flood deposits (Figure 7.4) show that the 90th percentile Zn concentrations in flood deposits are approximately 120 mg/kg for Bolin Billabong and 100 mg/kg for Willsmere Billabong, both under the trigger values for low probability toxic effects (ANZECC/ARMCANZ, 2000). Whilst sediments that are not deposited by floods are below these trigger values for Bolin Billabong, for Willsmere Billabong, the Zn concentration in non-flood deposits can exceed even the trigger value for high probability of toxic effects. As for Pb, Zn concentrations in flood and non-flood deposits exceed the background conditions (pre-anthropogenic pollution conditions) identified for both Bolin and Willsmere Billabong in Lintern *et al.* (submitted) from Chapter 4.

Heavy metal concentrations in flood deposits identified by the Flood Signal Strength method

The relationships between the heavy metals (Pb and Zn) in each 0.5-cm thick sediment deposit in Willsmere and Bolin Billabong, and the average daily flow in the Yarra River adjacent to the two

billabongs is shown in Figure 7.5. Figure 7.5 allows us to identify the heavy metal concentration likely to be in a sediment deposit in Willsmere Billabong and Bolin Billabong, if the average daily flow during the period of deposition of that 0.5-cm thick sediment layer is known. The average daily flow at the Banksia St stream gauge has a weak negative correlation to concentrations of Pb (ρ=-0.29, $p<0.05$) and Zn (ρ=-0.46, $p<0.05$) in Bolin Billabong sediment deposits. There are stronger negative correlations between the average daily flow at the Chandler Highway stream gauge and Pb (ρ=-0.79, $p<0.05$) and Zn (ρ=-0.71, $p<0.05$) concentrations in Willsmere Billabong sediment deposits. Below flows of 20 m^3/s at both the Chandler Highway and Banksia St stream gauges, Pb and Zn concentrations are above the sediment quality trigger values for low probability toxic effects (Figure 7.5). This suggests that smaller and more frequent events may be resulting in greater pollution of the aquatic system. It also indicates the importance local pollution sources (e.g., the urban stormwater connection) at Willsmere Billabong in contributing heavy metals to the aquatic system.

General discussion

There is some uncertainty associated with the pollutant distributions and relationships presented in Figure 7.3, Figure 7.4 and Figure 7.5. Firstly, these distributions and relationships are comprised of data obtained from 0.5-cm intervals in the sediment cores. However, the linear statistical models (Figure 7.1 and Figure 7.2) that were used to create these distributions and relationships were developed for coarser resolution data. The linear functions converting micro-XRF heavy metal abundances into heavy metal concentrations in terms of dry weight (Figure 7.1) were developed using data collected from the cores at 1-cm intervals. The functions used to convert the Flood Signal Strength to average daily flows (Figure 7.2) were developed for five year averages of both Flood Signal Strengths and average daily flows. Given the sediment accumulation rates of the billabongs, there potentially could have been up to 22.5 cm deposited in B5 over five years (between 1927 and 1922; see Chapter 5 for sediment chronologies). It is possible that these functions developed for coarser resolution sediment core data cannot fully represent the trends in high resolution sediment core data. In future work, the effect of these data agglomerations should be tested by seeing if the results change significantly when sediment core data at coarser intervals (e.g., 1 cm or 5 cm) are used.

Secondly, uncertainties in the age-depth model were not incorporated into the linear function that relates the Flood Signal Strength to average daily flow at the Chandler Highway and Banksia St stream gauges. It was instead assumed that this error was accounted for by averaging the Flood Signal Strength and the average daily flow data over five year intervals. Due to the inability to create a detailed chronology below 20-cm depth in B5, the uncertainties in the chronology below this point

could not be quantified. It is possible that age-depth model uncertainties below 20 cm in B5 exceed five years, which would undermine the choice to use five year averages of daily flows and Flood Signal Strengths for developing the linear function in Figure 7.2.

Heavy metals concentrations (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the water column at the Banksia St stream gauge have been measured approximately once a week between 1984-1986 and 1990-1997 (Department of Sustainability and Environment, 2013). However, only two of these grab samples occurred when the river was in minor flooding conditions at the stream gauge (i.e., river level greater than 6 m; Lintern *et al.*, in preparation-a). As such, these relationships could not be validated using existing heavy metal data of flood-deposited sediments or flood waters.

In spite of these uncertainties however, we have demonstrated the implementation of a methodology that could be applied to other billabongs to gain a better understanding of the heavy metal concentrations within fluvial flood-deposited sediments. Such understanding of the past is critical to understand the possible heavy metal concentrations of future flood deposits.

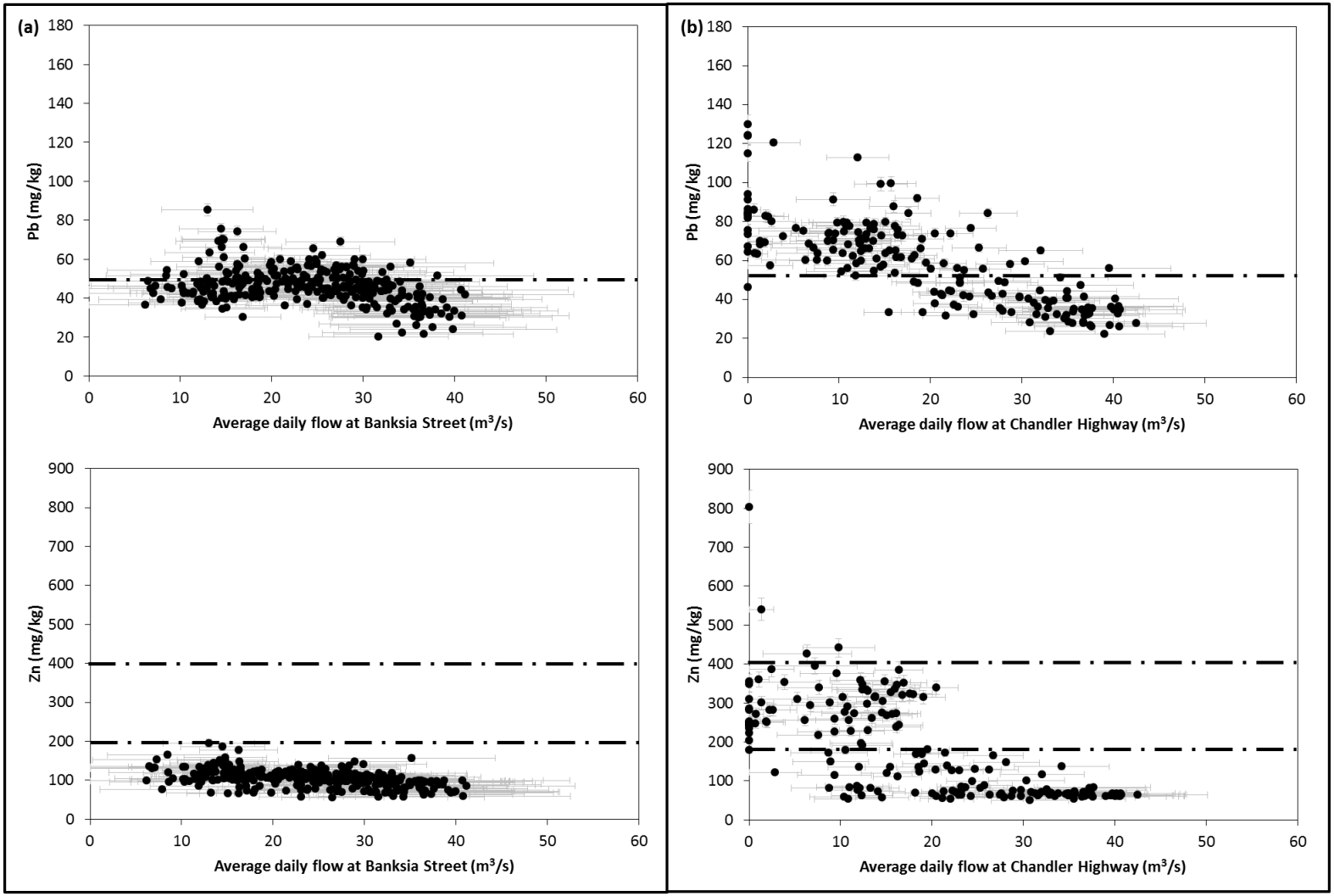

Figure 7.5: Relationship between average daily flow at the Banksia St stream gauge and the heavy metal (Pb, Zn) concentrations in Bolin Billabong deposits (a) and the relationship between average daily flow at the Chandler Highway stream gauge and the heavy metal (Pb, Zn) concentrations in Willsmere Billabong deposits (b). Error bars represent 95% confidence intervals. Black dashed lines indicate sediment quality trigger values (ANZECC/ARMCANZ, 2000).

7.4 Discussion

This chapter identified the relationship between the occurrence of fluvial river flooding and heavy metals in billabong bed sediments. This was determined by comparing the hydrologic trends of Willsmere and Bolin Billabongs (previously identified in Chapter 5 in Lintern *et al.*, in preparation-a) to heavy metal profiles. These comparisons suggested that high As levels in the sediments of Willsmere and Bolin Billabongs most likely result from overbank flood events of the Yarra River, which transported the As mobilized by mining activities in the upper Yarra River catchment in the late 19th and early 20th century into the billabongs. Similarly, the correlation between high Cr levels and the occurrence of discrete flood layers in the sedimentary records indicate that the Cr in the billabong sediments is largely deposited by overbank fluvial floods.

When the occurrence of flood-deposited sediments through the sediment cores were compared to high resolution pollution profiles, a slight correlation was detected between high Cu, Pb and Zn concentrations and the occurrence of flood-deposited sediments in Bolin Billabong in the latter part of the 20th century. This may be due to the input of stormwater into the river itself nearby Bolin Billabong. On the other hand, high Cu, Pb and Zn levels in the bed sediments of Willsmere Billabong appear to correlate negatively to the presence of overbank fluvial deposits. Furthermore, the fact that Willsmere Billabong has experienced a greater increase in Cu, Pb and Zn concentrations compared to Bolin Billabong suggests that local catchment sources such as the urban stormwater draining into Willsmere Billabong may be the key source of Cu, Pb and Zn in the Willsmere Billabong bed sediments.

In addition, understanding the relative contribution of overbank fluvial flooding to the contamination of billabong bed sediments allows us to pinpoint the mitigation strategies that should be implemented to reduce contamination levels in the billabong bed sediments. For example, the slight positive correlation between the occurrence of flood events and Cu, Pb and Zn levels in the Bolin Billabong bed sediments suggests that mitigation strategies of Bolin Billabong should focus on reducing the level of heavy metals entering the billabong via overbank flooding. This could be done by reducing the heavy metal inputs into the main river channel. On the other hand the negative correlation between the occurrence of flood events and Cu, Pb and Zn levels in the Willsmere Billabong bed sediments suggest that mitigation strategies of Willsmere Billabong should not focus on reducing heavy metal transport via overbank flooding of the Yarra River. Instead, the heavy metals entering through other sources, such as urban stormwater, should be reduced.

This chapter also provided Pb and Zn concentrations in Bolin Billabong and Willsmere Billabong flood deposits. The cumulative density functions of Pb and Zn concentrations in flood-deposited sediments (created using the flood deposits identified by the Traditional Method) show the range of Pb and Zn concentrations in flood-deposited sediments of approximately the last 100 years. In addition, a relationship was developed between Pb and Zn concentrations in sediment deposits of the two billabongs and the average daily flow in the river whilst each 0.5-cm thick sediment layer was being deposited in the billabong. Although there are uncertainties in these relationships, they provide rough estimates of the relationship between Pb and Zn concentrations occurring in the billabong deposits and river flow rates during the last 100 years.

7.5 Conclusion

The key messages of this chapter are the following:

- hydrologic trends, particularly the identification of discrete flood deposits in sediment cores, can be used in conjunction with the pollution profiles to better understand the sources and transport processes of heavy metals in aquatic systems,
- this understanding aids in the identification of the key mitigation strategies for reducing pollution of the aquatic systems, and
- the methodology presented in this chapter can assist in enhancing our understanding of the quality of flood-borne sediments deposited in inundated areas and the risk that these flood deposits pose to humans and the natural environment; as demonstrated by the creation of cumulative distribution functions of flood deposit quality in the 20th century, and the development of relationships linking river flow characteristics with sediment deposit quality in billabongs.

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CHAPTER 8
FINAL DISCUSSION AND CONCLUSIONS

8.1 Introduction

The main aim of this PhD was to determine the historical pollutant concentrations within sediments deposited by overbank fluvial floods, using sediment cores. In trying to achieve this aim, four key research objectives were addressed:

- to identify the historical contamination trends in the Yarra River billabongs using sedimentary records;
- to identify discrete fluvial flood deposits in sediment cores from the Yarra River billabongs;
- to assess the uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution trends in aquatic systems; and
- to use sediment cores to identify the contaminant levels in flood-deposited sediments in the Yarra River billabongs.

There were both strengths and weaknesses in the manner in which these four objectives were investigated. As such, this chapter will present the key conclusions and findings of this work after a detailed discussion of these strengths and weaknesses.

8.2 Strengths and Weaknesses

8.2.1 Research objective 1: To identify the historical contamination trends in the Yarra River billabongs using sedimentary records.

Strengths.

1. An understanding of the history of the Yarra River catchment was employed to identify the factors affecting the dated pollutant profiles identified using the sediment cores.

   This is the first time that historical pollution records have been reconstructed for the Yarra River catchment. One of the strengths in the work presented in Chapter 4 is that an understanding of catchment history was used to help explain the historical pollution trends identified in the dated Willsmere and Bolin Billabong sediment cores. The trends in toxicant concentrations through the sedimentary records (heavy metals for both Willsmere and Bolin Billabongs and persistent organic pollutants for just Willsmere Billabong) were compared to population, car ownership and catchment development data in order to identify the main factors affecting the dated pollutant profiles. Knowledge of when certain technologies and pollution mitigation policies were adopted was also utilized to understand why certain shifts occurred in the pollution states of the two billabongs. This understanding of the catchment (particularly of the local Willsmere Billabong catchment) helped us infer that urban stormwater even from purely residential catchments can have a deleterious effect on the

pollution states of aquatic systems. This finding suggests that aquatic systems are at risk from residential developments, and that the implementation of strategies (e.g., stormwater treatment tools) for the protection of existing waterways should beconsidered in future residential development plans.

2. The performance of a pollution mitigation tool (stormwater treatment wetland) was assessed using the dated pollutant records from Willsmere Billabong.

   A stormwater treatment device (a stormwater treatment wetland) was installed in the local Willsmere Billabong catchment in 2006 to treat urban stormwater from the 1.8 ha local residential catchment prior to its discharge into Willsmere Billabong. Whilst a decrease in heavy metal concentrations was detected in the dated pollution profiles of the Willsmere Billabong cores after the construction of this wetland, the heavy metal levels did not return to pre-disturbance levels. By including a field site that has recently experienced the implementation of a pollution reduction strategy, this thesis has helped demonstrate that sediment cores can be used to assess how successful structural pollution reduction strategies have been in reducing pollution states. This methodology has the potential to be applied to other aquatic systems currently undergoing remediation, to assess the success of these projects.

Weaknesses.

1. How pollution trends are affected by the proximity of the aquatic system to urban centres, was not fully explored.

   A sediment chronology could not be developed for the Yarra Flats Billabong due to sediment dredging that occurred in the late 1990s. Thus, the pollution trends at this site were not studied in this project. It was originally envisaged that a comparison between historical contamination trends of the billabongs within metropolitan Melbourne (Willsmere and Bolin Billabong) and the Yarra Flats Billabong (outside metropolitan Melbourne) would help elucidate and quantify how land use and proximity to urban areas affects pollution in aquatic systems. The catchment of the Yarra Flats Billabong has been used for agriculture and grazing over almost two centuries. However, even without the pollution trends from the Yarra Flats Billabong, Willsmere and Bolin Billabong had enough variability in their catchments (in terms of land-use) that the impact of residential stormwater and urban growth on pollution levels of aquatic systems could be demonstrated using these two billabongs.

2. Sub-samples from Willsmere Billabong sediment cores (W1 and W4) were not used to date the pollutant concentration profiles.

   In Chapter 4, W4 and W1 were dated by correlating these cores to a Willsmere Billabong sediment core for which a sediment chronology had been developed in a previous study (Leahy, 2007). Sub-samples from W4 were not analysed for radio-isotopic activities due to lack of access to a radiochemistry laboratory at the time that the work in Chapter 4 was being completed. Only one sample from W1 was outsourced to a commercial laboratory for ^{14}C dating due to financial limitations. The analysis of multiple sub-samples from W4 and W1 would have led to more precision in the dating of the pollution profiles.

   However, access to radiochemistry laboratories was gained later and as such, W4 was dated using ^{210}Pb and ^{137}Cs activities, and W1 was re-dated using two ^{14}C dates. This newer age-depth model was used in Chapters 5 to 7. The age-depth model used in Chapter 4 was very similar to the model developed in Chapter 5. This suggests that the core-correlation methodology used in Chapter 4 to date W4 and W1 did not have a significant impact on the interpretations of the pollution profiles.

3. The Bolin Billabong sediment cores did not contain extensive records of pre-European sediment accumulation.

   The Bolin Billabong sediment cores obtained specifically for this PhD project in 2013 did not contain pre-European sediments. This is because I could not gain permission to take cores more than 2-m long from the billabong. A longer core (2.9 m) had previously been taken from Bolin Billabong by Leahy (2007) in 2001 and analysed for heavy metal concentrations. As the longest core containing the oldest sediments, these previously obtained heavy metals data were used in Chapter 4. Four sediment sub-samples were obtained and analysed from the part of the sediment core deposited before 1850, which is assumed to be the start of disturbance in the Yarra River catchment. The temporal variability in heavy metal sediment concentrations prior to catchment disturbance therefore could not be assessed in detail and compared to post-disturbance sediment concentrations. Thus, it could not be verified that post-disturbance sediment concentrations were outside the range of natural variability in heavy metal concentrations under background conditions.

Longer sediment cores were obtained from Willsmere Billabong, which dated back to approximately the early 1300s CE. Given the minimal down-core variability in the heavy metal concentrations of seven pre-disturbance sediment sub-samples from W1, it is unlikely that there would have been large variations in the pre-disturbance heavy metal concentrations in Bolin Billabong.

8.2.2 Research objective 2: To identify discrete fluvial flood deposits in sediment cores from the Yarra River billabongs.

Strengths.

1. High resolution data from three locations in the Yarra River catchment were used to identify Zr/Rb as a proxy for particle size.

   An element or elemental ratio that can represent particle size was determined by using both laser diffraction to measure particle size on sediment sub-samples and micro-XRF to measure elemental composition at a high resolution (0.5 cm and 1 cm) through sedimentary records from three billabongs (Willsmere, Bolin and Yarra Flats Billabong). This resulted in the analysis of over 300 samples for the determination of a particle size proxy.

   The inclusion of sub-samples from three different billabongs enabled us to demonstrate the applicability of Zr/Rb as a proxy for median particle size (D_{50}) throughout the whole Yarra River catchment. The high resolution of the sub-sampling in addition to the large number of samples used for the analysis increases our confidence about both the precision and the accuracy of this proxy, allowing us to use Zr/Rb, instead of particle size measured using laser diffraction, to identify historical hydrologic trends in the sedimentary records. As discussed in the literature review, previous studies that assessed the applicability of Zr/Rb as a particle size proxy were not based on such rigorous methods. However, we acknowledge that based on the elemental composition of the geological deposits of catchments, the appropriate particle size proxy may vary. This study has demonstrated a methodology that should be adopted when validating the applicability of Zr/Rb as an indicator of particle size outside of the Yarra River catchment.

2. Multiple lines of evidence were used to identify both the overall historical trends in hydrology and discrete flood layers.

   A multi-proxy approach was adopted in this study to infer the historical hydrology of Willsmere and Bolin Billabongs using sedimentary records. This is especially apparent in the multiple lines of evidence used to calculate the Flood Signal Strength. In addition, the overall hydrologic trends and the flood layers identified in the sediment cores were checked using an additional line of evidence – historical measured flow records. The use of multiple lines of evidence enabled greater confidence that the hydrological trends and flood layers had been correctly identified using the sedimentary records.

Weaknesses.

1. The longest continuous dated sediment core from Willsmere Billabong could not be used to identify historical hydrologic trends due to errors in the micro-X-Ray Fluorescence (XRF) core scanning.

   As the ITRAX micro-XRF core scanner used in this study cannot scan a core that is more than 1.8 m long, sediment cores exceeding this length (e.g., W1) had to be scanned in several sections. However, when scanning W1 (introduced in Chapter 4) there were discrepancies in the micro-XRF readings between the ends of two adjacent sections from the same core. In other words, the elemental abundances detected at the bottom of one section (i.e., one end of the cut) were noticeably different to the elemental abundances detected at the top of the next section (i.e., the other end of the cut). The equipment settings were kept constant over the multiple sections and therefore, it is unclear why these discrepancies occurred in the micro-XRF readings. As sub-samples from this sediment core had previously been dated using ^{14}C and pollen assemblages, the original plan was to use this core to identify long-term changes in the hydrology of Willsmere Billabong.

   Micro-XRF results of W2001 (introduced in Chapter 5) were instead used to identify the long term changes in hydrology because there appeared to be no errors in the micro-XRF measurements for this core. W2001 was dated by correlating it to W1 using the magnetic susceptibility profiles. We believe that dating the Willsmere Billabong cores by correlating them to one another using their magnetic susceptibility profiles is a sound method because when comparing the Willsmere Billabong (W4 and W1) sediment chronologies developed in Chapter 4 and Chapter 5, it was demonstrated that sediment chronologies from one core can

be applied to another from the same billabong by correlating the magnetic susceptibility profiles.

2. It was assumed that all source rocks (i.e., sediment sources) from the Yarra River catchment were sampled and analysed. These sediment samples were used to identify the elements that were more concentrated in flood-borne sediment deposits compared to sediments conveyed by overland runoff from the local billabong catchments.

   Geological maps were used to identify the geological deposits in the Yarra River catchment upstream of Willsmere and Bolin Billabong, which contribute sediments to billabongs. However, resolutions of geological maps are quite coarse, and it is possible that some important sources of sediment into Willsmere and Bolin Billabong were not included on the map and therefore not sampled. Furthermore, it is uncertain whether variability in elemental composition within geological deposits has been adequately represented by the sampling methodology. Regardless of these uncertainties, validation of the reconstructed flood record using measured flow data suggests that the rock and sediment sampling procedure was adequate in identifying flood deposits within the sedimentary records.

3. The chronologies for the Bolin Billabong cores were not very precise.

   As discussed previously in Chapter 5, the sediments below approximately 20 cm could not be dated using ^{210}Pb, due to the non-monotonic decrease in the unsupported ^{210}Pb activities. Whilst ^{137}Cs and plutonium activities were also analysed in the top 70 cm of B5, detection was either too low (^{137}Cs) or no peak in activity could be detected (plutonium). As such, the chronology of B5 below 20-cm depth was developed by correlating B5 to the core from Willsmere Billabong (W4), for which there was a more precise sediment chronology. Whilst these are able to provide approximate dates, precise ages could not be assigned to the sediment deposits.

4. The pre-European hydrology of Bolin Billabong could not be determined because the cores were not long enough.

   In previous section (Section 8.2.1), it was discussed that sediment cores containing pre-European sediments could not be obtained and that this hindered our ability to identify background heavy metal concentrations. This also made it difficult to infer the pre-disturbance hydrological trends of Bolin Billabong. Although the Bolin Billabong core obtained in 2001 (Leahy, 2007; Leahy *et al.*, 2005) contained an approximately 30-cm thick layer of pre-European sediments, this core was no longer available for micro-XRF core scanning as it had

been opened and sub-sampled in 2001. As such, this sedimentary record could not be used to determine historical hydrologic trends. Whilst the pre-European hydrology of Bolin Billabong could not be identified in this study, previous works (Leahy, 2007; Leahy *et al.*, 2005) suggest that the characteristics of pre-European sediment deposits and the diatom flora in Bolin Billabong are similar to those of Willsmere Billabong. As such, it is assumed that the pre-European hydrological conditions of Bolin Billabong are similar to that determined for Willsmere Billabong.

5. Further checking of the reconstructed hydrological trends and identified flood layers is required.

   The long-term Yarra River streamflow observations used to check the hydrologic trends inferred from the sedimentary records were missing data between 1934 and 1959 and between 1969 and 1974. This was a period with a significant increase in water extractions, with the construction of the Upper Yarra Reservoir in 1957. It would therefore be expected that the flow regime of the river would have experienced a large shift during this period. We would be able to have more confidence in the method used to identify historical hydrologic trends if the dataset used to confirm the reconstructed trends was not missing this crucial period in the history of the Yarra River.

   Furthermore, there was some uncertainty in the age-depth model that was used to identify the timing of the flood-deposited layers. Being unable to obtain precise dates for sediment deposits meant that accuracy of the Flood Signal Strength was checked using five year averages. This means that we evaluated the ability of the Flood Signal Strength to identify the likelihood that a sediment layer deposited over a five year period was due to an overbank flood, rather than the effectiveness of the Flood Signal Strength in identifying the likelihood that a 0.5 cm sediment layer was due to an overbank fluvial flood.

   Regardless of these limitations, the promising comparison of the measured flow data and the reconstructed hydrological trends presented in this thesis suggest that it is likely that the framework used to identify historical trends in hydrology and identify flood layers is reliable, and will continue to improve with increased precision in sediment dating.

8.2.3 Research objective 3: To assess the uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution trends in aquatic systems.

Strengths.

1. A large dataset was used to identify the relationship between heavy metal abundances obtained by micro-XRF and heavy metal concentrations obtained by ICP-MS.

   Heavy metal abundances were measured using micro-XRF at 1-cm intervals through sediment cores from both Willsmere and Bolin Billabongs (W4 and B3). In addition, heavy metal concentration (in terms of dry weight) was determined at 1 cm intervals through both cores using ICP-MS. This resulted in a dataset of approximately 490 points that could be used to evaluate the accuracy and precision of micro-XRF heavy metal results.

   To our knowledge, previous studies have not used such large datasets to identify the relationships between micro-XRF heavy metal profiles and heavy metal profiles developed using more traditional analytical methods (e.g., ICP-MS or conventional XRF). The size of the dataset was critical in ensuring that correlations between the heavy metal levels obtained using micro-XRF and ICP-MS were statistically significant. Furthermore, the fact that the data were from cores from two different billabongs increased the robustness of the analysis, making it more likely that the relationships identified are applicable to sediment cores from other sites within the Yarra River catchment.

2. The spatial and temporal variability between heavy metal profiles from sedimentary records were assessed using high resolution heavy metal profiles.

   Previous studies have not systematically quantified the differences in heavy metal profiles due to spatial variability or post-depositional mobilisation. Spatial variability between the heavy metal profiles of three sediment cores from Willsmere Billabong was assessed using heavy metal measurements obtained at 0.5-cm intervals through the three cores. This high resolution enabled the assessment of spatial variability in short-term fluctuations in heavy metal trends. Similarly, the effects of post-depositional mobilization on sediment core heavy metal profiles was assessed using heavy metal concentrations obtained at a high resolution (1-cm intervals) through cores taken ten years apart from each other. This also enabled the assessment of the effect of post-depositional mobilization or transformation on short-term fluctuations.

The findings in Chapter 6 indicated that whilst overall trends in heavy metals may be similar regardless of the location from which the core was taken, there can be considerable short term fluctuations. Thus, to assess the true uncertainty in heavy metal profiles due to the spatial variability of heavy metal deposition and accumulation, it is critical to use high resolution measurements of heavy metals.

Weaknesses.

1. There were some uncertainties in the measurement of heavy metal inputs into Willsmere Billabong during the 12-month field monitoring, thereby introducing uncertainty in the comparisons between bed sediment heavy metal levels and heavy metal inputs into Willsmere Billabong.

   Firstly, overbank flooding of the Yarra River did not occur during the 12-month monitoring period of Willsmere Billabong. As such, the effect of overbank flooding on the quality of billabong sediment deposits and the billabong water column could not be determined. However, the contribution of non-flood metal sources (e.g., urban stormwater, atmospheric deposition) to heavy metal levels depositing on the bed sediments of Willsmere Billabong could be determined. This allowed us to find that the heavy metal masses deposited on the bed of Willsmere Billabong generally correlate to the heavy metal masses entering Willsmere Billabong.

   There were also difficulties in quantifying the heavy metal inputs into Willsmere Billabong via stormwater and atmospheric deposition. The diameter and the location of the stormwater drain into Willsmere Billabong did not allow for the installation of an auto-sampler. Whilst several stormwater grab samples were obtained, it is not certain how accurately these grab samples represent Event Mean Concentrations (EMCs). In addition, the dust-deposition gauge could not be collected as soon as it was filled with rainwater. Whilst (1) it was verified that the mass of heavy metals deposited in the dust deposition gauge had no relationship to the volume of overflow occurring, and (2) we corrected for this error, there is still some uncertainty in the atmospheric metal influxes evaluated for Willsmere Billabong. However, the modelled masses of particulates and heavy metals in stormwater and atmospheric deposition were comparable to literature values of total suspended solids and metals in urban stormwater and total particulates and metals in atmospheric deposition. This suggests that

the errors in the modelled particulates and heavy metals masses in stormwater and atmospheric deposition were negligible.

Finally, there were limitations in the sampling methodology of the water column. One grab sample was taken of the water column just before the sediment traps were retrieved each month. However, it would have been more effective to sample several locations through the billabong and at different depths in the water column to capture the spatial variability in heavy metals in the water column. Conversely, the use of a passive sampling device may have been able to more effectively capture fluctuations in water quality over time, so that these fluctuations could then be compared to the heavy metal content of sediments settled in the sediment traps. Despite the inability to accurately detect the heavy metal concentrations in the water column, we were able to verify that the heavy metal masses deposited on the bed sediments were representative of the heavy metal inputs (stormwater and atmospheric deposition) into the billabong, using a mass balance model.

2. Micro-XRF results were not consistent between cores, which meant that one core had to be excluded from the spatial variability uncertainty analysis and micro-XRF measurements of W4 and W2001 could not be used to assess the post-depositional mobilization uncertainties.

   Micro-XRF data for one group of sediment cores (B3, W4, W1-1, W3-1) were obtained in November of 2013, using the ITRAX core scanner. A second group of cores (W2001 and W5, which is discussed briefly in Chapter 4) was analysed in the same core scanner nine months later, in August 2014. It was intended that W4, W5, W1-1 and W3-1 would be used to assess spatial variability in heavy metal profiles and that the micro-XRF heavy metal trends of W2001 would be compared to W4 to evaluate the influence of post-depositional transformation on heavy metal profiles in sediment cores. However, the X-Ray molybdenum tube was replaced in the nine month period between the two micro-XRF core scans. As a result, the micro-XRF readings obtained for the cores scanned in August 2014 differed in magnitude to those of the cores scanned in November 2013 and the micro-XRF results for W5 and W2001 could not be compared to those of W4, W1-1, and W3-1.

   However, there were ICP-MS results that could be used to compare the heavy metal composition of W2001 and W4, and three cores (W1-1, W4, W3-1) scanned in November 2013 (the first round) already represented different coring locations within Willsmere Billabong. Thus the exclusion of W5 and W2001 did not greatly hinder the assessments of spatial

variability and post-depositional mobilisation. It is also for this reason that the micro-XRF heavy metal abundances of W2001 were not used to assess the ability of micro-XRF to accurately represent heavy metal concentrations in sediments, even though there were both micro-XRF heavy metal abundances and ICP-MS heavy metal concentrations available for W2001.

3. The sediment cores used to evaluate the effects of spatial variability and post-depositional mobilisation on sediment core heavy metal profiles were not dated.

   Some of the sediment cores used to assess spatial variability uncertainties (W1-1, W3-1) and post-depositional mobilization uncertainties (W2001) were not dated due to financial constraints. Therefore, the effect of spatial variability and post-depositional mobilization could not be assessed by comparing sediments deposited in the same time period (e.g., the same year or decade).

   Instead, the main sedimentary (or lithological) units in the cores were identified in the cores and these sedimentary units represent sediments that would have been deposited in the same time period. The heavy metal levels in each sedimentary unit were compared across the cores. Sedimentary units were identified primarily using visual assessment of the stratigraphy (i.e., using the optical and radiographic images of the cores) and magnetic susceptibility profiles. It is unlikely that dating all four cores would have significantly changed the spatial variability or post-depositional mobilization uncertainties presented in Chapter 6.

8.2.4 Research objective 4: To use sediment cores to identify the contaminant levels in flood-deposited sediments in the Yarra River billabongs.

Strengths.

1. Sediment cores were used to identify both historical hydrologic trends and historical pollution trends, and these two were compared to infer the sources and transport pathways of pollutants into the billabongs.

   In Chapter 7, the sources and transport processes of heavy metals into Willsmere and Bolin Billabong were identified by comparing the historical hydrologic trends with the historical pollution profiles identified in sedimentary records. This enabled us to identify pollution levels within stormwater, overland runoff, and fluvial flooding. For example, it confirmed previous

findings from Chapter 4, that elevated arsenic (As) levels in the Willsmere and Bolin Billabong cores were a result of As mobilized by mining in the upstream reaches of the Yarra River catchment, and transported into the billabongs by fluvial flooding. This method has the potential to be applied to other aquatic systems, to better understand the sources of pollution, and thereby design targeted plans for reducing pollution levels in these systems.

This methodology also enabled us to identify the heavy metal concentrations in flood-deposited sediments in Willsmere and Bolin Billabong. This is both the first time that the heavy metal concentrations in flood deposited sediments in the Yarra River catchment have been identified, and the first time that ranges and distributions in heavy metal concentrations in fluvial flood-deposited sediments have been presented. This methodology can be applied to other river systems, to enhance understanding about the risks of contamination of flood-inundated areas, and thereby develop appropriate risk management strategies.

2. Two billabongs with varying degrees of connectivity to the urban stormwater drainage network were compared.

When addressing research objective four, the historical hydrologic trends and pollution trends of two billabongs were compared. Whilst one billabong receives a direct urban stormwater input (Willsmere Billabong), the other does not (Bolin Billabong). This enabled us to identify the effect of stormwater on both the hydrology and the pollution levels of these billabongs. The historical hydrologic trends identified for Willsmere Billabong and Bolin Billabong in Chapter 5 showed that stormwater can be a source of water and sediments to billabongs, helping to maintain lake levels when the frequency and magnitude of overbank flooding decreases. However, it was found that urban stormwater also transports significant amounts of heavy metals (lead; Pb, zinc; Zn and copper; Cu) into the billabong. As such, whilst there has been a plan proposed at Bolin Billabong to fill the drying billabong with treated stormwater, the history of Willsmere Billabong indicates that such schemes may lead to increased pollutant levels in the billabongs, which would also have negative effects on the ecosystem.

Weaknesses.

1. There were uncertainties in the relationships that link average daily river flow to Pb and Zn concentrations in billabong deposits.

   Although the Pb and Zn concentrations in Willsmere Billabong and Bolin Billabong deposits were plotted against average daily river flow (at points in the river adjacent to Willsmere and Bolin Billabongs) in Chapter 7 (Figure 7.5), there are uncertainties associated with these relationships as represented by the error bars (95% confidence intervals). These uncertainties likely arise from the fact that there are few data points used to develop the functions used to convert Flood Signal Strength into average daily flows, due to the gap in measured streamflow data in the 20th century.

   Whilst these uncertainties hinder the use of these relationships for predicting the exact Pb and Zn concentrations in future Willsmere Billabong and Bolin Billabong sediment deposits, the relationships are still able to provide a range of heavy metal (Pb or Zn) concentrations expected in a sediment deposit in Willsmere or Bolin Billabong given the average daily flow of the Yarra River during the period of sediment deposition.

8.3 Key findings

8.3.1 Historical contamination trends in the Yarra River billabongs identified using their sedimentary records

Firstly, the main sources of contaminants such as heavy metals and POPs into an aquatic system were identified using a dated bed sediment core. The pollutant trends identified in the sedimentary records were compared to an understanding of catchment history. For example, it was found that urban development and the introduction of motor vehicles have contributed to heavy metal and persistent organic pollutants (POPs) pollution of Willsmere Billabong. The **sedimentary records from Willsmere Billabong also suggest that urban stormwater from purely residential catchments contribute to the heavy metal and POPs pollution of urban aquatic environments**. This emphasises the need to incorporate stormwater treatment strategies in future residential developments that are created near waterways. In addition, it was demonstrated that **sediment cores can be used to evaluate pollution reduction strategies** such as stormwater treatment tools or pollutant emission regulations (e.g., banning of Pb-based petrol).

It was also identified that generic sediment quality trigger values for heavy metals provided by existing water quality guidelines in Australia (ANZECC/ARMCANZ, 2000) differ from site-specific background sediment metal concentrations at Bolin and Willsmere Billabongs in the Yarra River catchment. This highlights the **importance of identifying site-specific background concentrations when developing sediment quality targets or when assessing the pollution state of aquatic environments**. We have shown that these site-specific background concentrations can be obtained using sediment cores that contain sediments deposited before catchment disturbance.

8.3.2 Historical hydrologic trends of the Yarra River billabongs identified using their sedimentary records

Long-term hydrologic trends of the Yarra River and its billabongs were reconstructed using sedimentary records from Willsmere and Bolin Billabongs. Overall trends in hydrology were identified using sediment characteristics such as magnetic susceptibility, organic matter, particle size and elemental composition. It was found that **prior to the 20th century Willsmere and Bolin Billabong received fluvial inputs regularly, but became increasingly disconnected from the river in the late 20th century**.

In addition, two methods for identifying discrete flood layers in sediment cores were identified. One of these methods used traditional flood layer identification methods (e.g., presence of laminations, high magnetic susceptibility, low organic matter, high grain size). The second method used the elemental composition of sediment deposits, in addition to the traditional markers to identify likely flood layers. Elemental composition had not previously been utilized as a proxy for identifying discrete flood events. The reconstructed overbank flood records were checked using actual flow records of the Yarra River through the 20th century. **The study demonstrated that the use of elemental composition of sediments, in conjunction with magnetic susceptibility, particle size and inorganic matter content, can be used to identify discrete flood-deposited sediment layers in sediment cores. This method could potentially be applied when analysing sediment cores from other river systems for environmental flow management purposes.**

8.3.3 Uncertainties associated with using sediment cores to reconstruct historical heavy metal pollution of aquatic systems

A framework that conceptualizes the uncertainties associated with reconstructing historical heavy metal pollution trends in aquatic systems using sediment cores was presented. This framework not only summarises the main sources of uncertainties, but also presents the linkages between them. The sources of uncertainties identified in this framework include: spatial variability, sub-sampling intervals, analytical methods, loss of metals during settlement and post-depositional mobilization. Whilst it is acknowledged that there can be large uncertainties when sediment cores are used to reconstruct historical environmental changes, these have not previously been quantified.

This work indicates that main source of uncertainty differs depending on the heavy metal being studied. The largest source of uncertainty for most metals appears to be the assumption that metal inputs into the billabongs are deposited on the bed sediment. However, the analysis has shown that over a 12-month monitoring period, **the fluctuations in the bed sediment metal masses reflected variability in the inputs, which increases confidence in the use of sediment core heavy metal profiles for identifying historical pollution trends.** It is envisaged that the uncertainty framework, and the quantified sources of uncertainties in Chapter 6 can be used by other researchers in the future to plan sediment core sampling strategies, and analyses that minimize and correct for these uncertainties.

8.3.4 Contaminants in flood-deposited sediments in the Yarra River billabongs identified using sediment cores

The trends in sediment properties (used to infer historical hydrologic trends), juxtaposed with pollutant profiles for the Willsmere and Bolin Billabong sediment cores helped to confirm the main drivers for heavy metal pollution, which were previously identified using just the dated pollutant profiles in Chapter 4. It was demonstrated that an understanding of sediment characteristics, and hence historical hydrological trends, greatly aids in identifying contaminant sources. In particular the negative relationship between the occurrence of flood-deposited sediments (as inferred from the two flood deposit identification methods proposed in the thesis) and the concentration of Cu, Pb and Zn in the sediment deposits suggested **the deleterious contribution of residential stormwater on Willsmere Billabong**. This indicates that heavy metal pollutant reduction strategies in Willsmere Billabong should focus on the stormwater drain. However, the slight positive correlation between the Flood Signal Strength and Cu, Pb and Zn concentrations in Bolin Billabong in the latter half of the 20th century suggests that Bolin Billabong has received contaminants mainly from fluvial flooding. The **method demonstrated in this work (i.e., using both historical hydrological and pollution trends using sediment cores to identify pollutant sources) should be applied in future studies that aim to identify pollution sources of aquatic environments.**

The cumulative distribution functions of Pb and Zn concentrations in sediments that have been deposited by floods through the 20th century contributes to a better understanding of the level of heavy metals contained within flood-deposited sediments of the Yarra River. Comparisons between the heavy metal (Pb and Zn) concentrations in flood-deposited sediments and guideline sediment quality trigger values indicates that if these trigger values were used as a criteria to assess the contamination extent of sediment deposits, Zn concentrations in flood-deposited sediments at both billabongs have been below heavy metal trigger values, but the sediments that deposited during non-flood periods in Willsmere Billabong have been above trigger values. On the other hand, Pb concentrations in flood deposits have often exceeded recommended trigger values for both billabongs. **Thus, a dataset of the heavy metal contamination (Pb and Zn) of historical flood deposits has been developed for Bolin and Willsmere Billabongs. This dataset could be used for future predictions of heavy metal concentrations in these areas, much like in flood-frequency analysis.**

Finally, a relationship between average daily river flow rate and heavy metal concentrations within billabong deposits was provided. Whilst further investigation is required to refine this relationship, **the presented methodology can be applied to other river catchments for providing rough estimates**

of the concentration of heavy metals contained in sediments deposited in floodplains. **Not only will this help us identify remediation or mitigation priorities to combat water quality degradation of billabongs, but it will also increase our understanding of the risk management and flood-clean-up strategies that must be implemented during and after river floods.**

8.4 Further Investigation

8.4.1 Further investigations into the practical applications of historical pollution trends obtained using sediment cores

Reconstructing historical water quality data.

An understanding of the toxicant concentrations within flood deposits is critical during flood clean-up efforts. However, the quality of flood water is also an important issue that must be addressed to equip future generations to better cope with the likely increase in the frequency and intensity of floods. It is therefore worthwhile investigating whether historical sediment concentration data can be used to model historical water quality. The sediment quality data collected in this project could be coupled with existing models of the fate of pollutants in aquatic environments. One example is STUMP (Vezzaro *et al.*, 2010) and although this is a model of pollutant fate in stormwater treatment units, the model could be modified to simulate a natural lake, and be used to back-calculate the water quality using sediment concentration data (i.e., the known fate of the pollutants).

Furthermore, if historical water quality can be successfully modelled using historical sediment deposit concentrations, background concentrations of historical water quality (in terms of mg/L) could be developed and be used to assess trigger values of water quality currently provided in water quality and environmental monitoring guidelines (e.g., ANZECC/ARMCANZ, 2000).

Exploring the effect of water quality management strategies on the heavy metal levels in the sediments of Willsmere and Bolin Billabong.

This thesis provided a brief exploration of the effect of water quality management strategies on heavy metal concentrations in the sediments accumulating on the billabong bed sediments (e.g., removal of lead additives, the regulation of DDT). However, in the future (due to further sediment deposition) we may be able to pinpoint the effects of further water quality mitigation strategies such as the implementation of stormwater wetlands and/or the installation of rainwater tanks in the billabong catchments. As such, sediment cores should be taken from Bolin Billabong and Willsmere Billabong one or two decades from now, and the heavy metal levels in recent sediment deposits should be compared to past trends and background levels.

Correlating the trends in historical toxicant concentrations to trends in historical ecological conditions.

It is recommended that further work be conducted to link the trends in sediment toxicant concentrations with trends in indicators of species health (e.g., diatoms or chironomids) in sediment cores. This would be one way of identifying and quantifying the site-specific toxicant levels that may be correlated to past ecological shifts. These correlations could be used to develop site-specific sediment and water quality targets, so that water quality management plans can be developed based on not only an understanding of background or pre-disturbance conditions, but also on the level of ecosystem protection that is desired.

Identifying historical trends in heavy metal masses in sediment cores.

Trends in pollutant concentrations through sediment cores were the primary focus of this study. The focus on pollutant concentrations is justified because these are the means by which sediment and water quality are generally assessed, particularly for lentic systems such as the Yarra River (ANZECC/ARMCANZ, 2000). However, one disadvantage of assessing historical pollution trends using pollutant concentrations is that the trends can be affected by the bulk amount of sediments being deposited on the sediment bed. Toxicant masses and toxicant concentrations have different uses in ecological management, and it would therefore be worthwhile investigating toxicant masses buried in sediment cores and to use these data to estimate historical mass influxes.

8.4.2 Further investigations into the use of sedimentary records to understand historical hydrological trends

Applying Bayesian change point algorithms to sedimentary records to infer historical hydrological trends.

In this study, overall trends in hydrology were identified using hierarchical constrained cluster analysis to identify the points in the sediment core at which sediment characteristics change. Constrained cluster analysis is a statistical method that assesses the similarity of variables through sediment cores based on the magnitude of the variables included in the cluster analysis. Although observed streamflow data confirmed the hydrological trends reconstructed by applying constrained cluster analysis to sediment core data, we acknowledge that there are Bayesian change point algorithms (e.g., Dynamic Connectivity Regression; Cribben *et al.*, 2012) which can also be used to identify significant changes in sediment characteristics through the cores. In particular, the benefit of Dynamic Connectivity Regression would be that changes in the variability of sediment characteristics, instead

of just the magnitudes of the sediment characteristics, would be considered when determining the main change points within the sedimentary record. It is recognised that there is a further opportunity for using advanced statistical methods to interpret sedimentary records, not just for identifying historical trends in hydrology, but also for identifying historical environmental changes such as climate variability or fire regimes.

Applying flood deposit identification methods to other catchments.

Whilst an attempt was made in the project to verify the inferred hydrological trends to known flood occurrences, this was made difficult by two issues. First, that there was a significant period (approximately 25 years) of missing flow data; and second, there were uncertainties in the ages assigned to sediment deposits. As such, it is recommended that the methods used in this project to identify historical hydrology and identify discrete flood events be applied to another river catchment, preferably one which has a continuous streamflow record spanning over 100 years. Furthermore, it would be ideal if the sedimentary records contained a greater number of chronological markers, allowing for a highly precise age-depth model. Successfully applying the framework for inferring historical hydrological trends to another river catchment would increase confidence in the wide applicability of this method.

Investigating the use of mixing models for identifying discrete flood deposits within sediment cores.

Preliminary work conducted in this thesis indicated that existing linear and Bayesian mixing models such as SourceTracker (Knights *et al.*, 2011) were not suited to identifying discrete flood deposits within sedimentary records, particularly if some of the sediment sources themselves are mixtures of upstream sediment sources. It should be further investigated whether existing models can be adapted to accommodate for these 'mixed sources'. Analysis of prepared and known mixtures of sediments could be used to help validate the performance of these adapted models.

8.4.3 Further investigation of uncertainties in the use of sediment cores to reconstruct historical pollution trends

Quantifying uncertainties associated with building sediment chronologies.

Previous studies have quantified the uncertainties in age-depth modelling, and as such these were not explored in the thesis. However, these age-depth modelling uncertainties have not previously been compared to other sources of uncertainty in the development of historical pollution trends (e.g., spatial, sub-sampling interval, post-depositional mobilisation). Quantifying the uncertainties due to

age-depth modelling for Willsmere Billabong, and then comparing these to the uncertainties quantified in the thesis, would yield a more holistic understanding of the potential errors associated with developing historical pollution records of aquatic environments.

Identifying uncertainties for other aquatic environments.

It would be worthwhile to apply the uncertainty framework proposed in this study to additional aquatic environments. Whilst uncertainties associated with (1) post-depositional mobilisation of metals; (2) sediment sub-sampling; (3) spatial variability and (4) loss of metals during sediment settlement, were quantified for Willsmere Billabong, it is likely that the magnitude and significance of these uncertainties vary according to the physical and chemical characteristics of aquatic systems. It would be beneficial to identify whether there is a relationship between the physical or chemical characteristics of the aquatic systems (and their catchments), and the contribution of each type of uncertainty to the overall uncertainty framework. This will enable greater understanding in the level of uncertainty expected in the reconstruction of historical heavy metal pollution trends using bed sediment cores. From this, it will be easier to estimate the expected uncertainty in reconstructed historical pollution trends for specific systems without undertaking extensive field monitoring and data collection.

Creating an uncertainty framework for reconstructing historical POPs contamination using sediment cores.

Given the toxicity of POPs to both humans and the ecosystem, accurate reconstruction of historical POPs trends is critical. In this study however, the effect of post-depositional mobility on the interpretation of sediment core POPs profiles has not been measured. The differences between POPs in bed sediments and the influx of POPs into the aquatic system have not been quantified either. The post-depositional mobility of POPs could not be quantified in this study because the sediment core taken in 2001 (W2001) used for assessing the extent of post-depositional mobilization of toxicants, was stored in a Polyvinyl Chloride (PVC) pipe for over 10 years, which may have resulted in the leaching of POPs from the PVC pipe into the sediments during storage. In addition, the link between POPs inputs into the billabong and POPs settlement onto the bed sediment of the billabong could not be determined because POPs were below detection levels in both the inputs and the settled bed sediments during period of long-term field monitoring at Willsmere Billabong. These uncertainties should be quantified in the future so that the magnitude of uncertainty associated with reconstructing historical POPs trends is better understood.

8.4.4 Further investigations into the use of sediment cores to identify contaminant levels in flood-deposited sediments

Reducing uncertainties in the relationships between heavy metal concentrations of billabong sediment deposits and average daily river flow.

As discussed previously, there were uncertainties in the relationship between heavy metal concentrations of billabong deposits, and the average daily flow during the period of sediment accumulation. One way to do this would be to address the uncertainties in the function that converts the flood signal strength to average daily flows. This could be done by (1) increasing the precision in the age-depth model or (2) filling the gaps in the dataset of average daily flows by modelling the Yarra River flows over the 20th century.

Developing a model that accounts for the impact of urbanisation on concentration of heavy metals within flood deposits.

Further work should be conducted to adjust the heavy metal concentration in flood deposits identified in Chapter 7 according to the extent of urban development in the catchment at the time of the flood. It is important to take into account not only the effect of flood characteristics on the contaminant levels within flood-deposited sediments, but also how the extent of pollution generation activities within the catchment affects contaminant levels in flood deposits. This would enable the quantification of heavy metal concentrations in flood-deposited sediments at different stages of urban development. Frequency distributions for contaminant concentrations in flood-deposits could be developed for various levels of urbanisation. Such a dataset would be of great use in predicting the heavy metal contamination of future flood deposits of the Yarra River. If would also enable us to approximate pollutant concentrations in sediments deposited by floods in other river systems around the world.

8.5 References

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APPENDICES

APPENDIX A SUPPLEMENTARY MATERIALS

Appendix A.1 Supplementary materials for 'Using sediment cores to establish targets for the remediation of aquatic environments' (Chapter 4)

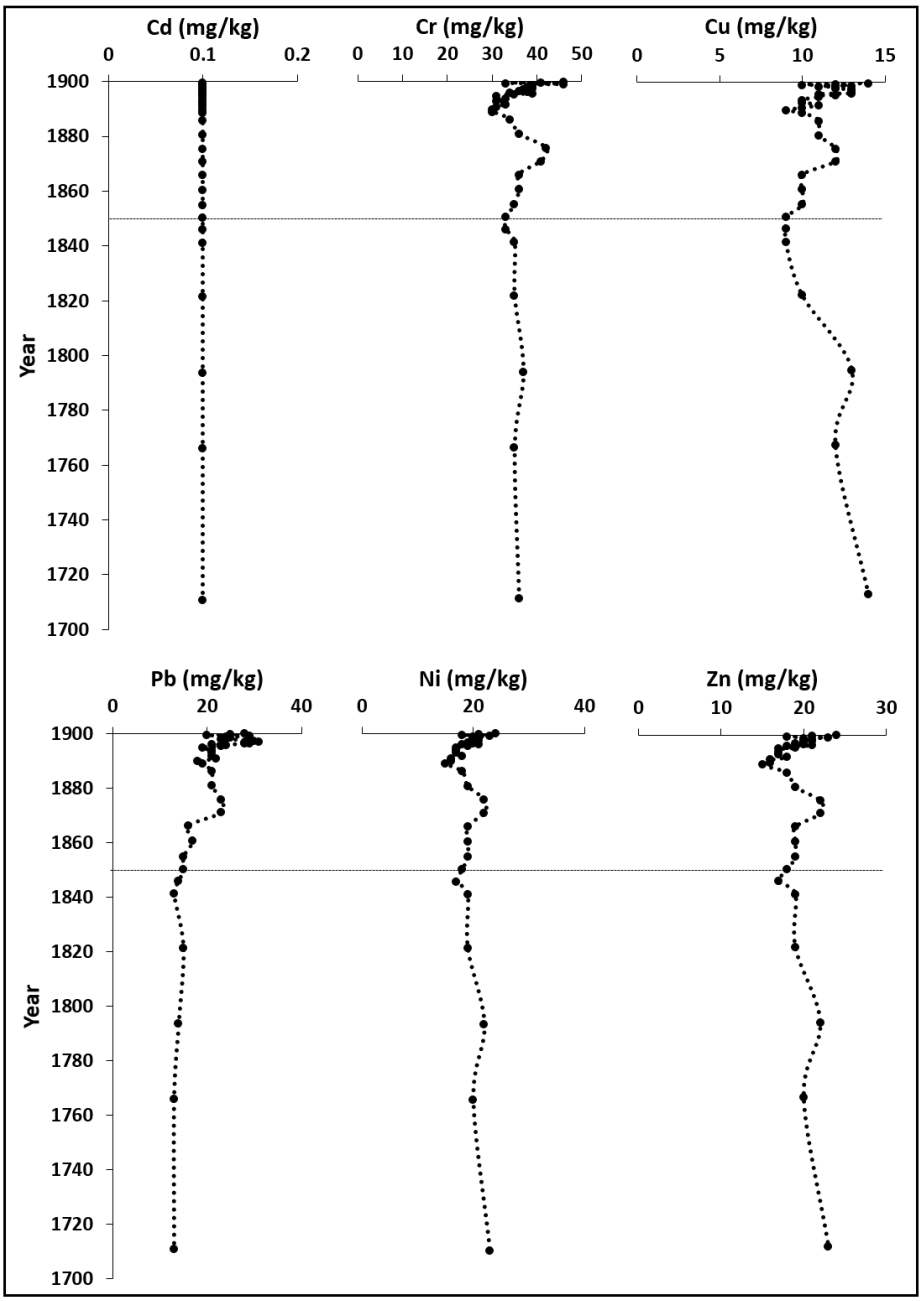

Figure S1: Heavy metal concentrations in 18th and 19th century deposits in the Willsmere Billabong sediment core (adapted from Lintern et al. 2015). Horizontal black dashed line represents 1850.

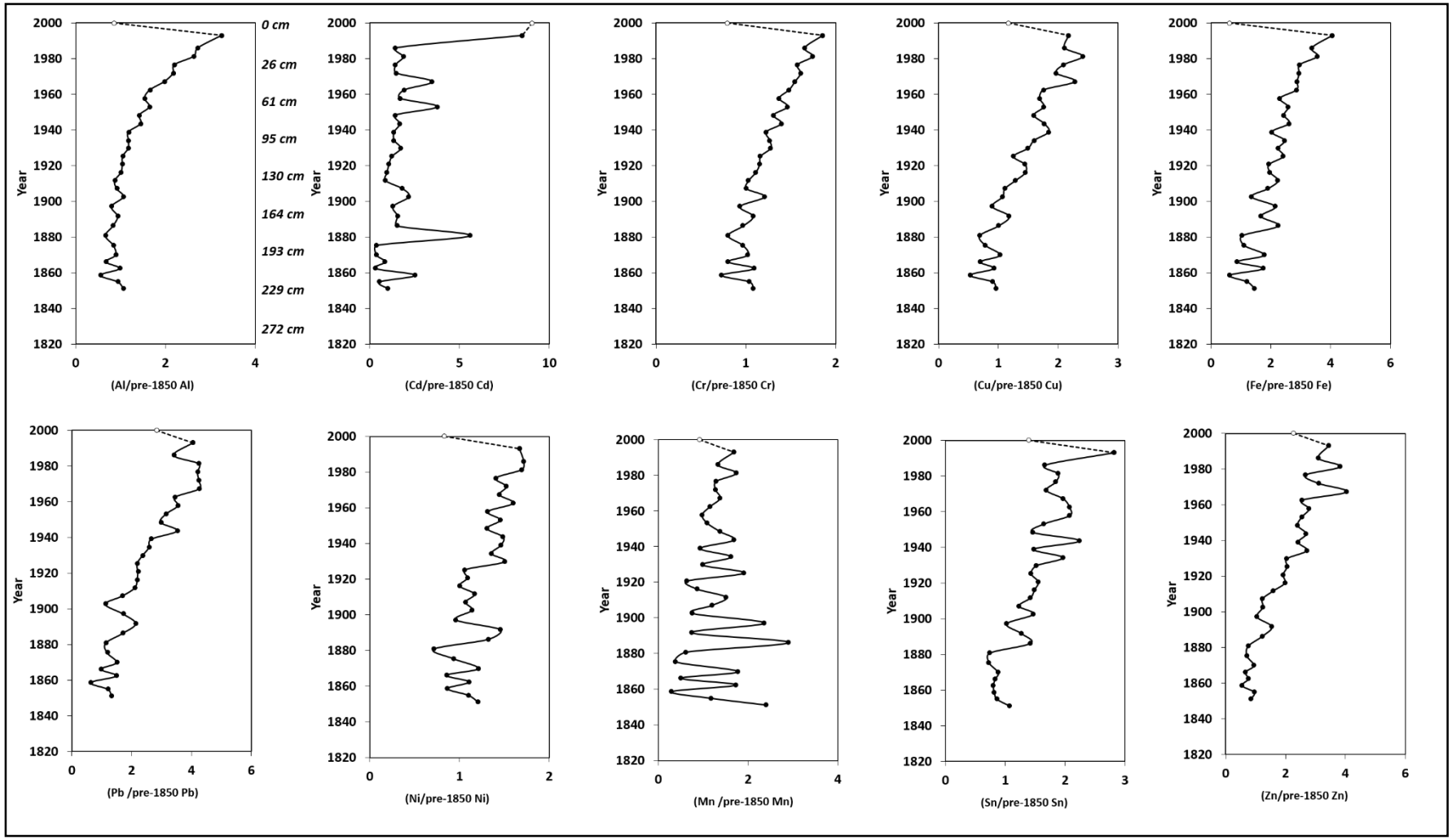

Figure S2: Metal profiles for Bolin Billabong, where metal concentrations are normalized by the average pre-1850 concentration of that metal. Sediment core depths provided on secondary Y axis of Al. Open circle and dashed line represents suspect data from the surface of the sediment core.

Table S1: P-values obtained in the Shapiro-Wilk test for normality of metal concentrations identified in the Bolin Billabong sediment core. Asterisks (*) denote normally distributed elements (p>0.05).

	Metal concentrations									
	Al	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Ni**	**Mn**	**Sn**	**Zn**
P-value	8.4×10^{-5}	3.1×10^{-7}	0.28*	0.23*	0.74*	0.012	0.45*	0.30*	0.095*	0.031

Table S2: Metal concentrations at 8 cm intervals through the Bolin Billabong sediment core.

Depth (cm)	Year	Element concentrations (mg/kg-dry weight)									
		Al	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Ni**	**Mn**	**Sn**	**Zn**
0	**2000**	1736.5	1.7	10.3	13.4	5768.0	39.7	7.6	137.9	0.2	79.6
8	**1993**	6644.7	1.6	23.9	24.8	36877.3	56.8	15.3	251.0	0.5	121.0
16	**1986**	5570.1	0.3	21.3	24.1	30650.0	47.8	15.7	198.1	0.3	109.0
24	**1981**	5380.6	0.3	22.5	27.5	32390.1	59.5	15.5	259.5	0.3	134.7
32	**1977**	4498.2	0.3	20.3	23.9	26950.8	59.0	12.9	191.9	0.3	93.8
40	**1972**	4442.5	0.3	20.7	22.5	26772.6	59.6	13.9	189.8	0.3	109.2
48	**1967**	4045.7	0.6	19.9	26.1	26176.2	59.8	13.2	205.5	0.3	142.2
56	**1962**	3380.2	0.4	19.1	20.1	25994.5	48.4	14.7	171.9	0.3	89.7
64	**1958**	3134.7	0.3	17.7	19.3	20925.2	49.8	12.0	145.0	0.3	98.1
72	**1953**	3362.9	0.7	18.9	20.1	23447.5	44.2	13.3	162.6	0.3	89.4
80	**1948**	2898.1	0.3	16.8	18.2	22150.4	41.7	12.0	205.4	0.2	84.5
88	**1944**	2968.9	0.3	18.0	20.1	23748.0	49.5	13.6	251.2	0.4	94.6
96	**1939**	2406.8	0.3	15.8	21.0	18441.1	37.2	13.4	138.8	0.2	85.2
104	**1934**	2401.4	0.3	16.3	18.3	22359.6	36.2	12.4	241.9	0.3	95.4
112	**1930**	2392.3	0.3	16.4	17.1	20425.0	33.1	13.8	147.3	0.3	71.9
120	**1925**	2134.9	0.2	15.0	14.3	22006.9	30.7	9.7	284.6	0.2	72.3
128	**1921**	2120.6	0.2	14.8	16.5	17589.0	31.0	10.0	94.6	0.3	67.3
136	**1916**	2059.2	0.2	14.3	16.6	17962.4	30.7	9.2	129.0	0.2	69.6
144	**1912**	1779.3	0.2	13.3	14.7	20350.4	29.5	10.7	225.1	0.2	55.7
152	**1907**	1865.5	0.3	13.0	12.7	17263.0	23.6	9.8	179.4	0.2	43.1
160	**1903**	2174.9	0.4	15.6	12.3	12307.4	15.7	10.4	112.4	0.2	44.0
168	**1897**	1626.2	0.2	12.0	10.3	19511.1	24.1	8.8	352.1	0.2	36.9
176	**1892**	1910.4	0.3	13.9	13.5	15198.3	30.0	13.3	111.1	0.2	54.3
184	**1886**	1698.9	0.3	12.5	11.5	20448.5	23.9	12.1	432.9	0.2	43.0
192	**1881**	1351.8	1.0	10.3	7.9	9486.9	16.0	6.5	91.8	0.1	26.7
200	**1875**	1720.4	0.1	12.4	9.0	10034.5	16.6	8.6	57.0	0.1	24.9
208	**1870**	1818.0	0.1	13.1	11.8	16221.6	21.1	11.1	264.7	0.1	33.3
216	**1866**	1370.4	0.2	10.3	8.0	7933.2	13.7	7.8	75.6	0.1	23.2
224	**1862**	2007.9	0.1	14.1	10.6	15951.3	20.9	10.1	258.2	0.1	26.9
232	**1859**	1121.7	0.5	9.4	6.1	5702.3	8.8	7.9	43.8	0.1	19.4
240	**1855**	1923.6	0.1	13.4	10.4	11034.5	17.0	10.1	174.9	0.1	33.7
248	**1851**	2164.9	0.2	14.0	11.0	13178.7	18.5	11.0	357.5	0.2	29.6
256	**1847**	1789.0	0.1	11.9	8.8	8189.5	14.4	9.0	121.4	0.1	25.4
264	**1844**	1973.1	0.1	12.0	9.1	7495.8	14.6	8.5	112.5	0.2	24.7
272	**1840**	2381.2	0.4	14.7	16.4	11554.3	13.1	9.9	213.3	0.2	55.3

Table S3: Spearman Rank Correlation Coefficient (ρ) matrix of heavy metal profiles obtained from the Bolin Billabong sediment core. Asterisks (*) represent statistically significant correlations (p<0.05).

	Year	Al	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Sn	Zn
Year	1	0.80*	0.46*	0.87*	0.89*	0.93*	0.94*	0.19	0.76*	0.86*	0.92*
Al	0.80*	1	0.40*	0.97*	0.92*	0.81*	0.82*	0.27	0.81*	0.86*	0.89*
Cd	0.46*	0.40*	1	0.42*	0.43*	0.38*	0.35*	-0.060	0.38*	0.48*	0.46*
Cr	0.87*	0.97*	0.42*	1	0.95*	0.88*	0.88*	0.31	0.86*	0.89*	0.94*
Cu	0.89*	0.92*	0.43*	0.95*	1	0.90*	0.92*	0.31	0.85*	0.91*	0.97*
Fe	0.93*	0.81*	0.38*	0.88*	0.90*	1.00	0.94*	0.52*	0.82*	0.86*	0.92*
Pb	0.94*	0.82*	0.35*	0.88*	0.92*	0.94*	1.00	0.32	0.81*	0.88*	0.93*
Mn	0.19	0.27	-0.060	0.31	0.31	0.52*	0.32	1.00	0.37*	0.26	0.34*
Ni	0.76*	0.81*	0.38*	0.86*	0.85*	0.82*	0.81*	0.37*	1.00	0.79*	0.82*
Sn	0.86*	0.86*	0.48*	0.89*	0.91*	0.86*	0.88*	0.26	0.79*	1.00	0.94*
Zn	0.92*	0.89*	0.46*	0.94*	0.97*	0.92*	0.93*	0.34*	0.82*	0.94*	1.00

Table S4: Results of Mann-Whitney U-test for equal distributions (W statistics and p-values), comparing pre-1850 (n=4) and post-1850 (n=30) metal concentrations in the Bolin Billabong sediment core. Asterisks (*) represent statistically significant differences (p<0.05).

	Metal concentrations									
	Al	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Ni**	**Mn**	**Sn**	**Zn**
W statistic	71	84	90	92	106	109	91	57	91	98
p-value	0.59	0.22	0.12	0.09	0.01*	5.22×10^{-3}*	0.10	0.90	0.10	0.04*

Table S5: Results of Mann-Whitney U-test for equal distributions (W statistics and p-values), comparing pre-1850 Bolin Billabong (n=4) and pre-1850 Willsmere Billabong (n=6) heavy metal concentrations. Asterisks (*) represent statistically significant differences (p<0.05).

	Metal concentrations					
	Cd	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**
W statistic	21	0	14	20	0	0
p-value	0.15	0.01*	0.99	0.29	0.01*	0.07

Table S6: Spearman Rank Correlation Coefficient (ρ) matrix comparing trends in heavy metal concentrations in the Bolin Billabong sediment core and the number of dwellings in the City of Manningham and in the Yarra River catchment upstream of Bolin Billabong between 1921 and 2011; and comparing trends in heavy metal concentrations in the Bolin Billabong sediment core and the population in the City of Manningham and in the Yarra River catchment upstream of Bolin Billabong between 1851 and 2011. Asterisk (*) represents statistically significant correlations (p<0.05).

	Dwellings		Population	
	Dwellings (in the City of Manningham)	**Dwellings (in the Yarra River catchment upstream of Bolin Billabong)**	**Population (in the City of Manningham)**	**Population (in the Yarra River Catchment upstream of Bolin Billabong)**
Al	0.99*	0.99*	0.98*	0.97*
Cd	0.50	0.50	0.68*	0.67*
Cr	0.90*	0.90*	0.95*	0.95*
Cu	0.88*	0.88*	0.92*	0.91*
Fe	0.73*	0.73*	0.75*	0.74*
Pb	0.73*	0.73*	0.82*	0.82*
Mn	0.55	0.55	0.14	0.11
Ni	0.89*	0.89*	0.92*	0.90*
Sn	0.48	0.48	0.67*	0.64*
Zn	0.85*	0.85*	0.88*	0.87*

Appendix A.2 Supplementary materials for 'Digging up the dirty past: evidence for stormwater's contribution to pollution of an urban floodplain lake' (Chapter 4)

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Supplementary material

Digging up the dirty past: evidence for stormwater's contribution to pollution of an urban floodplain lake

Anna Lintern[A,C], *Ana Deletic*[A], *Paul Leahy*[B] *and David McCarthy*[A]

[A]Monash Water for Liveability, Department of Civil Engineering, Monash University, Clayton, Vic 3800, Australia.

[B]EPA Victoria, Monitoring and Assessment Unit, Ernest Jones Drive, Macleod, Vic. 3085, Australia.

[C]Corresponding author. Email: anna.lintern@monash.edu

Discussion of data used for normalisation

There are visible shifts in S intensities over time (Fig. S1) with highest levels occurring in the late 20th century. This is expected to increase the absolute Hg concentrations within the sediment core. Fig. S1 shows that although there is minimal intra-core variability in Al concentrations, Al concentrations were markedly higher in W1 compared with W4. As discussed in the text, we hypothesise that this results from spatial variability within the billabong.

Organic matter levels (Fig. S1) decrease in *c*. 1840, and remain low until the late 19th century. An increasing trend in organic matter levels into the 20th century is apparent. This variability in organic matter through the cores highlights the need to normalise the POP concentrations to organic matter, to ensure that the variation in organic matter levels is not influencing our interpretation of the POP profiles.

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Table S1. Heavy metal concentrations in W4 and W1

Depth	Year	Metal concentrations (mg kg^{-1})															
		Al	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Ti	V	Zn
W4																	
0	2012.0	18000	6	170	0.6	33	9	25	16000	59	87	0.16	21	15	11	22	260
1	2011.3	18000	7	170	0.8	32	9	26	15000	62	92	0.12	22	16	8	23	300
2	2010.5	18000	7	180	0.6	33	9	24	15000	62	100	0.12	22	17	13	24	320
3	2009.8	18000	7	170	0.6	33	9	24	15000	64	100	0.12	22	16	10	24	320
4	2009.1	18000	7	150	0.6	33	8	25	15000	62	92	0.12	21	14	13	25	260
5	2008.4	18000	6	160	0.5	32	7	23	15000	59	81	0.12	19	13	13	24	210
6	2007.6	18000	6	150	0.5	32	8	25	17000	57	93	0.12	21	14	12	24	260
7	2006.9	18000	6	210	0.5	32	11	24	16000	54	130	0.11	24	20	10	24	360
8	2006.2	16000	8	190	0.5	29	12	23	18000	52	110	0.1	25	19	7	25	350
9	2005.5	18000	10	180	0.8	33	13	29	16000	73	130	0.13	28	22	18	27	510
10	2004.7	18000	9	190	0.8	32	11	25	17000	76	130	0.13	24	22	8	25	440
11	2004.0	19000	6	150	0.4	34	7	22	17000	72	87	0.14	18	15	13	24	230
12	2003.3	18000	6	170	0.1	33	6	22	15000	70	80	0.13	17	15	13	22	170
13	2002.6	19000	5	160	0.1	34	6	21	16000	73	76	0.13	17	14	12	23	140
14	2001.8	19000	5	160	0.1	34	6	21	16000	69	76	0.13	17	14	16	24	140
15	2001.1	18000	2.5	160	0.1	33	6	20	17000	68	75	0.13	16	14	16	24	130
16	2000.4	19000	6	170	1	33	9	21	17000	75	100	0.13	21	17	16	24	270
17	1999.7	18000	6	170	0.6	32	8	22	16000	86	100	0.13	19	17	16	25	230
18	1998.9	18000	5	180	0.4	31	7	20	17000	80	120	0.12	17	19	19	24	180
19	1998.2	19000	6	190	1	32	9	22	16000	94	130	0.13	21	21	16	26	340
20	1997.5	17000	6	160	0.3	30	6	24	17000	120	90	0.14	16	16	22	24	160
21	1996.8	19000	6	180	0.7	32	9	19	17000	67	130	0.12	21	19	14	26	320
22	1996.0	18000	7	170	0.5	31	8	17	20000	60	110	0.1	20	18	16	26	270
23	1995.3	18000	2.5	160	0.4	31	7	19	17000	70	92	0.12	17	16	11	23	170
24	1994.6	18000	6	190	0.6	32	9	20	16000	75	120	0.12	21	19	11	24	330
25	1993.9	17000	6	210	0.5	29	9	19	15000	64	140	0.11	20	21	12	23	320
26	1993.1	18000	6	170	0.5	30	10	19	15000	67	150	0.11	21	19	11	24	310
27	1992.4	18000	6	160	0.5	31	10	21	16000	78	150	0.12	20	18	11	25	260
28	1991.7	18000	6	160	0.5	30	10	22	16000	79	150	0.12	20	17	13	24	270
29	1991.0	15000	8	130	0.5	26	14	23	18000	82	220	0.11	21	19	12	27	310
30	1990.2	14000	7	120	0.5	26	11	32	16000	79	160	0.11	19	16	11	26	290
31	1989.5	16000	7	150	0.4	27	9	30	19000	70	200	0.1	18	16	10	26	220
32	1988.8	19000	6	170	0.4	30	10	17	21000	63	320	0.11	19	17	11	28	180
33	1988.1	16000	11	130	0.6	27	12	25	23000	100	350	0.12	22	17	20	27	420

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Depth	Year	Metal concentrations (mg kg^{-1})															
		Al	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Ti	V	Zn
34	1987.3	16000	9	160	0.5	29	9	23	22000	95	200	0.12	18	16	15	26	310
35	1986.6	18000	8	160	0.5	31	11	21	23000	85	190	0.1	21	16	17	28	290
36	1985.9	17000	9	150	0.6	28	12	24	19000	86	160	0.11	22	16	11	26	310
37	1985.2	18000	13	140	0.8	32	15	29	19000	130	210	0.15	26	20	11	29	550
38	1984.4	17000	15	150	0.7	30	14	27	28000	150	280	0.14	25	21	15	31	540
39	1983.7	19000	9	150	0.5	32	11	21	24000	90	200	0.12	23	17	12	30	280
40	1983.0	16000	2.5	150	0.3	29	10	16	18000	48	130	0.09	19	15	11	25	120
41	1982.3	16000	7	140	0.3	29	11	17	19000	56	150	0.11	20	15	12	27	180
42	1981.5	17000	6	150	0.4	32	11	18	19000	61	130	0.11	21	15	11	27	180
43	1980.8	18000	8	170	0.4	32	13	18	21000	59	150	0.12	23	17	11	29	180
44	1980.1	14000	5	130	0.3	31	11	17	19000	41	130	0.1	24	13	20	26	150
45	1979.4	15000	7	140	0.2	27	13	21	25000	53	120	0.1	39	23	7	19	170
46	1979.0	16000	2.5	130	0.1	26	11	15	19000	30	86	0.07	28	18	6	19	120
47	1978.1	15000	2.5	130	0.1	25	10	16	20000	28	89	0.07	31	23	8	16	110
48	1976.2	16000	8	160	0.4	29	12	19	19000	72	130	0.13	26	15	10	25	210
49	1974.4	19000	8	160	0.6	36	11	20	20000	56	130	0.11	25	16	10	28	270
50	1972.6	14000	11	140	0.8	45	12	26	19000	61	150	0.13	31	16	16	26	370
51	1972.0	18000	18	170	0.9	36	10	26	25000	76	110	0.16	23	14	9	29	330
52	1969.9	16000	12	150	1.1	43	10	21	22000	43	110	0.13	24	14	12	26	250
53	1966.9	16000	15	150	1.3	41	13	24	22000	57	140	0.13	27	16	13	29	300
54	1964.0	16000	9	150	0.4	29	10	14	18000	37	110	0.08	17	13	15	28	120
55	1961.0	14000	6	120	0.3	27	9	13	16000	24	94	0.07	16	12	18	24	85
56	1958.0	17000	9	150	0.4	31	8	14	20000	32	79	0.09	18	11	21	28	97
57	1954.4	18000	15	170	0.9	35	13	21	20000	47	130	0.12	24	16	14	30	180
58	1950.8	18000	9	170	0.4	30	12	16	19000	37	110	0.09	20	15	11	28	130
59	1947.2	16000	8	160	0.3	28	10	14	18000	33	100	0.08	18	15	12	26	110
60	1943.6	17000	9	160	0.3	28	10	14	19000	34	96	0.07	17	14	6	25	100
61	1940.0	17000	9	160	0.2	28	9	14	19000	33	91	0.08	17	14	11	27	88
62	1936.4	16000	10	160	0.2	27	9	14	19000	33	96	0.07	17	14	13	25	87
63	1932.8	16000	11	160	0.2	27	11	15	18000	34	110	0.08	18	15	10	26	100
64	1929.2	17000	11	160	0.1	27	8	16	20000	36	85	0.1	16	12	12	26	78
65	1925.6	16000	10	160	0.1	26	11	14	18000	31	110	0.09	17	14	8	25	84
66	1922.0	17000	10	160	0.2	31	9	14	21000	30	120	0.07	19	15	11	27	79
67	1921.2	16000	8	160	0.1	33	10	13	21000	27	170	0.05	22	17	15	27	73
68	1920.3	18000	22	170	0.2	29	12	16	22000	38	150	0.07	21	16	9	29	97
69	1919.5	18000	27	170	0.2	29	14	17	23000	39	150	0.09	21	16	12	29	110

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Depth	Year	Metal concentrations (mg kg^{-1})															
		Al	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Ti	V	Zn
70	1918.7	16000	11	160	0.1	28	10	14	21000	33	92	0.08	17	13	12	28	74
71	1917.8	15000	11	150	0.1	26	10	15	18000	35	99	0.06	17	13	9	25	75
72	1917.0	13000	10	140	0.1	25	9	16	18000	39	95	0.06	15	13	10	25	58
73	1916.2	15000	10	160	0.1	25	11	12	17000	25	110	0.06	17	14	8	24	80
74	1915.3	14000	8	150	0.1	24	10	11	16000	22	100	0.06	16	13	9	23	67
75	1914.5	16000	8	180	0.1	27	11	12	20000	25	200	0.06	18	15	13	27	72
76	1913.7	15000	8	150	0.1	26	9	11	22000	23	130	0.06	15	12	12	27	57
77	1912.8	14000	7	160	0.1	25	11	10	18000	22	140	0.05	16	13	9	25	61
78	1912.0	14000	6	150	0.1	24	9	9	16000	18	110	0.025	15	12	20	24	49
79	1911.2	14000	6	150	0.1	24	9	9	18000	19	160	0.025	14	13	8	24	49
80	1910.3	13000	6	150	0.1	24	9	10	17000	20	140	0.025	14	13	8	23	51
81	1909.5	14000	6	160	0.1	25	10	10	19000	23	180	0.06	16	13	9	25	57
82	1908.7	15000	6	170	0.1	26	11	11	20000	23	200	0.06	16	14	11	26	52
83	1907.8	16000	6	180	0.1	28	11	11	21000	24	220	0.07	17	14	9	26	52
84	1907.0	15000	6	170	0.1	27	9	10	18000	21	120	0.06	17	13	10	25	48
85	1906.2	14000	6	150	0.1	25	8	10	18000	20	100	0.06	15	12	10	24	41
86	1905.3	14000	6	170	0.1	25	9	10	17000	19	120	0.06	16	13	14	25	45
87	1904.5	13000	6	150	0.1	24	8	9	16000	18	110	0.05	15	12	19	24	42
88	1903.7	15000	7	180	0.1	27	9	11	20000	22	200	0.07	16	14	14	26	46
89	1902.8	16000	6	190	0.1	28	11	12	23000	23	270	0.07	17	15	16	26	48
90	1902.0	12000	2.5	140	0.1	21	8	8	15000	16	120	0.025	13	12	17	21	36
91	1901.2	14000	7	160	0.1	25	9	11	18000	22	98	0.06	15	13	9	24	51
92	1900.3	15000	6	170	0.1	26	10	10	19000	22	150	0.06	16	14	8	24	52
93	1899.5	15000	6	180	0.1	27	10	10	20000	21	200	0.06	16	15	10	25	52
94	1898.7	14000	6	160	0.1	26	9	10	20000	20	190	0.07	15	14	13	24	47
95	1897.8	14000	5	160	0.1	26	9	10	16000	20	96	0.06	15	14	8	24	46
96	1897.0	15000	6	170	0.1	26	9	10	18000	22	92	0.06	15	14	9	25	49
W1																	
0	1927.2	25000	6	210	0.2	41	11	24	19000	85	110	0.15	27	22	86	34	200
1	1926.3	28000	6	190	0.1	42	10	23	20000	73	110	0.13	25	22	90	35	170
2	1925.3	27000	7	200	0.2	41	10	22	21000	76	110	0.13	25	22	80	35	220
3	1924.3	29000	10	210	0.6	44	14	25	23000	80	120	0.14	30	23	78	36	460
4	1923.3	27000	7	210	0.3	40	13	22	22000	63	110	0.12	30	21	54	33	290
5	1922.3	27000	7	220	0.3	40	12	22	22000	64	120	0.12	28	23	47	35	230
6	1921.4	27000	7	220	0.1	40	10	22	22000	67	120	0.13	24	23	52	35	160
7	1920.4	27000	7	220	0.1	40	9	22	22000	69	130	0.14	22	22	47	35	160

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Depth	Year	Metal concentrations (mg kg^{-1})															
		Al	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Ti	V	Zn
8	1919.4	27000	7	200	0.3	40	12	22	29000	73	180	0.13	21	22	50	37	150
9	1918.4	26000	10	220	0.7	41	9	29	27000	110	190	0.16	22	23	42	37	270
10	1917.4	27000	12	220	0.7	42	10	26	30000	97	190	0.14	25	23	75	39	480
11	1916.5	32000	16	280	0.8	47	16	33	31000	120	160	0.17	33	27	67	44	590
12	1915.5	29000	12	190	0.5	44	13	23	30000	84	150	0.14	29	23	40	41	280
13	1914.5	25000	12	180	0.2	39	10	18	26000	39	110	0.11	22	17	39	38	100
14	1913.5	30000	14	220	0.2	47	12	18	32000	36	170	0.1	26	20	68	45	85
15	1912.5	28000	27	200	0.1	39	12	18	30000	46	160	0.12	23	20	62	41	90
16	1911.6	24000	15	170	0.1	35	10	16	24000	37	110	0.1	19	17	50	35	71
17	1910.6	24000	13	180	0.1	35	11	14	24000	27	120	0.1	20	17	61	36	69
18	1909.6	27000	11	200	0.1	39	11	14	26000	28	120	0.11	21	19	73	40	68
19	1908.6	36000	10	190	0.1	37	11	13	27000	26	170	0.09	21	19	110	39	65
20	1907.6	25000	9	190	0.1	37	11	12	26000	23	190	0.08	21	18	110	38	56
21	1906.7	24000	9	180	0.1	36	10	12	25000	23	160	0.07	19	17	120	37	55
22	1905.7	25000	9	190	0.1	37	11	12	25000	25	170	0.09	20	18	94	38	59
24	1903.7	28000	10	220	0.1	41	12	13	27000	26	170	0.14	22	20	150	41	60
25	1902.7	27000	9	210	0.1	41	11	13	25000	25	130	0.12	22	19	120	41	55
26	1901.9	21000	8	160	0.1	33	9	11	21000	20	110	0.09	18	16	110	33	44
27	1901.6	23000	8	190	0.1	36	10	12	23000	22	130	0.1	20	17	140	36	48
28	1901.3	24000	9	200	0.1	38	10	13	26000	24	190	0.11	21	18	92	38	53
29	1901.1	27000	9	230	0.1	41	12	14	30000	27	280	0.11	22	20	99	40	55
30	1900.8	23000	8	170	0.1	35	10	11	22000	22	130	0.09	19	18	93	34	51
31	1900.5	25000	9	210	0.1	39	11	13	25000	27	120	0.1	21	19	34	37	62
32	1900.2	25000	9	190	0.1	38	11	12	25000	23	180	0.09	20	19	88	38	55
33	1899.9	30000	9	240	0.1	46	12	14	31000	28	230	0.12	24	22	83	45	64
34	1899.6	27000	8	210	0.1	41	11	12	29000	25	240	0.1	21	20	110	41	57
35	1899.3	22000	7	170	0.1	33	9	10	21000	20	110	0.08	18	16	71	33	47
36	1899.0	32000	10	250	0.1	46	12	13	27000	29	110	0.11	23	23	110	46	61
37	1898.7	26000	8	200	0.1	39	11	11	25000	24	130	0.1	20	20	47	38	53
38	1898.4	26000	8	210	0.1	39	11	12	24000	25	110	0.1	21	20	45	38	58
39	1898.1	25000	8	200	0.1	38	10	12	23000	24	96	0.1	20	20	100	38	54
40	1897.8	26000	8	200	0.1	38	10	12	23000	23	93	0.09	20	19	100	38	51
41	1897.6	27000	10	210	0.1	39	12	13	27000	29	210	0.11	21	21	110	40	60
42	1897.3	25000	10	200	0.1	37	11	13	29000	30	270	0.13	20	20	43	38	64
43	1897.0	27000	11	210	0.1	38	11	13	27000	31	210	0.13	20	21	82	39	62
44	1896.7	25000	10	200	0.1	36	10	13	23000	28	91	0.12	19	19	65	37	66

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Depth	Year	Metal concentrations (mg kg^{-1})																
		Al	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Ni	Sr	Ti	V	Zn
45	1896.4	26000	10	210	0.1	37	10	13	23000	29	93	0.12	20	21	65	38	65
46	1896.1	26000	11	210	0.1	38	11	13	27000	28	180	0.12	21	21	89	40	58
47	1895.8	22000	8	170	0.1	34	10	11	23000	21	140	0.08	18	17	68	35	41
48	1895.5	27000	10	210	0.1	39	11	12	27000	24	190	0.1	19	21	100	39	47
49	1895.2	24000	10	190	0.1	35	11	11	25000	23	180	0.11	19	19	58	37	51
50	1894.8	20000	7	160	0.1	31	10	11	21000	19	120	0.09	17	17	48	32	40
51	1893.8	22000	7	160	0.1	33	9	10	23000	21	150	0.12	17	17	60	33	45
52	1892.8	21000	8	160	0.1	31	9	10	26000	21	230	0.12	17	17	72	33	44
53	1891.8	22000	7	170	0.1	33	10	11	26000	21	230	0.12	18	18	78	35	46
54	1890.8	21000	7	170	0.1	31	9	10	22000	22	130	0.12	16	18	37	32	42
55	1889.8	20000	7	150	0.1	30	9	9	20000	18	120	0.11	16	16	79	32	38
56	1888.9	20000	6	150	0.1	30	8	10	19000	19	91	0.08	15	16	63	31	37
61.75	1886.0	23000	8	170	0.1	34	9	11	22000	21	100	0.15	18	18	69	35	42
71.75	1880.8	23000	8	180	0.1	36	10	11	24000	21	180	0.15	19	20	43	35	38
81.75	1875.7	29000	8	220	0.1	42	12	12	29000	23	250	0.16	22	22	88	42	44
91.75	1870.9	26000	8	220	0.1	41	12	12	26000	23	160	0.19	22	21	85	41	46
101.75	1866.0	21000	5	160	0.1	36	9	10	23000	16	160	0.11	19	18	130	34	34
111.75	1860.4	24000	6	180	0.1	36	10	10	21000	17	100	0.14	19	19	83	35	36
121.75	1854.8	22000	7	170	0.1	35	11	10	20000	15	110	0.13	19	17	88	35	32
131.75	1850.2	21000	6	160	0.1	33	9	9	20000	15	160	0.17	18	18	120	33	32
141.75	1845.8	20000	6	160	0.1	33	9	9	20000	14	190	0.18	17	17	130	32	30
151.75	1840.9	21000	5	190	0.1	35	10	9	20000	13	170	0.12	19	18	200	34	35
161.75	1815.3	23000	5	200	0.1	35	10	10	19000	15	130	0.23	19	20	120	35	34
171.75	1778.7	27000	6	280	0.1	37	11	13	19000	14	150	0.06	22	25	200	39	58
181.75	1742.1	27000	2.5	260	0.1	35	10	12	17000	13	160	0.025	20	23	140	37	56
201.5	1701.7	27000	2.5	290	0.1	36	14	14	18000	13	200	0.05	23	26	130	40	64

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Table S2. PAH and OCP concentrations in W4 and W1

Depth (cm)	Year	PAHs (mg kg^{-1})														
		NA	ACL	AC	FL	PHE	AN	FLA	PY	BaA	CHR	BbkFA	BaP	IP	DBahA	BghiP
W4																
2	2010.9	0.025	<0.01	<0.01	0.048	0.063	0.012	0.13	0.13	0.054	0.07	0.069	0.025	0.071	0.017	0.1
6	2008.0	0.027	0.011	<0.01	0.035	0.063	0.012	0.13	0.14	0.067	0.077	0.075	0.034	0.089	0.021	0.13
10	2005.1	0.027	<0.01	<0.01	0.067	0.072	0.014	0.13	0.14	0.062	0.073	0.076	0.033	0.092	0.018	0.13
18	1999.3	0.022	<0.01	<0.01	0.021	0.055	0.01	0.1	0.11	0.052	0.063	0.057	0.025	0.089	0.024	0.13
22	1996.4	0.021	<0.01	<0.01	0.021	0.056	0.011	0.11	0.12	0.051	0.064	0.06	0.025	0.089	0.02	0.15
26	1993.5	0.021	<0.01	<0.01	0.018	0.049	<0.01	0.1	0.1	0.049	0.059	0.056	0.025	0.09	0.022	0.13
30	1990.6	0.023	<0.01	<0.01	0.066	0.063	0.012	0.087	0.085	0.045	0.057	0.079	0.03	0.11	0.025	0.16
34	1987.7	0.019	<0.01	<0.01	0.033	0.055	0.01	0.091	0.087	0.046	0.053	0.072	0.038	0.11	0.023	0.16
38	1984.8	0.018	<0.01	<0.01	0.021	0.041	<0.01	0.062	0.063	0.032	0.039	0.039	0.017	0.062	0.022	0.1
42	1981.9	0.017	<0.01	<0.01	0.011	0.043	<0.01	0.064	0.07	0.04	0.047	0.043	0.024	0.083	0.023	0.11
46	1978.4	0.01	<0.01	<0.01	<0.01	0.028	<0.01	0.053	0.057	0.027	0.027	0.02	<0.01	0.041	0.012	0.058
50	1971.0	0.035	0.012	0.011	0.041	0.12	0.019	0.16	0.16	0.063	0.076	0.061	0.034	0.1	0.031	0.14
54	1959.3	0.035	0.013	0.011	0.03	0.14	0.03	0.17	0.16	0.083	0.096	0.071	0.038	0.13	0.038	0.17
58	1945.4	0.037	0.017	0.011	0.025	0.13	0.029	0.24	0.23	0.1	0.12	0.093	0.051	0.17	0.05	0.22
62	1931	0.043	0.027	<0.01	0.026	0.15	0.034	0.33	0.27	0.15	0.17	0.14	0.079	0.26	0.074	0.34
66	1920.8	0.027	0.021	<0.01	0.02	0.14	0.031	0.32	0.27	0.15	0.16	0.13	0.076	0.25	0.066	0.31
70	1917.4	0.059	0.026	0.016	0.038	0.2	0.034	0.35	0.35	0.14	0.16	0.13	0.069	0.23	0.065	0.3
74	1914.1	0.022	0.005	<0.01	0.018	0.07	0.012	0.13	0.12	0.06	0.067	0.044	0.021	0.08	0.024	0.1
78	1910.8	0.023	0.011	<0.01	0.021	0.11	0.019	0.19	0.18	0.1	0.12	0.1	0.053	0.15	0.043	0.18
86	1904.1	0.014	<0.01	<0.01	0.011	0.058	<0.01	0.11	0.11	0.056	0.059	0.051	0.026	0.072	0.02	0.089
90	1900.8	0.012	<0.01	<0.01	0.01	0.067	0.011	0.13	0.13	0.064	0.071	0.061	0.034	0.084	0.024	0.1
94	1897.4	0.015	<0.01	<0.01	0.015	0.11	0.017	0.19	0.18	0.11	0.12	0.11	0.061	0.22	0.056	0.27
W1																
2	1925.8	0.046	<0.01	<0.01	0.019	0.066	0.011	0.13	0.13	0.048	0.072	0.058	0.033	0.079	0.012	0.11
6	1921.9	0.057	<0.01	<0.01	0.026	0.082	<0.01	0.14	0.14	0.053	0.075	0.051	0.027	0.062	<0.01	0.079
10	1917.9	0.039	<0.01	0.014	0.018	0.091	0.09	0.15	0.14	0.08	0.082	<0.01	0.12	0.78	<0.01	0.8
14	1914.0	0.088	0.028	<0.01	0.038	0.29	0.046	0.62	0.59	0.21	0.27	0.19	0.11	0.26	0.056	0.31
18	1910.1	0.047	0.012	0.014	0.035	0.17	0.026	0.32	0.3	0.11	0.15	0.1	0.053	0.11	0.029	0.13
22	1906.2	0.027	<0.01	<0.01	0.023	0.1	0.016	0.22	0.21	0.079	0.11	0.082	0.043	0.071	0.016	0.069
26	1902.5	0.025	<0.01	<0.01	0.016	0.083	0.011	0.16	0.16	0.062	0.077	0.064	0.034	0.049	0.017	0.053
30	1900.9	0.018	<0.01	<0.01	0.021	0.12	0.015	0.28	0.28	0.14	0.15	0.2	0.094	0.053	0.013	0.078
34	1899.7	0.031	<0.01	<0.01	0.021	0.15	0.02	0.33	0.34	0.12	0.17	0.077	0.073	0.12	0.055	0.13
38	1898.6	0.029	0.011	<0.01	0.022	0.16	0.022	0.37	0.36	0.14	0.19	0.15	0.079	0.13	0.059	0.14
42	1897.4	0.035	0.017	0.013	0.03	0.23	0.031	0.52	0.49	0.2	0.27	0.21	0.11	0.22	0.11	0.24

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Depth (cm)	Year	PAHs (mg kg^{-1})														
		NA	ACL	AC	FL	PHE	AN	FLA	PY	BaA	CHR	BbkFA	BaP	IP	DBahA	BghiP
46	1896.2	0.04	0.026	0.018	0.057	0.5	0.055	1.2	1.2	0.47	0.56	0.75	0.42	0.26	0.059	0.32
50	1894.8	0.041	0.023	0.016	0.048	0.38	0.052	0.73	0.71	0.3	0.38	0.27	0.17	0.31	0.092	0.33
54	1891.3	<0.01	<0.01	<0.01	0.01	0.12	<0.01	0.3	0.31	0.15	0.16	0.1	0.061	0.084	<0.01	0.13
58	1888.1	0.029	0.015	0.01	0.035	0.22	0.031	0.4	0.38	0.16	0.18	0.14	0.084	0.13	0.039	0.14
93	1870.4	0.018	<0.01	<0.01	0.015	0.061	<0.01	0.1	0.091	0.039	0.042	0.034	0.018	0.03	<0.01	0.032
143	1845.4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
194.5	1734.2	0.092	<0.01	<0.01	0.037	0.067	<0.01	0.054	0.032	0.034	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Table S3. OCP concentrations in W4 and W1

Depth (cm)	Year	OCPs (mg kg^{-1})				
		trans-Chlordane	Dieldrin	pp-DDE	pp-DDD	pp-DDT
W4						
2	2010.9	0.0078	0.0015	0.018	<0.001	<0.001
6	2008.0	0.0063	0.0012	0.012	<0.001	<0.001
10	2005.1	<0.001	<0.001	<0.001	<0.001	<0.001
18	1999.3	0.0059	0.0021	0.0093	<0.001	<0.001
22	1996.4	0.004	0.0013	0.0076	<0.001	<0.001
26	1993.5	<0.001	<0.001	0.011	<0.001	<0.001
46	1978.4	<0.001	<0.001	0.0095	<0.001	<0.001
50	1971.0	0.03	0.012	0.054	0.038	0.11
54	1959.3	<0.001	<0.001	0.019	<0.001	<0.001
58	1945.4	<0.001	<0.001	0.028	<0.001	<0.001
62	1931.0	<0.001	<0.001	0.03	<0.001	<0.001
66	1920.8	<0.001	<0.001	0.025	<0.001	<0.001
70	1917.4	<0.001	<0.001	0.0013	<0.001	<0.001
74	1914.1	<0.001	<0.001	<0.001	<0.001	<0.001
78	1910.8	<0.001	<0.001	<0.001	<0.001	<0.001
86	1904.1	<0.001	<0.001	<0.001	<0.001	<0.001
90	1900.8	<0.001	<0.001	<0.001	<0.001	<0.001
94	1897.4	<0.001	<0.001	<0.001	<0.001	<0.001
W1						
2	1925.8		0.051	0.027	0.062	0.0031
6	1921.9		<0.001	0.12	0.78	0.0029
10	1917.9		0.19	0.11	0.26	0.0021
14	1914.0		<0.001	0.053	0.11	0.0015

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Depth (cm)	Year	OCPs (mg kg^{-1})				
		trans-Chlordane	Dieldrin	pp-DDE	pp-DDD	pp-DDT
18	1910.1		<0.001	<0.001	<0.001	<0.001
22	1906.2		<0.001	<0.001	<0.001	<0.001
26	1902.5		<0.001	<0.001	<0.001	<0.001
30	1900.9		<0.001	<0.001	<0.001	<0.001
34	1899.7		<0.001	<0.001	<0.001	<0.001
38	1898.6		<0.001	<0.001	<0.001	<0.001
42	1897.4		<0.001	<0.001	<0.001	<0.001
46	1896.2		<0.001	<0.001	<0.001	<0.001
50	1894.8		<0.001	<0.001	<0.001	<0.001
54	1891.3		<0.001	<0.001	<0.001	<0.001
58	1888.1		<0.001	<0.001	<0.001	<0.001
93	1870.4		<0.001	<0.001	<0.001	<0.001
143	1845.4		<0.001	<0.001	<0.001	<0.001
194.5	1734.2		<0.001	<0.001	<0.001	<0.001

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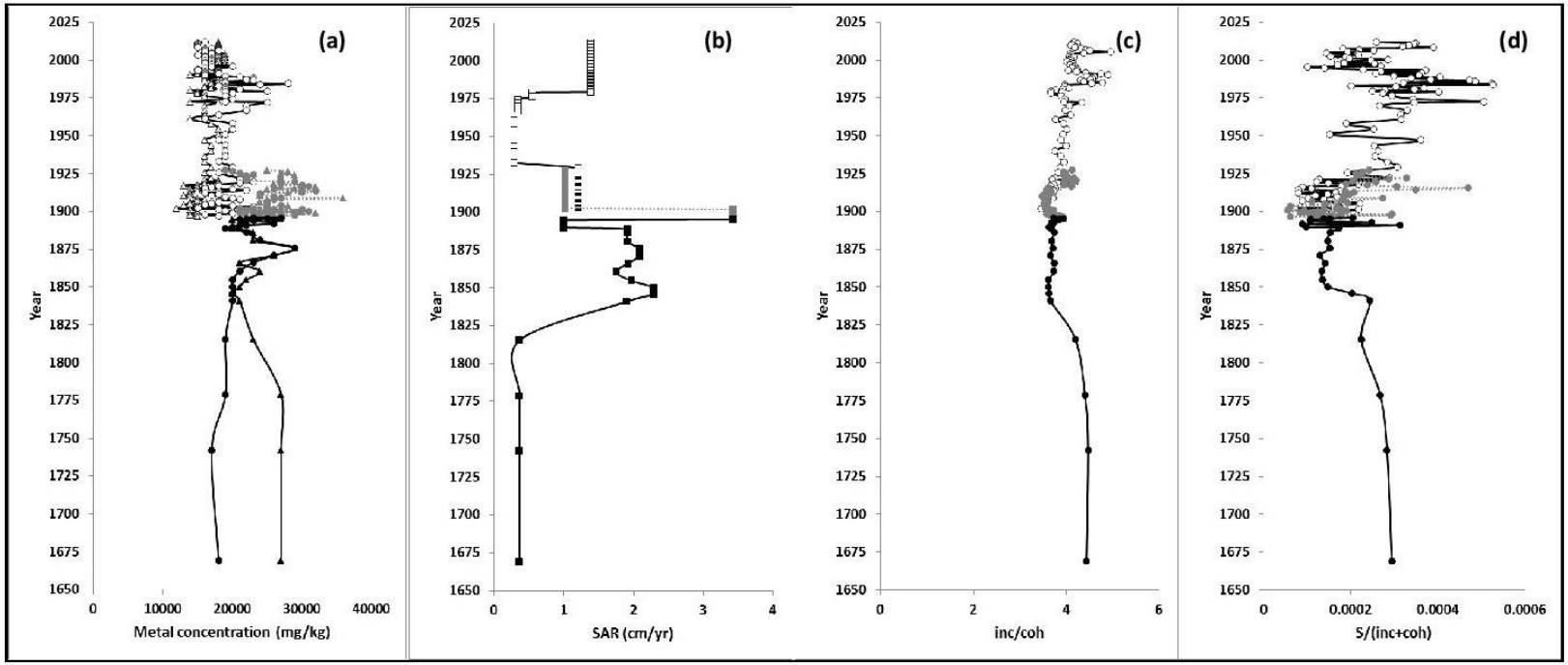

Fig. S1. Al, Fe, SAR, incoherent/coherent ratio (inc/coh) and S profiles of W1 and W4.

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Fig. S2. Photographs of significant features from sediment cores W1 and W4 showing (*a*) the distinct clay layer in W4, and (*b*) leaf matter on the surface of W4.

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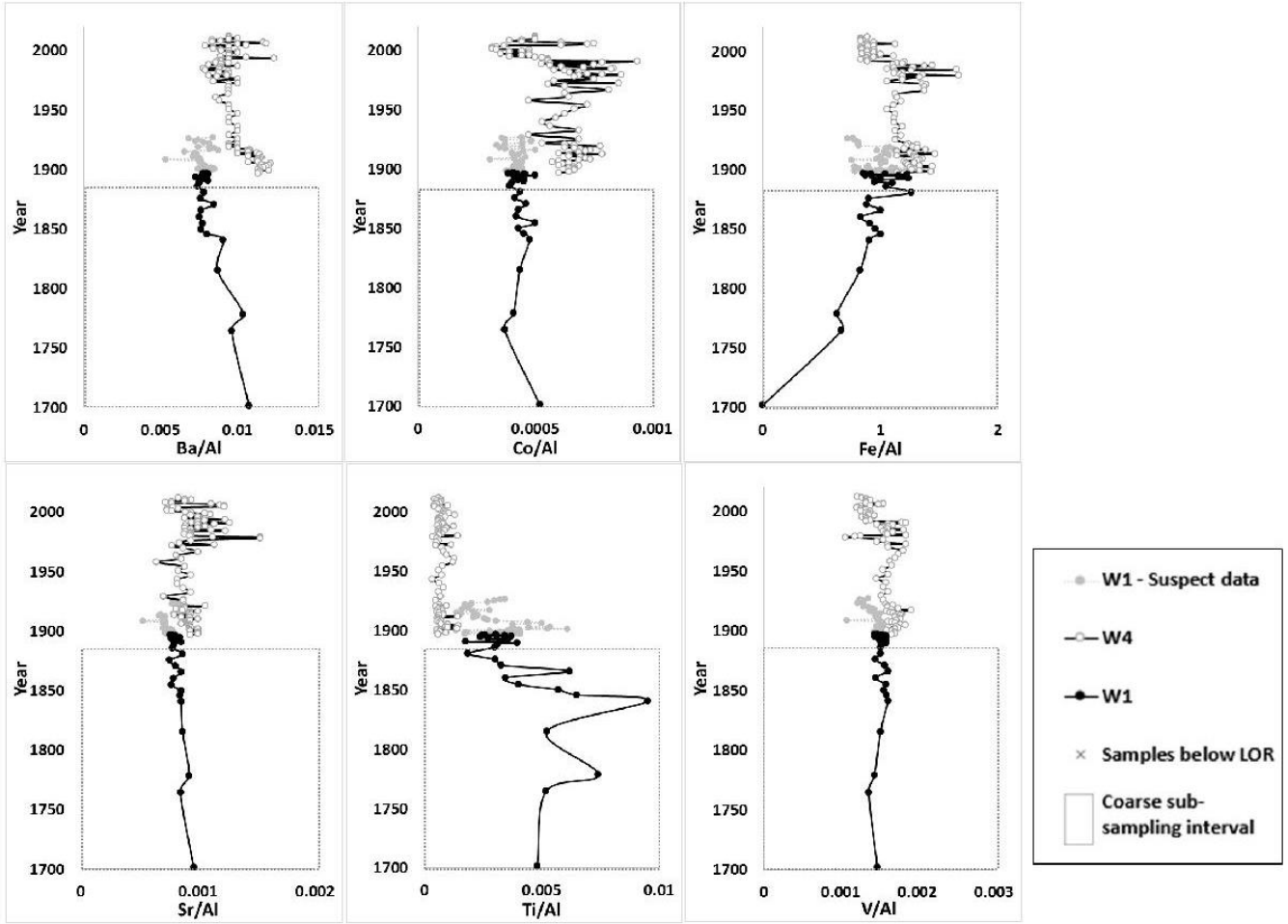

Fig. S3. Heavy metal profiles of W1 and W4 not included in manuscript.

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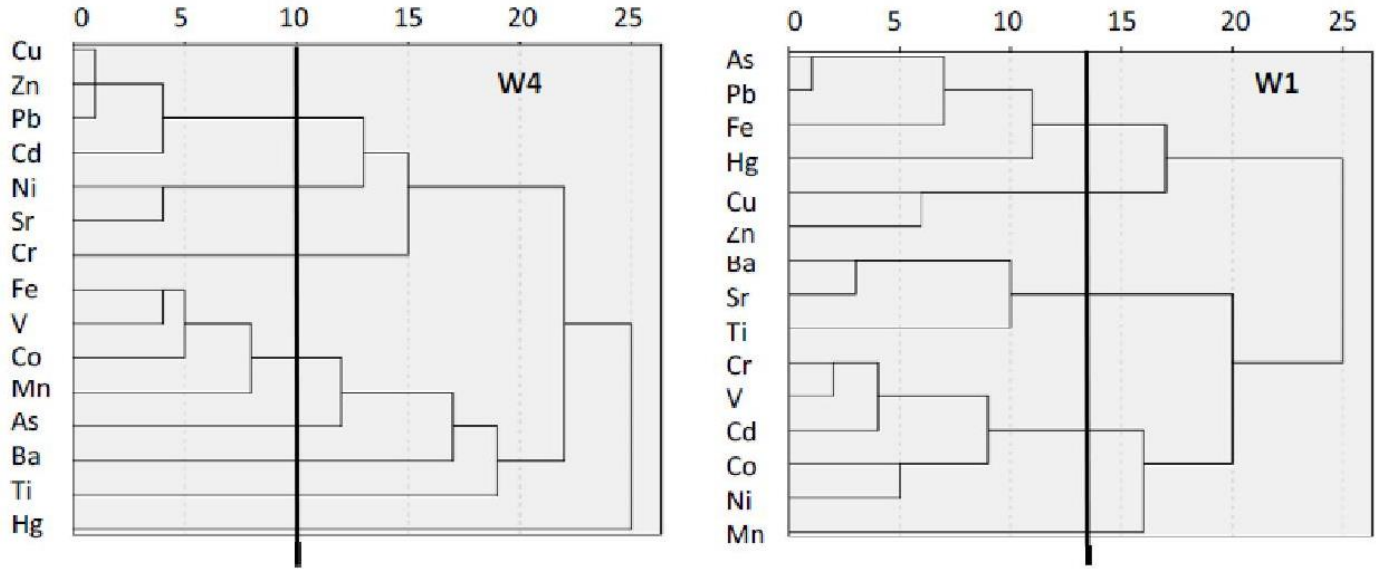

Fig. S4. Dendrograms from cluster analysis for W4 and W1 (thick lines represent the cut-off point of the dendrograms).

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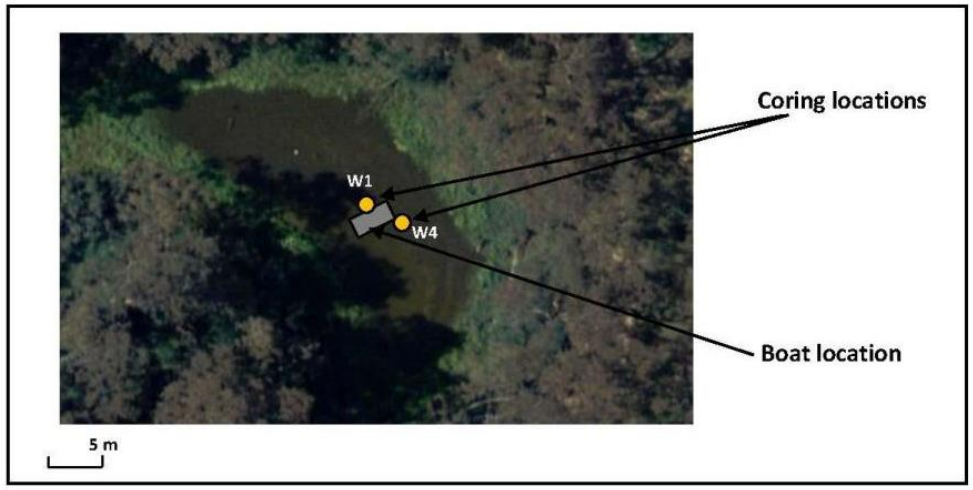

Fig. S5. Satellite image of Willsmere Billabong, showing location of boat and coring.

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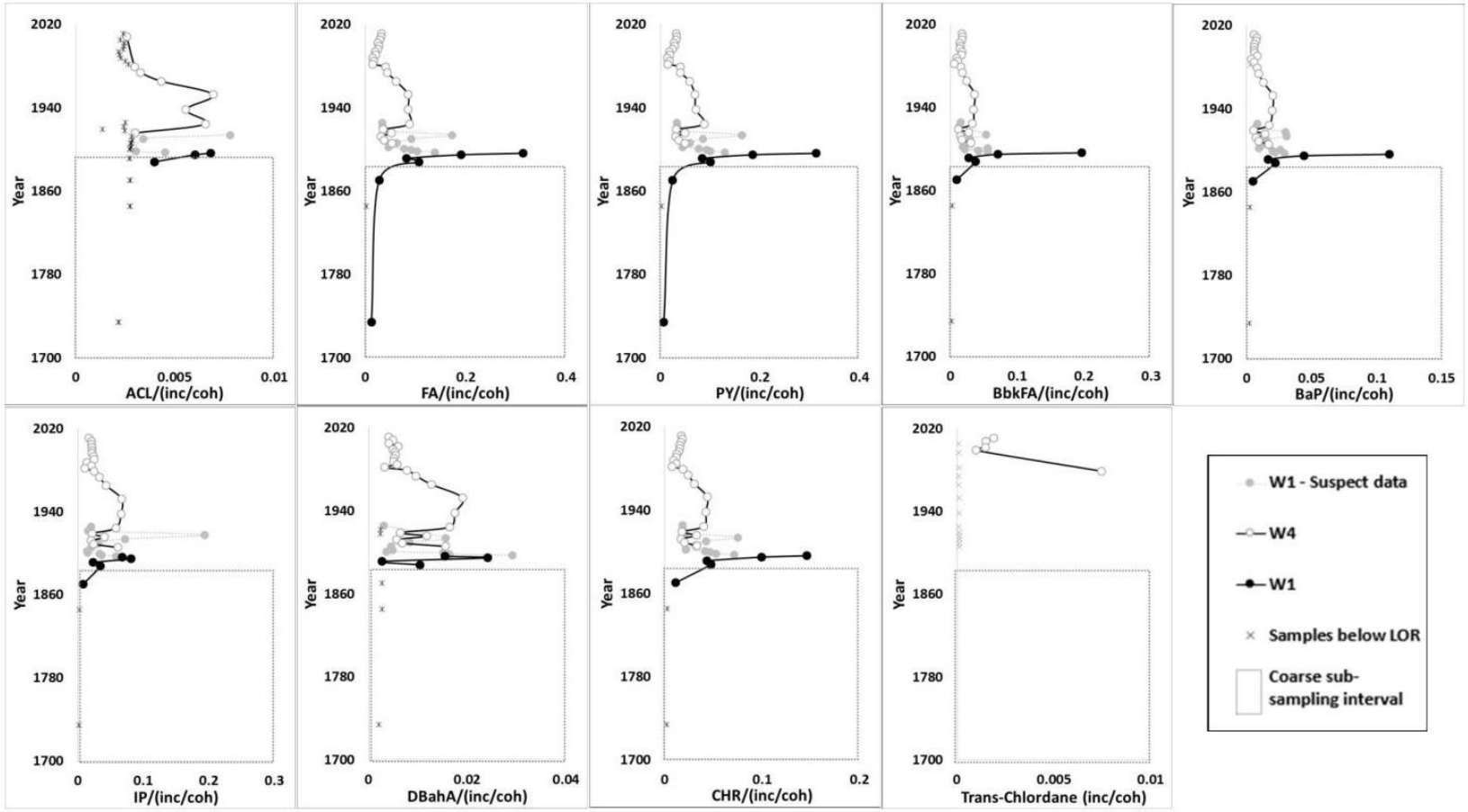

Fig. S6. PAH and OCP profiles of W1 and W4 not included in manuscript.

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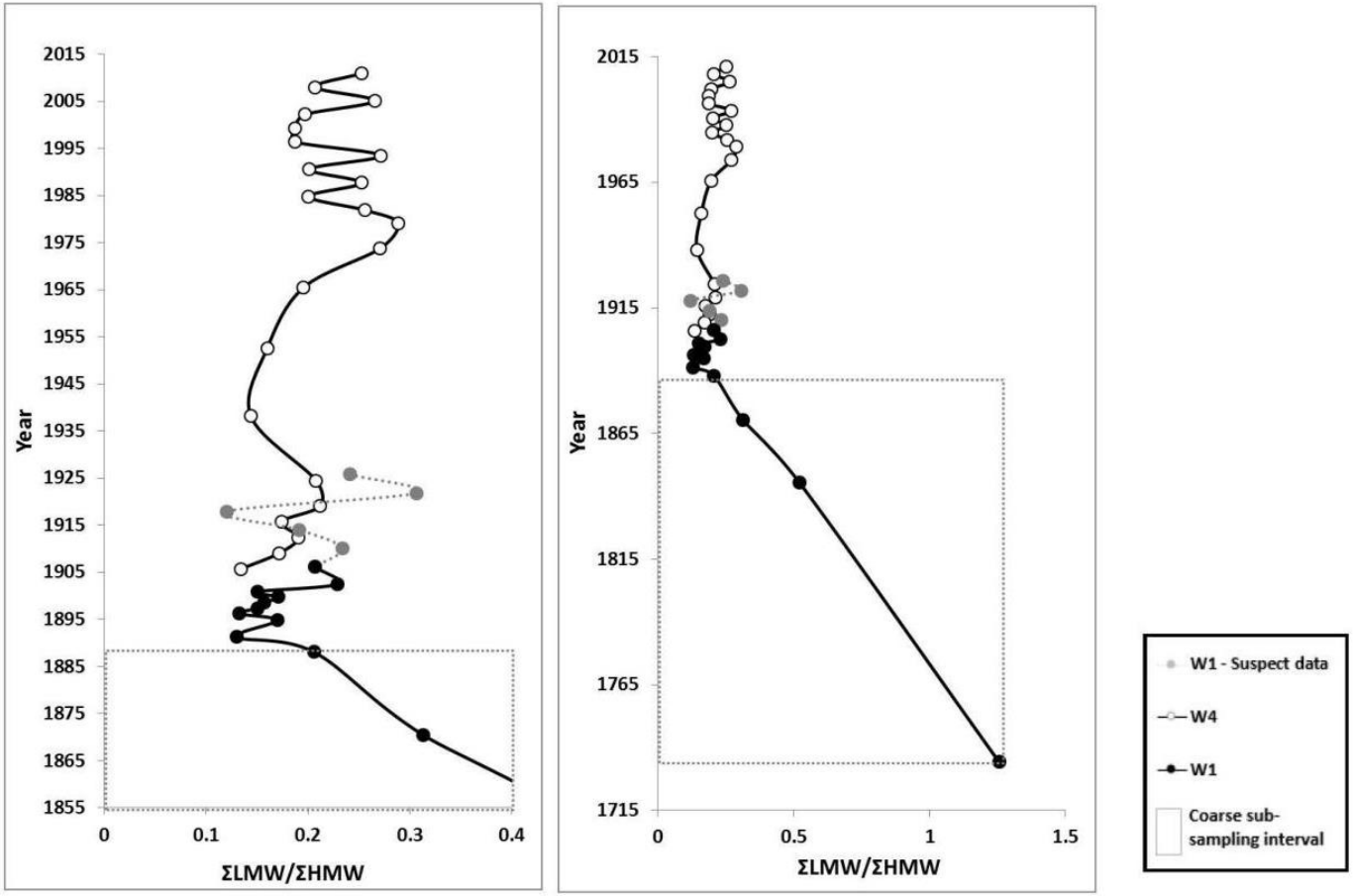

Fig. S7. Profile of the ratio of the sum of low molecular weight PAHs to high molecular weight PAHs for W1 and W4.

Appendix A.3 Supplementary materials for 'Using sediment cores to identify historical changes in floodplain lake hydrology' (Chapter 5)

Discussion S1:

Justification of the use of Zr/Rb as an indicator of particle size in the sediment cores

Methods

Sampling. Sediment cores from Willsmere Billabong (W4), Bolin Billabong (B5) and an additional billabong, the Yarra Flats Billabong were used to determine the elemental ratio that would act as a suitable particle size proxy. The sites and coring methods at Willsmere Billabong and Bolin Billabong are provided in the main body of the text and as such will not be discussed here.

The Yarra Flats Billabong (location provided in Figure 1 in the main body of the text) is outside the area of metropolitan Melbourne and is located in a rural area near the township of Yarra Glen. It has a local catchment area of 15 ha and a bank-full area of approximately 2.4 ha. It receives flows from the main river when the river is at 4 m at the Yarra Glen stream gauge, which is adjacent to the billabong (Vic SES, 2012b).

In August 2013, a sediment core was taken from the Yarra Flats Billabong (Figure 1 in the main body of the text). This core was taken in ten drives (bed surface to depth 17 cm; depth 17 cm to depth 46 cm; depth 46 cm to depth 71 cm; depth 71 cm to depth 100 cm; depth 100 cm to depth 131 cm; depth 131 cm to depth 167 cm; depth 167 cm to depth 202.5 cm; depth 202.5 cm to depth 244.5 cm; depth 244.5 cm to depth 298.5 cm; depth 298.5 cm to depth 353.5 cm) using the 40-mm diameter Livingstone corer (Livingstone, 1955). This will be referred to in this study as YG1. A map of the catchment of the Yarra Flats Billabong, showing the coring location is provided in Figure S2 in the supplementary material.

Sediment dredging in the Yarra Flats Billabong in 1998 resulted in the loss of approximately 10 to 15 cm of sediments from the sedimentary record (Rod Baker, VicRoads, pers. comm., 12 February 2015). Due to this sediment discontinuity, reliable sediment chronologies could not be developed for YG1. As a result, YG1 was used only for the determination of an element or element ratio that can act as a reliable grain size proxy.

Particle size analysis. Particle size of sediments can be strongly correlated to their elemental composition (Cuven *et al.*, 2010; Jones *et al.*, 2012). Using a particle size proxy allows us to develop an understanding of the particle size of sediments in cores that have not been directly analysed for particle size, if the elemental composition of sediments is known. Furthermore, it enables the identification of fluctuations in grain size at finer resolutions (e.g., 1-mm intervals) than could be

determined by destructive sub-sampling of the core. Therefore, W4, B5 and YG1 were sub-sampled for particle size analysis. Approximately 0.5 g of moist sediment was taken at 1-cm intervals from W4 and at 0.5-cm intervals from B5. Approximately 0.5 g of moist sediment was also taken at 0.5-cm intervals from three sections of YG1 (0-39.5 cm, 145-154.5 cm, 250-264.5 cm). These YG1 sections were selected so as to include clay, silt and sand deposits in the analysis. The sediment samples were suspended in de-ionized water and were treated using approximately 10 mL of hydrogen peroxide (H_2O_2) (30%) to remove the organic matter and 1 mL of sodium hexametaphosphate ($Na(PO_3)_6$) to disperse the solution. The samples were then ultrasonicated for 30 minutes prior to analysis in a Malvern Mastersizer 2000. Sixty additional sediment samples from sediment core regions in B5 with a large range in particle sizes (100-109.5 cm; 120-129.5 cm; 140-153 cm) were suspended in water and ultrasonicated until the obscuration stabilised (as per Kermode *et al.*, 2012) and their particle size distributions were measured in the Malvern Mastersizer 2000. The particle size results (10^{th} percentile of particle diameters, D_{10}; 50^{th} percentile of particle diameters, D_{50}; and 90^{th} percentile of particle diameters, D_{90}) of these sixty additional sub-samples from B5 were compared to their replicates that were subjected to chemical dispersion to assess whether the treatment of sediment samples prior to laser diffraction analysis significantly changes the particle size distribution of the sediments.

There was a strong correlation between the particle size distributions of the treated and untreated sediment sub-samples of B5, particularly for D_{50} and D_{90} (ρ=0.82); as shown in Figure S3 in the supplementary material. As such, it appears that the pre-treatment method of sediment sub-samples prior to laser diffraction analysis will not significantly affect the selection of a particle size proxy. Thus, laser diffraction results of the chemically dispersed samples were used to determine the optimal grain size proxy.

The particle size properties obtained from the Malvern Mastersizer 2000 for the chemically dispersed sediment samples were compared to K, Fe, Rb, Zr, Ti, Si, Zr/Rb, Ti/Rb, Fe/Rb, K/Rb and Zr/Ti chemical element profiles, which we obtained using the ITRAX core scanner (as described in the main body of the text). The above elements and element ratios were studied because they have been previously identified as possible grain size proxies in literature (Cuven *et al.*, 2010; Jones *et al.*, 2012; Kylander *et al.*, 2011). Correlations between grain size distributions and potential grain size proxies were assessed using the Spearman Rank Correlation Coefficient (ρ), where α=0.05, calculated in RStudio version 3.1.0 (Free Software Foundation, Inc. Boston).

Results

We compared the median particle size (D_{50}) of sub-samples from W4, B5 and YG1 and possible grain size proxies identified previously from the literature: K, Fe, Rb, Zr, Ti, Si, Zr/Rb, Ti/Rb, Fe/Rb, K/Rb and Zr/Ti (Cuven *et al.*, 2010; Jones *et al.*, 2012). This is shown in Figure S4 in the supplementary material. Although Al intensity is also recommended as an particle size proxy due to the abundance of Al in clay particles (Jones *et al.*, 2012), Al was not considered as a potential grain size proxy in this study due to its low detection in the ITRAX micro-XRF core scanner. The correlation plots and the results of the Spearman Rank Correlation Coefficient (ρ) in Figure S4 in the supplementary material indicate that Zr/Rb has the strongest correlation to D_{50}. As such, Zr/Rb was used to represent grain size through the sedimentary records.

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Tables

Table S1: Locations where geological deposits were sampled. The sampling locations listed in this table are shown in Figure 1 in the main body of the text and local billabong catchment sampling locations shown in Figure S1 in the supplementary material.

Geological deposit	Sampling location	Abbreviation used throughout the study
Early Devonian Sedimentary	Upper Yarra Reservoir Park	UYR
Upper Devonian Marysville Igneous Rhyodacite Complex	Fernshaw Picnic Ground	FPG
Silurian Sedimentary (Dargile Formation)	Mount Lofty Park	MLP
Silurian Sedimentary (Anderson Creek Formation)	Warrandyte State Park 100 steps lookout	100S
Quaternary Newer Volcanics	West Bank of Darebin Creek at Bridge Inn Road	WB
	Norris Bank Reserve	NBR
Quaternary Alluvium	Westerfolds Park	WP
	Birrarung Park (Templestowe)	BP
	Local Bolin Billabong catchment	BP
	Local Willsmere Billabong catchment (residential area)	WR
	Local Willsmere Billabong catchment (park area)	WP

Figures

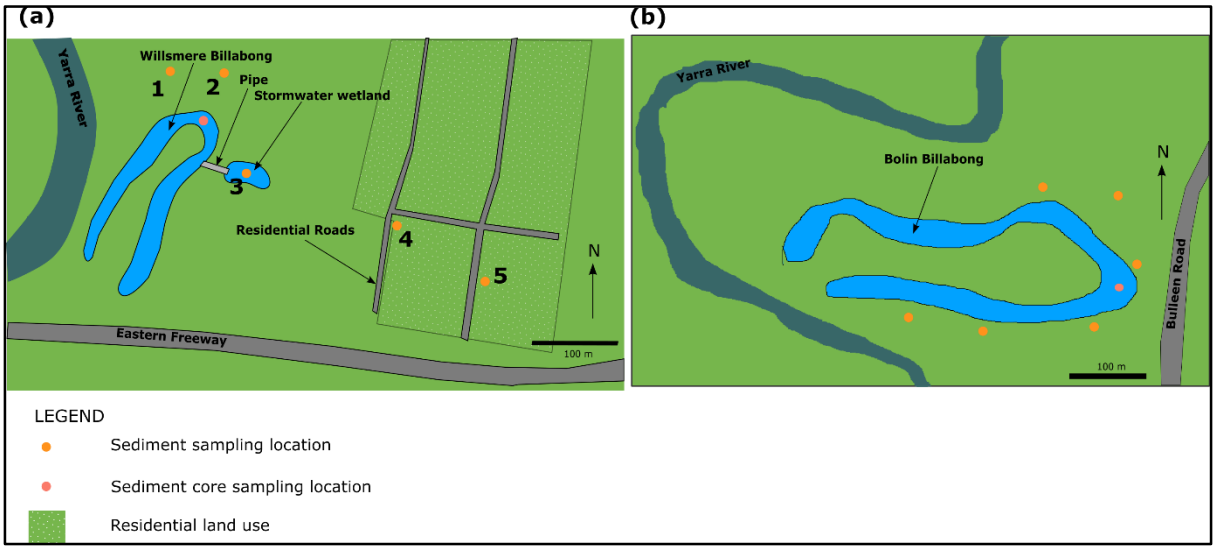

Figure S1: Coring and sampling locations within Willsmere Billabong catchment (a), Bolin Billabong catchment (b). For (a): sampling points 1 and 2 represent Quaternary Alluvium from parkland, (b) sampling points 3, 4 and 5 represent Quaternary Alluvium from urban catchment.

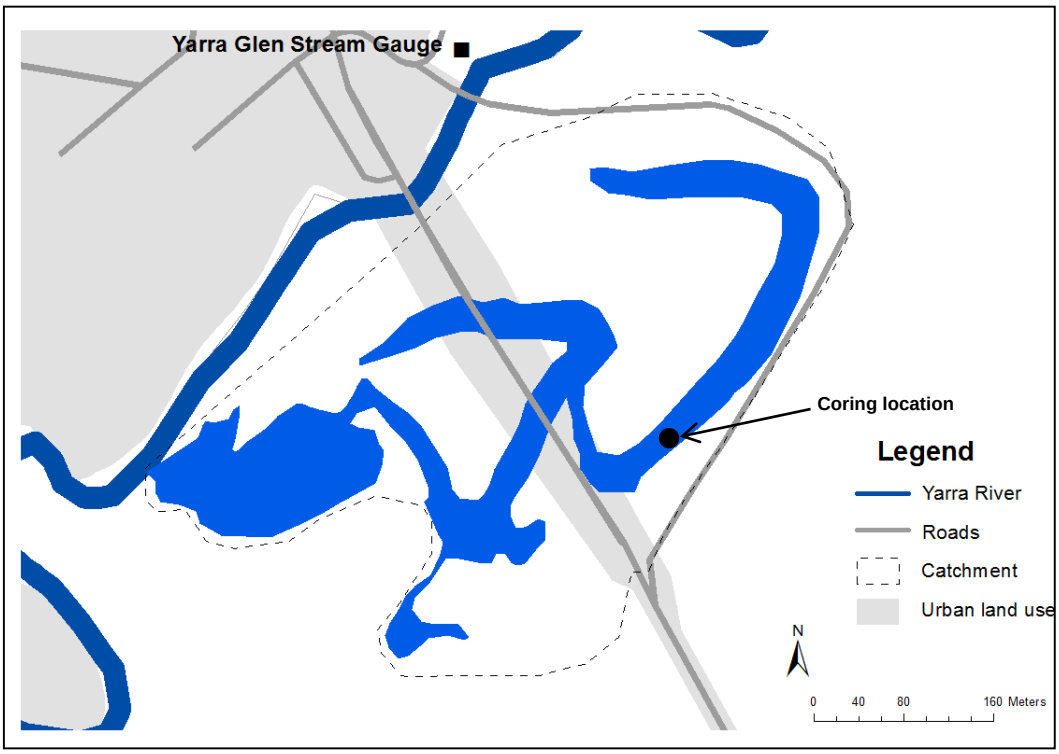

Figure S2: Yarra Flats Billabong catchment and the coring location.

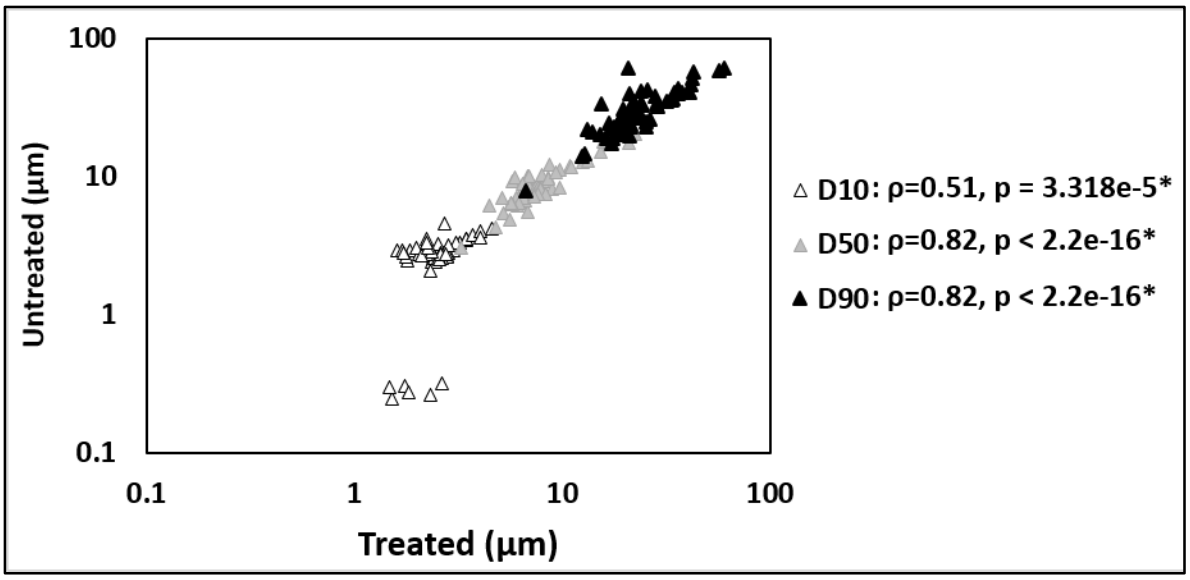

Figure S3: Comparison of grain size distributions determined with (treated) and without (untreated) chemical pre-treatment of sediment samples from B5. Spearman Rank Correlation Coefficient (ρ) and p-values are shown. Asterisk (*) denotes statistically significant correlations (p<0.05).

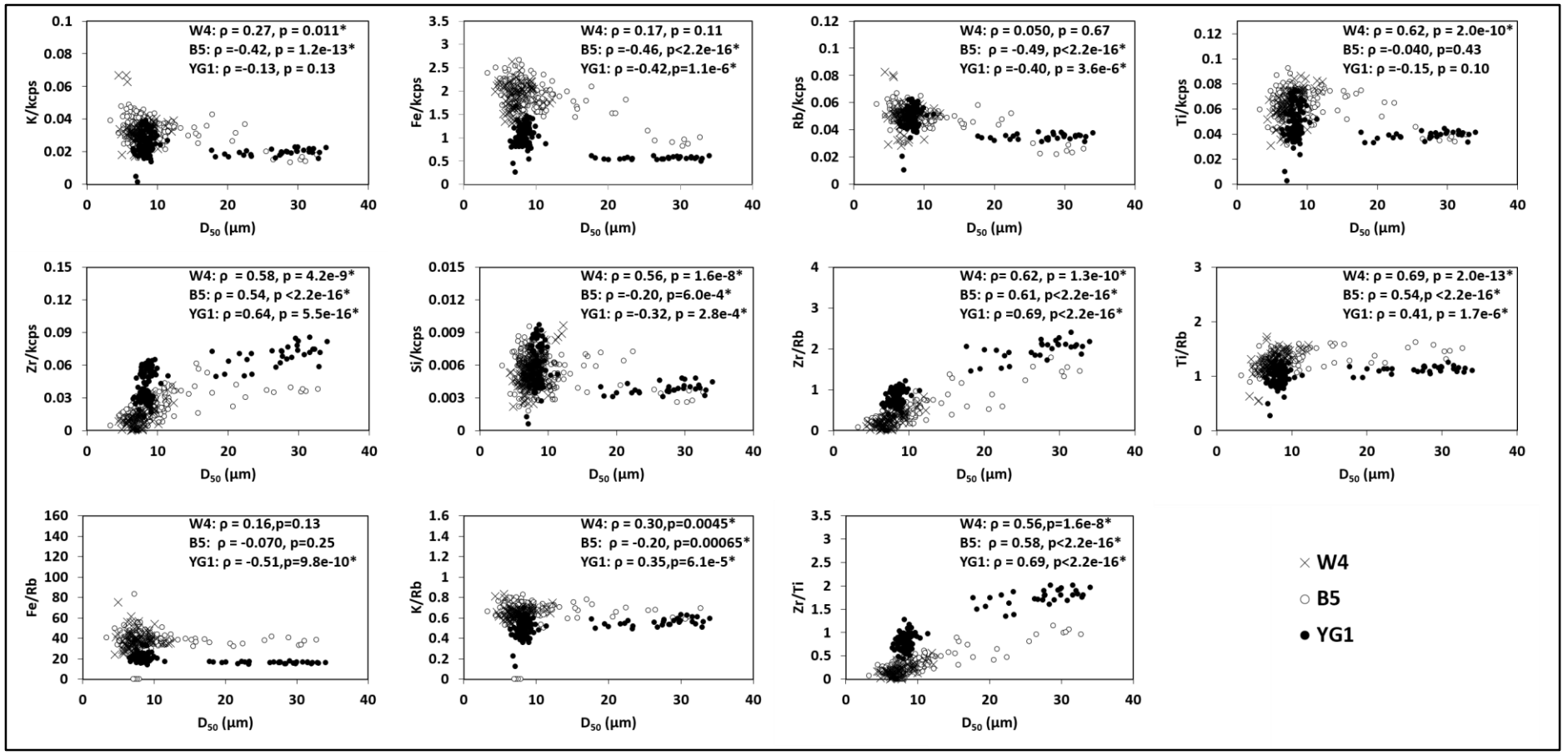

Figure S4: Correlations between D_{50} and grain size proxies for grain size data from W4, B5 and YG1. Spearman Rank Correlation Coefficient (ρ) and p-values shown. Asterisk (*) denotes statistically significant correlations (p<0.05).

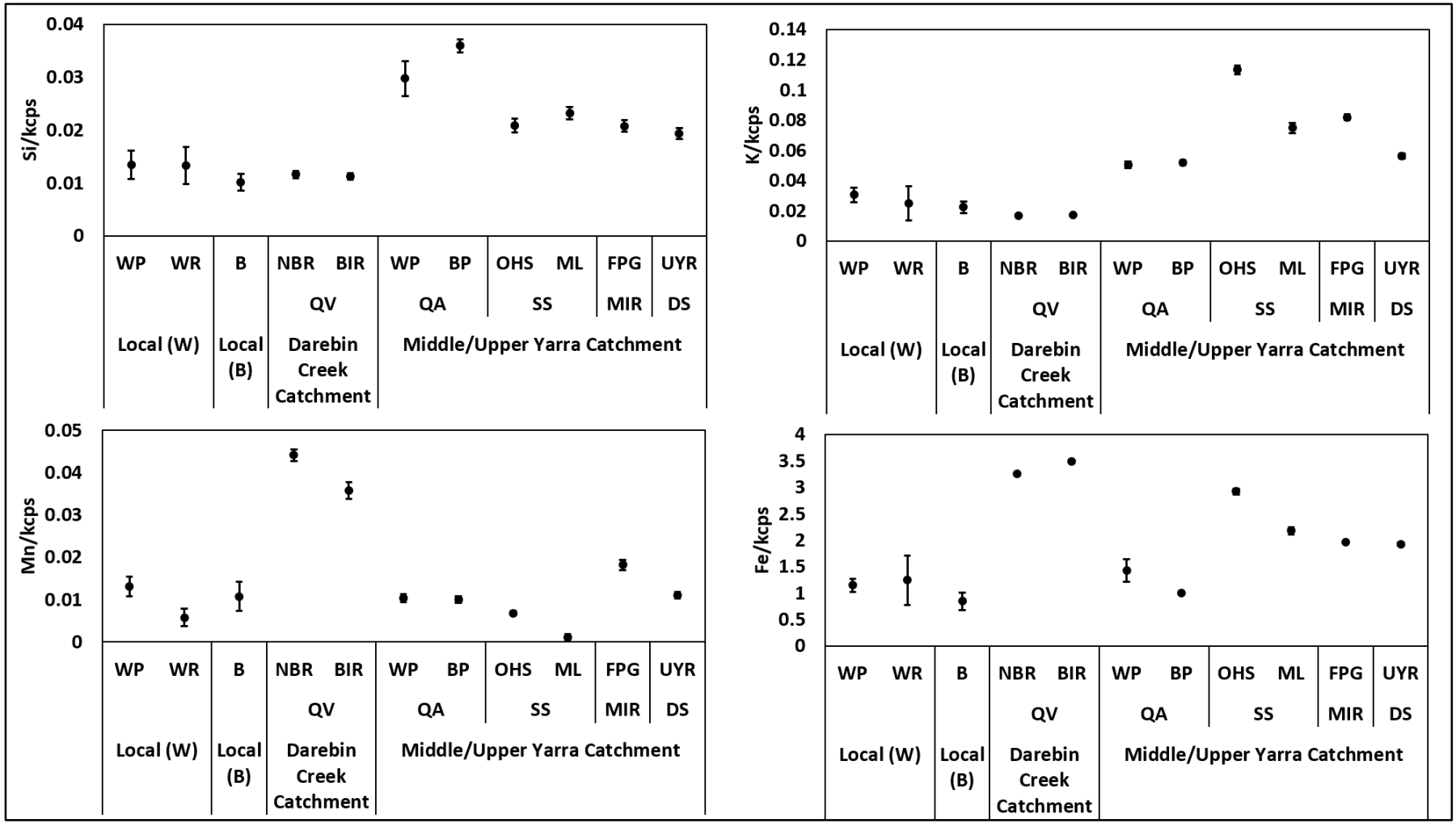

Figure S5: Average elemental composition of source rocks, with error bars representing standard deviation. WP: Willsmere Park (parkland), WR: Willsmere Residential (urban catchment), B: Bolin, Local (W): Local Catchment of Willsmere Billabong, Local (B): Local Catchment of Bolin Billabong, NBR: Norris Bank Reserve, BIR: Bridge Inn Rd, WP: Westerfolds Park, BP: Birrarung Park, OHS: Warrandyte State Park, ML: Mount Lofty, FPG: Fernshaw Picnic Ground, UYR: Upper Yarra Reservoir, QV: Quaternary Volcanics, QA: Quaternary Alluvium, SS: Silurian Sedimentary, MIR: Marysville Igneous Rhyodacite, DS: Devonian Sedimentary.

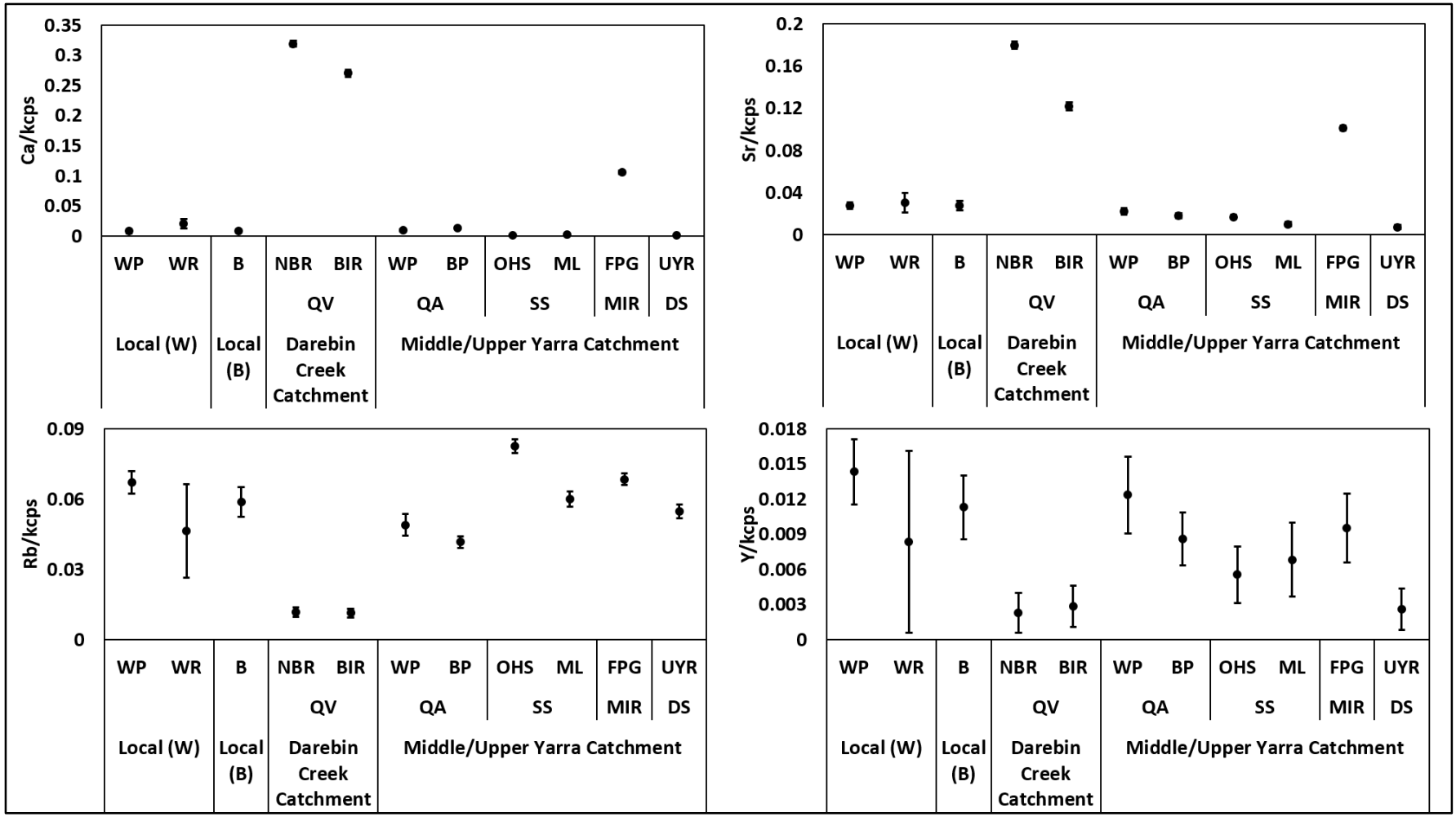

Figure S5 (continued): Average elemental composition of source rocks, with error bars representing standard deviation. WP: Willsmere Park (parkland), WR: Willsmere Residential (urban catchment), B: Bolin, Local (W): Local Catchment of Willsmere Billabong, Local (B): Local Catchment of Bolin Billabong, NBR: Norris Bank Reserve, BIR: Bridge Inn Rd, WP: Westerfolds Park, BP: Birrarung Park, OHS: Warrandyte State Park, ML: Mount Lofty, FPG: Fernshaw Picnic Ground, UYR: Upper Yarra Reservoir, QV: Quaternary Volcanics, QA: Quaternary Alluvium, SS: Silurian Sedimentary, MIR: Marysville Igneous Rhyodacite, DS: Devonian Sedimentary.

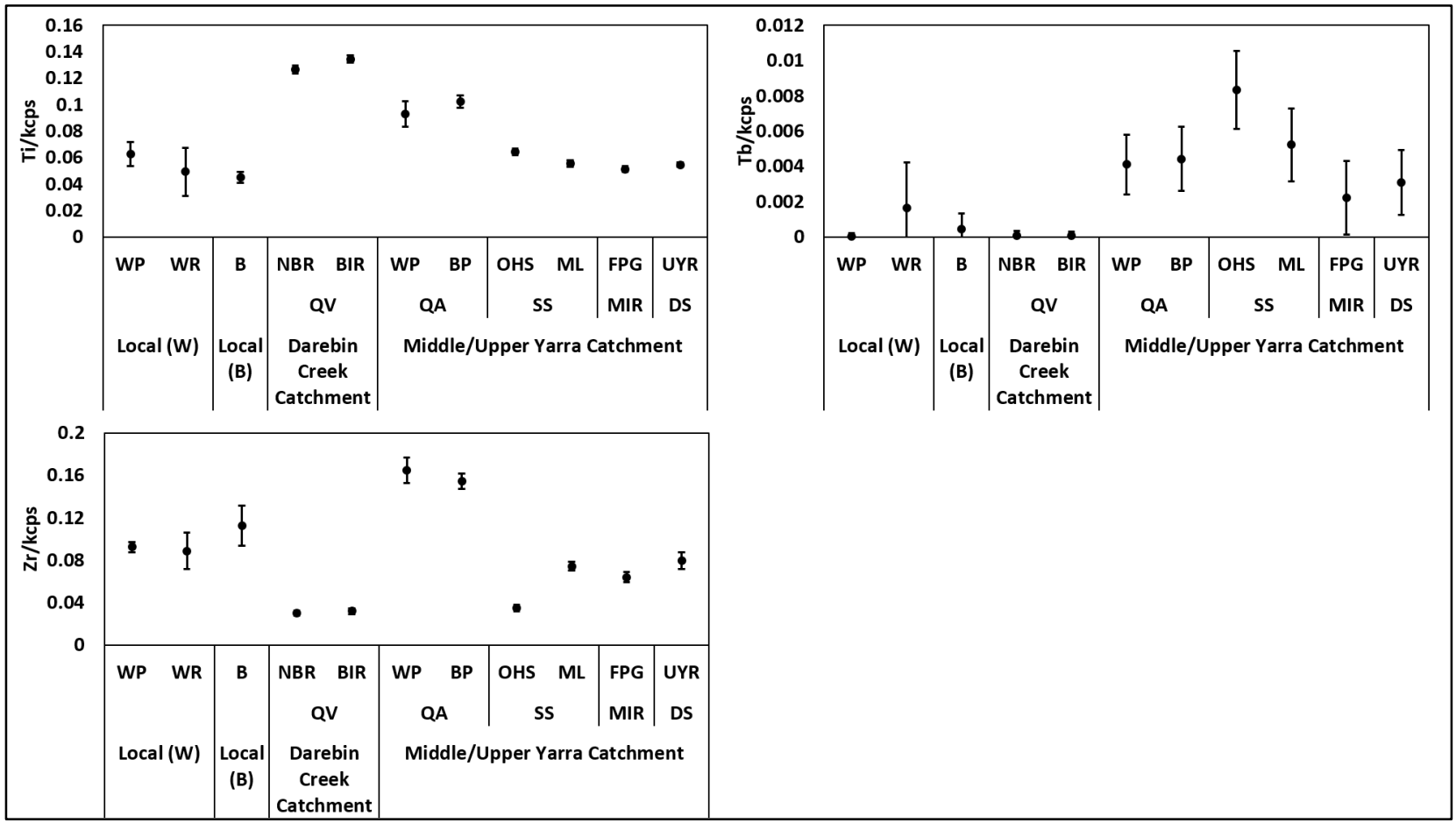

Figure S5 (continued): Average elemental composition of source rocks, with error bars representing standard deviation. WP: Willsmere Park (parkland), WR: Willsmere Residential (urban catchment), B: Bolin, Local (W): Local Catchment of Willsmere Billabong, Local (B): Local Catchment of Bolin Billabong, NBR: Norris Bank Reserve, BIR: Bridge Inn Rd, WP: Westerfolds Park, BP: Birrarung Park, OHS: Warrandyte State Park, ML: Mount Lofty, FPG: Fernshaw Picnic Ground, UYR: Upper Yarra Reservoir, QV: Quaternary Volcanics, QA: Quaternary Alluvium, SS: Silurian Sedimentary, MIR: Marysville Igneous Rhyodacite, DS: Devonian Sedimentary.

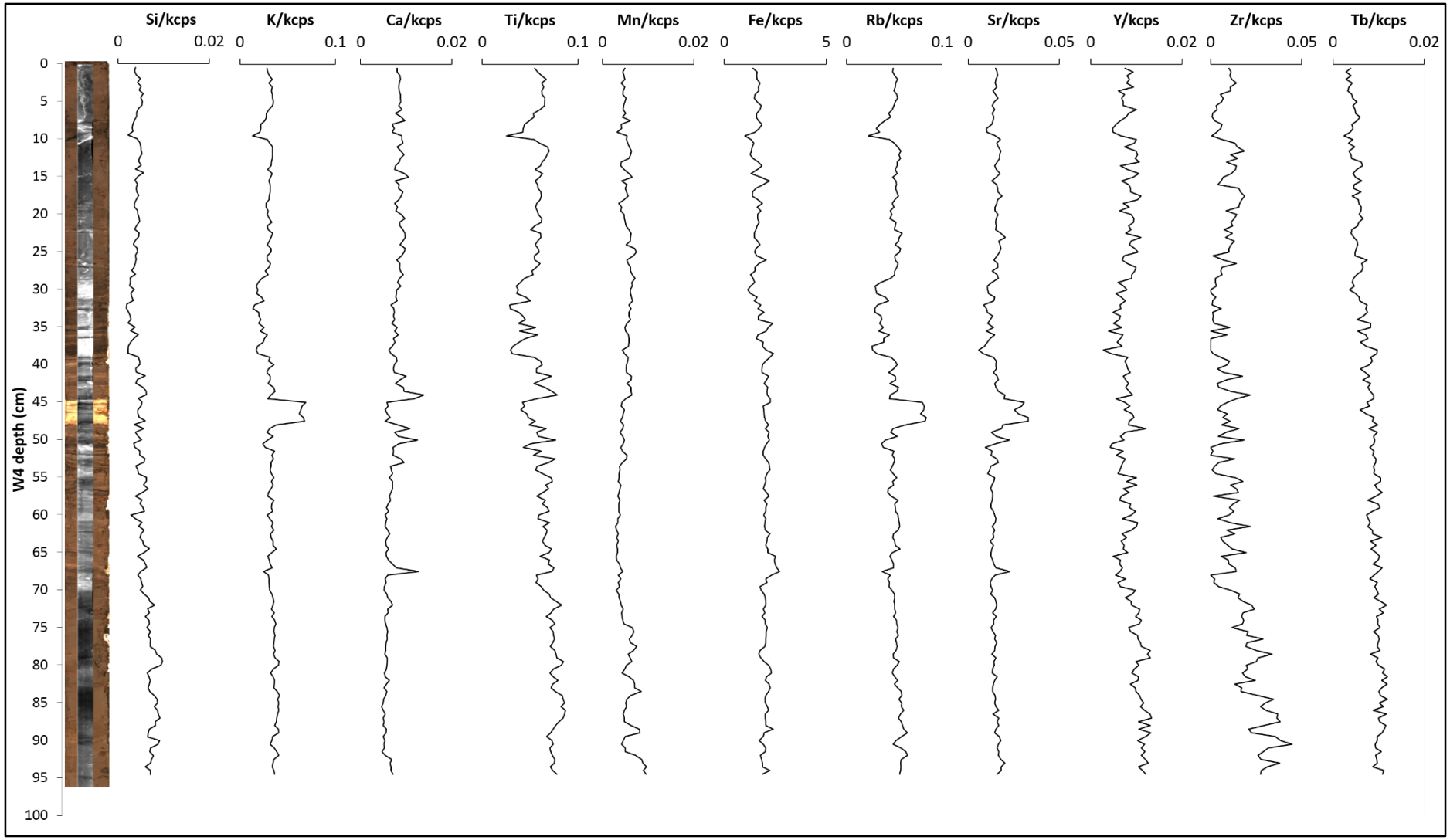

Figure S6: Selected element profiles obtained from micro-XRF core scan for W4.

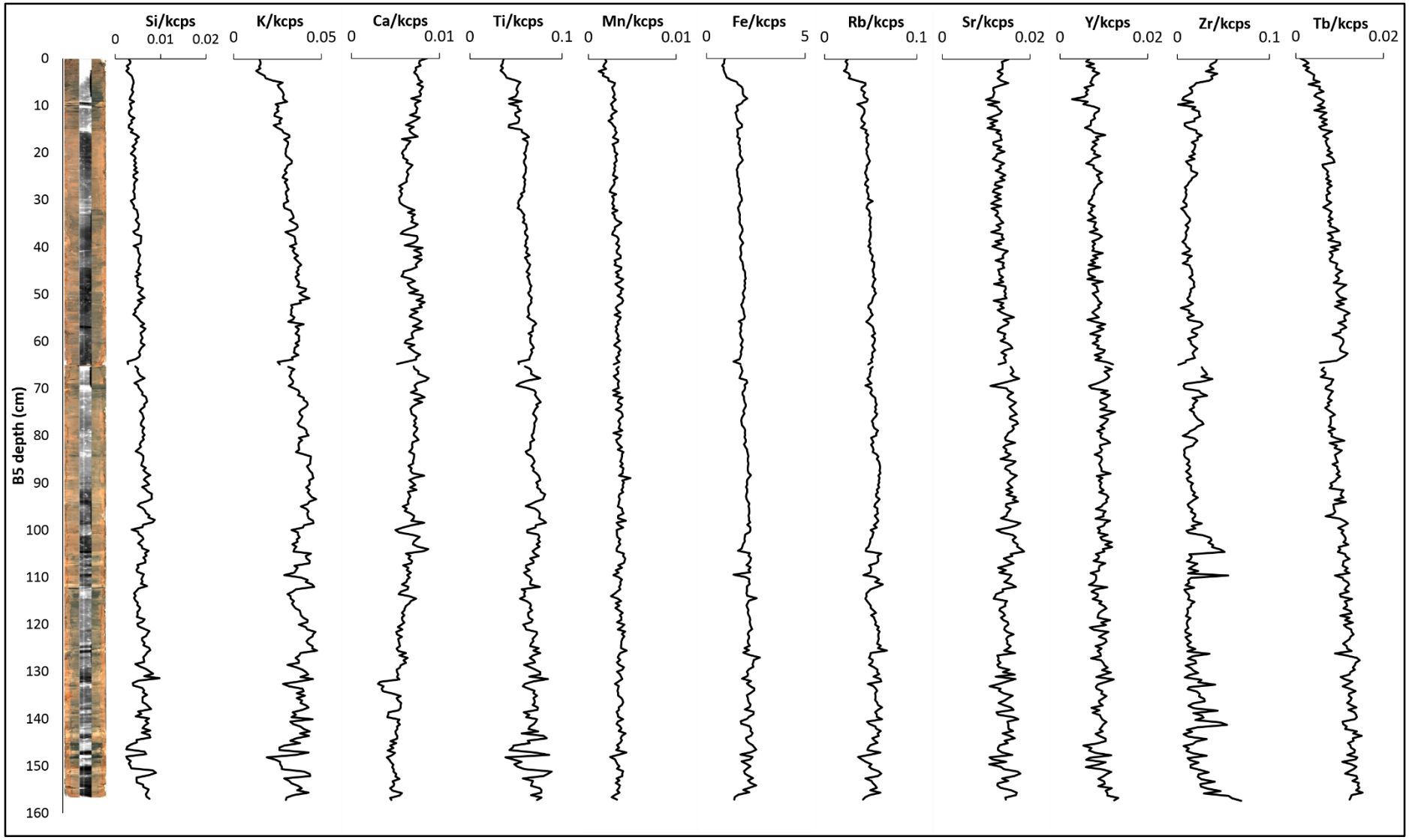

Figure S7: Selected element profiles obtained from micro-XRF core scan for B5.

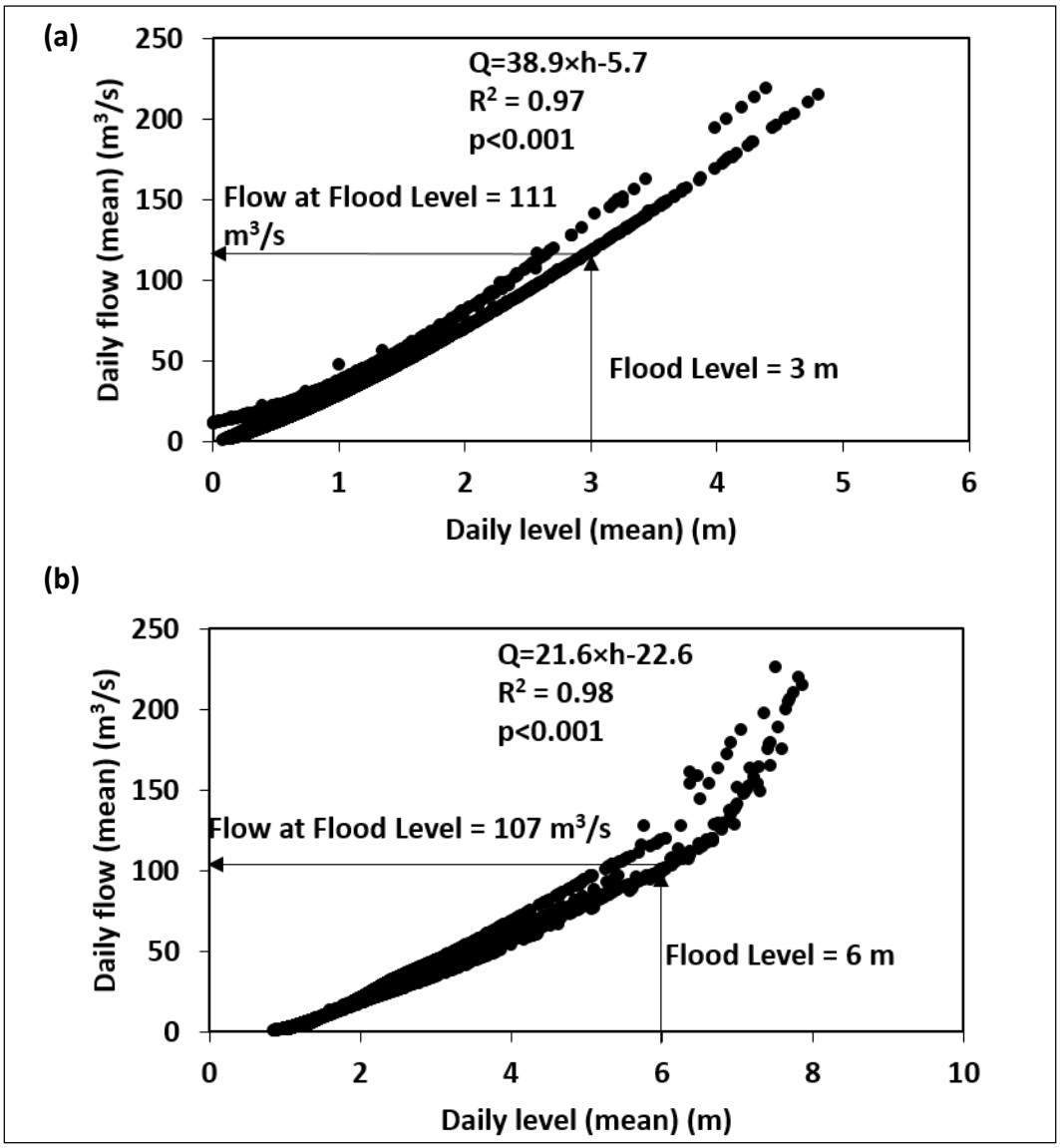

Figure S8: Rating curves for the stream gauges at Chandler Highway (a) and Banksia St (b), developed using available river level and average daily flow data from 1975 to 2013 (Department of Sustainability and Environment, 2013).

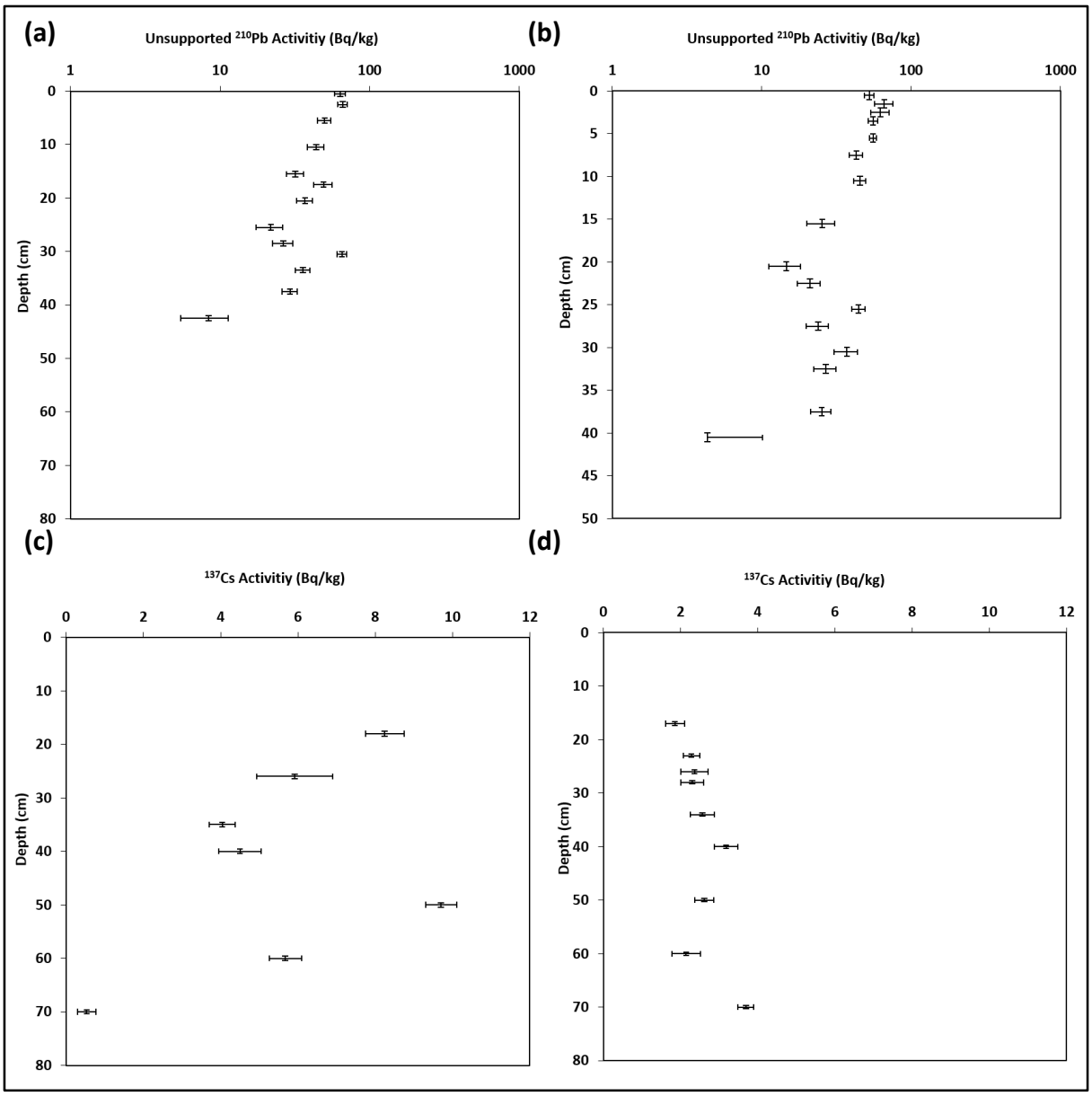

Figure S9: ^{210}Pb and ^{137}Cs activity for W4 (a, c) and B5 (b, d).

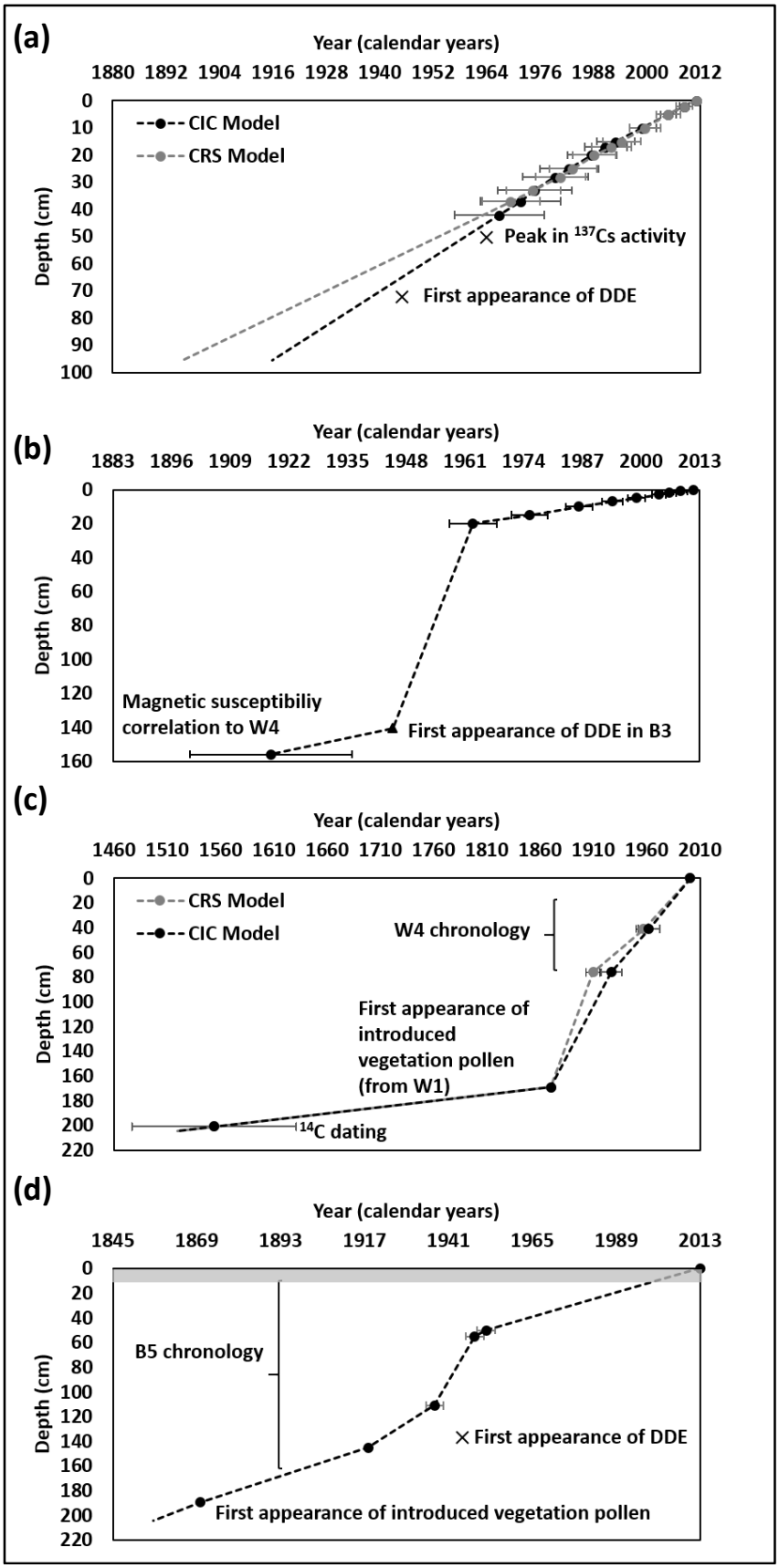

Figure S10: Age-depth models for W4 (a), B5 (b), W2001(c) and B3 (d). The grey box in (d) represents the top 13 cm of the core that was not analysed in the ITRAX micro-XRF core scanner.

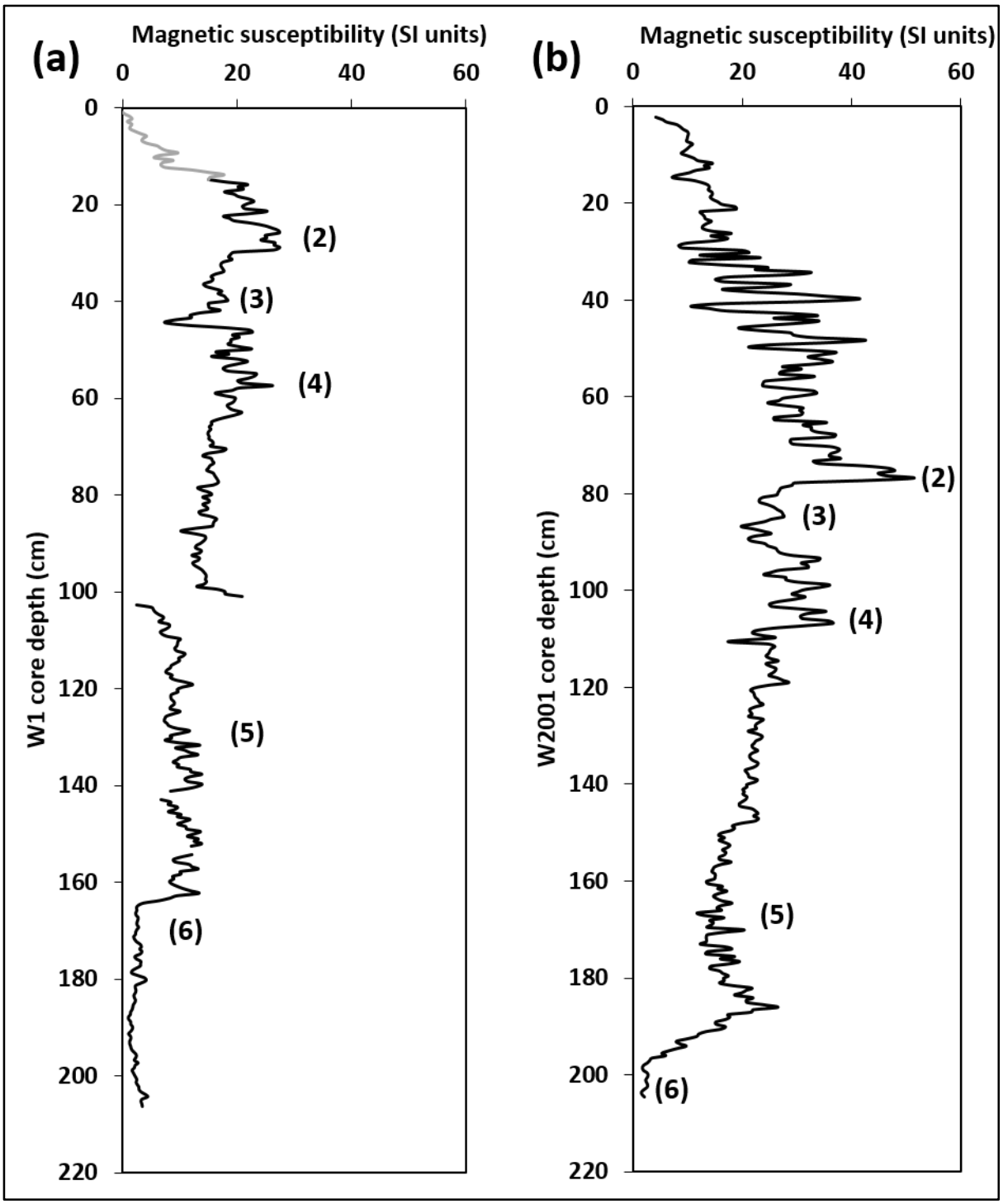

Figure S11: Magnetic susceptibility profiles of W1 (a) and W2001 (b). The grey line in (a) denotes the suspect data due to sediment compaction and loss during coring. The numbers in parentheses represent points where the two magnetic susceptibility curves correlate with each other and W4 (Figure 3).

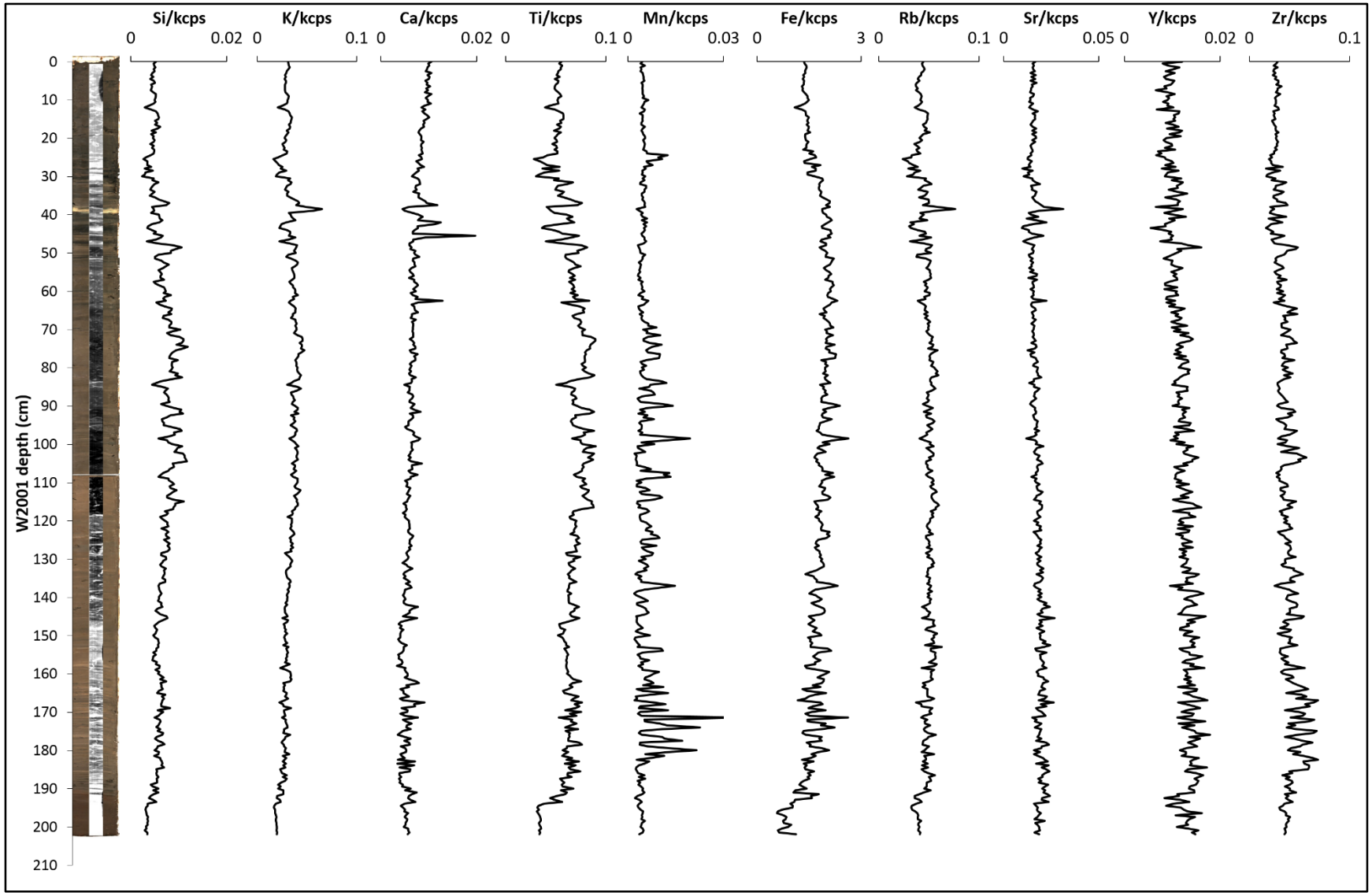

Figure S12: Element profiles obtained from micro-XRF core scanner for W2001.

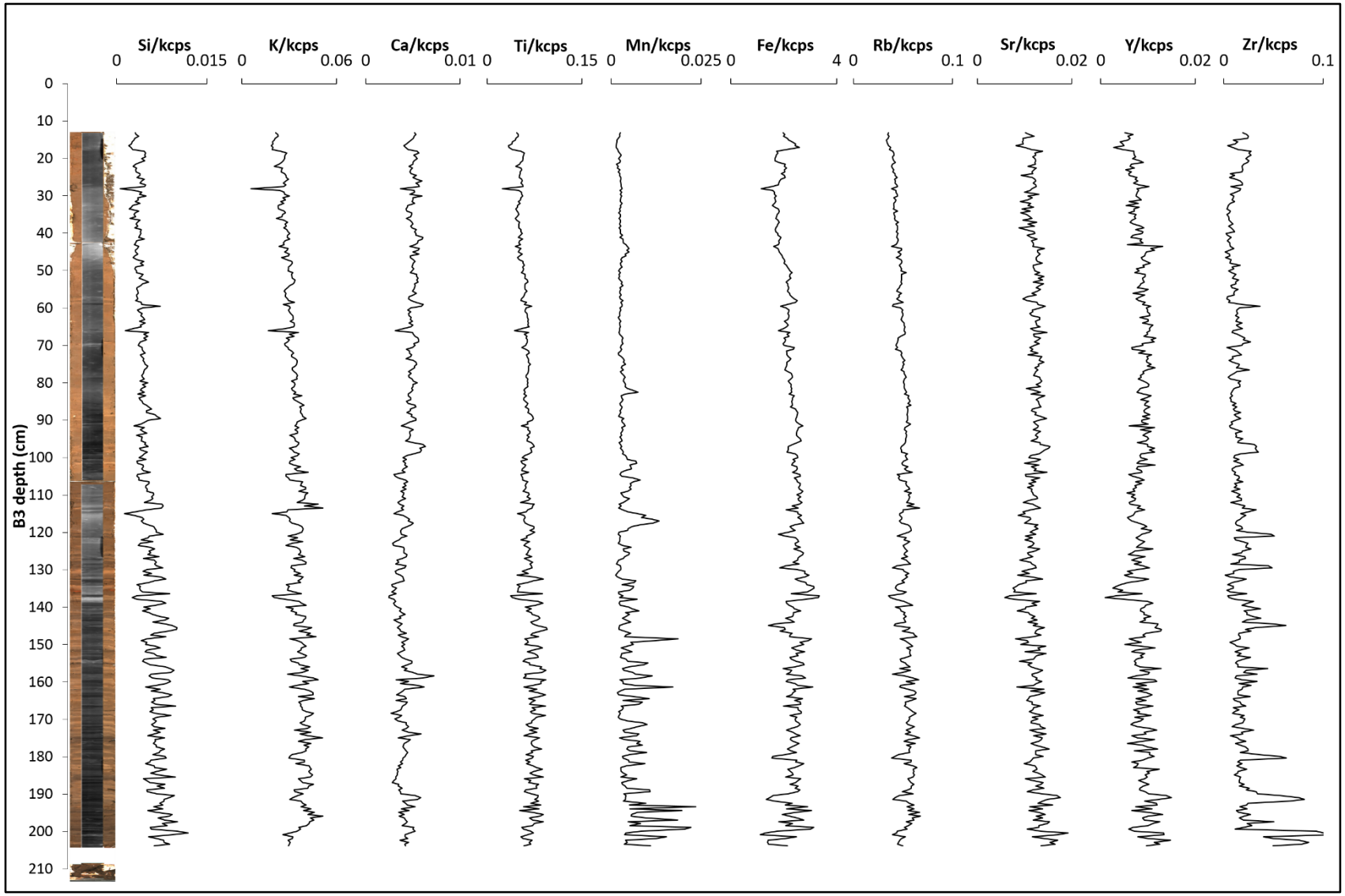

Figure S13: Element profiles obtained from micro-XRF core scanner for B3.

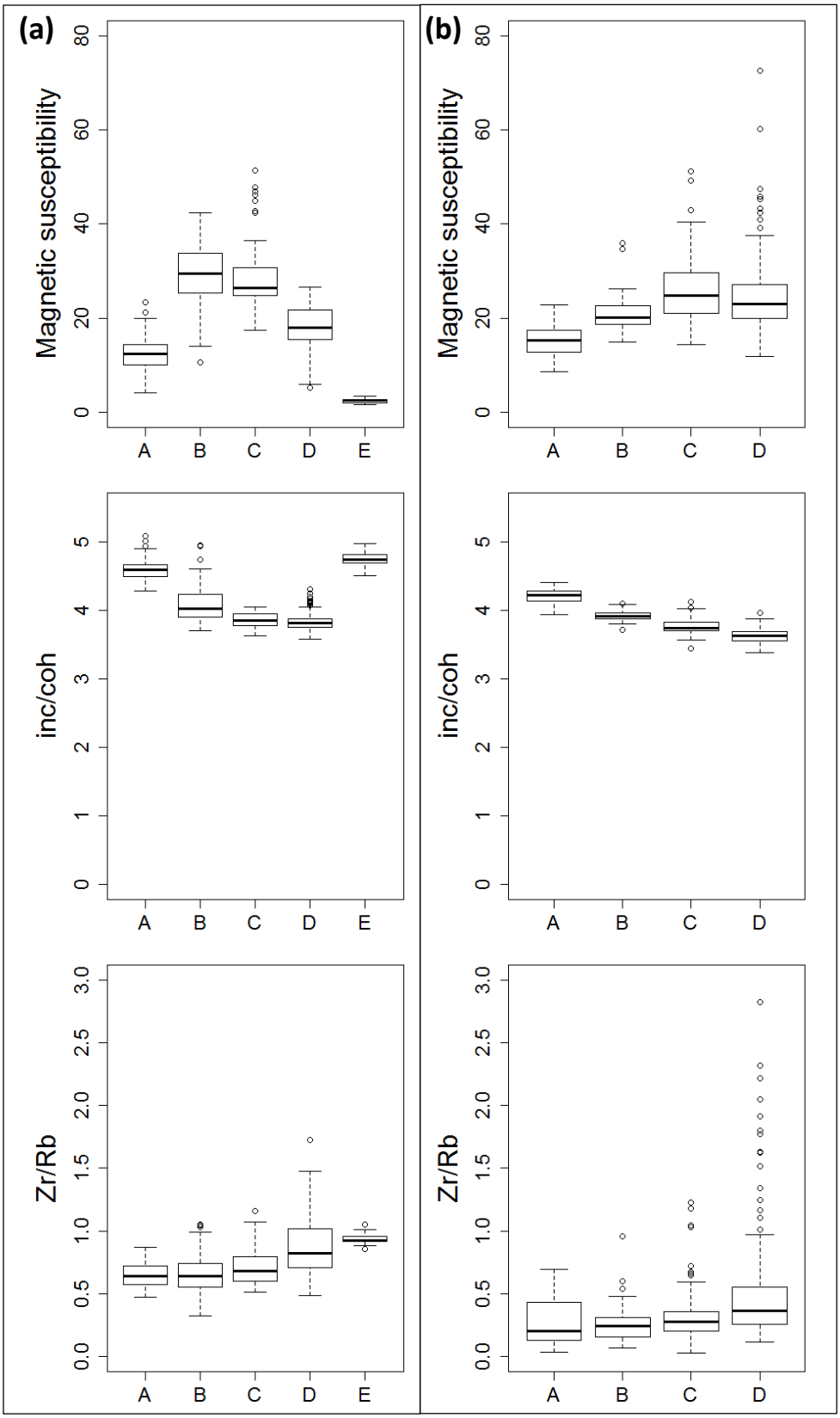

Figure S14: Boxplots showing the distribution of magnetic susceptibility, inc/coh, Zr/Rb and element levels (normalised to total counts, which is expressed as kilo-counts per second; kcps) within each zone for Willsmere Billabong core W2001 (a) and Bolin Billabong core B3 (b).

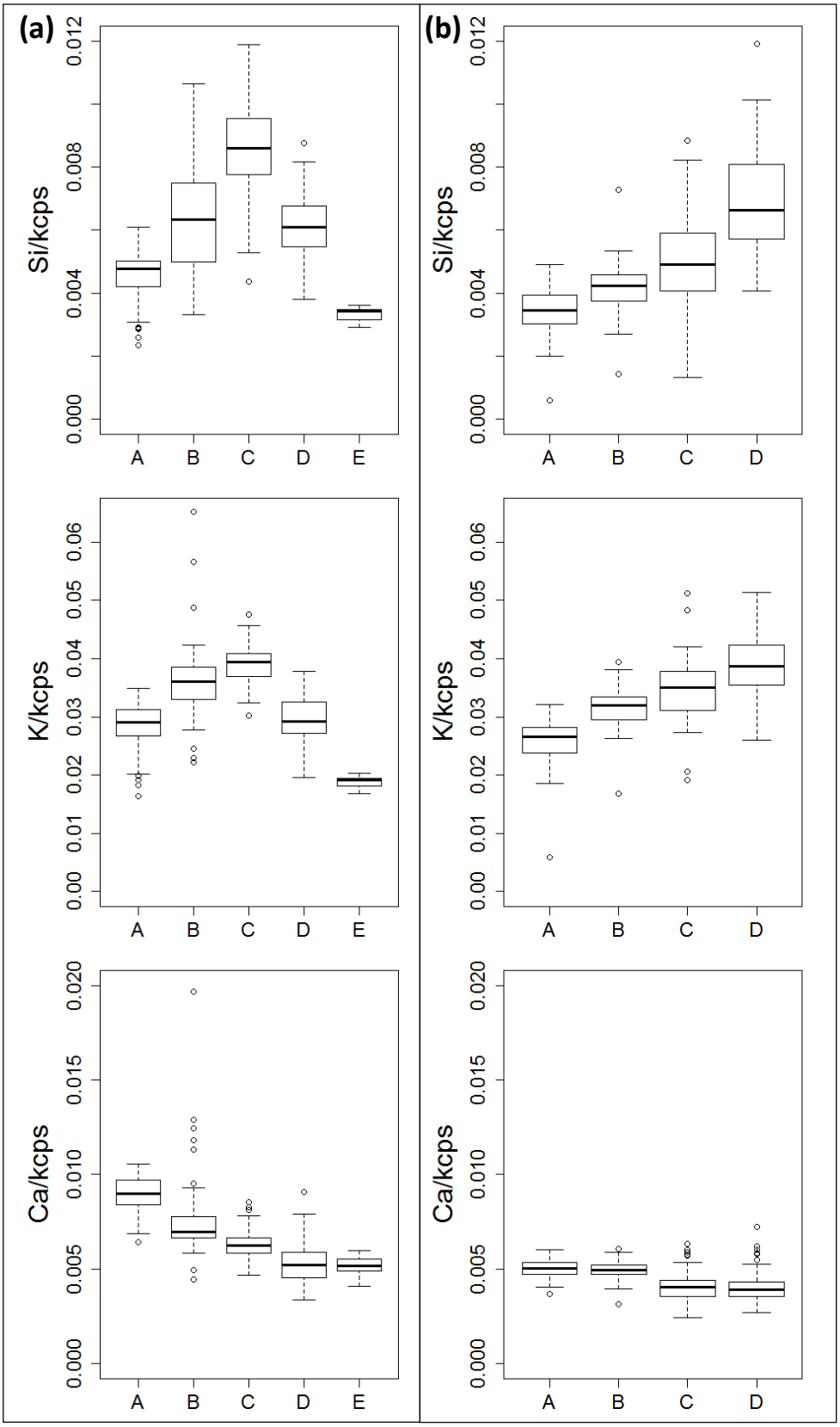

Figure S14 (continued): Boxplots showing the distribution of magnetic susceptibility, inc/coh, Zr/Rb and element levels (normalised to total counts, which is expressed as kilo-counts per second; kcps) within each zone for Willsmere Billabong core W2001 (a) and Bolin Billabong core B3 (b).

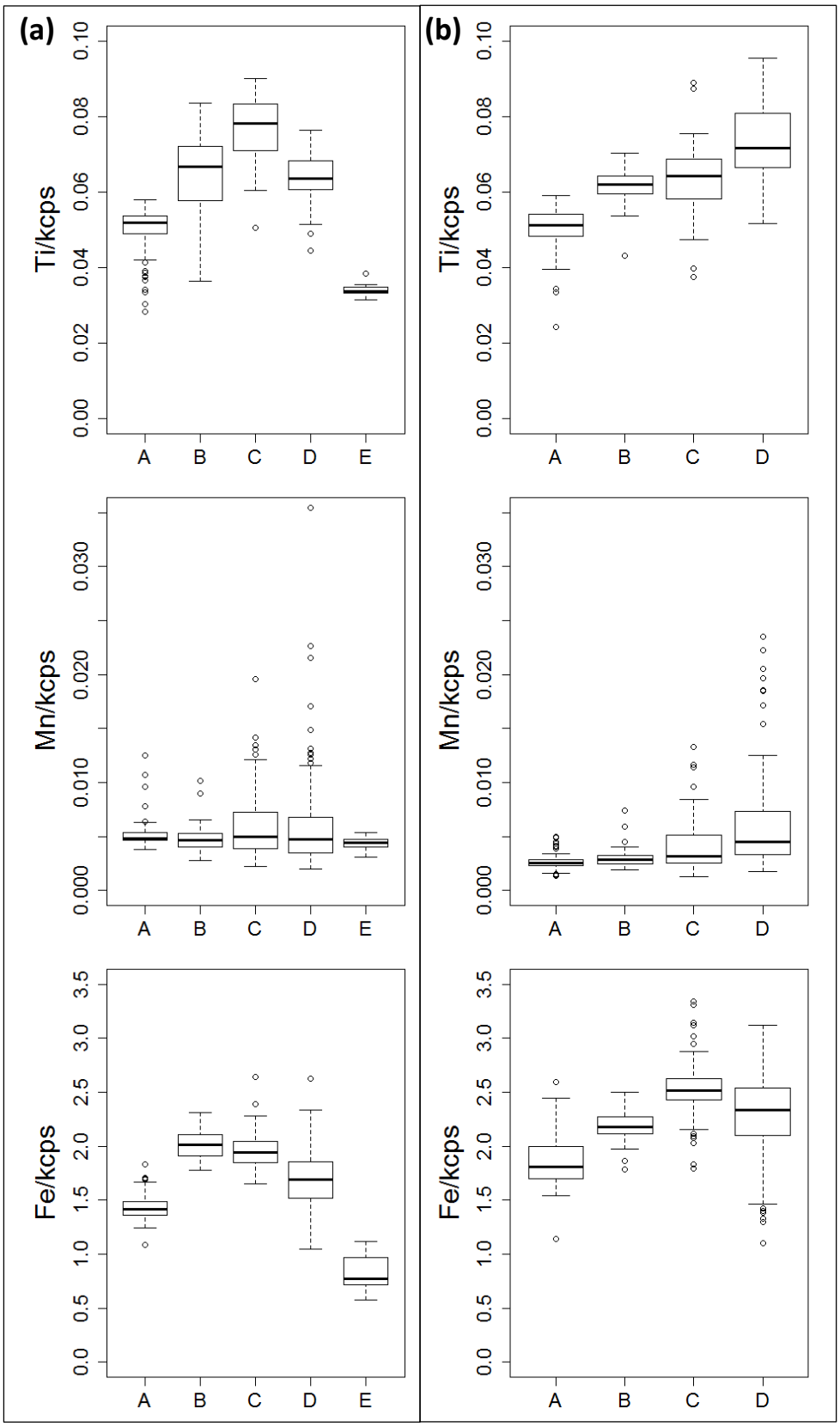

Figure S14 (continued): Boxplots showing the distribution of magnetic susceptibility, inc/coh, Zr/Rb and element levels (normalised to total counts, which is expressed as kilo-counts per second; kcps) within each zone for Willsmere Billabong core W2001 (a) and Bolin Billabong core B3 (b).

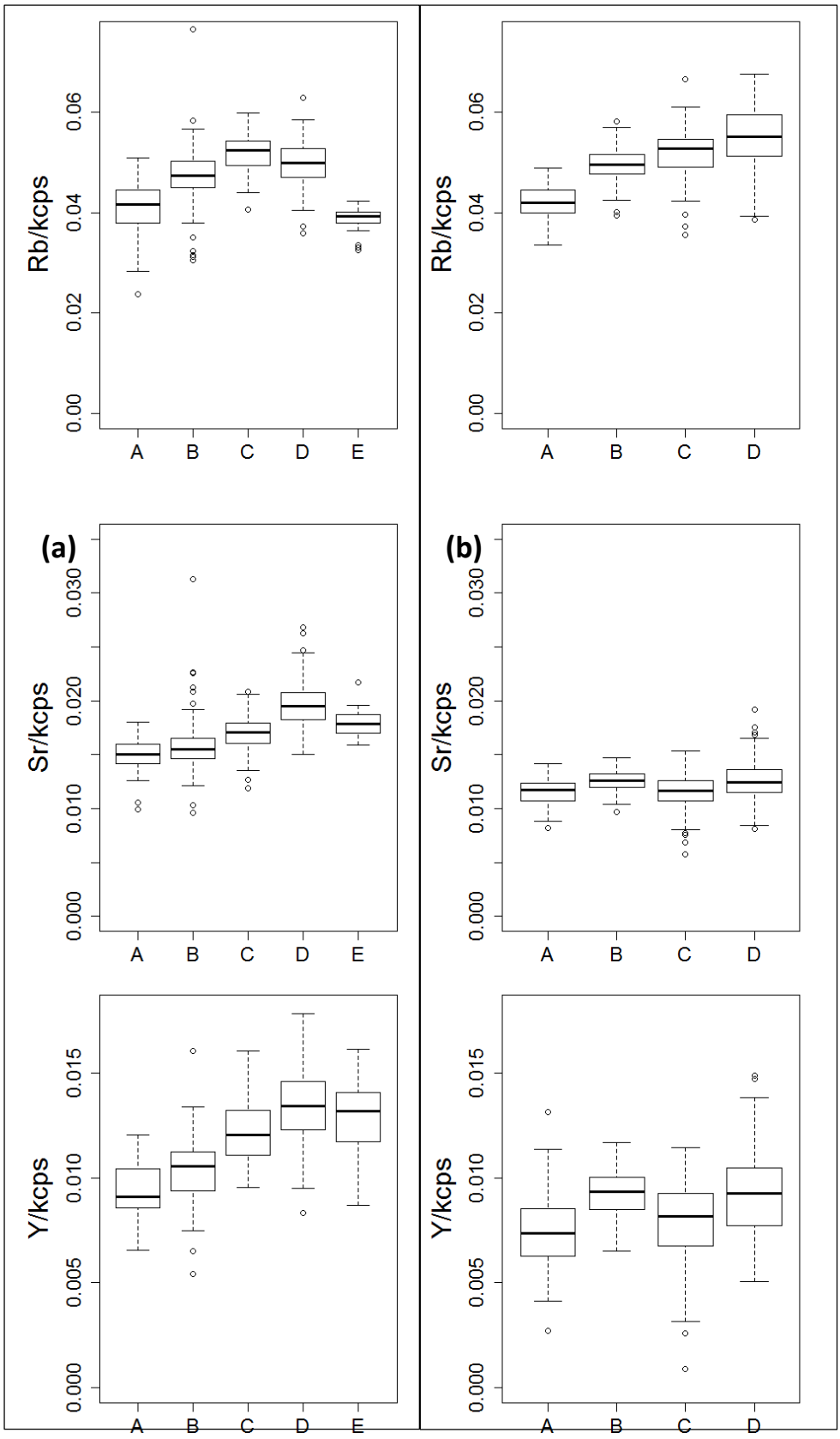

Figure S14 (continued): Boxplots showing the distribution of magnetic susceptibility, inc/coh, Zr/Rb and element levels (normalised to total counts, which is expressed as kilo-counts per second; kcps) within each zone for Willsmere Billabong core W2001 (a) and Bolin Billabong core B3 (b).

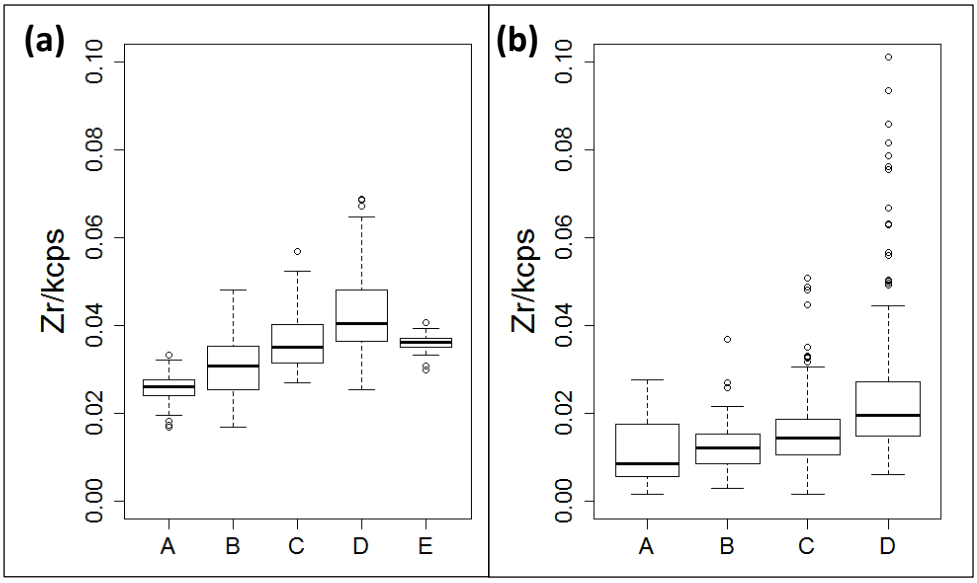

Figure S14 (continued): Boxplots showing the distribution of magnetic susceptibility, inc/coh, Zr/Rb and element levels (normalised to total counts, which is expressed as kilo-counts per second; kcps) within each zone for Willsmere Billabong core W2001 (a) and Bolin Billabong core B3 (b).

Appendix A.4 Supplementary materials for 'Uncertainties in pollution data from sedimentary records' (Chapter 6)

Figures

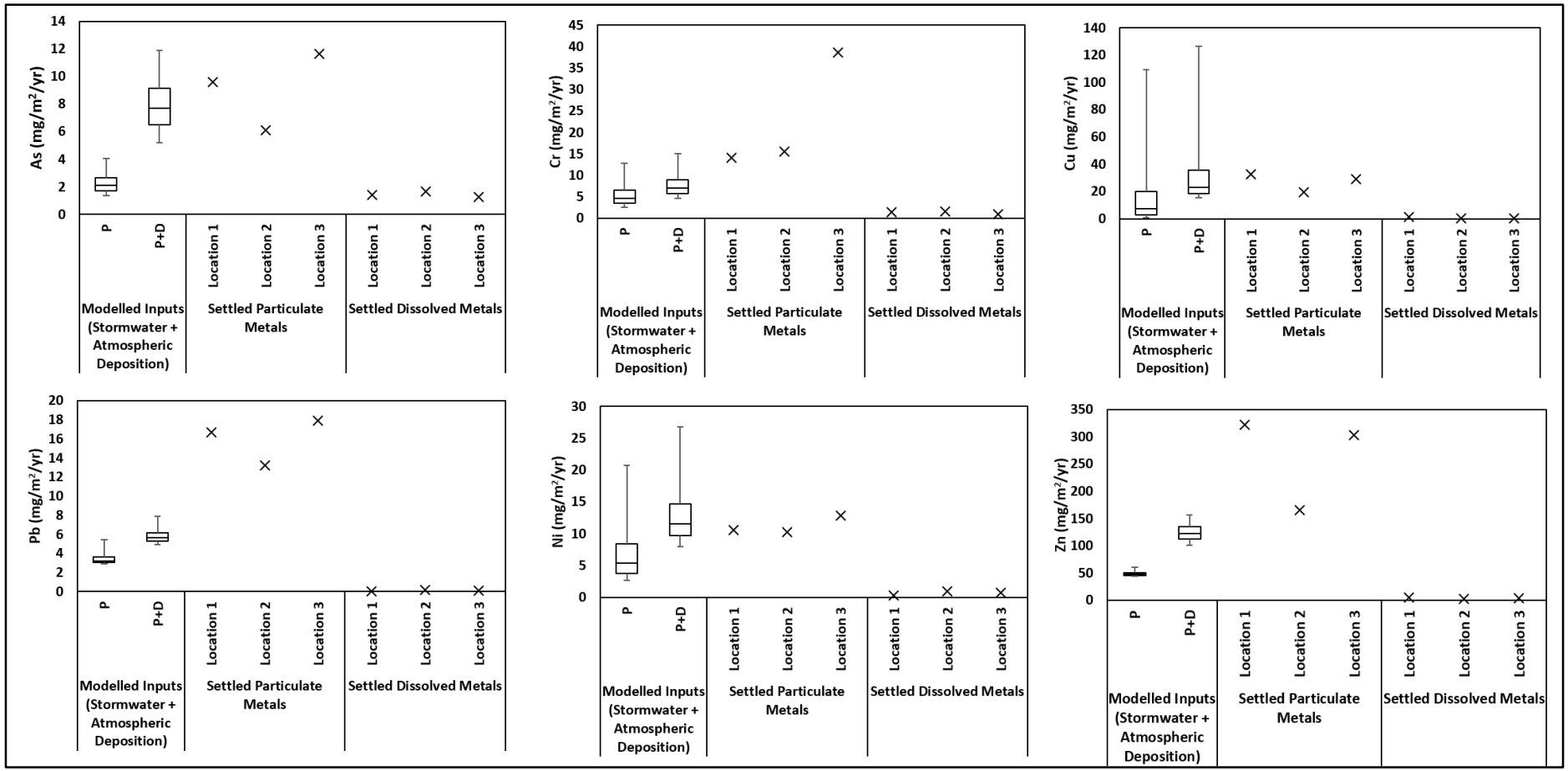

Figure S1: Mass of modelled metal inputs (stormwater discharge and atmospheric deposition) compared to the mass of settled metals in the particulate form and dissolved form over the 12-month monitoring period. Under modelled inputs, P represents inputs that are only in the particulate form, and P+D represents the total inputs (i.e., inputs that are in both particulate and dissolved form).

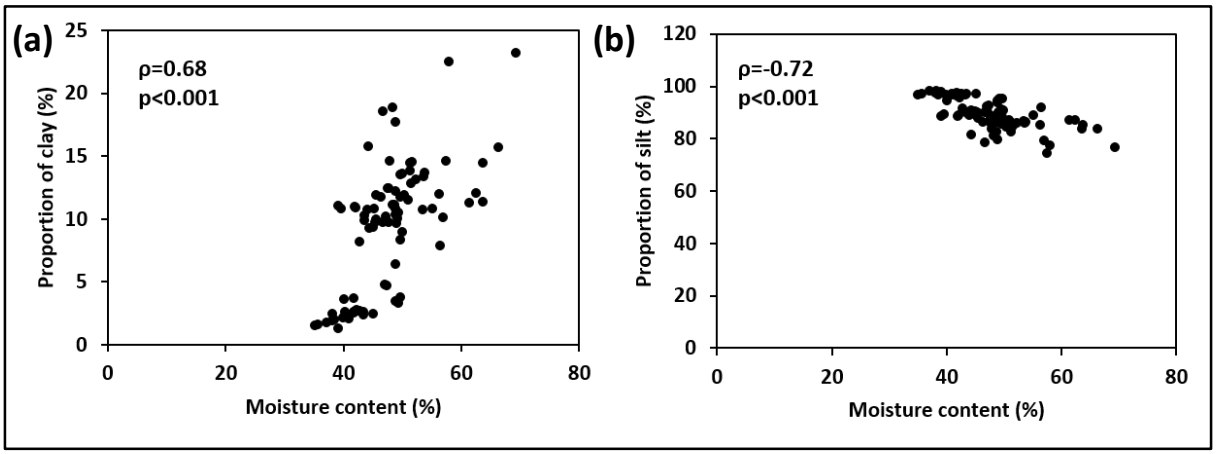

Figure S2: Moisture content (%) and proportion of clay (a) and proportion of silt (b) measured at 1-cm intervals through W4. Grain size data for W4 is from Lintern *et al.* (in preparation-a). Spearman Rank Correlation Coefficient (ρ) and p-values shown.

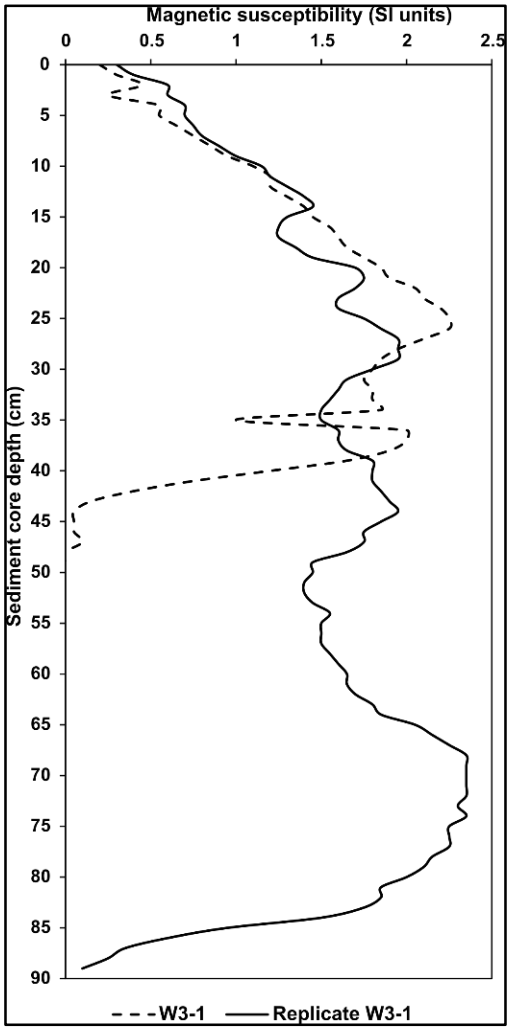

Figure S3: Magnetic susceptibility profiles of the two sediment cores taken from Location 3 (W3-1 and W3-2) using the Bartington MS Series One meter and core scanning loop.

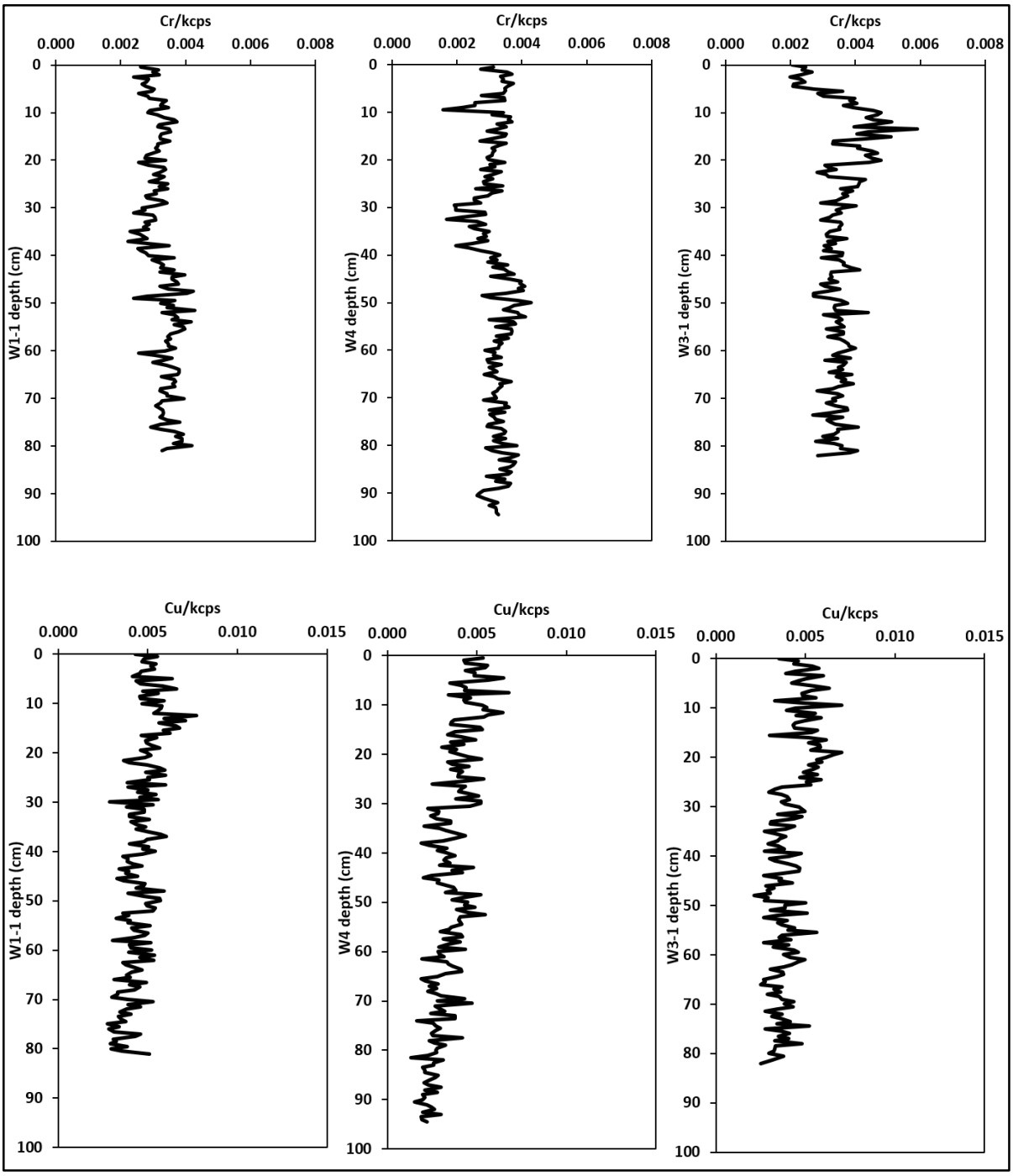

Figure S4: Heavy metal profiles (Cr, Cu, Pb, Ni, Zn) for three Willsmere Billabong cores (W1-1, W4, W3-1).

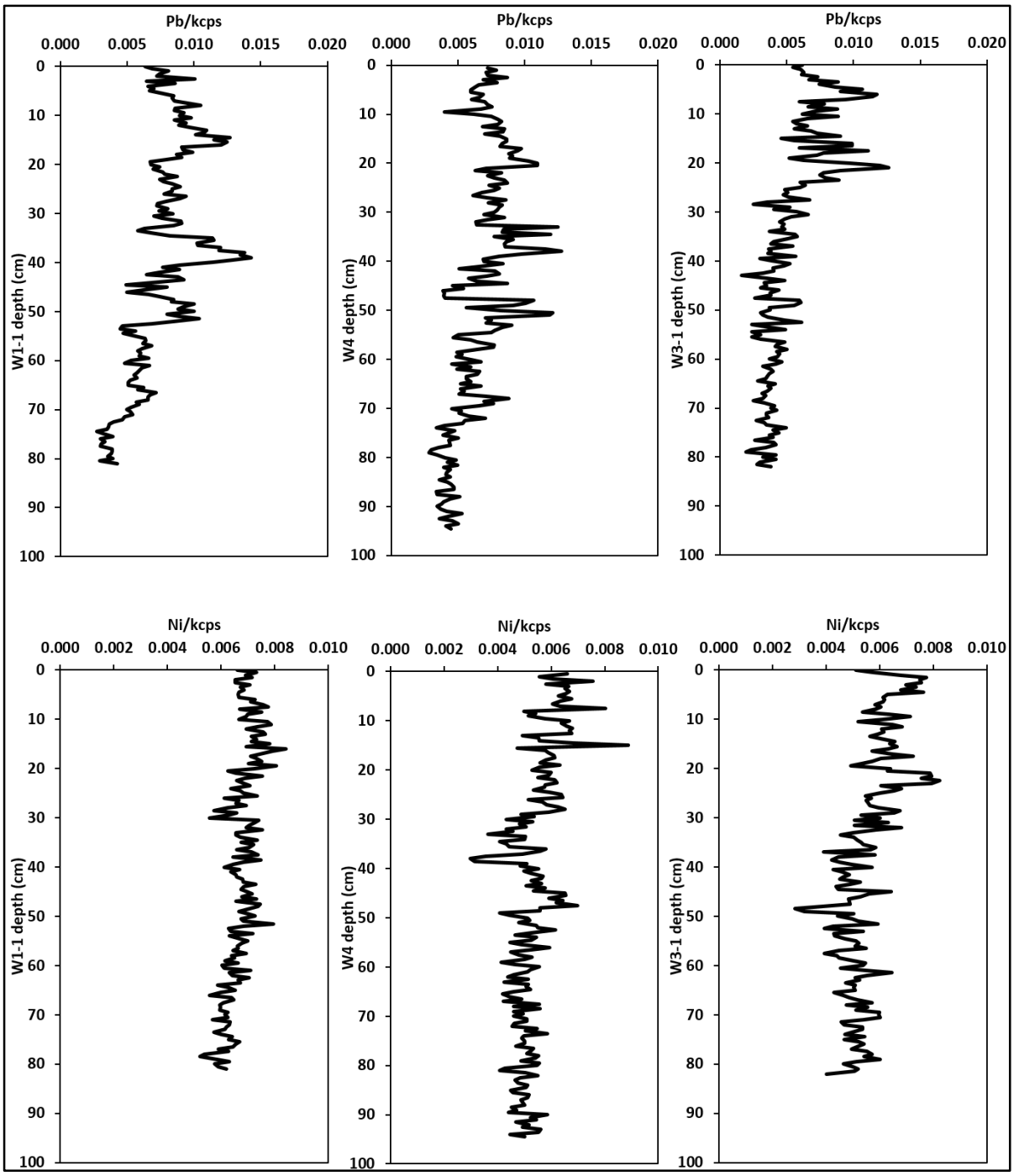

Figure S4 (continued): Heavy metal profiles (Cr, Cu, Pb, Ni, Zn) for three Willsmere Billabong cores (W1-1, W4, W3-1).

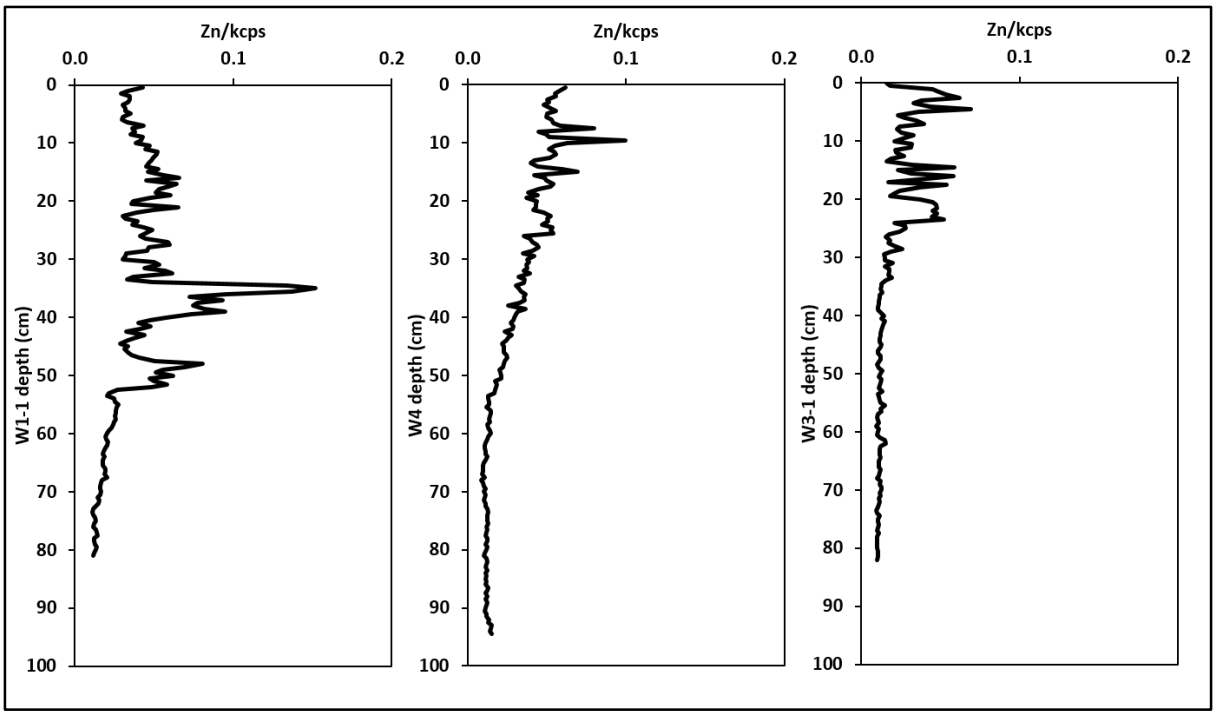

Figure S4 (continued): Heavy metal profiles (Cr, Cu, Pb, Ni, Zn) for three Willsmere Billabong cores (W1-1, W4, W3-1).

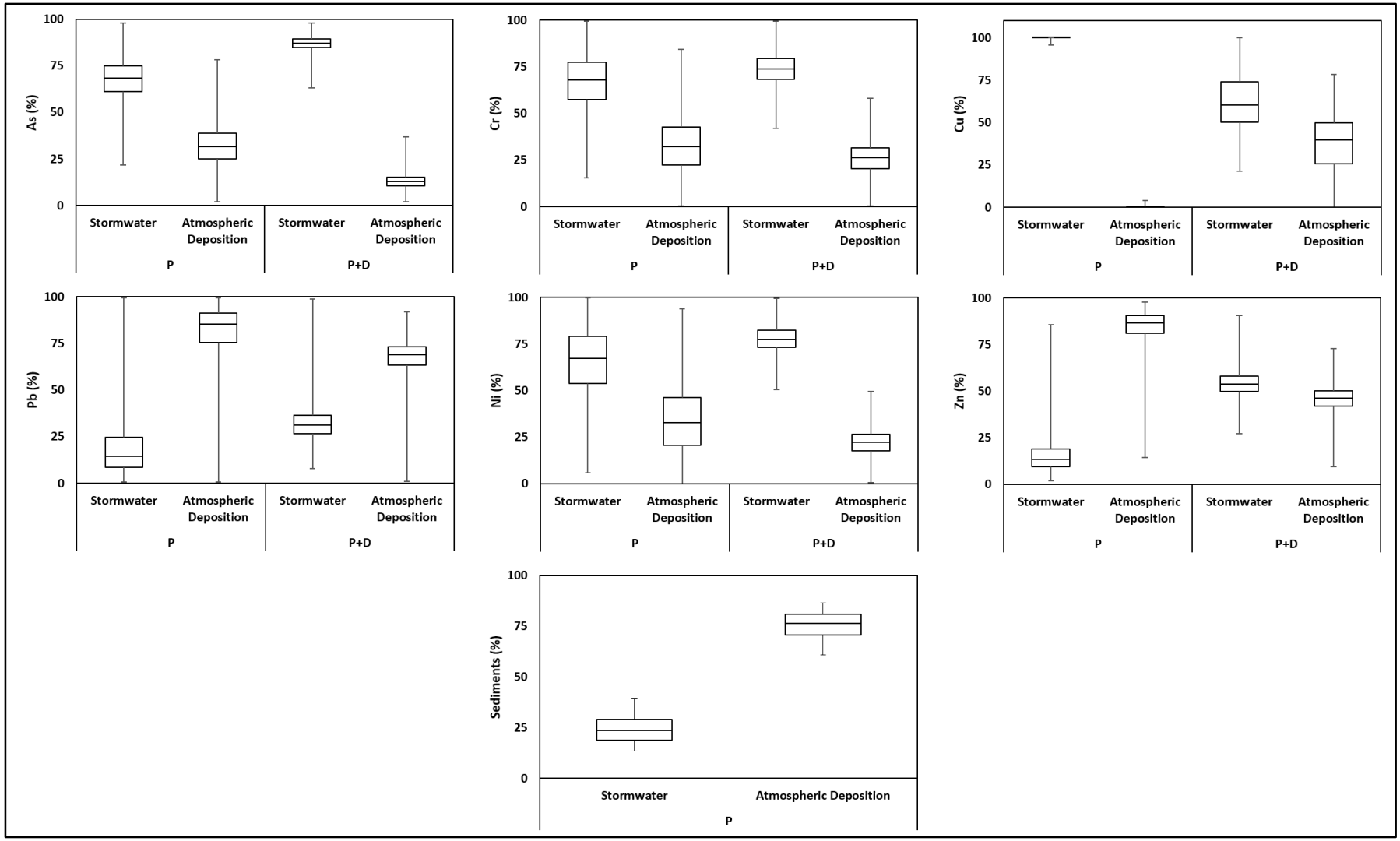

Figure S5: Proportion of heavy metals entering Willsmere Billabong by stormwater and by atmospheric deposition (cumulative over 12 months). P represents the mass of particulate matter entering by urban stormwater and atmospheric deposition, and P+D represents the total mass entering (sum of particulate matter and dissolved matter) by urban stormwater and atmospheric deposition.

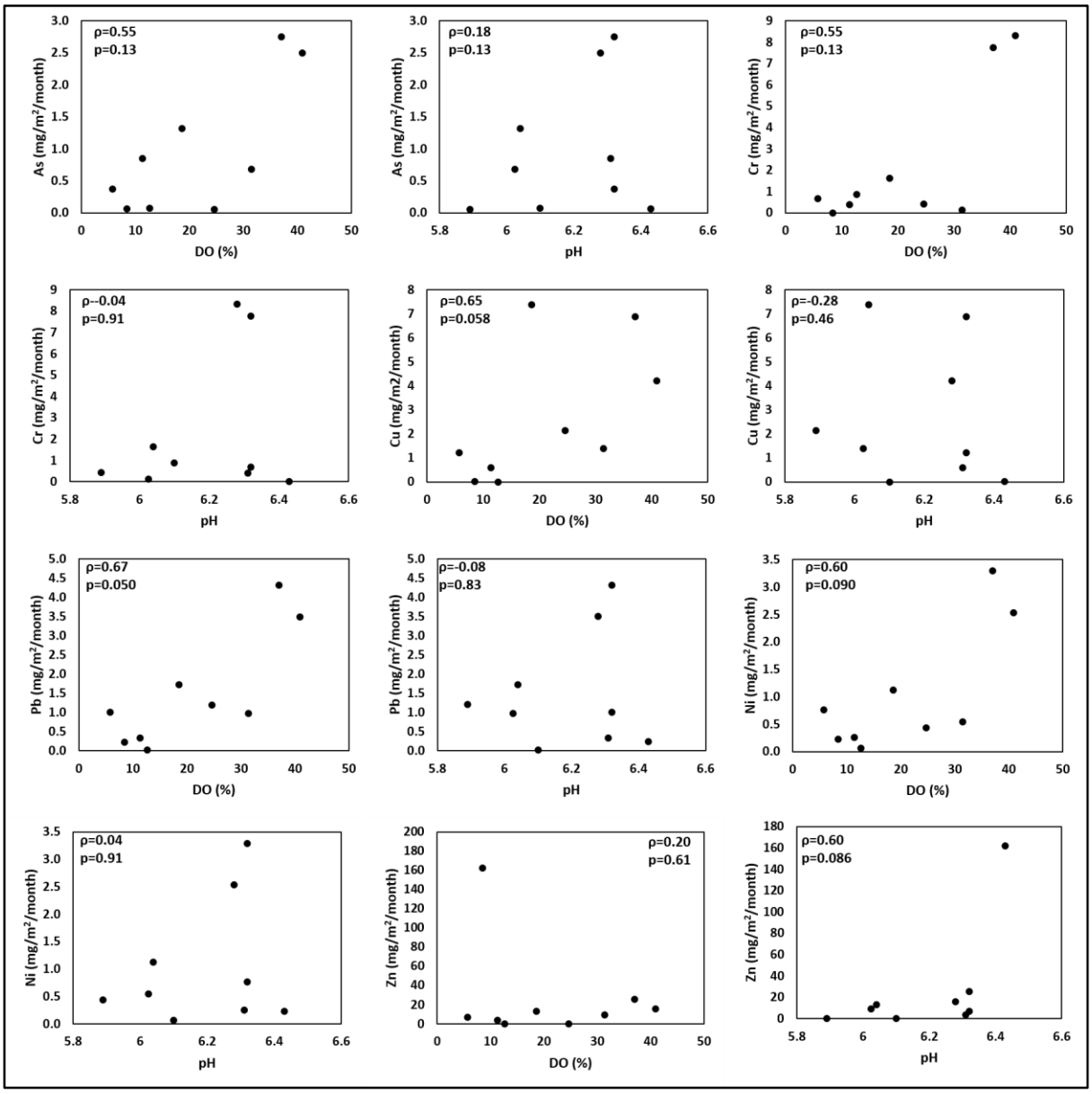

Figure S6: Correlation between DO (%), pH and heavy metal masses deposited on sediment bed each month (mg/m²/month). Spearman Rank Correlation Coefficients (ρ) and p-values shown for each metal.

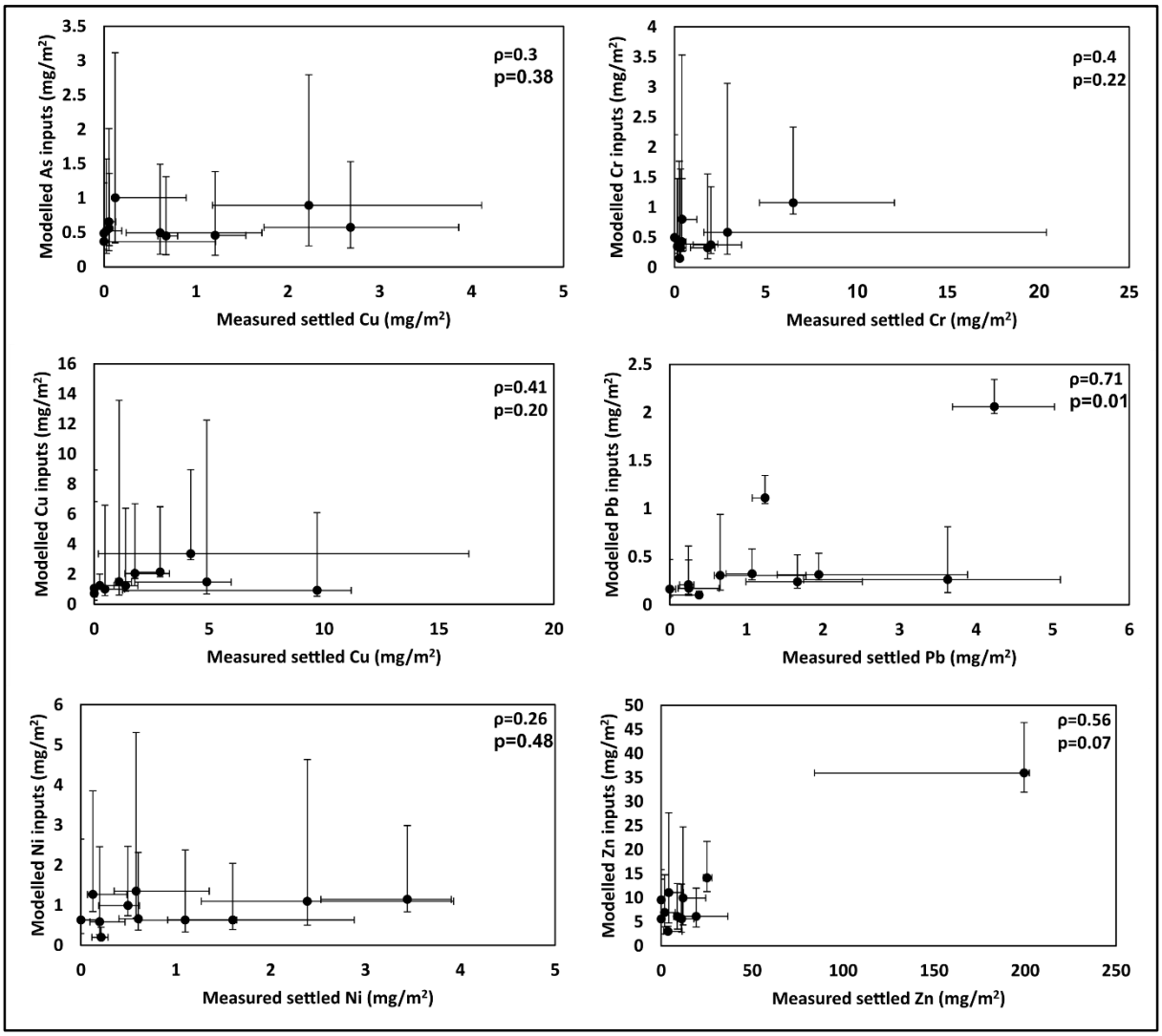

Figure S7: Correlation between median settled metal masses measured in the sediment traps and median modelled metal inputs each month. Error bars represent 95% confidence intervals. Spearman Rank Correlation Coefficients (ρ) and p-values shown for each metal.

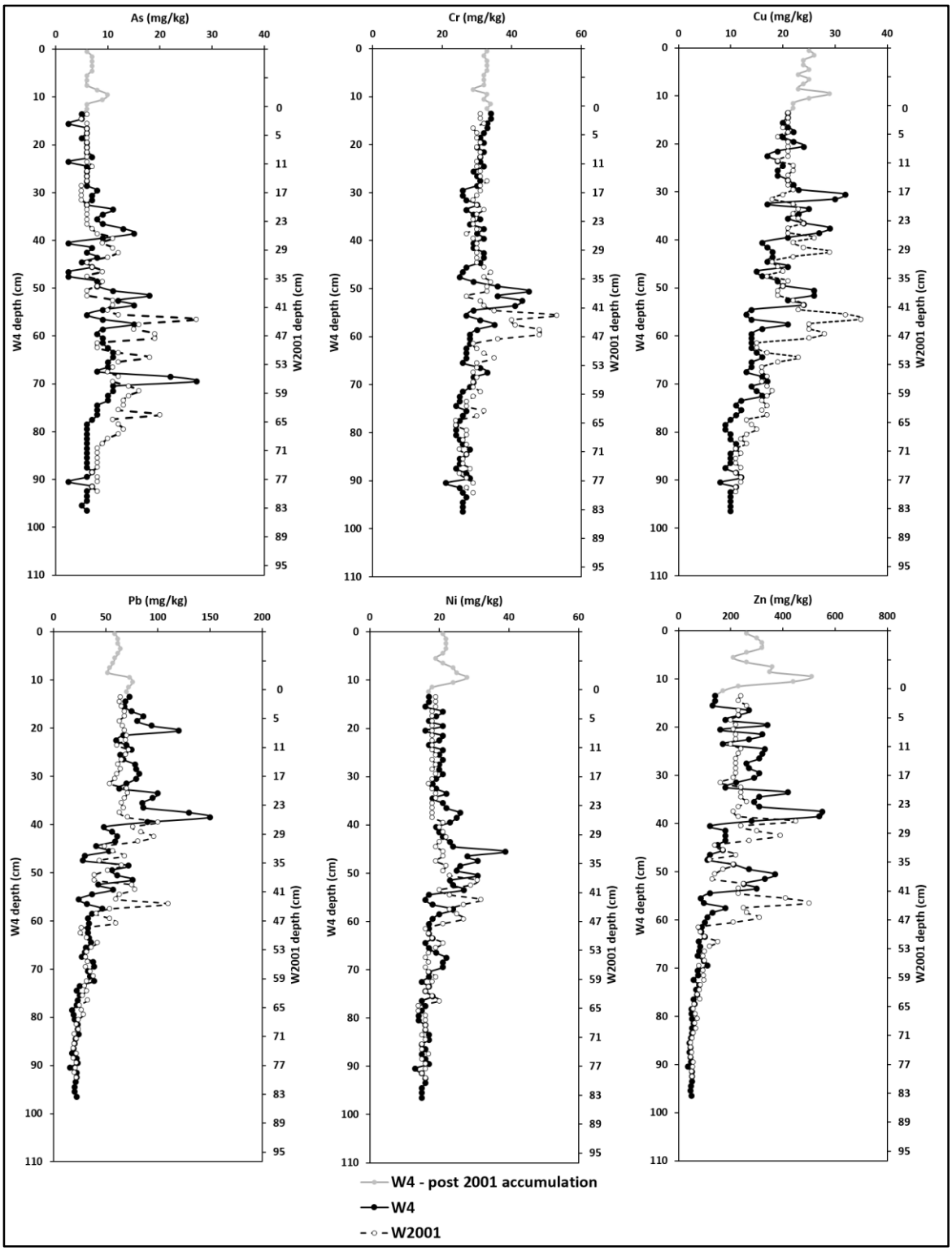

Figure S8: High resolution (1-cm interval) metal trends for Willsmere Billabong cores W4 (on primary y axis) and W2001 (on secondary y axis).

Tables

Table S1: Comparison between log-transformed measured stormwater heavy metal levels and stormwater heavy metal levels around the world. Shaded cells indicate where data are unavailable.

		Log-transformed data: mean (standard deviation)						
		TSS	**As**	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**
Measured stormwater concentrations in this study		1.93 (1.25)	-0.61 (0.83)	-3.14 (2.68)	-1.85 (3.33)	-0.65 (1.09)	-1.54 (2.29)	0.145 (2.38)
Measured stormwater concentrations around the world[a] (by land use)	**Roads**			-1.91 (0.25)	-1.09 (0.44)	-0.66 (0.55)		
	High urban roads	2.41 (0.46)						-0.33 (0.35)
	Low urban roads	1.84 (0.66)						-0.71 (0.37)
	Roofs	1.55 (0.38)			-1.62 (0.56)	-1.68 (0.7)		
	Roofs (zinc)							0.57 (0.7)
	Roofs (non-zinc)							-0.8 (0.55)
	Urban (high)	2.19 (0.48)				-0.84 (0.56)	-1.5 (0.3)	
	Urban (high, non-residential)			-1.48 (0.61)	-1.21 (0.49)			-0.49 (0.38)
	Urban (medium/low)			-1.71 (0.19)	-1.43 (0.19)	-1.35 (0.62)		-0.71 (0.54)
	Agricultural	2.27 (0.47)						
	Forest	1.90 (0.30))						
	Residential			-1.88 (0.66)	-1.44 (0.42)			-0.79 (0.45)

[a](Duncan, 1999)

Table S2: Comparison between modelled atmospheric deposition heavy metal concentrations and atmospheric deposition heavy metal concentrations measured in Sydney, Australia. Shaded cells indicate where data are unavailable.

		TSS ($mg/m^2/day$)	As ($\mu g/m^2/day$)	Cr ($\mu g/m^2/day$)	Cu ($\mu g/m^2/day$)	Pb ($\mu g/m^2/day$)	Ni ($\mu g/m^2/day$)	Zn ($\mu g/m^2/day$)
Total modelled deposition	**Minimum**	167	5.44	1.47	0.0486	3.02	1.38	26.0
	25th percentile	194	29.5	55.9	70.7	174	48.1	115
	Median	209	35.0	71.7	109	189	64.5	126
	75th percentile	222	41.3	86.9	136	201	73.2	138
	Maximum	237	101	159	215	252	136	199
Mean measured data from Sydney (by land use)[a]	**Background (low)**	19			11	12		131
	Background (high)	30			20	29		118
	Road (low)	58			28	39		238
	Road (medium)	212			184	83		865
	Road (high)	288			246	106		1354

[a](Davis and Birch, 2011)

Appendix A.5 Supplementary material for 'Recreating historical data from sediment cores; to protect aquatic environments' (Chapter 7)

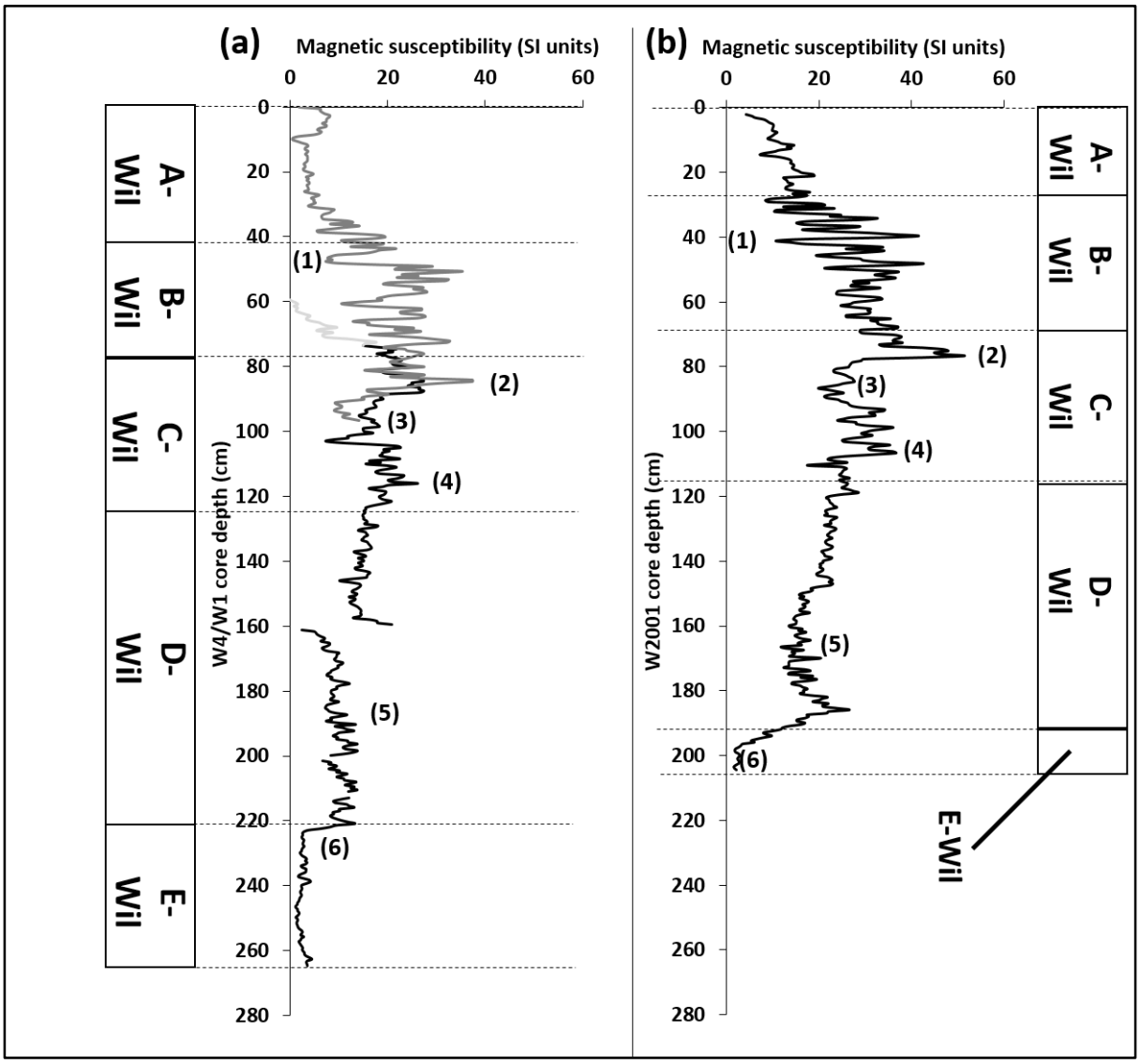

Figure S1: **The magnetic susceptibility profiles of W4 and W1 (a) and the magnetic susceptibility profile of the replicate Willsmere Billabong core W2001 that was studied in Lintern *et al.* (in preparation-a) (b). Numbers on magnetic susceptibility profile represent points of correlation between the profiles. Correlations between hydrologic or depositional zones in W2001 and W4 and W1 shown.**

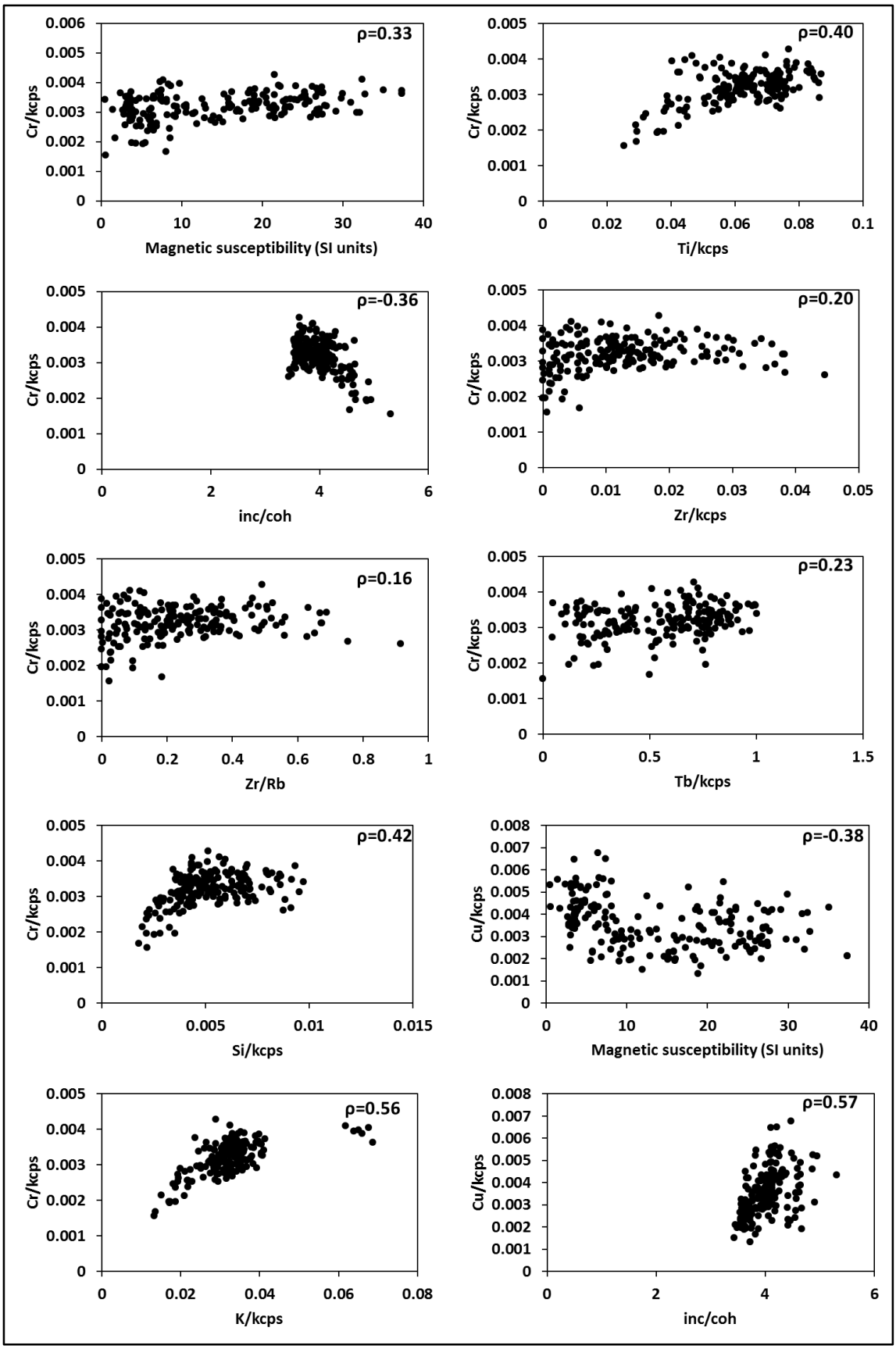

Figure S2: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Willsmere Billabong core W4. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant ($p<0.05$).

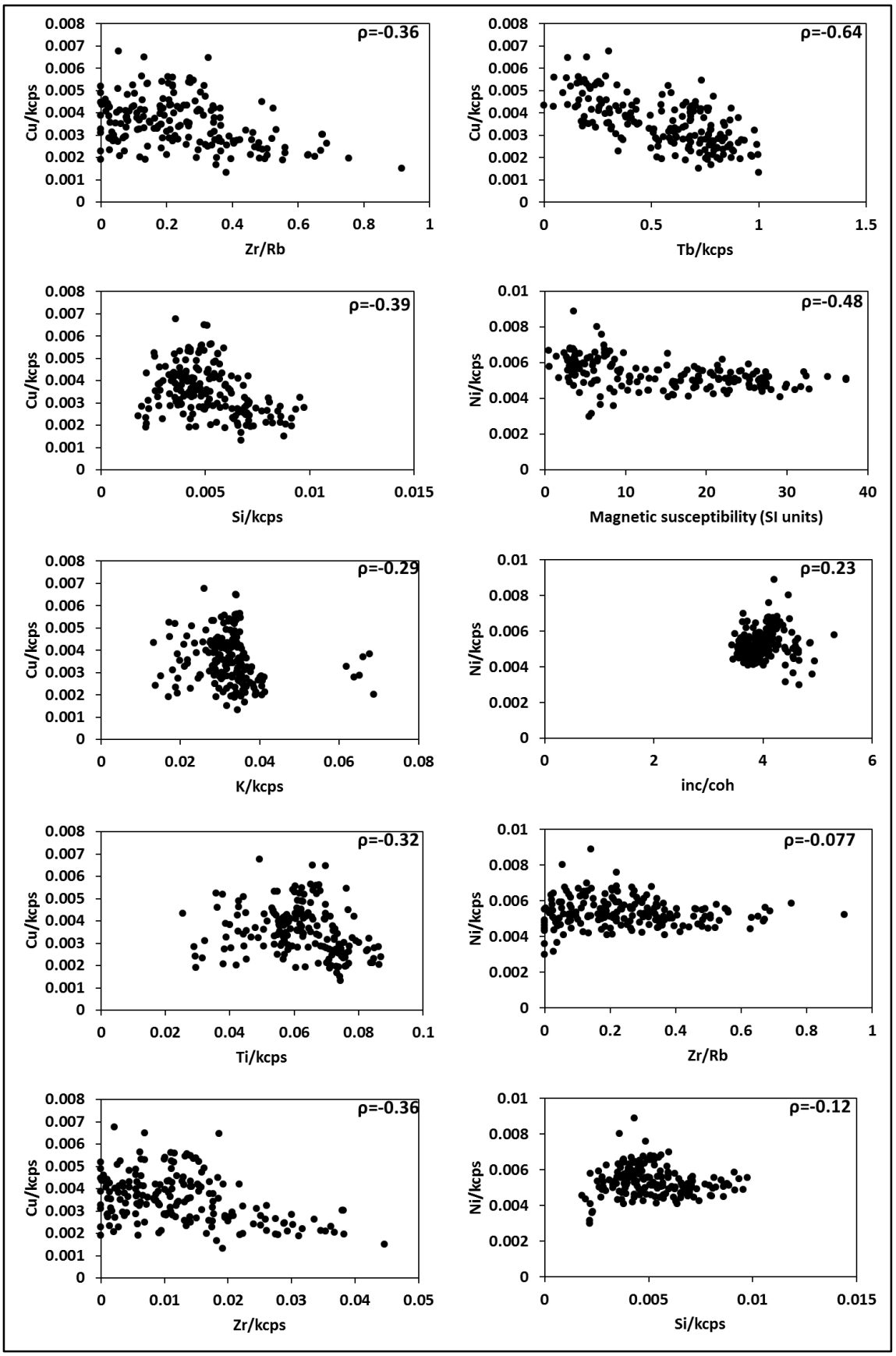

Figure S2 continued: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Willsmere Billabong core W4. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant (p<0.05).

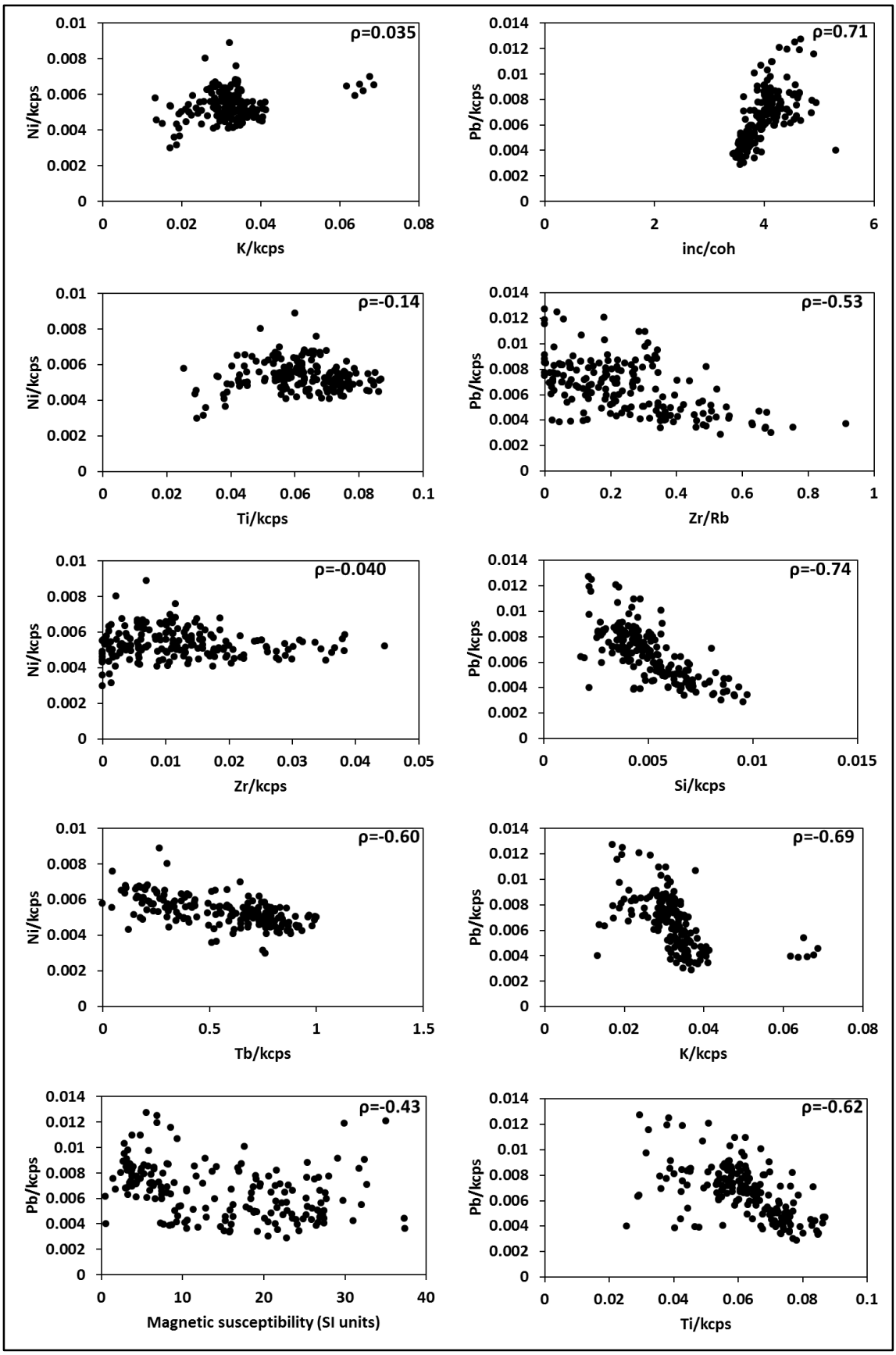

Figure S2 continued: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Willsmere Billabong core W4. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant ($p<0.05$).

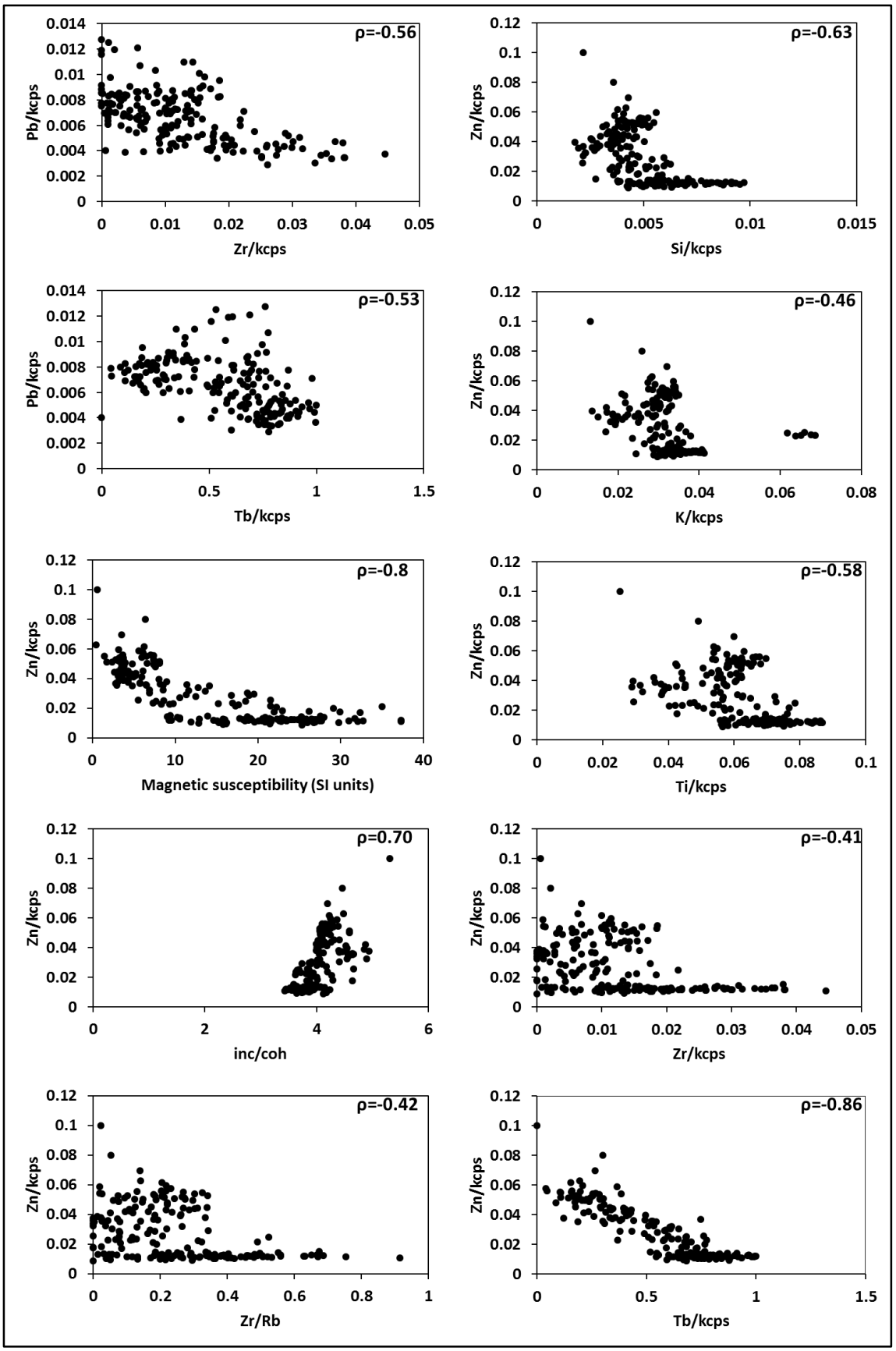

Figure S2 continued: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Willsmere Billabong core W4. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant (p<0.05).

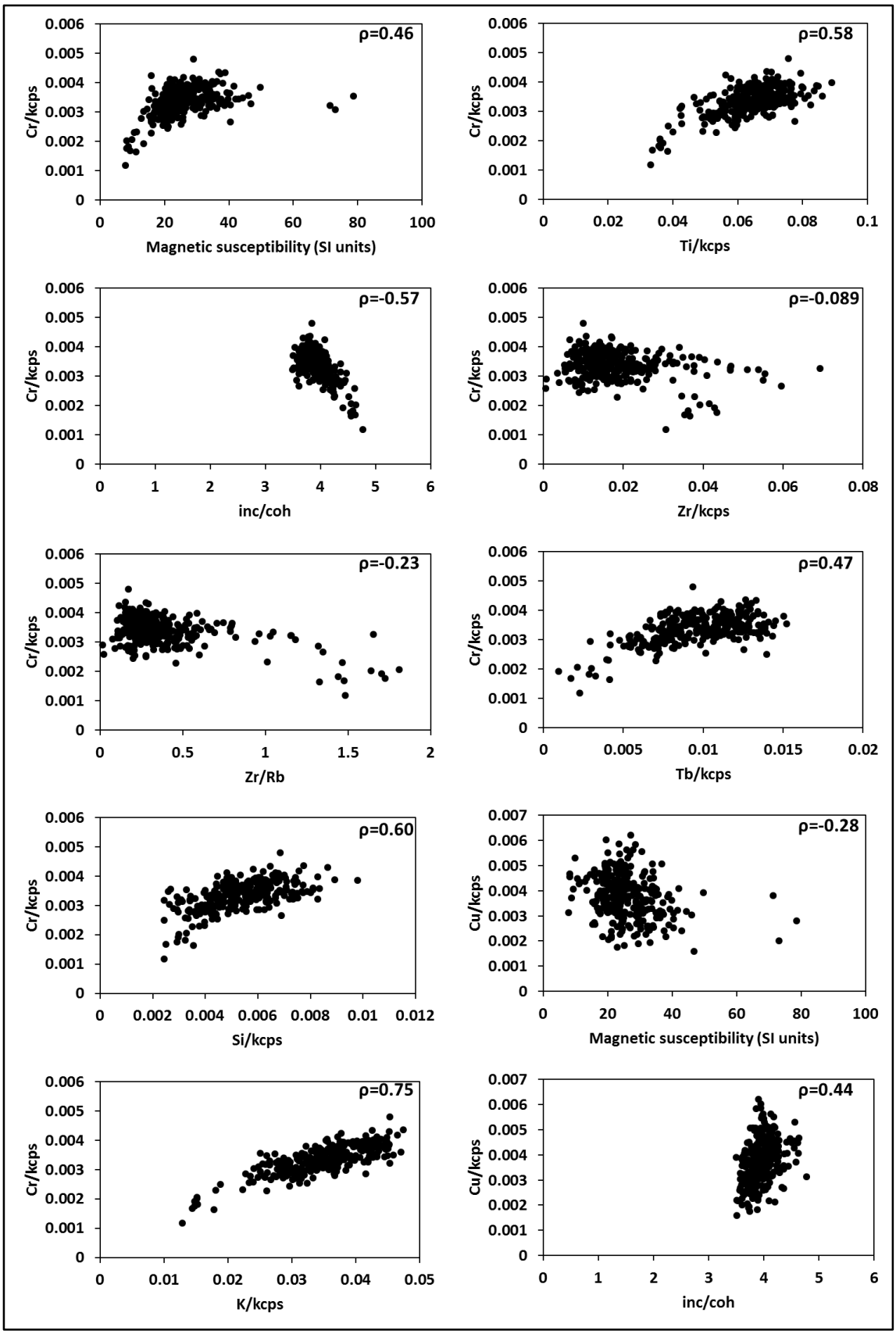

Figure S3: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Bolin Billabong core B5. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant ($p<0.05$).

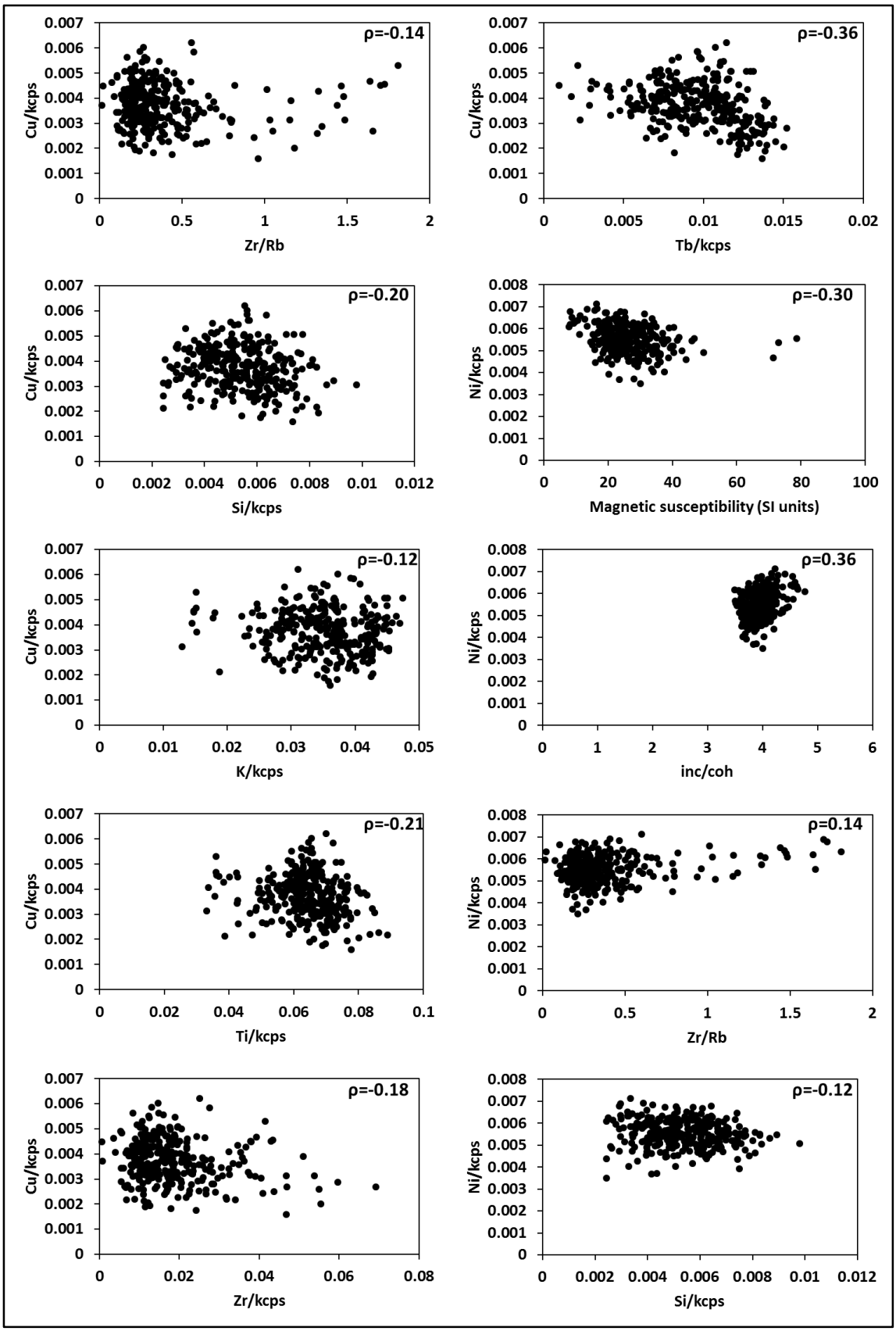

Figure S3 continued: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Bolin Billabong core B5. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant ($p<0.05$).

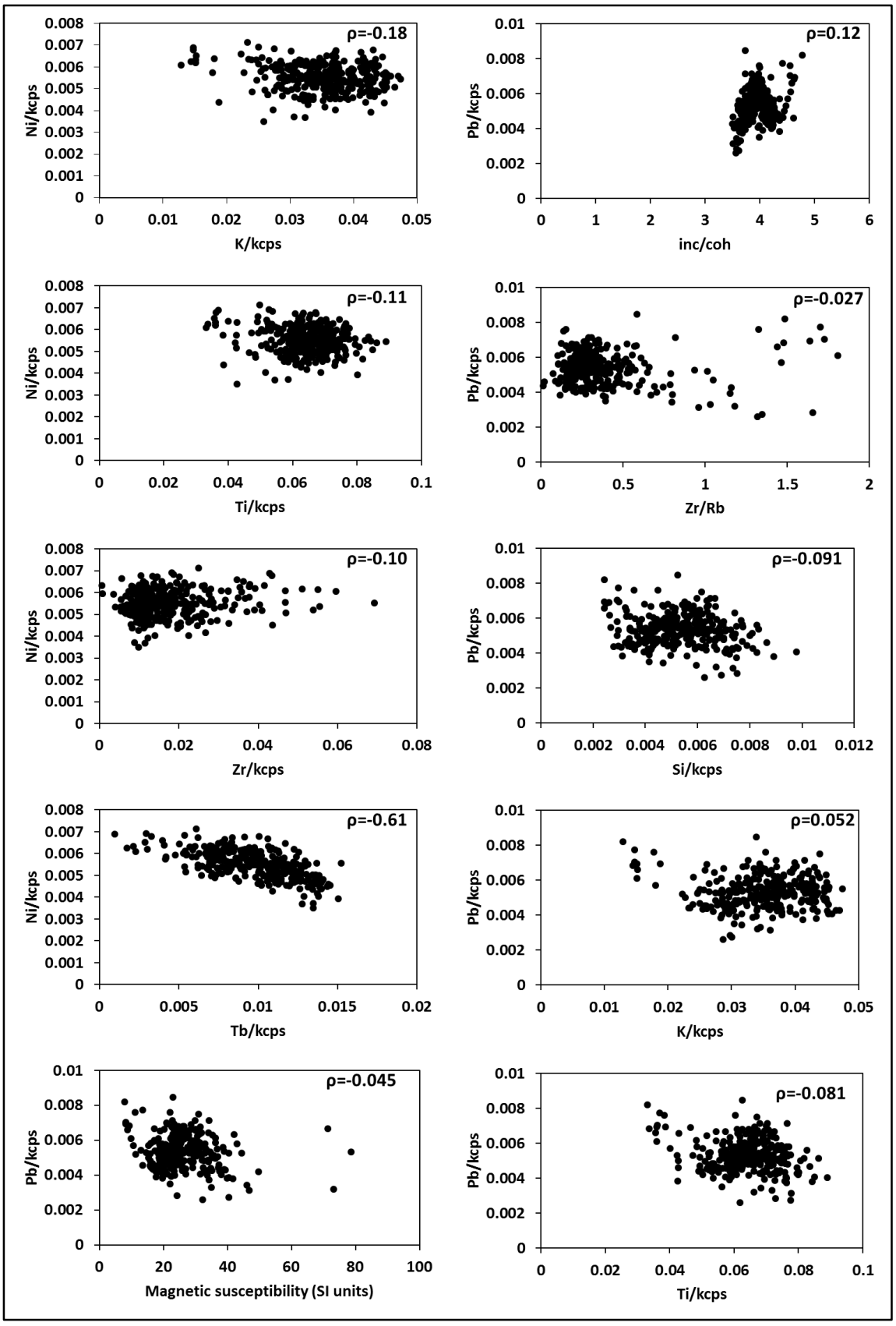

Figure S3 continued: Cross-correlation plots between parameters used to determine the Flood Signal Strength and heavy metals for Bolin Billabong core B5. Spearman's Rank Correlation Coefficients (ρ) shown were all statistically significant ($p<0.05$).

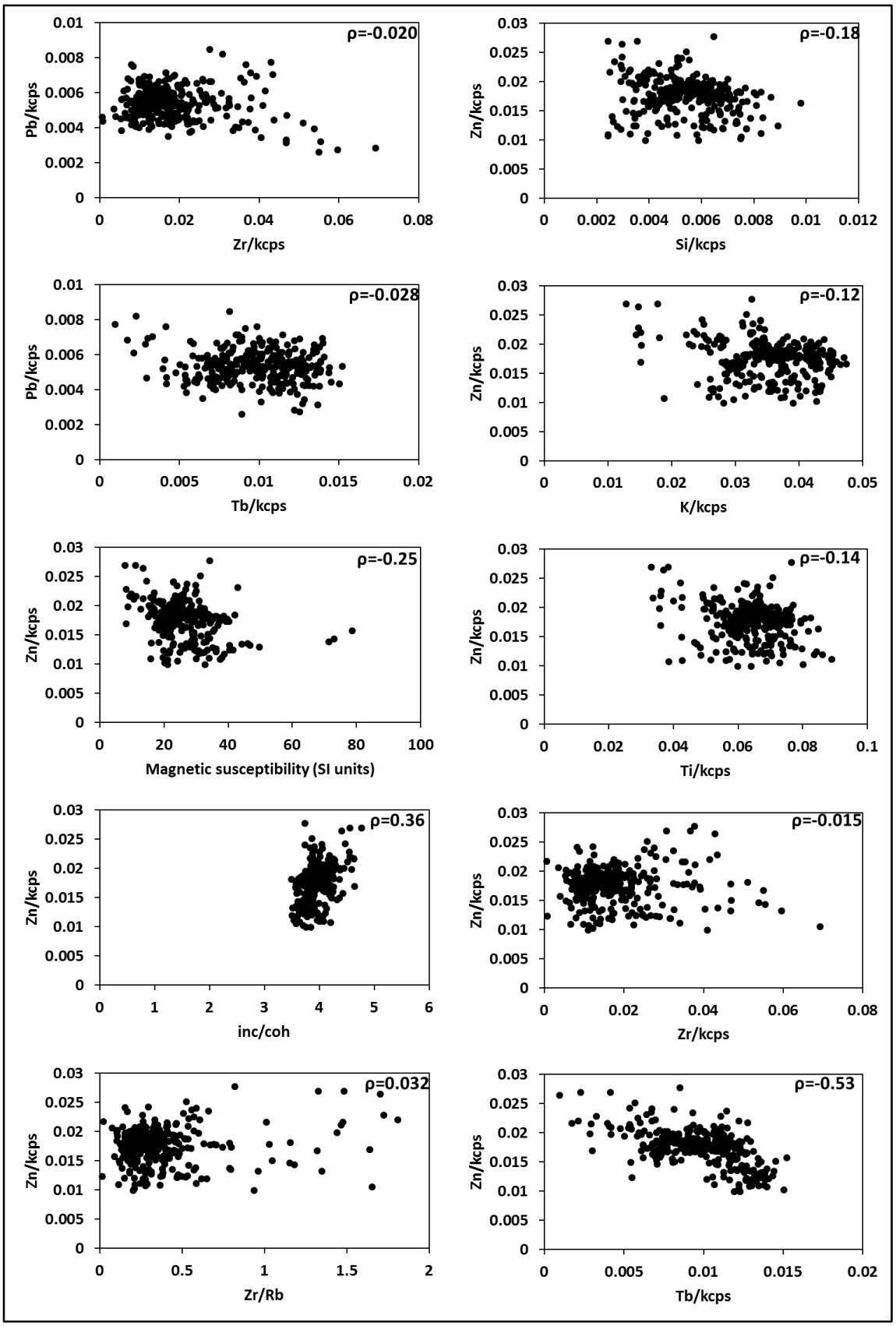

Figure S3 continued: Cross-correlation plots between parameters used to determine the flood signal strength and heavy metals for B5. Spearman's rank correlation coefficients shown were all statistically significant ($p<0.05$).

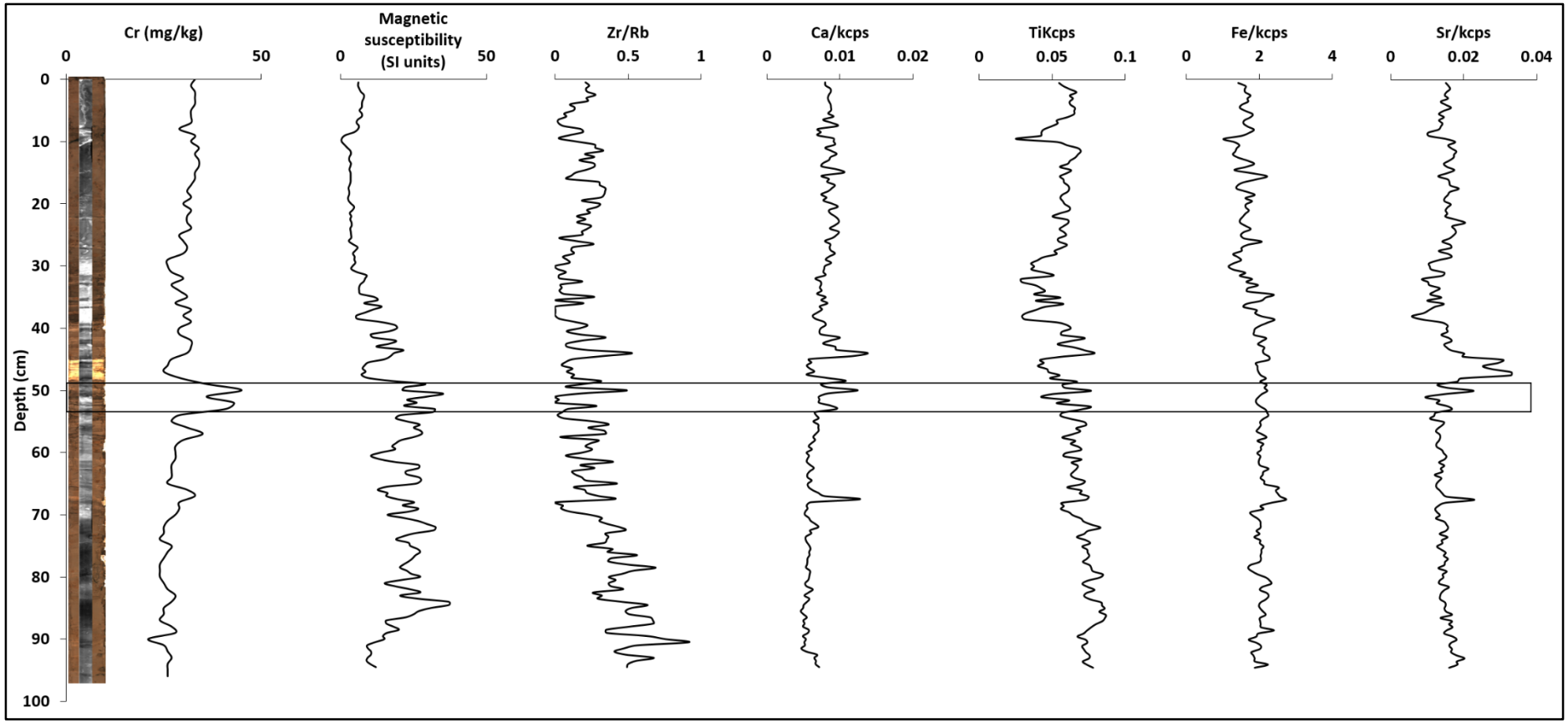

Figure S4: Cr (mg/kg) trends compared to trends in magnetic susceptibility and particle size (Zr/Rb) and selected elements (Ca, Ti, Fe, Sr) for Willsmere Billabong core W4. Black rectangle indicates region of elevated Cr levels. Optical and radiographic image of the core provided on the left.

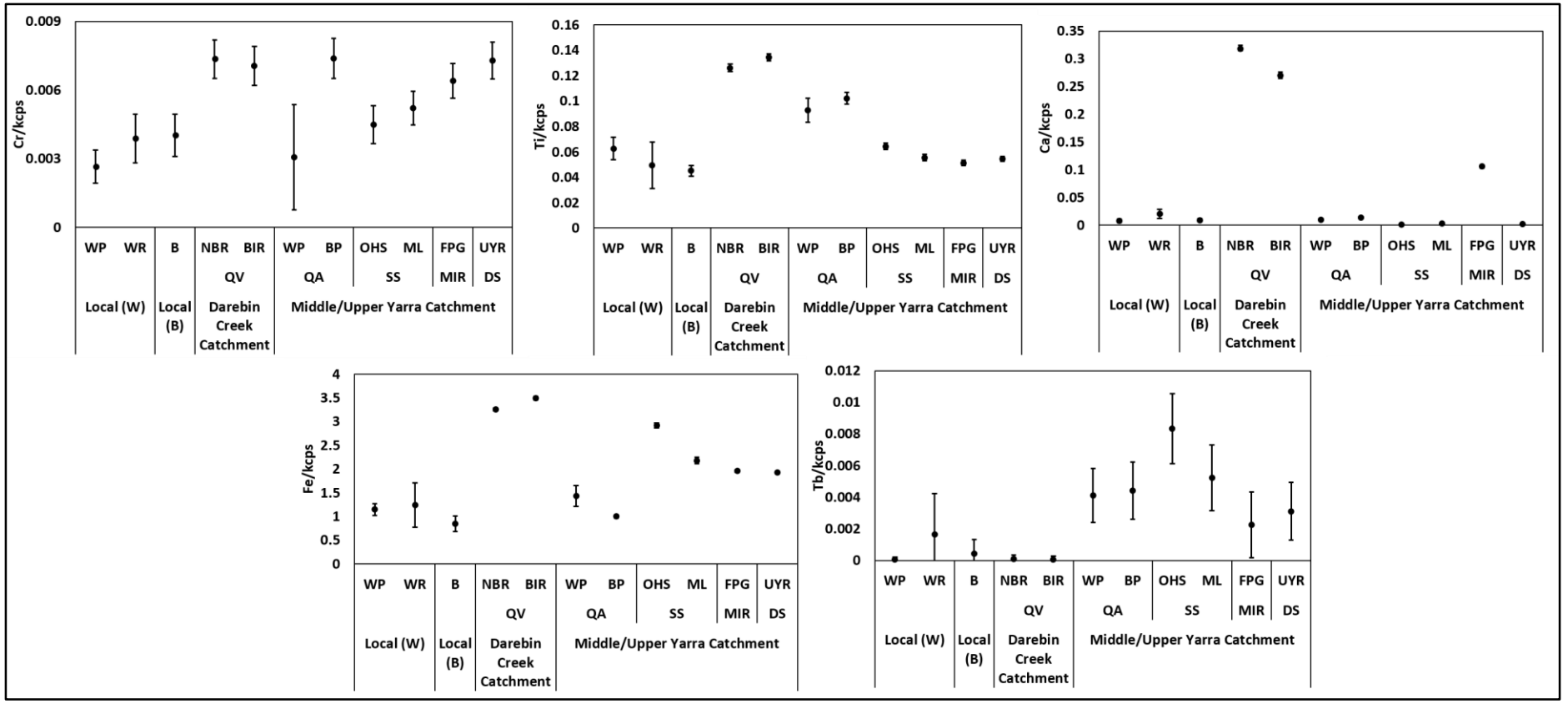

Figure S5: Cr/kcps, Ti/kcps, Ca/kps, Fe/kcps, Sr/kcps in source rocks and soils, with error bars representing standard deviation. WP: Willsmere Park (parkland), WR: Willsmere Residential, B: Bolin Billabong, Local (W): Local Catchment of Willsmere Billabong, Local (B): Local Catchment of Bolin Billabong, NBR: Norris Bank Reserve, BIR: Bridge Inn Rd, WP: Westerfolds Park, BP: Birrarung Park, OHS: Warrandyte State Park, ML: Mount Lofty, FPG: Fernshaw Picnic Ground, UYR: Upper Yarra Reservoir, QV: Quaternary Volcanics, QA: Quaternary Alluvium, SS: Silurian Sedimentary, MIR: Marysville Igneous Rhyodacite, DS: Devonian Sedimentary. Sampling locations and methodologies of the analyses of these sources rocks have previously been discussed in Lintern *et al.* (in preparation – a).

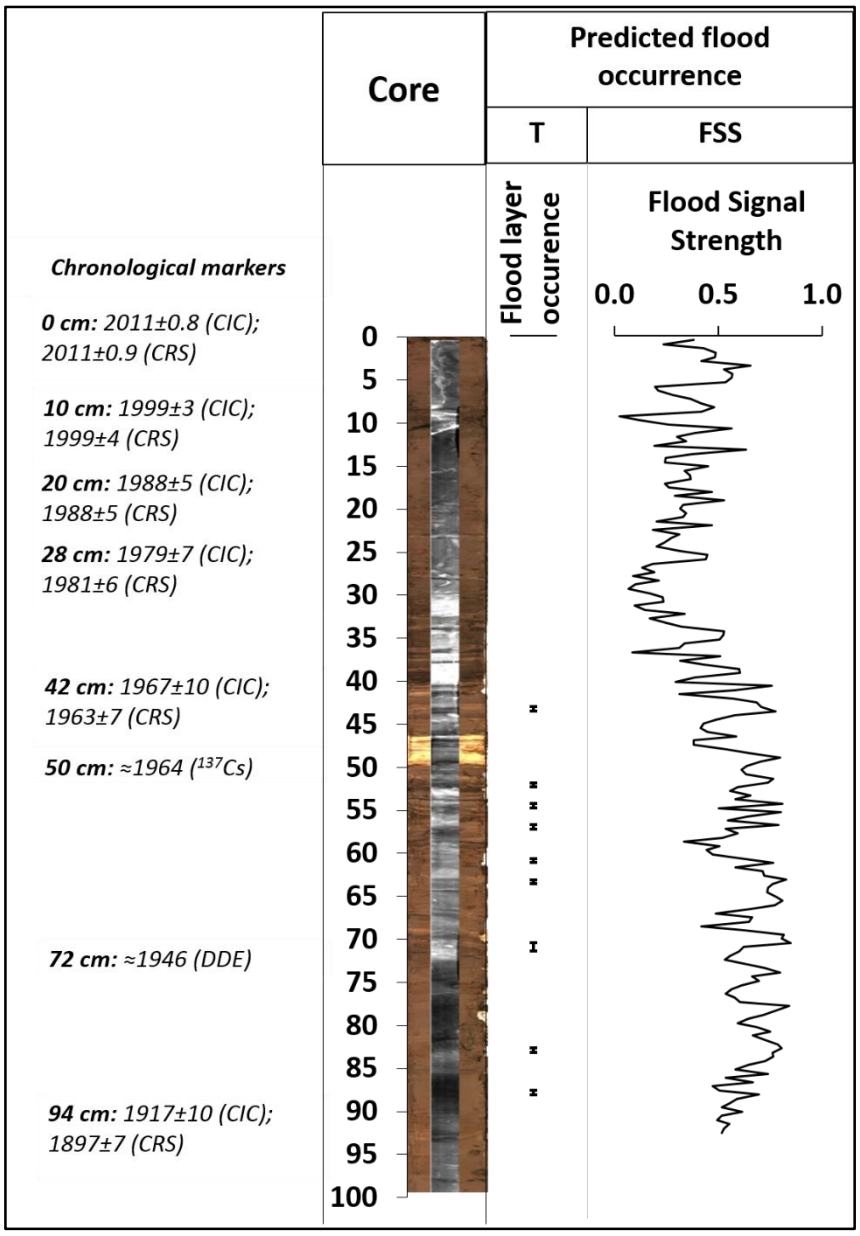

Figure S6: Flood deposits identified using the Traditional Method and Flood Signal Strength method for Willsmere Billabong core W4 (adapted from Lintern *et al.*, in preparation-a). Selected chronological markers and optical and radiographic images of the core provided on the left. Other chronological markers of W4 are provided in Lintern *et al.* (in preparation-a).

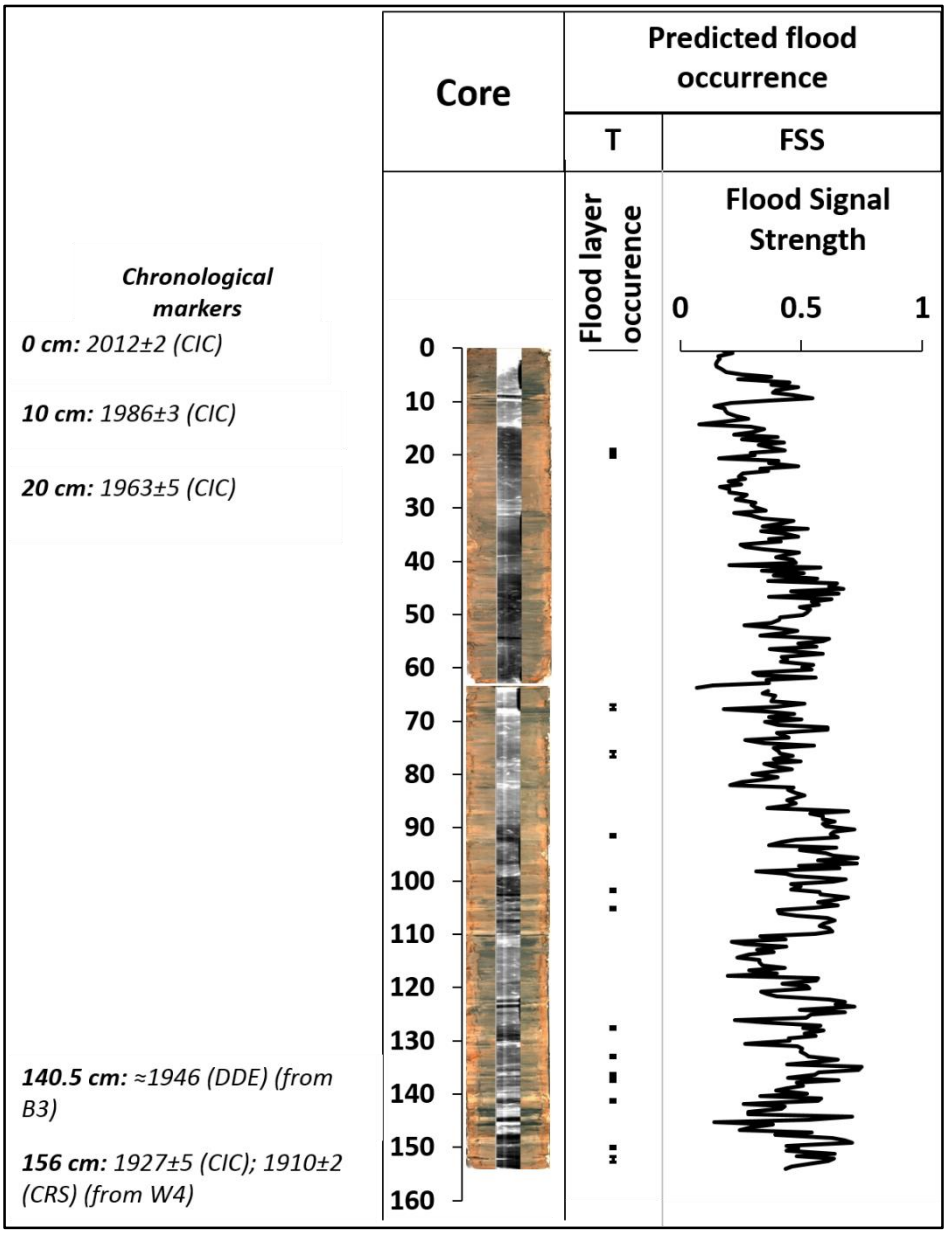

Figure S7: Flood deposits identified using the Traditional Method and Flood Signal Strength method for Bolin Billabong core B5 (adapted from Lintern *et al.*, in preparation-a). Selected chronological markers and optical and radiographic images of the core provided on the left. Other chronological markers of B5 are provided in Lintern *et al.* (in preparation-a).

APPENDIX B PHOTOGRAPHS OF FIELD SITES

Appendix B.1 Photographs of Willsmere Billabong

Figure B.1: Satellite photograph of Willsmere Billabong taken October 2012 (Source: Nearmap, www.nearmap.com).

Figure B.2: Photograph of Willsmere Billabong from north bank (October 2012).

Figure B.3: Photograph of Willsmere Billabong from east bank (October 2012).

Appendix B.2 Photographs of Bolin Billabong

Figure B.4: Satellite photograph of Bolin Billabong taken June 2013 (Source: Nearmap, www.nearmap.com).

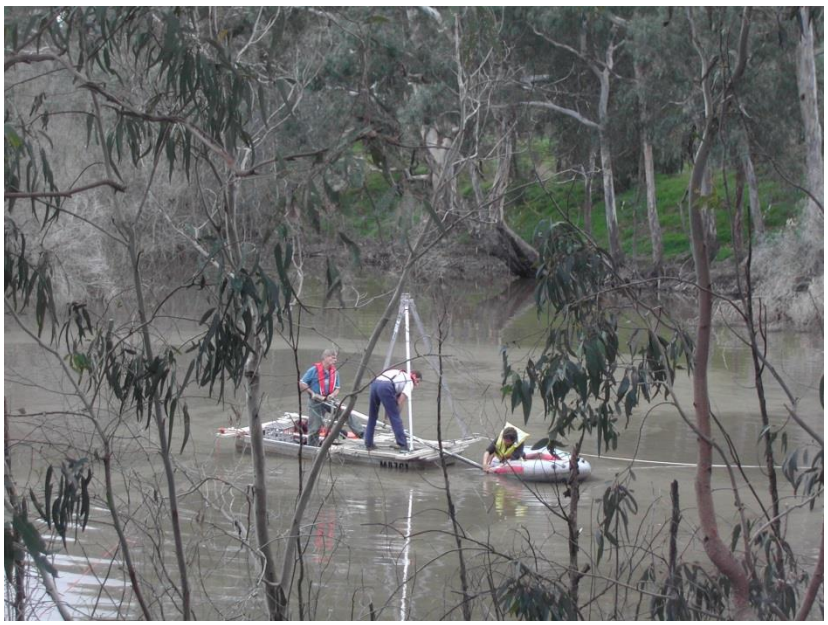

Figure B.5: Photograph of Bolin Billabong from south bank (July 2013).

Figure B.6: Photograph of Bolin Billabong from east bank (June 2013).

Appendix B.3 Photographs of Yarra Flats Billabong

Figure B.7: Satellite photograph of Yarra Flats Billabong taken April 2011 (Source: Nearmap, www.nearmap.com).

Figure B.8: Photograph of Yarra Flats Billabong from footbridge south bank looking west (June 2013).

Figure B.9: Photograph of Yarra Flats Billabong from footbridge south bank looking north (August 2013).