The interactions between macrophytes and sediments in urban river systems

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I hereby declare that the work presented in this thesis is my own and has not been submitted elsewhere for any award.

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Abstract

Many urban rivers receive significant inputs of metal-contaminated sediments from their catchments. Their restoration has the potential to increase the deposition and accumulation of these sediments from greater sediment supply and increased channel hydraulic complexity, creating a store of metals which could have negative impacts upon ecosystems and human health. Macrophytes often establish in restored channels and have the potential to stabilise these sediments and uptake metals through processes of phytoremediation, thus reducing the risk of the accumulated sediments becoming a source of metals. This thesis investigates the effects of river restoration upon sedimentation patterns and the interactions between macrophytes and sediments in terms of sediment trapping, stabilisation and metal uptake within urban river systems.

At a reach scale, greater finer sediment deposition and the accumulation of sediment around in-channel vegetation was found within restored stretches of tributaries of the River Thames London, reflecting sediment availability and hydraulic conditions. These sediments were important in terms of greater metal storage within stretches, and along with gravels showed particularly high metal concentrations.

Interactions between macrophytes, sediment and flow were investigated within the urban-influenced River Blackwater, Surrey. At the stand scale, the common emergent *Sparganium erectum* was found to significantly reduce flow velocities, accumulate fine sediments and retain them over winter. Research on individual plants revealed that, although three common emergent macrophytes (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) did not significantly phytoremediate metal contaminated sediments through metal uptake or bioconcentration, the reinforcement and stabilisation of these accumulated sediments (particularly by *Sparganium erectum* and *Typha latifolia*) and the creation of anoxic sediment conditions which strongly bind metals, were important in reducing the risk of metal mobilisation from the sediments.

These macrophyte sediment interactions illustrate the great potential of using emergent macrophytes in the restoration and management of urban rivers with metal contaminated sediments.

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Chapter 1

Introduction

Historically, rivers have been heavily altered and managed in response to urban development within their catchments (Wohl & Merritts, 2007; Downs & Gregory, 2004; and, Brookes, 1992). Urban development and associated river modification has a very significant effect upon hydrological processes, sediment and water quality, geomorphology and habitat quality, resulting in degraded urban river ecosystems (Everard & Moggridge, 2011; Bernhardt & Palmer, 2007; Findlay & Taylor, 2006; and, Paul & Meyer, 2001). Recently however, urban rivers are increasingly being restored in response to various environmental, legislative and social drivers (Lundy & Wade, 2011; Mainstone & Holmes, 2010; London Rivers Action Plan, 2009; Wharton & Gilvear, 2006; and, Downs & Gregory, 2004). Restoration techniques have the potential to affect in-channel sediment dynamics and vegetation growth as a result of increases in sediment availability (e.g. removal of bank and bed protection) and changes in flow hydraulics (e.g. increases in channel sinuosity). Within the context of urban river systems where sediments are often contaminated by metals and other pollutants, river restoration has the potential to alter the quantity of sediments that are retained, and thus the quantity of metal contaminated sediments stored within river channels. Increased storage of metals within river channels can have detrimental impacts upon ecosystem health and increase the risk to human health from recreation within the river channel (Scholes *et al*., 2008; CROCUS, 2006; Moore & Ramamoorthy, 1984; and, Forstner & Wittmann, 1981).

The above-ground and below-ground biomass of terrestrial, riparian and aquatic plants has the ability to trap and reinforce sediments and thus reduce their erosion and resuspension (Burylo *et al*., 2011; Liffen *et al.*, 2011; Docker & Hubble, 2008; and, Horppila & Nurminen, 2003). Furthermore, a range of plants have been shown to uptake metals from sediment and translocate them from below-ground to above-ground tissues (e.g. Vardanyan *et al*., 2008; Robinson *et al*., 2003; and, McGrath *et al*., 2001). In particular, aquatic macrophytes have the potential to reinforce metal contaminated sediments within urban rivers, reducing erosion and resuspension and thus reducing metal remobilisation. Additionally, macrophytes can potentially ameliorate metal contaminated sediments through metal uptake and translocation. However, the ability of particular macrophyte species to trap and accumulate sediment within urban rivers will impact upon the effectiveness of the processes of vegetation reinforcement, stabilisation and

phytoremediation of metal contaminated sediments, and thus their ability to reduce the risk of the sink of sediment associated metals turning into a source. These macrophyte-sediment processes of sediment trapping, stabilisation and phytoremediation within the context of urban river systems are the focus of this thesis.

This thesis begins with a review of literature relevant to the research, focussed around urban river restoration, sediments in urban rivers, stabilisation and phytoremediation of sediments by macrophytes and the interactions between macrophytes, flow and sedimentation (Chapter 2). Details of the overall research design are provided in Chapter 3 with a summary of the four complementary studies that were designed to answer the research questions identified in Chapter 2. Details on the choice of study sites are provided along with an overview of field and laboratory methods, with greater details being provided for common elements of field and laboratory work that appear throughout the thesis. The following four Chapters (4 to 7) present the results of the four studies. Chapter 4 investigates sedimentation patterns and the characteristics and metal concentrations of different bed sediment types in restored and unrestored stretches of urban rivers over one year at four sites within Greater London. Chapters 5 to 7 present results from detailed field investigations of macrophytes at sites on the urban River Blackwater, Surrey. This river was chosen as it is an urban river that supports abundant growth of most common macrophyte species. The biomechanical properties of three common emergent macrophyte species are assessed in Chapter 5. This research, conducted through a complete summer growing season, allows inferences to be made about the ability of these species to reinforce and stabilise river sediments. Chapter 6 describes the results of a study of metal uptake from sediments and their translocation from below-ground to above-ground tissues by the same three common emergent macrophytes investigated in Chapter 5. Finally, Chapter 7 focuses on the most common emergent macrophyte in Britain, *Sparganium erectum*, presenting observations of its local impact on flow velocity and sedimentation over two years. All results chapters follow a common structure. Study sites and field and laboratory methods are initially described, followed by presentation of study results and then a detailed discussion in the context of urban river restoration and other relevant studies in the literature. Finally, Chapter 8 provides a summary of the research and considers the key research findings in light of the initial research questions, and their wider implications for the restoration and management of urban rivers and the Water Framework Directive, concluding with an assessment of opportunities for future research.

Chapter 2

Literature Review and Research Questions

2.1 Introduction

This Chapter provides a review of the literature relevant to the present research, identifying research gaps and concluding with the overall aim and objectives and the specific research questions that will be investigated throughout this thesis.

The first section (Section 2.2) provides a review of the restoration of urban rivers. This is followed by a section on sediments in urban rivers in the context of metal contamination (Section 2.3) and provides a review of the behaviour of sediment-associated metals in terms of binding and spatial distribution, the impacts upon ecosystems and human health and their context within the Water Framework Directive. The final sections focus on the interaction between sediments and macrophytes. Section 2.4 reviews the stabilisation of sediments by plants and how this may be inferred through biomechanical measurements, Section 2.5 reviews the phytoremediation of metal contaminated aquatic environments by macrophytes and Section 2.6 reviews the effect of macrophytes upon flow and sedimentation. The various aspects of the literature review are summarised and synthesised in the context of this research in Section 2.7. Finally, the overall aim, objectives and specific research questions addressed by this thesis are identified in Section 2.8.

2.2 Restoration of Urban Rivers

2.2.1 Historical management of rivers

Historically, rivers have been highly altered and managed by humans for numerous uses including: flood control, navigation, water supply, waste disposal, agricultural drainage, irrigation, river stabilisation and training as well as reclamation of land for urban and industrial developments (Lemons & Victor, 2008; Wohl & Merritts, 2007; Adams *et al*., 2004; Downs & Gregory, 2004; Hey, 1997; and, Brookes, 1992). These modifications include channel and riparian physical modifications, an increase in discharges from agriculture, industry and urban developments and clearance of channel and riparian vegetation (Adams *et al*., 2004; Hey, 1997; and, Brookes, 1992). Physical modifications include: channel straightening, deepening and widening; installation of dams and weirs; dredging; creation of flood walls; bank and bed protection structures; and, culverting (Mainstone & Holmes, 2010; Lemons & Victor, 2008;

Adams *et al*., 2004; Downs & Gregory, 2004; Hey, 1997; and, Brookes, 1992). Physical modifications are particularly prevalent on lowland rivers in Britain with up to 96% of channels having been modified (Brookes & Shields, 1996) and over 40% of sites surveyed for the River Habitat Survey having bank resectioning, reinforcement and bridge structures (Raven *et al*., 1998).

Urban areas have historically developed around rivers as a result of their importance to humans for transport, water supply and sewage disposal (Francis, 2012). This close association of urban development with rivers has resulted in many rivers being overexploited and physically and chemically degraded, leading, in extreme circumstances, to them becoming covered over and completely hidden. For example, in London numerous rivers including the Westbourne, Fleet, Walbrook, Falcon and Effra, have been completely culverted (Brookes & Shield, 1996 and Barton, 1962). Moreover, urban areas have large ecological footprints whereby small areas of urbanisation cause large impacts upon stream ecosystems (USEPA, 2010 and Pickett *et al*., 2008). Currently, around 80% of the UK population live in urban areas and this is predicted to rise to around 86% by 2050 (United Nations, 2012), making improved understanding and sustainable management of urban rivers an increasingly pressing environmental issue.

2.2.2 Impact of urbanisation upon rivers

The adverse impact of urbanisation upon river ecosystems as a result of hydrological, physical and chemical deterioration has been termed the 'Urban Stream Syndrome' (Everard & Moggridge, 2011; Meyer *et al*., 2005; Walsh *et al*., 2005; and, Paul & Meyer, 2001). These impacts are caused by: an increase in impervious land cover, which induces a 'flashy' urban runoff regime; wastewater and stormwater discharges, which lead to degraded water quality; loss of riparian and channel vegetation; and, physical modifications to the river channel resulting in the disconnection of the river from riparian zones and floodplains (Everard & Moggridge, 2011; USEPA, 2010; Bernhardt & Palmer, 2007; Findlay & Taylor, 2006; Brown *et al*., 2005; and, Paul & Meyer, 2001). Overall, urban development results in very marked changes in hydrological processes, sediment and water quality, the geomorphology and habitat structure and the turnover of the river environment, with adverse consequences for the entire river ecosystem.

Several recent reviews (e.g. Everard & Moggridge, 2011; Bernhardt & Palmer, 2007; Gurnell *et al*., 2007; Findlay & Taylor, 2006; Brown *et al*., 2005; Walsh *et al*., 2005; and, Paul & Meyer, 2001) detail the complex impacts of urban development on river systems that are described below. In terms of hydrology an increase in impervious areas and in the density and efficiency of the drainage network causes a decrease in infiltration, increased runoff and peak flows,

decreased time to peak flows and decreased groundwater recharge and baseflows. An increase in wastewater and stormwater discharges in to rivers results in a decrease in sediment and also water quality in terms of increased suspended solids, nutrients, metals, hydrocarbons, bacteria plus a decrease in dissolved oxygen. In the UK combined sewer overflows and surface water outfalls are responsible for 35% of the annual total pollutant load to receiving watercourses despite operating only 2 to 3% of the time (Morrison *et al*., 1984). Removal of riparian vegetation and the impact of the urban heat island also cause an increase in water temperatures. Channels are physically altered through straightening, bed and bank lining, culverting and enlargement, which simplifies the channel structure and, with the loss of channel and riparian vegetation, decreases habitat complexity. Comparison of rural and urban watercourses by Pizzuto *et al*., (2000) found that urban watercourses were wider, had shallower pools, lower sinuosity and an overall lower channel roughness compared to rural watercourses. The sediment regime is altered with an initial increase in sediment supply and aggradation during the construction phase and a subsequent decrease in sediment supply and channel erosion once urban surfaces become protected by buildings, roads, pavements and other impervious, erosion-resistant surfaces. Disconnection of the river from its floodplain and riparian zone, plus the hydrological, chemical, geomorphological and habitat changes result in a decrease in the number of species that a river can support, with an increase in pollution tolerant and, frequently, exotic species and a decrease in sensitive, native species.

Recently, the impact of urbanisation upon the natural river continuum has been summarised in an 'urban watershed continuum' by Kaushal & Belt (2012). Impacts include interactions between groundwater and leaky pipes, urban infrastructure replacing first order streams and the temporal variations from land use and urban infrastructure development over time.

2.2.3 Restoration of urban rivers

Following a history of degradation, many urban rivers are now being restored in response to a number of environmental, legislative and social drivers. Environmentally, there is now widespread recognition and acceptance of the adverse environmental impact of historical river management (Lundy & Wade, 2011; Wheaton *et al*., 2008; Clifford, 2007; Wharton & Gilvear, 2006; and, Downs & Gregory, 2004) and acknowledgement of the ecosystem services and goods that urban rivers can provide if they are managed effectively (Everard & Moggridge, 2011; Lundy & Wade 2011; and, Dufour & Piegay, 2009). Similarly, there is recognition of the need for sustainable flood management and adaptation due to future climate change (Mainstone & Holmes, 2010; Wheaton *et al*., 2008; and, Wharton & Gilvear, 2006). Various pieces of legislation, including the Water Framework Directive, Habitats Directive and related Biodiversity Action Plans (Mainstone & Holmes, 2010; Wharton & Gilvear, 2006; and, Downs

& Gregory, 2004) and, in a social context, the renewal of urban spaces, provision of recreational spaces and attempts to connect people with the natural environment, are all driving urban river restoration (Lundy & Wade, 2011; Mainstone & Holmes, 2010; Wheaton *et al*., 2008; and, Wohl *et al*., 2005). Between 1994 and 2009 22 km of rivers within Greater London were improved or restored. Furthermore, the London Rivers Action Plan, launched in 2009 through a collaboration of the Environment Agency, Natural England, Greater London Authority and voluntary organisations, pledges restoration of a further 15 km by 2015 (London Rivers Action Plan, 2009).

The scope of urban river restoration can range from full restoration (complete structural and functional return to pre-disturbance state, as in Cairns (1991)) through rehabilitation (partial return to a pre-disturbance structure or function) and enhancement (any improvement in environmental quality) to creation (development of a resource that did not previously exist at the site) (Clifford, 2007; Findlay & Taylor, 2006; and, Brookes & Shields, 1996) (Figure 2.1).

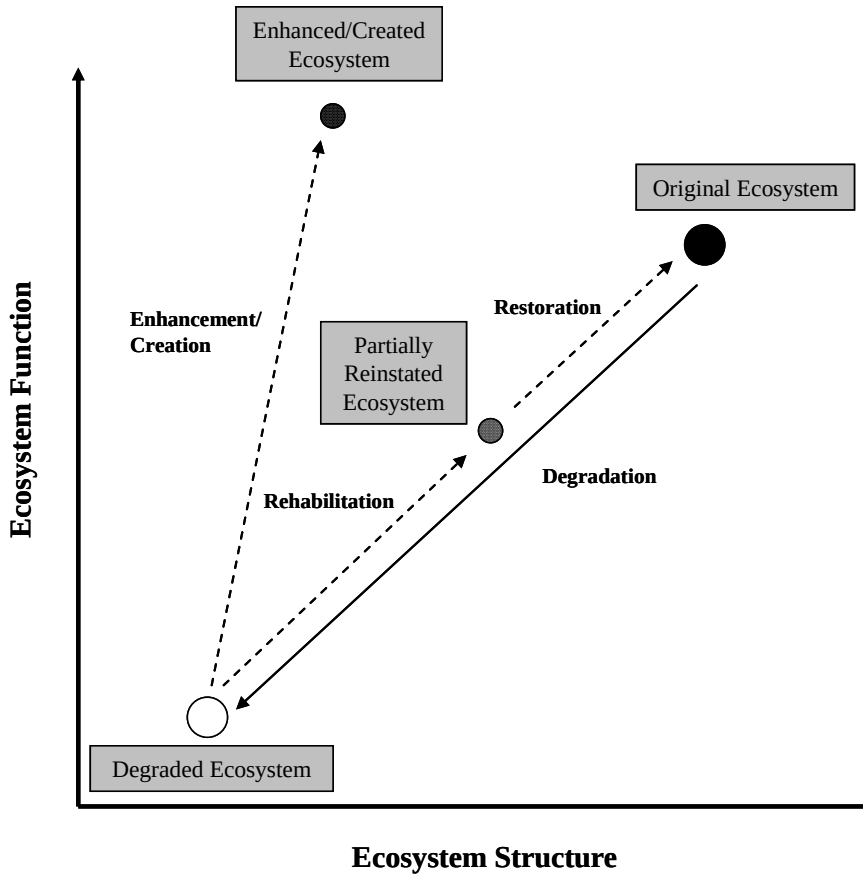


Figure 2.1: Distinction between restoration, rehabilitation and enhancement/creation. Ecosystem states represented by circles with descriptions in grey boxes. Processes for moving between the ecosystem states represented by arrows. (Adapted from Findlay & Taylor, 2006 and Downs & Gregory, 2004).

Full restoration is generally accepted as an idealistic vision, which in many contexts is neither feasible nor desirable, due to difficulties of defining the pre-disturbed state of the river and the potential inappropriateness of that pre-disturbed state to the current catchment context (Mainstone & Holmes, 2010; Wharton & Gilvear, 2006; Downs & Gregory 2004; Downs & Throne, 2000; and, Brookes & Shields, 1996), particularly in the urban river context (Gregory & Chin, 2002) where pressures of flood defence, infrastructure protection and contamination protection can dominate and restrain restoration efforts. Thus many 'restoration' schemes are technically rehabilitation, enhancement or creation schemes, but the term 'restoration' is often used in its broadest sense to describe all of these methods of enhancing the complexity of river systems (Mainstone & Holmes, 2010; Wheaton *et al*., 2008; and, Wohl *et al*., 2005).

The techniques applied to the restoration of urban rivers include: reinstatement of meanders, removal (or replacement with natural materials) of bank support, creation of wetlands and backwaters, removal of channel lining, de-culverting (daylighting), in-channel enhancements and providing improved public access (River Restoration Centre, 1999 and Brookes, 1992).

There have been few post-project appraisals or monitoring undertaken on river restoration schemes that document their impact on geomorphological, biological and social elements (Buchanan *et al*.; 2012; O'Donnell & Galat, 2008; Downs & Kondolf, 2002; and, Kondolf, 1995). Changes in channel complexity and increases in habitat heterogeneity are often inferred through monitored changes in macroinvertebrates and fish populations (for example, Albertson *et al.*, 2011; Sarriquet *et a*l., 2007; and, Hannaford & Resh, 1995). There is therefore a gap in the research in to the effects of urban river restoration upon sedimentation patterns and the growth of in-channel vegetation, which both affect the form and habitat structure of the river bed.

2.3 Sediments in Urban Rivers

2.3.1 Characteristics of urban river sediments

Differentiations can be made between the sources of sediment to rivers within non-urban and urban areas. Within non-urban areas, sediment sources include soil erosion from agricultural, pasture and forested land, bank erosion and atmospheric deposition (Taylor & Owens, 2009 and Salomon & Brils, 2004). In an urban area, however, these natural sources are often restricted or not available (*e.g.* bank protection prevents bank erosion) and anthropogenic sediment sources including industrial, sewage treatment works, combined sewer overflows, road deposited sediments and construction materials, dominate instead (Taylor & Owens, 2009 and Salomon & Brils, 2004). The differentiation in sediment sources between urban and non-urban areas is illustrated by work undertaken by Carter *et al.* (2003) on the River Aire in Yorkshire. Source

differentiation through suspended sediment fingerprinting showed that in the mainly agricultural upper reach the major sources were the channel banks (43 to 84%) and uncultivated (pasture and moorland) topsoil (16 to 57%). In the highly industrialised and urbanised middle and lower reaches (including the city of Leeds) agriculturally cultivated topsoil was a major source (20 to 45%) and a significant contribution came from urban sources such as road dust (19 to 22%) and sewage treatment work solids (14 to 18%).

As a result of the polluted nature of many urban sediment sources (Poleto *et al*., 2010; Taylor & Owen, 2009; and, Scholes *et al*., 2008), sediments accumulating within urban rivers are generally contaminated with elevated concentrations of metals, nutrients, coliforms and organic compounds (including hydrocarbons, PCBs and PAHs). Higher concentrations of P, Cr and PCBs were found in the sediments of the highly urbanised and industrialised River Aire/Calder catchment compared to the dominantly agricultural River Swale catchment in Yorkshire (Owens *et al*., 2001). Similarly, higher PAH and heavy metal concentrations were found in sediments of a stream receiving urban and motorway runoff compared to an unpolluted (reference) stream in Denmark (Christensen *et al.*, 2006). Gradients in sediment contamination levels through a catchment with changing land use have also been shown with decreasing Pb and Zn concentrations along an urban–suburban–rural gradient in the Chattahoochee River Basin (Callender & Rice, 2000) and an increase in P, Cr and PCBs along the River Aire/Calder catchment from the relatively unpolluted headwaters into the urban and industrial middle and lower reaches (Owens *et al*., 2001). The extent of contamination is illustrated by Wilson *et al.* (2005a) who found that sediment at four out of nine sites receiving urban runoff sampled across Scotland would be classified as special waste in the UK if dredged, due to the high hydrocarbon concentrations.

2.3.2 Metal contaminated sediments

Sources of metals

Sources of metals within the environment are both natural and anthropogenic. Metals are naturally found at varying levels in rocks and minerals providing background concentrations. However, elevated concentrations above these background levels can occur due to anthropogenic sources, with increasing anthropogenic sources since the 20th century from greater production, processing, usage and disposal of metals (Alloway & Ayres, 1997 and Foster & Charlesworth, 1996). For example, elevated concentrations (determined through calculation of enrichment factors) of Cd, Pb and Zn were found in sediments at industrial discharge outlets along the Nakivubo channelised stream, Kampala, Uganda (Sekabira *et al*., 2010) and elevated concentrations of Cd, Cr, Cu, Ni, Pb and Zn were found in sediments of the Yamuna River in the urban centres of Delhi and Agra, India (Singh, 2001). Within the urban

environment anthropogenic sources of metals include: landfill leachates (Cd, Cu, Pb, Zn); vehicular, including exhausts and tyre wear (Al, Cd, Cu, Ni, Pb, Zn); industrial discharges (Cd, Cu, Fe, Pb, Zn); metal corrosion (Cu, Cd, Pb, Zn); sewage sludge (Cd, Cu, Mn, Ni, Pb, Zn); gas work sites (Cd, Cu, Fe, Pb); batteries (Cd, Ni, Pb, Zn); pigments and paints (Cd, Pb, Zn); wastewater treatment (Al); electronic manufacture (Al, Cu, Pb, Zn); de-icing (Fe, Zn); and, fuel combustion (Cd, Cu, Fe, Mn, Pb, Zn) (Charlesworth *et al*., 2010; Chon *et al*., 2010; Duruibe *et al*., 2007; Paul & Meyer, 2001; Charlesworth & Lee, 1999; and, Alloway & Ayres, 1997). These sources can either be discharged directly into watercourses (e.g. wastewater), or deposited on land and enter the watercourses as runoff (e.g. vehicular and street).

Binding of metals in sediments

Metals within a river can either be in a dissolved, colloidal or particulate phase (Luoma & Rainbow, 2008 and Weiner, 2008). The dissolved phase is operationally defined as that <0.45 µm, the colloidal phase between 0.10 µm and 0.45 µm and the particulate phase >0.45 µm (Luoma & Rainbow 2008 and Salomon & Brils, 2004). These three phases of metals exist within four different reservoirs within a river: overlying water, suspended sediments, deposited sediment and porewater (Salomons & Forstner, 1984). Metals can move between the various phases/reservoirs within the aquatic environment. Figure 2.2 below shows a conceptual model of the different phases of metal within a river and the processes between them.

At pH neutral partitioning of metals favours the particulate phase (suspended sediments and sediments), therefore concentrations of metals in the particulate phase are orders of magnitude greater than the dissolved and colloidal phase, resulting in sediments being a significant sink of metals (Luoma & Rainbow, 2008 and Foster & Charlesworth, 1996).

The simplest phase in which a metal can be present in a river is as a dissolved ion (e.g. Fe^{2+}) (Weiner, 2008). These dissolved metal ions can move into particulate phase through either direct precipitation of metal compounds of (hydr)oxides, carbonates and sulphides when their solubility product is exceeded (Fergusson, 1990 and Forstner & Wittmann, 1981) or through some form of binding with a ligand (Luoma & Rainbow, 2008).

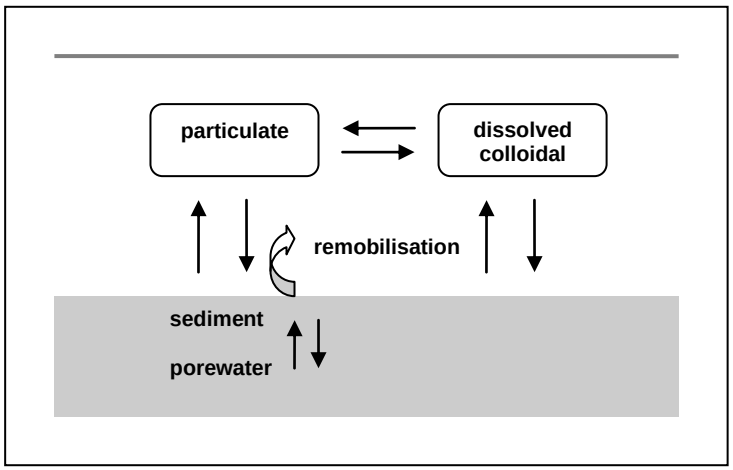


Figure 2.2: Conceptual model of phases of metals within a river and processes between them (adapted from Fergusson (1990) p275).

There are two main processes by which metal ions bind to ligands: adsorption and coprecipitation (Linge, 2008). Adsorption of metal ions occurs by the process of cation exchange whereby the negatively charged surfaces of the ligands attract the positively charged metal ions (Du Laing *et al*., 2009 and Forstner & Wittmann, 1981). Increasing adsorption occurs with a greater surface area of particles increasing the cation exchange capacity and the greater concentrations of metal ions in solution. Coprecipitation of metal ions is the process whereby the metal ion precipitates upon a precipitate already present.

The main ligands which are important for metal binding in oxidising conditions are: Fe and Mn (hydr)oxides; clay minerals; organic matter; and, carbonates; and, in reducing conditions sulphides.

In oxidising conditions Fe and Mn (hydr)oxides precipitate out of solution once their solubility product is exceeded (Luoma & Rainbow, 2008). They can form either discrete particles or coatings upon other minerals or particles (Rao *et al*., 2008; Miller & Orbock Miller, 2007; and, Warren & Haack, 2001). Metal ions are then either adsorbed, or coprecipitated onto these metal (hydr)oxides, thus taking them out of solution (Miller & Orbock Miller, 2007 and Forstner & Wittmann, 1981). These (hydr)oxides, even when in low quantities, have a significant ability to bind metals, particularly Fe (hydr)oxides which have a sorption capacity over 10 times that of Mn (hydr)oxides (Forstner & Wittmann, 1981).

Clay minerals are small particles (<4 μm) with a high cation exchange capacity onto which metal ions adsorb (Fergusson, 1990 and Forstner & Wittmann, 1981). Metal (hydr)oxides and

organic matter, which are more reactive, may also coat clay minerals and thus increase metal binding (Luoma & Rainbow, 2008).

Organic matter within the river can be from both autochthonous and allochthonous sources and comprise humic and fulvic acids, leaf detritus, chlorophyll and microorganisms. It can be present as discrete particles or adsorbed onto clay minerals or metal (hydr)oxides (Luoma & Rainbow, 2008; Allan & Stegemann, 2007; and, Forstner & Wittmann, 1981). Metals are either adsorbed or complexed on to the various organic matter compounds (Du Laing *et al*., 2009; Warren & Haack, 2001; and, Forstner & Wittmann, 1981), with organic matter being able to adsorb between 1 and 10% of its dry weight for certain metals (Forstner & Wittmann, 1981).

Carbonates, which precipitate out of solution when the solubility product is exceeded in the same process as Fe and Mn (hydr)oxides, are important ligands for metal binding when Fe and Mn (hydr)oxides and organic matter are less abundant (Rao *et al*., 2008). Metals are able to adsorb or coprecipitate onto carbonates (Rao *et al*., 2008 and Fergusson, 1990).

Under strongly reducing conditions, sulphates are reduced to sulphides on to which metals coprecipitate and form stable insoluble metal sulphide precipitates (Luoma & Rainbow, 2008 and Forstner & Wittmann, 1981).

The ligand to which metals are bound has implications on the behaviour and bioavailability of metals, for example metals bound to carbonates are more mobile than those bound to organic matter (Du Laing *et al*., 2009; Miller & Orbock Miller, 2007; and, Gleyzes *et al*., 2002).

Spatial variations in sediment-associated metals

Grain size is one of the greatest controls on metal concentrations in sediments (Foster & Charlesworth, 1996). Fine sediments (particularly silt and clay, <63 µm) generally have higher metal concentrations due to not only their greater surface areas, but also the fact that ligands which are important in metal binding (organic matter, Fe and Mn (hydr)oxides, clay and carbonates) are common in this grain size fraction (Luoma & Rainbow, 2008; Miller & Orbock Miller, 2007; Salomon & Brils, 2004; and, Foster & Charlesworth, 1996). For example, sediments from the Anllons River, Spain had higher concentrations of Cu, Fe, Ni, Pb and Zn in the silt and clay fraction (<63 µm) compared to the sand fraction (63 µm to 2 mm) (Devesa-Ray *et al*., 2011). Sediment metal concentrations have also been shown to have positive correlations with increasing proportions of silt and clay (% <63 µm) and negative correlations with increasing sand proportions (63 µm to 2 mm) (Rodriguez-Barroso *et al*., 2010; Cevik *et al*., 2009; and, Liu *et al*., 2003). However, in some studies high metal concentrations in coarser

sediments have also been shown, thought to be from either metal-enriched detrital minerals or metal-enriched discrete anthropogenic particles from pollution sources (Miller & Orbock Miller, 2007; Lin *et al*., 2003; Singh *et al*., 1999; and, Forstner & Wittmann, 1981). For example, sites near coal mining activities on the Damodar River basin, India showed higher metal concentrations in the coarser sediment fractions thought to be from inputs from the mining (Singh *et al*., 1999).

Due to the strong association of metals with sediment, the hydraulic processes of sediment erosion, transport and deposition have a role in determining how sediment-associated metals are moved and distributed within a river (Miller & Orbock Miller, 2007). These processes mean that sediment-associated metals are not uniformly distributed along or across a river channel, with differing patterns seen at a catchment and a river reach scale (Miller & Orbock Miller, 2007).

At a catchment scale, downstream decreases in sediment-associated metal concentrations are frequently seen with increasing distance from sources of metal pollution (e.g. mining sites and discharges) due to dilution effects from inputs of less contaminated sediment from tributaries and channel margins, deposition of contaminated sediment on the floodplain and in the channel and changes in chemical speciation of metals (Miller & Orbock Miller, 2007 and Foster & Charlesworth, 1996). For example, a decrease in sediment Pb and Zn concentrations were seen with increasing distance from Atlanta, USA along the Chattahoochee River Basin (Callender & Rice, 2000), and decreases in sediment metal concentrations downstream from mining sites have been shown on the River Tyne, northeast England (Hudson-Edwards *et al*., 1996), River Swale, Yorkshire (Walling *et al*., 2003) and Clark Fork River, Montana, USA (Axtmann & Luoma, 1991).

At a river reach scale, hydraulic sorting of sediment based on size and density results in the distribution of sediment-associated metals between geomorphological units with distinct hydraulic and sediment characteristics (Miller & Orbock Miller, 2007 and Paul & Meyer, 2001). Generally, higher sediment metal concentrations are found in areas of low flow velocity where fine organic rich sediment and associated metals accumulate and in areas of intermediate velocity with sand-sized minerals and metal particulates (Miller & Orbock Miller, 2007; Paul & Meyer, 2001; and, Rhoads & Cahill, 1999). Lower sediment metal concentrations are found in areas of higher flow velocity associated with coarser sediments (Miller & Orbock Miller, 2007; Paul & Meyer, 2001; and, Rhoads & Cahill, 1999). On rivers impacted by metal mining and urban discharges in Montana and Illinois, USA respectively, the highest sediment metal concentrations were found in eddy drop zones and bars and the lowest concentrations in glides,

pools and riffles (Rhoads & Cahill, 1999 and Ladd *et al*., 1998). Similarly, the highest sediment metal concentrations were found in hydraulic dead zones and close to river banks within the river channel, and the lowest concentrations were found in the zones of highest current, in a river in southern Poland impacted by domestic and industrial effluents (Ciszewski, 2004).

Effect of changing environmental conditions upon sediment-associated metals

Urban rivers tend to be dynamic systems with changing physiochemical conditions, reflecting their 'flashy' hydraulic nature and the potential for polluting discharges, which can cause the remobilisation of metals from sediments (Scholes *et al*., 2008). There are two main environmental conditions which, if altered, can change concentrations and mobilities of sediment-associated metals: pH and redox.

Lowering of the pH can cause the desorption (opposite process of adsorption) of metal ions from ligands due to increased competition from H^+ ions. Carbonate and sulphide compounds can also undergo dissolution (opposite process of precipitation) to become the soluble form, resulting in the release of metal ions (Du Laing *et al*., 2009; Weiner, 2008; Miller & Orbock Miller, 2007; and, Forstner & Wittmann, 1981). Such changes in pH could occur from waste discharges entering watercourses.

Changes in redox conditions have effects upon two key ligands in metal binding: Fe and Mn (hydr)oxides and sulphides (Miller & Orbock Miller, 2007). Under reducing conditions dissolution of Fe and Mn (hydr)oxides occurs which releases metal ions into solution, which may however then be precipitated as insoluble metal sulphides if sulphur is available, thus removing them from solution (Du Laing *et al*., 2009; Weiner, 2008; and, Miller & Orbock Miller, 2007). Under oxidising conditions metal sulphides undergo dissolution releasing metal ions into solution, however the released Fe and Mn ions can then precipitate as Fe and Mn (hydr)oxides on to which the dissolved metal ions are adsorbed or coprecipitated (Du Laing *et al*., 2009; Weiner, 2008; and, Miller & Orbock Miller, 2007). Oxidised sediments can become reduced from increased nutrient loading from sewage and eutrophication and reduced sediments can become oxidised from erosion, resuspension and bioturbation (Miller & Orbock Miller, 2007 and Forstner & Wittmann, 1981).

Metals and aquatic ecosystems and human health

Some metals are essential or beneficial to plants and animals and some are non-essential and can be toxic. For example, non-essential metals include Al, Cd, Pb and essential or beneficial metals for plants and animals include Cu, Mn, Ni and Zn (Kapustka *et al*., 2004). Plants can be exposed to metals in the aquatic environment from growing in contaminated sediment and

water. Animals can be exposed to metals from the ingestion of contaminated sediment and water and other plants and animals. Although plants and animals are able to successfully adapt to metal polluted environments and accumulate metals they are also adversely affected by metal contamination (Moore & Ramamoorthy, 1984). For example, Cu concentrations over 0.3 mgl^{-1} were found to inhibit growth of *Lemna Minor* (duckweed) with 70% growth inhibition at 0.5 mgl^{-1} (Khellaf & Zerdaoui, 2010). Similarly, research by Fargasova *et al.* (1999), investigating the effect of six metal ions upon the algae *Scenedesmus quadricauda*, found EC_{50} concentrations (the metal concentration where 50% of its maximal effect is observed) varied for different metals: growth inhibition (Cu^{2+} 0.27 mgl^{-1} to Mn^{2+} 4.98 mgl^{-1}), total chlorophyll production (Cu^{2+} 0.39 mgl^{-1} to Mo^{6+} 2.59 mgl^{-1}), chlorophyll a production (Cu^{2+} 0.41 mgl^{-1} to Mo^{6+} 3.85 mgl^{-1}) and chlorophyll b production (Cu^{2+} 0.26 mgl^{-1} to V^{5+} 2.66 mgl^{-1}). Macroinvertebrate community structures are affected by metal concentrations, with fewer mayflies and greater numbers of chironomids and oligochaetes being reported at sites with higher metal concentrations in streams in Yorkshire, UK (Beasly & Kneale, 2004) and similarly fewer mayflies at higher metal sites in the Southern Rocky Mountains, Colorado, USA (Clements *et al*., 2000). Fish diversity has been shown to decrease in relation to increased sediment metal concentrations in Ontario, Canada (Pyle *et al*., 2005) and higher Cd and Ni tissue concentrations were found in fish closer to the metal mining/smelting industries in lakes around the Norway/Russia border (Amundsen *et al*., 1997).

As with plants and animals some metals, such as Cu, Fe, Mn and Zn, are known to be essential and beneficial to humans in low quantities (Goyer & Golub, 2004). However, even when a metal is essential, it can become toxic to humans if it is present in excess quantities (Forstner & Wittmann, 1981). Other metals, such as Al, Cd, Hg and Pb, are nonessential with no known benefits to humans, and are toxic to humans even in low quantities (Goyer & Golub, 2004). Humans can be exposed to metals in the aquatic environment through ingestion (contaminated sediment, water, plants and animals), inhalation (metals volatised from contaminated sediment and water) or dermal contact (contaminated sediment and water) (Filipsson *et al*., 2009; Duruibe *et al*., 2007; Jarup, 2003; Albering *et al*., 1999; and, Alloway & Ayres, 1997). The adverse human health effects from excess metals can include renal damage, cancer and neurological problems (Duruibe *et al*., 2007 and Jarup, 2003). A well known example is the occurrence of Minamata disease in Japan. In the 1950s, fishermen and their families suffered from a neurological disease which was found to be caused by the consumption of seafood from Minamata Bay, which had been contaminated by methylmercury from an effluent discharging in to the bay from a local chemical plant (Forstner & Wittmann, 1981). In Bangladesh, metal-poisoning from naturally-occurring arsenic-contaminated groundwater that is used for drinking, was first identified in the 1980s with people suffering from skin lesions (Smith *et al.*, 2000).

Various sediment quality guidelines (SQG) have been developed, mainly in North America, in response to both regulation and recognition of the adverse ecological effects of high sediment metal concentrations (Burton, 2002). Commonly used guidelines include the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment, 2002) and the USA National Oceanic and Atmospheric Administration (NOAA) values (NOAA, 1999). The Environment Agency has also recently developed draft freshwater sediment quality criteria for England and Wales (Environment Agency, 2008).

Nevertheless, there appear to be no guidelines for assessing the potential impact of metal contaminated aquatic sediments upon human health, with contaminated land guidelines being used instead. In particular the Dutch target and soil remediation intervention values (Dutch Ministry of Housing, Spatial Planning and Environment 2009; Cheung *et al*., 2008; Bird *et al*., 2003; and, Macklin *et al.*, 2003) are frequently used. Risks to human health from recreational activities within waterbodies have been assessed using exposure models which compare total metal exposure levels (from ingestion and dermal contact with contaminated sediment and water) to tolerable daily intakes (Filipsson *et al*., 2009 and Albering *et al*., 1999).

Water Framework Directive and metal contaminated sediments

The Water Framework Directive (WFD, 2000/60/EC), which came into force in 2000, is a European-wide directive which requires all water bodies to achieve good ecological status by 2015 (Collins *et al*., 2012). This involves assessment of the biological, hydromorphological, physico-chemical and chemical quality of each water body. One aspect of the WFD is the development of ecological quality standards (EQS) for a range of specific pollutants (including some metals) for sediment, water and biota, which are then to be used in monitoring for compliance with the WFD (Carere *et al*., 2012; Borja *et al*., 2004; and, Crane, 2003). Whilst the setting of EQS's for overlying water has been successful and is now widely used under the WFD, there has been recognition of the difficulty in setting EQS's for sediment due to both the lack of toxicity data for benthic organisms and the uncertainties in relation to exposure as part of the risk assessment in sediments (Brils, 2008 and Crane & Babut, 2007). This has resulted in overlying water being the predominant matrix monitored for compliance (WFD UKTAG, 2012). However, sediment may still be monitored under the WFD for assessment of both the no-deterioration objective and spatial and temporal trends (WFD UKTAG, 2012; Brils, 2008; and, Crane & Babut, 2007). Therefore, any changes to the retention of metal contaminated sediments within a river have the potential to affect WFD assessment. Additionally, the potential release of metals from accumulated sediments into the overlying water and the adverse impacts upon ecology, may also result in detrimental impacts upon the WFD status.

In summary, urban river sediments are characterised by the accumulation of sediment-associated contaminants, including metals, which can have detrimental impacts upon ecosystems and human health. The characteristics of the sediment, and the environmental conditions in which they are retained, are very important in terms of determining the concentrations and mobilities of metals associated with the sediment. Much research has already been undertaken on sediment-associated metals in rivers in various contexts, and the potential impacts of it. Although there has been acknowledgement of the potential impacts of contaminated sediments in the restoration of urban rivers (Scholes *et al*., 2008 and CROCUS, 2006) there appears to be no research which has looked specifically at sediment quality, particularly sediment-associated metal concentrations and their potential impacts within the specific context of restored and unrestored urban rivers to see whether they are influenced by restoration practices.

2.4 Plant Sediment Stabilisation and Biomechanics

2.4.1 Sediment retention, stabilisation and protection by plants

Plants have been shown to stabilise soils/sediments and reduce erosion in various environments, through the functioning of their above-ground and below-ground components. Below-ground systems of roots and rhizomes affect the bulk physical properties of soil/sediment. Soil/sediment erodibility is reduced through: (i) an increase in bulk density from the growth of root/rhizome structures pushing soil/sediment particles together; (ii) in terrestrial environments, the growth of root/rhizome structures create pores which increase infiltration and decrease runoff; and, (iii) root/rhizome structures bind soil/sediment particles together, increasing aggregate stability (Stokes *et al*., 2009; Gyssels *et al*., 2005; and, Abernethy & Rutherford, 2001). Additionally, soil/sediment reinforcement is increased by an increase in shear strength due to the soil-root/rhizome matrix. The stabilisation of soil/sediment by riparian vegetation has been shown along river banks (e.g. Docker & Hubble, 2008; Marden *et al.*, 2005; Wynn *et al*., 2004; Micheli & Kirchner, 2002; Simon & Collison, 2002; Abernethy & Rutherford, 2001; and, Coops *et al*., 1996) and in terrestrial environments vegetation can increase slope stability and decrease erosion by overland flow (e.g. Burylo *et al*., 2011; Abdi *et al*., 2010; Bischetti *et al*., 2009; Burylo *et al*., 2009; Stokes *et al*., 2009; and, Reubens *et al*., 2007). For example, Simon & Collinson (2002), looking at the effect of riparian trees and grasses on stream bank stability in Goodwin Creek, Mississippi, found that the presence of roots from trees increased soil strength by 2 to 8 kPa and the presence of roots from grasses increased soil strength by 6 to 18 kPa. Coops *et al.* (1996) undertook some experiments in a wave tank to quantify differences in wave reduction and bank erosion along un-vegetated and vegetated (*Phragmites australis* and *Scirpus lacustris*) sections. Net erosion was reduced in the vegetated sections (*P. australis* 0.21

± 0.006 m^3m^{-1} and *S. lacustris* 0.50 ± 0.11 m^3m^{-1}) compared to the unvegetated section (0.75 ± 0.01 m^3m^{-1}). Similarly, Burylo *et al*., (2011), investigating the effect of terrestrial plants in reducing debris flows in the marly mountainous region of Alpes-de-Haute-Provence, France, found increases in soil strength of up to 10 kPa.

In lakes the above-ground biomass of macrophytes has also been shown to reduce sediment resuspension due to the dissipation of wave energy and decreased flow velocities (e.g. James *et al*., 2004; Horppila & Nurminen, 2003; Horppila & Nurminen, 2001; and, Dieter, 1990). For example, Horppila & Nurminen (2003) measured rates of sediment suspension five metres within (inner zone), on the edge of, and five metres out from (outer zone), a *Typha angustifolia* stand on a lake in Finland. The rate of suspension in the outer zone of 20g dwm^{-2} statistically exceeded the edge (12 to 22 g dwm^{-2}) and the inner zone (12 g dwm^{-2}).

2.4.2 Plant biomechanics

Plant biomechanics, at the interface between biology and engineering, is the understanding of how physical laws and processes have an influence upon the growth, survival and reproduction of plants (Niklas, 1992). This can include the ability for plants to withstand forces acting upon them. This can be quantified through two biomechanical measurements: the force required for stem breakage, and the force required for uprooting, with greater forces indicating a greater ability of the plants to withstand the forces. Many studies involving biomechanical measurements of plants have been undertaken on both aquatic macrophytes (e.g. Miler *et al*., 2012; Liffen et *al*., 2011; Schutten *et al*., 2005; Bociag *et al*., 2009; Usherwood *et al*., 1997; and, Brewer & Parker, 1990) and terrestrial plants (Liu *et al*., 2011; Burylo *et al*., 2009; and, Mickovski *et al*., 2005). The size and mechanical properties of the stem, size and properties of the root system and cohesive strength of the soil/sediment in which the plant is rooted all affect plant biomechanical strength, and some studies have related measures of above-ground and below-ground plant growth/traits and sediment cohesion to the biomechanical measurements (e.g Liu *et al*., 2011; Bociag *et al*., 2009; Burylo *et al*., 2009; Mickovski *et al*., 2005; Schutten *et al*., 2005; and, Brewer & Parker, 1990). For example, Mickovski *et al*., (2005), investigating the uprooting resistance of vetiver grass, *Vetiveria zizanioides*, (a terrestrial plant), found significant positive correlations between uprooting resistance and plant height and lateral root spread, and Brewer & Parker (1990) modelled stem breakages of seven macrophytes as a function of increasing stem cross-sectional area. Some studies have also used biomechanical measurements to infer sediment reinforcement and reduction in susceptibility to erosion and resuspension (e.g. Burylo *et al*., 2011; Liffen *et al*., 2011; Burylo *et al*., 2009; Mickovski *et al*., 2005; Schutten *et al*., 2005; and, Schutten & Davy, 2000).

Although research has already been undertaken on the biomechanical properties of macrophytes and inferences have been made from these measurements in terms of sediment reinforcement and reduction in erosion and resuspension, there appears to be little research specifically on the biomechanics of common emergent macrophytes in urban rivers and the potential implications of these biomechanical properties for reinforcement and reduction of erosion and resuspension of metal-contaminated sediments.

2.5 Phytoremediation

Many plants have the ability to remove, transfer or stabilise contaminants from the soil, sediment or water in which they are growing, in a process which is known as phytoremediation (Dhir *et al.*, 2009). Macrophytes growing within rivers and wetlands are no exception and have the ability to remove contaminants such as heavy metals, radionuclides and other organic and inorganic contaminants from the aquatic system (Dhir *et al.*, 2009). The major processes of phytoremediation for metals within the aquatic system, phytostabilisation and phytoextraction/rhizofiltration, are outlined below.

Phytostabilisation: this process reduces the mobility and bioavailability of metals within sediments. Metals are not actually taken up, or removed from the sediments, instead they are held in place and so made less mobile. For example, root systems physically hold contaminated sediments in place, therefore reducing their mobility and resuspension (Dean, 2007 and McCutcheon & Schnoor, 2003, and discussed above in Section 2.4). Erosion, which would resuspend contaminated sediments, is reduced through the protective cover provided by the above-ground parts of aquatic plants (Srivastava *et al.*, 2008, and discussed above in Section 2.4).

Whilst stabilising sediments, wetlands and macrophytes may also alter environmental conditions within the sediment (redox, pH and organic matter content), which can alter metal mobility. Waterlogged sediments generally provide a reducing environment which is advantageous for the immobilisation of metals through the precipitation of sulphides to which metals strongly adsorb or co-precipitate (Jacob & Otte, 2003). However, the presence of macrophytes can alter this environment and subsequent metal mobility, particularly in a confined area around the roots and rhizomes known as the rhizosphere (Cambrolle *et al*., 2008). Redox conditions can become more oxic through the release of oxygen from plant roots, causing the oxidation of sulphides and the release of bound metals (Jacob & Otte, 2003 and Lacerda *et al*., 1997). Conversely, the oxic environment can cause Fe and Mn (hydr)oxides to precipitate to which metals readily co-precipitate and adsorb (Jacob & Otte, 2003). Higher metal concentrations have been found in sediments within the root/rhizome area than from

beyond the root zone by Cambrolle *et al*. (2008) for *Spartina densiflora* and by Almeida *et al*. (2004) for *Juncus maritimus*.

A decrease in pH around macrophytes from the exudation of inorganic acids from roots and the decomposition of organic matter, can increase the mobility of metals in sediments through increased solubility of sulphides and carbonates, and the subsequent release of bound metals, and a lowering of the cation exchange capacity (and thus a lowering of the available binding sites for metals) of organic matter, clay and Fe and Mn oxides (Du Laing *et al*., 2009). Mucha *et al*. (2005) undertook a sediment metal extraction experiment using oxalic, malonic and citric acids, which are commonly exuded by plants. Metals, particularly Cr, Cd and Ni, were released by the acids, in particular oxalate.

Increased organic matter around macrophytes can help to maintain reducing conditions and thus sulphide precipitation and the associated metal adsorbtion and co-precipitation (Jacob & Otte, 2003). Metals also adsorb directly with organic matter due to its high cation exchange capacity (Du Laing *et al*., 2009). Almeida *et al.* (2006), investigating the effect of *Scripus maritimus* and *Juncus maritimus* on sediment characteristics, found that seasonally the lowest metal concentrations in sediment surrounding the plants coincided with the lowest organic matter content in spring. However, dissolved organic ligands can also form soluble metal complexes (Jacob & Otte, 2003).

The particular effect that macrophytes have upon metal mobility within sediment varies depending upon the species and the sediment characteristics (Jacob & Otte, 2003). Annual senescence of macrophytes can however reduce phytostabilisation, thus making metals potentially more available.

Phytoextraction/Rhizofiltration: this process is the uptake of metals by plants from sediments or water and the translocation and accumulation of metals within the rhizomes, roots and above-ground tissue (stems and leaves) (Rai, 2009). Metals are captured by the cell wall via ion-exchange, taken up across the cell, and reach the xylem which translocates them around the plant (Clemens *et al.*, 2002). In order for metals to be taken up by macrophytes, they need to be in a form which is available to them, this is the bioavailable form (Clemens *et al.*, 2002). The most bioavailable metals are those in the water soluble and exchangeable form; potentially available are those precipitated as inorganic compounds, complexed with large molecular weight humic materials and adsorbed to hydrous oxides; and, unavailable metals are those precipitated as insoluble sulphides and bound within the crystalline lattice of minerals (Weis & Weis, 2004). Changes in environmental conditions can alter the form in which the metals are

held and hence their bioavailability. Metals will generally become more bioavailable with: a decrease in pH, which increases metals in solution (Weis & Weis, 2004); an increase in redox (oxidation), which decreases the metals tightly bound to sulphides (Dhir *et al.*, 2009); a decrease in suspended solids, which decreases the binding sites for metals (Rai, 2009); and, a decrease in organic matter, clay content and Fe and Mn (hydr)oxides in sediments which decreases the binding sites for metals (Fergusson, 1990). As was discussed above, some of these changes can occur around macrophytes within the rhizosphere, but they can also occur within the wider aquatic environment.

Research on the uptake of metals by macrophytes has shown that differences are found between species, with generally submerged species having higher metal concentrations than emergent species (e.g. Vardanyan *et al*., 2008; Pajevic *et al*., 2003; and, Sparling and Lowe, 1998), and also in the location within the plant where metals are stored, with below-ground tissues generally having higher metal concentrations than above-ground tissues (e.g. Deng *et al*., 2004; Mays & Edwards, 2001; and, Fergusson, 1990).

Phytoremediation has been studied and used for many years in the treatment of contaminated wastewater, urban runoff, and acid mine drainage (AMD) through the development of constructed wetlands and detention ponds (e.g. Ladislas *et al*., 2012; Sundberg-Jones & Hassan, 2007; Maine *et al*., 2006; Karathanasis & Johnson, 2003; Mays & Edwards, 2001; Hares & Ward, 1999; Scholes *et al*., 1998; and, Ellis *et al*., 1994), and in rivers and lakes which receive, or have received, contaminated discharges (e.g. Sasmaz *et al*., 2008; Cardwell *et al*., 2002; and, Samecka-Cymerman & Kempers, 2001), with many studies demonstrating the ability for constructed wetlands to reduce metal loadings in water. For example, a constructed wetland used for treating runoff from the M25 in Surrey, UK, showed removal efficiencies for a range of metals ranging from 87% for Zn to 93% for Cu and V (Hares & Ward, 1999) and Karathanasis and Johnson (2003), investigating a constructed wetland for treating AMD in Kentucky, USA, found removal efficiencies for Al, Fe and Mn of 96%, 99% and 98%, respectively. The same processes that operate in constructed wetlands can also be seen in rivers where water flows slowly through beds of vegetation over long distances (Haslam, 2006). Fewer studies have focussed on the processes of phytoremediation that occur naturally in watercourses affected by general urban and agricultural runoff where diffuse rather than point discharges are the focus (e.g. Zhang *et al*., 2010 and Vardanyan *et al*., 2008).

Although much is known about phytoremediation, particularly in the context of constructed wetlands, less research has been undertaken on the phytoremediation processes occurring within

urban rivers and the potential for common emergent macrophytes to be used in urban river restoration schemes to reduce sediment metal concentrations.

2.6 Macrophytes, Flow and Sedimentation

The characteristics of flow within a river channel affect the presence of macrophytes, and conversely the presence of macrophytes within a river channel affects the characteristics of flow (Franklin *et al*, 2008; Clarke, 2002; and, Madsen *et al.*, 2001). Flow velocities within rivers are considered to be the key factor regulating the ability of macrophytes to colonise and grow (Franklin *et al.*, 2008). High velocities impede macrophyte colonisation and growth with Chambers *et al.* (1991) finding that where flow velocities exceeded 1 ms^{-1} macrophytes were only present in negligible quantities or were completely absent.

The presence of macrophytes within a river channel creates an obstruction to flow causing a slowing down of flow velocities within, and around, the macrophyte stands, to the extent that bottom shear stresses are decreased and suspended sediment is deposited and accumulates (Jones *et al*., 2011; Luhar *et al*., 2008; Haslam, 2006; Pluntke & Kozerski, 2003; and, Schulz *et al*., 2003).

Much research has focused on this hydraulic effect, with investigations of the effects at the reach, stand and individual plant scale both in the field and in the laboratory. For example, a ten-fold decrease in flow velocities were recorded within individual *Ranunculus penicillatus* plants in the River Wylye, Wiltshire UK (Green, 2005a). A similar ten-fold decrease in flow velocities at all depths within *Sparganium emersum*, *Potamogeton pectinatus* and *Sagittaria sagittifolia* stands were recorded in the River Spree, Germany (Schulz *et al*., 2003) and a two- to three-fold increase in Mannings 'n' (indication of channel roughness) on a reach of the River Blackwater, Hampshire, UK during summer was attributed to the growth of submerged macrophytes, notably *Sparganium emersum* and *Potamogeton* spp. (Naden *et al*., 2006). Commonly, research comparing the hydraulic impacts of different macrophyte species has focussed on their differing flexibilities and morphologies and how they interact with flow velocity profiles (Bal *et al*., 2011; Vereecken *et al*., 2006; Dodds & Biggs, 2002; and, Stephan & Gutknecht, 2002). For example, Sand-Jensen & Pedersen (1999) and Sand-Jensen & Mebus (1996) conducted research on stands of the submerged macrophytes *Batrachium peltatum*, *Callitriche cophocarpa*, *Elodea canadensis* and *Sparganium emersum* in Danish streams. They found that although flow velocities were reduced within stands of all species, *S. emersum* showed the smallest reduction in flow velocities due to the long, stream-lined morphology of the leaves. Other variables which influence the impact of plants upon flow velocities include

plant size, density, spatial arrangement and biomass (Montakhab *et al*., 2012; Dijkstra & Uittenbogaard, 2010; Franklin *et al*., 2008; Luhar *et al*., 2008; and, Sand-Jensen, 2008).

Less research has focussed on the effects of macrophytes upon sedimentation than on their effects on flow velocities. Horvath (2004) clearly showed increased sediment retention rates in the presence of macrophytes (submerged, emergent and riparian) through experimental particle release and capture experiments on the Breitenbach, Germany before, and after, macrophyte removal (retention rates of 0.28 to 1 with macrophytes and 0.02 to 0.26 without macrophytes). Direct measurement of sedimentation has focussed mainly on submerged macrophytes, and in particular *Ranunculus* (Trimmer *et al*., 2009; Cotton *et al*., 2006; and, Wharton *et al*., 2006), although there has been some research on emergent macrophytes, including *Sparganium erectum* and *Sparganium americanum* (Asaeda *et al*., 2010 and Koetsier & McArthur, 2000) and in flume experiments (Gorrick & Rodriguez, 2012; Zong & Nepf, 2010; Bennett *et al*., 2008; and, Sharpe & James, 2006).

Interactions between macrophytes, flow and sediment can result in macrophytes forming patches in rivers associated with low flow velocities and fine sediment retention, and separated by areas of higher velocity and coarser substrates (Gurnell *et al*., 2006; Clarke, 2002; Large & Prach, 1999; and, Sand-Jensen & Mebus, 1996) which in the short- to medium-term can have an impact upon river morphology (Gurnell *et al*., 2012, and Clarke, 2002) resulting in macrophytes being termed 'ecosystem engineers' due to their ability to "modify, maintain and/or create habitats" (Jones *et al*., 1994, p374).

Corenblit *et al.* (2007) have described the four-phase evolution of fluvial landforms through the interactions of riparian plants, flow and sediment in the 'Fluvial Biogeomorphic Succession Concept'. During the first phase (geomorphic phase) the vegetation is destroyed (e.g. in a flood) and the channel is in a transitory phase. Following this, pioneer vegetation recruitment occurs on the previously bare sediment (pioneer phase) and riparian plants begin interacting with biogeomorphic processes and fluvial landforms develop (biogeomorphic phase). Finally, fluvial landforms stabilise and the vegetative communities become increasingly disconnected from fluvial processes as the land surface aggrades (ecologic phase). This concept has been extended recently by Gurnell *et al*., (2012) to incorporate a wider range of river types of different energies and to include aquatic and wetland plants as well as riparian plants. Plants which have an effect upon sediment stabilisation and pioneer landform development act at the junction between the plant (resistance) dominated and fluvial-disturbance (force) dominated zones of river corridors which vary both through time and along and between rivers. Different plants are important in different energy environments for driving this pioneer landform

development with the *Salicaceae* (riparian willows and poplars) being particularly influential in high energy rivers and emergent macrophytes being drivers of landform development in low energy rivers.

Much research has been undertaken on the hydraulic effects of macrophytes, with research into the effects on sedimentation particularly focussing on submerged species. Less research has focussed on the effects of common emergent macrophytes on sedimentation, particularly in the context of urban rivers, with their potential to accumulate metal contaminated sediments.

2.7 Summary and Synthesis

Restoration of urban rivers has the potential to affect sedimentation and in-channel vegetation growth patterns with banks and beds being released from artificial reinforcement and some degree of morphodynamics being reinstated. A possible consequence of this restoration is that urban river channels are potentially becoming sinks for metal contaminated sediments delivered to the river from the urban area. This could then potentially have detrimental impacts upon ecosystem and human health. Common emergent macrophytes in urban rivers have the potential to reinforce metal-contaminated sediment and reduce its erosion and resuspension, with differences in these processes induced by differing macrophyte biomechanical properties. Similarly, these common emergent macrophytes could also reduce the sediment-associated metals through processes of phytoremediation. Overall these macrophyte-sediment interactions could reduce the potential for sediment-associated metals to be remobilised within urban rivers. However, these processes of sediment reinforcement, stabilisation and phytoremediation depend upon the ability of common emergent macrophytes to trap and accumulate sediments within urban rivers.

Therefore, understanding the degree of contamination and accumulation of such sediments, their association with macrophytes growing within restored reaches, and the potential for macrophyte reinforcement and phytoremediation of the sediment could inform the future design and management of urban river restoration schemes and provide best practice for minimising sedimentation and sediment quality issues and the associated ecological and human health issues.

2.8 Aim, Objectives and Research Questions

The overall aim of this research is to investigate the interactions between sediments and macrophytes in urban river systems, in terms of sediment trapping, sediment stabilisation and metal uptake by common emergent macrophytes from metal contaminated sediments in order to

understand the implications for restoration and management practices in urban rivers. The main objectives of this research are:

(i) At a reach-scale, to compare restored and unrestored stretches of urban rivers to:

- Determine the extent of differing sedimentation and in-channel vegetation growth patterns.
- Determine the characteristics (including metal concentrations) of sediments accumulating within restored and unrestored river reaches and assess sediment quality.

(ii) At a patch/individual plant-scale, explore macrophyte–sediment interactions in urban rivers to:

- Determine the biomechanical properties of some common emergent macrophytes.
- Determine the potential phytoremediation of metal-contaminated sediment by common emergent macrophytes by determining the concentrations of metals in sediment, overlying water and macrophyte tissues.
- Determine the effect of the most commonly-occurring emergent macrophyte species in British rivers, *Sparganium erectum,* upon flow velocity and fine sediment accumulation throughout its growth cycle.

The following research questions will be answered in response to the research objectives.

1. Are there differences in the pattern and extent of sedimentation and in-channel vegetation growth between restored and unrestored stretches of urban rivers in London?

2. What are the characteristics of sediment (metal concentrations, grain size etc.) retained within restored and unrestored stretches of urban rivers in London and to what extent do these characteristics vary in space and time?

3. What factors explain the observed variations in metal concentrations and sediment characteristics in restored and unrestored urban rivers in London?

4. To what extent are the sediments in London urban rivers potentially harmful to humans and ecosystems?

5. How does the ability of three commonly occurring emergent macrophyte species (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) to retain and reinforce fine

sediment and thus reduce sediment erosion and resuspension, vary between species and through their annual growth cycles?

6. What is the distribution of metals between three commonly occurring emergent macrophytes (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) and associated overlying water and sediments?

7. To what extent do the characteristics and metal concentrations of overlying water and sediment associated with these three commonly occurring emergent macrophytes vary between the species?

8. How does the uptake and storage of metals in three commonly occurring emergent macrophyte species vary?

9. To what extent do three commonly occurring emergent macrophyte species bioconcentrate and translocate metals?

10. To what extent does the presence of *S. erectum* affect sedimentation and flow velocities?

11. To what extent does sedimentation vary through the annual growth cycle of *S. erectum*?
Following a review of the broad methodologies and field sites used in this research (Chapter 3), research questions 1 to 4 will be answered in Chapter 4, research question 5 in Chapter 5, research questions 6 to 9 in Chapter 6 and research questions 10 and 11 in Chapter 7. Lastly, Chapter 8 draws together the outcomes of the research to place a perspective on the role of emergent macrophytes in the functioning of restored reaches of urban rivers and to provide recommendations for enhanced restoration and management of urban rivers.

Chapter 3

Research Design, Research Sites and Methodologies

3.1 Introduction

This Chapter provides details on the overall research design adopted to answer the research questions set out at the end of Chapter 2. It provides an overview of the study sites, field and laboratory methods used in each study as well as detailed descriptions of common elements of field and laboratory work that are relevant to the research presented in the following chapters of this thesis.

3.2 Research Design

3.2.1 Overview of research design

In order to answer the research questions set out at the end of Chapter 2 four complementary studies were designed:

- A study of sediment characteristics and metal concentrations of bed sediments in contrasting restored and unrestored London urban rivers (Chapter 4) to answer research questions 1 to 4.
- A study of the biomechanical properties of three common emergent macrophyte species: *Sparganium erectum, Typha latifolia* and *Phalaris arundinacea* (Chapter 5) to answer research question 5.
- A study of the uptake and translocation of metals by three common emergent macrophytes: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea* (Chapter 6) to answer research questions 6 to 9.
- A study of the effect of *Sparganium erectum* upon flow velocity and sedimentation (Chapter 7) to answer research questions 10 and 11.

These four studies involved varying combinations of fieldwork and laboratory work and were undertaken at differing spatial and temporal scales. Table 3.1 briefly outlines the studies in terms of field sites, spatial and temporal scales and field and laboratory work.

Table 3.1: Overview of spatial and temporal scales and field and laboratory work components of each study.

Study/Chapter	Site	Spatial Scale	Temporal Scale	Fieldwork	Laboratory Work
Chapter 4 **Sediment characteristics and metal concentrations of bed sediments in contrasting restored and unrestored London urban rivers**	London rivers (four sites)	River stretch	Three occasions over one year	Mapping different bed sediment types, bank protection and sediment depths in adjacent restored and unrestored stretches. Sampling sediments from different bed sediment types. Sediment pH and redox (via porewater collection and analysis).	Sediment samples analysed for various properties including metals concentrations. Porewater samples analysed for Fe (II) for redox.
Chapter 5 **Biomechanics of three common emergent macrophytes*: Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea***	River Blackwater (research site one)	Individual macrophyte plant	Five occasions over one year	Stem strength and uprooting resistance of macrophyte plants. Measurements of above-ground and below-ground plant size/biomass.	None
Chapter 6 **The uptake and translocation of metals by three common emergent macrophytes: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea***	River Blackwater (research site one)	Individual macrophyte plant	Two occasions over one year	Collection of common macrophytes (both above-ground and below-ground tissues). Collection of adjacent sediment sample and overlying water sample. Sediment pH and redox (via porewater collection and analysis). Overlying water pH and dissolved oxygen.	Macrophytes and overlying water analysed for metals. Sediment analysed for various properties including metal concentrations. Porewater samples analysed for Fe (II) for redox.
Chapter 7 **Effect of *Sparganium erectum* upon flow and sedimentation**	River Blackwater (research site two)	Stand of macrophytes	Several occasions over two years	Flow velocities, water depth, fine sediment depth and macrophyte coverage measured within, and outside of, S. *erectum* stands. Maximum leaf length measured and quadrat of *S. erectum* collected for biomass measurement.	*S. erectum* quadrat sample dried to measure biomass.

3.2.2 Site selection

London sites (Chapter 4)

In order to undertake a study of sediment characteristics and metal concentrations in bed sediments, within contrasting restored and unrestored urban rivers (Chapter 4), it was necessary to identify sites which: were along rivers that had been impacted and modified by urbanisation; had adjacent restored and unrestored stretches; were widely distributed in space to give different background sediment chemistry and styles of unrestored and restored stretch; and, had safe access in to the river.

It was decided to focus on sites within the Thames catchment, in Greater London. The city of London has developed around the Thames and its tributaries. Ever increasing urban development has increased the pressures upon the rivers and encroached upon their channels and floodplains (Francis *et al*., 2008). As a result, many rivers have been highly modified, placed into concrete channels and culverts, and impacted by increasing urban pollution. Some rivers, for example the Fleet, Tyburn and Efra, have been lost completely underground and integrated into the city's sewerage system (Bazelegette, 1865). However, there has been increasing recognition of the need to restore London's rivers as a part of urban regeneration and renewal, both for environmental benefits (improved flood storage and biodiversity) and social benefits (increased connection of communities to the local environment), with 22 km being improved or restored between 1994 and 2009 (London Rivers Action Plan, 2009 and Environment Agency, 2001). This restoration has been consolidated in the London Rivers Action Plan, which pledges to restore a further 15 km by 2015 (London Rivers Action Plan, 2009). The numerous rivers within Greater London, their historical management and the current restorative drive means that the Thames catchment within Greater London provided an ideal area to identify sites with very different characteristics.

Potential sites were identified through the London Rivers Action Plan database (http://www.therrc.co.uk/lrap.php), a literature search and information from practitioners working on river restoration within the Thames catchment. Several sites were visited and assessed for their suitability based upon: proximity of the restored and unrestored stretches; contrasts in morphology between the stretches; and, safe access in to the river. Four sites on three different rivers were chosen: one within the River Wandle catchment and three sites within the Ravensbourne River catchment (two sites on the River Quaggy and one site on the Pool River) (Figure 3.1). Full details of the catchments and the individual sites are detailed in Section 4.2 of Chapter 4.

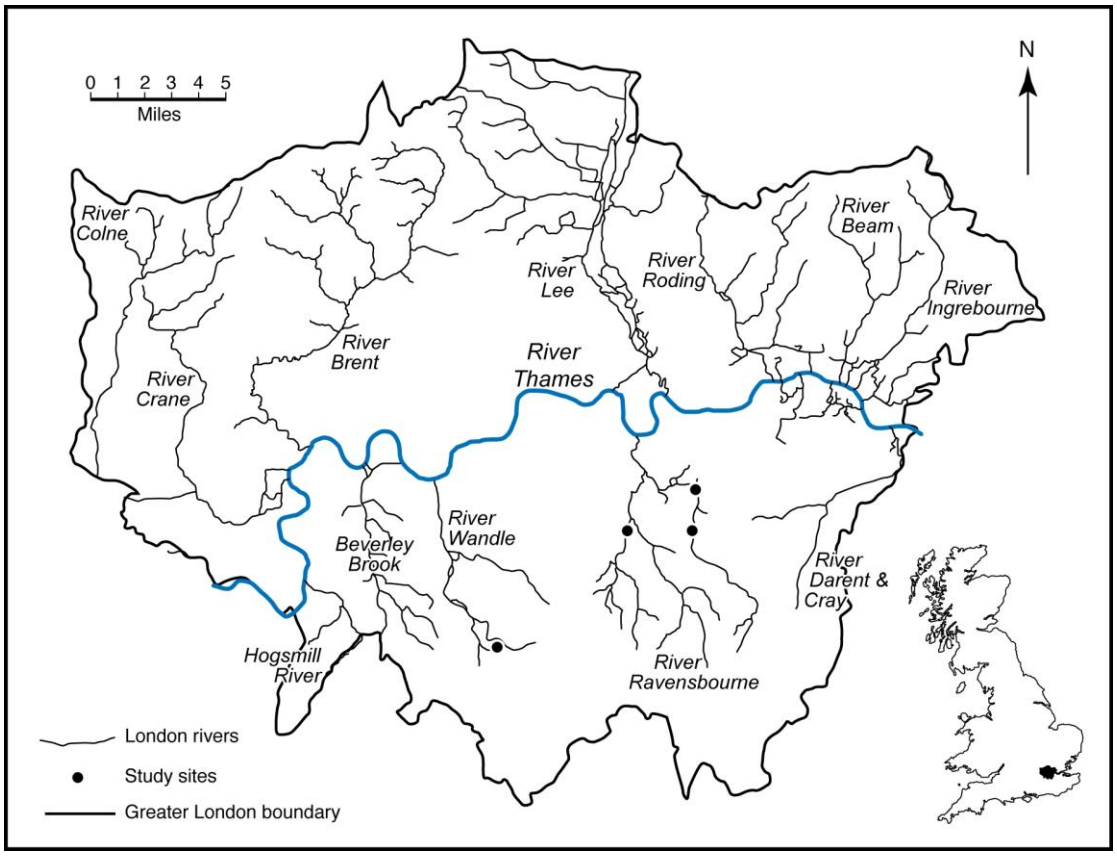


Figure 3.1: Research sites within the Thames catchment in Greater London.

River Blackwater sites (Chapters 5, 6 and 7)

In order to undertake detailed field studies of the biomechanical properties and uptake and translocation of metals in common emergent macrophytes, and the effect of the most common macrophyte, *S. erectum*, upon flow and sedimentation, it was necessary to identify sites which: were along urban rivers; had abundant macrophyte growth; permission would be granted for destructive research; at least one site would be secure from the public to prevent human disturbances that would adversely affect sediment accumulation measurements; and, had safe access in to the river.

It was decided to focus upon sites on the River Blackwater, Surrey, UK. The River Blackwater, a lowland river in southeast England, rises at Rowhill Nature Reserve near Aldershot and flows for 34 km in a northwesterly direction in to the River Loddon, near Eversley (Blackwater Valley Countryside Partnership, 2012). The River Loddon, a tributary of the River Thames, flows in to the Thames near Reading. There are various tributaries of the River Blackwater, the larger ones being Cove Brook which enters at Hawley (approximately 15 km downstream from the source) and the River Whitewater which enters at Swallowfield (approximately 2.5 km upstream from the confluence with the River Loddon) (Blackwater Valley Countryside Partnership, 2012).

The catchment of the River Blackwater has been heavily impacted by gravel extraction, transportation development and increasing urbanisation, particularly over the past 50 years. This has resulted in extensive modifications to the river and valley and confined the river to a narrow corridor. Extensive gravel and sand deposits within the valley have resulted in widespread gravel extraction since World War II, resulting in modifications to the river channel and the development of many lakes (Blackwater Valley Countryside Partnership, 2012). Construction of the A331 link road in the early 1980s necessitated management and relocation of many sections of the river (Brookes *et al*., 1998). Additionally, the Blackwater flows through the highly urbanised areas of Aldershot, Farnborough, Frimley, Camberley and Sandhurst (Figure 3.2). This increasing urbanisation has encroached upon the valley and also resulted in high inputs from sewage treatment works. In summer, flows upstream of the confluence with the River Whitewater can be comprised of up to 85% treated sewage effluent (Daniels *et al*., 2000). The river is therefore a highly modified and contaminated urban river. However, there have been significant improvements in landscaping, water quality, riparian vegetation and habitats since the 1980s through management undertaken by local councils in partnership with the Blackwater Valley Countryside Partnership (Surrey Heath Borough Council, 2012).

The river supports abundant macrophyte growth along its course and also transports a significant load of fine silt and organic sediment. As a result, various sites along the river have been used previously for research looking at contaminated sediments (House & Denison, 2002 and Daniels *et al*., 2000) and macrophytes (Liffen *et al*., 2011; Pollen-Bankhead *et al*., 2011; and, Naden *et al*., 2006) and thus provides suitable locations for the present research.

Permission had already been granted to undertake research (including destructive measurements) at various sites along the River Blackwater as part of a NERC funded project (Ref: NE/014597/1), and so two of these sites were also used in this complementary research (Figure 3.2).

Research site 1, Hawley Meadows, is a site maintained by the Blackwater Valley Countryside Partnership with public access and easy access in to the river. The presence of extensive stands of different emergent macrophyte species and easy access for heavy equipment and removal of large samples of plants and sediments meant that this site was suitable for the studies of biomechanical plant properties and the uptake and translocation of metals by common macrophytes (Chapters 5 and 6).

Research site 2, Mytchett, is on private land with no public access to the river and no cattle grazing. This meant that the site was suitable for the study of sediment retention and flow

properties (Chapter 7) since there was a low risk that the river bed would be disturbed by humans or animals over the period of the study.

Full details of each field site is provided in the relevant results chapters (see Section 5.22 of Chapter 5, Section 6.2 of Chapter 6 and Section 7.2 of Chapter 7).

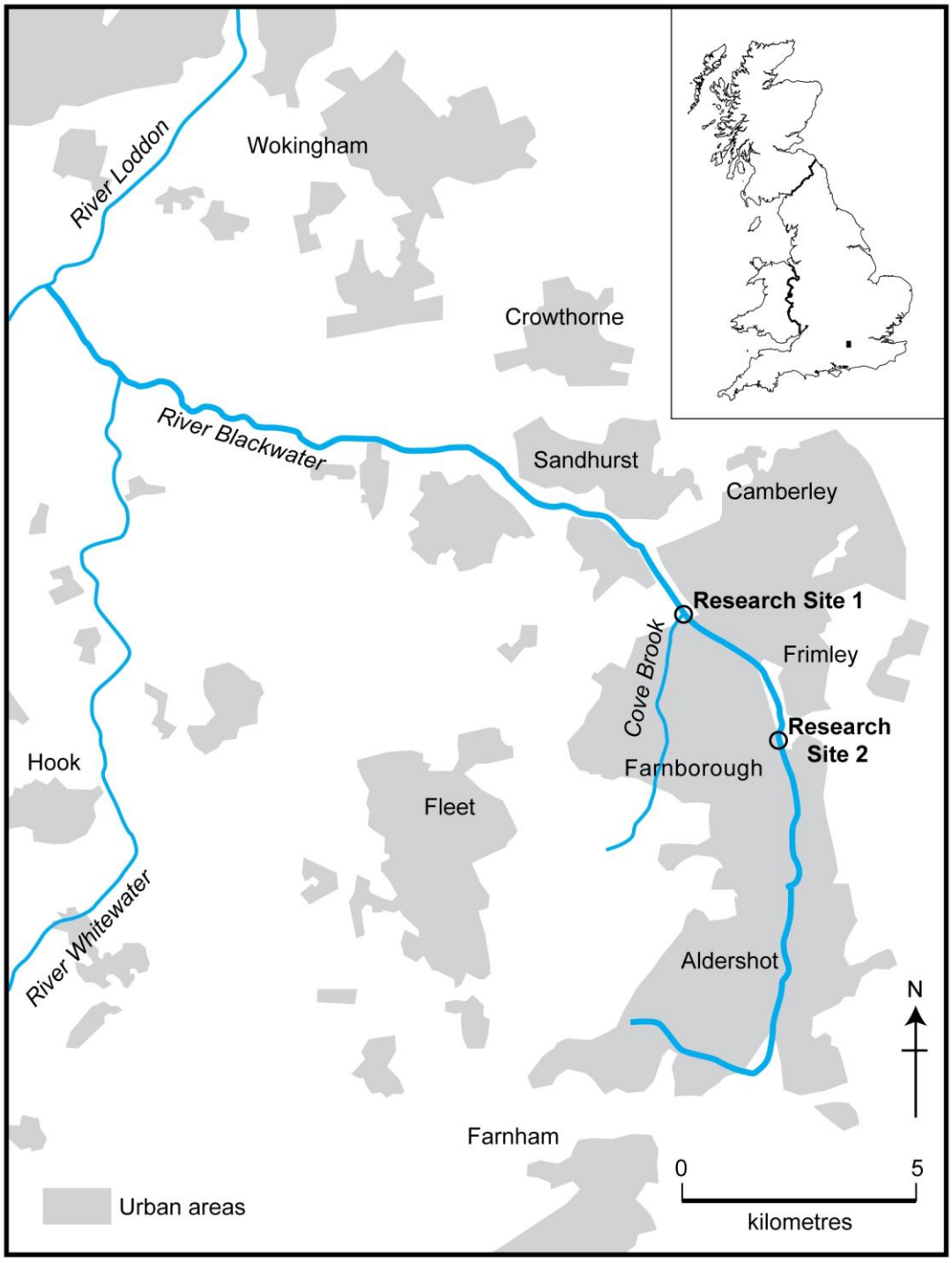


Figure 3.2: Research sites on the River Blackwater.

3.3 Field and Laboratory Methods

All research studies reported in this thesis involved fieldwork and most also involved some laboratory analysis (Table 3.1). The majority of field methods employed were very specific to the individual study and so are reported in detail in the relevant research chapters. Conversely, many of the laboratory methods were common across the studies. Therefore, detailed information about field methods employed in more than one of the field studies are provided below (Section 3.3.1) along with detailed information about all laboratory methods (Section 3.3.2). Greater details of the fieldwork components specific to each study are provided in the relevant results chapters.

3.3.1 Fieldwork

Sediment pH

Sediment pH can change during sampling and storage, therefore pH was determined in the field with fresh samples. pH can either be measured directly in-situ by insertion of a pH probe into the sediment, or through the creation of a sediment:water suspension and measuring the pH of the resulting supernatant. As damage could potentially occur to the pH probe if it is inserted into coarse sediments, a sediment:water suspension approach was used in this research. pH results will vary depending upon the ratio of sediment to water and whether the pH is measured in the resultant overlying supernatant or in the sediment (Radojevic & Bashkin, 1999 and Rowell, 1994). Therefore consistency is very important in the measuring protocol.

Sediment samples were collected and a 1:2.5 sediment:deionised water suspension was created through shaking in a sealed sample bag for 5 minutes. pH was measured in the overlying supernatant once it had been allowed to settle with a calibrated VWR pH100 meter (Nguyen *et al*., 2009).

Sediment redox - porewater Fe (II) concentrations

Porewater Fe (II) concentrations can be used as a proxy for redox (Storey *et al*., 2004). A series of redox reactions occur within the environment under increasingly anoxic conditions. As oxygen levels decrease, and the environment changes from oxidising to reducing, a series of redox reactions occur (Sigg, 1999). Each redox reaction will occur around a specific redox potential (Eh), although this is also mediated by the pH. Figure 3.3 shows at what redox potential each redox reaction will occur at both pH 7 (dark arrow) and pH 8 (light arrow).

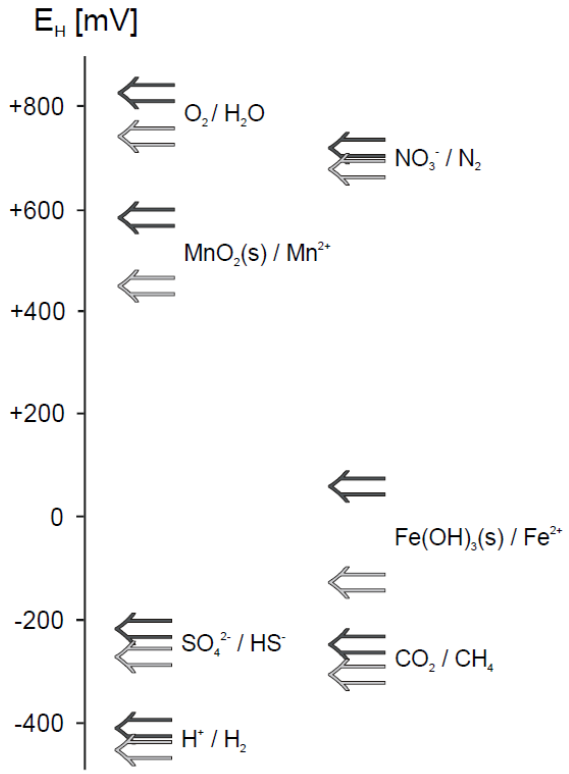


Figure 3.3: Redox potential (Eh) of redox reactions at pH 7 (dark arrow) and pH 8 (light arrow) (taken from Sigg, 1999).

From Figure 3.3 an indication of the constraint on the range of redox conditions that will be detected by only analysing Fe (II) can be determined. Assuming the sediments are within the pH neutral range (pH 7 to 8) the range of redox values that will be captured is limited to around +100 mV to -100 mV. A limitation of this method is that if redox conditions are greater than +100 mV then the sample would have 0 mgl^{-1} Fe (II) as no reduction of Fe (III) to Fe (II) will have occurred. Conversely, if the redox conditions are less than -100 mV then the sample would have a consistently high Fe (II) concentration as all Fe (III) will have been reduced to Fe (II), but the presence of redox reactions further down the sequence (e.g. $SO_4^{2-} \rightarrow HS^-$) will not be detected. Greater Fe (II) concentrations in the porewater indicate lower redox conditions.

Since significant changes in the redox conditions of sediments may occur during sediment sampling, these were determined in the field prior to any disturbance of the sediment through collection of sediment samples. Porewater samplers were inserted at the sampling locations and left to allow the sediment to settle. Porewater was extracted from the sediment and filtered through a nitrogen-flushed 0.45 µm filter into buffered phenanthroline (1:5, porewater:buffered phenanthroline) and stored in the dark on the day of collection. Buffered phenanthroline is a

complexing agent which changes Fe (II) into a strongly coloured compound, making it suitable for analysis on a spectrophotometer (Perkampus, 1992).

3.3.2 Laboratory analysis

A range of laboratory analysis methods were undertaken on various sediment, macrophyte, porewater and water samples (Table 3.2). The use of specific analysis methods are referred to in each chapter, but the background and justification for each are given here.

Analytical grade chemicals and ultrapure water were used for all analysis. Additionally, all glassware used for metal analysis was acid-washed in 10% HNO_3.

Table 3.2: Summary of laboratory analysis of sample types for each study.

	Sediment Analysis	Macrophyte Analysis	Porewater Analysis	Water Analysis
Chapter 4	•		•	
Chapter 6	•	•	•	•
Chapter 7		•		

Laboratory analysis quality control

Various procedures were employed throughout the laboratory analysis to ensure the quality of the data produced. Three measures commonly employed were those of accuracy, precision and analytical blanks. Accuracy is a measure of how close to the real value the measured value is, and accuracy is a measure of the closeness of repeated measurements. These allowed the replicability of laboratory analyses across batches to be assessed.

Accuracy can be assessed by using certified reference materials and calculating percentage recovery (R, %):

$$R = (M_c / K_c) * 100$$

where M_c is the measured concentration and K_c is the known concentration. Certified reference materials were used in analysis of sediment and macrophyte metal concentrations and water total hardness. Each of these are referred to in the relevant sections below.

Precision can be assessed through triplicate analysis of samples and calculation of relative standard deviation (RSD, %):

$$RSD = (\sigma / \bar{x}) * 100$$

where σ is the standard deviation and $\bar{x}$ is the mean. Measures of accuracy were used throughout the laboratory analysis and are referred to in the relevant sections below.

Analytical blanks were also used as a measure of any contamination.

Sediment analysis

(i) Sediment preparation

The preparation of sediment samples prior to analysis can have a significant effect upon their physiochemical composition as a result of changes to environmental conditions, particularly pH, temperature and redox (Bordas & Bourg, 1998). Ideally, analysis should be undertaken on fresh sediment (Bordas & Bourg, 1998). However, this is not always possible, particularly when large numbers of samples are being collected in a short period of time. Therefore, all sediment samples were stored in the freezer on the day of collection and were kept frozen until they were analysed.

For longer-term storage sediment needs to be dried (Bordas & Bourg, 1998). The process of drying has a significant effect upon the partitioning of metals within the sediment (Petrovic *et al*., 2007). Investigations into the effect of different drying methods (air, oven and freeze) upon metal partitioning have identified the importance of the particular extraction method used, the metal being extracted and the character of the sediment itself (Capilla *et al*., 2007 and Bordas & Bourg, 1998). Although metal partitioning is affected by drying, total metal concentrations within sediment are not affected. Additionally, determination of organic matter content and moisture content requires that sediment is dried at 105°C. Therefore, in this research the frozen sediment samples were defrosted in the fridge and then oven-dried at 105°C overnight (16 hours) prior to further analysis. An investigation was undertaken to identify the effect of this drying temperature upon acetic acid extractable metals in these sediments (Section 3.3.2 (v)).

(ii) Sediment moisture, dry bulk density and sieving

Sediment was dried in the oven at 105°C overnight (16 hours) to a constant weight to remove all moisture (Rowell, 1994). Sediment moisture content (MC, %) was then calculated as:

$$MC = 100 - ((W_{105} / W_{wet}) * 100)$$

where W_{105} is sediment weight after drying at 105°C (g) and W_{wet} is sediment weight before drying (g).

Sediment dry bulk density (DBD, gcm^{-3}) is the weight of dried sediment in a known volume:

$$DBD = W_{105} / V_t$$

where W_{105} is sediment weight after drying at 105°C (g) and V_t is total volume of the sample prior to drying (cm^3).

The total volume (V_t) of the sediment sample prior to drying comprises not just sediment particles (V_s, cm^3) but also water content (V_w, cm^3) (Avnimelech *et al*., 2001). As not all sediment samples were of a known, or constant, volume, then total volume (V_t) was calculated as:

$$V_t = V_s + V_w$$

$$\text{Where } V_s = W_{105} / SD$$
$$\text{And } V_w = (W_{wet} - W_{105}) / WD$$

Sediment density (SD, gcm^{-3}) is commonly taken as 2.65 gcm^{-3} (Rowell, 1994). However, a correction for organic matter content should also be included, with organic matter density being 1.25 gcm^{-3} (Boyd, 1995). Therefore sediment density (SD, g/cm^3) is calculated as:

$$SD = (1.25 * (OM / 100)) + (2.65 * (1 - (OM / 100)))$$

where organic matter content (OM, %) is calculated as below in Section 3.3.2 (iii).

Water density (WD, gcm^{-3}) is commonly taken as 1 gcm^{-3} (Rowell, 1994).

Sediment samples were then sieved to 2 mm, and the proportion of sample >2 mm and <2 mm weighed. Sub-samples of the <2 mm (sand, silt and clay) fraction were used for analysis of organic matter content, absolute particle size and metal concentrations. Although it is known that the <63 µm fraction (silt and clay) frequently contains the greatest concentration of metals (Section 2.3.2 in Chapter 2) the <2 mm fraction was used in these analyses due to the range of

sediment calibres sampled in these studies (particularly in the Chapter 4 study). In particular, the coarser (i.e. sand and gravel) samples were likely to have a low proportion of sediment <63 µm, therefore the <2 mm fraction was preferable for comparing sediment properties across the four bed sediment types used in Chapter 4. Furthermore, coatings on sand particles (63 µm to 2 mm), such as organic and Fe and Mn (hydr)oxides, can also be important for metal binding (Forstner, 2004).

(iii) Organic matter content

Loss on ignition (LoI) is a simple and frequently used method for estimating organic matter content of sediments, which can allow easy processing of a large number of samples. The principle of the method is that the change in weight of a sediment sample after ignition in a furnace equates to the loss of organic matter. However, at high temperatures losses of water from clay minerals and metal oxides and losses of inorganic carbon can also occur which may cause an over-estimation of the organic matter content (Santisteban *et al.*, 2004 and Heiri *et al*., 2001).

Heiri *et al.* (2001) undertook a series of investigations to look at the effect of furnace temperature, duration, sample size and position in the furnace on organic matter content determination. The results suggested that 550°C for four hours was optimal in terms of organic matter combustion and reducing the effect of differences in sample size and position in the furnace. Additionally, Heiri *et al.* (2001) stated that consistency in the LoI method is important with clearly stated sample sizes, furnace temperature and duration.

In this research 1 g ± 0.1 g of the <2 mm fraction of dried sediment was placed in the furnace at 550°C for four hours. The furnace programming setting was used so that the timer began once the furnace reached 550°C and the furnace automatically switched off after four hours. Once samples were cool enough, they were transferred to the dessicator to prevent reabsorption of moisture during the cooling process. Organic matter content (OM, %) was calculated as:

$$OM = ((W_{105} - W_{550}) / W_{105}) * 100$$

where W_{105} is sediment weight after drying at 105°C (g) and W_{550} is sediment weight after ignition at 550°C (g).

To check the precision of the method, triplicate LoI was undertaken on three sediment samples and relative standard deviation (RSD, %) was calculated.

Table 3.3 shows that there was little variation in the calculated organic matter contents for each triplicate, resulting in RSD values below 6%.

Table 3.3: Organic matter content and calculated relative standard deviations (RSD) for triplicate loss on ignitions on three sediment samples.

Sample	Organic Matter Content (%)	% RSD
1	3.00 2.80 3.13	5.56
2	24.12 23.24 22.13	4.30
3	17.25 18.32 16.28	5.90

(iv) Sediment absolute particle size

The absolute (mineral) particle size distribution of the <2 mm fraction (sand, silt and clay) was determined using a Beckmann Laser Diffractor Particle Size Analyser (PSA) in order to determine the % by volume of the <2 mm fraction that was <63 µm. As only the mineral component of the sediment was required, and organic matter can bind minerals together, organic matter was removed from the sediment prior to analysis by oxidation with hydrogen peroxide (H_2O_2) and heating on the hotplate (Rowell, 1994). Once no further reaction occurred with H_2O_2, the samples were shaken in the dispersing agent Calgon (sodium hexametaphosphate and anhydrous sodium carbonate) overnight to ensure disaggregation (Rowell, 1994). Three samples underwent this process in triplicate to test the precision (measured as relative standard deviation) of sub-sampling and organic matter removal, with all samples having an RSD below 15% (Table 3.4). Also, three samples underwent triplicate analysis on the PSA to check the precision of the machine, with all samples having an RSD below 6% (Table 3.5).

Table 3.4: Percentage <63 µm and calculated relative standard deviations (RSD) for triplicate determinations of % <63 µm for three sediment samples to check precision of sub-sampling and organic matter removal.

Sample	% <63 µm	% RSD
1	22.6 24.7 18.4	14.65
2	22.2 19.7 22.5	7.16
3	46.9 55.8 42.6	13.90

Table 3.5: Percentage <63 µm and calculated relative standard deviations (RSD) for triplicate determinations of % <63 µm for three sediment samples to check precision of the PSA.

Sample	% <63 µm	% RSD
1	47.5 48.8 47.3	1.70
2	100 100 100	0.00
3	9.49 10.5 10.4	5.49

During analysis of the samples on the PSA, a reference material (Micromeritics medium particle size reference material) with a known median particle size was run at the beginning and end of a batch of samples to check the PSA was running correctly, and also to check that there was no carry over of sediment in the bottom of the machine in between samples. The median particle size of the reference material was 3.77 µm ± 0.14 µm, which gave an acceptable range in median particle size of 3.63 to 3.91 µm. When median particle sizes were outside the acceptable range the samples were re-run.

(v) Metal extractions

There are many different methods used for the extraction of metals from sediments. The main distinction can be made between single, selective and sequential extractions (Rao *et al.*, 2008). A single (aqua regia) and a selective (acetic acid) extraction were used in this research.

Aqua regia metals extraction (pseudo-total metals)

A single extraction, undertaken using strong acid, can provide a total or pseudo-total concentration of metals within sediment (Rao *et al.*, 2008). Strong acids that can be used for

this include hydrofluoric acid (HF), hydrochloric acid (HCl) and nitric acid (HNO_3) (Radojevic & Bashkin, 1999). Although HF is the most effective acid as it fully digests the sediment rather than just providing an extraction, and thus provides a total metal concentration, it is very dangerous and specific laboratory facilities and training are required for its use (Radojevic & Bashkin, 1999). Alternatively, the use of an aqua regia mixture as a single extraction (3:1 HCl:HNO_3) is a widely-used method in studies of the contamination of aquatic sediments (e.g. Li *et al.*, 2009; Korfali *et al.*, 2006; Old *et al.*, 2004; and, Walling *et al.*, 2003). Although this method does not provide a total metal extraction of the sediment (metals bound to silicate structures in particular will not normally be extracted) most metals from anthropogenic inputs are not bound to the silicate matrix (Ure, 1996) and the very strong acid digest will release the majority of metals and thus provide a pseudo-total metal concentration (Rao *et al.*, 2008 and Radojevic & Bashkin, 1999).

There are many variations of the aqua regia method, with differences in the weight of sediment used, volume of acids used, length of heating and heating method. Therefore, an investigation was undertaken of four different aqua regia methods to select the method to be used in this research:

Method 1: microwave aqua regia (Bettinelli *et al*., 2000).
Method 2: microwave reverse aqua regia (USEPA, 2007).
Method 3: hotplate reverse aqua regia with hydrogen peroxide (USEPA, 1996).
Method 4: hotplate aqua regia (based on Chen & Ma, 2001).

The four different methods were assessed for their accuracy using a certified reference material (for % recovery, reference material LGC6187 – aqua regia extractable metals) (Table 3.6), and their precision (through % relative standard deviation) was determined from triplicate extractions (Table 3.7).

Table 3.6: Summary of recoveries of certified reference material LGC6187 for four aqua regia methods.

	% Recovery			
Metal	**Method 1**	**Method 2**	**Method 3**	**Method 4**
Cd	93	90	85	105
Cr	107	87	73	77
Cu	98	97	93	88
Fe	145	114	95	96
Mn	85	82	79	75
Ni	104	93	74	82
Pb	91	89	85	78
Zn	96	90	86	87

Table 3.7: Summary of relative standard deviations (RSD) for four aqua regia methods.

	% RSD			
Metal	**Method 1**	**Method 2**	**Method 3**	**Method 4**
Al	9.9	8.7	6.5	4.6
Cd	35.4	11.9	10.5	3.0
Cr	15.4	5.5	6.3	1.2
Cu	53.5	22.5	7.0	0.4
Fe	2.0	3.8	3.0	1.7
Mn	16.1	7.0	4.0	0.5
Ni	22.6	7.0	5.5	2.5
Pb	13.9	5.0	1.5	1.4
Zn	5.2	1.3	3.4	1.1

The microwave methods generally showed a greater accuracy than the hotplate methods, but the hotplate methods had greater precision (Tables 3.6 and 3.7). However, there were issues with the reliability of the microwave as there was a lag in the microwave reaching maximum temperature within the ramp up time and the pressure sensor did not appear to be working. Additionally, only 12 samples (including any blanks, CRM's and triplicates) were able to be extracted at a time compared to 20 samples plus blanks, CRM's and triplicates on the hotplate. Method 3 showed slightly lower precision than method 4 and was more time consuming due to it being a two day extraction. Method 4 was therefore chosen as the extraction method.

In order to understand how this aqua regia extraction compared to undertaking a total metals digest (i.e. with HF), method 4 was undertaken on a specific total metals CRM (BCR 320R total metals in channel sediment) (Table 3.8).

Table 3.8: Percentage recovery of aqua regia extraction on total metals certified reference material BCR 320R.

% Recovery	
Metal	**Method 4**
Cd	91
Cr	35
Cu	80
Fe	82
Mn	72
Ni	64
Pb	70
Zn	77

Table 3.8 shows that as expected the aqua regia extraction gives a lower recovery in terms of total metals for all metals. In particular Cr has a very low recovery, which has been reported in other research, due to the presence of insoluble Cr minerals (Chen & Ma, 2001 and Scancar *et al*., 2000).

Pseudo-total metal extraction was undertaken via a hotplate aqua regia extraction. Twelve ml of aqua regia was added to 0.5 g ± 0.01 g of the <2 mm fraction of dried sediment and refluxed on the hotplate at a gentle simmer for five hours. The extraction was then filtered (Whatman number 542 filters) and the filtrate made up to 50 ml with ultrapure water.

Acetic acid metals extraction

Whilst single extractions can provide total or pseudo-total metal concentrations, selective extractions can be used to target metals that are bound to one particular fraction within the sediment (Rao *et al.*, 2008). These fractions are operationally defined, e.g. reducible or residual. Commonly, a series of single extractions is undertaken (known as a sequential extraction) to provide detail on the partitioning of metals within the sediment (Linge, 2008). Each successive extraction targets a fraction of metals associated with lesser mobility. Most sequential extractions have between three and eight stages (Filgueiras *et al*., 2002). One of the most common sequential extractions is the BCR (Community Bureau of Reference, now the Standards, Measurements and Testing Programme) sequential extraction, which has been used to study the fractionation of metals within contaminated river sediments (e.g. Byrne *et al*., 2010; Linge, 2008; Rao *et al*., 2008; Tuzen, 2003; and, Svete *et al*., 2001) (Table 3.9).

Table 3.9: Summary of the stages, fractions, metal associations, sources and mobilisation processes for the BCR sequential extraction (Trujillo-Cardenas *et al*., 2010; Filgueiras *et al*., 2002; and, Gleyzes *et al*., 2002).

Stage	Operationally – defined fraction	Association of metals	Source of metals	Mobilised by
1	Exchangeable and acid-soluble	Weakly sorbed and associated with carbonates	Anthropogenic	Changing ionic-strength and pH
2	Reducible	Associated with Fe and Mn (hydr)oxides	Scavenging	Reducing conditions
3	Oxidisable	Associated with various organic materials and sulphides	Scavenging	Oxidising conditions
4	Residual	Associated with crystalline lattice	Natural	Weathering

Although sequential extractions are commonly used there are some criticisms of the methods. There is a lack of selectivity of the reagents used to extract metals from each fraction and readsorption and redistribution of metals can occur during extraction (Linge, 2008; Filgueiras *et al*., 2002; and, Gleyzes *et al*., 2002). The specific sediment drying method will alter the distribution of metals across the fractions, and this, along with variations in the specific method used for each fraction extraction, can cause variations in results (Linge, 2008; Filgueiras *et al*., 2002; and, Gleyzes *et al*., 2002).

Undertaking one of the selective extractions of the sequential extraction provides information on the concentration of metals within that one particular fraction. The bioavailability of metals depends upon how easily they can become mobilised from the sediment and become available to organisms. In terms of the sequential extractions (Table 3.9) the most mobile metals are those extracted in BCR stage 1 with acetic acid. This extracts those metals which are soluble in water or slightly acidic conditions and the exchangeable metals (Alvarez-Valero *et al*., 2009). The standard stage 1 acetic acid extraction method was used (Alvarez-Valero *et al*., 2009). 1 g ± 0.01 g of the <2 mm fraction of dried sediment with 40 ml 0.11 mol/l acetic acid (CH_3COOH) was shaken overnight for 16 hours at room temperature. The extraction was then filtered (Whatman number 542 filters) and the filtrate made up to 50ml with ultrapure water.

Drying the sediment at the higher temperature of 105°C as opposed to 40°C (as recommended for the BCR sequential extraction) will make no difference to total or pseudo-total metal concentrations. However it could alter the proportions of metals held in the different fractions and thus make a difference to the acetic acid extractable metals content. Drying at 105°C was

necessary in this study in order to determine the dry weight of the sediment and to calculate organic matter content. An investigation was therefore undertaken on five samples to assess the effect of drying at 105°C, as opposed to 40°C, upon the acetic acid extractable metal content so as to provide some context for the results (Table 3.10).

Table 3.10: Comparison of acetic acid extracted metal concentrations in five samples (A to E) dried at 40°C and 105°C.

	Concentration ($mgkg^{-1}$)							
Samples	**Al**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
A40	35.06	<LoD	0.65	5,807.23	75.48	5.33	<LoD	179.57
A105	140.29	0.28	2.70	2,005.56	95.39	4.76	<LoD	171.22
B40	50.43	<LoD	1.21	5,081.44	98.86	5.83	<LoD	196.63
B105	173.67	0.37	4.19	2,666.36	92.39	6.24	<LoD	214.13
C40	41.83	<LoD	0.65	5,243.83	87.22	5.96	<LoD	202.91
C105	145.47	0.34	2.63	2,235.70	81.52	5.01	<LoD	187.95
D40	44.87	<LoD	0.91	4,786.66	140.27	6.16	<LoD	191.45
D105	155.81	0.30	3.08	1,616.79	71.69	4.65	<LoD	151.68
E40	45.02	<LoD	0.96	4,189.06	108.19	3.25	<LoD	131.33
E105	153.07	0.28	3.81	1,192.03	112.07	4.21	<LoD	162.21

The results indicate that drying at 105°C increases the exchangeable metal concentrations for Al, Cr and Cu. The exchangeable metal concentration is decreased for Fe. There was no clear increase or decrease for Mn, Ni and Zn. Unfortunately the Pb concentrations in the samples used were low so <LoD concentrations were found for both 40°C and 105°C.

Sediment samples were extracted in triplicate for both the aqua regia and acetic acid extractions in order to measure the precision of the methods (through % RSD). Additionally, certified reference materials were extracted to measure accuracy (through % recovery):

- LGC6187 (sediment aqua regia extractable metals).
- BCR701 (extractable trace elements in sediment following a sequential extraction, acetic acid extraction).

Analytical blanks were also included as a measure of any contamination. Uncorrected metal concentrations (i.e. not corrected for % recoveries calculated from extraction of certified reference materials) are reported throughout this thesis.

The triplicate extractions, certified reference materials and analytical blanks were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

(vi) ICP-OES

The filtrates were then analysed by ICP-OES (inductively coupled plasma optical emission spectrometry) on the Varian Vista Pro CCD Simultaneous ICP-OES in order to measure the concentration of metals. Elemental analysis by ICP-OES is one of the most widely used techniques and all metals of interest in this research can be determined by ICP-OES (Walsh, 1999). The sample is introduced as a mist to the plasma flame, and the resulting wavelengths from the radiation produced are measured and compared to the standards to interpret the presence and concentration of metals. The advantages of ICP-OES are that it has limited interference due to the high temperatures, can produce many spectral lines for single elements and good detection limits can be produced as the background signal from the plasma is low (Walsh, 1999). However, there can be problems of spectral interference and matrix effects (Olesik, 1991). Matrix effects can be reduced by matrix matching samples and standards. Spectral interference can be reduced by carefully selecting specific wavelengths of analysis for each metal and screening data.

The aqua regia extraction samples were run both with no dilution and with a 1:20 dilution (used to calculate Al and Fe concentrations), the dilution being undertaken with 24% aqua regia. The acetic acid extraction samples were run with no dilution. The samples were analysed for a range of metals: Aluminium (Al), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn). The specific wavelengths of analysis for each metal are presented below (Table 3.11).

Table 3.11: Determined optimum wavelengths, limits of determination (LoD) and standard concentrations for measuring metal concentrations by ICP-OES for both aqua regia and acetic acid sediment extractions.

	Aqua Regia	Acetic Acid	Aqua Regia	Acetic Acid		
Metal	**Wavelength measured on (nm)**		**LoD (mgl^{-1}) 3 s.f.**		**Standard**	**Concentration (mgl^{-1})**
Al	328.068	328.068	0.0141	0.0280	**1**	0
Cd	228.802	228.802	0.0100	0.0100	**2**	0.2
Cr	267.716	267.716	0.00247	0.00520	**3**	0.6
Cu	327.395	327.395	0.00150	0.00475	**4**	1
Fe	238.204	238.204	0.0376	0.0150	**5**	5
Mn	257.610	257.610	0.00138	0.00419	**6**	10
Ni	230.299	227.021	0.00930	0.0300	**7**	50
Pb	220.353	220.353	0.0251	0.0400		
Zn	213.857	213.857	0.00300	0.00966		

Seven multi-element standards were made over a range of concentrations (0 mgl^{-1} to 50 mgl^{-1}) and matrix matched (24% aqua regia and 0.11mol l^{-1} acetic acid) (Table 3.11). The standards were run on the ICP-OES at the start of every run to calibrate the machine. Some samples had very low metal concentrations which were below instrumental detection on the ICP-OES. Many of these were identified on the ICP-OES as negative values, or had a 'uv' suffix, indicating a reading lower than the zero point on the calibration. Additionally, the levels of determination (LoD) for each metal and matrix on the ICP-OES were calculated. Twelve matrix matched blank samples were run on the ICP-OES and the standard deviation of the measured concentrations (mgl^{-1}) calculated. According to Walsh (1999), three times the standard deviation is the 'detection limit', the limit at which the presence of a peak can be detected, but it is too small to be quantitatively measured. Six times the standard deviation is the 'limit of determination', the threshold for confidence in a quantitative analysis of a trace element. The limits of determination were therefore calculated initially. However, these are theoretical limits so the data was screened and all peaks checked, especially those below the lowest standard (0.2 mgl^{-1}) to ensure they showed a clear peak. Combining these two methods, a set of LoDs were defined which were used to screen the data from the ICP-OES (Table 3.11).

Once the data from the ICP-OES had been screened for <LoD, the concentration of metals in the sediment (C_m, $mgkg^{-1}$) were calculated as:

$$C_m = ((C_e * V) / W) * \text{dilution factor}$$

where C_e is the concentration in the extractant measured by ICP-OES (mgl^{-1}), V is the volume extractant made up to (ml) and W is the weight of the sediment sample used (g).

Lab standards of a known concentration were run every eight samples to check for drift of the instrument and during long sample runs the instrument was re-calibrated halfway through. Samples were analysed on the ICP-OES in triplicate to measure the precision of the instrument. These were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

Macrophyte analysis

(i) Macrophyte preparation

On return to the laboratory the macrophyte samples were carefully washed with tap water and then deionised water, until the water ran clear, to remove any surface sediment which could potentially have an impact upon biomass and metal extraction results (Campbell & Plank, 1998 and Markert, 1995).

Due to the varying water content of plants between, and even within, species vegetation biomass measurements are generally given as dry weights per area. The temperature, and duration, of drying is a balance between ensuring full water removal and preventing any thermal decomposition (Radojevic & Bashkin, 1999). Additionally, macrophyte samples need to be dried prior to metal extraction.

The cleaned vegetation was dried in the oven for 72 hours at 85°C and then weighed (Asaeda *et al.*, 2010). To calculate the dry weight biomass the dry weight was then multiplied up to per m^2 and presented as grams dry weight (gdw) /m^2.

(ii) Macrophyte metals extraction

The procedure for extracting metals from vegetation is based on extracting the metals into solution, similar to sediment metal extraction. The main steps with vegetation is the destruction of the organic matter through an oxidation reaction and an acid extraction on the residues (carbonates, silicates and oxides). Two main methods exist for this: dry ashing and wet ashing. Dry ashing is the combustion of organic matter at very high temperatures in a furnace (around 500°C) followed by dissolution of the residue in acid (Sasmaz *et al.*, 2008; Du Laing *et al.*, 2003; and, Miller, 1998). Wet ashing follows the same basic procedure as used for sediment, with organic matter being destroyed through the use of acids and heat (various combinations of HNO_3, $HClO_4$ and H_2O_2) (Liu *et al*., 2007; Samecka-Cymerman & Kempers, 2001; and, Sparling & Lowe, 1998). As with sediment extractions microwaves have also been utilised in vegetation metal extractions (Vardanyan *et al.*, 2008 and Du Laing *et al*., 2003). The full dissolution of samples which have a high silica content will not occur unless HF is used (as similarly seen in sediment), which particularly affects the full extraction of Al which tends to associate with silica in vegetation (Hansen *et al*., 2009 and Griepink, 1987).

A disadvantage of dry ashing is the potential loss of volatile metals (As, Cd, Hg, Pb and Zn (Benjamin & Honeyman, 1992)) and the potential low recovery of Al, Fe and Zn in material high in silica (Miller, 1998 and Mills & Jones, 1996). However, dry ashing allows numerous samples to be analysed at once, small volumes of acid are used and it requires less supervision (Soon, 1998 and Hoenig & Kersabiec, 1996). A disadvantage of wet ashing is the potential incomplete solubilisation of the sample due to the lower temperatures and the high volumes of acid used if numerous samples are being analysed (Soon, 1998 and Hoenig & Kersabiec, 1996). Higher recoveries of Al, Fe and Zn from materials high in silica have been recorded from wet ashing (Mills & Jones, 1996).

An investigation was undertaken to choose the specific method for this study through a comparison of four different methods. A microwave method was not tested as it had previously been tried for the sediment extractions and found not to be reliable. Additionally, a method involving the use of HF was not used due to health and safety concerns. The four methods investigated were:

Method 1: hotplate aqua regia (based on Chen & Ma, 2001, same as sediment extraction).
Method 2: hotplate aqua regia (Wilson *et al*., 2005b).
Method 3: hotplate nitric acid and hydrogen peroxide (Wilson *et al*., 2005b).
Method 4: dry ashing with hydrochloric acid (Miller, 1998).

The four different methods were assessed for their accuracy using a certified reference material (for % recovery, reference material BCR060, Lagarosiphon major) (Table 3.12), and their precision (through % relative standard deviation) was determined from triplicate extractions (Table 3.12).

Table 3.12: Summary of recoveries of certified reference material BCR060 and relative standard deviations (RSD) for four macrophyte metal extraction methods.

	% Recovery			
Metal	**Method 1**	**Method 2**	**Method 3**	**Method 4**
Al	19.06	16.83	20.07	17.50
Cd	65.94	77.17	95.15	22.76
Cu	69.96	67.99	88.25	63.11
Mn	64.22	67.54	84.39	62.79
Pb	62.58	70.45	85.26	28.02
Zn	71.11	70.43	86.80	63.89

	% RSD			
Metal	**Method 1**	**Method 2**	**Method 3**	**Method 4**
Al	4.5	6.9	1.2	9.8
Cd	14.0	11.6	7.8	47.9
Cr	5.1	11.1	10.6	5.8
Cu	2.3	6.6	1.7	9.5
Fe	5.1	2.4	2.9	6.1
Mn	2.1	13.8	2.2	2.9
Ni	3.4	9.8	2.0	2.7
Pb	1.8	4.0	3.0	8.9
Zn	2.0	6.2	2.4	3.5

As noted earlier, all extractions showed low recoveries for Al as HF was not used (Table 3.12). Method 3 showed the highest recoveries and also showed good precision and was therefore chosen as the digest method.

Metal extraction was therefore undertaken via a hotplate nitric acid and hydrogen peroxide method. Prior to metal digest, the macrophyte samples were milled to a fine powder in a non-metallic ball mill to ensure homogenization of the sample. Fourteen ml of nitric acid was added to 0.5 g ± 0.01 g of the finely milled macrophyte sample and refluxed for 90 minutes on the hotplate. After cooling, 1 ml of hydrogen peroxide was added, the sample heated until effervescence subsided and a further 1 ml of hydrogen peroxide added and the sample refluxed for a further 30 minutes. The extraction was then filtered (Whatman number 542 filters) and the filtrate made up to 100 ml with ultrapure water.

Macrophyte samples were extracted in triplicate in order to measure precision of the methods. Additionally, certified reference materials were extracted to measure accuracy:

- BCR060 (Aquatic Plant, Lagarosiphon major).

Analytical blanks were also included as a measure of any contamination. Uncorrected metal concentrations (i.e. not corrected for % recoveries calculated from extraction of certified reference materials) are reported throughout this thesis.

The triplicate extractions, certified reference materials and analytical blanks were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

(viii) ICP-OES

The filtrates were then analysed by ICP-OES. The vegetation extraction samples were run both with no dilution and with a 1:20 dilution (for Fe concentrations), the dilution being undertaken with a 14% HNO_3 and 2% H_2O_2 solution. The samples were analysed for a range of metals: Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn). Aluminium (Al) was not analysed for due to the low recoveries. The specific wavelengths of analysis for each metal are presented below (Table 3.13).

Table 3.13: Determined optimum wavelengths, limits of determination (LoD) and standard concentrations for measuring metal concentrations by ICP-OES for macrophyte metal extractions.

Metal	Wavelength measured on (nm)	LoD (mgl^{-1}) 3 s.f.	Standard	Concentration (mgl^{-1})
Cd	228.802	0.02	**1**	0
Cr	267.716	0.001	**2**	0.2
Cu	327.395	0.01	**3**	0.6
Fe	238.204	0.06	**4**	1
Mn	257.610	0.003	**5**	5
Ni	230.299	0.021	**6**	10
Pb	220.353	0.092	**7**	50
Zn	213.857	0.07		

Seven multi-element standards were made over a range of concentrations (0 mgl^{-1} to 50 mgl^{-1}) and matrix matched (14% HNO_3 and 2% H_2O_2) (Table 3.13). Once the run was completed all measured peaks were checked.

As with the sediment samples, some samples had very low metal concentrations and the same methodology was used to calculate LoDs (Table 3.13) and identify samples with concentrations below the LoD.

Once the data from the ICP-OES had been screened for <LoD, the concentration of metals in the macrophyte (C_m, $mgkg^{-1}$) were calculated as:

$$C_m = ((C_e * V) / W) * \text{dilution factor}$$

where C_e is the concentration in the extractant measured on the ICP-OES (mgl^{-1}), V is the volume extractant made up to (ml) and W is the weight of the macrophyte sample used (g).

Lab standards of a known concentration were run every eight samples to check for drift of the instrument and during long sample runs the instrument was re-calibrated halfway through. Samples were analysed on the ICP-OES in triplicate to measure the precision of the instrument. These were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

Porewater analysis

(i) Porewater Fe (II) concentrations – UV-VIS spectrophotometry

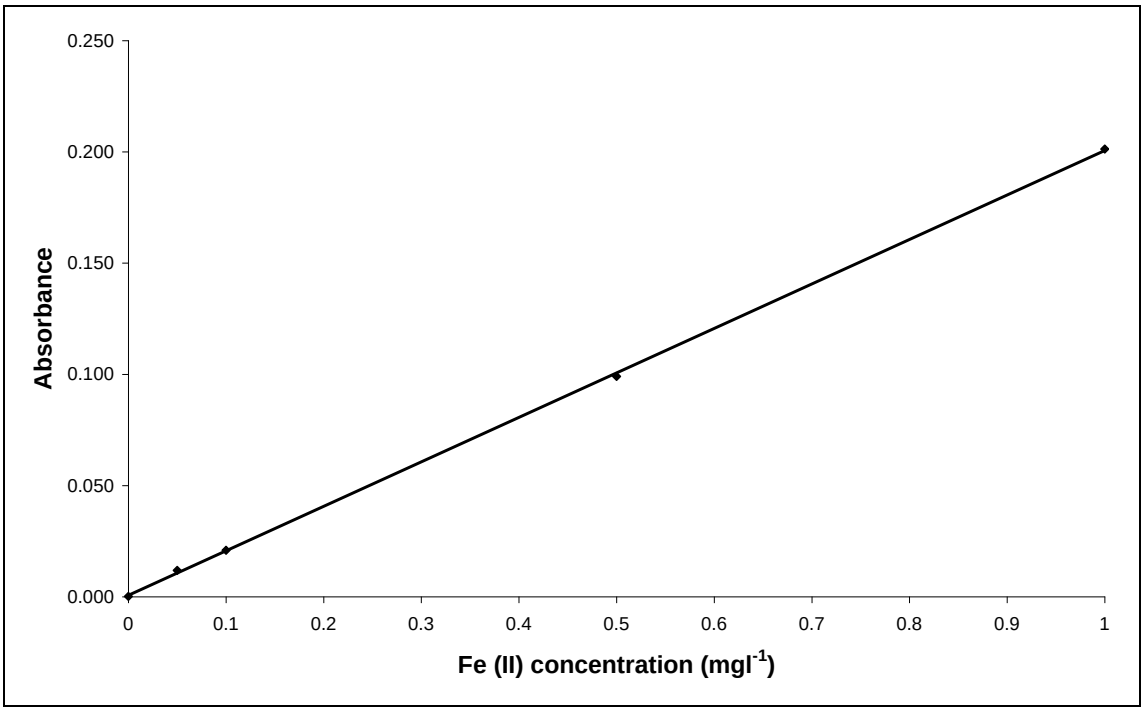
As stated earlier, porewater Fe (II) concentrations can be used as a proxy for redox conditions within the sediment (Storey *et al.*, 2004). The porewater samples in buffered phenanthroline were analysed for Fe (II) concentrations by UV-VIS spectrophotometry on the Evolution 100 Thermo Scientific Spectrophotometer.

Spectrophotometry measures the amount of light at a particular wavelength which is absorbed by a sample. Light is passed through a filter to select the desired wavelength. The light then passes through the sample and hits a detector which measures it (Clark *et al.*, 1993). The absorbance of light is then calculated based upon the difference between the light intensity before it passed through the sample to after it has passed through the sample. The amount of light absorbed is directly proportional to the concentration of the element of interest. Different elements are measured at different wavelengths based upon which part of the spectrum they absorb light in, known as the wavelength of maximum absorption (Perkampus, 1992).

Prior to sample analysis the exact wavelength of maximum absorbance for Fe (II) on the spectrophotometer was checked. A 1 mgl^{-1} Fe (II) sample was scanned for absorbance across the range of wavelengths, with the maximum absorbance being observed at 510 nm. Five Fe (II) standards were made over a range of concentrations (0 mgl^{-1} to 1.0 mgl^{-1}) with the buffered phenanthroline solution (Table 3.14). The spectrophotometer was zeroed with the 0 mgl^{-1} standard. The five standards were run and the calculated absorbances used to create a calibration curve (see example in Table 3.14 and Figure 3.4). Samples were initially run undiluted, with samples having absorbances >0.200 being diluted using the 0 mgl^{-1} standard and re-run. The standards 0 mgl^{-1} and 1 mgl^{-1} were run after every 11 samples, in order to identify any drift. After analysis on the spectrophotometer, the absorbance values were converted in to Fe (II) concentrations using the equation from the calibration curve (see example in Figure 3.4).

Table 3.14: Fe (II) standard concentrations and associated measured absorbances analysed on the spectrophotometer.

Standard	Fe (II) concentration (mgl^{-1})	Absorbance (example of calibration)
1	0	0.000
2	0.05	0.012
3	0.1	0.021
4	0.5	0.099
5	1.0	0.201



$y = 0.1999 x + 0.0007$

where y is absorbance and x is Fe (II) concentration (mgl^{-1}).

$\therefore$ Fe (II) concentration (mgl^{-1}) = ((absorbance – 0.0007) / 0.1999) * dilution factor

Figure 3.4: Example calibration curve and associated equation for determination of Fe (II) concentrations analysed on the spectrophotometer.

Water analysis

(i) Dissolved metals analysis – ICP-OES

The dissolved metal concentrations of the water samples were analysed by ICP-OES. As the water samples had already been filtered and preserved in nitric acid no further preparation was needed. The water metal samples were run with no dilution. The samples were analysed for a range of metals: Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn). The specific wavelengths of analysis for each metal are presented below (Table 3.15).

Table 3.15: Determined optimum wavelengths, limits of determination (LoD) and standard concentrations for measuring dissolved metal concentrations by ICP-OES in water samples.

Metal	Wavelength measured on (nm)	LoD (mgl^{-1}) 3 s.f.	Standard	Concentration (mgl^{-1})
Cd	228.802	0.00199	**1**	0
Cr	267.716	0.00217	**2**	0.2
Cu	327.395	0.00333	**3**	0.6
Fe	238.204	0.00783	**4**	1
Mn	257.610	0.00109	**5**	2
Ni	227.021	0.00640	**6**	6
Pb	220.353	0.0940	**7**	10
Zn	213.857	0.0351		

Seven multi-element standards were made over a range of concentrations (0 mgl^{-1} to 10 mgl^{-1}) and matrix matched (0.5% HNO_3) (Table 3.15). The standards were run on the ICP-OES at the start of every run to calibrate the machine. Once the run was completed all measured peaks were checked.

As with the sediment and macrophyte samples some samples had very low metal concentrations and the same methodology was used to calculate LoDs (Table 3.15) and identify samples with concentrations below the LoD.

Once the data from the ICP-OES had been screened for <LoD, the concentration of metals in the water samples were taken from the ICP-OES results.

Lab standards of a known concentration were run every eight samples to check for drift of the instrument. Samples were analysed on the ICP-OES in triplicate to measure precision of the instrument. These were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

(ii) Total water hardness

Total water hardness (sum of calcium hardness and magnesium hardness) affects the solubility of metals with harder water decreasing metal solubility (Radojevic & Bashkin, 1999). Total water hardness is determined through a complexation titration using EDTA (ethylenediaminetetraacetic acid). A buffer solution is added to the sample to adjust the sample to pH 10. The indicator is then added which complexes with all the Ca^{2+} and Mg^{2+} ions turning the sample red. Slowly titrating EDTA displaces the ions from the indicator complex and forms more stable complexes with the EDTA. Once all Ca^{2+} and Mg^{2+} is complexed with EDTA the

sample turns blue which is the end point of the titration. (Radojevic & Bashkin, 1999 and Chapman, 1998). The volume of EDTA required to cause the colour change is then used to calculate the total hardness of the water sample.

A Hach Lange digital titrator (model 16900) was used along with the associated Hach Lange buffer solution (Hardness 1 buffer solution), indicator (ManVer 2 Hardness Indicator Powder Pillow) and EDTA solution (EDTA titration cartridge, 0.800 M EDTA).

Water samples were placed in the fridge on the day of collection and samples were analysed the next day after being allowed to return to room temperature. One hundred ml of a well-mixed sample was added to a conical flask. Two ml of the buffer solution and one indicator powder pillow were added to the sample and swirled to mix. The sample was now red. Whilst continuously swirling the flask, EDTA was titrated in until the sample turned blue. The number of digits on the digital titrator was recorded. Total hardness (H_t, mgl^{-1} as $CaCO_3$) of the sample was calculated as:

$$H_t = \text{digits} * (100 / V)$$

where V is volume of sample used (ml).

To check the precision and accuracy of the method, three water samples were tested in triplicate and a standard solution (1,000 mgl^{-1} as CaCO3) was tested in triplicate (Table 3.16).

Samples were analysed in triplicate to measure precision and a certified reference standard (Hach Lange 1,000 mgl^{-1} $CaCO_3$ standard solution) was analysed as a measure of accuracy. Uncorrected total water hardness values are reported. These were included in the laboratory protocol so as to equate to at least 10% of the total samples (USEPA, 2001).

Table 3.16: Total water hardness and calculated relative standard deviations (RSD) for triplicate determinations of $CaCO_3$ (mgl^{-1}) for three water samples to check recoveries and precision of the method.

Sample	$CaCO_3$ (mgl^{-1})	% RSD	Sample	% Recovery
1	230 239 239	2.20	**1**	100
2	340 330 335	1.49	**2**	95
3	198 205 203	1.78	**3**	96

3.4 Data Analysis

The large data sets were analysed through a range of techniques using the statistical packages Microsoft Excel 2003, XLSTAT Pro 2011 and 2012 and SPSS version 16.0. A review of the initial preparation of the data in terms of values below the level of determination is provided here, along with the granulometric normalisation of sediment metal concentrations. A brief overview of statistical techniques is provided, although specific details of the techniques used, the reasons for them and study specific data analyses in each study are provided in the relevant chapters.

3.4.1 Data points below the level of determination (LoD)

Analytical data sets often contain values which are below the limit of determination (LoD). Decisions have to be made about how to deal with these prior to undertaking statistical analysis of the data set as the method used will affect the results and thus potentially alter the interpretation of the data. There are three possible ways to deal with <LoD data points: delete the data points; substitute all <LoD data points with a new value; or, use a more robust distributional method to compute a value for <LoD (Helsel, 2006 and Farnham *et al*., 2002). The first option of deleting the data points is not appropriate as this significantly alters the original data set (Helsel, 2006). Substitution of <LoD with either 0, LoD or a fraction of LoD is the most common method, but does have its criticisms particularly if there are different LoD values due to changes in machines or data coming from different laboratories (Helsel, 2006 and Farnham *et al*., 2002). Computing a value for LoD is less common in geochemistry and many of these methods assume that the data has a normal or log-normal distribution and they do not work well on small data sets (Helsel, 2006 and Farnham *et al*., 2002). Helsel (2006) compared

the effect of substitution as opposed to a distributional method upon statistical analysis of a data set, and found that distributional methods produced the same, or better, results than substitution. However, the results also indicated that different fractions for substitution may produce better results for different data sets. Helsel (2006) also stated that substitution may be appropriate if:

- geochemical analysis has relatively high precision and low detection limits;
- geochemical analysis is performed by one laboratory;
- the detection limits stay fairly constant;
- there are many data points (in the hundreds); and,
- below 60% of the data points are <LoD.

Farnham *et al*., (2002) looked at different substitution methods for a data set which had neither a normal or log-normal distribution. They found that substitution with 0.5 LoD produced better results than substitution with 0 or LoD, and that substitution of over 30% of the data points produced poor results. Substitution of LoD with 0.5 LoD was also used by Sparling & Lowe (1998) investigating metal uptake by macrophytes.

In these studies, all analysis was carried out in one laboratory by one worker. The LoDs were therefore constant as the same methodology and instrumentation was used throughout. Therefore looking at the distribution of the data, size of data set and the % data points <LoD will help to determine the most appropriate method to deal with <LoD in each study.

3.4.2 Granulometric normalisation of metal concentrations

As previously discussed (Section 2.3.2 in Chapter 2) fine sediments (<63 µm) are known to have a significant influence upon metal concentrations with increasing proportions of <63 µm (silt and clay) generally resulting in increased metal concentrations. This strong influence of grain size upon metal concentrations can mask other trends in metal concentrations and hinder any real comparisons of metal concentrations between sediment samples of varying grain size composition (Luoma & Rainbow, 2008; Kerste & Smedes, 2002; Clark *et al*., 2000; Loring, 1991; and, Horowitz & Elrick, 1988). Therefore a grain-size correction can be undertaken to differentiate between metal concentrations that are due to natural variability (i.e. grain size influenced) and those that are due to factors, such as anthropogenic inputs (Kersten & Smedes, 2002 and Loring, 1991). This correction, known as granulometric correction, involves the calculation of a dilution factor (DF) for each sediment sample, based upon the fraction of the sample that is < 63 µm, and then applying the dilution factor to correct the pseudo-total metal concentration (Luoma & Rainbow, 2008 and Horowitz, 1991). It is important to note that the

resultant value is no longer a metal concentration and is now a normalised metal ratio (Luoma & Rainbow, 2008).

$$\text{Dilution Factor (DF)} = 100 / \% \text{ sample} < 63\mu m$$

$$\text{Normalised metal ratio} = DF * \text{sediment metal concentration } (mgkg^{-1})$$

3.4.3 Data presentation and statistical analysis

A brief overview of the range of techniques and analyses is provided here, with specific details of techniques and reasons for them in each results chapter.

Distribution

An initial step in data analysis is to understand the form of the frequency distribution as this allows appropriate statistical tests to be chosen. Parametric tests, which are generally more 'powerful', often rely on the data (or the population from which it is drawn) being normally distributed (Dytham, 2011). Non-parametric tests, although generally less 'powerful', do not have this assumption (Dytham, 2011). The frequency distribution of a data set can be tested visually through histograms and statistically tested with the one sample Kolmogorov-Smirnov (K-S) test by comparing the observed frequency distribution to an expected (normal) distribution to test the null hypothesis that there are no significant differences between the observed and expected distributions.

If data sets show a non-normal distribution then they can often be transformed to conform to a normal distribution (Dytham, 2011). Common transformations include $\log_{10}$ (x) and Arcsin (x) for percentage data. However, if the results of the statistical analysis of different data sets are to be compared then it is preferable if all data sets have undergone similar transformations.

Due to the prevalence of non-normal frequency distributions in the present research, non-parametric tests were used throughout.

Correlations

Correlation tests are used to identify the strength and significance of correlations between measured variables. The non-parametric Spearman's Rank-order correlation (S-R) has no underlying assumptions regarding the distribution of the populations from which the samples have been drawn and so was applied in this research

Testing differences

Differences between groups were initially visualised using boxplots and comparison of median values. Median values were used, as opposed to means, due to the prevalence of non-normal frequency distributions throughout the research. Mann-Whitney U-tests (M-W) and Kruskal – Wallis (K-W) tests were used to test whether there were statistically significant differences between groups, with the former applied when comparing two groups and the latter applied to multiple groups. These non-parametric statistical tests assess the null hypothesis that the medians of groups are the same. Where K-W tests identified a significant difference between groups, the post-hoc multiple-comparison Steel-Dwass-Critchlow-Fligner (S-D-C-F) test was applied to identify which groups were statistically significantly different from one another.

Principal Component Analysis

Multivariate analysis was undertaken using Principal Component Analysis (PCA). PCA is a data reduction technique which takes account of intercorrelation between variables and allows these properties to be synthesised into a series of new Principal Components (PCs) (Dytham, 2011). The first PC explains the largest proportion of the variance in the multivariate data set and each subsequent PC explains progressively less variability (Dytham, 2011). In this way, much of the variance in a large multivariate data set can be reduced to a relatively small number of PCs. Each PC describes an environmental gradient that can be interpreted by reference to the original variables that have the highest loadings on it. Each sample then has a score on each PC (known as a factor score), which shows its relative location along the PC in comparison with other samples and the strength of the association of each sample to that PC (Reid & Spencer, 2009). Additionally, samples which have similar factor scores can be indicative of similar sources and/or chemical behaviour (Reid & Spencer, 2009). PCA thus allows interpretation of the key environmental gradients and related variables that provide the greatest discrimination between the samples that have been analysed.

Due to the non-normal frequency distributions of the data in this research, PCA was applied to a Spearman's Rank correlation matrix of the variables (Webster, 2001). Interpretation of the PCA results focussed on PCs with eigenvalues greater than one as this is the level of variation expected by chance when there are no strong correlations among variables (McKillup, 2012). A varimax rotation was applied to these PCs in order to aid their interpretation (Field, 2009), and interpretation of the PCs focussed on variables with loadings >0.6, although those >0.4 were also identified (Reid & Spencer, 2009).

Chapter 4

Sediment Characteristics and Metal Concentrations of Bed Sediments in Contrasting Restored and Unrestored London Urban Rivers

4.1 Introduction

Currently there are numerous environmental, legislative and social drivers to restore urban rivers. These include acknowledgement of the environmental degradation of urban rivers from historical management, legislation including the Water Framework Directive, Habitats Directive and Catchment Flood Management Plans and a drive to increase recreational spaces and reconnect people with the natural environment (Lundy & Wade, 2011; Mainstone & Holmes, 2010; London Rivers Action Plan, 2009; Wharton & Gilvear, 2006; and, Downs & Gregory, 2004). The scope of river restoration can range from full restoration (complete return to pre-disturbance structural and functional state (as in Cairns, 1991)) through rehabilitation (partial return to pre-disturbance structure or function) to enhancement (any improvement in environmental quality) and creation (development of resource that did not previously exist at the site) (Brookes & Shields, 1996). Full restoration is generally accepted as an idealistic vision, which in many contexts is neither feasible nor desirable (Wharton & Gilvear, 2006 and Downs & Thorne, 2000), particularly in the urban river context where pressures of flood defence, infrastructure protection and contamination protection can dominate and restrain restoration efforts. Thus many restoration schemes are technically rehabilitation, enhancement or creation schemes, but 'restoration' is often used in its broadest sense to describe all of these methods of enhancing the complexity of river systems (Wheaton *et al*., 2008).

Restoration schemes, which alter the hydraulic and physical conditions of the river, can create river environments favourable to sediment accumulation and in-channel vegetation growth. Removal of bank and bed protection, and increased connection with floodplains, results in greater sediment availability. Increased heterogeneous and slower flow patterns, from the creation of more complex channel forms, results in the deposition of these sediments and in increased habitat complexity suitable for in-channel vegetation colonisation, which in turn increases sediment deposition and accumulation (Riis *et al*., 2009 and Franklin *et al*., 2008).

Sediments within rivers often act as stores for various contaminants including metals (Scholes *et al*., 2008). The potential of sediments to store metals, and therefore affect their quality, is

dependent upon a number of physiochemical characteristics including grain size, redox, pH and organic matter content (Forstner & Wittman, 1981). Sediment-associated contamination can have detrimental impacts upon ecology, human health and both surface and groundwater quality (Salomons & Brils, 2004 and Forstner & Wittmann, 1981). Additionally, the accumulated sediments which are acting as a sink for contamination, may turn into a source through sediment resuspension or changes in water chemistry (Scholes *et al*., 2008 and Salomons & Brils, 2004). Significant consideration has not yet been given to understanding how river restoration practices impact upon sediment-related contaminant storage and therefore ecosystem health, and hence their implications for the design, management and use of restored urban rivers.

This Chapter reports on a study into sedimentation patterns and sediment characteristics and metal concentrations of different bed sediment types within paired restored and unrestored stretches of urban rivers in London. The research was undertaken in order to answer the following research questions:

- Are there differences in the pattern and extent of sedimentation and in-channel vegetation growth between restored and unrestored stretches of urban rivers in London?

- What are the characteristics of sediment (metal concentrations, grain size etc.) retained within restored and unrestored stretches of urban rivers in London and to what extent do these characteristics vary in space and time?

- What factors explain the observed variations in metal concentrations and sediment characteristics in restored and unrestored urban rivers in London?

- To what extent are the sediments in London urban rivers potentially harmful to humans and ecosystems?

4.2 Research Sites

The research was undertaken on rivers within the Thames River catchment, Greater London, UK. Potential sites, with adjacent restored and unrestored stretches, were identified through the London Rivers Action Plan database (http://www.therrc.co.uk/lrap.php), a literature search and information from practitioners working on river restoration within the Thames catchment. Several sites were visited and assessed for their suitability based upon: proximity of the restored and unrestored stretches; contrasts in morphology between the stretches; and, safe access to the rivers. Four sites with paired restored and unrestored stretches were chosen, one site within the River Wandle catchment and three sites within the Ravensbourne River catchment (two sites on the River Quaggy and one on the Pool River) (Figure 4.1).

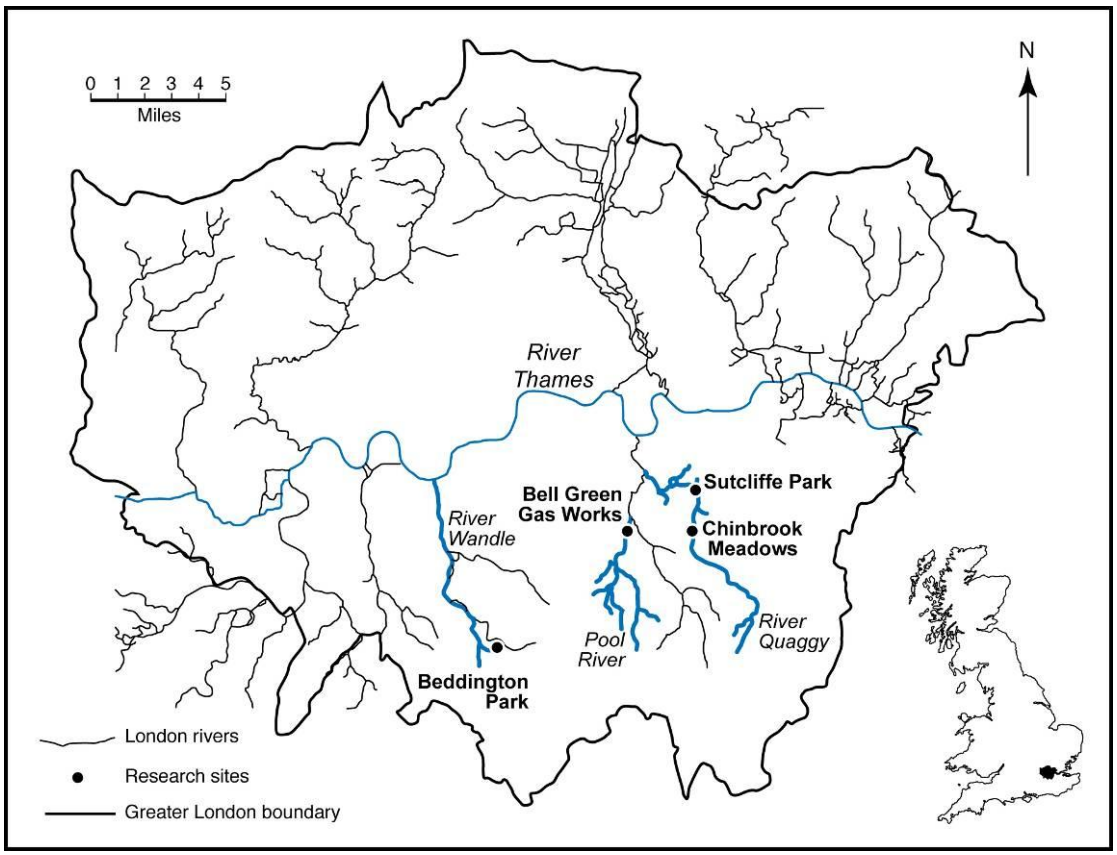


Figure 4.1: Map showing the research sites within the Thames catchment.

4.2.1 River Wandle catchment

The River Wandle has a catchment area of 200 km^2 (to its confluence with the Thames) and flows 27 km from its two sources at Waddon Ponds and Carshalton Ponds, west of Croydon in south London, to its confluence with the River Thames at Wandsworth. In addition to the two source streams, which join at Hackbridge, the river has two major tributaries; the River Graveney which enters at South Wimbledon and the Beddington corner branch which joins at

Mitcham. Historically, the Wandle has been heavily utilised by industry with numerous mills and factories having used the river (Solomon & Thomson, 2009). The historical uses of the river, plus the inputs from Beddington sewage treatment works and the urban setting of the river, suggest that the river sediments are potentially contaminated.

Site 1: Beddington Park, River Wandle

The Waddon Pond branch of the River Quaggy flows through Beddington Park approximately 1.7 km downstream from the source. Much of the River Wandle within Beddington Park is reinforced and straightened, but removal and decay of wooden toe boarding provides a restored stretch which was compared with an unrestored stretch within the park (Figure 4.2).

(i) Restored stretch

During the 1970s the River Wandle within Beddington Park was channelised with the construction of wooden boarding along the banks resulting in a uniform channel with little marginal habitat (Moore, 2001). In 1998 a series of works were undertaken along one stretch of the river within the park with the aim of enhancing the ecological value of the channel (Moore, 2001). Sections of wooden boarding were removed, banks re-profiled, weirs removed and a reed bed planted by a surface water outflow (Figures 4.3 and 4.4) (Moore, 2001).

Since the enhancement works were undertaken the reed bed has fully developed. A small channel flows through the reed bed area in which there is a dense mix of vegetation (Figure 4.4). There is some development of in-stream marginal vegetation and there is a vegetated island within the main channel. There are still some areas of wooden boarding, although in many areas this is beginning to decay and disintegrate.

(ii) Unrestored stretch

Approximately 100 m downstream, still within Beddington Park and just before the river flows into a pond, the Wandle flows within a straight channel with concrete bank protection along the full length of the right bank and partially along the left bank (Figure 4.3).

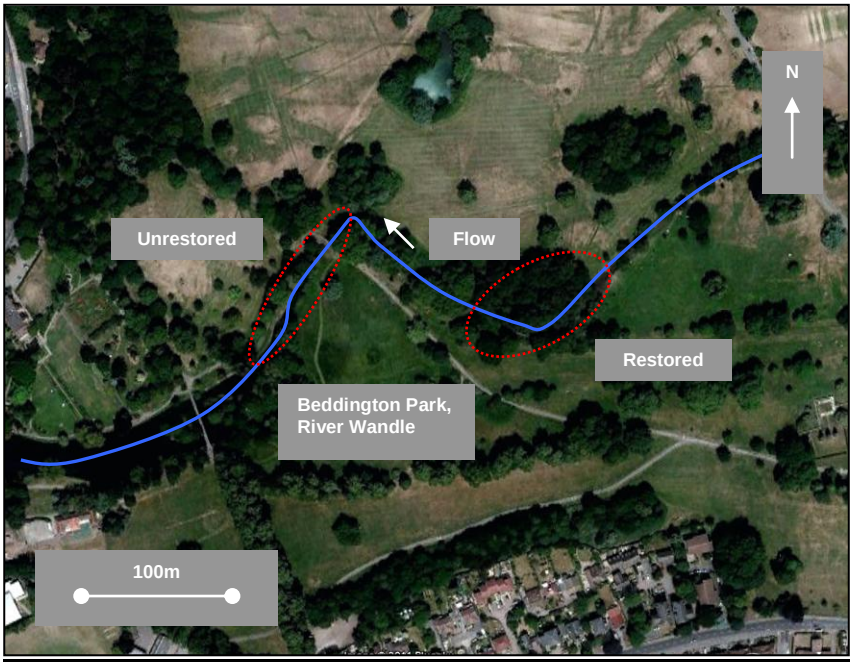


Figure 4.2: Map showing the location of the restored and unrestored stretches of the River Wandle at the Beddington Park site.

Figure 4.3: Photos of the restored (left) and unrestored (right) stretches of the River Wandle at the Beddington Park site.

Figure 4.4: The constructed reed bed in Beddington Park in August 1998 (left) (taken from Moore, 2001) and November 2009 (right).

4.2.2 Ravensbourne River catchment

The Ravensbourne River flows 18 km from its source in Keston, south of Bromley in south London, to the River Thames at Deptford Creek. The catchment covers 180 km^2 and there are many tributaries to the river, with the major ones being the River Quaggy, The Beck and the Pool River. The Pool River rises near West Wickham, east of Croydon, and flows for 5 km before joining the Ravensbourne at Catford. The River Quaggy rises at Locksbottom, east of West Wickham, and flows for 17 km before joining the Ravensbourne River at Lewisham, downstream of the Pool River/Ravensbourne River confluence. During the 1920s and 30s many sections of the river were straightened and deepened in association with urban building development (Lewisham Council, 2010). In the 1960s and 70s further reinforcement and culverting of the river channel for flood protection was undertaken, often involving lining of the channel with concrete (Lewisham Council, 2010). It is estimated that over 50% of the river channels in the Ravensbourne catchment are artificial to some extent and there are over 70 culverts (Lewisham Council, 2010).

Site 2: Bell Green Gas Works, Pool River

The former Bell Green Gas Works site lies about 4 km downstream from the source of the Pool River, 1 km upstream from its confluence with the Ravensbourne River in Catford. Stretches of the Pool River alongside the former Bell Green Gas Works site, and upstream alongside a sports field, were used as a paired restored and unrestored stretch respectively (Figure 4.5).

(i) Restored stretch

Historically the Pool River had been placed within a concrete culvert 3 m beneath the ground as it flowed through the Bell Green Gas Works site (Howes, 2000). In the late 1980s the gas

works site was closed and decommissioned (Lewisham Council, 2009), and in 1994 a new channel for the Pool River was created to the east of the former gas works site, diverting the river and providing a focus for the new Pool River Linear Park (Lewisham Council, 2009 and Cameron Taylor Bedford, 2005). The new channel was placed outside of a bentonite cut-off wall constructed around the old gas works site to prevent the river from being affected by land contamination (Cameron Taylor Bedford, 2005). This left the old channel for land drainage, discharging directly to the foul sewer (Cameron Taylor Bedford, 2005). The new concrete-lined channel was constructed with a sinuous (meandering) course that included cascades, in-stream planters and gravels that were introduced into the channel (Howes, 2000) (Figure 4.6). Its course is bordered by the old gas works site and a supermarket beyond the left bank of the river, and a grassed bank leading up to a railway line and residential housing area on the right bank.

Since the restoration, the river has developed by moving sediment within the concrete channel. Sediment has accumulated both within and between the in-channel planters creating a sinuous course within the concrete meandering channel (Figure 4.6), with vegetation growing in the accumulated sediments.

(ii) Unrestored stretch

Approximately 400 m upstream of the former Bell Green Gas Works site the Pool River flows within a relatively straight channel with bank protection along both banks before flowing under Meadowview Road (Figure 4.6). There are some industrial units and sports fields on the right bank and a pathway and residential housing on the left bank.

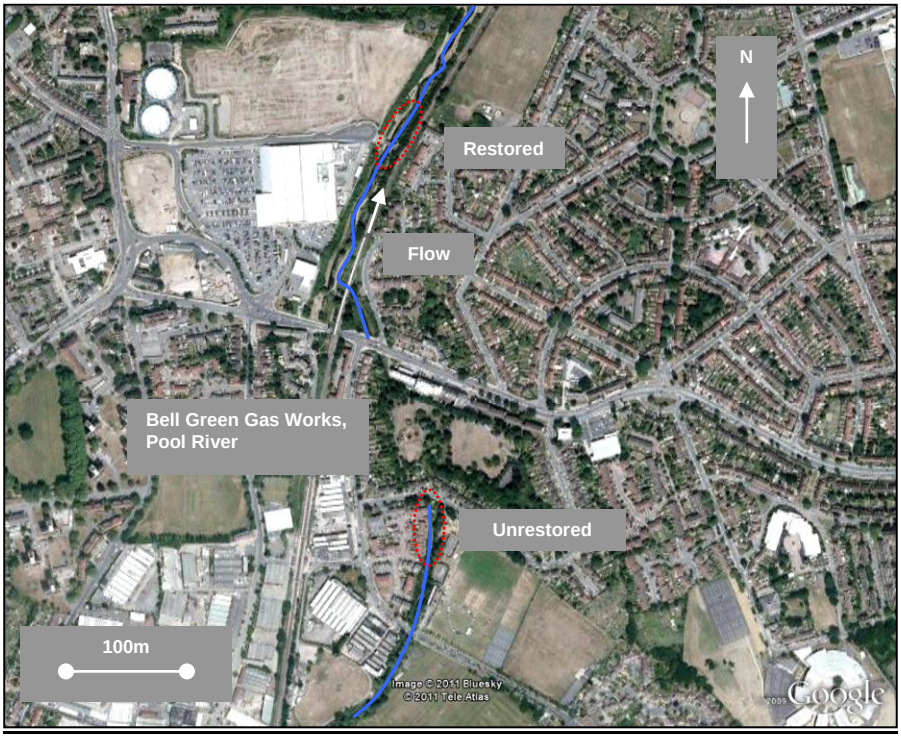


Figure 4.5: Map showing the location of the restored and unrestored stretches of the Pool River at the Bell Green Gas Works site.

Figure 4.6: Photos of the restored (left) and unrestored (right) stretches of the Pool River at the Bell Green Gas Works site.

Site 3: Chinbrook Meadows, River Quaggy

Approximately 10 km downstream from its source, the River Quaggy flows within Chinbrook Meadows, a public park. Stretches of the River Quaggy within Chinbrook Meadows, and downstream alongside a sports field, were used as a pair of restored and unrestored stretches, respectively (Figure 4.7).

Figure 4.7: Map showing the location of the restored and unrestored stretches of the River Quaggy at the Chinbrook Meadows site.

(i) Restored stretch

During the 1960s the River Quaggy, flowing through Chinbrook Meadows, was straightened, enlarged, lined with concrete and obscured behind a large hedge and fence (Figure 4.8) (Baxter, 2003), dividing the park and deterring people from seeing or using the river (Wigmore, 2009 and CABE space, 2005). In 2002 a 300 m stretch of the Quaggy within the park was restored with the aims of improving flood management, increasing wildlife habitats and enhancing people's access and enjoyment of the park (Figure 4.8) (Quaggy Waterways Action Group, 2011; River Restoration Centre, 2007; and, Baxter, 2003). The concrete channel, hedges and fences were removed and a new, smaller, sinuous channel was cut, following as far as possible the river's historical course and reconnecting the river with the floodplain (River Restoration Centre, 2007). Flood storage ponds, boardwalks and wetland areas were also created and the marginal areas were planted with native vegetation (River Restoration Centre, 2007).

In the eight years since the restoration there has been a lot of vegetation growth along the river bank and in the flood storage ponds. The river channel itself is relatively clear of vegetation, although there is some marginal in-channel vegetation and over-hanging riparian vegetation (Figure 4.9).

(ii) Unrestored stretch

Downstream from Chinbrook Meadows, the Quaggy flows through a trapezoidal channel that is fully-reinforced with concrete. The unrestored study stretch is located within this concrete-lined section, approximately 400 m downstream from Chinbrook Meadows, with sports fields on the right bank and residential housing on the left bank (Figure 4.9).

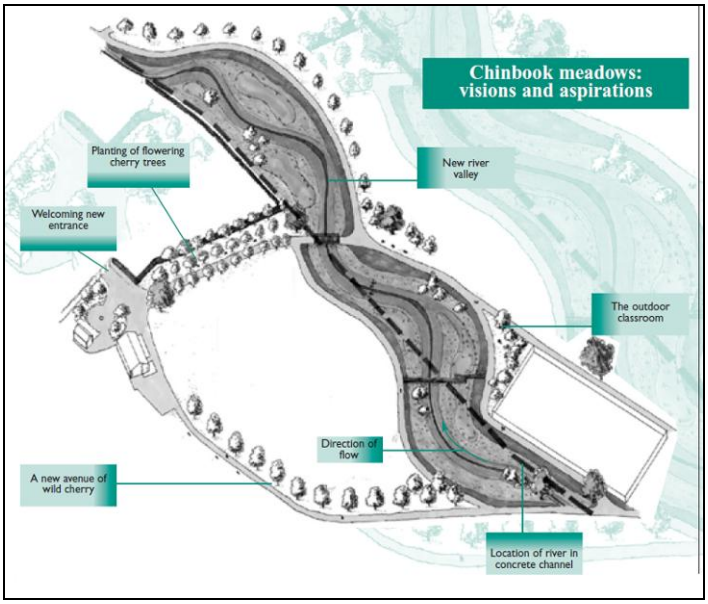


Figure 4.8: Photo of River Quaggy in Chinbrook Meadows prior to restoration (top) and plan of the restoration scheme (bottom) (taken from Baxter, 2003).

Figure 4.9: Photos of the restored (left) and unrestored (right) stretches of the River Quaggy at the Chinbrook Meadows site.

Site 4: Sutcliffe Park, River Quaggy

Approximately 3 km downstream from Chinbrook Meadows the Quaggy flows through Sutcliffe Park, a public park, 4 km upstream from its confluence with the River Ravensbourne. Stretches of the River Quaggy within Sutcliffe Park, and downstream within a sports field, were used as a pair of restored and unrestored stretches, respectively (Figure 4.10).

(i) Restored stretch

During the 1960s the River Quaggy was placed in a culvert beneath Sutcliffe Park (Figure 4.11) (Evans, 1994). Although not normally visible, the river flowed out of the culvert to flood local homes during high rainfall events (River Restoration Centre, 2008). In 2003 restoration was undertaken on a 500 m stretch of the Quaggy within the park, lowering the level of the park to create flood storage and alleviate flooding of 600 homes and businesses and introducing a new sinuous channel following the course of the river in the 19th century to make the park more attractive for local people (Quaggy Waterways Action Group, 2011; Environment Agency, 2009; and, River Restoration Centre, 2008). A series of ponds, boardwalks, reedbeds and a lake were constructed across the lowered park surface, creating a floodplain with a capacity of 85,000 m^3 of water (Figure 4.11) (Quaggy Waterways Action Group, 2011 and River Restoration Centre, 2008). The old culvert was retained with a sluice regulating flow between the culvert and the new channel to allow excess flow during high floods to pass through the old culvert (River Restoration Centre, 2008).

Seven years since the restoration, dense vegetation has developed around and within the channel and a lot of fine sediment has accumulated in some sections (Figure 4.12), probably as a result of flood peak flows being diverted through the culvert rather than being retained within the river channel.

(ii) Unrestored stretch

Approximately 600 m downstream from Sutcliffe Park the Quaggy flows in a relatively straight channel between sports fields. Although the river is not within a fully protected channel there is some bank protection along both banks (Figure 4.12).

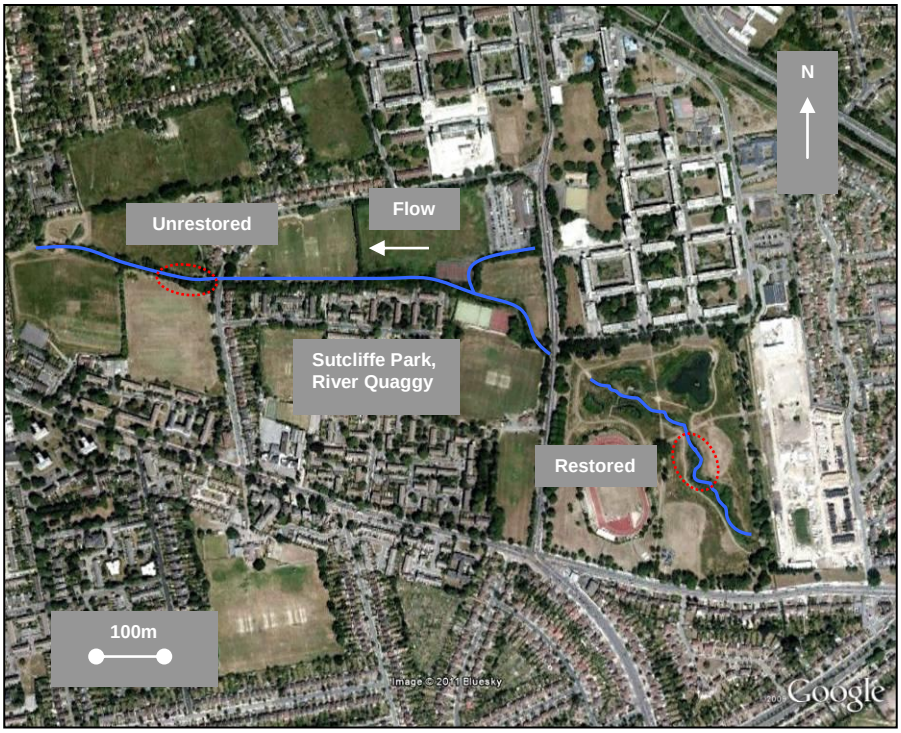


Figure 4.10: Map showing the location of the restored and unrestored stretches of the River Quaggy at the Sutcliffe Park site.

Figure 4.11: Photos showing Sutcliffe Park before (left) and after (right) restoration (taken from Wild *et al*., 2011).

Figure 4.12: Photos of the restored (left) and unrestored (right) stretches of the River Quaggy at the Sutcliffe Park site.

Table 4.1 provides the grid references of the upstream and downstream ends of the four pairs of restored and unrestored stretches. The four sites are referred to in the remainder of the chapter as: Beddington Park, Bell Green, Chinbrook Meadows and Sutcliffe Park.

Table 4.1: Grid references of the upstream and downstream points of the restored and unrestored stretches at each site.

	Restored Stretch	Unrestored Stretch
Beddington Park, River Wandle		
Upstream grid reference	TQ 29277 65323	TQ 29075 65351
Downstream grid reference	TQ 29165 65311	TQ 29015 65304
Bell Green Gas Works, Pool River		
Upstream grid reference	TQ 36947 72017	TQ 37036 71360
Downstream grid reference	TQ 36990 72096	TQ 37050 71471
Chinbrook Meadows, River Quaggy		
Upstream grid reference	TQ 41016 71871	TQ 41126 72524
Downstream grid reference	TQ 41014 71947	TQ 41140 72596
Sutcliffe Park, River Quaggy		
Upstream grid reference	TQ 41030 74866	TQ 40199 75161
Downstream grid reference	TQ 41016 74951	TQ 40124 75181

4.3 Methods

4.3.1 Fieldwork

Fieldwork at the study sites was undertaken in May, August and November 2010 to coincide with the growth and senescence of the in-channel vegetation. Mapping and sediment sampling was undertaken at all sites in all three time periods. Additionally, analysis of sediment redox and pH was undertaken at Sutcliffe Park in August 2010 in order to provide a more detailed data set for analysis at a site which showed strong contrasts in terms of bed sediment types between the restored and unrestored stretch.

(i) Mapping

Prior to sediment sampling, sketch maps were made of each stretch at each site in order to determine the presence and spatial extent of each bed sediment type. The extent of patches of bed sediment of differing calibre was mapped, visually distinguishing between four broad types: exposed (unvegetated) gravel, sand and finer and sediment that had accumulated around in-channel vegetation. These maps were then used to guide sediment sampling locations.

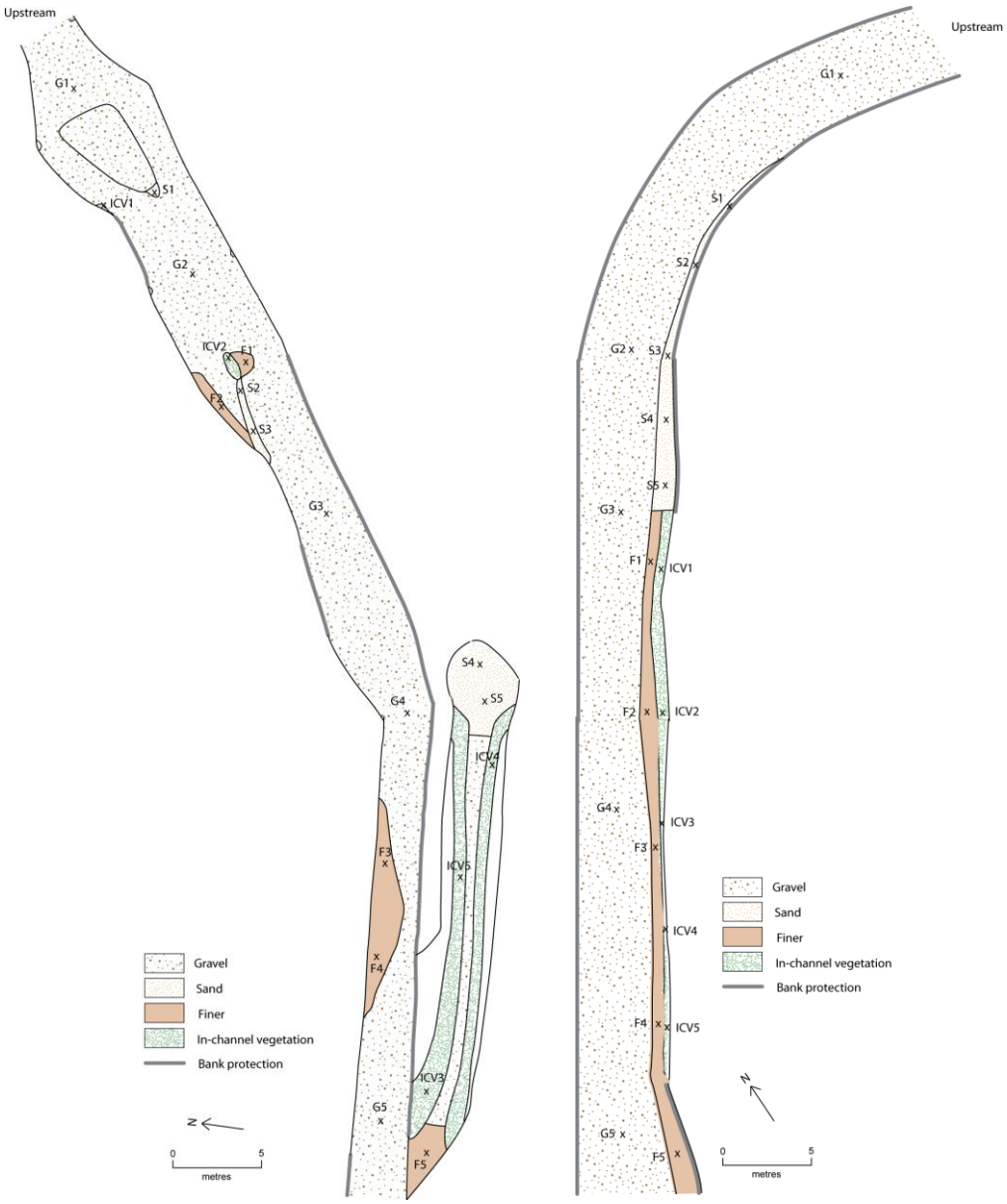
In July 2010, just prior to the August 2010 sediment sampling, more detailed mapping was undertaken. Channel cross-sections were established at 10m spacing, the boundaries of the four

bed sediment types were recorded across each section, and then the boundaries mapped between the cross sections guided by a tape measure stretched along the bank. Where a natural bed was exposed, all stretches had a gravel bed. Superficial sediment depths were measured to the underlying gravel or, where present, to the substrate. Gravel depths were measured in the top loosely compacted layer.

(ii) Sediment sampling design

Sampling was stratified according to the different bed sediment types present within each stretch as identified in the mapping (Figure 4.13). Five samples were obtained for each bed sediment type present within each stretch. Sampling locations were chosen to maximise spatial coverage and thus independence of samples within each stretch and were obtained, as far as was possible, from the centre of sediment patches. Although the maps showed some changes in the spatial distributions of the bed sediment types over the three time periods, these changes were small, allowing sediment samples to be obtained from the central area of the same patches during each sampling occasion (May, August and November 2010).

Surface sediments were sampled to a depth of 2 cm using a corer wherever possible or alternatively a plastic scoop. The corer and scoop were rinsed in river water between samples and all samples were sealed in plastic bags, with the excess air removed, and frozen on the day of collection.

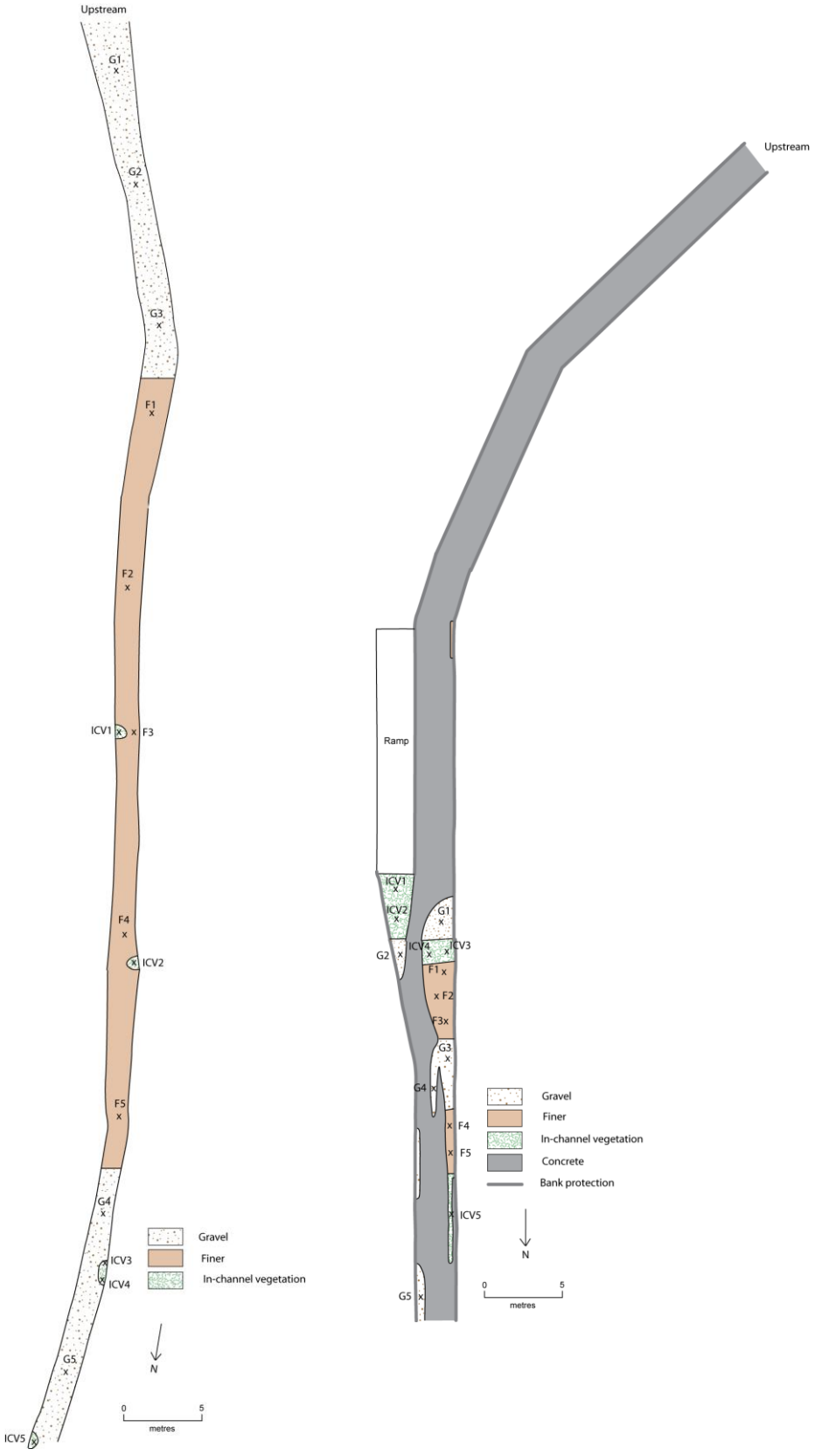


(a) Beddington Park.

Figure 4.13: Maps of bed sediment sampling locations in the restored (left) and unrestored (right) stretches at (a) Beddington Park (b) Bell Green (c) Chinbrook Meadows and (d) Sutcliffe Park. Mapping undertaken in July 2010 (*continued overleaf*).

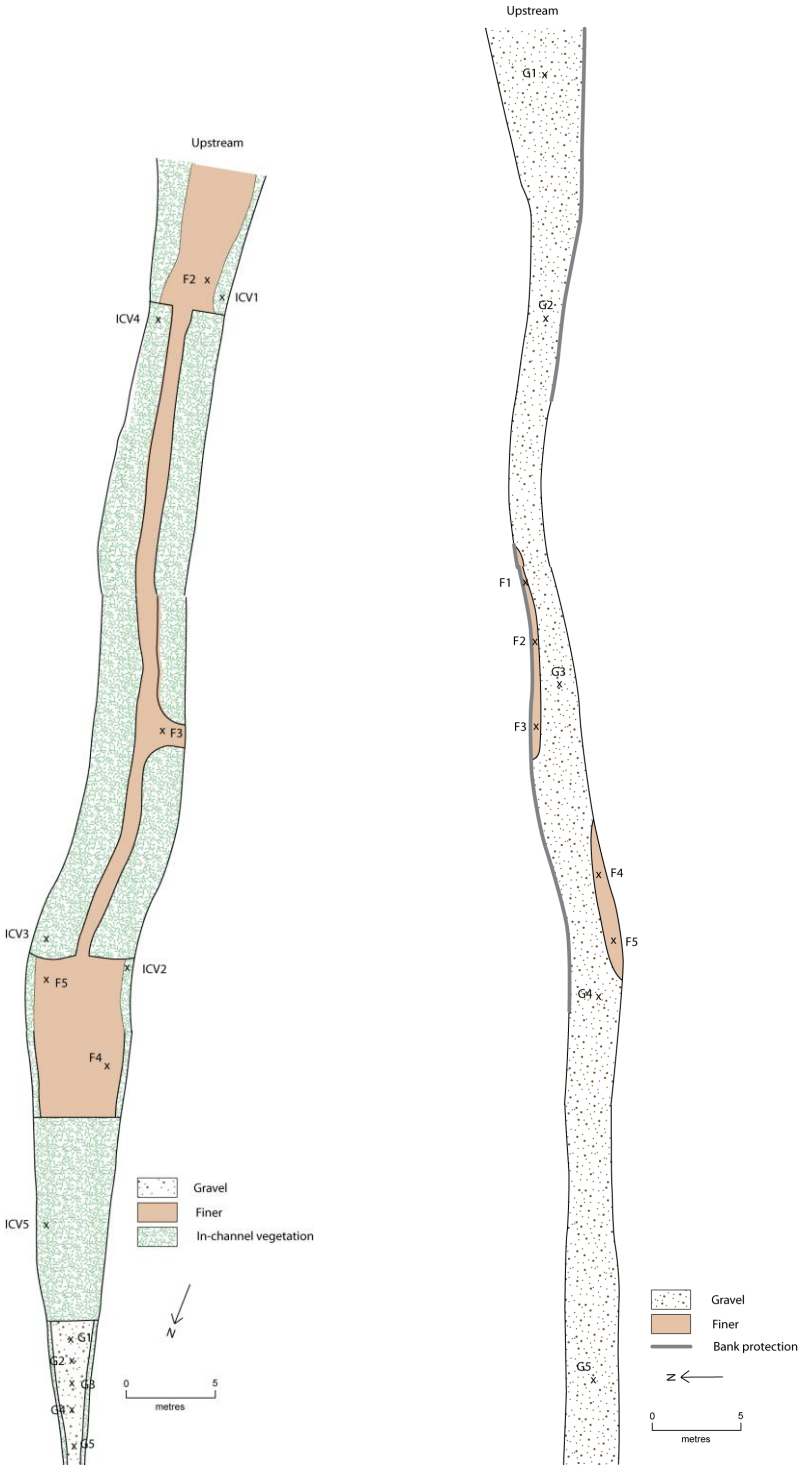
(b) Bell Green.

Figure 4.13: Maps of bed sediment sampling locations in the restored (left) and unrestored (right) stretches at (a) Beddington Park (b) Bell Green (c) Chinbrook Meadows and (d) Sutcliffe Park. Mapping undertaken in July 2010 (*continued overleaf*).



(c) Chinbrook Meadows.

Figure 4.13: Maps of bed sediment sampling locations in the restored (left) and unrestored (right) stretches at (a) Beddington Park (b) Bell Green (c) Chinbrook Meadows and (d) Sutcliffe Park. Mapping undertaken in July 2010 (*continued overleaf*).



(d) Sutcliffe Park.

Figure 4.13: Maps of bed sediment sampling locations in the restored (left) and unrestored (right) stretches at (a) Beddington Park (b) Bell Green (c) Chinbrook Meadows and (d) Sutcliffe Park. Mapping undertaken in July 2010 (*continued*).

(iii) Sediment redox and pH

Sutcliffe Park was selected for additional investigation of sediment redox and pH conditions during August 2010. These are two key environmental conditions that have an effect upon metal binding and behaviour within sediments (Du Laing *et al*., 2009 and Jacob & Otte, 2003).

Sediment redox conditions were determined using porewater Fe (II) concentrations as a proxy (Section 3.3.1 in Chapter 3). Prior to sediment sampling, porewater samplers were inserted at the sampling locations and left to allow the sediment to settle. Porewater was extracted from the sediment and filtered through a nitrogen-flushed 0.45 µm filter into buffered phenanthroline and stored in the dark on the day of collection (full details in Section 3.3.1 of Chapter 3).

An additional sediment sample was taken from the same location as the main sediment sample and used to create a 1:2.5 sediment:deionised water suspension that was shaken for 5 minutes. pH was measured in the overlying supernatant with a calibrated VWR pH100 meter (full details in Section 3.3.1 of Chapter 3).

4.3.2 Laboratory analysis

This section provides an overview of the laboratory analysis undertaken on the samples collected for this study, including the quality control results. Full details and discussion of each laboratory method and quality control procedures are provided in Chapter 3 (Section 3.3.2). Analytical grade chemicals and ultrapure water were used for all analyses. Additionally, all glassware used for metal analysis was acid-washed in 10% HNO_3.

(i) Methods

In the laboratory, all sediment samples were defrosted, weighed, dried at 105°C and then reweighed in order to calculate moisture content. The dried samples were sieved to 2 mm and the weight of the >2 mm and <2 mm fractions was determined. Subsamples of the <2 mm fraction were used in determination of % organic matter content, pseudo-total metal concentrations (aqua regia extraction: Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and absolute particle size (% <63 µm). Metal concentrations were analysed by ICP-OES (Varian Vista Pro CCD Simultaneous ICP-OES). Absolute particle size (% <63 µm) was analysed on the Beckman Coulter Laser Diffraction particle size analyser. The measurements of moisture content, organic matter content and dry sediment weight were used to calculate dry bulk density. The sequence of analyses is summarised in Figure 4.14.

The sediment samples obtained during August 2010 from Sutcliffe Park underwent an additional acetic acid metals extraction (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and the

porewater samples were analysed by UV-VIS spectrophotometry (Evolution 100 Thermo Scientific Spectrophotometer) for Fe (II) concentrations. Acetic acid extractable metal concentrations provide an indication of the concentration of metal which is more bioavailable than a pseudo-total metal concentration, being only weakly sorbed and associated with carbonates (Trujillo-Cardenas *et al*., 2010; Filgueiras *et al*., 2002; and, Gleyzes *et al*., 2002).

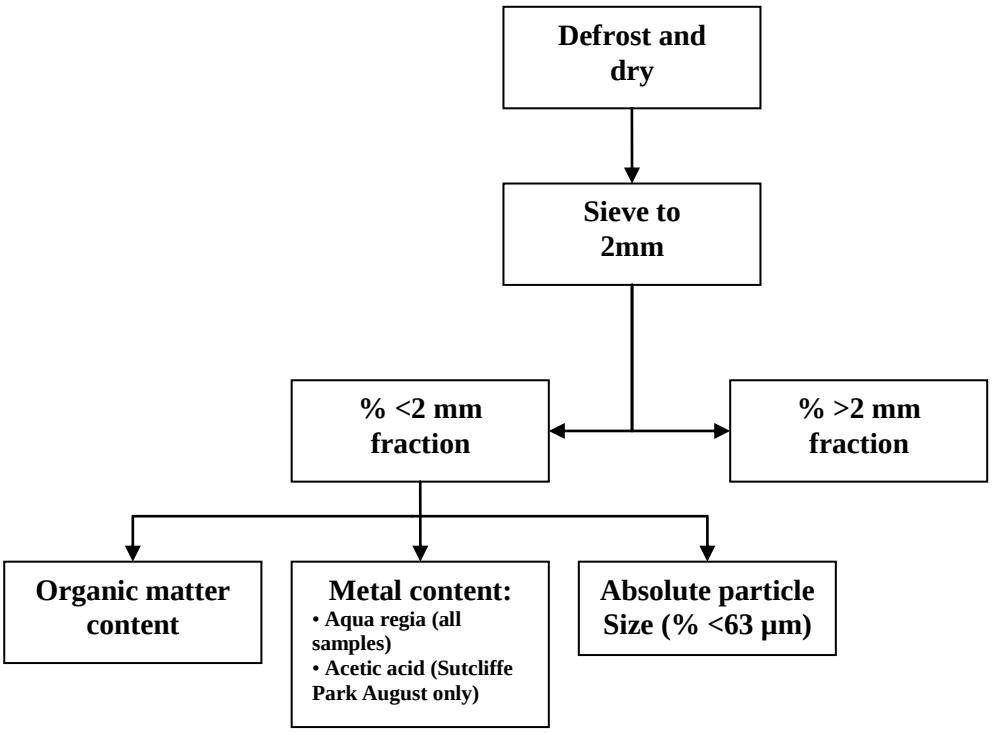


Figure 4.14: Flow diagram summarising laboratory analysis of sediment samples.

(ii) Quality control

As detailed in Chapter 3 (Section 3.3.2) quality control procedures were employed to ensure the quality of the laboratory analysis. The accuracy of sediment extractions and the particle size analyser were determined using certified reference materials. The precision of sediment extractions and the ICP-OES were determined by calculation of relative standard deviations. Analytical blanks were used to identify any contamination. Full results of the quality control procedures are provided in Appendix I. Sediment metal extractions generally had recoveries over 80%, with some Cr, Ni and Mn recoveries of 70 to 80%. Sediment metal extractions generally had relative standard deviations below 15%, although some higher values were recorded, likely due to the heterogeneous nature of the sediments. The majority of analytical blanks were <LoD, although higher concentrations were recorded for Al, Fe and Zn. All analytical relative standard deviations were below 5%.

4.3.3 Data analysis

Analysis focussed on sediment metal concentrations and characteristics for four different bed sediment types sampled from restored and unrestored stretches at four different sites at three different time periods. A more detailed data set was collected from one site (Sutcliffe Park) during the August 2010 sampling period.

The bed sediment type mapping undertaken in July 2010 was drawn to scale and digitised on Adobe Illustrator CS3 (Version 13.0). The files were then georeferenced in ArcGIS (Version 9.2) and the different bed sediment types subsequently digitised and areas calculated.

Each study site and stretch had differing areal coverages of the different bed sediment types. Therefore in order to compare metal storage within these study sites and stretches, sediment metal storage was calculated based upon sediment weights and average metal concentrations. The storage of each metal for each different bed sediment type within each stretch (in the <2 mm fraction, mg) was calculated as below (Table 4.2):

$$= \text{average metal concentration } (mgkg^{-1}) * \text{weight of sediment } <2 \text{ mm } (kg)$$

Table 4.2: Variables used in calculation of sediment metal storage.

Variable 1: Average metal concentration ($mgkg^{-1}$)	
Average metal concentration ($mgkg^{-1}$)	Mean metal concentration for each bed sediment type at each stretch throughout the year (May, August and November 2010 sampling).

Variable 2: Weight of sediment <2 mm (kg)	
Where:	
Weight of sediment <2 mm (kg) = total weight of sediment (kg) * proportion of sediment (by weight) that is <2 mm (%)	
And: Total weight of sediment (kg) = Total sediment volume (m^3) * Whole sediment sample dry bulk density (kgm^{-3})	
And: Total sediment volume (m^3) = sediment area (m^2) * average sediment depth (m)	
Sediment area (m^2)	Calculated using ArcGIS using digitisation of mapping undertaken in July 2010
Average sediment depth (m)	Mean of five depths for each bed sediment type in each stretch measured during the July 2010 mapping (sediment depths measured at same location as sediment samples taken).
Whole sediment sample dry bulk density (kgm^{-3})	Mean of five sediment dry bulk densities calculated for each sediment sample taken in August 2010.
Proportion by weight of sediment that is <2 mm (%)	Mean of five sediment <2 mm proportions calculated for each sediment sample taken in August 2010.

All data analysis was undertaken using Microsoft Excel 2003, XLSTAT Pro 2011 and 2012 and SPSS version 16.0. Prior to statistical analysis, the data was screened for values below the level of determination (LoD) and a decision made on how to treat these values (Section 3.4.1 in Chapter 3). The frequency distributions of the variables were determined through visual inspection of histograms and statistically tested for normality using the Kolmogorov-Smirnov (K-S) test. The strength of associations between the variables were analysed using the non-parametric Spearmans Rank test (S-R). Sediment metal concentrations were granulometrically normalised to produce normalised metal ratios using % <63 µm values. Differences in sediment metal concentrations and characteristics between restored/unrestored stretches, sampling times, sites and bed sediment types were statistically tested by using non-parametric Mann-Whitney U-tests when there were two groups to compare and Kruskal-Wallis tests (K-W) when there

were more than two groups to compare. If the K-W test indicated that there were significant differences, then post-hoc Steel-Dwass-Critchlow-Fligner tests (S-D-C-F) tests were undertaken to identify the significant differences between the sampling times, sites and bed sediment types. Multivariate analysis of the properties of the sampled sediments was undertaken using Principal Component Analysis (PCA) on a Spearmans-Rank correlation matrix and with a varimax rotation on Principal Components with eigenvalues over one. Differences in factor scores from the PCA of samples grouped by restored/unrestored, sampling time, site and bed sediment types were visually observed and statistically tested using non-parametric Mann-Whitney U-tests when there were two groups to compare and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner tests (S-D-C-F) tests when there were more than two groups to compare.

4.4 Results

4.4.1 Presence and coverage of the four bed sediment types within the studied stretches

Strong contrasts were identified in the presence and coverage of the four bed sediment types and bank protection within the restored and unrestored stretches of each of the four study sites in July 2010 (Figures 4.15 to 4.18). Table 4.3 summarises which bed sediment types were present at each site and Figure 4.19 displays the percentage coverage of the channel by each bed sediment type.

Table 4.3: Presence of bed sediment types at each site.

		Bed Sediment Type			
Site	**Stretch**	**Gravel**	**Sand**	**Finer**	**In-channel vegetation**
Beddington Park	Restored	●	●	●	●
	Unrestored	●	●	●	●
Bell Green	Restored	●			●
	Unrestored	●			●
Chinbrook Meadows	Restored	●		●	●
	Unrestored	●		●	●
Sutcliffe Park	Restored	●		●	●
	Unrestored	●		●	

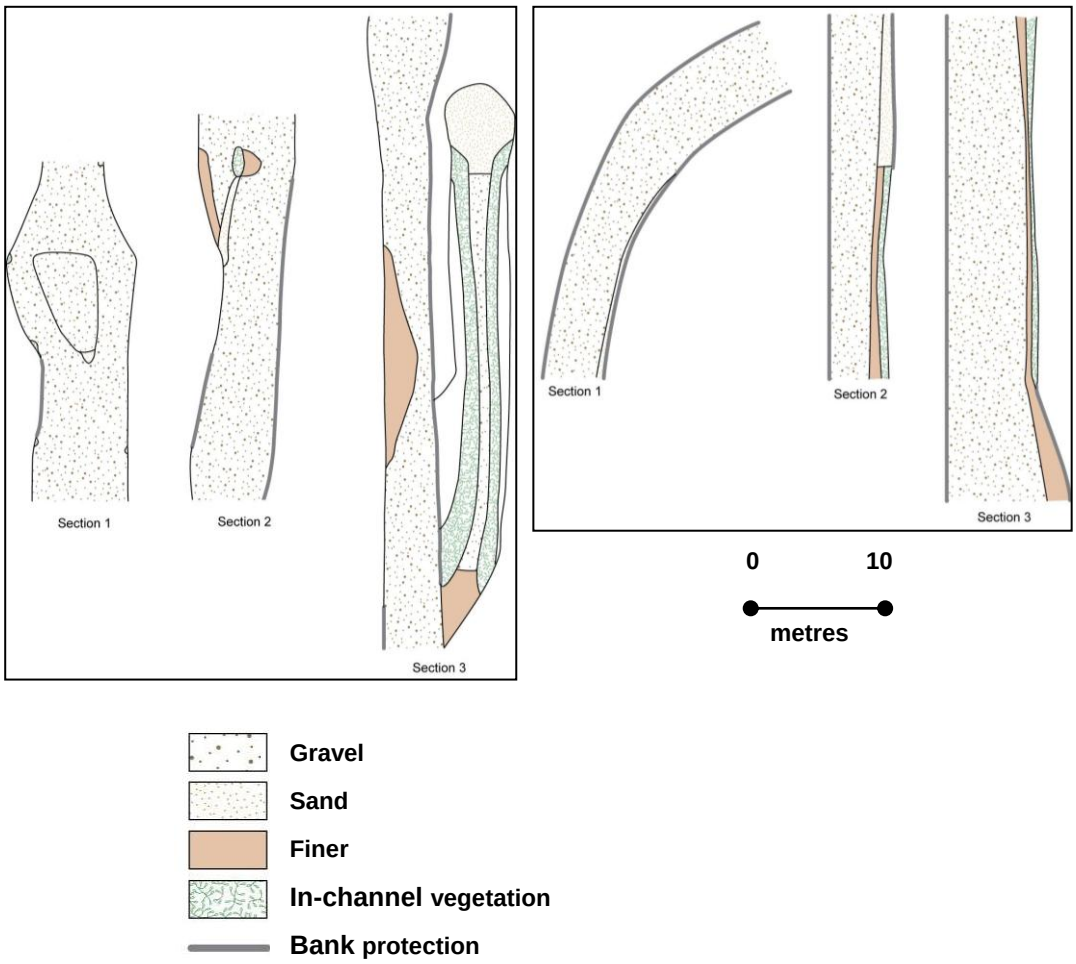


Figure 4.15: Distribution of bed sediment types and bank protection in the restored (left) and unrestored (right) stretches at Beddington Park.

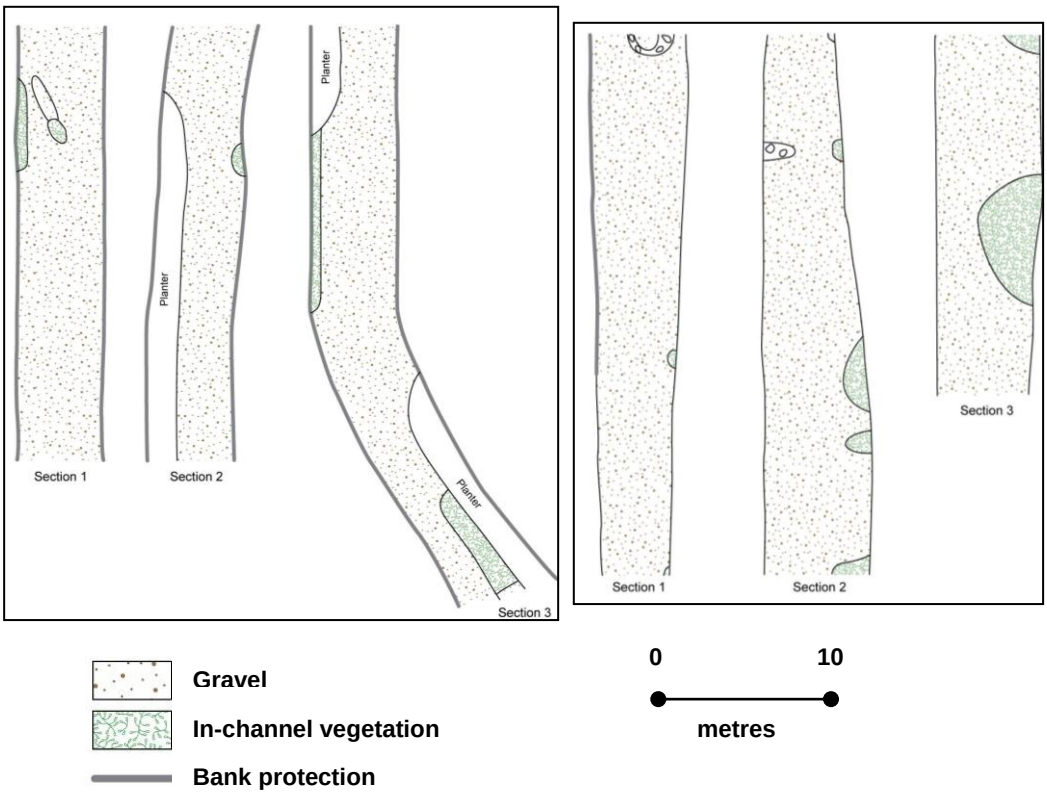


Figure 4.16: Distribution of bed sediment types and bank protection in the restored (left) and unrestored (right) stretches at Bell Green.

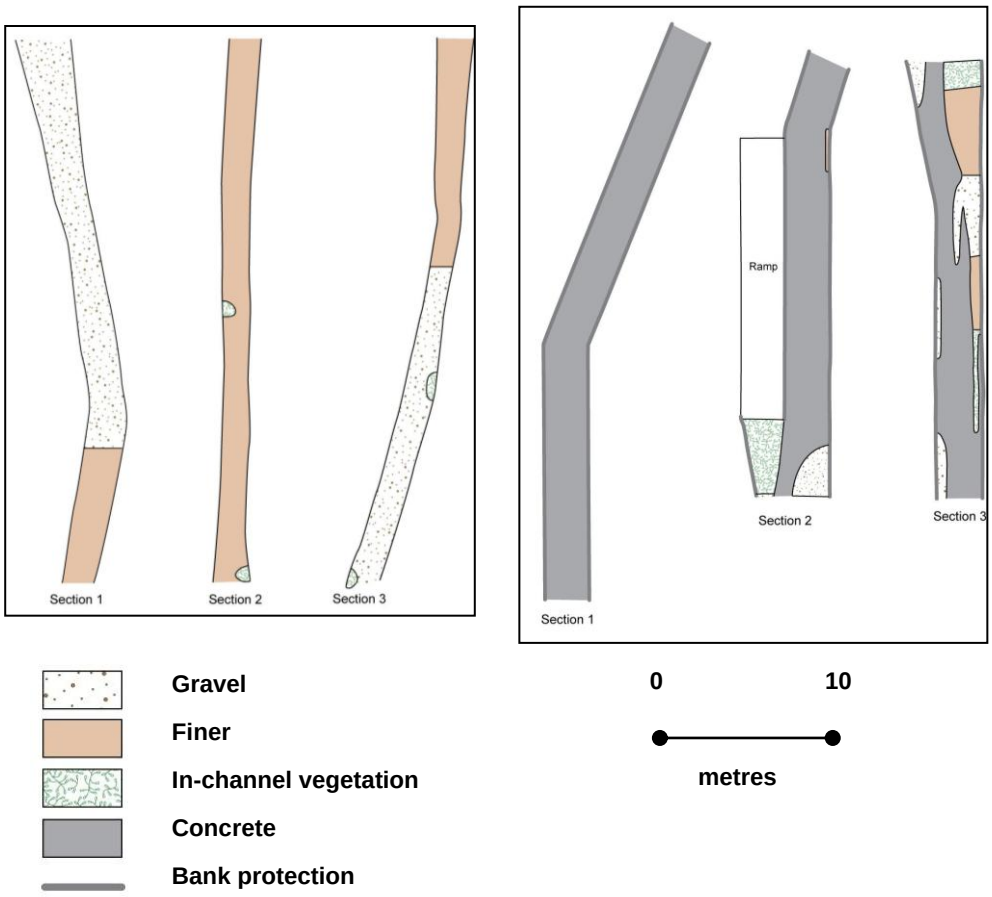


Figure 4.17: Distribution of bed sediment types and bank protection in the restored (left) and unrestored (right) stretches at Chinbrook Meadows.

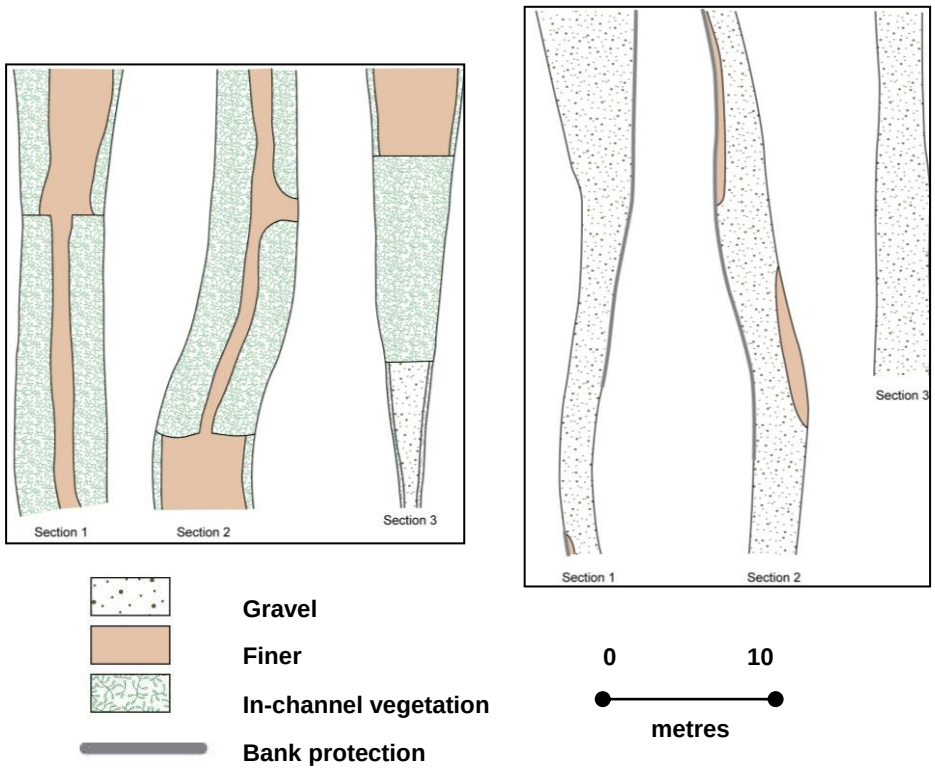


Figure 4.18: Distribution of bed sediment types and bank protection in the restored (left) and unrestored (right) stretches at Sutcliffe Park.

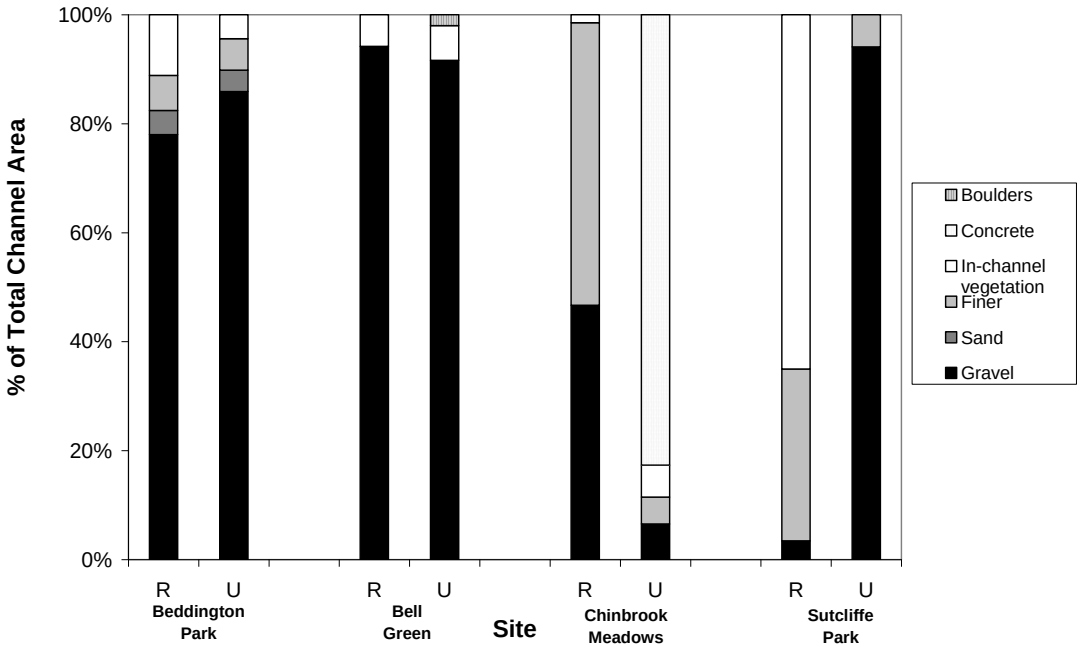


Figure 4.19: Percentage coverage of channel by different bed sediment types.

The four study sites represent very different levels of engineering within the unrestored stretches and strongly contrasting coverages and distributions of the different bed sediment types.

At Beddington Park, there was some bank protection within both stretches, however it was only intermittent along the left bank of the restored stretch, and both the restored and unrestored stretches had gravel, sand, finer and in-channel vegetation bed sediment types present (Figure 4.15). The coverage of the channel by the different bed sediment types was similar in both the restored and the unrestored stretch (Figure 4.19). The dominant bed sediment type within both stretches was gravel with the finer and in-channel vegetation sediment covering less than 20% of the channel. However, there were differences in the spatial distribution of bed sediment types between the stretches. In the unrestored stretch all sand, finer and in-channel vegetation sediment depositions were long, thin and linear, parallel to the bank. In contrast, in the restored stretch (particularly in the main channel as opposed to the reed bed area) the sand, finer and in-channel vegetation sediment depositions were far less thin and linear, extended further in to the channel and were more 'patchy'. Also there were more extensive areas of finer sediment and sediment associated with in-channel vegetation. In both stretches finer and in-channel vegetation sediment was present adjacent to unreinforced banks. In the unrestored stretch the finer sediment was located adjacent to the in-channel vegetation sediment and extended further downstream than the in-channel vegetation sediment where the channel widened. Sand was present in the unrestored stretch upstream of the finer and in-channel vegetation sediment. In the restored stretch a large area of in-channel vegetation sediment was present within the reed bed area, and there was also an island of in-channel vegetation in the centre of the channel, along with a few smaller patches located next to the bank at the upstream end of the stretch. The finer sediment areas were generally associated with areas of in-channel vegetation, although there was an additional more isolated area towards the downstream end of the stretch.

At Bell Green both the restored and unrestored stretches had gravel and in-channel vegetation bed sediment types, and the unrestored stretch additionally had some areas of boulders (Figure 4.16). The coverage of the channel by the bed sediment types was similar in both the restored and the unrestored stretch (Figure 4.19). Again, the dominant bed sediment type within each stretch was gravel (over 90% cover) and in-channel vegetation sediment covered less than 10% of the channel, with additionally a small area of boulders in the unrestored stretch. Due to the nature of the restoration works at this site, the restored stretch had full bank and bed protection (concrete), in contrast to the unrestored stretch, which had bank protection only. Although the in-channel vegetation sediment was adjacent to the banks in both stretches, there was a clear difference in the shape of these deposits. Within the restored stretch, the in-channel vegetation

sediment areas were generally long, thin and linear, parallel to the bank, whereas in the unrestored stretch they were less thin and linear, and extended further in to the channel. There was also a small in-channel vegetation sediment area in the centre of the restored channel at the upstream end of the stretch.

At Chinbrook Meadows both the restored and unrestored stretch had gravel, finer and in-channel vegetation bed sediment types present (Figure 4.17). Additionally, the unrestored stretch had some areas without deposited sediment where the concrete channel bed was visible. There were clear differences between the restored and unrestored stretch in the coverage by the different bed sediment types (Figure 4.19). The dominant bed sediment types in the restored stretch were finer and gravel (52% and 47% cover respectively), whereas in the unrestored stretch the dominant bed 'sediment' was the bare concrete bed (83% cover). There was solid bank protection present along the entire unrestored stretch, whereas there was no bank protection in the restored stretch. Areas of sedimentation in the unrestored stretch were spatially distributed to where the channel was widest, being long and linear, adjacent to the banks. In contrast, the finer sediments in the restored stretch were occupying the full channel in the central part of the stretch. Smaller, more lobe-shaped, areas of in-channel vegetation sediment were present in the restored stretch adjacent to the banks.

At Sutcliffe Park there were differences between the restored and unrestored stretch for both the presence and coverage of the channel by the bed sediment types (Figures 4.18 and 4.19). Both stretches had gravel and finer bed sediment types present, whereas only the restored stretch had in-channel vegetation sediment (Figure 4.18). The dominant bed sediment type in the unrestored stretch was gravel (94% cover), whereas in the restored stretch finer and in-channel vegetation sediment dominated (32% and 65% cover respectively) (Figure 4.19). There was no bank protection in the restored stretch, but some intermittent protection was present along both banks of the unrestored stretch. The spatial distribution of finer sediment varied between the restored and unrestored stretch. In the unrestored stretch, the areas were long, thin and linear, adjacent to the banks, whereas in the restored stretch, finer sediment was present across the centre of the channel between the patches of in-channel vegetation sediment, apart from in the downstream part of the stretch. Here the channel narrowed and there was less in-channel vegetation and some gravel was exposed.

4.4.2 Sediment characteristics and metal concentrations

Integrated analysis of data from all four study sites

(i) Data preparation and description

All sediment samples had detectable concentrations of all of the metals of interest apart from Cd which had concentrations <LoD for 253 out of the 345 samples (73%). Due to the very high proportion of samples with <LoD concentrations (Section 3.4.1 in Chapter 3), Cd was excluded from further analysis. Therefore, analysis focussed on 11 variables determined for 345 sediment samples (Al, Cr, Cu, Fe, Mn, Ni, Pb, Zn, % organic matter, % fine of the <2 mm fraction (<63µm) and % gravel (>2 mm)). The complete data set is shown in Appendix II, and is summarised in boxplots in Figure 4.20.

None of the 11 variables were normally distributed (Kolmogorov-Smirnov test, $p < 0.001$). All variables showed a positively-skewed distribution apart from % >2 mm, which showed a bimodal distribution (Figure 4.20). The variables were subjected to a range of transformations, including the commonly used $\log_{10}$ transformation and Arcsin transformation for % data, in an attempt to normalise their distributions (Table 4.4). Different transformations were required to normalise different variables, and no transformation could be found to normalise the bimodal % >2 mm variable. As a result, non-parametric methods were used to analyse the data set.

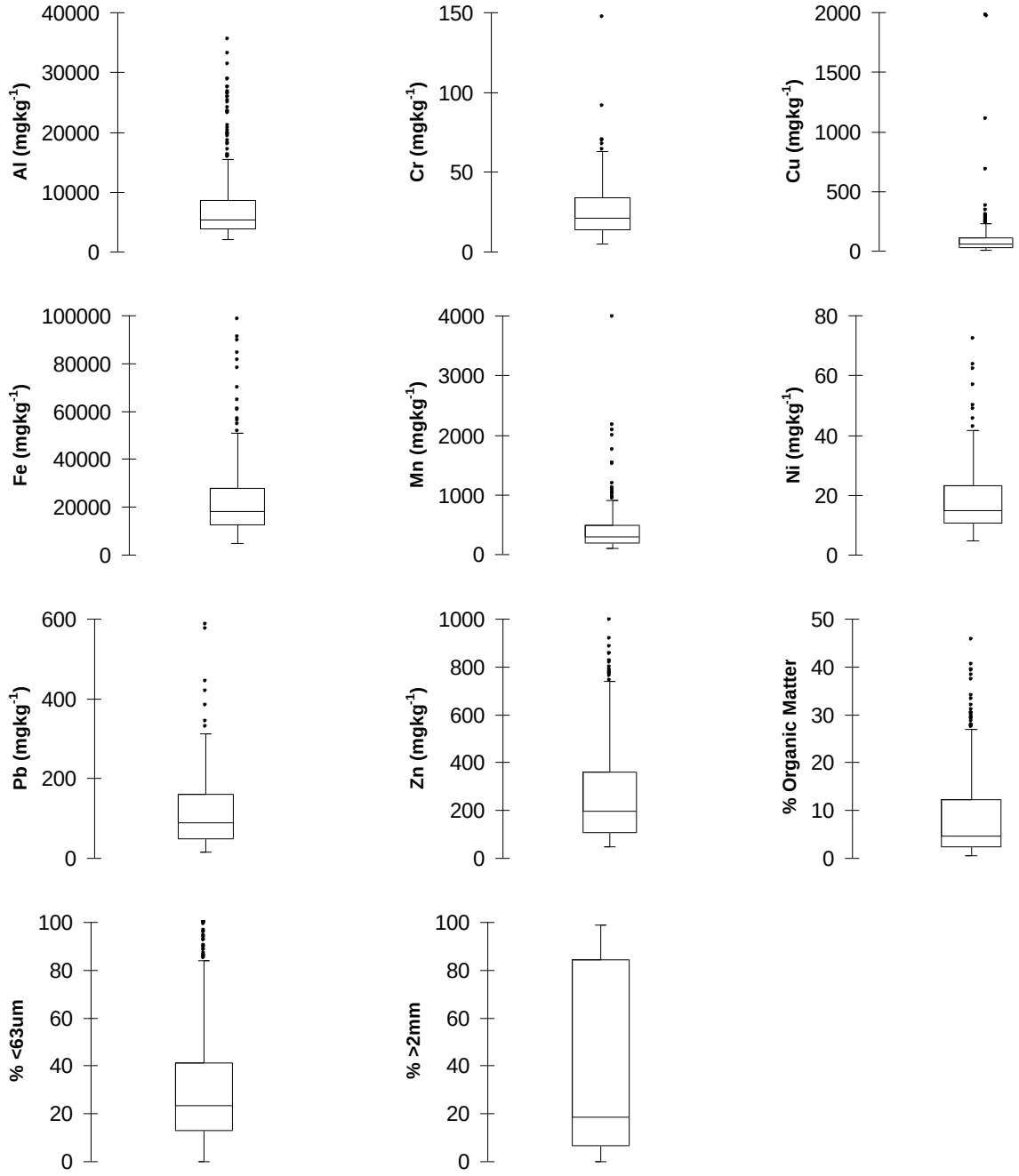


Figure 4.20: Boxplots of each variable for the whole data set.

Table 4.4: Transformations applied in an attempt to normalise variable distributions. With transformations which produce a normal distribution (p >0.05) shown in bold.

Variable	Normalising transformation and K-S p value
Al	$\log_{10}$ = 0.002
	1/x = 0.366
Cr	$\log_{10}$ = 0.036
	1/√x = 0.132
Cu	**$\log_{10}$** = 0.291
Fe	**$\log_{10}$** = 0.687
Mn	**$\log_{10}$** = 0.379
Ni	**$\log_{10}$** = 0.385
Pb	**$\log_{10}$** = 0.156
Zn	**$\log_{10}$** = 0.084
% Organic matter	$\log_{10}$ = 0.013
	Arcsin = 0.000
	1/√(x+1) = 0.056
% <63 µm	**$\log_{10}$** = 0.185
	Arcsin = 0.000
% >2 mm	$\log_{10}$ (x+1) = 0.000
	Arcsin = 0.000
	1/(x+1) = 0.000
	x^2 = 0.000
	1/√(x+1) = 0.000

Spearman's Rank (S-R) correlation coefficients were calculated to explore the associations between the 11 variables across the entire data set, and in particular the relationships between sediment metal concentrations and sediment characteristics. There were statistically significant correlations (S-R, $p < 0.05$) between all variables, apart from between Al and % >2 mm (Figure 4.21). There were positive correlations between all metals and % organic matter and % <63 µm (S-R, $p < 0.01$). Organic matter and % <63 µm were highly positively correlated (S-R, r_s = 0.700, $p < 0.01$). Percentage >2 mm was positively correlated with Al, Fe, Mn and Ni and negatively correlated with Cr, Cu, Pb and Zn, with all correlations significant apart from with Al. Organic matter and % <63 µm showed significant negative correlations with % >2 mm. Visual analysis of the scatterplots indicates that the relationships between some variables are more complicated that the correlation coefficients suggest (Figure 4.21): the scatterplots between Al and Cr, Cu, Fe, Mn, Ni and Pb suggest a subset of the samples which had low Al

concentrations but high Cr, Cu, Fe, Mn, Ni and Pb concentrations; the scatterplots between % >2 mm and metal concentrations suggest a subset of samples with high % >2 mm and high metal concentrations; and, the scatterplots between organic matter content and metal concentrations suggest a subset of samples with low organic matter content but high metal concentrations (though lesser so for Al and Zn). These will be analysed further and discussed in Section 4.5.2. There were two groups of metals whose concentrations were strongly intercorrelated: Cr, Cu, Pb and Zn ($r_s > 0.6$); and, Al, Fe, Mn and Ni ($r_s > 0.5$).

(ii) Contrasts in sediment properties through time and across space

The median values for metal concentrations, % organic matter content, % <63 µm and % >2 mm of the whole data set, within restored and unrestored stretches, within the different time periods, within each study site and for each bed sediment type are presented in Tables 4.5, 4.6 and 4.7. Mann-Whitney U (M-W), Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these sediment properties between restored and unrestored stretches, sampling times, sampling sites and the four bed sediment types (Table 4.8).

Within the whole data set there were large differences in concentrations between different metals. The highest concentrations were for Fe and Al (median concentrations 18,300 $mgkg^{-1}$ and 5,360 $mgkg^{-1}$ respectively) and the lowest concentrations for Ni and Cr (median concentrations 14.9 $mgkg^{-1}$ and 21.0 $mgkg^{-1}$ respectively) (Table 4.5). The medians of the two descriptors of grain size (% <63 µm and % >2 mm) were similar (23.6% and 18.5%, respectively) (Table 4.5).

Overall, the restored stretches had higher median concentrations of all metals, (apart from Cu, Pb and Zn), % organic matter, % <63 µm and % >2 mm than the unrestored stretches (Table 4.5), although none of these differences were statistically significant (M-W, $p > 0.05$, Table 4.8). The lowest median metal concentrations, % organic matter, % <63 µm and % >2 mm were found in the November samples and the highest were found in the May samples, apart from the Cr concentration (Table 4.5). However, the only statistically significant differences were for Al, Cu, Pb, Zn concentrations and % organic matter which were significantly higher in May then in November (K-W, $p < 0.05$, Table 4.8).

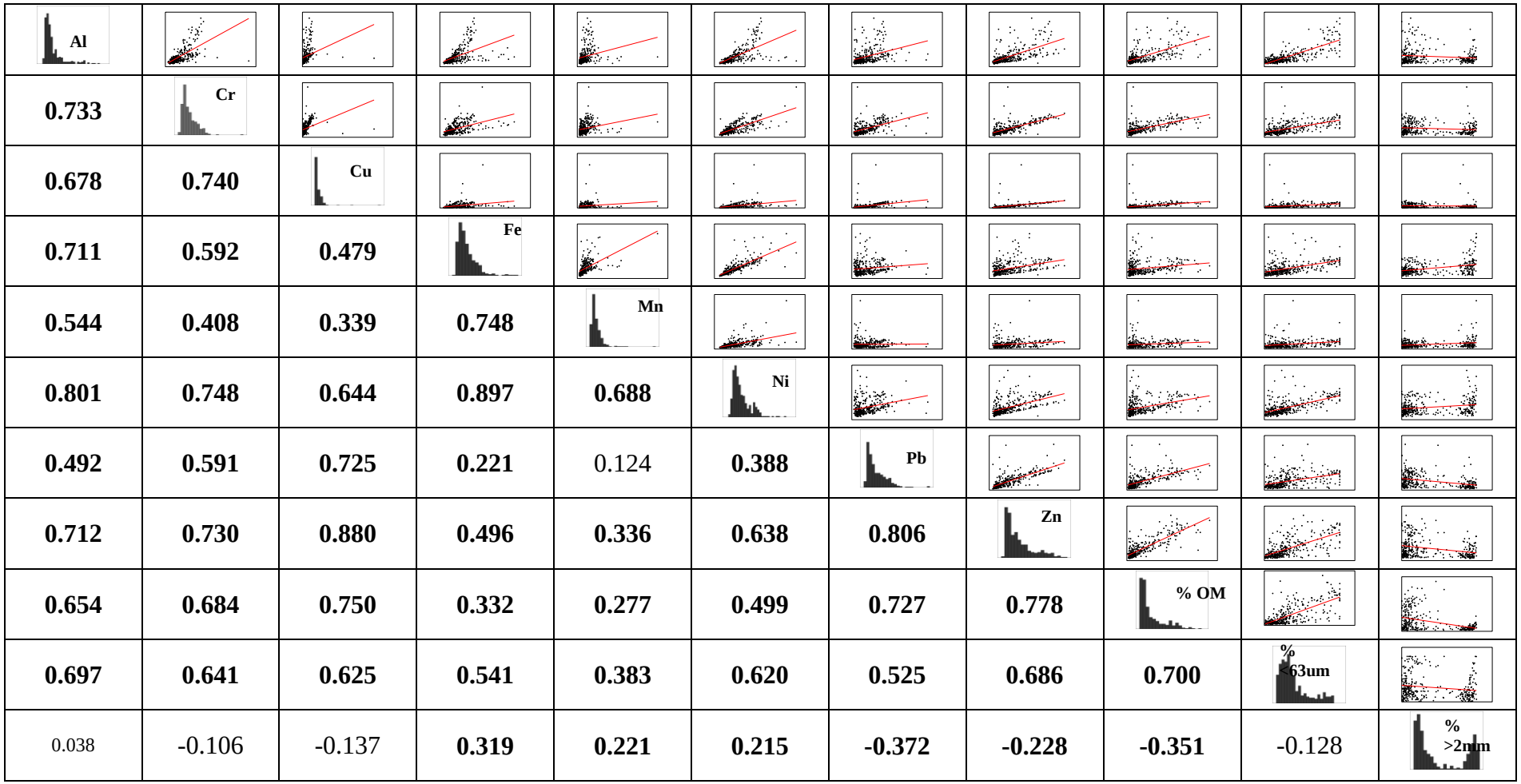


Figure 4.21: Scatter plots, histograms and correlations between all 11 variables across the whole data set. Spearmans Rank correlation coefficients significant at p <0.01 are shown in large and bold font, those significant at p <0.05 are shown in large font, and those not significant (p >0.05) are shown in small font.

Table 4.5: Median sediment pseudo-total metal concentrations and characteristics for the whole data set, restored/unrestored stretches and different time periods (to 3 s.f.).

Variable	Whole	Restored	Unrestored	May	August	November
Al (mgkg^{-1})	5,360	5,390	5,290	6,260	5,360	4,870
Cr (mgkg^{-1})	21.0	21.5	19.6	21.2	22.9	18.4
Cu (mgkg^{-1})	58.0	57.8	58.0	73.9	59.8	43.8
Fe (mgkg^{-1})	18,300	18,600	17,900	19,300	18,400	17,300
Mn (mgkg^{-1})	302	312	299	347	315	270
Ni (mgkg^{-1})	14.9	15.7	14.5	16.7	15.4	13.5
Pb (mgkg^{-1})	88.8	84.7	89.6	100	91.9	69.1
Zn (mgkg^{-1})	198	190	211	221	202	171
% Organic matter	4.61	4.88	4.37	5.09	4.50	3.88
% <63 µm	23.6	24.8	22.9	24.2	23.9	22.2
% >2 mm	18.5	20.1	14.8	20.3	19.8	15.7

Across the four sites, Sutcliffe Park had the highest median concentration of all metals (statistically significant for Al, Cr, Cu, Fe, Ni and Zn), % organic matter and % <63 µm (Table 4.6 and K-W, $p < 0.01$, Table 4.8). The lowest median metal concentrations were found at Beddington Park and Chinbrook Meadows (Table 4.6), with Fe, Mn and Ni concentrations being the significantly lowest at Beddington Park and Pb concentrations being the significantly lowest at Chinbrook Meadows (K-W, $p < 0.01$, Table 4.8). Organic matter content was significantly lowest at Bell Green (K-W, $p < 0.01$, Table 4.8) and the lowest % <63 µm and % >2 mm was found at Beddington Park, although this was not statistically significant (Table 4.6, K-W, $p > 0.05$, Table 4.8).

Table 4.6: Median sediment pseudo-total metal concentrations and characteristics for the sites (to 3 s.f.).

Variable	Beddington Park	Bell Green	Chinbrook Meadows	Sutcliffe Park
Al (mgkg^{-1})	4,620	5,160	4,890	11,800
Cr (mgkg^{-1})	19.2	18.5	17.9	35.2
Cu (mgkg^{-1})	59.6	56.6	44.5	90.9
Fe (mgkg^{-1})	11,400	18,700	20,400	36,900
Mn (mgkg^{-1})	181	350	418	437
Ni (mgkg^{-1})	10.8	16.2	13.8	31.6
Pb (mgkg^{-1})	91.3	92.1	67.8	104
Zn (mgkg^{-1})	155	210	132	324
% Organic matter	3.86	2.85	4.69	6.26
% <63 µm	17.0	22.8	21.5	68.1
% >2 mm	13.6	50.3	14.9	30.5

In relation to bed sediment type, the lowest median, and statistically significantly lowest, metal concentrations were found in the sand samples, apart from Pb which was lowest in the gravel samples (Table 4.7, K-W, $p < 0.01$, Table 4.8). In-channel vegetation sediments had the highest median metal concentrations, apart from Fe which was highest in the gravel samples (Table

4.7), although these were not all statistically significant (Table 4.8). Finer and in-channel vegetation sediment samples had significantly higher concentrations of Cu and Zn than the other bed sediment types, and in-channel vegetation sediment samples had significantly higher concentrations of Cr and Pb (K-W, $p < 0.01$, Table 4.8). Gravel and in-channel vegetation sediment samples had significantly higher concentrations of Fe and Mn (K-W, $p < 0.01$, Table 4.8). Three bed sediment types (gravel, finer and in-channel vegetation sediment) had significantly higher concentrations of Al than sand (K-W, $p < 0.01$, Table 4.8). In-channel vegetation and finer sediments had the highest median % organic matter and % <63 µm contents (Table 4.7). These were significantly greater than the gravel and sand sediments (K-W, $p < 0.01$, Table 4.8), and gravel sediments had the significantly highest % >2 mm (K-W, $p < 0.01$, Table 4.8).

Table 4.7: Median sediment pseudo-total metal concentrations and characteristics for the different bed sediment types (to 3 s.f.).

Variable	Gravel	Sand	Finer	In-channel vegetation
Al ($mgkg^{-1}$)	5,160	3,210	5,280	7,150
Cr ($mgkg^{-1}$)	15.4	12.6	23.0	28.6
Cu ($mgkg^{-1}$)	44.0	25.1	73.5	90.4
Fe ($mgkg^{-1}$)	25,200	8,370	15,700	19,000
Mn ($mgkg^{-1}$)	350	149	234	363
Ni ($mgkg^{-1}$)	16.9	7.79	13.9	17.1
Pb ($mgkg^{-1}$)	49.1	57.8	131	150
Zn ($mgkg^{-1}$)	131	98.6	245	305
% Organic matter	2.56	2.11	9.00	11.6
% <63 µm	16.3	6.25	29.5	33.7
% >2 mm	89.4	8.38	9.54	9.69

Table 4.8: Statistically significant spatial and temporal differences in sediment pseudo-total metal concentrations and characteristics identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s. = not significant, R = restored, U = unrestored, M = May, A = August, N = November, BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park, G = Gravel, S = Sand, F = Finer, ICV = In-channel vegetation).

	Restored/Unrestored		Time		Site		Bed sediment type	
Variable	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**	**K-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
Al ($mgkg^{-1}$)	0.150	n.s.	0.023	M > N	<0.0001	SP > BP, BG, CM	<0.0001	ICV, F, G > S ICV > G
Cr ($mgkg^{-1}$)	0.074	n.s.	0.117	n.s.	<0.0001	SP > BP, BG, CM	<0.0001	ICV > F > G > S
Cu ($mgkg^{-1}$)	0.547	n.s.	0.002	M > N	<0.0001	SP > BP, BG, CM	<0.0001	F, ICV > G > S
Fe ($mgkg^{-1}$)	0.327	n.s.	0.568	n.s.	<0.0001	SP > BG, CM > BP	<0.0001	G, ICV > F > S
Mn ($mgkg^{-1}$)	0.716	n.s.	0.066	n.s.	<0.0001	BG, SP, CM > BP	<0.0001	G, ICV > F > S
Ni ($mgkg^{-1}$)	0.072	n.s.	0.065	n.s.	<0.0001	SP > BG, CM > BP	<0.0001	ICV > F ICV, F, G > S
Pb ($mgkg^{-1}$)	0.135	n.s.	0.009	M > N	0.0000	BP, BG, SP > CM	<0.0001	ICV > F > G, S
Zn ($mgkg^{-1}$)	0.600	n.s.	0.034	M > N	<0.0001	SP > BP, BG, CM BG > CM	<0.0001	ICV, F > G > S
% Organic matter	0.610	n.s.	0.007	M > N	<0.0001	SP > BP, CM > BG	<0.0001	F, ICV > G, S
% <63 µm	0.075	n.s.	0.372	n.s.	<0.0001	SP > BP, BG, CM	<0.0001	F, ICV > G > S
% >2 mm	0.529	n.s.	0.528	n.s.	0.001	SP > BP, CM	<0.0001	G > S, F, ICV

Fine sediments (<63 µm, silt and clay) are known to have a large influence upon metal concentrations with increasing proportions of silt and clay generally resulting in increased metal concentrations in sediment samples (Section 2.3.2 in Chapter 2). This can impede comparisons of metal concentrations between sediment samples of varying grain size by masking underlying trends in metal concentrations which are due to other factors, such as anthropogenic inputs, as opposed to natural (grain size) variability (Luoma & Rainbow, 2008; Kersten & Smedes, 2002; Clark *et al*., 2000; Loring, 1991; and, Horowitz & Elrick, 1988). The influence of grain size upon metal concentrations is illustrated in the current data set by: the significant positive correlations between % <63 µm and the concentrations of each metal (Figure 4.21); the corresponding differences in median % <63 µm and metal concentrations in different bed sediment types (Table 4.7); and, the significant differences in metal concentrations between the different bed sediment types (Table 4.8). Therefore, granulometric correction (correction for % of sample < 63 µm) of metal concentrations was undertaken to determine normalised metal ratios (Section 3.4.2 in Chapter 3) and the data reanalysed for temporal and spatial differences to explore the degree to which these differences were entirely a function of grain size or reflected underlying differences in metal inputs, or metal behaviour, in the environment (Table 4.9).

Following granulometric correction, there were no significant differences between the restored and unrestored stretches with the exception of Pb_{correc} and Zn_{correc} (M-W, $p = 0.009$ and $p = 0.031$ respectively, Table 4.9) which showed significantly greater normalised metal ratios in unrestored stretches. Similarly, there were no significant differences in normalised metal ratios between the three sampling times (K-W, $p > 0.05$, Table 4.9). However, there were significant differences for all normalised metal ratios (K-W, $p < 0.01$) apart from Al_{correc} (K-W, $p = 0.097$) between the four study sites (Table 4.9). Beddington Park had significantly greater normalised metal ratios of Cr_{correc}, Cu_{correc} and Pb_{correc} than the other three sites. Sutcliffe Park had significantly lower normalised metal ratios of Cr_{correc}, Mn_{correc} and Pb_{correc} than the other three sites. There were fewer significant differences between the study sites for Fe_{correc} and Ni_{correc}. There were also significant differences in all of the normalised metal ratios (K-W, $p < 0.01$) between bed sediment types (Table 4.9). Sand samples had significantly higher normalised metal ratios of Al_{correc}, Cr_{correc}, Cu_{correc}, Pb_{correc} and Zn_{correc} than the other bed sediment types. For Fe_{correc}, Mn_{correc} and Ni_{correc} both gravel and sand samples had significantly higher normalised metal ratios than both finer and in-channel vegetation sediment samples.

Table 4.9: Statistically significant spatial and temporal differences in normalised metal ratios identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K0W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (n.s. = not significant, R = restored, U = unrestored, M = May, A = August, N = November, BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park, G = Gravel, S = Sand, F = Finer, ICV = In-channel vegetation).

	Restored/Unrestored		Time		Site		Bed sediment type	
Variable	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**	**K-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
Al_{correc}	0.821	n.s.	0.722	n.s.	0.097	n.s.	<0.0001	S > G > F, ICV
Cr_{correc}	0.521	n.s.	0.467	n.s.	<0.0001	BP > BG, CM > SP	<0.0001	S > G, F, ICV
Cu_{correc}	0.643	n.s.	0.055	n.s.	<0.0001	BP > BG, SP, CM	0.006	S > G, F, ICV
Fe_{correc}	0.269	n.s.	0.507	n.s.	0.003	BG > SP	<0.0001	G, S > F, ICV
Mn_{correc}	0.055	n.s.	0.406	n.s.	<0.0001	BG, CM > BP > SP	<0.0001	G, S > F, ICV
Ni_{correc}	0.383	n.s.	0.145	n.s.	0.001	BP, BG > SP	<0.0001	G, S > F, ICV
Pb_{correc}	0.009	U > R	0.594	n.s.	<0.0001	BP > BG > CM > SP	<0.0001	S > G, F, ICV
Zn_{correc}	0.031	U > R	0.750	n.s.	<0.0001	BP, BG > SP, CM	0.001	S > G, F, ICV

(iii) Factors explaining the variations in sediment properties

Principal Component Analysis (PCA) was used to explore the data set in order to understand the underlying factors that explain the variations in sediment properties (Section 3.4.3 in Chapter 3). PCA reduces much of the variance in a large multivariate data set to a relatively small number of Principal Components (PCs), with the first explaining the largest proportion of variance and each subsequent PC explaining less variability. Additionally, each sample has a score on each PC (known as a factor score), which shows its relative location along the PC in comparison with other samples and the strength of the association of each sample to that PC.

This was initially undertaken on the raw data set (not granulometrically corrected) and then on the granulometrically corrected data set (with normalised metal ratios). Differences in the sample factor scores for different groupings (restored/unrestored, site, time and bed sediment type) were then explored through scatter plots and Mann-Whitney U and Kruskal-Wallis tests. However, differences in bed sediment types in the granulometrically corrected data set were not explored since the grain size influence had been removed through use of normalised metal ratios. Interpretation of the PCs, and separation of groupings along the PCs, is discussed in Section 4.5.3.

Raw data set (not granulometrically corrected)

With the raw data set two PCs were extracted with eigenvalues >1 which accounted for 78% cumulative variance after a varimax rotation (Table 4.10). Cr, Cu, Pb, Zn, % organic matter and % <63 μm were all heavily positively loaded on PC1, which explained 44% of the variance, and Al, Fe, Mn and Ni were heavily positively loaded on PC2, which explained 34% of the variance (Table 4.10).

Figure 4.22 plots the factor scores of each sample on PC1 and PC2 and codes the samples according to their representation of restored/unrestored stretches, sampling time, study site and bed sediment type to assess whether there is any discrimination between these properties of the samples in relation to their scores on PC1 and/or PC2.

Visually there is no clear separation of restored and unrestored stretch samples or samples obtained at different sampling times within the plot. However, the study sites and bed sediment types do occupy different areas of the plot. The study sites appear to be discriminated most strongly by their scores on PC2. Beddington Park samples generally have relatively low (negative) scores on PC2, whilst Sutcliffe Park samples have relatively high (positive) scores, and Bell Green and Chinbrook Meadows samples have intermediate scores. The bed sediment types appear to discriminate by their scores on both PC1 and PC2. Along PC1 the finer and in-

channel vegetation sediment samples show generally high (positive) scores and the gravel and sand samples show low (negative) scores. Along PC2 gravel samples generally show higher (positive) scores than the other three bed sediment types. In general, sand samples are confined to the lower left quadrant of the plot, gravel samples are confined to the left of the plot and finer and channel vegetation samples extend widely across the right side of the plot.

Table 4.10: Percentage variance explained and variable loadings on the first two components following the application of Principal Component Analysis to the whole raw data set (not granulometrically corrected) (loadings >0.6 are large and bold, loadings >0.4 but <0.6 are large, loadings <0.4 are small and italic).

	Principal Component	
	1	**2**
Eigenvalue	6.5	2.1
Variance Explained	44%	34%
	Principal Component Loadings after Rotation	
Al	0.588	**0.672**
Cr	**0.702**	0.507
Cu	**0.813**	*0.369*
Fe	*0.209*	**0.921**
Mn	*0.069*	**0.810**
Ni	0.411	**0.861**
Pb	**0.882**	*0.028*
Zn	**0.870**	*0.338*
% Organic Matter	**0.882**	*0.190*
% <63µm	**0.676**	0.443
% >2mm	-0.559	0.566

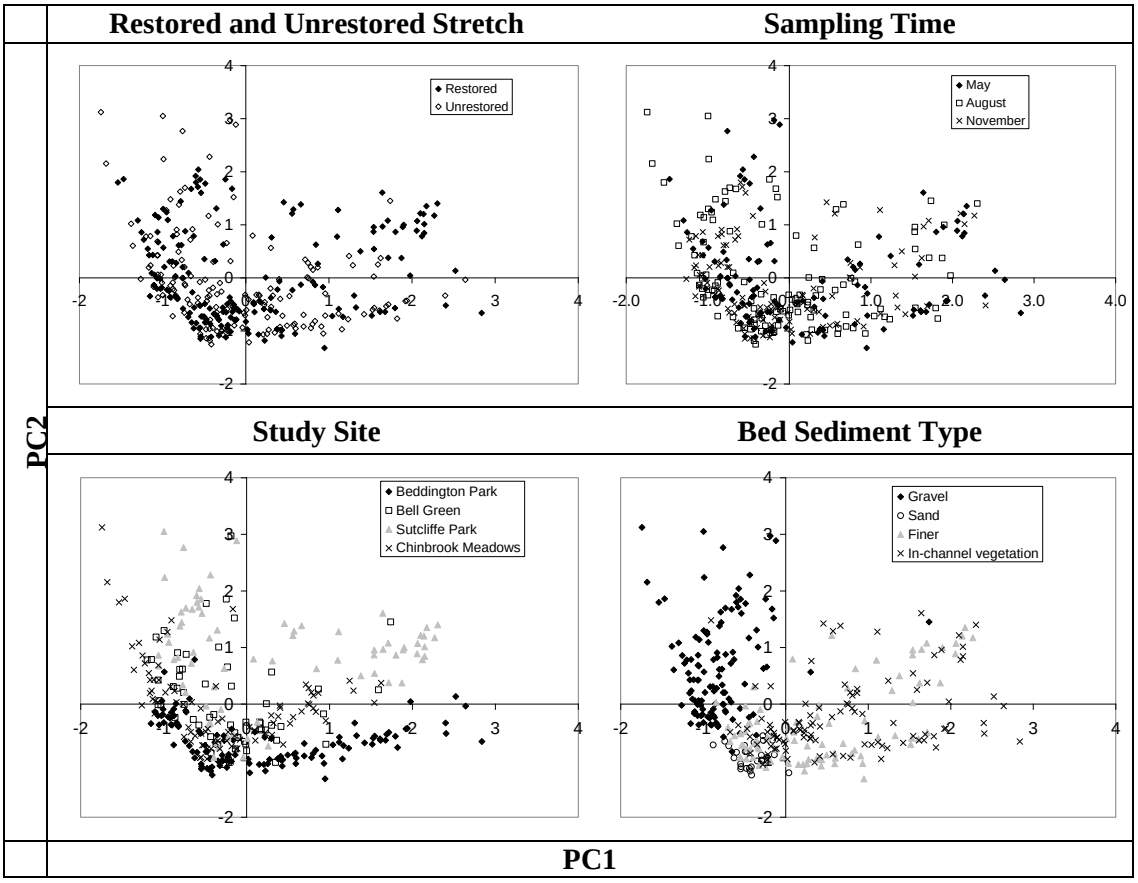


Figure 4.22: Plots of sample factor scores on PC1 and PC2 coded by restored and unrestored stretch, sampling time, study site and bed sediment type for the entire raw data set (no granulometric correction).

M-W, K-W and post-hoc S-D-C-F tests were applied to the factor scores on PC1 and PC2 to test whether the apparent separation of the groupings was statistically significant (Table 4.11). M-W and K-W tests undertaken on the sample factor scores on PC1 grouped according to restored/unrestored stretches, sampling time, study sites and bed sediment types indicated statistically significant differences between study sites and bed sediment types (K-W, $p = 0.002$ and $p < 0.0001$ respectively). Post-hoc S-D-C-F tests indicated that the scores on PC1 from both the Sutcliffe Park and Beddington Park samples were significantly greater than those for Chinbrook Meadows samples. In terms of bed sediment type, the scores of the finer and in-channel vegetation sediment samples on PC1 were significantly greater than those for both the sand and gravel samples. Additionally, the scores for the sand samples were significantly greater than the scores for the gravel samples.

M-W and K-W tests applied to sample factor scores on PC2 indicated that there were some statistically significant differences in factor scores of samples obtained from different study

sites and bed sediment types (both K-W, $p < 0.0001$). The factor scores from the Sutcliffe Park and Beddington Park site samples were both significantly different from the other three study sites, with Sutcliffe Park samples having significantly greater factor scores and Beddington Park samples having significantly lower factor scores than samples from the other sites. Sample factor scores associated with different bed sediment types were significantly different from each other, with gravel samples having the greatest factor scores on PC2 and sand samples having the lowest.

Table 4.11: Results of Mann-Whitney (M-W) U and Kruskal-Wallis (K-W) tests applied to sample factor scores on the first two Principal Components estimated from the whole raw data set according to the restored/unrestored, sampling time, study site and bed sediment type characteristics of the samples (n.s. = not significant, BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park, G = Gravel, S = Sand, F = Finer, ICV = In-channel vegetation).

	Restored/ Unrestored		Time		Site		Bed sediment type	
PC	**M-W p value**	**Signif diff**	**K-W p value**	**Signif diff**	**K-W p value**	**Signif diff**	**K-W p value**	**Signif diff**
PC1	0.568	n.s.	0.089	n.s.	0.002	SP, BP > CM	<0.0001	F,ICV > S > G
PC2	0.064	n.s.	0.481	n.s.	<0.0001	SP > CM, BG > BP	<0.0001	G > ICV > F > S

Granulometrically corrected data set

PCA applied to the granulometrically corrected data set identified two PCs with eigenvalues >1 which accounted for 79% cumulative variance after a varimax rotation (Table 4.12) (%<63 µm variable has been removed as this was used to granulometrically correct the metal concentrations). Cr_{correc}, Cu_{correc}, Pb_{correc} and Zn_{correc} were highly positively loaded on PC1, which explained 40% of the variance, and Al_{correc}, Fe_{correc}, Mn_{correc}, Ni_{correc} and % >2 mm highly positively loaded, and % organic matter highly negatively loaded, on PC2, which explained 39% of the variance (Table 4.12).

Figure 4.23 plots the factor scores of each sample on PC1 and PC2 and codes the samples according to their source from a restored/unrestored stretch, sampling time and study. Visually there is no clear separation between samples from restored and unrestored stretches, different sampling times and study sites.

Table 4.12: Percentage variance explained and variable loadings on the first two components following the application of Principal Component Analysis to the granulometrically corrected whole data set (loadings >0.6 are large and bold, loadings >0.4 but <0.6 are large, loadings <0.4 are small and italic, the %<63 µm variable was excluded from the analysis because it was used to granulometrically correct the metal concentrations).

	Principal Component	
	1	**2**
Eigenvalue	5.8	2.1
Variance Explained	40%	39%
	Principal Component Loadings after Rotation	
Al_{correc}	0.574	**0.629**
Cr_{correc}	**0.762**	0.519
Cu_{correc}	**0.877**	*0.138*
Fe_{correc}	*0.363*	**0.889**
Mn_{correc}	*0.336*	**0.820**
Ni_{correc}	0.503	**0.825**
Pb_{correc}	**0.878**	*0.120*
Zn_{correc}	**0.916**	*0.211*
% Organic Matter	*0.162*	**-0.795**
% >2 mm	*-0.348*	**0.605**

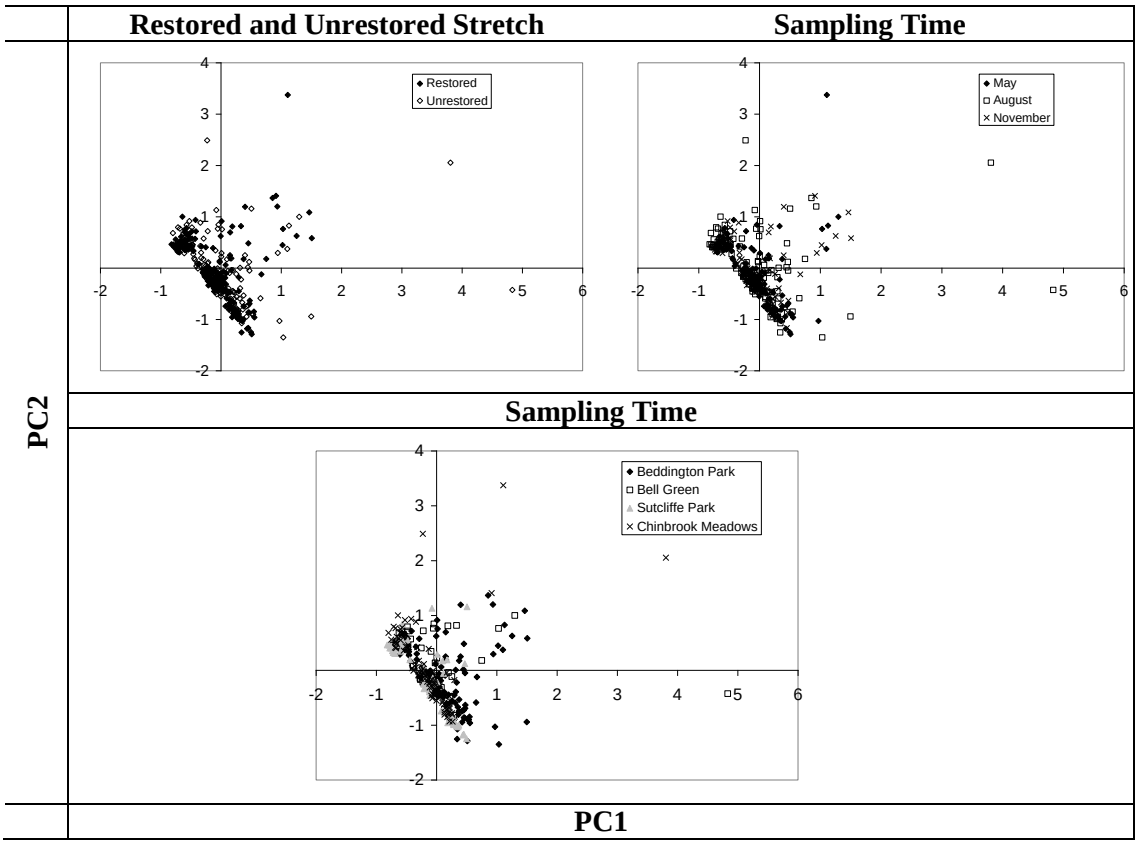


Figure 4.23: Plots of sample factor scores on PC1 and PC2 coded by restored and unrestored stretch, sampling time and study site for the granulometrically corrected data set.

M-W, K-W and post-hoc S-D-C-F tests were applied to the sample factor scores to test whether there was any statistically significant difference in scores on PC1 or PC2 according to whether the samples were drawn from restored or unrestored stretches, different times or different study sites (Table 4.13). M-W and K-W tests applied to sample factor scores on PC1 showed statistically significant differences in sample factor scores from different sampling sites (K-W, $p < 0.0001$). Post-hoc S-D-C-F tests indicated that Beddington Park samples had significantly greater factor scores on PC1 than the other three sites

M-W and K-W tests indicated that there were significant differences in sample factor scores on PC2 among study sites (K-W, $p=0.003$). Post-hoc S-D-C-F tests indicated that Bell Green samples had significantly greater factor scores on PC2 than Beddington Park and Sutcliffe Park samples.

Table 4.13: Results of Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests applied to sample factor scores on the first two Principal Components estimated from the granulometrically corrected data set according to the restored/unrestored, sampling time and study site characteristics of the samples (n.s. = not significant, BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park).

	Restored/Unrestored		**Time**		**Site**	
PC	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
PC1	0.698	n.s.	0.265	n.s.	<0.0001	BP > BG, SP, CM
PC2	0.556	n.s.	0.396	n.s.	0.003	BG > BP, SP

Analysis of detailed Sutcliffe Park August data set

In addition to the variables in the multi-site data set analysed above (sediment aqua regia extractable metals (referred to as pseudo-total metals), organic matter content and particle size), three further variables (sediment acetic acid extractable metals, porewater Fe (II) concentrations (as a proxy for redox) and sediment pH) were collected from the Sutcliffe Park sampling site during the August sampling. This then created a more detailed data set in which to analyse further the additional roles of the environmental conditions of redox and pH and as well as the more bioavailable fraction of metals (acetic acid extractable). This is referred to as the Sutcliffe Park August data set.

(i) Data preparation and description

All sediment samples had detectable concentrations of all of the pseudo-total metals of interest apart from Cd and detectable concentrations of Al, Cu, Fe, Mn and Zn acetic acid extractable metals. 52%, 56%, 72%, 12% and 44% of samples showed concentrations of Cd_{total} , Cd_{acetic}, Cr_{acetc}, Ni_{acetic} and Pb_{acetic} , respectively, that were <LoD. Due to the high proportions of samples <LoD (Section 3.4.1 in Chapter 3), Cd_{total}, Cd_{acetic} and Cr_{acetc} were removed from the data set. As <50% samples were <LoD for Ni_{acetic} and Pb_{acetic} these samples were replaced with 0.5 LoD values (Ni 0.75 $mgkg^{-1}$ and Pb 1 $mgkg^{-1}$) to allow their inclusion in statistical analyses (Section 3.4.1 in Chapter 3). However, for interpretation of analysis it should be noted that Pb_{acetic} <LoD samples were concentrated on restored gravel samples (5 out of 5 samples), unrestored gravel samples (4 out of 5 samples) and restored in-channel vegetation sediment samples (2 out of 5 samples).

Analysis therefore focussed on 20 variables determined for 25 samples (Al_{total}, Cr_{total}, Cu_{total}, Fe_{total}, Mn_{total}, Ni_{total}, Pb_{total}, Zn_{total}, Al_{acetic}, Cu_{acetic}, Fe_{acetic}, Mn_{acetic}, Ni_{acetic}, Pb_{acetic}, Zn_{acetic}, % organic matter, % fine of <2mm fraction (<63 µm), % gravel (>2 mm), Fe (II) concentrations (proxy for redox) and pH). The complete data set is shown in Appendix III and is summarised in boxplots in Figure 4.24.

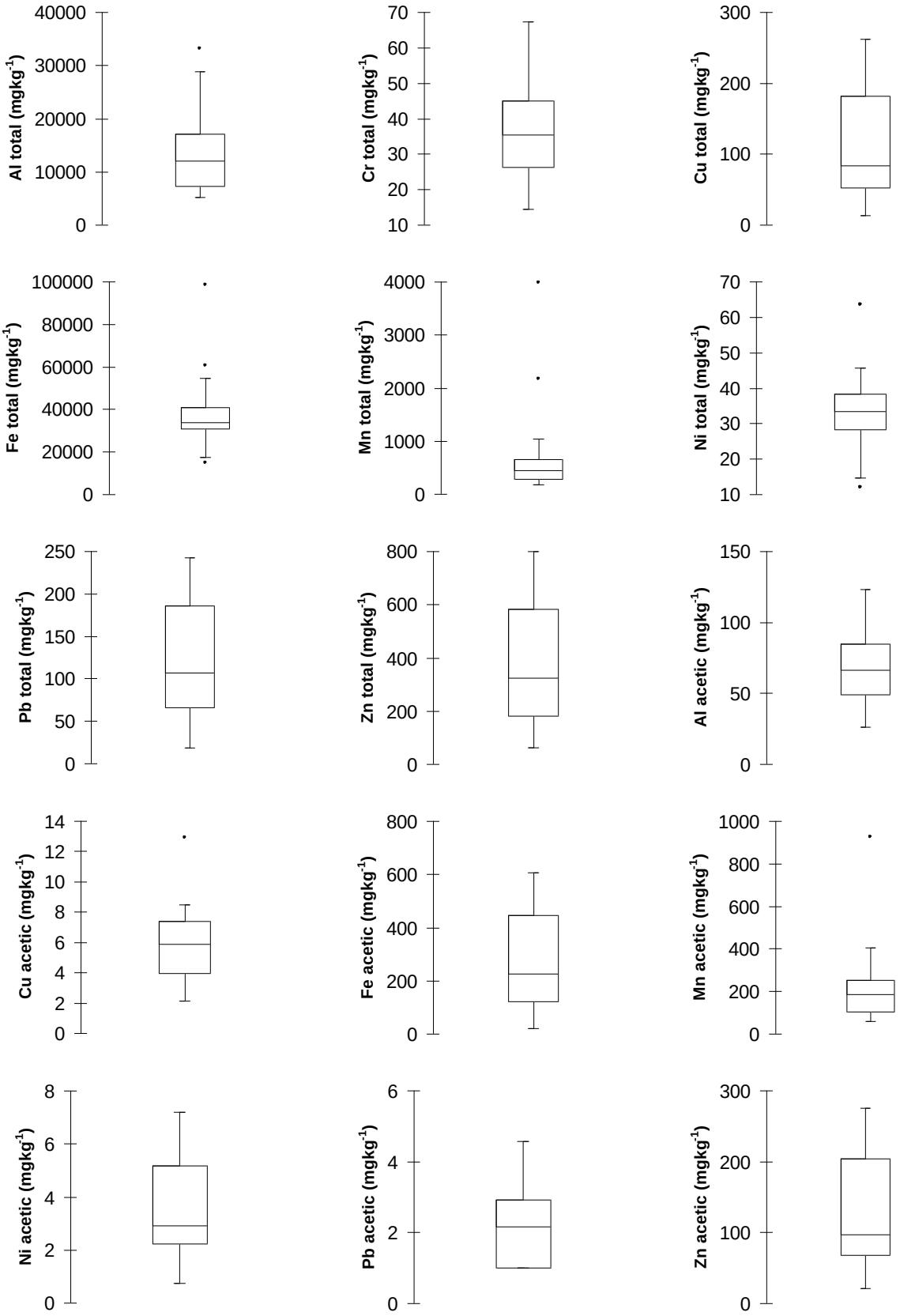


Figure 4.24: Boxplots of each variable for the Sutcliffe Park August data set (*continued overleaf*).

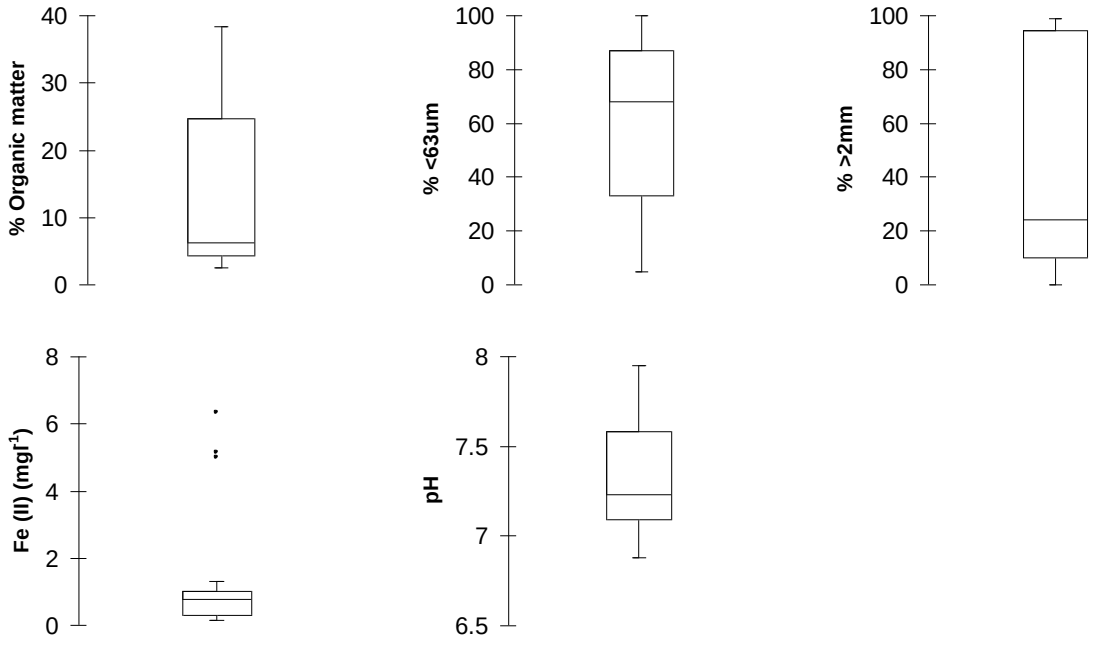


Figure 4.24: Boxplots of each variable for the Sutcliffe Park August data set (*continued*).

In contrast to the whole data set, the 20 variables of the Sutcliffe Park August data set were normally distributed (K-S, $p > 0.05$, Figure 4.25). However, with smaller data sets non-normality is less likely to be detected. Additionally, there can be some difficulties in comparing results of analyses when different statistical tests have been applied. Therefore, non-parametric methods were used to analyse the Sutcliffe Park August data set.

Spearman's Rank correlation coefficients were calculated to explore the associations between the 11 variables across the entire data set, and in particular the relationships between sediment metal concentrations and sediment characteristics (Figure 4.25).

There were fewer statistically significant correlations (S-R, $p < 0.05$) compared to the whole data set, reflecting the much smaller sample size. However, there were significant positive correlations between % organic matter and all metals apart from Fe_{total}, Mn_{total}, Ni_{total} and Cu_{acetic} (S-R, $p > 0.05$). Percentage <63 µm was significantly positively correlated with both all acetic acid and all pseudo-total metal concentrations, apart from Al_{acetic}, Fe_{total}, $Mn_{total,}$ Mn_{acetic}, Ni_{total}, Cu_{acetic} Pb_{total} and Pb_{acetic}. The majority of metals were negatively correlated with % >2 mm, with statistically significant negative correlations for Pb_{total}, Al_{acetic}, Fe_{acetic}, Pb_{acetic} and Zn_{acetic} (S-R, $p < 0.01$). Fe (II) was significantly positively correlated with Pb_{total}, Al_{acetic}, Fe_{acetic}, Pb_{acetic}, Zn_{acetic} (S-R, $p < 0.01$) and Zn_{total} (S-R, $p < 0.05$), and pH was significantly negatively

correlated with all pseudo-total and acetic acid metal concentrations apart from Fe_{total} , Mn_{total}, Ni_{total}, Cu_{acetic} and Mn_{acetic} (S-R, $p > 0.05$).

Apart from Fe (and Cr which did not have an acetic acid concentration), there were significant positive correlations between the pseudo-total and acetic acid concentrations of all metals (S-R, $p < 0.01$ for Cu, Mn, Ni, Pb and Zn, $p < 0.05$ for Al). There were three groups of metal concentrations which were particularly strongly intercorrelated: Cu_{total}, Pb_{total} and Zn_{total} ($r_s > 0.7$) and, Al_{acetic}, Fe_{acetic}, Ni_{acetic} and Zn_{acetic} ($r_s > 0.6$).

Organic matter was significantly positively correlated with % <63 µm (S-R, $r_s = 0.636$, $p < 0.01$) and significantly negatively correlated with % >2 mm (S-R, $r_s = -0.402$, $p < 0.05$). Fe (II) was significantly positively correlated with % organic matter ($r_s = 0.535$, $p < 0.01$) and significantly negatively correlated with % >2 mm ($r_s = -0.681$, $p < 0.01$). pH was significantly negatively correlated with % organic matter, % <63 µm and Fe (II) and significantly positively correlated with % >2 mm (S-R, $p < 0.05$).

Al total																			
0.782	Cr total																		
0.476	**0.794**	Cu total																	
0.341	**0.558**	0.355	Fe total																
0.061	0.348	0.441	**0.572**	Mn total															
0.412	**0.665**	0.401	**0.785**	0.523	Ni total														
0.352	0.495	**0.798**	-0.027	0.190	-0.042	Pb total													
0.455	**0.740**	**0.932**	0.389	**0.544**	0.338	**0.824**	Zn total												
0.472	**0.612**	**0.816**	-0.029	0.088	0.038	**0.868**	**0.768**	Al acetic											
0.302	0.628	**0.595**	0.418	0.245	0.482	0.225	0.418	0.535	Cu acetic										
0.515	**0.525**	**0.605**	-0.225	-0.250	-0.042	**0.678**	**0.533**	**0.785**	0.278	Fe acetic									
0.010	0.368	**0.550**	0.457	**0.879**	0.449	0.342	**0.624**	0.222	0.237	-0.127	Mn acetic								
0.536	**0.801**	**0.895**	0.320	0.458	**0.570**	**0.659**	**0.837**	**0.704**	0.462	**0.604**	**0.541**	Ni acetic							
0.100	0.130	0.424	-0.284	-0.150	-0.355	**0.755**	0.480	**0.735**	-0.027	**0.632**	0.067	0.292	Pb acetic						
0.503	**0.634**	**0.832**	-0.058	0.315	0.106	**0.929**	**0.888**	**0.851**	0.232	**0.708**	0.443	**0.792**	**0.643**	Zn acetic					
0.546	**0.675**	**0.845**	0.108	0.296	0.177	**0.835**	**0.867**	**0.805**	0.285	**0.697**	0.400	**0.801**	0.504	**0.902**	OM				
0.562	**0.514**	**0.578**	0.125	0.151	0.392	0.394	0.493	0.367	0.254	0.465	0.177	**0.690**	0.033	0.482	**0.636**	% <63um			
-0.265	-0.128	-0.238	0.405	0.359	0.422	**-0.630**	-0.288	**-0.600**	0.138	**-0.684**	0.224	-0.155	**-0.770**	**-0.549**	-0.402	-0.009	% >2mm		
0.090	0.054	0.337	-0.481	-0.266	-0.496	**0.597**	0.403	**0.592**	-0.100	**0.649**	-0.016	0.234	**0.731**	**0.562**	**0.535**	0.181	**-0.681**	Fe (II)	
-0.466	**-0.578**	**-0.759**	0.096	-0.029	0.013	**-0.807**	**-0.732**	**-0.822**	-0.343	**-0.740**	-0.223	**-0.620**	**-0.576**	**-0.797**	-0.808	**-0.434**	**0.582**	**-0.630**	pH

Figure 4.25: Scatter plots, histograms and correlations between all 20 variables across the Sutcliffe Park August data set. Spearmans Rank correlation coefficients significant at p <0.01 are shown in large and bold font, those significant at p <0.05 are shown in large font, and those not significant (p > 0.05) are shown in small font.

(ii) Contrasts in sediment properties across space

The median values for metal concentrations, % organic matter, % <63 µm, % >2 mm, Fe (II) concentrations and pH in the whole Sutcliffe Park August data set, for the restored and unrestored stretch and for the different bed sediment types are presented in Table 4.14. Mann-Whitney U (M-W), Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in sediment properties between the restored and unrestored stretch and the three bed sediment types that were present at the site (Table 4.15).

As seen previously in the multi-site data set, there were large differences in concentrations for different metals. The highest median pseudo-total metal concentrations were Fe_{total} and Al_{total} (median concentrations 33,800 $mgkg^{-1}$ and 12,000 $mgkg^{-1}$ respectively) and the lowest concentrations for Ni_{total} and Cr_{total} (median concentrations 33.4 $mgkg^{-1}$ and 35.5 $mgkg^{-1}$ respectively) (Table 4.14). In comparison however, the highest median acetic metal concentrations were Fe_{acetic}, Mn_{acetic} and Zn_{acetic} (median concentration 227 $mgkg^{-1}$, 185 $mgkg^{-1}$ and 97 $mgkg^{-1}$ respectively) and the lowest median concentrations were Pb_{acetic}, Ni_{acetic} and Cu_{acetic} (2.15 $mgkg^{-1}$, 2.90 $mgkg^{-1}$ and 5.90 $mgkg^{-1}$ respectively) (Table 4.14). The medians of the grain size descriptors were different from those found for the multi-site data set, with a higher median % <63 µm (68.2%) than % >2 mm (24.2%) (Table 4.14). The median pH (7.23) indicates that the sediments were pH neutral.

Overall, the restored stretch had higher median concentrations of all metals apart from Fe_{total}, Mn_{total}, Mn_{acetic} and Pb_{acetic} than the unrestored stretch (Table 4.14), although the only significant differences were for Al_{total}, Cr_{total}, Fe_{acetic} (M-W, $p < 0.05$, Table 4.15). Similarly, median % organic matter, Fe (II) concentrations and % <63 µm were higher in the restored stretch as opposed to the unrestored stretch (Table 4.14), although again this was only statistically significant for % <63 µm (M-W, $p < 0.01$, Table 4.15). The median % >2 mm and pH were greater in the unrestored stretch as opposed to the restored stretch (Table 4.14). However these were not statistically significant (K-W, $p = 0.934$ and $p = 0.174$, respectively Table 4.15).

In relation to bed sediment type (note that there were no sand samples at Sutcliffe Park), in-channel vegetation sediment samples had the highest median metal concentrations for all metals apart from Fe_{total}, Mn_{total} and Mn_{acetic} which were highest in the gravel samples and Pb_{acetic} which was highest in the finer samples (Table 4.14). Gravel samples had the lowest median metal concentrations for all metals apart from $Fe_{total,}$ Ni_{total} and Fe_{acetic} which were lowest in the finer samples and Mn_{total} and Mn_{acetic} which were lowest in the in-channel vegetation sediment samples (Table 4.14). Some of these differences were statistically significant (Table 4.15). In-

channel vegetation sediment samples had significantly higher concentrations of Al_{total}, Cr_{total} , Cu_{total} and Ni_{acetic} than the gravel samples and finer samples had significantly higher concentrations of Pb_{acetic} than gravel samples (K-W, $p < 0.05$, Table 4.15). $Pb_{total,}$ Zn_{total}, Al_{acetic}, Fe_{acetic} and Zn_{acetic} concentrations were significantly higher in both the finer and in-channel vegetation sediment samples than the gravel samples (K-W, $P < 0.05$, Table 4.15).

In-channel vegetation samples and gravel samples had the highest and lowest, respectively, median % organic matter and % <63 µm, and conversely the lowest and highest, respectively, % >2 mm (Table 4.14). Statistically, % organic matter was significantly higher in the finer and in-channel vegetation sediment samples than the gravel samples (K-W, $p = 0.001$, Table 4.15) and % <63 µm significantly higher in the in-channel vegetation sediment samples than the gravel samples (K-W, $p = 0.034$, Table 4.15). Percentage >2 mm were significantly higher in the gravel samples than both the finer and in-channel vegetation sediment samples (K-W, $p = 0.000$, Table 4.15). Median Fe (II) concentrations were highest, and statistically significantly greater, in the finer and in-channel vegetation sediment samples (Table 4.14, K-W, $p = 0.000$, Table 4.15).

Although pH median values were neutral for all bed sediment types (Table 4.14), they were significantly higher in the gravel samples as opposed to the finer and in-channel vegetation sediment samples (K-W, $p = 0.000$, Table 4.15).

Table 4.14: Median pseudo-total and acetic acid sediment metal concentrations and characteristics for the site (Sutcliffe Park August), restored/unrestored stretch and bed sediment types (3 s.f.). (Note Pb_{acetic} concentrations in Gravel are affected by replacement of <LoD and there were no sand samples at the Sutcliffe Park site).

Variable	Site	Restored	Unrestored	Gravel	Finer	In-channel vegetation
Al_{total} ($mgkg^{-1}$)	12,000	16,000	7,230	7,720	13,400	26,800
Cr_{total} ($mgkg^{-1}$)	35.5	42.1	26.6	30.3	34.0	47.0
Cu_{total} ($mgkg^{-1}$)	83.8	162	57.3	52.8	111	196
Fe_{total} ($mgkg^{-1}$)	33,800	33,700	37,600	38,400	32,000	36,600
Mn_{total} ($mgkg^{-1}$)	444	379	650	587	394	363
Ni_{total} ($mgkg^{-1}$)	33.4	33.8	28.9	34.1	30.0	38.4
Pb_{total} ($mgkg^{-1}$)	107	142	94.1	47.0	157	186
Zn_{total} ($mgkg^{-1}$)	324	452	272	187	396	595
Al_{acetic} ($mgkg^{-1}$)	66.1	76.8	61.0	44.1	80.1	84.7
Cu_{acetic} ($mgkg^{-1}$)	5.90	6.54	3.96	5.09	4.98	7.41
Fe_{acetic} ($mgkg^{-1}$)	227	416	122	119	341	504
Mn_{acetic} ($mgkg^{-1}$)	185	165	230	226	172	165
Ni_{acetic} ($mgkg^{-1}$)	2.90	4.74	2.40	2.44	3.63	5.26
Pb_{acetic} ($mgkg^{-1}$)	2.15	2.09	2.18	1.00	2.86	2.09
Zn_{acetic} ($mgkg^{-1}$)	97.0	172	92.3	52.5	151	204
% Organic matter	6.26	17.8	5.17	4.20	12.3	27.9
% <63 µm	68.2	85.9	26.1	49.6	56.5	87.1
% >2 mm	24.2	24.2	51.9	95.2	10.0	19.8
Fe (II) (mgl^{-1})	0.77	0.81	0.62	0.25	1.07	0.94
pH	7.23	7.11	7.46	7.64	7.14	7.01

Table 4.15: Statistically significant spatial differences in sediment metal concentrations (not granulometrically corrected) and characteristics of sediment samples in the Sutcliffe Park August data set identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s. = not significant, R = Restored, U = Unrestored, G = Gravel, F = Finer and ICV = In-channel vegetation).

	Restored/Unrestored		Bed sediment type	
Variable	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
Al_{total} ($mgkg^{-1}$)	0.004	R > U	0.028	ICV > G
Cr_{total} ($mgkg^{-1}$)	0.016	R > U	0.033	ICV > G
Cu_{total} ($mgkg^{-1}$)	0.091	n.s.	0.016	ICV > G
Fe_{total} ($mgkg^{-1}$)	0.978	n.s.	0.075	n.s.
Mn_{total} ($mgkg^{-1}$)	0.305	n.s.	0.373	n.s.
Ni_{total} ($mgkg^{-1}$)	0.360	n.s.	0.052	n.s.
Pb_{total} ($mgkg^{-1}$)	0.560	n.s.	0.001	F, ICV > G
Zn_{total} ($mgkg^{-1}$)	0.390	n.s.	0.026	F, ICV > G
Al_{acetic} ($mgkg^{-1}$)	0.212	n.s.	0.001	F, ICV > G
Cu_{acetic} ($mgkg^{-1}$)	0.063	n.s.	0.058	n.s.
Fe_{acetic} ($mgkg^{-1}$)	0.007	R > U	0.000	F, ICV > G
Mn_{acetic} ($mgkg^{-1}$)	0.212	n.s.	0.857	n.s.
Ni_{acetic} ($mgkg^{-1}$)	0.051	n.s.	0.045	ICV > G
Pb_{acetic} ($mgkg^{-1}$)	0.750	n.s.	0.001	F > G
Zn_{acetic} ($mgkg^{-1}$)	0.360	n.s.	0.001	F, ICV > G
% Organic matter	0.102	n.s.	0.001	F, ICV > G
% <63 µm	0.001	R > U	0.034	ICV > G
% >2 mm	0.934	n.s.	0.000	G > F, ICV
Fe (II) (mgl^{-1})	0.560	n.s.	0.000	ICV, F > G
pH	0.174	n.s.	0.000	G > F, ICV

As stated earlier, fine sediments (<63 µm, silt and clay) are known to have a large influence upon metal concentrations with increasing proportions of silt and clay resulting in increased metal concentrations in sediments, as was seen in the whole data set (Section 4.4.2 (ii)). This can hinder comparisons of metal concentrations between sediment samples of varying grain size. Focusing on the statistically significant correlations, the smaller Sutcliffe Park August data set also showed positive correlations between % <63 µm and metals and negative correlations between >2 mm (gravel) and metals (Figure 4.25). Therefore, granulometric correction of metal concentrations was made to produce normalised metal ratios (Section 3.4.2 in Chapter 3) and the data reanalysed for spatial differences, to see if there were underlying differences in metal concentrations between the different bed sediment types which were not due to grain size differences (Table 4.16).

Following granulometric correction of metal concentrations, there were more significant differences between the restored and unrestored stretches than between the different bed sediment types. All metals, apart from $Cu_{totalcorrec}$ and $Fe_{aceticcorrec}$, showed a significant difference between the restored and unrestored stretch (M-W, p = <0.05) with the unrestored stretch having higher normalised metal ratios than the restored stretch. Only $Fe_{totalcorrec}$ and $Fe_{aceticcorrec}$ were significantly different (K-W, p = 0.047 and p = 0.007 respectively) between the different bed sediment types. Gravel samples had significantly higher normalised metal ratios of $Fe_{totalcorrec}$ than the in-channel vegetation sediment samples, and the finer samples had significantly higher normalised metal ratios of $Fe_{aceticcorrec}$ than the gravel samples.

Table 4.16: Statistically significant spatial differences in normalised metal ratios of sediment samples in the Sutcliffe Park August data set identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests followed by Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s. = not significant, R = Restored, U = Unrestored, G = Gravel, F = Finer, ICV = In-channel vegetation).

	Restored/Unrestored		**Bed sediment type**	
Variable	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
$Al_{totalcorrec}$	0.038	U > R	0.792	n.s.
$Cr_{totalcorrec}$	0.016	U > R	0.936	n.s.
$Cu_{totalcorrec}$	0.142	n.s.	0.164	n.s.
$Fe_{totalcorrec}$	0.002	U > R	0.047	G > ICV
$Mn_{totalcorrec}$	0.000	U > R	0.185	n.s.
$Ni_{totalcorrec}$	0.001	U > R	0.106	n.s.
$Pb_{totalcorrec}$	0.001	U > R	0.084	n.s.
$Zn_{totalcorrec}$	0.002	U > R	0.298	n.s.
$Al_{aceticcorrec}$	0.001	U > R	0.169	n.s.
$Cu_{aceticcorrec}$	0.014	U > R	0.909	n.s.
$Fe_{aceticcorrec}$	0.760	n.s.	0.007	F > G
$Mn_{aceticcorrec}$	0.000	U > R	0.288	n.s.
$Ni_{aceticcorrec}$	0.003	U > R	0.475	n.s.
$Pb_{aceticcorrec}$	0.004	U > R	0.066	n.s.
$Zn_{aceticcorrec}$	0.003	U > R	0.151	n.s.

(iii) Proportion of acetic acid metals of pseudo-total metals

The proportion of the acetic acid extractable metal concentrations in the samples in relation to the pseudo-total metal concentrations is presented in Table 4.17 (care should be given to interpretation due to the replacement of <LoD acetic acid Pb concentrations in the gravel samples). Acetic acid extractable metal concentrations provide an indication of the

concentration of metal which is more bioavailable, being only weakly sorbed and associated with carbonates (Trujillo-Cardenas *et al*., 2010, Filgueiras *et al.*, 2002 and Gleyzes *et al*., 2002). Therefore increasing proportions of acetic acid extractable metal concentrations to pseudo-total metal concentrations suggests greater bioavailability of those metals to the environment. Across the site there were large differences in the mean proportion of acetic acid extractable concentrations between the different metals. Al, Fe and Pb had the lowest mean proportions (<5%) and Mn and Zn had the highest mean proportions (>30%) (note: the higher sediment drying temperature was found to increase and decrease the acetic acid extractable concentrations for Al and Fe respectively). The restored stretch samples had higher mean proportions of acetic acid extractable concentrations for all metals, apart from Al and Zn, than the unrestored stretch samples. There was no clear difference between the different bed sediment types. Gravel samples had the lowest and in-channel vegetation or finer sediment samples the highest, mean proportion of acetic acid extractable concentrations of Fe, Mn and Ni. Conversely, in-channel vegetation sediment samples had the lowest, and gravel samples the highest, mean proportion of acetic acid extractable concentrations of Cu and Pb. Finer samples had the highest mean proportion of acetic acid extractable concentrations of Al and Zn.

Table 4.17: Mean (± 1 standard deviation) proportion (%) of sediment acetic acid metal concentration to pseudo-total metal concentration.

Metal	Site	Restored	Unrestored	Gravel	Finer	In-channel vegetation
Al	0.53 ± 0.33	0.44 ± 0.18	0.83 ± 0.36	0.53 ± 0.30	0.72 ± 0.37	0.47 ± 0.25
Cu	7.65 ± 4.96	8.89 ± 6.43	7.31 ± 1.11	11.34 ± 5.73	5.38 ± 2.29	4.83 ± 2.29
Fe	0.89 ± 0.64	1.01 ± 0.49	0.72 ± 0.68	0.29 ± 0.20	1.30 ± 0.58	1.29 ± 0.33
Mn	40.18 ± 13.96	41.27 ± 14.09	38.57 ± 14.36	33.84 ± 17.90	43.63 ± 7.93	43.63 ± 11.77
Ni	11.16 ± 5.28	12.40 ± 6.03	9.29 ± 3.38	6.50 ± 2.44	13.94 ± 4.46	14.91 ± 4.25
Pb	2.40 ± 1.46	2.47 ± 1.59	2.30 ± 1.32	3.01 ± 1.67	2.23 ± 1.35	1.51 ± 0.63
Zn	34.97 ± 8.80	34.54 ± 4.23	35.62 ± 13.34	29.53 ± 9.03	40.77 ± 7.12	34.26 ± 2.85

(iv) Factors explaining the variations in sediment properties

Principal Component Analysis (PCA) was used to explore the data set to understand the underlying factors explaining the variations in sediment properties (Section 3.4.3 in Chapter 3). PCA reduces much of the variance in a large multivariate data set to a relatively small number

of Principal Components (PCs), with the first explaining the largest proportion of variance and each subsequent PC explaining less variability. Additionally, each sample has a score on each PC (known as a factor score), which shows its relative location along the PC in comparison with other samples and the strength of the association of each sample to that PC.

This was initially undertaken on the raw data set (not granulometrically corrected) and then on the granulometrically corrected data set. Differences in the sample factor scores for different groupings (restored/unrestored and bed sediment type) were then explored through scatter plots and Mann-Whitney U and Kruskal-Wallis tests. However differences in bed sediment types in the granulometrically corrected data set were not explored since the grain size influence had been removed through use of normalised metal ratios. Interpretation of the PCs, and separation of groupings along the PCs, is discussed in Section 4.5.3.

Raw data set (not granulometrically corrected)

With the raw data set, three PCs were extracted with eigenvalues >1 which accounted for 81% cumulative variance after a varimax rotation (Table 4.18). Cu_{total}, Pb_{total}, Zn_{total}, Al_{acetic}, Fe_{acetic}, Pb_{acetic}, Zn_{acetic}, % organic matter and Fe (II) had high positive loadings, and % >2 mm and pH had high negative loadings, on PC1, which accounted for 42% of the variance. Al_{total}, Cr_{total}, $Ni_{total,}$ $Cu_{acetic,}$ Ni_{acetic} and % <63 µm had high positive loadings on PC2, which accounted for 22% of the variance. The final PC, PC3, just had high positive loadings of Mn_{total} and Mn_{acetic}, which accounted for 17% of the variance.

Table 4.18: Percentage variance explained and variable loadings on the first three components following the application of Principal Component Analysis to the Sutcliffe Park August raw data set (not granulometrically corrected) (loadings >0.6 are large and bold, loadings >0.4 but <0.6 are large, loadings <0.4 are small and italic).

	Principal Component		
	1	**2**	**3**
Eigenvalue	9.9	4.7	1.8
Variance Explained	42%	22%	17%
	Principal Component Loadings after Rotation		
Al_{total}	*0.337*	**0.771**	*-0.171*
Cr_{total}	0.413	**0.832**	*0.221*
Cu_{total}	**0.708**	0.512	0.412
Fe_{total}	*-0.246*	0.594	0.554
Mn_{total}	*0.007*	*0.175*	**0.931**
Ni_{total}	*-0.217*	**0.783**	0.446
Pb_{total}	**0.925**	*0.101*	*0.197*
Zn_{total}	**0.738**	*0.378*	0.513
Al_{acetic}	**0.896**	*0.254*	*0.051*
Cu_{acetic}	*0.123*	**0.628**	*0.198*
Fe_{acetic}	**0.810**	*0.331*	*-0.350*
Mn_{acetic}	*0.207*	*0.081*	**0.929**
Ni_{acetic}	0.597	**0.608**	*0.378*
Pb_{acetic}	**0.844**	*-0.264*	*-0.077*
Zn_{acetic}	**0.895**	*0.245*	*0.261*
% Organic Matter	**0.822**	*0.376*	*0.223*
% <63 µm	*0.354*	**0.623**	*0.018*
% >2 mm	**-0.751**	*0.171*	0.411
Fe (II)	**0.811**	*-0.279*	*-0.227*
pH	**-0.858**	*-0.260*	*0.002*

Figure 4.26 plots the sample factor scores on PC1, PC2 and PC3, coded according to their location in the restored or unrestored stretch and their bed sediment type to see if there is any separation within these groupings along PC1, PC2 or PC3. Visually there appears to be a separation of the restored and unrestored stretch samples along PC2, with the restored stretch samples showing positive factor scores and the unrestored stretch samples showing negative factor scores. The bed sediment types appear to be separating along PC1 with the gravel samples showing negative factor scores and the finer and in-channel vegetation sediment samples showing positive factor scores, and along PC2 with the gravel samples showing negative factor scores and the in-channel vegetation samples showing positive factor scores.

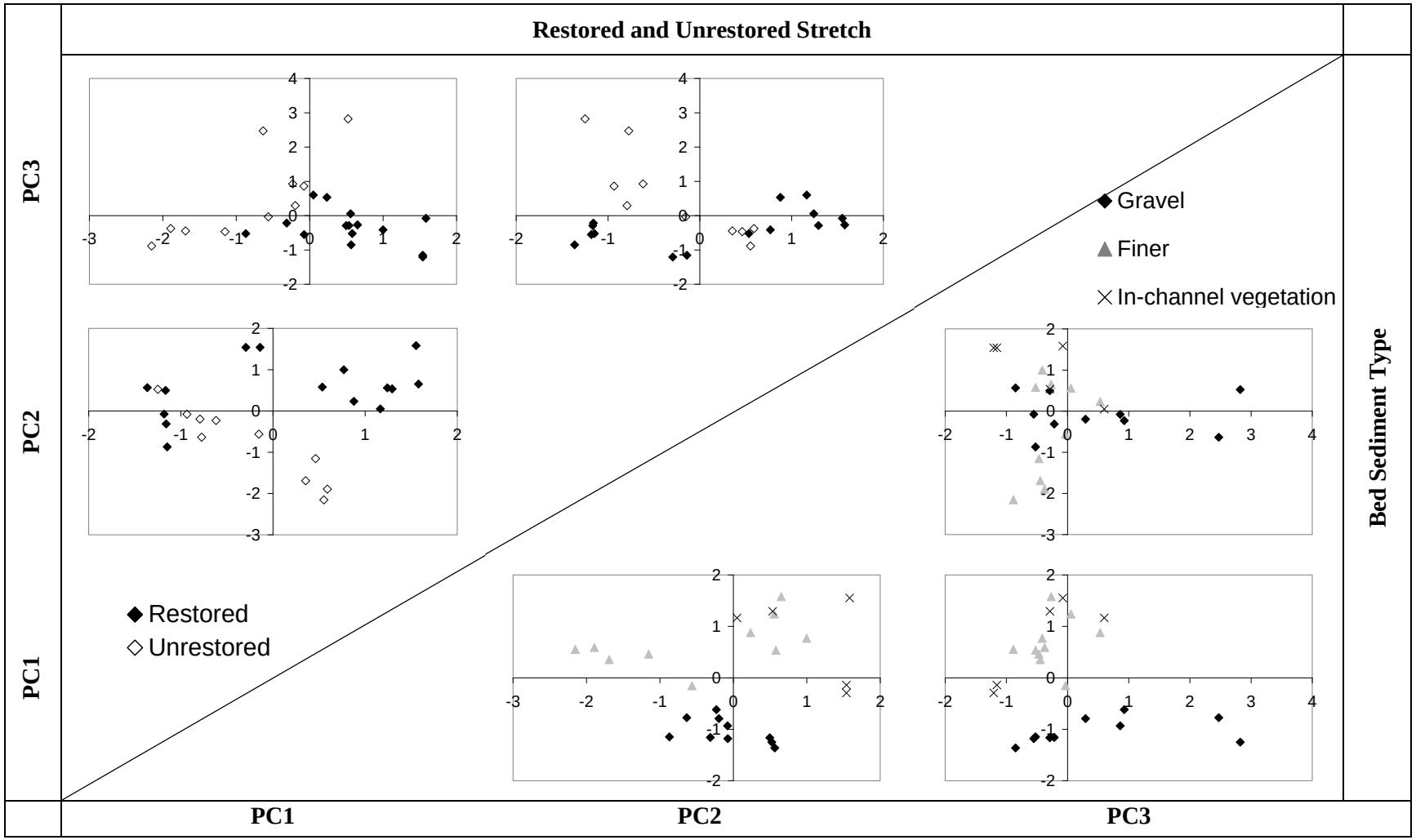


Figure 4.26: Plots of sample factor scores on PC1, PC2 and PC3 coded by restored and unrestored stretch and bed sediment type for the Sutcliffe Park August raw data set (no granulometric correction).

These apparent separations were confirmed through M-W, K-W and post-hoc S-D-C-F tests (Table 4.19). K-W tests and post-hoc S-D-C-F tests applied to the sample factor scores on PC1 identified that both finer and in-channel vegetation sediment samples had significantly greater scores on PC1 than the gravel samples (K-W, p = 0.000). The in-channel vegetation samples had significantly greater scores on PC2 than the gravel samples (K-W, p = 0.042). Also on PC2 the restored stretch samples had significantly greater factor scores than the unrestored stretch samples (M-W, p = 0.001).

Table 4.19: Results of Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests applied to sample scores on the first three Principal Components estimated from the raw Sutcliffe Park August data set according to the restored/unrestored and bed sediment type characteristics of the samples (n.s. = not significant, G = Gravel, F = Finer, ICV = In-channel vegetation).

	Restored/Unrestored		**Bed sediment type**	
PC	**M-W p value**	**Significant differences**	**K-W p value**	**Significant differences**
PC1	0.332	n.s.	0.000	F, ICV > G
PC2	0.001	R > U	0.042	ICV > G
PC3	0.091	n.s.	0.368	n.s.

Granulometrically corrected data set

With the granulometrically corrected data set, three PCs were extracted with eigenvalues >1 which accounted for 85% cumulative variance after a varimax rotation (Table 4.20) (%<63 µm variable has been removed as this was used to granulometrically correct the metal concentrations). $Cr_{totalcorrec}$, $Cu_{totalcorrec}$, $Mn_{totalcorrec}$, $Pb_{totalcorrec}$, $Zn_{totalcorrec}$, $Al_{aceticcorrec}$, $Cu_{aceticcorrec}$, $Mn_{aceticcorrec}$, $Ni_{aceticcorrec}$, $Pb_{aceticcorrec}$ and $Zn_{aceticcorrec}$ had high positive loadings on PC1, which accounted for 44% of the variance. PC2 had high positive loadings of $Fe_{totalcorrec}$, $Ni_{totalcorrec}$ and pH and high negative loadings of $Fe_{aceticcorrec}$ and % organic matter, which accounted for 21% of the variance. PC3 had a high positive loading of $Fe_{aceticcorrec}$ and Fe (II) and high negative loading of % >2 mm, which accounted for 20% of the variance.

Table 4.20: Percentage variance explained and variable loadings on the first three components following the application of Principal Component Analysis to the Sutcliffe Park August granulometrically corrected data set (loadings >0.6 are large and bold, loadings >0.4 but <0.6 are large, loadings <0.4 are small and italic).

	Principal Component		
	1	**2**	**3**
Eigenvalue	10.3	4.5	1.4
Variance Explained	44%	21%	20%
	Principal Component Loadings after Rotation		
$Al_{totalcorrec}$	0.482	0.534	0.479
$Cr_{totalcorrec}$	**0.745**	0.446	*0.269*
$Cu_{totalcorrec}$	**0.828**	*-0.174*	*0.391*
$Fe_{totalcorrec}$	0.434	**0.863**	*0.007*
$Mn_{totalcorrec}$	**0.851**	*0.271*	*-0.265*
$Ni_{totalcorrec}$	0.555	**0.779**	*-0.062*
$Pb_{totalcorrec}$	**0.811**	*0.040*	0.456
$Zn_{totalcorrec}$	**0.937**	*0.102*	*0.278*
$Al_{aceticcorrec}$	**0.771**	*0.278*	0.477
$Cu_{aceticcorrec}$	**0.622**	0.543	*0.211*
$Fe_{aceticcorrec}$	*0.326*	**-0.102**	**0.828**
$Mn_{aceticcorrec}$	**0.916**	*0.140*	*-0.223*
$Ni_{aceticcorrec}$	**0.927**	*0.074*	*0.224*
$Pb_{aceticcorrec}$	**0.724**	*0.171*	0.537
$Zn_{aceticcorrec}$	**0.880**	*0.055*	0.414
% Organic Matter	*0.151*	**-0.850**	*0.241*
% >2 mm	*-0.096*	*0.251*	**-0.842**
Fe (II)	*0.126*	-0.505	**0.639**
pH	*-0.186*	**0.727**	-0.502

Figure 4.27 plots the factor scores of each sample on PC1, PC2 and PC3 and codes the samples according to restored and unrestored stretch. Visually, the plots appear to show a separation between restored and unrestored stretch samples along both PC1 and PC2, with the restored stretch samples generally showing low (negative) factor scores and the unrestored stretch samples generally showing high (positive) factor scores.

These separations were confirmed to be statistically significant using M-W, K-W and post-hoc S-D-C-F tests (Table 4.21). On PC1, a M-W test indicated that the unrestored stretch samples had significantly greater factor scores than the restored stretch samples (M-W, $p = 0.005$). A similar separation was seen for PC2, with unrestored stretch samples having significantly greater factor scores than restored stretch samples (M-W, $p = 0.016$).

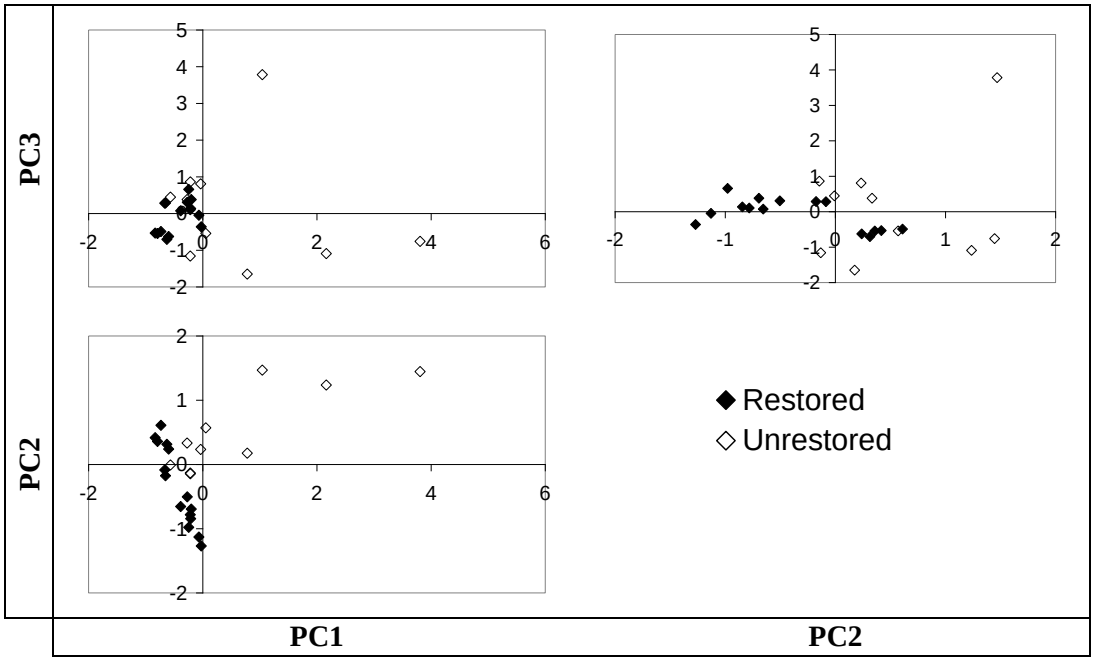


Figure 4.27: Plots of sample factor scores on PC1, PC2 and PC3 coded by restored and unrestored stretch for the Sutcliffe Park August data set granulometrically corrected.

Table 4.21: Results of Mann-Whitney U (M-W) tests applied to sample factor scores on the first three Principal Components estimated from the granulometrically corrected Sutcliffe Park August data according to the restored/unrestored characteristics of the samples (n.s. = not significant, R = Restored, U = Unrestored).

	Restored/Unrestored	
PC	**M-W p value**	**Significant differences**
PC1	0.005	U > R
PC2	0.016	U > R
PC3	1.000	n.s.

4.4.3 Metal storage

The storage of each metal in the sediment (in the <2 mm sediment fraction) was calculated for each site and restored/unrestored stretch at each site in order to allow a comparison to be made whilst taking in to account the varying depths and the spatial coverage of each bed sediment type at individual sites and within each restored and unrestored stretch. Calculations were made based on the mapped areas (Figures 4.15 to 4.18) and measured depths of the sediment types that were sampled within each stretch, and are presented in Table 4.22. Sutcliffe Park had the highest storage of Al, Cr, Cu and Zn and Bell Green the highest storage of Fe, Mn, Ni and Pb. Chinbrook Meadows had the lowest storage of all metals. At all sites, except for Bell Green, the restored stretch had greater storage of all metals as opposed to the unrestored stretch.

Conversely, at Bell Green all metals had greater storage in the unrestored stretch as opposed to the restored stretch.

Table 4.22: Calculated storage of metals in sediment (in the <2 mm fraction) at each site and within the restored and unrestored stretches at each site.

	Metal Storage (mg, in <2 mm fraction) (to 3 s.f.)							
	Al	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Beddington Park								
Site	189,000	785	2,110	476,000	7,830	510	3,630	6,700
Restored	143,000	599	1,580	374,000	6,010	404	2,700	4,920
Unrestored	45,600	186	537	102,000	1,820	106	928	1,780
Bell Green								
Site	269,000	1,090	14,300	1,480,000	18,000	1,150	5,860	10,600
Restored	84,900	484	1,030	402,000	6,070	387	1,200	3,010
Unrestored	185,000	604	13,300	1,080,000	11,900	760	4,660	7,540
Chinbrook Meadows								
Site	55,700	174	557	171,000	4,530	138	833	1,640
Restored	43,900	133	438	123,000	3,260	103	662	1,240
Unrestored	11,800	41.7	119	47,700	1,270	34.9	171	395
Sutcliffe Park								
Site	582,000	1,300	4,770	1,050,000	14,200	966	4,580	14,700
Restored	554,000	1,220	4,580	941,000	11,500	832	4,260	13,900
Unrestored	26,800	79.9	197	110,000	2,660	83.9	315	847

However, since all of the stretches had channels of differing dimensions (Figures 4.15 to 4.18), the metal storage was standardised to mg per m^2 channel, in order to allow for a more valid comparison (Table 4.23). Comparison on a per m^2 basis accounts for the changes in channel dimensions (widths and lengths (in terms of planform)) which exist between restored and unrestored stretches.

Table 4.23 shows that when standardised to mgm^{-2} channel Sutcliffe Park had the greatest metal storage of the sites for all metals, apart from Cu at Bell Green. Beddington Park had the lowest metal storage for the majority of metals (Al, Cu, Fe, Mn, Ni and Zn) and Chinbrook Meadows had the lowest metal storage for Cr and Pb. The three sites Beddington Park, Chinbrook Meadows and Sutcliffe Park still had a greater metal storage per m^2 of channel in the restored stretch as opposed to the unrestored stretch for all metals, although there were variations in the magnitude of difference between the restored and unrestored stretches at the sites. At Beddington Park the differences in the metal storage per m^2 channel between the restored and

unrestored stretch were small. At Chinbrook Meadows and Sutcliffe Park, however, the metal storage per m^2 channel were at least an order of magnitude greater in the restored as opposed to the unrestored stretch, apart from Ni at Chinbrook Meadows and Pb at Sutcliffe Park. At Bell Green, the majority of storage of metals per m^2 were greater in the unrestored as opposed to the restored stretch, apart from Cr.

Analysis of the data set in terms of the different bed sediment types shows that for all of the metals the storage per m^2 of channel consistently decreased in the order: in-channel vegetation sediment > finer sediment > sand sediment > gravel sediment, clearly showing the differences in metal storage per m^2 of channel cover of the different bed sediment types (Table 4.23).

Table 4.23: Calculated storage of metals in sediment (in the <2 mm sediment fraction) per m^2 of channel at each site, within the restored and unrestored stretches at each site and for each bed sediment type.

	Metal Storage (mgm^{-2} of channel, in <2 mm fraction)) (to 3 s.f.)							
	Al	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Beddington Park								
Site	149	0.62	1.67	376	6.18	0.40	2.87	5.29
Restored	157	0.66	1.73	409	6.58	0.44	2.96	5.39
Unrestored	129	0.53	1.52	290	5.15	0.30	2.63	5.04
Bell Green								
Site	225	0.91	12.0	1,240	15.0	0.96	4.90	8.82
Restored	202	1.15	2.46	959	14.5	0.92	2.86	7.18
Unrestored	237	0.78	17.1	1,390	15.3	0.98	6.00	9.70
Chinbrook Meadows								
Site	184	0.58	1.84	565	15.0	0.46	2.76	5.42
Restored	393	1.19	3.92	1,100	29.2	0.92	5.92	11.1
Unrestored	62.0	0.22	0.63	251	6.69	0.18	0.90	2.08
Sutcliffe Park								
Site	873	1.95	7.18	1,560	21.3	1.45	6.88	22.1
Restored	1,220	2.67	10.0	2,060	25.3	1.94	9.35	30.5
Unrestored	128	0.37	0.95	466	12.7	0.40	1.50	4.04
Bed Sediment Type								
Gravel	129	0.512	1.10	652	7.47	0.564	2.55	3.85
Sand	357	1.35	2.97	945	14.57	0.888	5.93	10.71
Finer	762	2.16	7.88	1590	25.7	1.43	10.4	25.5
In-channel vegetation	1070	2.83	9.97	2180	31.6	1.96	11.9	31.5

4.4.4 Sediment quality

Metal concentrations from the whole data set were analysed using sediment quality guidelines to assess the potential impact upon both the aquatic ecosystem (Environment Agency draft freshwater quality guidelines, 2008) and human health (Dutch Intervention Values for human, plant and/or animal life, 2009).

Draft freshwater quality guidelines were published by the Environment Agency in 2008 for As, Cd, Cr, Cu, Pb, Ni and Zn (Environment Agency, 2008). These draft guidelines define two levels of concentrations for metals: the 'Threshold Effect Level' (TEL) and the 'Predicted Effect Level' (PEL) (Table 4.24). The TEL is the concentration below which sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms. The PEL is the lower limit of the range of concentrations associated with adverse biological effects. However, these concentrations are just triggers for further investigation since other environmental conditions, such as pH and organic matter content, have an impact upon the potential bioavailability of these metals to aquatic organisms.

Table 4.24: Environment Agency draft freshwater sediment quality guidelines Threshold Effects Level (TEL) and Predicted Effects Level (PEL) concentrations for the metals of interest (Environment Agency, 2008).

	TEL	PEL
Metal	**($mgkg^{-1}$ dry weight)**	
Cr	37.3	90
Cu	36.7	197
Ni	18	35.9
Pb	35	91.3
Zn	123	315

Figure 4.28 shows the percentage of samples in the whole data set which were below the TEL concentration, exceeded the TEL concentration (but were below the PEL concentration) and exceeded the PEL concentration for Cr, Cu, Ni, Pb and Zn. The TEL and PEL was exceeded for some samples for every metal. A greater percentage of samples exceeded the PEL than just TEL for Pb. Cu, Pb and Zn had a greater percentage of samples exceeding the guidelines than falling below the guidelines.

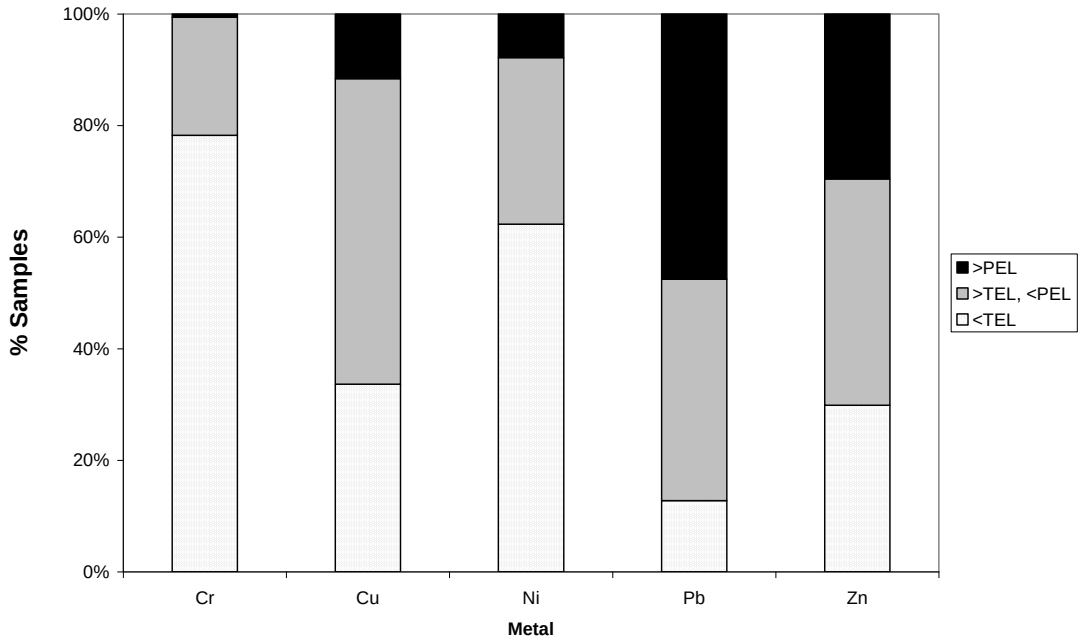


Figure 4.28: Percentage of samples in the whole data set exceeding Environment Agency sediment quality guidelines.

In relation to the sampling sites, all sites had some samples which exceeded TEL for every metal (Figure 4.29). Sutcliffe Park had the greatest percentage of samples exceeding the TEL for Cr, Cu and Ni. For Pb, Beddington Park and Bell Green had the greatest percentage of samples exceeding the guidelines, although Sutcliffe Park had the greatest percentage of samples exceeding PEL. For Zn, Bell Green and Sutcliffe Park had the greatest percentage of samples exceeding guidelines, but again Sutcliffe Park had the greatest percentage exceeding the PEL.

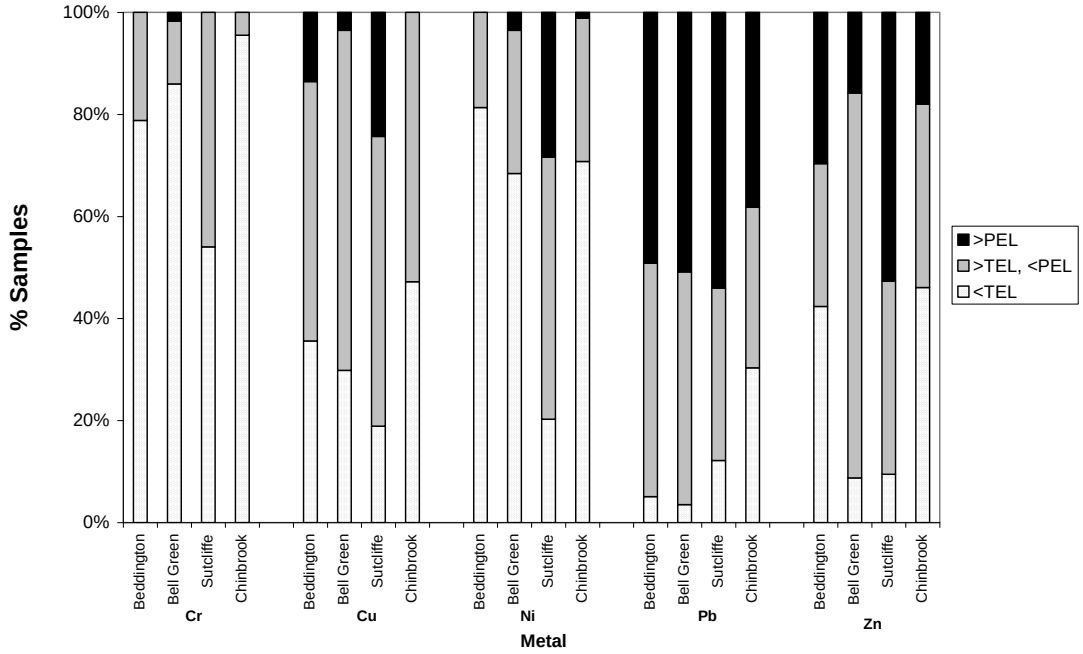


Figure 4.29: Percentage of samples by site exceeding Environment Agency sediment quality guidelines.

In comparison to the Environment Agency guidelines which focus solely upon hazards to aquatic organisms, those published by the Dutch Ministry of Housing, Spatial Planning and Environment focus upon hazards to humans, plants and animals (Dutch Ministry of Housing, Spatial Planning and Environment, 2009). The guidelines define intervention values for metals above which there is considered to be a serious case of contamination, and the functional properties of the soil for humans, plants and animals is seriously impaired or threatened (Table 4.25).

Table 4.25: Dutch sediment intervention values for the metals of interest (Dutch Ministry of Housing, Spatial Planning and Environment, 2009).

Metal	Intervention Value ($mgkg^{-1}$ dry weight)
Cu	190
Ni	100
Pb	530
Zn	720

The majority of samples in the whole data set did not exceed the intervention values (Figure 4.30). There were no exceedances of the intervention value for Ni and Pb. However, some samples exceeded the intervention value for Cu and Zn, with the greatest percentage of exceedances for Cu.

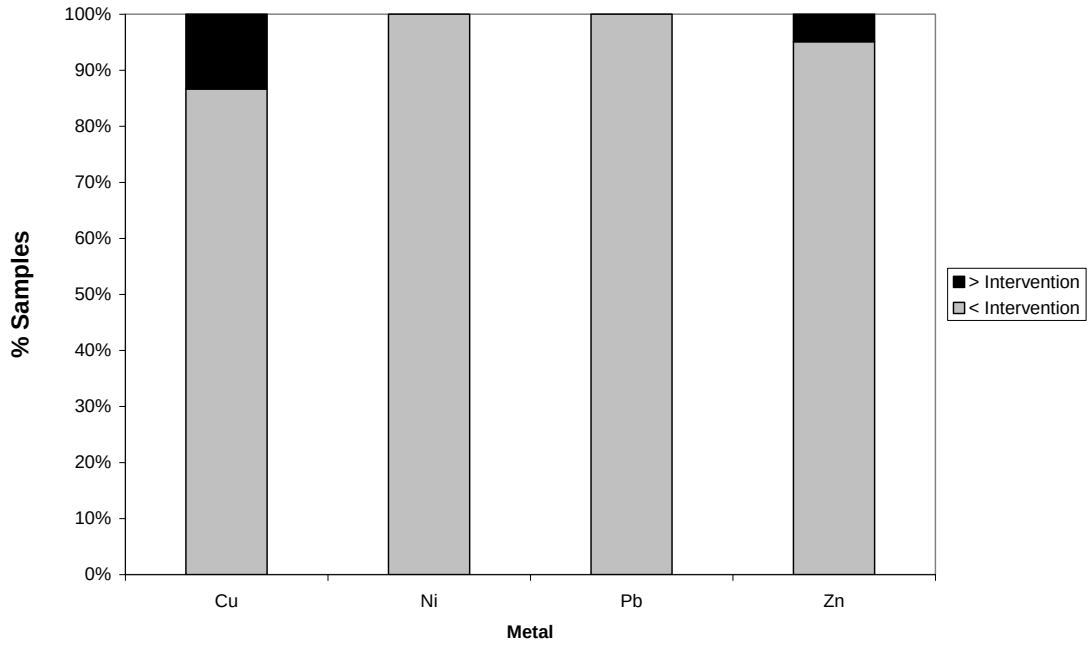


Figure 4.30: Percentage of samples in the whole data set exceeding Dutch intervention guidelines.

In terms of sites, no samples at any site exceeded the intervention value for Ni and Pb (Figure 4.31). Beddington Park, Bell Green and Sutcliffe Park had some samples which exceeded the intervention value for Cu, with Sutcliffe Park having the greatest percentage of exceedances. For Zn only Beddington Park and Sutcliffe Park had some samples which exceeded the intervention value, again with Sutcliffe Park having the greatest percentage of exceedances.

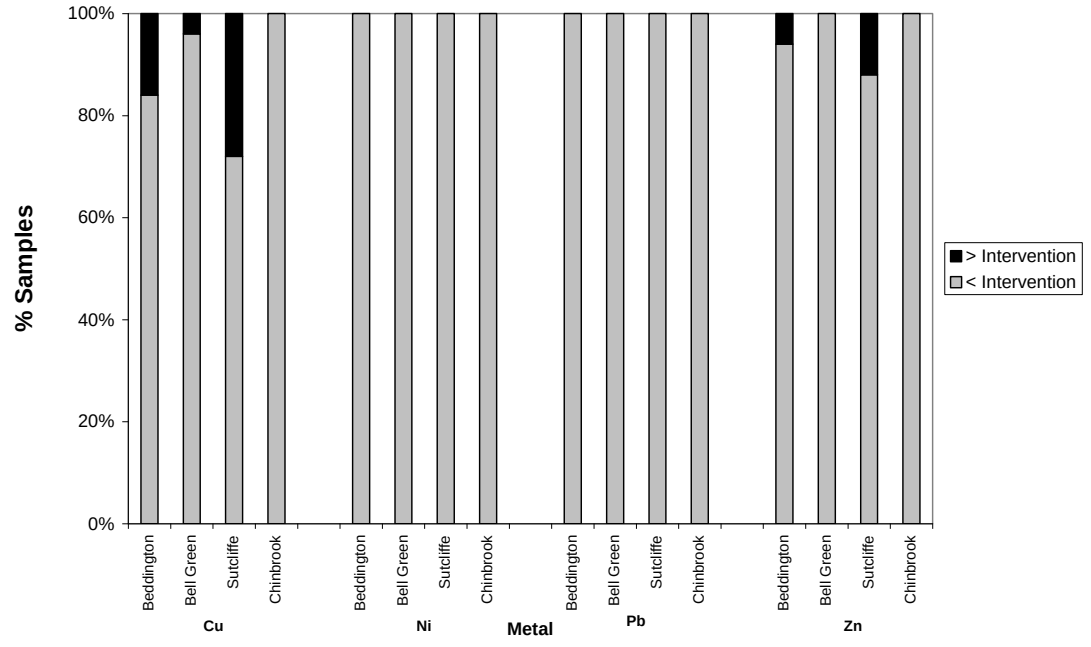


Figure 4.31: Percentage of samples by site exceeding Dutch intervention guidelines.

4.5 Discussion

In the following section the following research questions are discussed.

- Are there differences in the pattern and extent of sedimentation and in-channel vegetation growth between restored and unrestored stretches of urban rivers in London?

- What are the characteristics of sediment (metal concentrations, grain size etc.) retained within restored and unrestored stretches of urban rivers in London and to what extent do these characteristics vary in space and time?

- What factors explain the observed variations in metal concentrations and sediment characteristics in restored and unrestored urban rivers in London?

- To what extent are the sediments in London urban rivers potentially harmful to humans and ecosystems?

4.5.1 Contrasts in pattern and extent of sedimentation and in-channel vegetation growth between restored and unrestored stretches of urban rivers in London

Although all are classified as 'restored' stretches in the broad sense of the term, the four restored stretches used in this research have undergone different types and degrees of restoration. The restored stretches at Sutcliffe Park, Chinbrook Meadows and Bell Green are all newly created river channels (Quaggy Waterways Action Group, 2011; River Restoration Centre, 2007; and, Cameron Taylor Bedford, 2005). At Sutcliffe Park and Chinbrook Meadows these are river channels created following historical river channel courses, defining them as 'restoration' or 'rehabilitation' schemes (Clifford, 2007; Findlay & Taylor, 2006; and, Brookes & Shields, 1996). At Bell Green, a new course for the river was created in order to avoid contamination issues from a historical gas works site, defining it as a 'creation' scheme (Clifford, 2007; Findlay & Taylor, 2006; and, Brookes & Shields, 1996). At Beddington Park, the river channel has undergone minor modifications, defining it as an 'enhancement' scheme (Clifford, 2007; Findlay & Taylor, 2006; and, Brookes & Shields, 1996).

Another way of comparing the river stretches is to consider the degree of engineering that has been imposed. This can be done by using the planform type, cross-section type and reinforcement level descriptions used in the Urban River Survey (Gurnell *et al*., 2011; Boitsidis *et al.*, 2006; and, Davenport *et al*., 2004). At one end of the scale a typical highly modified unrestored urban river would have an engineered straight planform, an enlarged, two-stage

and/or resectioned cross-section and full reinforcement. At the other extreme, a typical restored urban river would have an engineered sinuous planform, a restored cross-section and no reinforcement. Table 4.26 defines each of the restored and unrestored stretches at the study sites according to its planform, cross-section and reinforcement.

In terms of planform, all unrestored stretches were engineered straight. The majority of the restored stretches were engineered sinuous, although at Beddington Park where minimal restoration work was undertaken the planform is classed as recovering. In terms of cross-section, the majority of sites had unrestored stretches which were resectioned and/or enlarged and restored stretches which were restored. At Bell Green however, due to the extent of engineering the restored stretch was also resectioned and enlarged. In terms of reinforcement, all unrestored stretches had some reinforcement. The restored stretch at Bell Green had full reinforcement and at Beddington Park the restored stretch had partial reinforcement by wooden toe boarding on both banks.

Table 4.26 indicates that a typical unrestored urban river is shown at the Chinbrook Meadows unrestored stretch, and a typical restored urban river is shown at the Chinbrook Meadows and Sutcliffe Park restored stretches. Bell Green restored stretch was closer to a typical unrestored urban river in terms of its cross-section and reinforcement due to the highly engineered nature of the stretch due to contamination issues.

Table 4.26: Styles of stretch engineering at the study sites in terms of planform type, cross-section type and reinforcement level (descriptions from the Urban River Survey, Gurnell *et al*., 2011) U = unrestored R = restored.

	Planform				Cross-section						Reinforcement						
Site	**Engineered Straight**	**Engineered Sinuous**	**Recovering**	**Semi-natural**	**Enlarged**	**Two-stage**	**Resectioned**	**Cleaned**	**Restored**	**Semi-natural**	**Full**	**Both banks**	**Bed and one bank**	**One bank**	**Partial both banks**	**Bed**	**None**
Beddington Park	**U**		**R**				**U**		**R**					**U**	**R**		
Bell Green	**U**	**R**			**R&U**		**R**		**R**		**R**	**U**					
Chinbrook Meadows	**U**	**R**			**U**		**U**		**R**		**U**						**R**
Sutcliffe Park	**U**	**R**					**U**		**R**						**U**		**R**

Differences in the patterns of sediment deposition in the stretches can be explained by differences in flow patterns (Figures 4.15 to 4.18). If sediment is available, areas of sand and finer sediment deposition and in-channel vegetation growth will develop within a river channel in areas of lower flow velocities, due to the lower velocities required for sand and finer sediment to be deposited out of the water column compared to coarser sediments and the lower velocities required for macrophyte colonisation (Charlton, 2009 and Franklin *et al*., 2008). Flow velocity within a river channel is controlled primarily by channel slope, cross-section and roughness (Charlton, 2009). River channels with a straight planform and a near-trapezoidal (resectioned) cross-section will generally have a higher overall velocity than river channels with a meandering planform and complex cross-section due to the increased channel slope and lower roughness in the channel. In the straight, near trapezoidal river channels a simpler flow pattern will occur with highest flow velocities in the centre of the channel and lowest flow velocities, and hence areas of sand and finer sediment deposition and in-channel vegetation growth, along the banks (Allen, 1977). However, in over-widened straight channels this deposition may occur more widely across the channel bed, due to the increased wetted perimeter and thus channel resistance (Charlton, 2009). In the more complex river channel forms, more variable flow patterns will occur which will result in a more heterogeneous sediment deposition and in-channel vegetation growth pattern (Charlton, 2009). For example, meandering river planforms result in low flow velocities and associated finer sediment deposition on the inside of bends (Dietrich, 1987).

All of the unrestored stretches had depositions of sand and finer sediment and in-channel vegetation growth areas adjacent to the banks, which were particularly long and linear at Beddington Park and Sutcliffe Park (Figures 4.15 to 4.18). This is due to the unrestored stretches having engineered straight planforms resulting in greater channel slopes and thus overall higher flow velocities, with the areas of sediment deposition along the banks associated with bank resistance (Charlton, 2009) (Table 4.26).

At the restored sites, although having sediment deposition and in-channel vegetation growth associated with the banks, more complex patterns also occurred (Figures 4.15 to 4.18). Both Beddington Park and Bell Green had some mid-channel vegetation growth, with associated finer and sand sediment deposits at Beddington Park (Figures 4.15 and 4.16). At Chinbrook Meadows and Sutcliffe Park finer sediment was deposited across the whole channel in some areas and additionally at Sutcliffe Park there was an area of in-channel vegetation growth across the whole channel (Figures 4.17 and 4.18). This more complex pattern of sediment deposition can be related to the planform and cross-sections of the restored stretches. All had engineered sinuous planforms, apart from Beddington Park which was recovering and was more sinuous

than its adjacent unrestored stretch. All, apart from Bell Green, did not have resectioned cross-sections, meaning overall lower flow velocities and more complex flow patterns (Charlton, 2009) (Table 4.26). The time elapsed since the restoration of the stretch may also have an impact upon the observed accumulation of sand and finer sediment and in-channel vegetation growth. However, the two youngest stretches (Sutcliffe Park and Chinbrook Meadows, seven and eight years since restoration respectively) showed the highest proportion of finer sediment and that accumulating around in-channel vegetation of the restored stretches. The oldest stretch, Bell Green (16 years since restoration), showed the lowest proportion of finer sediment accumulation (Figure 4.19), suggesting that time was not a factor at these study sites.

At Beddington Park and Bell Green the extent of the different bed sediment types was very similar between the restored and the unrestored stretch (Figure 4.19). However, at Chinbrook Meadows and Sutcliffe Park there were significant differences in the extents of the different bed sediment types between the restored and unrestored stretches (Figure 4.19).

All of the restored stretch at Chinbrook Meadows had sediment present, with the dominant bed sediment types being gravel and finer sediment and only a small proportion of in-channel vegetation present (Figure 4.17). However, in the unrestored stretch less than one-fifth of the channel had sediment present, with gravel, finer and sediment accumulated around in-channel vegetation being of roughly equal proportions (Figure 4.17). Potential sources of sediment to a stretch of river include: downstream transfer of upstream sources; adjacent hillslope erosion; in-channel bank erosion; reworking of floodplain deposits; and, inputs from tributaries (Charlton, 2009 and Prosser *et al*., 2001). The full reinforcement (concrete bed and banks) at Chinbrook Meadows unrestored stretch will reduce the in-channel supply of sediment, and also the height of the banks will disconnect the river from the floodplain reducing another potential sediment supply. Additionally, the full concrete reinforcement will reduce roughness within the channel, and thus increase flow velocities (Bathurst, 1993). The only area of sediment deposition in this reinforced channel is where the river channel widened and turned a bend, increasing the wetted perimeter and thus increasing channel resistance and causing a slowing of flow velocity (Charlton, 2009). The Bell Green restored stretch, which although had similar reinforcement levels with concrete bed and banks, had sediment present across the full channel. This is due to the introduction of gravels during the restoration process, thus mitigating the lack of sediment supply (Howes, 2000). The small proportion of sediment accumulated around in-channel vegetation in the restored stretch at Chinbrook Meadows is likely due to shading by the dense riparian vegetation which limits in-channel macrophyte colonisation (Franklin *et al*., 2008).

At Sutcliffe Park the dominant bed sediment types in the restored stretch were finer and that accumulated around in-channel vegetation, with only a small proportion of gravel sediment (Figure 4.18). In the unrestored stretch the majority of the channel bed was covered by gravel sediment, with only a small proportion of finer sediment (Figure 4.18). The lack of bed and bank protection, and the strong connection between the channel and its restored floodplain, means that sources of sediment are readily available to the restored stretch (Charlton, 2009 and Prosser *et al*., 2001). The highly sinuous restored planform will reduce the channel slope and thus slow flow velocities and result in the accumulation of sediments. Additionally, the diversion of flood flows around the park in the pre-restoration culvert rather than passing through the new channel (River Restoration Centre, 2008) will mean the accumulated sediments are not flushed through. The one area of gravel sediment within the restored stretch occurs where the channel is constricted so flow velocities increase, reducing the deposition of finer sediments (Charlton, 2009). The river enters the old culvert as it exits Sutcliffe Park, so the unrestored stretch downstream will be receiving higher flows (River Restoration Centre, 2008). Additionally, the unrestored stretch is comparatively narrower and straighter, resulting in overall higher flow velocities being maintained and resulting in overall less deposition of finer sediment (Charlton, 2009). The lack of sediment accumulated around in-channel vegetation in this unrestored stretch is likely due to higher flow velocities coupled with the dense overhanging riparian vegetation in comparison to the restored stretch, conditions which are unfavourable to in-channel vegetation colonisation (Franklin *et al*., 2008).

There appears to be little published research on the effects of urban river restoration upon sedimentation patterns. Much of the research has focussed on the effects of river restoration upon macroinvertebrates and fish populations in terms of the assumed improvements in habitats or direct stream bed modification (for example, Albertson *et al*., 2011; Sarriquet *et a*l., 2007; and, Hannaford & Resh, 1995). However, Lorenz *et al*., (2012) compiled information on macrophyte, habitat and channel parameters in restored and unrestored stretches of 40 streams in German lowland and mountain rivers. Results indicated that the increased variation in depth, velocity and substrate in the restored stretch compared to the unrestored stretch resulted in increased macrophyte colonisation.

Analysis of the presence of bed sediment types at the study sites has shown that the patterns and extents of finer sediment and that accumulated around in-channel vegetation was a reflection of both the availability of sediment (determined by the degree of bed and bank engineering and the degree of connection to the floodplain) and the hydraulic conditions prevalent within the channel (determined by the channel planform and cross-profile) controlling the transport and deposition of sediment and the colonisation of in-channel vegetation. It is the significant

alterations to these two factors (sediment availability and channel hydraulics) between the unrestored and restored stretches at Sutcliffe Park and Chinbrook Meadows which has resulted in the greater presence of these sediments. This study has therefore shown that in the design of urban river restoration schemes consideration of the potential effect upon sediment availability and channel hydraulics and the consequence of these upon in-channel vegetation growth and sedimentation patterns should be given.

4.5.2 Sediment metal concentrations and characteristics and spatial and temporal variations in restored and unrestored stretches of urban rivers in London

Four different bed sediment types (gravel, sand, finer and that around in-channel vegetation) were sampled in restored and unrestored stretches at four study sites in May, August and November 2010.

The range of sediment metal concentrations recorded at each study site throughout the sampling period is summarised in Table 4.27 along with data from other studies on urban rivers. As with this study, there is a considerable range in the concentrations of metals, particularly Cu, Mn, Pb and Zn which can show an order of magnitude difference between the minimum and maximum concentrations. The concentrations and range of concentrations in this study are consistent with those found in other studies.

Table 4.27: Summary of metal concentrations in sediments of urban rivers from this study and other studies (updated from Scholes *et al*., 2008) (*continued overleaf*).

	Range/max/ average	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mgkg^{-1} dry weight							
River Wandle, Beddington Park, London, UK (This study)	Range	2,210 – 13,000	4.89 – 70.3	12.3 - 340	4,880 – 33,700	98.7 - 537	4.79 – 29.8	28.6 - 996	62.6 - 996
Pool River, Bell Green, London, UK (This study)	Range	2,320 – 18,200	7.98 – 91.7	16.5 - 383	10,700 – 60,900	170 – 1,010	7.34 – 62.2	34.0 - 419	108 - 669
River Quaggy, Chinbrook Meadows, London, UK (This study)	Range	2,030 – 16,300	5.22 – 45.3	9.99 - 169	9,250 – 90,900	148 – 2,080	6.00 – 42.8	16.1 - 330	48.1 - 573
River Quaggy, Sutcliffe Park, London, UK (This study)	Range	2,930 – 35,600	11.3 – 69.6	13.8 - 284	10,500 – 89,700	110 – 2,180	9.61 – 50.1	18.2 - 263	63.7 - 824
Dandenong Creek, Melbourne, Australia Marshall *et al.* (2010)	Range		17 – 35	7 – 59			7 – 19	16 – 120	52 – 890
Nakivubo stream, Kampala, Uganda Sekabira *et al.* (2010)	Range			27.15 – 63.75	30085.33 – 58352.00	363.47 – 1467.47		64.05 – 147.40	177.89 – 442.40
Brunette River catchment, Vancouver, Canada Li *et al*. (2009)	Range			30 – 225	15386 - 33335	217 – 628		63 – 722	
Olobok River and Pilawa River, SW Poland Samecka-Cyerman & Kempers (2007)	Range		4.9 – 28.5	2.1 – 10.6	748 – 1962	37 – 155	7.5 – 15.2	15 – 57	6.8 – 458
	Range		17 – 85.2	9.5 – 43.7	5790 - 9583	47 – 242	14.5 – 39.0	17 – 97	22.9 – 174

Table 4.27: Summary of metal concentrations in urban rivers from other studies and this study (updated from Scholes *et al*., 2008) (*continued*).

	Range/max/ average	Al	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mgkg^{-1} dry weight							
River Seine, Paris, France. Thevenot *et al.* (2007)	Average		47	31				43	140
Lerma River, Mexico City, Mexico Tejeda *et al.* (2006)	Range			9 – 165	11520 - 88489	215 - 1115		12 – 64	38 – 1467
Louro River, Galicia, Spain Filgueiras *et al.* (2004)	Range		78 – 139	30.5 – 55.9			32.5 – 60.7	4.6 – 91.1	
Store Vejlea, Denmark Christensen *et al.* (2006)	Max			120			160	200	560
Bradford Beck, Bradford, UK Old *et al.* (2004)	Range	14200 - 19000	65.8 - 158	72.4 - 481	40500 - 61900		36.1 – 55.2	53.9 – 318	169 - 5500
River Aire River Calder, Bradford/Leeds, UK. Walling *et al.* (2003)	Range		21 – 181	118 - 198				90 – 237	274 – 580
	Range		65 – 313	141 - 235				199 – 343	397 – 907
River Seine, Paris, France Carpenter *et al.* (2002)	Range	<5 – 13	4 – 78	<5 – 172	2300 - 36859	9 – 509	<5 – 30	<5 – 278	39 – 563
East Tullos, Scotland Wilson & Clarke (2002)				440.6			80.9		407.0
Kaskaskia River basin, Illinois, USA Rhoads & Cahill (1999)	Range		9 – 328	6 – 55			8 – 244	10 – 225	29 – 528

The large differences in concentrations between different metals are due to the varying prevalence of the metals within the environment. Fe and Mn are the two most abundant metals in the environment (Forstner & Wittman, 1981). Additionally, Al and Fe are major constituents of clay minerals.

The most significant differences in metal concentrations and sediment characteristics were found between the study sites and bed sediment types, rather than between sampling times and restored and unrestored stretches (Table 4.8).

Temporally, the sampled sediments had significantly higher organic matter content and Al, Cu, Pb and Zn concentrations in May than November (Table 4.8). Although high organic matter contents may be expected towards the end of the growing season (November) due to accumulation of plant material, any high flows would potentially wash the plant material away and thus reduce the organic matter content. Organic matter is an important ligand for metal binding due to its high surface area and cation exchange capacity, and thus sediments with high organic matter content would be expected to have high metal concentrations (Du Laing *et al*., 2009; Luoma & Rainbow, 2008; Horowitz, 1991; and, Forstner & Wittmann, 1981, Section 2.3.2 in Chapter 2). The strong association between organic matter content and metal concentrations in this data set is shown by the significant positive correlations between these variables (Figure 4.21), particularly for Al, Cu, Pb and Zn. Similar positive correlations have been shown in other research (for example, Cevik *et al*., 2009; Liu *et al.*, 2003; Lin & Chen, 1998; and, Coquery & Welbourn, 1995). Therefore, in this data set it is likely that the higher concentrations of Al, Cu, Pb and Zn in May are due to the higher organic matter contents of the sediments at this time.

There were no significant differences between the restored and unrestored stretches in terms of metal concentrations and sediment characteristics (Table 4.8). However, after granulometric correction the Pb and Zn normalised metal ratios were higher in the unrestored stretches as opposed to the restored stretches, indicating less of a grain size control on these metals in the unrestored stretches, and the possibility of some discrete anthropogenic particles (Table 4.9).

In terms of the study sites, Sutcliffe Park was found to have the significantly highest concentrations of Al, Cr, Cu, Fe, Ni and Zn than the other three study sites (Table 4.8). The high metal concentrations were likely due to the strong influence of organic matter content and % <63 µm upon metal concentrations (significant positive correlations, Figure 4.21). As mentioned above, organic matter is an important ligand for metal binding in sediment due to high surface area and cation exchange capacity, and this is also true for fine sediments (<63 µm), thus sediments with high organic matter content and a high proportion of % <63 µm would be expected to have high metal concentrations (Du Laing *et al*., 2009; Luoma & Rainbow, 2008; Horowitz, 1991; Fergusson, 1990; and, Forstner & Wittmann, 1981, Section 2.3.2 in Chapter 2). It is likely that the high metal concentrations at Sutcliffe Park are due to the sediments at this sites having the significantly highest organic matter content and % <63 µm

(Table 4.8). The influence of fine sediments (< 63 μm) on metal concentrations at the site is also illustrated by the site not having the highest normalised metal ratios after granulometric correction of metal concentrations (Table 4.9). Instead, Beddington Park and Bell Green generally have the highest normalised metal ratios (apart from Chinbrook Meadows along with Bell Green for Mn) (Table 4.9), indicating that factors other than grain size are having an influence on metal concentrations at these two sites. This could potentially be caused by inputs of discrete anthropogenic particles. A small wetland at the Beddington Park restored stretch receives inputs from a surface water discharge pipe (Figure 4.15 and Section 4.2.1) and the Bell Green study site is adjacent to a road and a railway line and as such may be receiving direct runoff from these areas (Section 4.2.2). Some research has been undertaken which has identified these discrete anthropogenic particles within rivers impacted by urban runoff. Taylor *et al*., (2003) used electron microscope images to identify metalliferous particles in sediments sampled from Salford Quays in Manchester, UK. Prior to restoration of the quays, which hydrologically isolated the waterbody, coarse grained (up to 2 mm) metal-rich particles were identified. These included metal rich glass fragments, likely from furnace industries, and anthropogenic individual grains. Similarly, Rees *et al*., (1999) sampling sediments from the Rivers Sow, Idle, Aire and Don (all of which have been heavily impacted by urbanisation and industry) identified glass spheres and sharp fragments using X-Ray Fluorescence, thought to be derived from furnace industries. Taylor & Robertson (2009) also analysed road deposited sediments (which could enter urban watercourses through the drainage network) and using electron microscopes identified a dominance of anthropogenic grains, including Fe glass slag grains, Fe oxides from steel erosion and Fe oxides and Fe-rich glass from combustion processes. The glasses and oxides were also found to be major hosts of other metals.

Strong differences were seen between the different bed sediment types in terms of metal concentrations and sediment characteristics.

Analysis of the differences in metal concentrations between the different bed sediment types indicated that there were three bed sediment types which were of importance in terms of high metal concentrations, these were: finer, that accumulated around in-channel vegetation and gravel (Table 4.8). The highest Cr, Cu, Pb and Zn concentrations occurred in the finer and/or in-channel vegetation samples and the highest Fe and Mn concentrations in the gravel and in-channel vegetation samples (Table 4.8). The highest Al and Ni concentrations were in all three bed sediment types (Table 4.8). Although many studies have solely reported increasing metal concentrations with decreasing grain size (e.g. Rodriguez-Barroso *et al*., 2010; Cevik *et al*., 2009; and, Liu *et al*., 2003), some studies have found a similar bimodal distribution of metal concentrations with grain size as in this study. High metal concentrations in fine sediments and

also in coarse sand and gravel sediments have been reported in: two polluted rivers in Taiwan (Lin *et al*., 2003); at two sites on the Damodar River, India (Singh *et al*., 1999); in rivers receiving urban runoff in Poland (Ciszewski, 1998); in streams in New York state (Whitney, 1975); and, in the Severn Estuary (Thorne & Nickless, 1981).

The occurrence of high metal concentrations in the finer and in-channel vegetation samples are to be expected due to the significantly highest % < 63 µm (silt and clay) and organic matter content of the samples (Table 4.8) both of which are very important ligands for metal binding in sediments as discussed above (and Section 2.3.2 in Chapter 2). The importance of fine sediments (< 63 µm) within these two bed sediment types for metal concentrations is also illustrated by the fact that these two bed sediment types had the lowest normalised metal ratios after granulometric correction of the metal concentrations (Table 4.9).

The occurrence of high metal concentrations in the gravel samples is also shown in detailed analysis of the previous scatterplots (Figure 4.21) which indicates that the subset of samples with high % >2 mm and high metal concentrations (in some cases similar to the finer and in-channel vegetation sample concentrations) are gravel samples (Figure 4.32a). These high metal concentrations within these coarser gravel sediments could occur either due to the presence of organic matter (as flocs within the gravel or as coatings on the coarse particles), the presence of fine sediments (<63 µm), or some other factor (such as discrete anthropogenic particles). The low organic matter content associated with the gravel samples (Figure 4.32b and Table 4.8) suggests that organic matter coatings or flocs were not important in these gravel samples for causing the high metal concentrations. Low quantities of fine sediments (<63 µm) were present within these samples (Table 4.8), and further detailed analysis of the scatterplots shows that, particularly for Fe, Mn and Ni, high metal concentrations occur within the gravel samples despite low Al concentrations (which can be used as a geochemical indicator for fine particles as it is associated with clay minerals (Loring, 1991 and Horowitz, 1991)) (Figure 4.32c). This suggests that fine sediments were not important in these gravel sediments for high metal concentrations. Additionally, the gravel samples show high normalised metal ratios after granulometric correction (which removes the influence of grain size on metal concentrations (Luoma & Rainbow, 2008; Loring, 1991; and, Horowitz, 1985)) (Table 4.9). This indicates that some factor other than grain size is important for metal concentrations in these samples (Table 4.9).

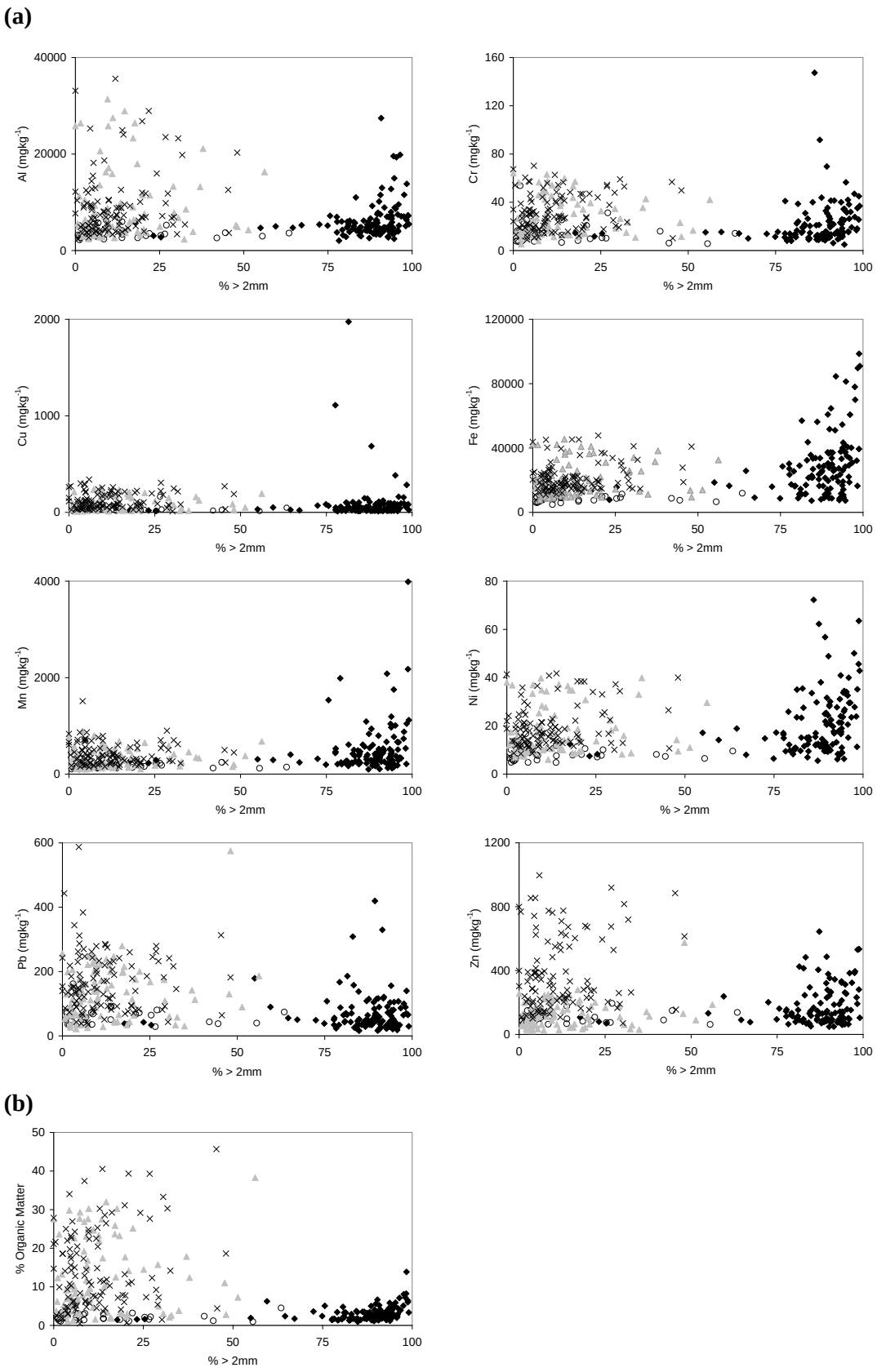


Figure 4.32: Detailed analysis of selected scatterplots between (a) % >2 mm and metal concentrations (b) % >2 mm and % organic matter (c) Fe, Mn, Ni concentrations and Al concentrations (*continued overleaf*).

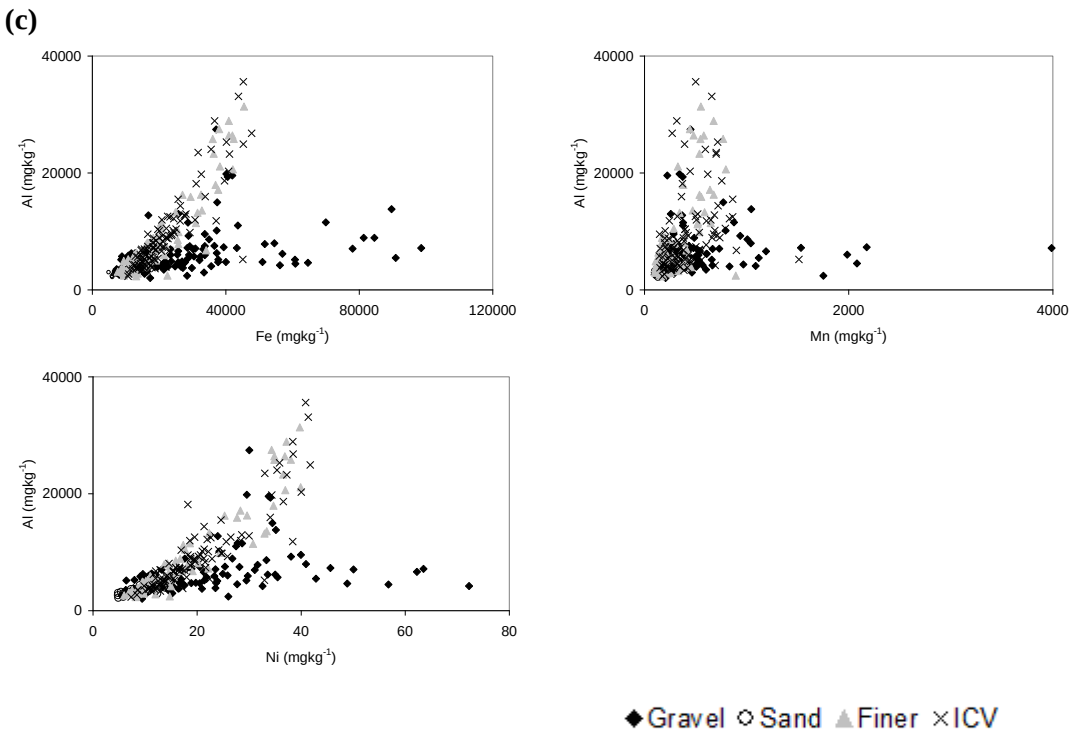


Figure 4.32: Detailed analysis of selected scatterplots between (a) % >2 mm and metal concentrations (b) % >2 mm and % organic matter (c) Fe, Mn, Ni concentrations and Al concentrations (*continued*).

Following granulometric correction, sand samples as well as gravel samples had higher normalised metal ratios than the finer and in-channel vegetation samples (Table 4.9). This indicates, as discussed previously, that particle size (in terms of the presence of fine particles, <63 µm) is having a greater influence on metal concentrations within the finer and in-channel vegetation samples. However, some factor(s) other than grain size are influencing the metal concentrations in the gravel and sand samples. The normalised metal ratios fall in to two groupings: for Cr, Cu, Pb and Zn sand is greater than gravel; and, for Al, Fe, Mn and Ni gravel and sand are greater than finer and in-channel vegetation. Two main processes have been suggested within the literature for higher metal concentrations within coarser sediments: the presence of Fe and Mn (hydr)oxides and the presence of discrete anthropogenic particles (Miller & Orbock Miller, 2007; Lin *et al.*, 2003; Singh *et al*., 1999; and, Whitney, 1975).

Fe and Mn, as redox sensitive metals, precipitate out as Fe and Mn (hydr)oxides under oxic conditions, either as discrete individual particles or as coatings on other minerals (Du Laing *et al*., 2009; Miller & Orbock Miller, 2007; Warren & Haack, 2001; and, Forstner & Wittmann, 1981). The environmental conditions within the gravel and sand deposits, which will be more oxic than within the finer and in-channel vegetation deposits due to the higher permeability and

therefore higher oxygen penetration, could result in greater Fe and Mn (hydr)oxide precipitation. These (hydr)oxides could occur not only as discrete individual particles, but it has been suggested that the larger grain size of coarser sediments, and the greater residence time of these sediments, allows for the development of thicker (hydr)oxide coatings in comparison to finer sediments (Singh *et al*., 1999 and Whitney 1975). This could therefore explain the higher normalised metal ratios of Fe and Mn within the gravel and sand samples.

Fe and Mn (hydr)oxides are effective scavengers of other metals, with metals accumulating on the (hydr)oxides via coprecipitation and adsorption (Du Laing *et al.*, 2009; Luoma & Rainbow, 2008; Miller & Orbock Miller, 2007; Siegel, 2002; Warren & Haack, 2001; and, Forstner & Wittmann, 1981). Scavenging could help to explain the higher normalised metal ratios in the gravel and sand samples for Al and Ni, and in the sand samples for Cr, Cu, Pb and Zn. Greater scavenging could possibly occur by the sand particles compared to the gravel samples as the sand samples were found to have significantly lower % <63 μm than the gravel samples (Table 4.8) in their <2 mm fraction, which implies a greater proportion of coarser particles in the <2 mm fraction for the sand samples and thus (as mentioned earlier) longer residence time and thicker Fe and Mn (hydr)oxide coatings.

Alternatively, the higher normalised metal ratios could be due to discrete anthropogenic particles. Other studies have suggested that inputs of mine and industrial discharges to watercourses could be responsible for discrete anthropogenic particles increasing metal concentrations in coarser sediments (Singh *et al*., 1999 and Thorne & Nickless, 1981). Anthropogenic sources of Al, Cr, Cu, Ni, Pb and Zn which could be relevant at the study sites include vehicular (including exhausts and tyre wear), industrial discharges, metal corrosion, de-icing and fuel combustion (Charlesworth *et al*., 2010; Chon *et al*., 2010; Duruibe *et al*., 2007; Paul & Meyer, 2001; Charlesworth & Lees, 1999; and, Alloway & Ayres, 1997). Additionally, Taylor & Robertson (2009) found that discrete anthropogenic particles of Fe oxides from steel corrosion and Fe-rich glass grains were important hosts for other metals in road-deposited sediments, indicating that these discrete anthropogenic particles could be effective scavengers of other metals too. It is also of note that sand samples in this data set were only found at the Beddington Park study site (Table 4.3) and for Cr, Cu and Pb Beddington Park had the significantly highest normalised metal ratio (Table 4.9), suggesting that the high normalised metal ratios for sand samples were due to the site, and therefore inputs of individual discrete anthropogenic particles.

The occurrence of differing metal concentrations in contrasting bed sediment types has also been explained in previous research in terms of hydraulic conditions and geomorphological

units. Different geomorphological units are characterised by different hydraulic conditions and thus differing sediment accumulation patterns. The highest metal concentrations have been found in dead channel zones, on point bars and alongside river banks, and the lowest metal concentrations in the zones supporting the main current and thus consistently highest flow velocities (Ciszewski, 2004; Rhoads & Cahill, 1999; and, Ciszewski, 1998). Although in the present research the sediment sampling was not stratified by geomorphological units, stratification based upon grain size characteristics implies different hydraulic conditions. Rhoads & Cahill (1999) concluded from their research that the highest metal concentrations occurred in two particular areas of a river channel based upon hydraulic conditions:

(i) regions of low velocity and stagnation zones which promote accumulation of fine sediment, organic matter and the associated metals; and
(ii) regions of intermediate velocity with sand-sized minerals and metal particulates.

Miller & Orbock Miller (2007) expand upon this by listing the controls upon variations in metal concentrations between different geomorphological units as:

(i) grain size distribution of sediment – geomorphological units with greater proportion of fine sediments will contain higher metal concentrations;
(ii) density dependent variations – some metals will associate with dense particles, allowing accumulation in high energy environments;
(iii) timing and frequency of deposition – inundation frequency affects opportunities to accumulate sediments; and,
(iv) geochemical dependent variations – physiochemical conditions of the sediment deposits will affect the behaviour and extent of metal contamination.

With the Sutcliffe Park August data set, a very similar pattern was seen as to the whole data set with the greatest significant differences in metal concentrations and sediment characteristics being between the different bed sediment types rather than between the restored and unrestored stretch (Table 4.15).

The only metal concentrations which were significantly greater in the restored stretch as opposed to the unrestored stretch were Al_{total}, Cr_{total} and Fe_{acetic} (Table 4.15).

In terms of different bed sediment types, compared to the whole data set there were fewer significant differences between the bed sediment types for the metal concentrations, although where these were present both the pseudo-total and acetic acid extractable metal concentrations

were significantly higher in the finer and/or in-channel vegetation samples as opposed to the gravel samples (no sand samples present at Sutcliffe Park) (Table 4.15). As discussed above, this is likely due to the higher organic matter contents and proportion of fine sediments (% <63 µm) in these sediments as opposed to the gravels, and the importance of these as ligands for metal binding in sediments (Table 4.15, Section 2.3.2 in Chapter 2). When the metal concentrations were granulometrically normalised, there were few significant differences between the bed sediment types in terms of normalised metal ratios (Table 4.16), with only Fe_{total} and Fe_{acetic} showing different normalised metal ratios between bed sediment types. This indicates that for the vast majority of metals at this site grain size was the predominant factor determining sediment metal concentrations in all of the bed sediment types, which was illustrated previously with Sutcliffe Park being the site showing the lowest normalised metal ratios of all the sites Table 4.9. However, the main emphasis of this data set is to look at differing environmental conditions, in terms of redox (porewater Fe (II) concentrations) and pH, between the different bed sediments, and also the potential bioavailability of metals (acetic acid extractable metals).

The presence of Fe (II) in all samples suggests that all samples were anoxic to some extent. However, Fe (II) concentrations were significantly higher in the finer and in-channel vegetation as opposed to the gravel samples, indicating more anoxic conditions in the finer and in-channel vegetation samples (Table 4.15). The finer sediments and that accumulating around in-channel vegetation will have a lower permeability compared to the gravel sediments and thus lower oxygen penetration, resulting in lower redox conditions (Huettel *et al*., 2003). Additionally, these sediments also had significantly higher organic matter content compared to the gravel samples (Table 4.15). The decomposition of organic matter by micro-organisms uses up oxygen, and thus sediments higher in organic matter have greater rates of decomposition and thus lower oxygen (more anoxic) conditions (Bronmark & Hansson, 2005; and, den Heyer & Kalff, 1998). Once all the oxygen has been used up, organic matter decomposition is then operating under anoxic conditions, and the micro-organisms will begin to reduce Fe (III) to Fe (II), and thus higher Fe (II) concentrations occur (Lovely & Phillips, 1986).

Although all samples were pH neutral, the gravel samples had a significantly higher pH than the finer and in-channel vegetation sediment samples (Table 4.15). The slightly lower pH conditions in the finer and in-channel vegetation sediments could be caused by the decomposition of organic matter which releases organic acids (Robertson & Paul, 2000), which was significantly higher in the finer and in-channel vegetation sediment than the gravel samples (significant strong negative correlation between organic matter content and pH, Figure 4.25).

The restored stretch at Sutcliffe Park had a higher proportion of acetic acid metals than the unrestored stretch for all metals apart from Al and Zn (Table 4.17). However the actual difference was small (1 to 3 % differences), suggesting little difference in bioavailabilities of metals between the sediments in the restored and the unrestored stretch. Although there was no one bed sediment type which had greater bioavailability of metals than the others, finer and in-channel vegetation samples had greater bioavailability of all metals (apart from Cu and Pb) than the gravel samples (Table 4.17).

The prevailing redox and pH conditions within sediment affect the importance of different ligands for metal binding, and thus metal mobility. Redox conditions affect the behaviour of two important ligands for metal binding: sulphides and Fe and Mn (hydr)oxides. In anoxic sediments, sulphides precipitate out and strongly bind metals, however Fe and Mn (hydr)oxides are reduced and bound metals released (Du Laing *et al*., 2009 and Jacob & Otte, 2003). In oxic sediments, sulphides are oxidised and bound metals released, and Fe and Mn (hydr)oxides precipitated to which metals also strongly bind (Du Laing *et al*., 2009 and Jacob & Otte, 2003). Decreases in pH can increase the mobility of metals in sediments from the increased solubility of sulphides and carbonates releasing bound metals, and a decrease in the metal binding sites on organic matter, clay and Fe and Mn (hydr)oxides from decreased cation exchange capacity (Du Laing *et al*., 2009). The lower redox conditions in the finer and in-channel vegetation sediments suggests a greater dominance of sulphides for metal binding within these bed sediments as opposed to the gravel sediments. However, the slightly lower pH conditions within the finer and in-channel vegetation samples, as opposed to the gravels, could account for the greater bioavailability of metals in these sediments from the increased solubility of sulphides and carbonates and fewer binding sites on organic matter, clay and Fe and Mn (hydr)oxides (Table 3.9, Chapter 3).

Al, Fe and Pb consistently had the lowest proportion of acetic acid extractable metals in the samples and Mn and Zn the highest proportion (Table 4.17), indicating differences in the potential bioavailability of different metals from the sediments. The low bioavailability of Al and Fe is to be expected given that they are major constituents of clays and Fe (hydr)oxides, which are naturally occurring in the environment, and thus most likely to be present in the residual fraction (Li *et al*., 2009 and Tuzen, 2003 Table 3.9, Chapter 3). In comparison, Mn shows a high bioavailability, which is contrary to studies which have reported its low bioavailability attributed again to its natural occurrence in the environment, particularly as Mn (hydr)oxides (Li *et al*., 2009; Sakan *et al*., 2009; and, Akcay *et al*., 2003). Some studies have however found higher bioavailabilities of Mn (Sakan *et al*., 2009 and Tuzen 2003), with Sakan *et al.* (2009) noting that these more mobile fractions of Mn are unlikely to be from

anthropogenic sources, and are more likely to be stable phases of Mn in carbonate minerals and ion-exchangeable forms (Table 3.9, Chapter 3). Several studies have reported low bioavailabilities of Pb, with it predominantly binding to organic matter (Aleksander-Kwaterczak & Helios-Rybicka, 2009; Li *et al.*, 2009; Tuzen, 2003; Svete *et al*., 2001; and, Yu *et al*., 2001, Table 3.9, Chapter 3). High bioavailabilities of Zn have been reported in several studies (Aleksander- Kwaterczak & Helios-Rybicka, 2009; Sakan *et al*., 2009; Svete *et al.*, 2001; and, Yu *et al*., 2001), which may be due to its highly anthropogenic source and therefore association with the acetic acid extractable phase (Table 3.9, Chapter 3).

The bioavailable metals analysed for in this study (Stage 1 of BCR sequential extraction, acetic acid extractable, Table 3.9, Chapter 3) can be mobilised by changes in pH and ionic strength, indicating that Mn and Zn are most at risk of being mobilised at this site if there were to be a decrease in pH or ionic strength, particularly in the finer and in-channel vegetation sediments.

Combining information on sediment volumes and metal concentrations allowed the storage of metals within the stretches to be calculated and compared.

In terms of the different bed sediment types, consistently higher metal storage per m^2 of channel were found in the following sequence: in-channel vegetation sediment > finer sediment > sand sediment > gravel sediment for all metals (Table 4.23). The high metal storage in the in-channel vegetation and finer sediments are a reflection of the high metal concentrations and low proportion of sediment >2 mm in these bed sediment types (Table 4.7). Despite having high Fe and Mn concentrations, the high % >2 mm in the gravel and sand samples resulted in these bed sediment types having low metal storage (Tables 4.7 and 4.23). This clearly shows that despite high metal concentrations being found in the <2 mm fraction of both finer, in-channel vegetation and gravel samples, when the grain size distribution of the bulk sediment sample is taken into consideration these concentrations are diluted by the high proportion of >2 mm fraction in the gravel samples.

The prevalence of finer and in-channel vegetation sediment in the restored stretch at Sutcliffe Park results in the site having the highest storage per m^2 channel of all metals (Figure 4.19 and Table 4.23). Beddington Park had the lowest storage per m^2 of channel for all metals apart from Cr and Pb.

The higher metal storage per m^2 of channel in the restored as opposed to the unrestored stretch at Sutcliffe Park and Chinbrook Meadows are a reflection of the differing areal coverage of bed sediment types between the restored and unrestored stretches and the differing storage from

each bed sediment type (Table 4.23). Sutcliffe Park restored stretch had a greater coverage of finer and in-channel vegetation sediment than the unrestored stretch, resulting in higher metal storage and Chinbrook Meadows unrestored stretch having very low sediment coverage, resulting in low metal storage as opposed to the restored stretch (Figure 4.19). The smaller difference between restored and unrestored stretches at Beddington Park, and the unclear difference at Bell Green are due to the similar coverage of bed sediment types between the restored and unrestored stretches at these sites (Figure 4.19).

These differing metal storages from the different bed sediment types is shown when comparing the percentage cover of the channel by the different bed sediment types to the percentage contribution to the total storage of metals within the stretch by the different bed sediment types (Figure 4.33). In both the restored and unrestored stretches at Beddington Park and Bell Green, the unrestored stretch at Sutcliffe Park and the restored stretch at Chinbrook Meadows, where the channel area is dominated primarily by gravel, the low contribution of gravel sediments and the high contribution of both the finer and in-channel vegetation sediments towards total metal storage in comparison to channel area is shown, particularly for the metals Pb and Zn. A similar pattern is seen in the unrestored stretch at Chinbrook Meadows. However, this is more of a reflection of the dominance of a concrete bed with no sediment deposition. In the restored stretch at Sutcliffe Park, the channel area is already dominated by finer and in-channel vegetation sediment, therefore no significant increase in contribution to total metal storage from these sediments is seen.

This study has clearly shown that the greatest differences in metal concentrations are between different bed sediment types rather than between restored and unrestored stretches. Three bed sediment types were important for high metal concentrations: finer sediment and that accumulating around in-channel vegetation due to their high organic matter content and high proportion of fine sediment; and, gravel sediment likely due to Fe and Mn (hydr)oxides and discrete anthropogenic particles. Metals were also found to generally be more bioavailable in the finer sediment and that accumulating around in-channel vegetation. However, the gravel sediments proved less significant in terms of metal storage due to the high proportion of sediment >2 mm within this bed sediment type, hence reinforcing the importance of finer sediment and that accumulating around in-channel vegetation for both metal concentrations, metal storage and bioavailabilities of metals.

This suggests that restoration per se does not alter sediment metal concentrations and bioavailability, but rather consideration should be given to the effect of restoration practices upon the distributions and extents of bed sediments, particularly finer sediments and those

accumulating around in-channel vegetation. Sutcliffe Park is a clear example of this with restoration resulting in a large increase in finer sediment and that accumulating around in-channel vegetation and thus high metal storage and potentially high metal bioavailabilities. Chinbrook Meadows is a slightly different example whereby restoration has resulted in a significant overall increase in sediment within the channel and thus high metal loadings.

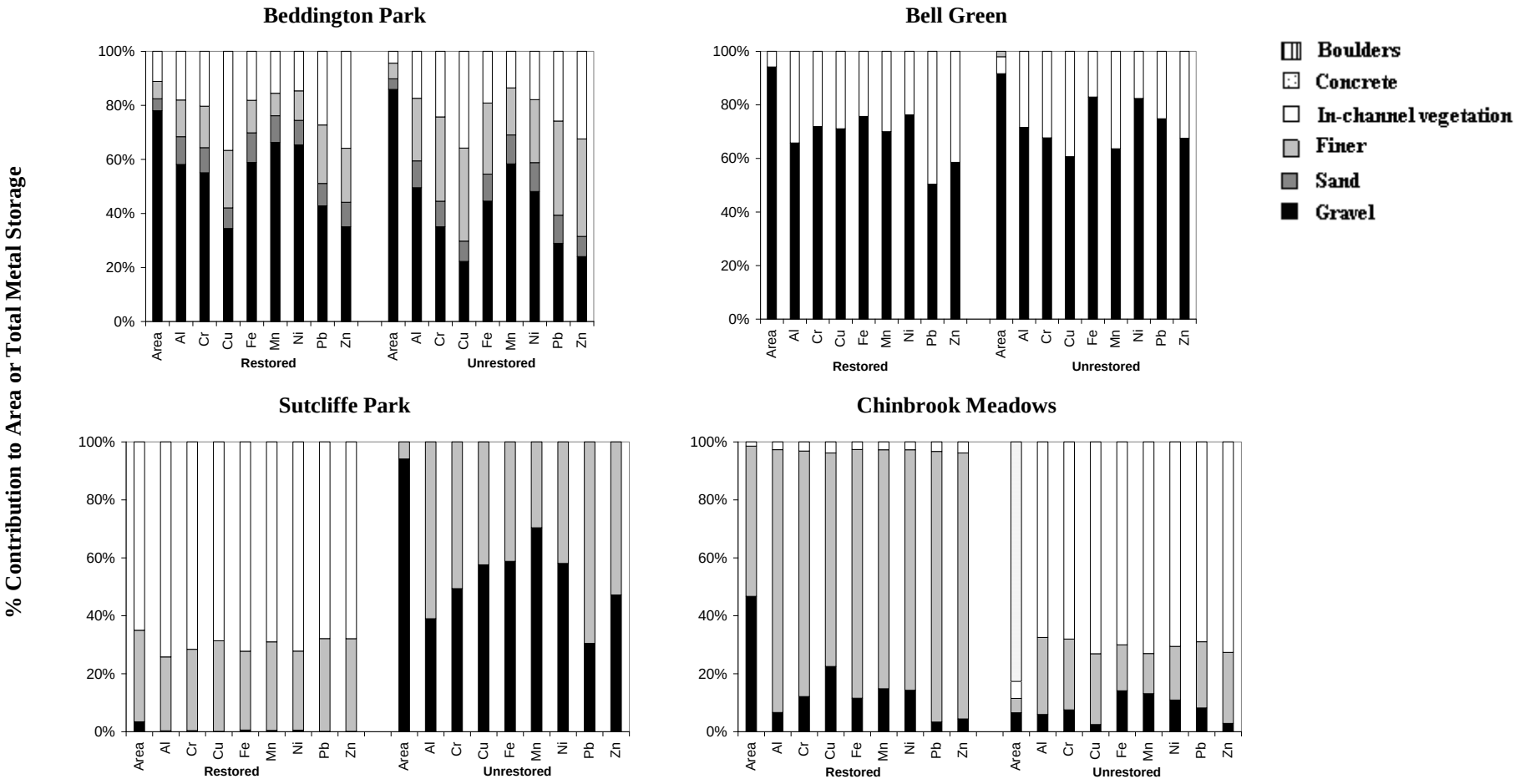


Figure 4.33: Comparison of % channel cover within the studied channels to % contribution to total metal storage of the different bed sediment types.

4.5.3 Factors explaining the variations in metal concentrations and sediment characteristics in restored and unrestored urban rivers in London

The underlying factors which can explain the variations in metal concentrations and sediment characteristics in the samples from the study sites can be understood from interpretation of the loadings of the variables on the PC's extracted through Principal Component Analysis (Tables 4.10, 4.12, 4.18 and 4.20).

Based on an interpretation of the highest loadings, the greatest variation (44%) within the whole data set (prior to granulometric correction) appears to be explained by anthropogenic metals and their association with fine sediment and organic matter. PC1 appears to represent a gradient of increasing concentrations of anthropogenic metals (Cr, Cu, Pb and Zn) and proportions of fine sediment (<63 µm) and organic matter which are all heavily loaded on this PC (Tables 4.10 and 4.28).

The next greatest variation (34%) in the whole data set (prior to granulometric correction) appears to represent coarser sediments which are enriched in Al, Fe, Mn and Ni which are all heavily loaded on PC2 (Tables 4.10 and 4.28). This could be the prevalence of Fe and Mn (hydr)oxides in the coarser, oxygenated gravels and/or discrete anthropogenic particles of Al, Fe, Mn and Ni as discussed above in Section 4.5.2.

There were significant differences between the sites and bed sediment types along these Principal Components (Tables 4.11 and 4.28). As would be expected from the interpretation of both PC1 and PC2, the finer and in-channel vegetation samples were more associated with fine, organic rich sediments and the associated anthropogenic metals (PC1) and the gravel samples were more associated with the coarser sediments and the associated Al, Fe, Mn and Ni (PC2) (Figure 4.22 and Table 4.11). The sediments at Sutcliffe Park and Beddington Park were more associated with fine, organic rich sediments and anthropogenic metals (PC1), which is to be expected for Sutcliffe Park which had the significantly greatest organic matter content and % <63 µm in its sediments (Table 4.8). The sediments at Sutcliffe Park were also more associated with the coarser gravel sediments than the other sites, which could indicate that this site receives greater inputs of discrete anthropogenic particles than the other sites, or its gravels are more oxygenated than at the other sites and thus have increased precipitation of Fe and Mn (hydr)oxides (PC2) (Figure 4.22 and Table 4.11).

The results of PCA applied to the entire raw data set (not granulometrically corrected) are summarised below in Table 4.28.

Table 4.28: Summary of the results of applying Principal Component Analysis followed by Kruskal-Wallis/Mann-Whitney U tests to the entire raw data set (not granulometrically corrected) (BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park, G = Gravel, S = Sand, F = Finer, ICV = In-channel vegetation).

Principal Component and Variance Explained		**Interpretation and notable loadings on the PCs** (loadings >0.4 listed, those >0.6 in bold)	**Significantly different sample groupings** (mean within-group sample factor score in brackets)
PC1	44%	Anthropogenic metals and association with fine sediment and organic matter Positive – Al, **Cr**, **Cu**, Ni, **Pb**, **Zn**, **organic matter**, **% <63µm** Negative - % >2mm	Site: SP (0.326), BP (0.160) > CM (-0.300) Bed sediment type: F (0.433), ICV (0.698) > S (-0.422) > G (-0.822)
PC2	34%	Coarser sediments Positive – **Al**, Cr, **Fe**, **Mn**, **Ni**, % <63µm ,%>2mm	Site: SP (0.901) > CM (0.001), BG (0.093) > BP (-0.653) Bed sediment type: G (0.649) > ICV (-0.214) > F (-0.372) > S (-0.913)

Following granulometric correction of the whole data set, the greatest variation (40%) appears to be explained by anthropogenic metals, with PC1 representing a gradient of increasing normalised metal ratios of the anthropogenic metals (Cr_{correc}, Cu_{correc}, Pb_{correc} and Zn_{correc}) which are all highly positively loaded on PC1 (Tables 4.12 and 4.29). These could be discrete particles of anthropogenic metals from industrial discharges or urban runoff.

The next greatest variation (39%) appears again to represent discrete Al, Fe, Mn and Ni particles (which are highly positively loaded) which are associated with the coarser sediments (>2 mm), but not associated with organic matter content (which scores negatively) on PC2 (Tables 4.12 and 4.29). This could be the prevalence of Fe and Mn (hydr)oxides in the gravels and/or discrete anthropogenic particles of Al, Fe, Mn and Ni as discussed above in Section 4.5.2 which are not associated with organic matter.

Again, as with the non-granulometrically corrected data set, there were significant differences between the sites along these Principal Components (Figure 4.23 and Table 4.13). The sediments at Beddington Park were more associated with the normalised anthropogenic metal ratios (PC1), and the sediments at Bell Green were more associated with the Al, Fe, Mn and Ni normalised metal ratios (PC2). Both sites were shown earlier as having the highest normalised

metal ratios (Table 4.9). Inputs of these discrete, individual metal particles could be from the small wetland at the Beddington Park restored stretch which receives inputs from a surface water discharge pipe (Figure 4.15 and Section 4.2.1) and at Bell Green, direct runoff from the road and railway line which are adjacent to the study site (Section 4.2.2).

The results of the PCA for the granulometrically corrected whole data set are summarised below in Table 4.29.

Table 4.29: Summary of the results of applying Principal Component Analysis followed by Kruskal-Wallis/Mann-Whitney U tests to the granulometrically corrected data set (BP = Beddington Park, BG = Bell Green, CM = Chinbrook Meadows, SP = Sutcliffe Park).

Principal Component and Variance Explained		**Interpretation and notable loadings on the PCs** (loadings >0.4 shown, those >0.6 in bold)	**Significantly different groups** (mean within-group sample score in brackets)
PC1	40%	Discrete anthropogenic metals Positive – Al_{correc}, **Cr_{correc}**, **Cu_{correc}**, Ni_{correc}, **Pb_{correc}**, **Zn_{correc}**	Sites: BP (0.141) > BG (-0.076), SP (-0.177), CM (-0.129)
PC2	39%	Discrete metals associated with coarser sediments Positive – **Al_{correc}**, Cr_{correc}, **Fe_{correc}**, **Mn_{correc}**, **Ni_{correc}**, %>2mm Negative – **organic matter**	Site: BG (0.159) > BP (-0.122), SP (-0.149)

Similarly to the whole data set, the greatest variation (42%) in the Sutcliffe Park August data set (non-granulometrically corrected) appears to be explained by sediment environmental conditions (Fe (II) concentrations (redox) and pH) and composition (organic matter and grain size) and some of the associated metals, representing a gradient from coarse sediments with higher pH and lower metal concentrations to organic rich sediments that are anoxic (high Fe (II) concentrations) and higher metal concentrations (Tables 4.18 and 4.30).

The next two PCs represent far less variation in the data set than PC1 (22% and 17% respectively), making interpretation more tentative. PC2 again appears to represent fine sediments (<63 µm) and clay minerals (Al and Fe) and also some high metal concentrations associated with them (Cr, Cu and Ni) (Tables 4.18 and 4.30). The final PC (PC3) is only highly positively loaded by Mn_{total} and Mn_{acetic} (Tables 4.18 and 4.30).

Again, bed sediment types were discriminated by PC1 and PC2 (Figure 4.26 and Table 4.19). The finer and in-channel vegetation samples were more associated with organic rich, anoxic sediments with high metal concentrations (positive factor scores on PC1), and the gravel samples more associated with coarser, higher pH sediments with lower metal concentrations (negative factor scores on PC1) (Table 4.19). Similarly, the in-channel vegetation samples were more associated with the fine sediments and associated metal concentrations on PC2 than the gravel samples (Table 4.19). The restored stretch had higher (positive) factor scores on PC2 than the unrestored stretch, indicating the importance of fine sediments in the restored stretch as opposed to the unrestored stretch (Table 4.15).

The results of the PCA for the Sutcliffe Park August raw data set is summarised below in Table 4.30.

Table 4.30: Summary of the results of applying Principal Component Analysis followed by Kruskal-Wallis/Mann-Whitney U tests to the raw Sutcliffe Park August data set. (R = restored, U = unrestored, G = gravel, F = finer and ICV = in-channel vegetation).

Principal Component and Variance Explained		**Interpretation and notable loadings on the PCs** (loadings >0.4 shown, those >0.6 in bold)	**Significantly different groups** (mean within-group sample score in brackets)
PC1	42%	Sediment composition, environmental conditions and associated metals Positive – Cr_{total}, **Cu_{total}**, **Pb_{total}**, **Zn_{total}**, **Al_{acetic}**, **Fe_{acetic}**, Ni_{acetic}, **Pb_{acetic}**, **Zn_{acetic}**, **OM**, **Fe (II)** Negative - **% >2mm**, **pH**	Bed sediment type: F (0.681), ICV (0.715) > G (-1.039)
PC2	22%	Fine sediment and associated metals Positive – **Al_{total}**, **Cr_{total}**, Cu_{total}, Fe_{total}, **Ni_{total}**, **Cu_{acetic}**, **Ni_{acetic} <63µm**	Restored: R (0.538) > U (-0.807) Bed sediment type: ICV (1.050) > G (-0.082)
PC3	17%	Mn Positive – Cu_{total}, Fe_{total}, **Mn_{total}**, Ni_{total}, Zn_{total}, **Mn_{acetic}**, >2mm	None

Following granulometric correction of the Sutcliffe Park August data set, the greatest variation (44%) in the data set was explained by the anthropogenic metals, with PC1 representing a

gradient in normalised anthropogenic metal ratios (Cr, Cu, Pb, Ni and Zn) which were all highly positively loaded on this PC (Tables 4.20 and 4.31). These could be discrete particles of anthropogenic metals from industrial discharges or road runoff.

The next two PC's represented far less variation in the data compared to PC1 (21% and 20% respectively), making interpretation more tentative. PC2, representing 21% variation in the data set, appears to be explaining variations in sediment environmental conditions and composition and associated metals, with PC2 representing a gradient from organic matter rich, anoxic (high Fe (II) concentrations) sediments to high pH sediments associated with discrete metal particles (Tables 4.20 and 4.31).

Twenty percent of the remaining variation in the data set was explained by a range of metal concentrations and the coarse grain size (>2 mm), with PC3 representing a gradient in the remaining metals with high positive loadings for Fe_{acetic} and high negative loading of % >2 mm (Tables 4.20 and 4.31).

There were significant differences between the restored and unrestored stretch samples along PCs 1 and 2 (Figure 4.27 and Table 4.21). The unrestored stretch was more associated with normalised anthropogenic metal ratios (positive scores on PC1) and the high pH sediments associated with discrete metal particles (positive scores on PC2) than the restored stretch, suggesting that the unrestored stretch was receiving greater inputs of discrete metal particles. This could be explained by high flows being diverted around the restored stretch and entering the unrestored stretch at Sutcliffe Park, thus discrete metal particles which could come from runoff during high precipitation events could be entering the unrestored stretch and thus accumulating there (Section 4.2.2).

The results of applying PCA, K-W and M-W tests to the Sutcliffe Park August granulometrically corrected data set are summarised below in Table 4.31.

Table 4.31: Summary of the results of applying Principal Component Analysis followed by Kruskal-Wallis/Mann-Whitney U tests to the Sutcliffe Park August granulometrically corrected data set. (R = restored and U = unrestored).

Principal Component and Variance Explained		**Interpretation and notable loadings on the PCs** (loadings >0.4 shown, those >0.6 in bold)	**Significantly different groups (mean within-group sample score in brackets)**
PC1	44%	Anthropogenic metals Positive – $Al_{totalcorrec}$, **$Cr_{totalcorrec}$**, **$Cu_{totalcorrec}$**, $Fe_{totalcorrec}$, **$Mn_{totalcorrec}$**, $Nit_{totalcorrec}$, **$Pb_{totalcorrec}$**, **$Zn_{totalcorrec}$**, **$Al_{aceticcorrec}$**, **$Cu_{aceticcorrec}$**, **$Mn_{aceticcorrec}$**, **$Ni_{aceticcorrec}$**, **Pb_{aceti}**$_{ccorrec}$, **$Zn_{aceticcorrec}$**	Restored/unrestored: U (0.654) > R (-0.436)
PC2	21%	Sediment composition, environmental conditions and associated metals Positive – $Al_{totalcorrec}$, $Cr_{totalcorrec}$, **$Fe_{totalcorrec}$**, **$Ni_{totalcorrec}$**, **pH** Negative – **$Fe_{aceticcorrec}$**, **organic matter,** Fe (II)	Restored/unrestored: U (0.518) > R (-0.345)
PC3	20%	Coarse sediment and remaining metals Positive – $Al_{totalcorrec}$, $Pb_{totalcorrec}$, $Al_{aceticcorrec}$, **$Fe_{aceticcorrec}$**, $Pb_{aceticcorrec}$, $Zn_{aceticcorrec}$, Fe (II) Negative - **>2mm**, pH	None

Overall, interpretation of the PCA results has clearly shown again the strong influence that grain size has upon metal concentrations in the sediments. In the whole data set, the influence of both the finer and coarser grained sediments was demonstrated, and in the Sutcliffe Park August data set the dominating influence of fine grained sediments was demonstrated. Following the removal of grain size, discrete metal particles appeared to be of importance. Other researchers undertaking PCA on similar data sets have demonstrated the strong influence of grain size on metal concentrations (for example, Reid & Spencer, 2009; Poot *et al*., 2007; and, Gorenc *et al*., 2004). This again reinforces the importance of understanding the influence of restoration practices upon alteration of sedimentation patterns as grain size has such a strong influence upon metal concentrations.

4.5.4 Sediment quality in London urban rivers

Analysis of the metal concentrations in the sediment in the sampled urban rivers in London using sediment quality guidelines indicates that it is potentially more harmful to ecosystems than to humans in terms of its metal concentrations, with far greater exceedances of ecosystem sediment quality guidelines than human health guidelines (Figures 4.28 and 4.30). In terms of specific metals, Cu and Zn concentrations are of greatest concern with the greatest exceedances for both ecosystem and human sediment quality guidelines (Figures 4.28 and 4.30). Additionally, Pb concentrations are a concern in terms of ecosystem health (Figure 4.28). Of the study sites, Sutcliffe Park generally had the greatest exceedances, with its sediments being of greatest concern in terms of both ecosystem and human sediment quality (Figures 4.29 and 4.31), which is related to the nature of the sediments at the site, being predominantly fine grain and organic rich, which results in the sediments at the site having many of the highest metal concentrations (Table 4.8) (discussed previously in Section 4.5.2).

Other studies, using a range of sediment quality guidelines, have highlighted similar metals as being at concentrations in river sediments that could potentially be harmful to ecosystems. Research on a section of the River Po in Italy found that the greatest exceedances of the Probable Effects Level (considered toxic to sediment-dwelling organisms) were for Cu, Ni and Zn (Farkas *et al*., 2007). Cheung *et al*., (2003) sampled sediments in the Pearl River Delta, South China and found concentrations of Cd, Pb and Zn exceeded Hong Kong standards at most sites. Sediments sampled in Lake Macquarie, New South Wales, Australia, had the greatest exceedances of the Effects Range Median (concentrations at which adverse biological effects are observed) for Cd, Hg, Pb and Zn (Roach, 2005).

Similarly, other studies using the Dutch intervention values to assess the potential risk of metal contaminated river sediments to human health have reported similar results to this study in terms of the metals of concern and also the low proportion of intervention value exceedances. Carpentier *et al*., (2002) assessed sediment from the River Seine basin, France, and found only two samples exceeded the intervention value for Hg. Analysis of river sediments from the Danube River, Serbia and Montenegro, near a hydroelectric power plant, for Cd, Cr, Cu, Ni and Zn found no exceedances of the Dutch intervention values (Milenkovic *et al*., 2005). Other studies which have found greater exceedances of the intervention values have been undertaken on rivers which have been impacted by metal mining. A study on the River Aries, Romania, which had active metal mines along its course by Bird *et al*., (2005) found the greatest exceedances of the intervention values were for Cu (77% of sites), Zn (38% of sites) and Cd (15% of sites). Similarly, a study on two river catchments in Romania (the Viseu/Tisa River and the Lapus/Somes River) which were affected by mine tailing dam failures by Macklin *et al*.,

(2003) found that there were exceedances of the intervention values at some sites for all metals (Cd, Cu, Pb and Zn), with the greatest exceedances for Zn (60%) and Cu (54%).

Although concentrations of Cu, Pb and Zn were at concentrations that could potentially cause adverse biological effects, there was no clear visual evidence of this with the growth of macrophytes seemingly healthy, particularly in Sutcliffe Park which had abundant macrophyte growth (Figure 4.11). The lesser risk to human health from sediment metal concentrations, with low exceedances of Dutch intervention values, is encouraging and indicates a low risk to people using the rivers for recreation.

4.6 Conclusions

This study has shown that the main factor affecting metal concentrations in the channel sediment of the surveyed urban rivers was the presence and extent of certain bed sediment types, and not whether they were in restored or unrestored stretches. Three bed sediment types were important for high metal concentrations: finer sediment, that accumulating around in-channel vegetation and gravel sediment, although when metal storage was considered gravel sediment was not as important due to the high proportion of >2 mm fraction within this bed sediment type. Metals were also found to generally be more bioavailable in the finer and in-channel vegetation sediments, hence reinforcing the importance of these two bed sediment types.

Overall, the concentrations of metals in the sediments of the urban rivers surveyed were of greater risk to ecosystems than to human health, indicating that use of the rivers for recreation was of low risk.

The presence and extent of the finer sediment and that accumulated around in-channel vegetation were a reflection of both the availability of sediment (determined by the degree of bed and bank engineering and the degree of connection to the floodplain) and the hydraulic conditions prevalent within the channel (determined by channel planform and cross-section) controlling the colonisation of in-channel vegetation and the transport and deposition of these sediments. Therefore, the design of urban river restoration schemes, in terms of their potential effect upon sediment availability and channel hydraulics, is critical in terms of managing the impact upon sediment related contaminant storage, with consideration given to the potential increases in deposition of finer sediment and that accumulating around in-channel vegetation. As illustrated in this study, the poor design of the restored stretch of the River Quaggy in Sutcliffe Park in terms of its hydraulics, has resulted in a stretch of river with extensive deposition and accumulation of finer sediment and that around in-channel vegetation, resulting in this stretch of

river generally having the highest storage of metals per m^2 of river channel and the greatest exceedances of sediment quality guidelines.

Although this has created a potentially important store of sediment associated metals within the river channel, the risk of the sink turning in to a source is dependent upon not only changes in water chemistry and hydraulics, but also the protection and stabilisation to the sediments provided by the in-channel vegetation. The reinforcement of sediments by macrophytes in urban rivers, as inferred by biomechanical measurements, is considered in Chapter 5.

Chapter 5

Biomechanical Properties of Three Common Emergent Macrophyte Species: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*

5.1 Introduction

In urban rivers, where sediments are more likely to be contaminated, reduced flow velocities and associated sediment accumulation induced by macrophytes, may result in contaminated sediments being retained within macrophyte stands. Although this is potentially an important sink for sediment-associated contaminants (including metals), dependent upon the ability of the macrophytes to reinforce the sediment and reduce sediment erosion and resuspension, there is the possibility for the sink to turn into a source, and metals to be released into overlying water (Scholes *et al*., 2008 and Salomons & Brils, 2004).

A macrophyte's ability to reinforce sediment, particularly fine organic-rich sediment, and thus to reduce erosion and resuspension is dependent upon the capability of the above-ground (leaves and stems) and below-ground (roots and rhizomes) tissues to withstand the flow forces acting upon them.

Above-ground tissues (leaves and stems) slow flow velocities, thus reducing shear stresses imposed on the underlying sediments and their potential to be eroded and resuspended (Franklin *et al*, 2008; Clarke, 2002; and, Madsen *et al.*, 2001). If leaves and stems break off then the sediment surface is exposed to relatively higher flow velocities, increasing the potential for sediment erosion and resuspension. Below-ground tissues (roots and rhizomes) can reinforce sediment (Edmaier *et al*., 2011; Corenblit *et al*., 2007; and, Schutten *et al*., 2005). If these are pulled out of the sediment then sediment is physically dislodged and the remaining sediment is no longer reinforced, rendering it more susceptible to erosion and resuspension by river flows.

Undertaking biomechanical measurements on macrophytes in order to determine the resistance of particular species to uprooting and stem or root/rhizome failure can provide an indication of the ability of those species to reinforce sediment (uprooting resistance) and to retain sediment, reducing its susceptibility to erosion and resuspension (stem strength) (Liffen *et al*., 2011; Schutten *et al*., 2005; and, Schutten & Davy, 2000).

This Chapter reports on a study into the biomechanical properties of three common emergent macrophyte species that are often found in urban river systems, recording changes in these properties through the annual growth cycle. The research was undertaken to answer the research question 'How does the ability of three commonly occurring emergent macrophyte species (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) to retain and reinforce fine sediment and thus reduce sediment erosion and resuspension, vary between species and through their annual growth cycles?'.

5.2 Selection of Macrophyte Species and Research Site

5.2.1 Selection and characteristics of macrophyte species

Three macrophytes were chosen to be studied in this research: *Sparganium erectum* (branched bur-reed), *Typha latifolia* (cattail) and *Phalaris arundinacea* (reed canary grass) (Figure 5.1). Studying *S. erectum* maintained continuity with the parallel study of macrophyte flow and sedimentation effects presented in Chapter 7. Undertaking the research on two further emergent species allowed additional inter-species comparisons to be made whilst ensuring the species are subject to similar flow and sediment conditions by sampling at the same time in the same reach. Additionally, all three macrophyte species were abundant at the research site and therefore could be subjected to intensive destructive sampling throughout the year.

An analysis of 1,653 Mean Trophic Rank (MTR) surveys obtained from sites across Great Britain revealed that *S. erectum* and *P. arundinacea* are the two most commonly occurring linear emergent macrophytes and *T. latifolia* is the ninth most common (Table 5.1) (data set supplied by Dr M.O'Hare, Centre for Ecology and Hydrology). Additionally, although all are linear emergents, the three macrophyte species display different physical characteristics particularly in terms of stem diameters and stem heights (Figure 5.1), which suggests that their biomechanical properties may also be different.

Table 5.1: Frequency of occurrence of nine linear emergent macrophyte species across 1,653 sites in Great Britain.

Linear Emergent Macrophytes	
Ranking	**Species**
1	*Sparganium erectum*
2	*Phalaris arundinacea*
3	*Glyceria maxima*
4	*Glyceria fluitans*
5	*Phragmites australis*
6	*Schoenoplectus lacustris*
7	*Iris pseudoacorus*
8	*Butomus umbellatus*
9	*Typha latifolia*

The three macrophyte species show similar growth characteristics. They all have below-ground systems of roots and rhizomes (Haslam, 2006; Adams & Galatowitsch, 2005; and, Dickerman & Wetzel, 1985). The growth of below-ground rhizomes, on which daughter plants develop, enables the macrophytes to reproduce vegetatively. They also reproduce sexually through seed production, and show a seasonal growth pattern with leaves emerging and growing during spring and summer and then collapsing and senescing in the autumn with negligible above-ground biomass remaining over winter.

All three macrophyte species are commonly found in either standing water bodies or in slow flowing watercourses (Haslam, 2006 and Rodwell *et al*., 1995). However, the species vary in their tolerance of inundation and water depth, and so the species tend to occupy different positions across the river channel bed and banks (Haslam, 2006). *S. erectum*, which does not tolerate long periods free of inundation, is found in the centre of shallow watercourses or in the shallower waters near the banks of deeper watercourses (Haslam, 2006). In comparison, *T. latifolia* and *P. arundinacea* are more tolerant of fluctuating water levels. *P. arundinacea* grows at the highest elevations of the three species, often growing in areas which are above the water level throughout the summer months but are flooded during the winter months (Rodwell *et al*., 1995). *T. latifolia* occupies areas of intermediate elevation relative to the other two species, tolerating a wide-range of water levels during which the soil can be wet, saturated or flooded (Haslam, 2006).

As all three macrophytes are commonly found within river margins, they are potentially important for fluvial sediment retention and reinforcement (Haslam, 2006 and Gran & Paola, 2001).

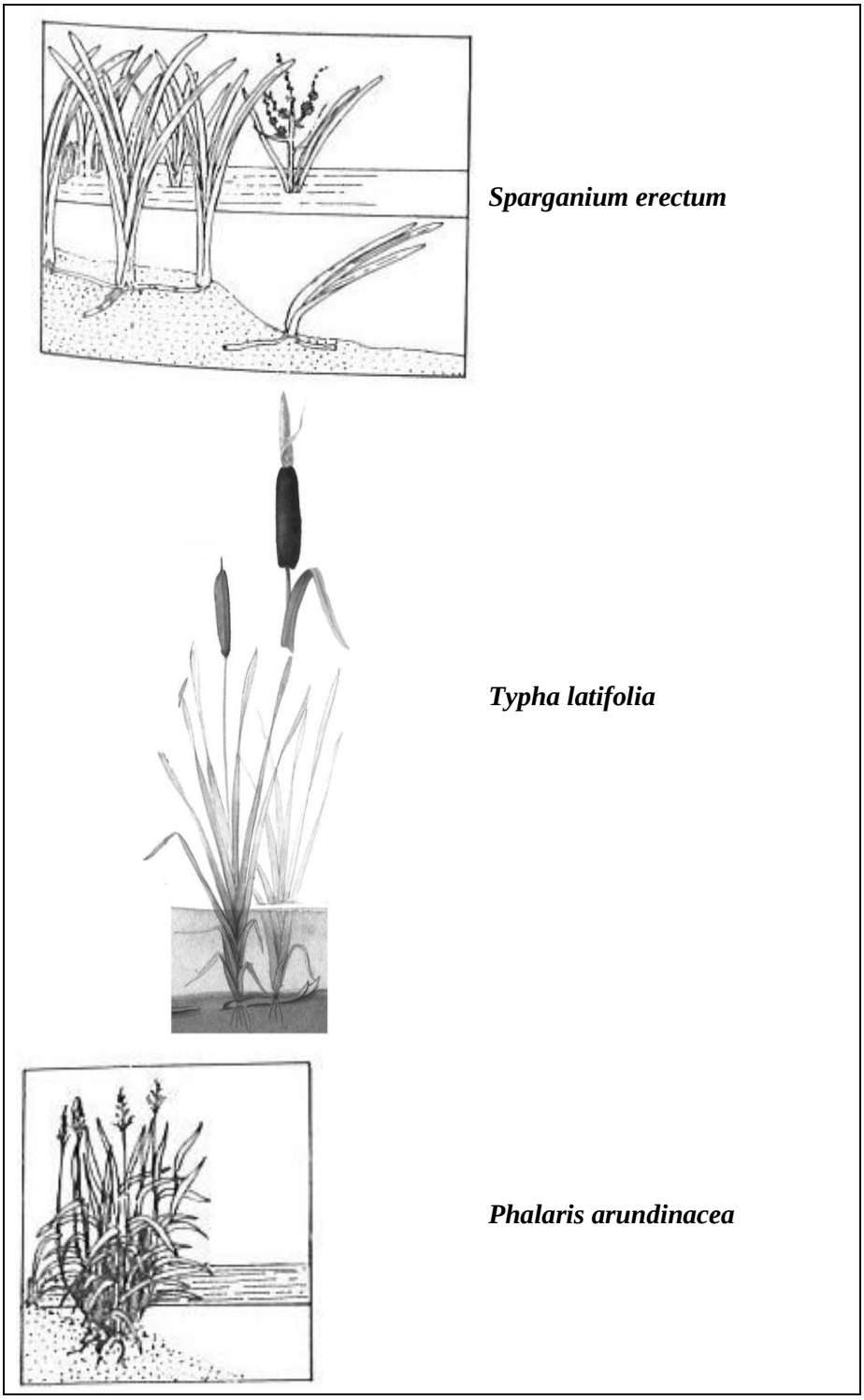


Figure 5.1: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea* (taken from Haslam, 2006 (*S. erectum* and *P. arundinacea)* and Orton *et al*., 2000 (*T. latifolia*)).

5.2.2 Research site

Having selected three of the most common emergent macrophytes for study, a research site was needed that was easily accessible, where all three species grew in sufficient abundance to support a detailed destructive biomechanical study through the entire growing season and where there was safe access into the river. A research site was found on the River Blackwater in Surrey, UK (Figure 5.2), which supports abundant growth of all three of the chosen emergent macrophyte species: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*. The site was easily accessible by vehicle, with only a short distance over which heavy equipment had to be carried to access sizeable stands of the three species (Figure 5.3).

The River Blackwater, a lowland river in southeast England, rises at Rowhill Nature Reserve near Aldershot and flows for 34 km in a northwesterly direction in to the River Loddon, near Eversley (Blackwater Valley Countryside Partnership, 2012). The River Loddon, a tributary of the River Thames, joins the Thames near Reading. The river supports abundant macrophyte growth along its course and also transports a significant load of fine silty and organic sediment. As a result, various sites along the river have been used previously for research into contaminated sediments (House & Denison, 2002 and Daniels *et al*., 2000) and macrophytes (Liffen *et al*., 2011; Pollen-Bankhead *et al*., 2011; and, Naden *et al*., 2006)

The river reach (study site) where macrophyte biomechanical properties were measured was approximately 15 km downstream from the source, within Hawley Meadows (central grid reference: SU 86078 58985; Figures 5.3 and 5.4), an area maintained by The Blackwater Valley Countryside Partnership. On the right bank the meadows are bounded by the A331 with industrial and residential areas beyond, and on the left bank by a railway line with residential areas beyond. During construction of the A331 in the 1980s the study site was particularly affected. The river was re-aligned and the meadows lowered to increase flood storage capacity. However, in 1987/88 the channel was dredged to narrow and deepen it in an attempt to reduce the excessive macrophyte growth (Daniels *et al*., 2000) and since then work has been undertaken to restore its floodplain meadows with improvements to habitats and the introduction of cattle grazing (Blackwater Valley Countryside Partnership, 2012). The upstream section of the river channel at the study site contains stands of *Typha latifolia* and the middle and downstream sections contain stands of *Sparganium erectum* and *Phalaris arundinacea*, making the site ideal for the present research (Figure 5.4).

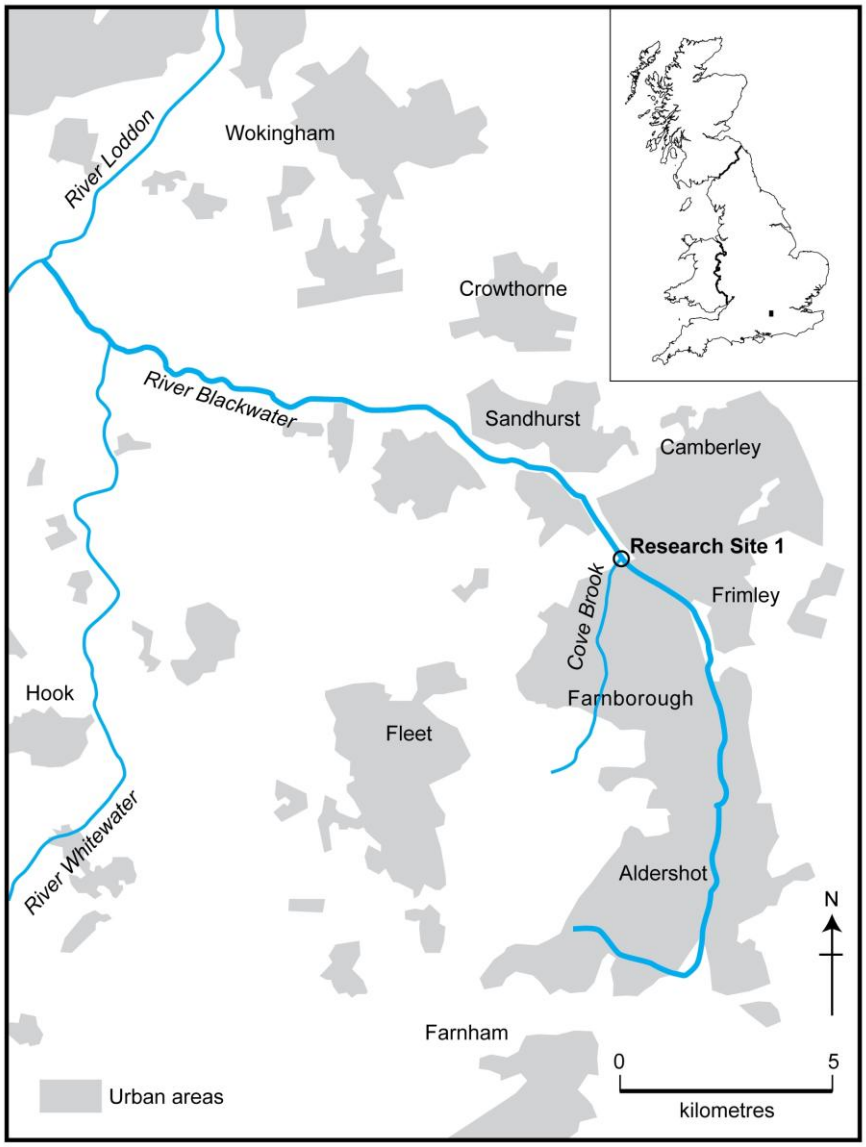


Figure 5.2: Map showing the location of the research site, Hawley Meadows, on the River Blackwater.

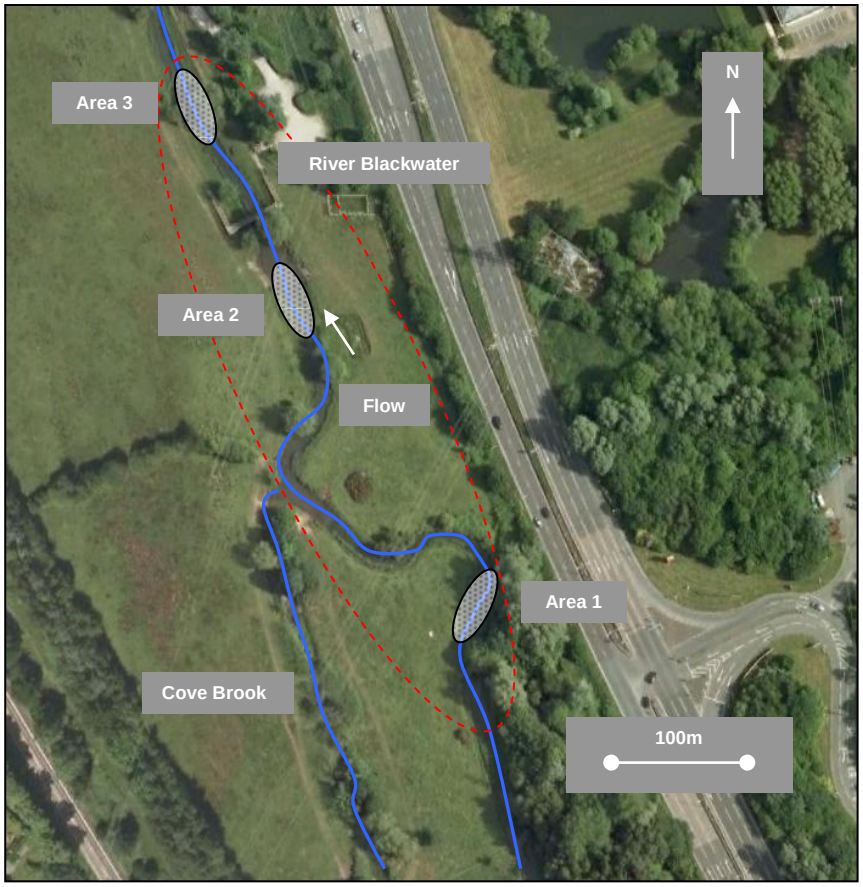


Figure 5.3: Detailed map of research site one, Hawley Meadows, on the River Blackwater. Area 1: upstream section with *T. latifolia*. Area 2: middle section with *S. erectum* and *P. arundinacea*. Area 3: lower section with *S. erectum* and *P. arundinacea*.

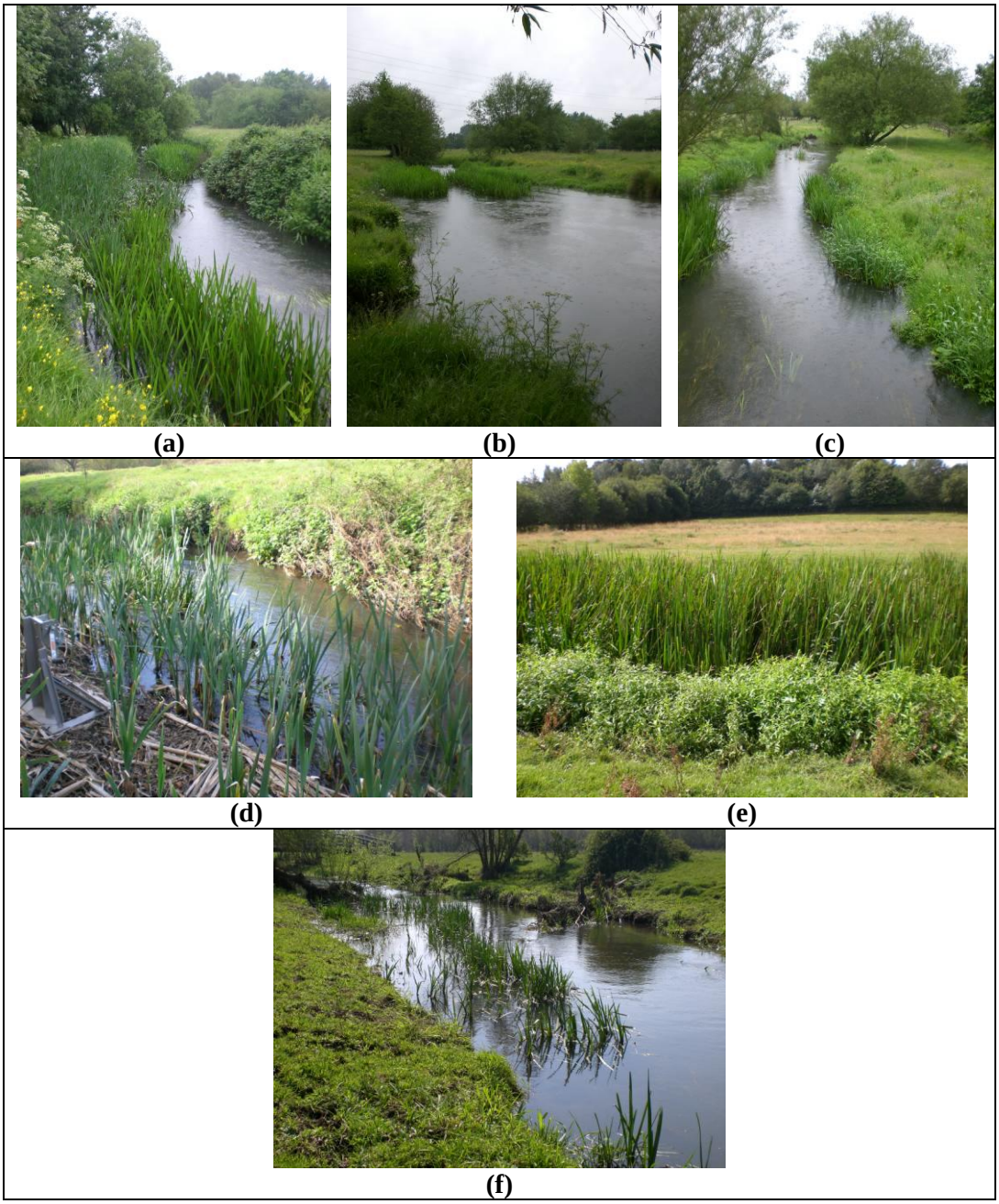
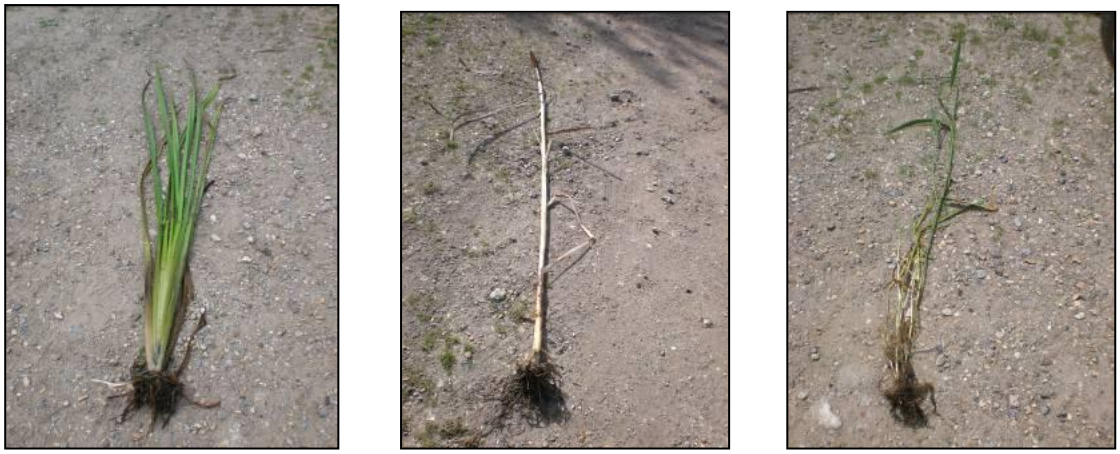


Figure 5.4: Overview photographs of research site one, Hawley Meadows, on the River Blackwater (a) upstream section with *T. latifolia*, (b) middle section with *S. erectum* and *P. arundinacea* (c) lower section with *S. erectum* and *P. arundinacea* (d) *T. latifolia* in upstream section in April 2011 (e) *S. erectum* and *P. arundinacea* in middle section in August 2011 (f) *S. erectum* and *P. arundinacea* in middle section in April 2011.

5.3 Methods

5.3.1 Fieldwork

Biomechanical measurements of the three emergent macrophyte species (Figure 5.5) were undertaken on five occasions during the macrophyte growth season (April to November) in 2011 in order to capture the full extent of the growing period of the macrophytes (Table 5.2).



S. erectum ***T. latifolia*** ***P. arundinacea***

Figure 5.5: Photographs of *S. erectum*, *T. latifolia* and *P. arundinacea* plants.

Table 5.2: Dates of the five measuring periods.

Measuring Period	Date	
1	11/04/11	(mid-April)
2	31/05/11	(end-May)
3	14/07/11	(mid-July)
4	22/08/11	(end-August)
5	11/10/11	(mid-October)

The field methodology was based upon that used by Liffen *et al.*, (2011) to investigate the biomechanical properties of *S. erectum*. For each species, and at each measuring period, a count of the number of plants within a 0.5m x 0.5m quadrat located at the centre of a stand was recorded in order to determine stem density per m^2. A sample of ten plants were then randomly chosen within and around the quadrat for biomechanical measurements, resulting in a sample of ten plants for each species on each monitoring occasion. The maximum leaf/stem length and stem basal diameter (two measurements for the non-symmetrical *S. erectum* and *T. latifolia* stems, and one measurement for the symmetrical *P. arundinacea* stem) of each plant was recorded (Figure 5.6). The plants were then subjected to a simulated drag force using a pulling device, consisting of a winch mounted on a heavy metal frame, constructed and supplied by the United States Department of Agriculture, Agricultural Research Service. A cable, with an attached load cell and data logger, ran from the winch to the macrophyte where it was attached

towards the base of the stem with a U-bolt clamp. The cable was then winched in gently until the cable was taut and the load cell was zeroed. An increasing stress was then steadily applied to the macrophyte using the winch until the macrophyte uprooted or the stem snapped (failed). The maximum force applied to the macrophyte was recorded and whether the force was associated with plant uprooting or stem failure. Plants were pulled at 10 to 20° from the horizontal in order to simulate the impact of river flows on uprooting or stem breakage. If the plant was uprooted then the following additional data were recorded: maximum root length; number of rhizomes; and, maximum diameter of largest rhizome (Figure 5.6). The plant pulling device installed on the river bank is shown in Figure 5.7.

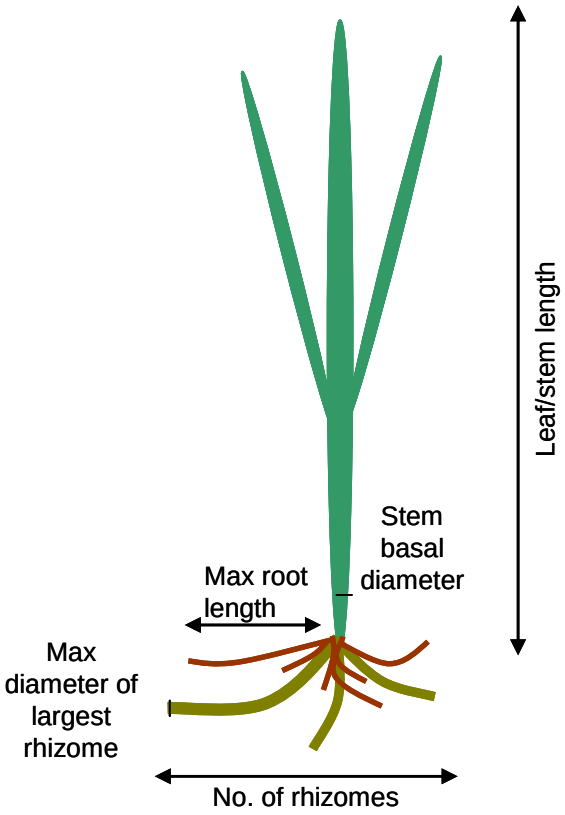


Figure 5.6: Diagram of measurements undertaken on the macrophytes.

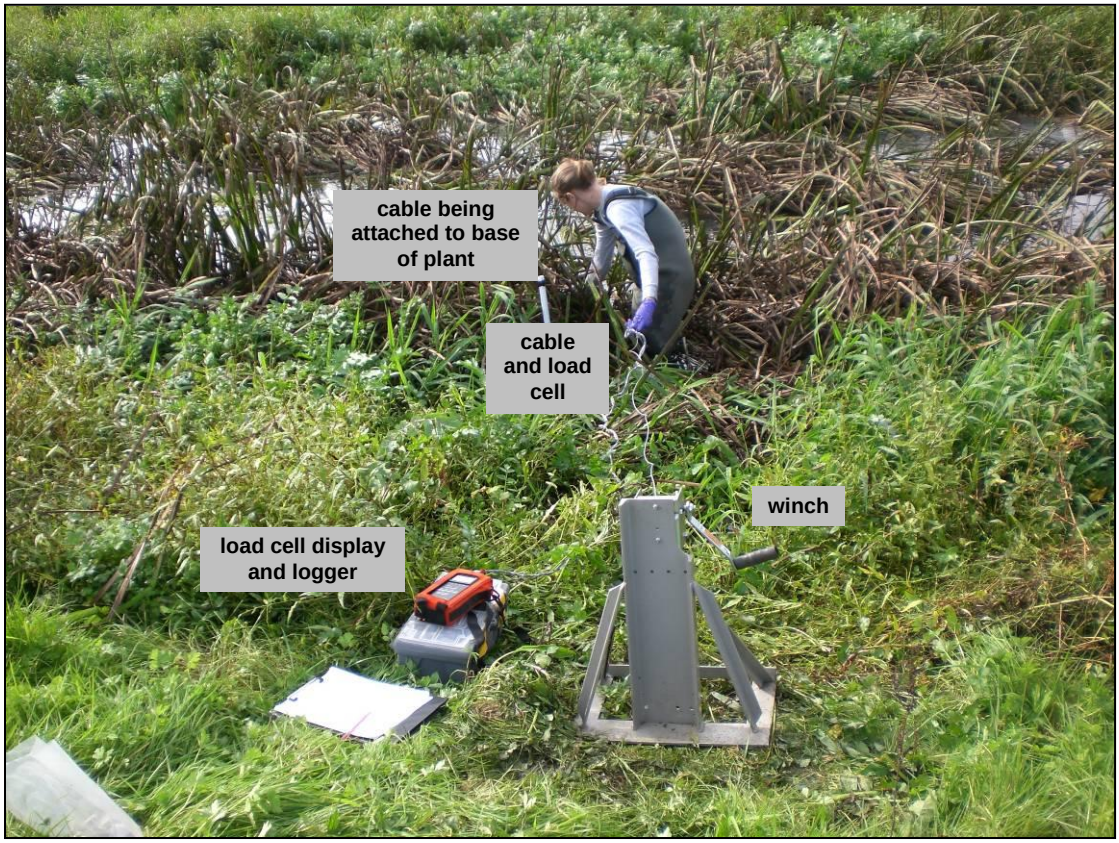


Figure 5.7: The plant pulling device installed in the field.

5.3.2 Data analysis

Analysis focussed on nine variables. There were three measures of the plant's resistance to failure: (i) uprooting resistance or (ii) stem strength at failure (referred to hereafter as stem strength) depending upon whether the plant was uprooted or suffered stem failure (the two measures are collectively referred to as plant failure resistance), and also (iii) stem breaking stress, which standardises stem strength based on stem cross-section area. There were three measures of above-ground plant size/biomass: (i) maximum leaf/stem length, (ii) stem cross-section area, and (iii) stem density. Lastly, there were three measures of below-ground plant size/biomass: (i) maximum root length, (ii) number of rhizomes per plant and (iii) maximum rhizome diameter. All nine variables were measured for the three different species on five occasions between April and November 2011 (the macrophyte growth season).

Stem cross-section areas were calculated using the measurements of stem basal diameter. Cross-section areas (CSA, cm^2) were calculated as:

$$CSA = (\pi \times ((D1 / 2) * (D2 / 2))) / 100$$

where D1 and D2 were the two measurements of stem basal diameter (mm).

Where stem failure occurred, the stem breaking stress (SBS in MNm^2, the force per cross-section area the stem can withstand before snapping) was calculated as:

$$SBS = SS / (CSA / 10000)$$

where SS is stem strength (N).

All data analysis was undertaken using Microsoft Excel 2003, XLSTAT Pro 2011 and 2012 and SPSS version 16.0. Prior to statistical analysis of the data set the form of the frequency distributions of the variables was determined through visual inspection of histograms and statistically tested for normality using the Kolmogorov-Smirnov (K-S) test (see Appendix IV for full results). All of the variables were found to conform to a normal distribution (K-S, $p > 0.05$) apart from plant failure resistance for *P. arundinacea* (K-S, $p = 0.034$), stem cross-section areas for *S. erectum* (K-S, $p = 0.015$), maximum root lengths for *P. arundinacea* (K-S, $p = 0.009$) and number of rhizomes per plant for *T. latifolia* and *P. arundinacea* (K-S, $p = 0.003$ and $p = 0.040$ respectively). Although these variables could have been transformed to achieve a normal distribution (Section 3.4.3, Chapter 3) comparisons can not be easily made between the results of analyses applied to a mix of transformed data and untransformed data, or between parametric and non-parametric analysis results. Therefore non-parametric methods were used to analyse the entire data set. Species and temporal differences in plant biomechanical properties and measures of plant size/biomass were observed from boxplots and statistically tested using the Mann-Whitney U test (M-W) when there were two groups to compare and the Kruskal-Wallis test (K-W) when there were more than two groups to compare. If the K-W test indicated a significant difference post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were undertaken to identify which species or measuring periods were significantly different from each other. Finally, the strength of associations between the biomechanical and plant size/biomass measurements were analysed using the Spearmans Rank correlation test (S-R).

5.4 Results

5.4.1 Data preparation and description

The nine variables for each of the three studied macrophyte species are summarised as boxplots in Figure 5.8.

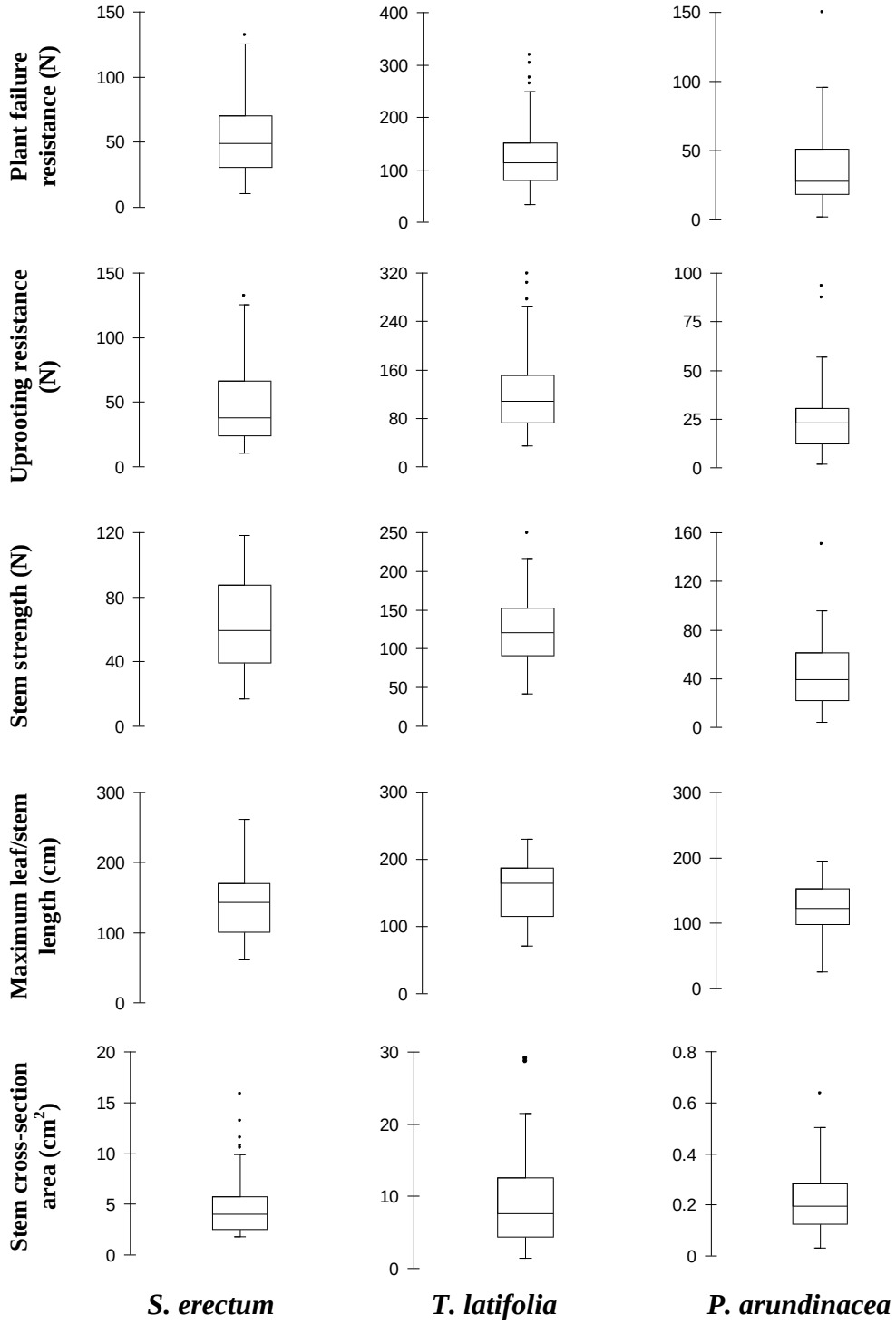


Figure 5.8: Boxplots of each of the nine measured variables for each macrophyte species (*continued overleaf*).

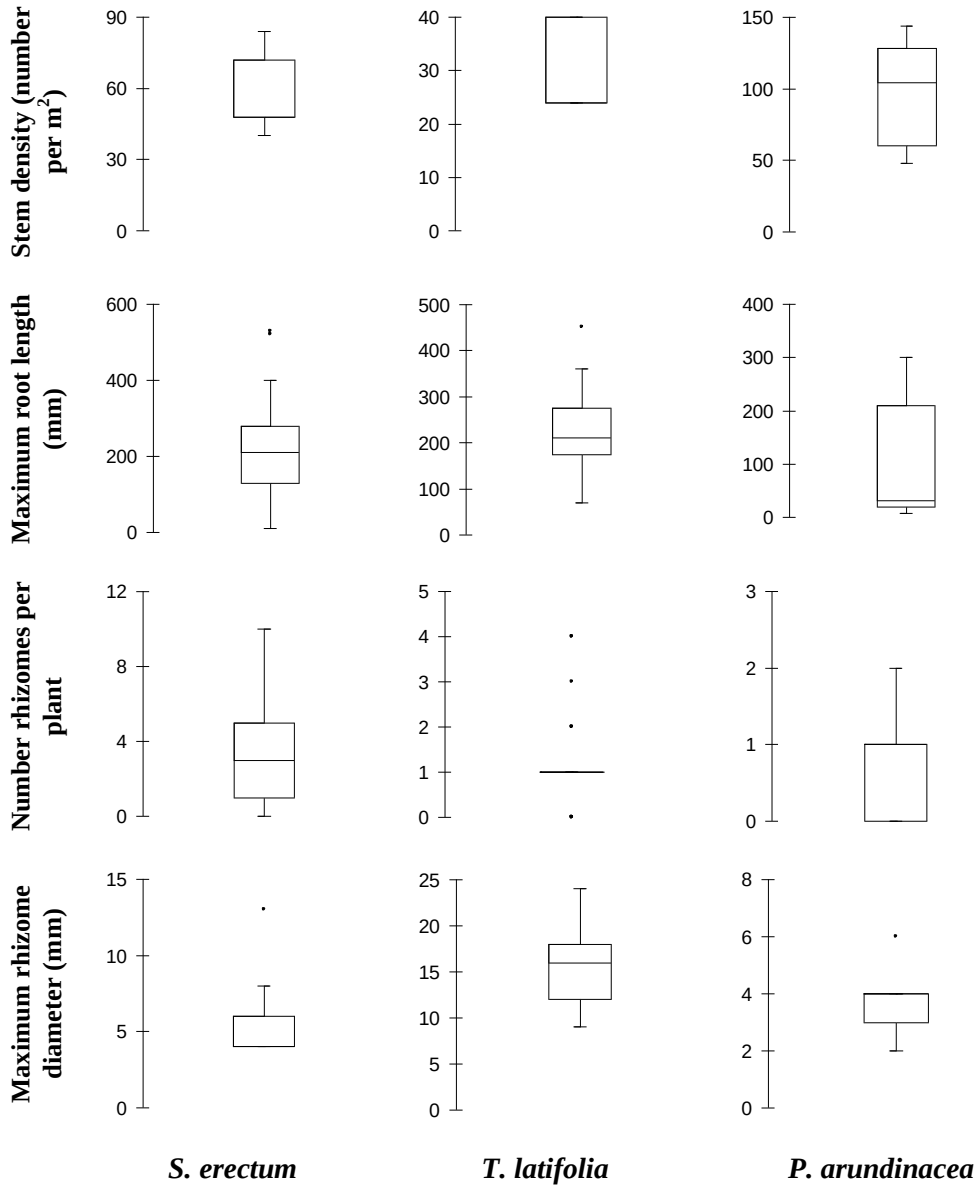


Figure 5.8: Boxplots of each of the nine measured variables for each macrophyte species (*continued*).

5.4.2 Differences in biomechanical properties through time and between species

Species differences

The median values and range of plant failure resistance, uprooting resistance, stem strength and stem breaking stress for each species are shown in Table 5.3. Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences between the macrophyte species in these properties (Table 5.4).

Plant failure resistances showed statistically significant differences between species when the data were aggregated across all five measuring periods (Table 5.4). *T. latifolia* had the

significantly highest (median 114 N) and *P. arundinacea* the significantly lowest (median 28 N) plant failure resistance (K-W, $p < 0.00001$, Tables 5.3 and 5.4). Splitting the plant failure resistances into uprooting resistances and stem strength (based upon whether the plant was uprooted or the stem snapped) all species had greater median stem strengths than median uprooting resistances (Table 5.3). However, the difference was only statistically significant for *P. arundinacea* (M-W, $p = 0.014$, Table 5.5). There were significant differences in uprooting resistances between all three species, with *T. latifolia* showing the greatest (median 108 N) and *P. arundinacea* the lowest (median 23 N) uprooting resistance (K-W, $p < 0.0001$, Tables 5.3 and 5.4). Additionally, *T. latifolia* had a significantly greater stem strength than both *S. erectum* and *P. arundinacea* (K-W, $p < 0.0001$, Table 5.4). Stem breaking stresses were significantly greater for *P. arundinacea* (median 2.7 MNm^2) than for both *S. erectum* and *T. latifolia* (median 0.13 and 0.20 MNm^2 respectively) (K-W, $p < 0.0001$, Tables 5.3 and 5.4). Between species there were no differences in the proportion of uprootings and stem failures across the whole monitoring period with roughly equal proportions of both (Figure 5.9).

Table 5.3: Range, median and sample size for the four biomechanical measurements for each species across the five measuring periods.

	S. erectum	***T. latifolia***	***P. arundinacea***
Plant failure resistance (N)	10 - 132 49 n = 50	34 - 319 114 n = 50	2 - 150 28 n = 50
Uprooting resistance (N)	10 - 132 38 n = 25	34 - 319 108 n = 26	2 - 93 23 n = 24
Stem strength (N)	17 - 118 59 n = 25	42 - 249 121 n = 24	4 - 150 39 n = 26
Stem breaking stress (MNm^2)	0.08 – 0.48 0.13 n = 25	0.08 – 1.00 0.20 n = 24	0.57 – 11.96 2.70 n = 26

Table 5.4: Statistically significant differences in biomechanical measurements between species (S = *S. erectum*, T = *T. latifolia*, P = *P. arundinacea*) across the five measuring periods identifed using Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests.

	K-W p value	**S-D-C-F Significant differences ($p < 0.05$)**
Plant failure resistance	<0.0001	T > S > P
Uproot resistance	<0.0001	T > S > P
Stem strength	<0.0001	T > S, P
Stem breaking stress	<0.0001	P > S, T

Table 5.5: Statistically significant differences in uprooting resistance (U) and stem strength (S) for each species identified using Mann-Whitney U (M-W) tests across the five measuring periods (n.s. = not significant).

	M-W p value	**Significant differences**
S. erectum	0.095	n.s.
T. latifolia	0.749	n.s.
P. arundinacea	0.014	S > U

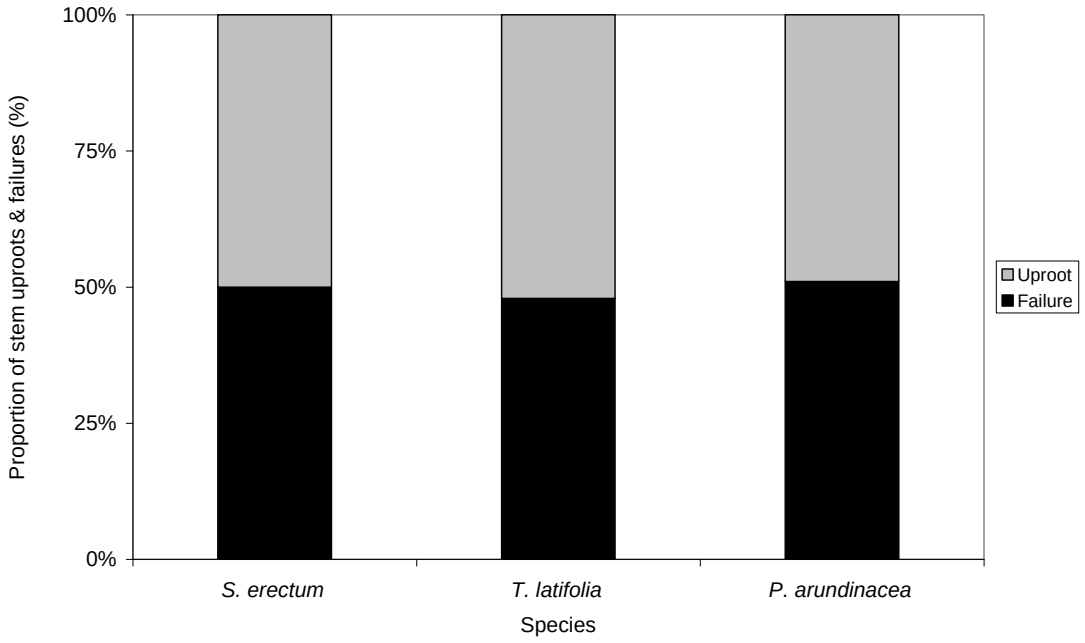


Figure 5.9: Proportion of plant uprooting and stem failures observed for each of the three studied species.

Changes through the growing season

Due to differing proportions of stems uprooting and failing, there were variations in the number of uprooting resistance and stem strength measurements for each species between measuring periods. Measuring periods for each species with sample numbers less than five are identified in Table 5.6, and they were excluded from statistical analysis.

Table 5.6: Measuring periods for each variable with sample numbers below five for each species. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

	S. erectum	***T. latifolia***	***P. arundinacea***
Uprooting resistance	1, 2	1, 5	3, 4, 5
Stem strength	3, 4, 5	2	1 (no data)

Plant failure resistance, uprooting resistance and stem strength in each of the five measuring periods for each of the species was plotted as boxplots to visualise any differences in these variables over time (Figure 5.10). Mann-Whitney U (M-W) and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these variables over time for each macrophyte species for measuring periods with five or more observations (Tables 5.6 and 5.7).

All species showed the same pattern of plant failure resistance across the five measuring periods with minimum resistance in measuring period 1 and maximum resistance in measuring period 2 (Figure 5.10). This was followed by a large decrease to measuring period 3 and then a smaller increase followed by a smaller decrease in measuring periods 4 and 5 (Figure 5.10). Plant failure resistances for *S. erectum* were significantly greater in measuring periods 2 and 4 than measuring period 1, and additionally significantly greater in measuring period 2 than measuring periods 1, 3 and 5 (K-W, $p < 0.0001$, Table 5.7). *T. latifolia* had significantly greater plant failure resistances in measuring period 2 than measuring period 1 (K-W, p 0.010, Table 5.7). *P. arundinacea* had significantly greater plant failure resistances in measuring periods 2, 3 and 4 than at the beginning and end of the growing season (measuring periods 1 and 5) (K-W, $p < 0.0001$, Table 5.7). Uprooting resistance and stem strength for both *S. erectum* and *T. latifolia* showed a similar pattern through the growth season as plant failure resistance. Stem strengths in measuring period 2 were significantly greater than in measuring period 1 for *S. erectum* (M-W, $p = 0.001$, Table 5.7, measuring periods 3, 4 and 5 data excluded from the analysis). There were no significant differences for uprooting resistance (*S. erectum* and *T. latifolia*) and stem strength (*T. latifolia*) (K-W, $p = 0.447$, $p = 0.115$ and $p = 0.121$ respectively, Table 5.7) between measuring periods with a sufficient sample size for statistical testing. *P. arundinacea* showed a similar pattern for uprooting resistance to the other species, except for having minimum median values in measuring period 5 and stem strength showed a clear decrease throughout the measuring periods (Figure 5.10). Uprooting resistance was significantly greater in measuring period 2 than measuring period 1 (M-W, $p = 0.008$, Table 5.7, measuring periods 3, 4 and 5 data excluded from the analysis) and stem strength was significantly greater in measuring periods 2 and 3 than in measuring period 5 (K-W, $p = 0.009$, Table 5.7, no data for measuring period 1).

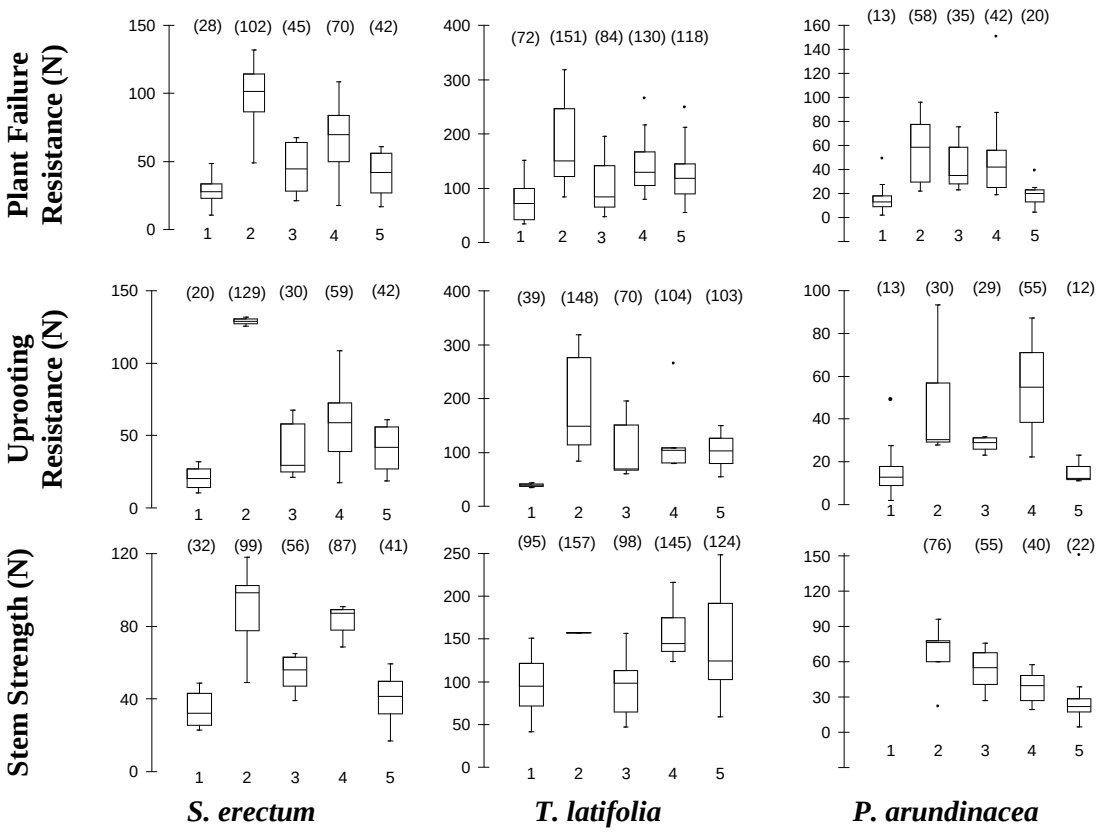


Figure 5.10: Boxplots of biomechanical measurements during each measuring period for the three studied species with median values shown in brackets (note: some boxplots n <5 – see Table 5.6). (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

Table 5.7: Statistically significant differences in biomechanical measurements over time for each species identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) and tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

	S. erectum		***T. latifolia***		***P. arundinacea***	
	p value	**S-D-C-F Significant differences ($p < 0.05$)**	**p value**	**S-D-C-F Significant differences ($p < 0.05$)**	**p value**	**S-D-C-F Significant differences ($p < 0.05$)**
Plant failure resistance	K-W <0.0001	2 > 1, 3, 5 2, 4 > 1	K-W 0.010	2 > 1	K-W <0.0001	2, 3, 4 > 1, 5
Uprooting resistance	K-W 0.447	n.s.	K-W 0.115	n.s.	M-W 0.008	2 > 1
Stem strength	M-W 0.001	2 > 1	K-W 0.121	n.s.	K-W 0.009	2, 3 > 5

Between the three species there were different temporal patterns in the proportion of plant uprootings and stem failures (Figure 5.11). The minimum proportion of stem failures occurred in measuring period 4 for *S. erectum* (30%), measuring period 2 for *T. latifolia* (10%) and measuring period 1 for *P. arundinacea* (0%). The maximum proportion of stem failures occurred in measuring period 2 for *S. erectum* (80%), measuring period 1 for *T. latifolia* (70%) and measuring period 4 for *P. arundinacea* (78%). *S. erectum* showed a general decrease in the proportion of stem failures towards the end of the measuring periods. *T. latifolia* showed a large decrease in the proportion of stem failures from measuring period 1 to 2, then a general increase towards the end of the measuring periods. *P. arundinacea* showed a clear pattern of increasing proportion of stem failures through the measuring periods.

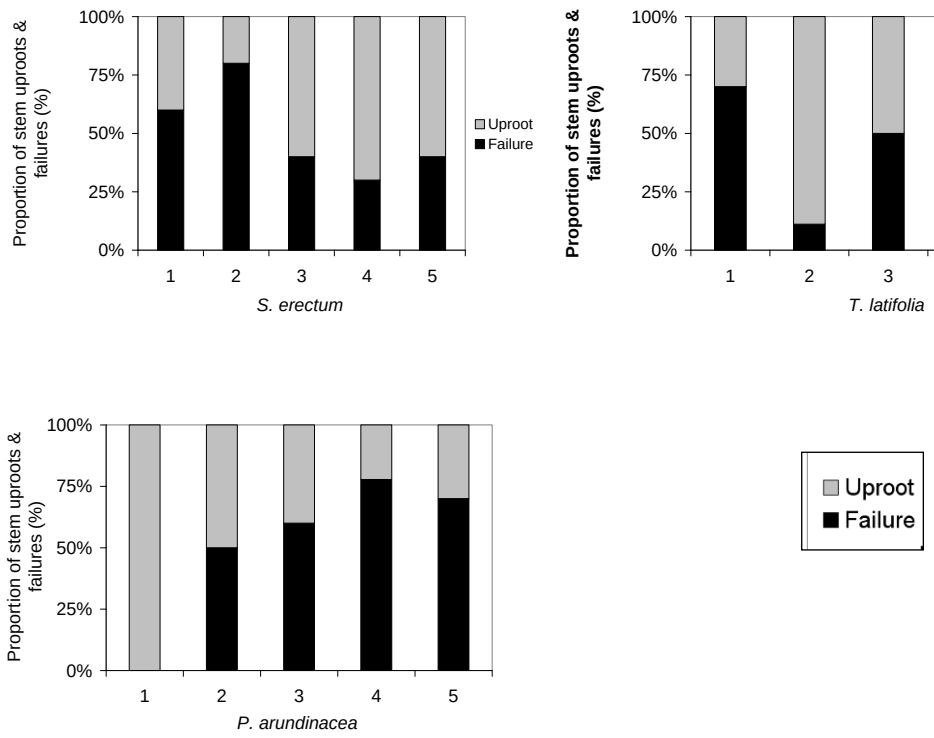


Figure 5.11: Proportion of plant uprootings and stem failures over time for each species. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

5.4.3 Differences in above-ground plant size/biomass through time and between species

Species differences

The median values and range of above-ground plant/size biomass measurements for each species are shown in Table 5.8. Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these properties between the macrophyte species (Table 5.9).

There were differences between the three species for all three measures of above-ground plant size/biomass. All three species showed a large range in recorded maximum leaf/stem lengths (Table 5.8). *T. latifolia* had a significantly greater maximum leaf/stem length (median 165 cm) than *P. arundinacea* (median 123 cm) (K-W, $p = 0.002$, Tables 5.8 and 5.9). There were significant differences in stem cross-section area between the three species (K-W, $p < 0.0001$, Table 5.9), with *T. latifolia* having the significantly greatest (median 7.56 cm^2) and *P. arundinacea* the significantly smallest (median 0.20 cm^2) stem cross section area (Tables 5.8 and 5.9). *S. erectum* and *P. arundinacea* had a significantly greater stem density (median 48 per m^2 and 104 per m^2 respectively) than *T. latifolia* (median 24 per m^2) (K-W, $p = 0.006$, Tables 5.8 and 5.9).

Table 5.8: Range, median and sample size for the three above-ground plant size/biomass measurements for each species across the five measuring periods.

	S. erectum	***T. latifolia***	***P. arundinacea***
Median maximum leaf/stem length (cm)	61 – 262 144 n = 50	71 - 230 165 n = 50	26 - 195 123 n = 50
Median stem cross-section area (cm^2)	1.81 – 15.83 4.03 n = 50	1.41 – 29.04 7.56 n = 50	0.03 – 0.64 0.20 n = 50
Median stem density (stems per m^2)	40 – 84 48 n = 5	24 - 40 24 n = 5	48 - 144 104 n = 5

Table 5.9: Statistically significant differences in the three above ground plant size/biomass measurements for the three studied species (S = *S. erectum*, T = *T. latifolia*, P = *P. arundinacea*) identified using Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests.

	K-W p value	**S-D-C-F Significant differences ($p < 0.05$)**
Max leaf /stem length	0.002	T > P
Stem cross-section area	<0.0001	T > S > P
Stem density	0.006	S, P > T

Temporal differences

Above-ground measures of plant biomass for each of the species were plotted as boxplots and bar charts to visualise any differences in these variables over time (Figure 5.12). Mann-Whitney U (M-W) and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these variables over time for each macrophyte species (Table 5.10).

All three species had lowest maximum leaf/stem lengths in measuring period 1 (Figure 5.12). The highest maximum leaf/stem lengths were in measuring period 5 for *S. erectum* and *T. latifolia* and in measuring period 4 for *P. arundinacea* (Figure 5.12). *S. erectum* showed a clear temporal pattern of steadily increasing maximum leaf/stem lengths through the measuring periods (Figure 5.12) with each measuring period significantly different from the others (K-W, $p < 0.0001$, Table 5.10). A similar pattern was shown by *T. latifolia*, with the exception of a decrease between measuring periods 2 and 3 (K-W, $p < 0.0001$, Table 5.10). *P. arundinacea* showed no clear temporal pattern, with measuring period 1 having the significantly lowest maximum leaf/stem lengths and measuring period 4 the significantly highest (K-W, $p < 0.0001$, Table 5.10).

The maximum stem cross-section areas were observed in measuring period 2 for *S. erectum* and *T. latifolia* and in measuring period 1 for *P. arundinacea* (Figure 5.12). The minimum stem cross-section areas were observed in measuring period 5 for *S. erectum* and *P. arundinacea* and in measuring period 1 for *T. latifolia* (Figure 5.12). *P. arundinacea* showed a clear temporal pattern of decreasing stem cross-section areas through the measuring periods (Figure 5.12), with stem cross-section areas significantly greater in measuring periods 1 and 2 than the rest of the measuring periods, and additionally measuring period 3 significantly greater than measuring period 5 (K-W, $p < 0.0001$, Table 5.10). The temporal patterns were less clear for *S. erectum* and *T. latifolia*, though for both species the cross-section areas at the beginning and end of the measuring periods (measuring periods 1 and 5) were significantly lower than some of the measurements in between (K-W, $p = 0.002$ and $p < 0.0001$ for *S. erectum* and *T. latifolia* respectively, Table 5.10).

S. erectum and *T. latifolia* showed an increase in stem density to a maximum in measuring periods 3 and 4 and a decrease in measuring period 5 (Figure 5.12). *P. arundinacea* had maximum stem density in measuring periods 2 and 3 and minimum in measuring periods 1 and 5 (Figure 5.12).

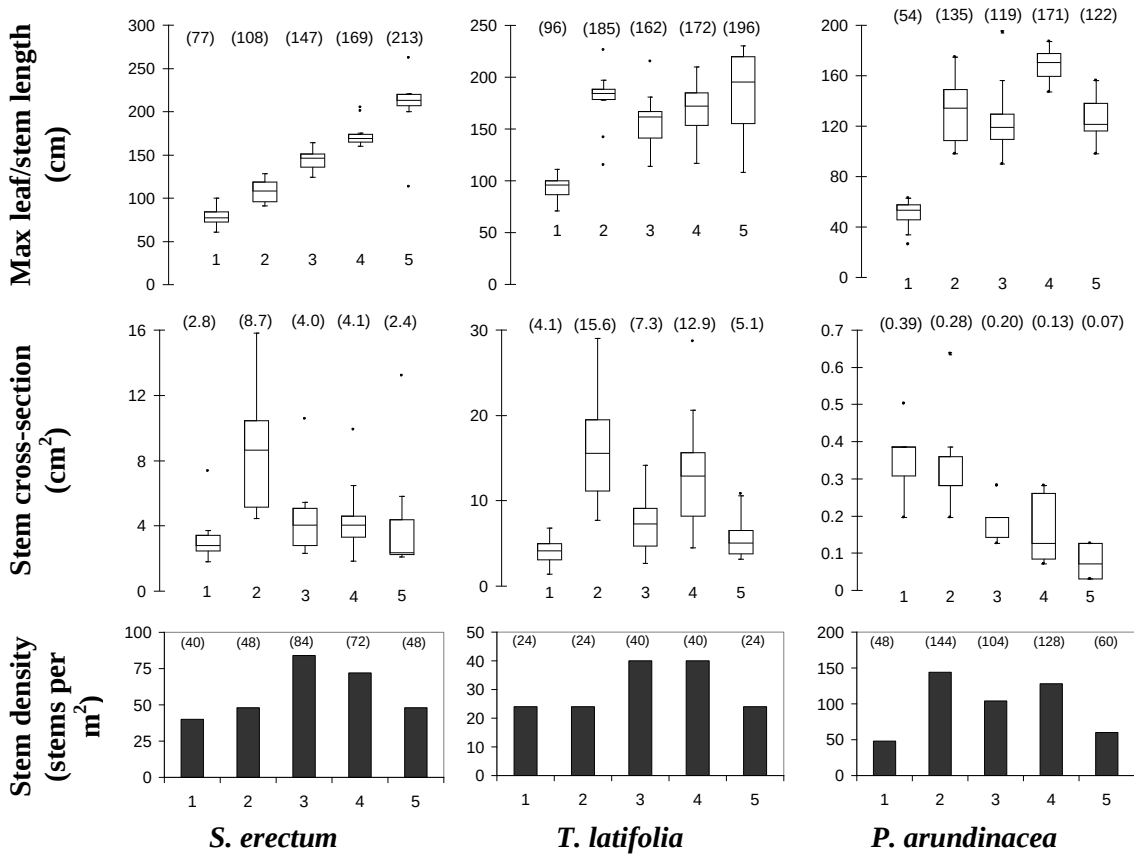


Figure 5.12: Boxplots and bar charts of maximum leaf/stem length, stem cross-section area and stem density over the five measurement periods for all three studied species with median values shown in brackets. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

Table 5.10: Statistically significant differences in above-ground plant size/biomass measurements over time for each of the three studied species assessed using Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

	S. erectum		***T. latifolia***		***P. arundinacea***	
	K-W p value	**S-D-C-F Significant differences ($p < 0.05$)**	**K-W p value**	**S-D-C-F Significant differences ($p < 0.05$)**	**K-W p value**	**S-D-C-F Significant differences ($p < 0.05$)**
Max leaf /stem length	< 0.0001	5 > 4 > 3 > 2 > 1	< 0.0001	2, 3, 4, 5 > 1	< 0.0001	4 > 2, 3, 5 > 1
Stem cross-section area	0.002	2 > 1, 5	< 0.0001	2, 4 > 1, 5 2 > 3	< 0.0001	1, 2 > 3, 4, 5 3 > 5

5.4.4 Species and temporal differences in measures of below-ground plant size/biomass

Species differences

The range and median values of below-ground plant/size biomass measurements for each species are shown in Table 5.11. Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these properties between the macrophyte species (Table 5.12).

There were differences between the species for all three measurements of below-ground plant size/biomass (Table 5.11). *S. erectum* and *T. latifolia* had significantly greater maximum root lengths (median 210 mm and 193 mm respectively) compared to *P. arundinacea* (median 31 mm) (K-W, p = 0.002, Tables 5.11 and 5.12). *S. erectum* had a significantly greater number of rhizomes per plant compared to both *T. latifolia* and *P. arundinacea* (medians 3, 1 and 1 respectively, K-W, p = 0.000, Tables 5.11 and 5.12) and a significantly greater maximum rhizome diameter than *P. arundinacea*. However, *T. latifolia* had a significantly greater maximum rhizome diameter than both *S. erectum* and *P. arundinacea* (K-W, p < 0.0001, Table 5.12). These differences were also clear from visual observations (Figure 5.13). Overall, *S. erectum* plants had many rhizomes, which were long and relatively thick, and they also had long roots which were observed to extend primarily from the base of the stem. *T. latifolia* plants had only a few rhizomes, which were long and thick, and long roots which were observed to extend

primarily from the rhizomes. *P. arundinacea* plants had few rhizomes, which were thin and short, and also short roots.

Table 5.11: Range, median and sample size for the three measures of below-ground plant size/biomass measurements for each species across the five measuring periods.

	S. erectum	***T. latifolia***	***P. arundinacea***
Maximum root length (mm)	10 - 530 210 n = 25	0 - 452 193 n = 26	8 - 300 31 n = 24
Number of rhizomes per plant	0 - 10 3 n = 25	0 - 4 1 n = 26	0 - 2 1 n = 24
Maximum rhizome diameter (mm)	4 - 13 4 n = 20	9 - 24 16 n = 21	2 - 6 4 n = 13

Table 5.12: Significant differences in below-ground plant size/biomass measurements between the three studied species. (S = *S. erectum*, T = *T. latifolia*, P = *P. arundinacea*) identified using Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests.

	K – W p value	**S-D-C-F Significant differences ($p < 0.05$)**
Maximum root length	0.002	S, T > P
Number rhizomes per plant	0.000	S > T, P
Maximum rhizome diameter	<0.0001	T > S > P

Figure 5.13: Photographs of root and rhizome systems of *S. erectum*, *T. latifolia* and *P. arundinacea*.

Temporal differences in measures of below ground plant size/biomass

Due to the below-ground plant growth measurements being undertaken only on the uprooted plants, there were variations in the number of samples between measuring periods for each species (Figure 5.11). Measuring periods for each species with sample numbers less than five are identified in Table 5.13, and they were excluded from statistical analysis.

Table 5.13: Measuring periods for which there were less than five observations of the different measures of below ground plant size/biomass for each of the studied species. (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

	S. erectum	***T. latifolia***	***P. arundinacea***
Maximum root length	1, 2	1, 5	3, 4, 5
Rhizomes per plant	1, 2	1, 5	3, 4, 5
Maximum rhizome diameter	1, 2, 3	1, 3, 4, 5	2, 3, 4, 5

Below-ground measures of plant biomass for each of the species were plotted as boxplots to visualise any differences in these variables over time (Figure 5.14). Mann-Whitney U (M-W) and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were employed to identify significant differences in these variables over time for each macrophyte species for measuring periods with five or more observations (Tables 5.13 and 5.14).

Minimum values of maximum root length were observed in measuring period 1 for *S. erectum* and *T. latifolia* (median 15 mm and 136 mm respectively) and measuring period 2 for *P. arundinacea* (median 13 mm), and maximum values of maximum root length were observed in measuring period 2 for *S. erectum* and *P. arundinacea* (median 525 mm and 263 mm respectively) and measuring period 3 for *T. latifolia* (median 225 mm) (Figure 5.14). *S. erectum* showed a gradual decrease after maximum, with *T. latifolia* and *P. arundinacea* then showing a slight increase again in measuring period 5, with a wide range of values in measuring period 5 for *P. arundinacea* (Figure 5.14). For *S. erectum*, measuring period 3 maximum root lengths were significantly greater than measuring periods 4 and 5 (K-W, $p = 0.003$, Table 5.14, measuring periods 1 and 2 data omitted from analysis). There were no significant differences between the measuring periods with large enough samples for *T. latifolia* and *P. arundinacea* (K-W, $p = 0.631$ and M-W, $p = 0.098$ respectively, Table 5.14).

No clear temporal differences were seen in the number of rhizomes per plant for *T. latifolia* and *P. arundinacea*, with low numbers throughout the measuring periods (Figure 5.14) and with no significant differences between the measuring periods with large enough samples for statistical testing (K-W, p = 0.323 (*T. latifolia*) and M-W, p = 0.074 (*P. arundinacea*), Table 5.14). The maximum number of rhizomes were observed on *S. erectum* in measuring period 5 (median 9) and these were significantly greater than the numbers observed in both measuring periods 3 and 4 (K-W, p = 0.001, Table 5.14, measuring periods 1 and 2 data omitted from analysis).

Maximum rhizome diameter generally showed a decrease through the growing season, with minima in measuring periods 3, 4 and 5 for *S. erectum* (median 4 mm), measuring period 4 for *T. latifolia* (median 12 mm) and measuring periods 2 and 5 for *P. arundinacea* (median 2 mm and 3 mm respectively, Figure 5.14). However, there were no significant differences in the rhizome diameters between the measuring periods with a large enough sample for *S. erectum* (M-W, p = 0.870, Table 5.14) and there were insufficient measuring periods with a large enough sample for either *T. latifolia* or *P. arundinacea*.

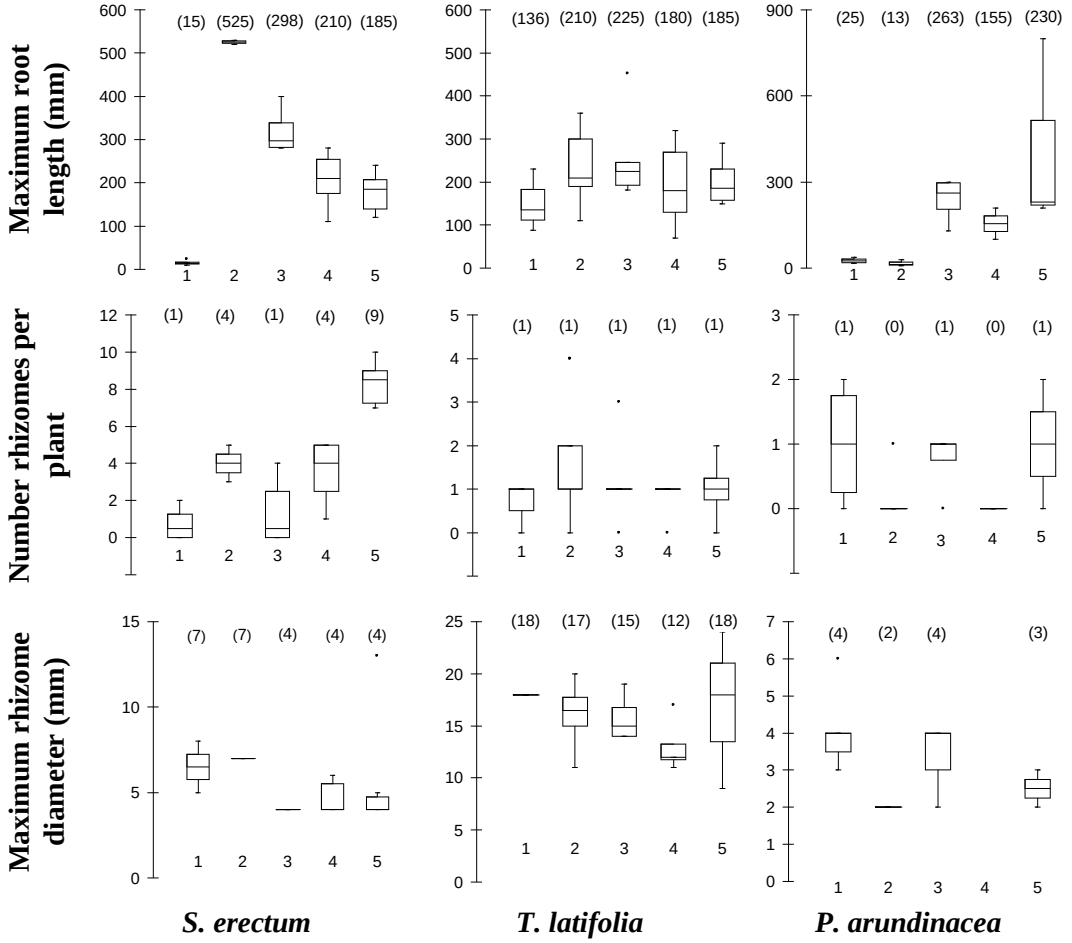


Figure 5.14: Boxplots of maximum root length, number of rhizomes per plant and maximum rhizome diameter observed in each of the measuring periods for each species with median values shown in brackets (note: some boxplots n < 5 – see Table 5.13). (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

Table 5.14: Statistically significant differences in below-ground plant size/biomass measurements over time for each species identified using Mann-Whitney U (M-W) and Kruskal-Wallis (K-W) tests followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s = not significant, * = test not undertaken due to insufficient measuring periods with enough samples). (Measuring period 1 = mid-April, 2 = end-May, 3 = mid-July, 4 = end-August and 5 = mid-October).

	S. erectum		***T. latifolia***		***P. arundinacea***	
	p value	**S-D-C-F Significant differences ($p < 0.05$)**	**p value**	**S-D-C-F Significant differences ($p < 0.05$)**	**p value**	**S-D-C-F Significant differences ($p < 0.05$)**
Maximum root length	K-W 0.003	3 > 4, 5	K-W 0.631	n.s.	M-W 0.098	n.s.
Number rhizomes per plant	K-W 0.001	5 > 3, 4	K-W 0.323	n.s.	M-W 0.074	n.s.
Maximum rhizome diameter	M-W 0.870	n.s.	*	*	*	*

5.4.5 Relationships between biomechanical measurements and measures of plant size/biomass

Spearman's Rank correlation coefficients were calculated to explore the associations between the biomechanical measurements and measures of above-ground and below-ground plant size/biomass for each species (Figures 5.15 and 5.16).

Both *S. erectum* and *T. latifolia* showed positive correlations between all biomechanical measurements and measures of above-ground plant size/biomass (Figure 5.15). These correlations were all significant for *T. latifolia* (S-R, $p < 0.01$ and 0.05, Figure 5.15). *S. erectum* showed significant positive correlations between stem cross-section area and both plant failure resistance and stem strength (S-R, $r_s = 0.512$ and $r_s = 0.705$ respectively, $p < 0.01$, Figure 5.15). *P. arundinacea* showed significant positive correlations between maximum leaf/stem length and both plant failure resistance and uprooting resistance (S-R, $r_s = 0.407$ and $r_s = 0.694$ respectively, $p < 0.01$, Figure 5.15) as well as between stem cross-section area and stem strength (S-R, $r_s = 0.591$, $p < 0.01$, Figure 5.15).

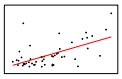
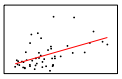
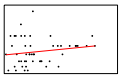
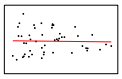
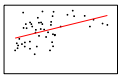
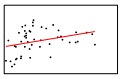
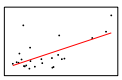
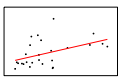
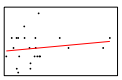
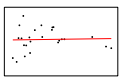
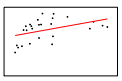
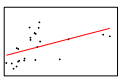
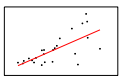
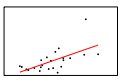
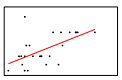
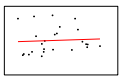
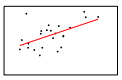
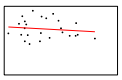
	S. erectum	*T. latifolia*	*P. arundinacea*
Stem cross-section area	 **0.512**	 **0.502**	 0.161
Max leaf/stem length	 0.055	 **0.475**	 **0.407**
	Plant failure resistance	**Plant failure resistance**	**Plant failure resistance**
Stem cross-section area	 0.375	 0.476	 0.103
Max leaf/stem length	 0.090	 **0.573**	 **0.694**
	Uprooting resistance	**Uprooting resistance**	**Uprooting resistance**
Stem cross-section area	 **0.705**	 **0.637**	 **0.591**
Max leaf/stem length	 0.240	 0.482	 -0.114
	Stem strength	**Stem strength**	**Stem strength**

Figure 5.15: Scatter plots and correlations between biomechanical measurements and measures of above-ground plant size/biomass for each macrophyte species. Spearmans Rank correlation coefficients (r_s) significant at $p < 0.01$ are shown in large and bold font, those significant at $p < 0.05$ are shown in large font, and those not significant ($p > 0.05$) are shown in small font.

There were fewer statistically significant correlations between uprooting resistance and the measures of below-ground plant size/biomass. *S. erectum* showed a significant positive correlation between maximum root length and uprooting resistance (S-R, $r_s = 0.516$, $p < 0.01$, Figure 5.16). *P. arundinacea* showed a significant negative correlation between number of rhizomes and uprooting resistance (S-R, $r_s = -0.435$, $p < 0.01$, Figure 5.16).

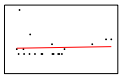
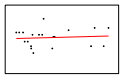
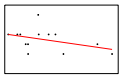
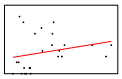
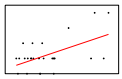
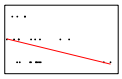
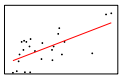
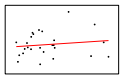
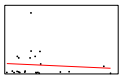
	S. erectum		*T. latifolia*		*P. arundinacea*	
Max rhizome diameter		0.109		0.087		-0.395
Number rhizomes		0.381		0.315		-0.435
Max root length		**0.516**		0.150		-0.059
	Uprooting resistance		**Uprooting resistance**		**Uprooting resistance**	

Figure 5.16: Scatter plots and correlations between uprooting resistance and measures of below-ground plant size/biomass for each macrophyte species. Spearmans Rank correlation coefficients (r_s) significant at p <0.01 are shown in large and bold font, those significant at p <0.05 are shown in large font, and those not significant (p >0.05) are shown in small font.

5.5 Discussion

This discussion centres on interpreting the biomechanical measurements to answer the research question 'How does the ability of three commonly occurring emergent macrophyte species (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) to retain and reinforce fine sediment and thus reduce sediment erosion and resuspension, vary between species and through their growth cycle?'. To do this the biomechanical properties are interpreted as follows:

- *Plant failure resistance*: provides a measure of the degree to which the macrophyte is able to remain in-situ providing some protection and reinforcement to the underlying sediment under varying flow stresses;
- *Uprooting resistance*: provides a measure of the degree to which the macrophyte can maintain root and rhizome reinforcement of underlying sediments under varying flow stresses;
- *Stem strength*: provides a measure of the degree to which the macrophyte can retain an above-ground canopy that can trap sediment and provide some protection to the underlying sediment surface from high shear stresses under varying flow stresses; and
- *Stem breaking stress*: provides similar information to stem strength, but is standardised for stem cross-section area, allowing comparison between individual stems of different sizes.

5.5.1 Species differences in ability to reinforce sediment and reduce sediment erosion and resuspension

There were clear differences in observations of all of the biomechanical measures obtained across the entire monitoring period among the three studied species, inferring clear contrasts in their ability to reinforce and protect the underlying sediment.

T. latifolia showed the greatest plant failure resistance, uprooting resistance and stem strength inferring it thus had the greatest overall ability to reinforce sediment and protect the sediment surface from erosion and resuspension (Table 5.4). Conversely, *P. arundinacea* showed the lowest plant failure resistance, uprooting resistance and, along with *S. erectum*, stem strength, inferring it thus had the lowest ability to reinforce sediment and protect the sediment surface from erosion and resuspension (Table 5.4). None of the species had a greater tendency to uproot or suffer stem breakage than the others, with equal proportions of both occurring across the entire monitoring period (Figure 5.9).

There were also statistically significant associations between the various measures of plant size/biomass and biomechanical strength for each of the studied species (Figures 5.15 and 5.16). For all species, increasing stem strength was statistically significantly correlated ($p < 0.05$) with increasing stem cross-section area. Plant failure resistance was also statistically significantly positively correlated ($p < 0.05$) with stem cross-section area for *S. erectum* and *T.latifolia*. Leaf/stem length was significantly positively correlated with uprooting resistance and plant failure resistance for *T. latifolia* and *P. arundinacea*. These statistically significant positive correlations between the two measures of plant size/biomass (stem-cross section area and maximum leaf/stem length) and stem strength and uprooting resistance illustrate that within each of the three species larger plants are more difficult to uproot and have stems that are more difficult to break. Overall, *T. latifolia* had the greatest stem strength and both the greatest leaf/stem length and stem cross-section area (Tables 5.4 and 5.9).

Similar positive relationships between biomechanical measurements (both stem strength and uprooting resistance) and stem cross-section areas and leaf/stem lengths have been observed in other macrophytes (Liffen *et al*., 2011; Bociag *et al*., 2009; Schutten *et al*., 2005; and, Brewer & Parker, 1990) and terrestrial plants (Liu *et al*., 2011; Burylo *et al*., 2009; and, Mickovski *et al*., 2005). Due to this relationship, above-ground plant size/biomass measurements have been suggested as simple and non-destructive measures for indirectly assessing the biomechanical strength of plants (Liffen *et a*l., 2011 and Burylo *et al*., 2009), particularly as 'plants that invest more in the above-ground parts would also invest more in the proliferation of their root system' (Mickovski *et al*., 2005, p 40). This study has confirmed this trend and has also illustrated the

degree to which the three study species have different associations between biomechanical measurements and above-ground plant measurements as well as contrasting overall strength.

The differences in below-ground plant growth structures between the species were reflected in differing uprooting resistances. *P. arundinacea* had the lowest, and *T. latifolia* and *S. erectum* the highest, uprooting resistance, maximum root length and maximum rhizome diameter (Tables 5.4 and 5.12). However, the relationships between uprooting resistances and below-ground plant size/biomass differed between the species (Figure 5.16). Increasing uprooting resistances were significantly correlated ($p < 0.01$) with increasing maximum root lengths for *S. erectum*. Conversely, increasing uprooting resistances were significantly correlated ($p < 0.05$) with decreasing number of rhizomes for *P. arundinacea*.

Other research has shown the influence of below-ground root and rhizome structures upon the uprooting resistance of plants. Liffen *et al*., (2011) concluded that rhizomes were important in uprooting resistance for *S. erectum* and Burylo *et al*., (2009) in research on terrestrial plants found that rooting depth and vertical anchorage were key in uprooting resistance and resulted in increased root-soil contact. Similarly, Mickovski *et al*., (2005), again in research on a terrestrial plant, found lateral root spread the significant below-ground morphological trait associated with uprooting resistance. However, although below-ground root and rhizome structures are clearly important in terms of a plant's uprooting resistance, sediment conditions, particularly in terms of cohesiveness, can also have a large effect upon a plants ability to withstand uprooting (Schutten *et al*., 2005 and Handley & Davy, 2002) with Pollen-Bankhead *et al*., (2011) and Schutten *et al*., (2005) including sediment cohesion measurements in their modelling of plants uprooting resistance. The lack of association between below-ground plant growth structures and uprooting resistance for *P. arundinacea* imply that below-ground root and rhizome structures may be of less importance to this species and sediment conditions may be of greater importance. The below-ground root and rhizome structures are clearly important in terms of uprooting resistance for *S. erectum* and *T. latifolia*, something that has previously been identified for *S. erectum* by Liffen (2011).

Overall, the below-ground plant growth structure and high stem cross-section of *T. latifolia* imply that it is the species most able to reinforce sediment and reduce sediment erosion and resuspension of the three macrophyte species investigated in this study. Although having the lowest plant failure resistance, uprooting resistance and, along with *S. erectum*, stem strength, *P. arundinacea* had the significantly greatest stem breaking stress, indicating that although not being a strong plant overall, on a per unit stem area basis the stem was the strongest of the three species.

Pollen-Bankhead *et al.,* (2011) modelled the drag forces acting upon *S. erectum* plants at the Mytchett site on the River Blackwater (upstream of the study site used in this research). Drag forces were calculated based upon river cross-section average velocities and species-specific regression parameters related to the number of stems per plant. Therefore, these calculated drag forces are specific to *S. erectum* and would vary for *T. latifolia* and *P. arundinacea* with varying regression parameters. The maximum drag force at mean monthly flow depth occurred in April and was 0.0058 N. This is a few orders of magnitude lower than the lowest plant failure resistance recorded for *S. erectum* and also for *T. latifolia* and *P. arundinacea* (Table 5.3), suggesting a low risk of plants being uprooted or stems failing as a result of drag forces at this site.

Similar biomechanical measurements have been undertaken on other macrophyte and terrestrial species allowing comparison with these three emergent macrophyte species (Table 5.15). Stem strength studies have focused mainly on submerged macrophytes (Table 5.15) with the range of values recorded for these submerged species considerably lower than the median values for the three emergent species in this study. The median stem strength from the other *S. erectum* study is very similar to the *S. erectum* value found in this study, and the mean stem strength for the other emergent species that has been reported (*G. fluitans,* Miler *et al.,* 2012) is greater then for the submerged species, but still lower than values recorded in this study.

Few studies have looked specifically at the uprooting resistance of macrophytes (Table 5.15). A study by Schutten *et al*., (2005) of nine submerged macrophytes produced a range of uprooting resistances (0.25 to 12 N), which are considerably lower than values produced in this study. The median uprooting resistance for the other *S. erectum* study (106 N, Liffen *et al.,* 2011) is considerably greater than the value found for *S. erectum* in this study, and is closer to the *T. latifolia* uprooting resistance. This could be a reflection of the greater number of plants sampled over a longer period of time in the Liffen *et al*., (2011) study compared to this one. In comparison with values for terrestrial plants, the uprooting resistance of a willow tree is an order of magnitude greater than *T. latifolia*, and the uprooting resistance of vetiver grass is approximately four times greater than *T. latifolia*. The lower end of the range of uprooting resistance values recorded by Burylo *et al*., (2009) is comparable to *T. latifolia*, with *Anthyllis vulneraria* (Woundwort – a herbaceous plant) having a mean of 102.7 N and *Quercus pubescens* (Downy Oak tree) having a mean of 108.7 N.

The stem breaking stresses, calculated for the three species in this study, appear to be lower than values recorded for a range of other macrophytes (predominantly submerged/floating leaf species) (Table 5.15). The median stem breaking stress from the *S. erectum* study of Liffen *et*

al. (2011) (0.15 MNm^2) is very similar to the value recorded for *S. erectum* in this study. The mean stem breaking stress for the other emergent species that has been reported (*G. fluitans*, Miler *et al.*, 2012) is greater than the values recorded in this study. However, inter-species variation is apparent with *E. spicatum* recorded in two studies with means of 3.25 MNm^2 by Schutten *et al*., (2005) and 10.0 MNm^2 by Brewer & Parker (1990).

Table 5.15: Summary of stem strengths, uprooting resistances and stem breaking stresses from other studies and this study. (E = emergent macrophyte, S = submerged macrophyte, F = floating leaf macrophyte, T = terrestrial species) (*continued overleaf*).

Stem strength (N)			
Median	*S. erectum* (E)	59	This study
	T. latifolia (E)	121	
	P. arundinacea (E)	39	
Median	*S. erectum* (E)	62	Liffen *et al*. 2011
Mean	*G. fluitans* (E)	26.6	Miler *et al.*, 2012
	F. antipyrectica (S)	2.9	
	R. penicillatus (S)	3.8	
	M. alterniflorum (S)	3.1	
Median	*P. natans* (S/F)	15.6	Bociag *et al*., 2009
	P. pectinatus (S)	3.3	
	B. fluitans (S)	2.6	
	C. fragilis (S)	0.6	
Mean	*R. peltatus* (S)	3.29	Usherwood *et al*., 1997
	R. fluitans (S)	2.26	
Uprooting resistance (N)			
Median	*S. erectum* (E)	38	This study
	T. latifolia (E)	108	
	P. arundinacea (E)	23	
Median	*S. erectum* (E)	106	Liffen *et al*., 2011
Mean	*Salix alba* (T) (Willow tree)	1284.1	Liu *et al*., 2011
Range of means	12 species – trees, shrubs, herbaceous (T)	102.7 – 333.3	Burylo *et al*., 2009
Range of means	Nine macrophytes (S)	0.25 – 12	Schutten *et al*., 2005
Mean	*V. zizanioides* (T) (Vetiver Grass)	466.97	Mickovski *et al*., 2005

Table 5.15: Summary of stem strengths, uprooting resistances and stem breaking stresses from other studies and this study. (E = emergent macrophyte, S = submerged macrophyte, F = floating leaf macrophyte, T = terrestrial species) (*continued*).

Stem breaking stress (MNm^2)			
Median	*S. erectum* (E)	0.13	This study
	T. latifolia (E)	0.20	
	P. arundinacea (E)	2.70	
Median	*S. erectum* (E)	0.15	Liffen *et al*., 2011
Mean	*G. fluitans* (E)	4.18	Miler *et al*., 2012
	F. antipyrectica (S)	19.3	
	R. penicillatus (S)	0.97	
	M. alterniflorum (S)	1.82	
Range of means	9 macrophytes (S)	3 – 10	Schutten *et al*., 2005
Mean	*R. peltatus* (S)	0.72	Usherwood *et al*., 1997
	R. fluitas (S)	1.98	
Mean	*M. spicatum* (S)	10.0	Brewer & Parker, 1990
	R. aquatilis (S/F)	9.6	
	E. canadensis (S)	10.0	
	P. alpinus (S/F)	12.4	
	P. richardsonii (S)	1.9	
	P. filiformis (S)	33.8	

These comparisons have shown that both the stem strength and uprooting resistances of the three emergent macrophytes in this study are greater than the submerged species and that *T. latifolia* has a similar uprooting resistance to small terrestrial plants. Overall, this infers that the three emergent macrophytes have a greater ability to retain and reinforce fine sediment than submerged macrophytes.

Based upon their differing tolerance of water depths, the three emergent macrophyte species occupy varying positions along the river bank profiles (Section 5.2.1) resulting in them potentially performing a series of successive roles in the stabilisation of fine sediments across bank profiles and the development of shelves, benches and ultimately an extension of the river bank. *S. erectum*, positioned at the bottom of the river bank, would be the first macrophyte accumulating and retaining fine sediments. As the fine sediments stabilise and aggrade, *T. latifolia* and then *P. arundinacea* may successively replace *S. erectum* as the aggrading fine sediments develop in to submerged shelves, marginal benches and eventually extensions of the entire river bank profile, providing different inundation / water table environments suitable for different macrophyte species. This process has been termed plant-associated pioneer landform development by Gurnell *et al*., (2012) (Figure 5.17).

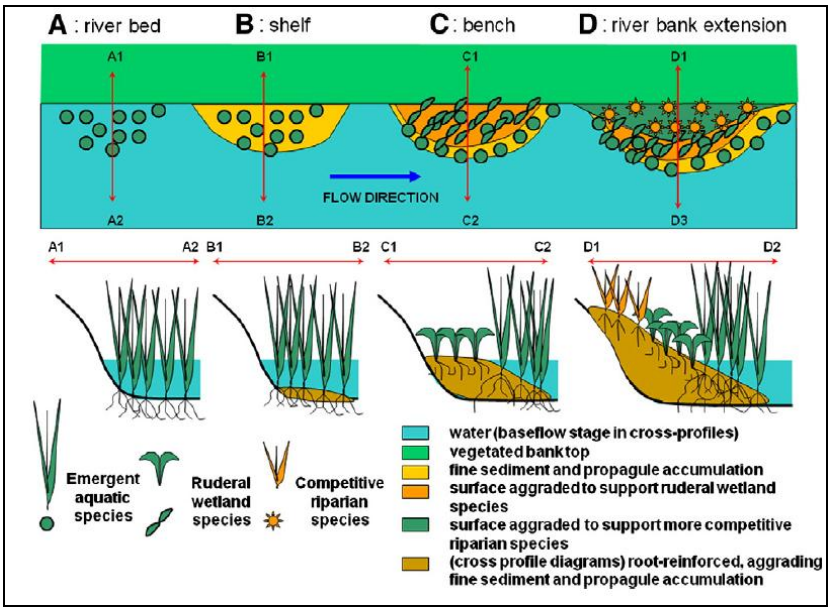


Figure 5.17: Diagram of plant-associated pioneer landform development. Emergent macrophytes trapping sediment (A) to build a submerged shelf (B), marginal bench (C) and finally an extension of the river bank (D), with associated changes in plant types. (Taken from Gurnell *et al*., (2012)).

Therefore, as *S. erectum* is the initial species in this pioneer landform development process it needs to have the ability to successfully accumulate and retain fine sediments. This study has shown that, although not having the greatest uprooting resistance and stem strength of the three emergent macrophyte species studied, compared to other macrophytes (particularly submerged species) *S. erectum* has sufficient ability to withstand uprooting and stem breakage to retain fine sediments and initiate the process of fine sediment stabilisation and aggradation. *P. arundinacea*, although having the lowest uprooting resistance and stem strength, is subject to the lowest flow stresses because of its relatively higher growing position on river banks, and thus it may continue to retain fine sediments in locations where the process has been initiated and sustained by the mechanically stronger species *S. erectum* and *T. latifolia.* This process of stabilisation and aggradation of fine sediments in restored urban rivers by macrophytes is a potentially important process in the storage of sediment associated metals.

5.5.2 Temporal differences in ability to reinforce sediment and reduce sediment erosion and resuspension

There were clear temporal differences in observations of the biomechanical measurements inferring clear changes through time in the macrophytes ability to reinforce and protect the underlying sediment.

All biomechanical measurements were highest in late-May and lowest in mid-April for *S. erectum* and *T. latifolia* (although only statistically significant for both species for plant failure resistance and for stem strength for *S. erectum* due to low sample numbers for some months) inferring the greatest and lowest reinforcement and protection of the underlying sediment by the above-ground canopy of these species was in late-May and mid-April respectively (Figure 5.10). For *P. arundinacea* uprooting resistances were highest in late-August and lowest in mid-October inferring the greatest and lowest sediment reinforcement was in late-August and mid-October respectively, and highest stem strength was in late-May, with a gradual decrease, inferring the greatest protection of underlying sediments was in late-May with a gradual decrease through the growing season (Figure 5.10).

During the growing season, *S. erectum* and *T. latifolia* both had relatively low uprooting resistances and an equal tendency to be uprooted or stem failing in mid-July inferring that the sediments surrounding these species were at the greatest risk of erosion, resuspension and not being reinforced in mid-Summer (Figures 5.10 and 5.11). However, this was the time of greatest stem density for *S. erectum* (Figure 5.12), suggesting that lower median strength of individual plants may be in part compensated by denser plant stands (as new plants emerge from rhizomes between the older established plants). *P. arundinacea* had the greatest tendency to uproot and a low uprooting resistance in mid-April, inferring that sediments surrounding this species were at the greatest risk of erosion, resuspension and not being reinforced in Spring (Figures 5.10 and 5.11).

During the growing season, both *S. erectum* and *T. latifolia* showed a large increase in all biomechanical measurements between mid-April and late-May and a large decrease between late-May and mid-July (Figure 5.10). Section 5.5.1 discussed strong associations between plant failure resistance and stem cross-section area for both *S. erectum* and *T. latifolia* and between plant failure resistance and maximum leaf/stem length for *T. latifolia*. Temporal changes in stem cross-section area and in biomechanical measurements for *S. erectum* and *T. latifolia*, indicate that the greater stem-cross section areas of the plants in late-May, and the lower cross-section areas of the plants in mid-July, are useful indicators of changes in biomechanical strength measurements (Figures 5.10 and 5.12). Additionally, the maximum leaf/stem lengths

for *T. latifolia* show the same temporal pattern as the biomechanical measurements, providing a further surrogate for biomechanical strength whereas this was not the case for *S. erectum*, which showed a steady increase in leaf length throughout the monitoring period (Figures 5.10 and 5.12).

In Section 5.5.1, the strong association between uprooting resistance and maximum root length for *S. erectum* was also discussed. Although maximum root length for *S. erectum* coincides with maximum uprooting resistance (late-May) this measure of below-ground plant size/biomass does not show the same temporal pattern throughout the growing season as uprooting resistance (Figures 5.10 and 5.14). This may be explained by the rapid extension of rhizomes following the late May measurements as rooting length declines (Figure 5.14). The increased number of rhizomes from each plant late in the growing season, when rooting length is very small is a particular property of *S. erectum* and may explain how the sediment retained in submerged patches by this species is protected from erosion through the winter period when no above-ground biomass remains. In contrast, *T. latifolia* shows little variation in roots or rhizomes through time, whereas *P. arundinacea* increases its rooting length through the growing season, with little change in the number or diameter of rhizomes supported by each plant (Figure 5.14)

All three macrophytes have the ability to reproduce both sexually through seed production and vegetatively through rhizome growth and development of daughter plants. However, all species, and particularly *T. latifolia*, predominantly reproduce vegetatively once well-developed stands have been established (Inoue & Tsuchiya, 2006; Maurer & Zedler, 2002; Grace & Wetzel, 1982; and, Cook, 1962). Both *S. erectum* and *T. latifolia* have been observed to produce up to three cohorts of plants within a single growth season, a result of the development of second and third daughter plants from the below-ground rhizomes (Asaeda *et al*., 2010 and Inoue & Tsuchiya, 2006). As noted above, the distinctive decrease in stem-cross section in mid-July may be a result of a second cohort of growth and the resultant smaller daughter plants reducing the size distribution of sampled stems.

The gradual decrease in stem strength over the monitoring period for *P. arundinacea* can be related to stem cross-section area, which shows the same temporal pattern (Figures 5.10 and 5.12). In Section 5.5.1, the little influence of below-ground plant growth upon uprooting resistance for *P. arundinacea* was described, and again maximum uprooting resistance occurred when the sampled species supported no rhizomes. *P. arundinacea* has been observed to grow in two distinct phases. The first stage is characterised by rapid growth in which the plant invests predominantly in above-ground biomass and in the second stage the plant predominantly invests

in below-ground biomass (Adams & Galatowitsch, 2005). This is thought to be a competitive trait which has resulted in *P. arundinacea* being a successful invasive plant in North America (Lavergne & Molofsky, 2004). The gradual decrease in stem-cross section area through the monitoring period could be a reflection of the decreasing investment in above-ground plant biomass by the species through the growing season.

5.6 Conclusions

This study has shown that there are clear differences between emergent macrophyte species in both their overall biomechanical measurements and variations through the growth season which infers clear species differences in both their ability to reinforce and protect underlying sediments and variations through the growing season. These variations have implications in terms of differing risks of sediment-associated contaminants (including metals) being released from the underlying sediments in urban rivers.

Biomechanical measurements of *T. latifolia* indicate that due to it being the species most able to reinforce and protect underlying sediment due to its morphological characteristics of high stem cross-sections and large roots and rhizomes, it was the macrophyte whose underlying sediments would be at the lowest risk of releasing metals. Conversely, biomechanical measurements of *P. arundinacea* indicate that it was the species least able to reinforce and protect underlying sediment and therefore the underlying sediments would be at the greatest risk of releasing metals. However, given the growing position of *P. arundinacea* higher up the river bank, the macrophyte is likely to be subject to lower flow stresses than the other two species. Temporally, biomechanical measurements infer that sediments underlying *S. erectum* and *T. latifolia* would be most at risk of releasing metals in the middle of the growth season (mid-July), whereas sediments underlying *P. arundinacea* would be most at risk of releasing metals at the beginning of the growth season (mid-April) and also during the winter when no above-ground biomass is present. Overall however, comparison of published biomechanical measurements inferred that the studied emergent macrophytes had a greater ability to reinforce and protect underlying sediments than submerged macrophytes and the well-developed below-ground biomass of all three species during winter (although achieved by different root and rhizome development) provides an ability to retain sediments when the above-ground biomass is negligible. These different properties of the three species are highly relevant to species selection and use for the management of metal contaminated sediments in urban rivers.

Inter-species variations in risks of underlying sediments releasing metals have been shown through biomechanical measurements which infer sediment reinforcement and protection. However, the risk is also dependent upon the uptake of metals in to macrophyte tissues and

translocation of those metals from below-ground to above-ground tissues which may reduce the storage of sediment-associated metals. The uptake and translocation of metals by different macrophyte species in urban rivers is considered in Chapter 6.

Chapter 6

The Uptake and Translocation of Metals by Three Common Emergent Macrophytes: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*

6.1 Introduction

As well as reducing the risk of underlying sediments releasing metals through reinforcement and protection, macrophytes can ameliorate metal contaminated sediments through processes of phytoremediation including uptake into plant tissues and translocation from below-ground to above-ground tissues. Phytoremediation has been used and studied extensively in constructed wetlands and detention ponds for the treatment of heavily contaminated wastewaters and runoff or in rivers or lakes which are either currently, or have historically, been heavily impacted by known contaminant discharges (e.g. sewage treatment discharges) (e.g. Fawzy *et al*., 2012; Ladislas *et al*., 2012; Yeh *et al*., 2009; Sasmaz *et al*., 2008; Liu *et al*., 2007; Sundberg-Jones & Hassan, 2007; Maine *et al*., 2006; Karathanasis & Johnson, 2003; Cardwell *et al*., 2002; Mays & Edwards, 2001; Samecka-Cymerman & Kempers, 2001; Hares & Ward, 1999; Scholes *et al*., 1998; and, Ellis *et al*., 1994). Fewer studies have looked at phytoremediation occurring naturally in watercourses affected by general urban and agricultural runoff where no specific direct discharges are the focus (e.g. Zhang *et al*., 2010 and Vardanyan *et al*., 2008).

This Chapter reports on an investigation into the concentrations of metals in three common emergent macrophyte species that are often found in urban river systems and their associated overlying water and sediment, along with their abilities to uptake and bioconcentrate metals from the sediment and translocate them from below-ground to above-ground tissues. The research was undertaken to answer the following research questions:

- What is the distribution of metals between three commonly occurring emergent macrophytes (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) and associated overlying water and sediments?

- To what extent do the characteristics and metal concentrations of overlying water and sediment associated with these three commonly occurring emergent macrophytes vary between the species?

- How does the uptake and storage of metals in three commonly occurring emergent macrophyte species vary?

- To what extent do three commonly occurring emergent macrophyte species bioconcentrate and translocate metals?

6.2 Research Site

Research was undertaken at research site one within Hawley Meadows on the River Blackwater in Surrey, UK, a lowland urban river which has been heavily impacted by gravel extraction, transportation development and urbanisation (Figures 6.1 and 6.2 and Section 3.2.2 in Chapter 3). Hawley Meadows is approximately 15 km downstream from the source of the river (central grid reference: SU 86078 58985). On the right bank the meadows are bounded by the A331 with industrial and residential areas beyond, and on the left bank a railway line with residential areas beyond (Figure 6.2). During construction of the A331 in the 1980's this site was particularly affected. The river was re-aligned and the meadows lowered to increase flood storage capacity. However, in 1987/88 dredging of the channel occurred to narrow and deepen the channel in an attempt to reduce excessive macrophyte growth (Daniels *et al*., 2000) and since then work has been undertaken to restore the site as a floodplain meadow, with improvements to habitats and the introduction of cattle grazing (Blackwater Valley Countryside Partnership, 2012). The upstream section of the river channel at the study site contains extensive stands of *Typha latifolia* and the middle and downstream sections contain stands of *Sparganium erectum* and *Phalaris arundinacea* (Figure 6.3).

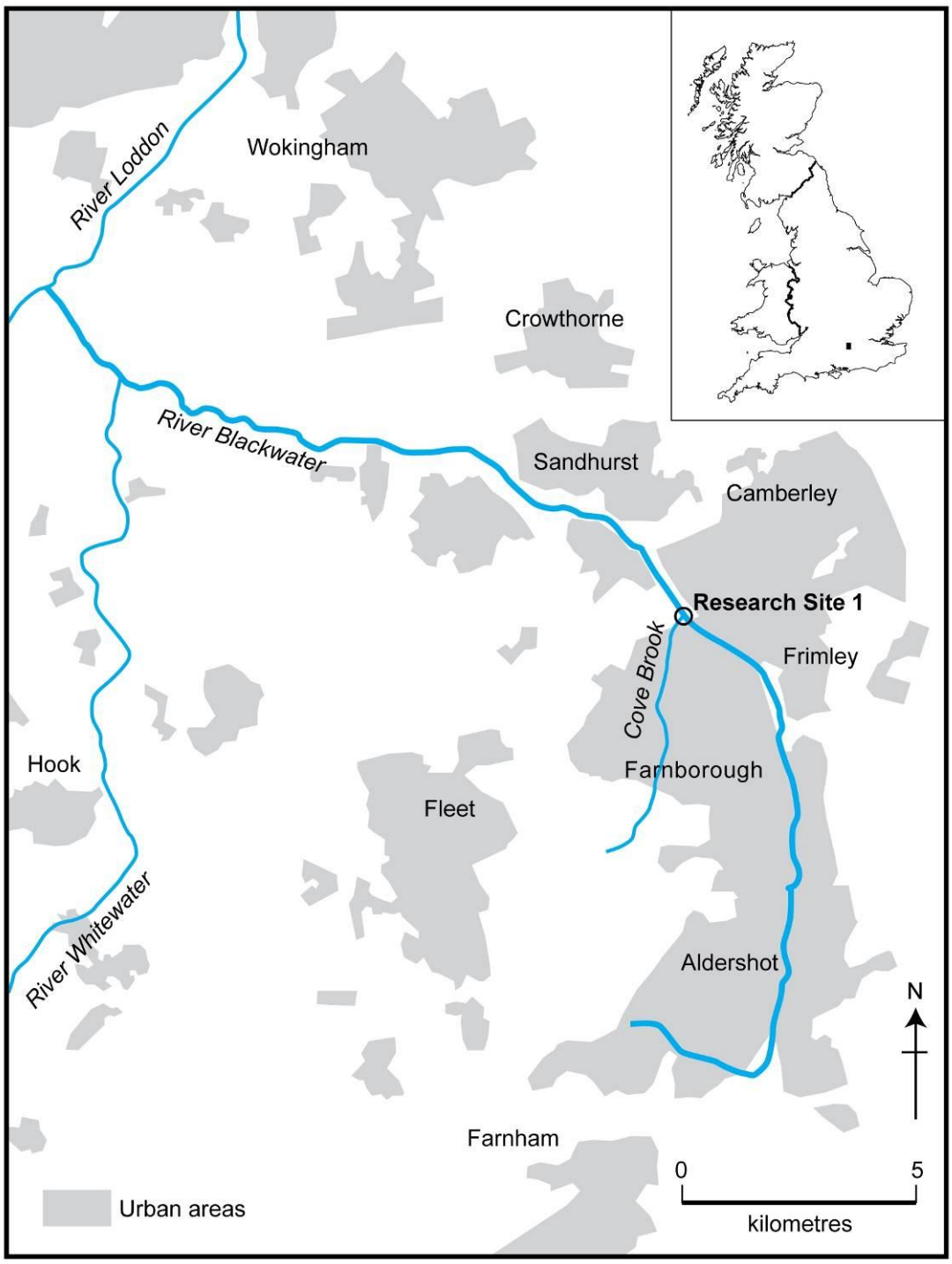


Figure 6.1: Location of research site one, Hawley Meadows, on the River Blackwater.

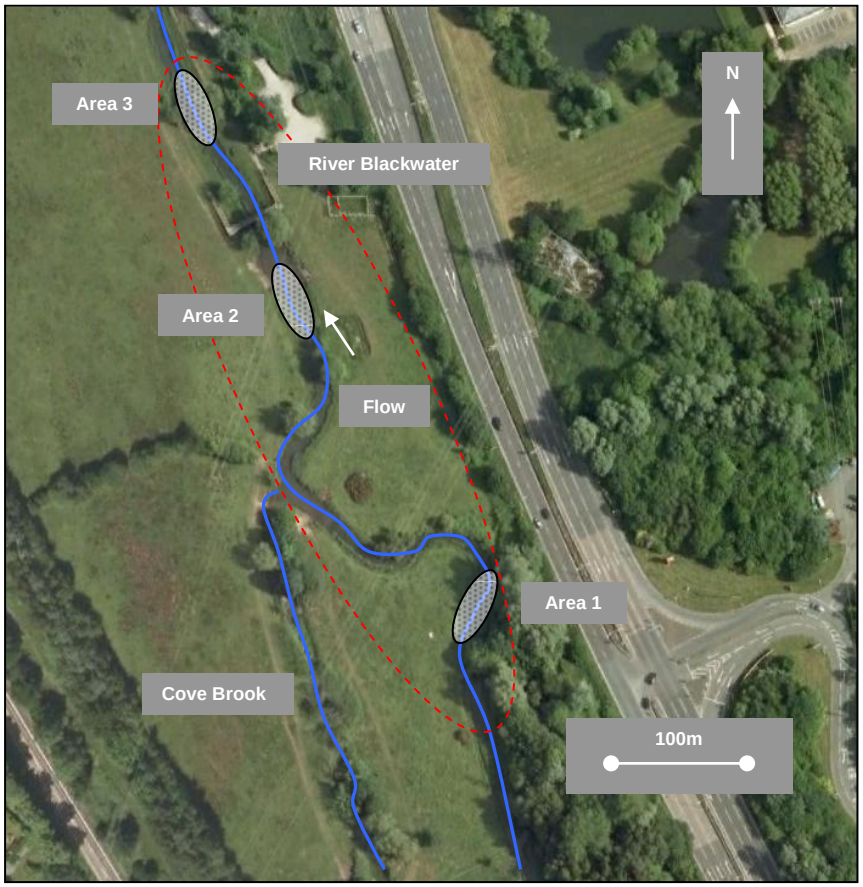


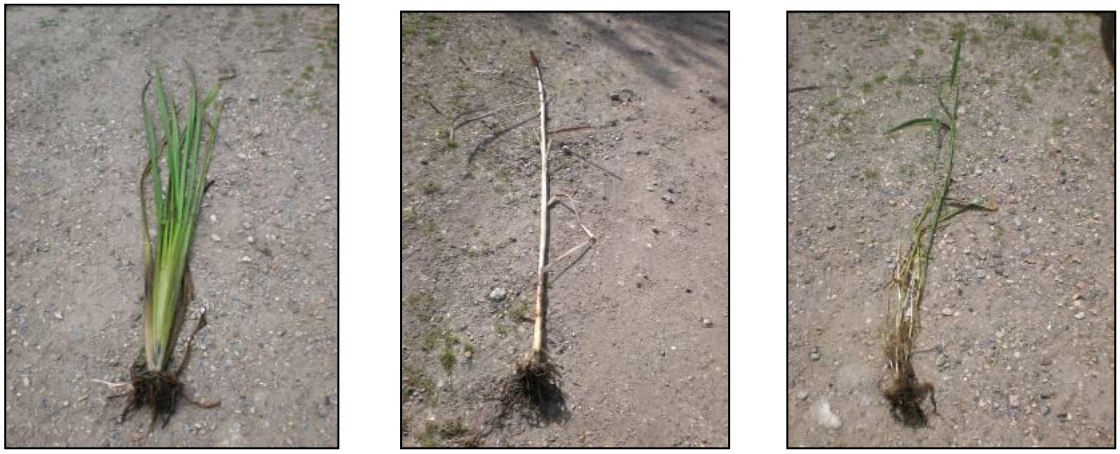
Figure 6.2: Detailed map of research site one, Hawley Meadows, on the River Blackwater. Area 1: upstream section with *T. latifolia*. Area 2: middle section with *S. erectum* and *P. arundinacea*. Area 3: lower section with *S. erectum* and *P. arundinacea*.

Figure 6.3: Overview photographs of research site one, Hawley Meadows, on the River Blackwater (a) upstream section with *T. latifolia* (June 2012), (b) middle section with *S. erectum* and *P. arundinacea* (June 2012) (c) lower section with *S. erectum* and *P. arundinacea* (June 2012) (d) *T. latifolia* in upstream section in November 2011 (e) *S. erectum* and *P. arundinacea* in downstream section in November 2011.

6.3 Methods

6.3.1 Fieldwork

Fieldwork was undertaken on two occasions: November 2011 and June 2012. The November sampling was used as an exploratory study to investigate the levels of metals in the river environment and to inform the research undertaken in June, at the peak of macrophyte growth. Measurements were undertaken on the same three macrophyte species that were used for biomechanical measurements (Chapter 5) (*Sparganium erectum, Typha latifolia* and *Phalaris arundinacea*) (Figure 6.4).



S. erectum ***T. latifolia*** ***P. arundinacea***

Figure 6.4: Photographs of *S. erectum*, *T. latifolia* and *P. arundinacea* plants.

Fieldwork focussed upon collection of three types of samples: overlying water, sediment and macrophytes. In the November sampling, as the macrophytes had begun to collapse, three composite samples of each macrophyte species were collected. Associated sediment and overlying water samples were collected from the centre of the area of the composite macrophyte sample. In June, due to the large biomass of *T. latifolia*, five individual *T. latifolia* plants were collected along with adjacent overlying water, sediment and porewater samples. However, due to the lower biomass of the other macrophyte species five replicates of two adjacent *S. erectum* and five adjacent *P. arundinacea* plants were collected along with overlying water, sediment and porewater samples from in-between the adjacent plants.

(i) Overlying water

Overlying water samples were collected first to prevent disturbance of the sediment affecting water samples and readings. Water pH and dissolved oxygen concentrations were measured in-situ since these parameters can significantly alter once a sample is taken. pH and dissolved oxygen content (mgl^{-1}) were taken just below the surface with a calibrated VWR pH100 and YSI dissolved oxygen meter (model 550A) respectively.

Metal concentrations in water can be determined as either total concentrations or dissolved concentrations, with dissolved concentrations operationally defined as < 0.45 µm (Radojevic & Bashkin, 1999 and Chapman, 1998). As dissolved metal concentrations in waters are often at very low concentrations, care needs to be taken to preserve the samples once collected and to prevent contamination. To prevent contamination all sampling equipment was acid-washed prior to use and water samples were acidified immediately after collection (pH <2) in order to preserve the sample and prevent changes in metal concentrations (USEPA, 1992). A 500 ml

overlying water sample was collected approximately 10 cm below the water surface in an acid-washed sample bottle. This bottle was then shaken and a 10 ml sample removed using an acid-washed syringe. The sample was filtered through a 0.45 µm filter into an acid-washed vial containing 0.5 ml concentrated HNO_3 up to the 10 ml mark (5 ml concentrated HNO_3 for every 1 litre of sample) and shaken (USEPA, 1992). The samples were then put in the fridge on the same day as collection.

For total water hardness a 500 ml overlying water sample was collected approximately 10 cm below the surface. The samples were stored in the fridge on the same day as collection.

(ii) Sediment

In the June sampling, sediment redox conditions were determined using porewater Fe (II) concentrations as a proxy (Section 3.3.1 in Chapter 3). Prior to sediment sampling, porewater samplers were inserted at the sampling locations and left to allow the sediment to settle. Porewater was extracted from the sediment and filtered through a nitrogen-flushed 0.45 µm filter into buffered phenanthroline (1:5 porewater:buffered phenanthroline) and stored in the dark on the day of collection.

Surface sediments were sampled to a depth of 10 cm using a 45 mm diameter plastic corer, which was rinsed in river water between samples. The sediment sample was composited in a sample bag and a sub-sample taken and used to create a 1:2.5 sediment:deionised water suspension that was shaken for 5 minutes. pH was measured in the suspension with a calibrated VWR pH100 meter (Section 3.3.1 in Chapter 3). Excess air was removed and the sample bag was then sealed and frozen on the day of collection.

(iii) Macrophytes

Both the above-ground (leaf and stems) and below-ground (roots and rhizomes) tissues of each plant were collected, with excess sediment being removed in the river.

6.3.2 Laboratory analysis

This section provides an overview of the laboratory analysis undertaken on the samples collected for this study, including the quality control results. Full details and discussion of each laboratory method and quality control procedures is provided in Chapter 3, Section 3.3.2. Analytical grade chemicals and ultrapure water were used for all analyses. Additionally, all glassware used for metal analysis was acid-washed in 10% HNO_3.

(i) Overlying water analysis

The dissolved metal concentrations (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the overlying water samples were analysed directly by ICP-OES (Varian Vista Pro CCD Simultaneous ICP-OES) as soon as possible after collection. Total hardness (as $CaCO_3$) was analysed by an EDTA titration (Radojevic & Bashkin, 1999).

(ii) Sediment analysis

Sediment underwent the same analysis as described in Chapter 4 (Figure 6.5). All sediment samples were defrosted, weighed and dried at 105°C. The dried samples were sieved to 2 mm and the weight of the >2 mm and <2 mm fractions was determined. Subsamples of the <2 mm fraction were used in determinations of % organic matter content, metal concentrations (pseudo-total via aqua regia extraction and acetic acid extractions: Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and absolute particle size (% <63 µm). Metal concentrations were analysed by ICP-OES. Absolute particle size was analysed on the Beckman Coulter Laser Diffraction particle size analyser.

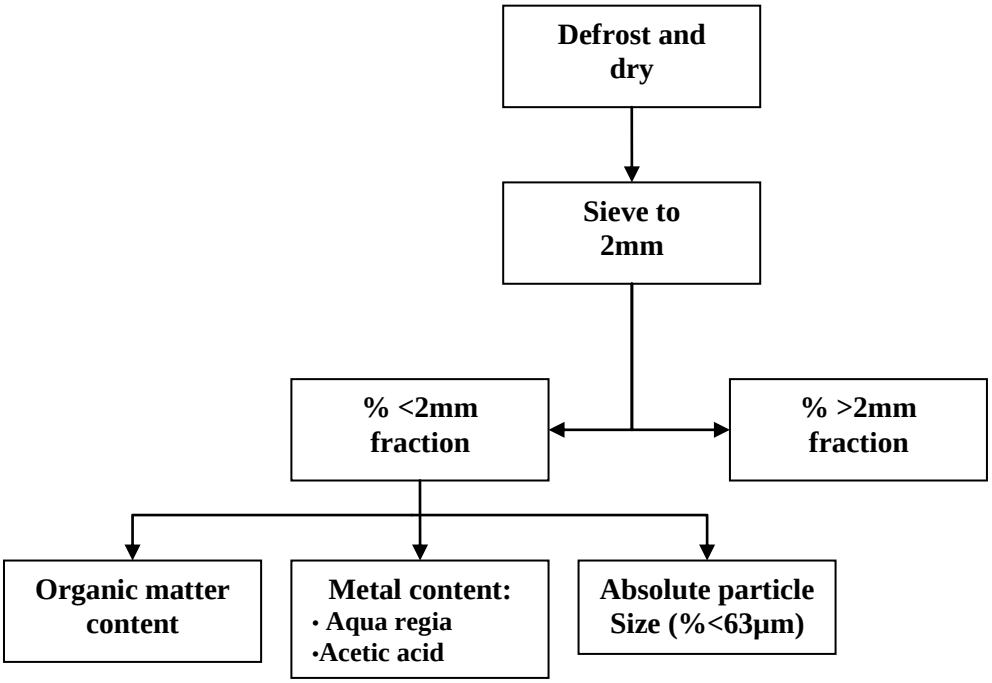


Figure 6.5: Flow diagram summarising laboratory analysis of sediment samples.

(iii) Macrophyte analysis

In the laboratory the macrophyte samples were carefully washed with tap water and then deionised water until the water ran clear to remove all sediment. They were then patted dry and split in to the separate tissues for each macrophyte (Table 6.1). As the *P. arundinacea* plants

had a very low biomass in November, the root and rhizome samples had to be combined. In June sufficient material was collected for these to be separated.

Table 6.1: Macrophyte tissue samples analysed in November 2011 and June 2012.

	November 2011	**June 2012**
S. erectum	Roots	Roots
	Rhizomes	Rhizomes
	Leaf/Stem	Leaf/Stem
T. latifolia	Roots	Roots
	Rhizomes	Rhizomes
	Leaf/Stem	Leaf/Stem
P. arundinacea	Roots & Rhizomes	Roots
	Leaf/Stem	Rhizomes
		Leaf/Stem

The tissues were dried in the oven at 85°C for 72 hours and then milled to a fine powder in a ball-mill. Sub-samples were then used in the determination of metal concentrations (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) through a nitric acid and hydrogen peroxide extraction and analysed by ICP-OES. With the June samples, the dry weights of the roots, rhizomes and leaf/stem of each individual plant for each macrophyte species was also recorded after oven drying.

(iv) Porewater analysis

Porewater samples were analysed by UV-VIS spectrophotometry (Evolution 100 Thermo Scientific Spectrophotometer) for Fe (II) concentrations.

(v) Quality control

As detailed in Chapter 3 (Section 3.3.2) quality control procedures were employed to ensure the quality of the laboratory analysis. The accuracy of sediment and macrophyte extractions, total water hardness determinations and the particle size analyser were determined using certified reference materials. The precision of extractions, water hardness determinations and the ICP-OES were determined by calculation of relative standard deviations. Analytical blanks were used to identify any contamination. Full results of the quality control are provided in Appendix V. Metal extractions generally had recoveries over 80%, with some Ni and Pb acetic acid sediment recoveries of 70 to 80%. Metal extractions had relative standard deviations below 15%. The majority of analytical blanks were <LoD, although higher concentrations were recorded for Fe. Analytical relative standard deviations were generally below 5%, although higher values were recorded for Cr and Cu in macrophytes and Fe and Zn in the overlying water, thought to be due to the low concentrations.

6.3.3 Data analysis

Analysis focussed on metal concentrations in overlying water, sediment (both pseudo-total and acetic acid extractable) and macrophytes (in roots, rhizomes and leaf/stems) samples and overlying water and sediment characteristics for the three different macrophyte species. Although samples were taken at two different time periods, data were collated and analysed as one data set, since the November sampling was an exploratory sampling round (Section 6.3.1). As *P. arundinacea* samples in November were only combined root and rhizome samples, these data points were removed from analysis.

Bioconcentration factors (BCF, both root, rhizome and leaf/stem), which evaluate the ability of the macrophyte to concentrate metals within their tissues from the surrounding sediment, were calculated as (Romero Nunez *et al*., 2011; Yeh *et al*., 2009; and, Sasmaz *et al*., 2008):

$$BCF = M / S$$

where M is the concentration of metal in the macrophyte tissue (either root or rhizome or leaf/stem, in $mgkg^{-1}$) and S is the concentration of metal in the sediment (pseudo-total, in $mgkg^{-1}$).

Translocation factors (TF), which evaluate the ability of the macrophyte to translocate metals from below-ground tissues to above-ground tissues, were calculated as (Romero Nunez *et al*., 2011; Yeh *et al*., 2009; Sasmaz *et al*., 2008; and, Deng *et al*., 2004):

$$TF = LS / (RT + RZ)$$

where LS is the concentration of metal in the leaf/stem ($mgkg^{-1}$), RT is the concentration of metal in the root ($mgkg^{-1}$) and RZ is the concentration of metal in the rhizome ($mgkg^{-1}$).

In order to compare metal storage between macrophyte species, which takes into account the differing dry biomasses of the tissues between the macrophyte species, the mass of each metal (MM, mg/plant) within each macrophyte species was calculated as:

$$MM = (RTW * RT) + (RZW * RZ) + (LSW * LS)$$

where RTW, RZW and LSW are the median dry weight biomass of the roots, rhizomes and leaf/stems of each macrophyte species (kg) and RT, RZ and LS are the median metal

concentration in the root, rhizome and leaf/stem of each macrophyte species ($mgkg^{-1}$) (Windham *et al*., 2003).

In order to compare the storage of metals in the different macrophyte species on an areal basis (per m^2 of channel), which takes into account the differing growing densities of the macrophyte species, macrophyte metal storage on a per m^2 channel basis (MMC, mgm^{-2}) was calculated as (Karathanasis & Johnson, 2003):

$$MMC = MM * \text{number of plants per } m^2$$

where MM is the mass of metal within each plant, calculated above.

In order to compare the storage of metals in the macrophytes (MMC, above) to storage in the underlying sediments, sediment metal storage on an areal basis (per m^2 of channel) was calculated (Karathanasis & Johnson, 2003). This would then provide information on where the greatest storage of metal was. Since detailed sediment depth measurements were made for *S. erectum* in the Chapter 7 study, this calculation was only undertaken for *S. erectum*.

The storage of metals in the sediment underlying the *S. erectum* plants was calculated on the basis of a similar method used in Chapter 4 (Section 4.3.3) based upon sediment weights and metal concentrations.

The storage of each metal in the underlying sediment per m^2 of channel (mgm^{-2}, (in the <2 mm fraction)) was calculated as (Table 6.2):

= average metal concentration ($mgkg^{-1}$) * weight of sediment <2 mm per m^2 of channel (kgm^{-2})

Table 6.2: Variables used in calculation of metal storage in the sediment.

Variable 1: Average metal concentration ($mgkg^{-1}$)	
Average metal concentration ($mgkg^{-1}$)	Mean sediment pseudo-total metal concentration in this study in the <2 mm fraction of the *S. erectum* sediment samples.

Variable 2: Weight of sediment <2 mm per m^2 of channel (kgm^{-2})	
Where:	
Weight of sediment <2 mm per m^2 of channel (kgm^{-2}) = total weight of sediment per m^2 of channel (kgm^{-2}) * proportion of sediment (by weight) that is <2 mm (%)	
And: Total weight of sediment per m^2 of channel (kgm^{-2}) = total sediment volume per m^2 of channel (m^3m^{-2}) * whole sediment sample dry bulk density (kgm^{-3})	
Total sediment volume per m^2 of channel (m^3m^{-2})	Mean sediment volume per m^2 of channel with *S. erectum* growth calculated in Chapter 7 study.
Whole sediment sample dry bulk density (kgm^{-3})	Mean dry bulk density calculated for all *S. erectum* sediment samples from this study (method detailed in Section 3.3.2, Chapter 3).
Proportion of sediment that is <2 mm	Mean proportion of whole sediment sample that is <2 mm (by weight) for all *S. erectum* sediment samples from this study.

All data analysis was undertaken using Microsoft Excel 2003, XLSTAT Pro 2011 and 2012 and SPSS version 16.0. Prior to statistical analysis, the data were screened for values below the level of determination (LoD) and a decision made on how to treat these values (Section 3.4.1 in Chapter 3). The frequency distributions of the variables were determined through visual inspection of histograms and statistically tested for normality using the Kolmogorov-Smirnov (K-S) test (full results in Appendix VI). Overlying water and sediment metal concentrations and characteristics (apart from sediment % >2 mm) were normally distributed (K-S, $p > 0.05$). Macrophyte metal concentrations were non-normally distributed (K-S, $p < 0.05$). Non-normality is less likely to be detected in smaller data sets and there can be difficulties in comparing results of analyses when different statistical tests have been applied. Therefore, non-parametric methods were used throughout the study. Differences in metal concentrations and characteristics in overlying water and sediment between the macrophyte species were statistically tested using non-parametric Kruskal-Wallis tests (K-W). If the K-W test indicated a significant difference, post-hoc Steel-Dwass-Critchlow-Fligner tests (S-D-C-F) tests were undertaken to identify which macrophyte species were significantly different from each other.

Similarly, differences in metal concentrations between the macrophytes and in metal concentrations in the different tissues within the macrophytes were statistically tested using non-parametric Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner tests (S-D-C-F) tests. The strength of associations between the variables were analysed using the non-parametric Spearmans Rank test (S-R). The bioconcentration and translocation of metals were assessed by calculating bioconcentration factors (BCFs) and translocation factors (TF's) (see above, earlier in this Section).

6.4 Results

6.4.1 Overlying water

(i) Data preparation and description

Of the metals of interest, the overlying water samples only had detectable concentrations of dissolved Fe, Mn and Zn, with the remaining all being <LoD. Therefore, analysis focussed on dissolved Fe, Mn and Zn concentrations, pH and dissolved oxygen concentrations. The data set is shown in Appendix VII and is summarised in boxplots in Figure 6.6.

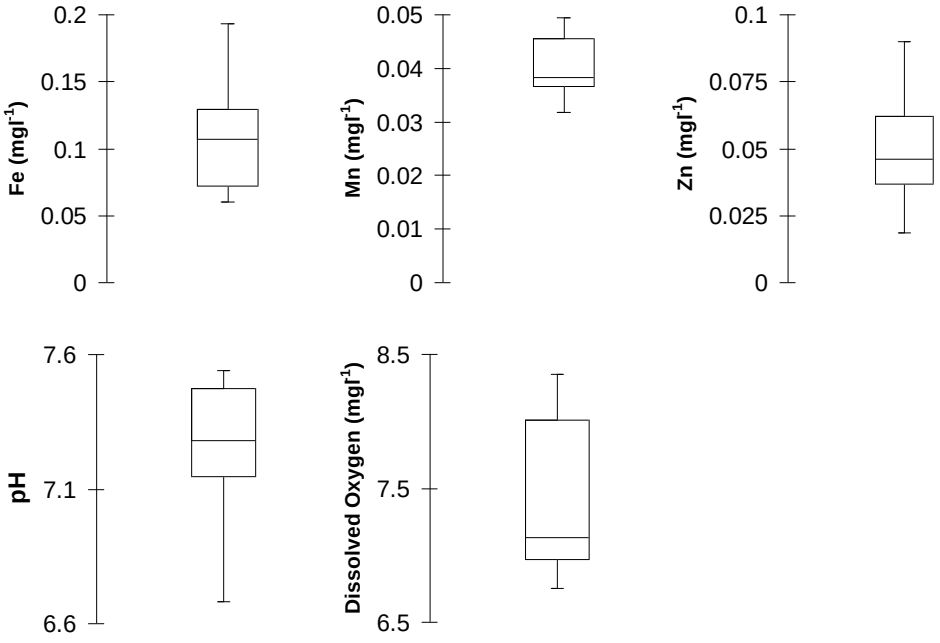


Figure 6.6: Boxplots of the overlying water dissolved metal concentrations, pH and dissolved oxygen data set.

(ii) Overlying water dissolved metal, pH and dissolved oxygen concentrations and differences between macrophyte species

The range and median dissolved metal concentrations, pH and dissolved oxygen in the overlying water for each macrophyte species are presented in Table 6.3. Comparison of the median dissolved metal, pH and dissolved oxygen concentrations to water quality standards (Table 6.4) (using the median total water hardness values shown in Table 6.5 as appropriate for Zn) showed that there were no exceedances indicating that overlying water dissolved metal concentrations were not very high, pH was in the acceptable range and dissolved oxygen levels were not too low.

Table 6.3: Range and median dissolved metal concentrations in overlying water samples (n = 8).

	Range and median metal concentration (2 s.f.)		
Macrophyte	**Fe (mgl^{-1})**	**Mn (mgl^{-1})**	**Zn (mgl^{-1})**
S. erectum	0.070 – 0.15	0.037 – 0.047	0.032 – 0.090
	0.12	0.037	0.041
T. latifolia	0.060 – 0.13	0.032 – 0.048	0.019 – 0.070
	0.69	0.033	0.049
P. arundinacea	0.074 – 0.19	0.038 – 0.049	0.032 – 0.080
	0.13	0.043	0.056
	pH	**Dissolved oxygen (mgl^{-1})**	
S. erectum	6.68 – 7.28	6.75 – 8.10	
	7.14	7.09	
T. latifolia	7.14 – 7.54	6.93 – 8.35	
	7.50	7.12	
P. arundinacea	7.13 – 7.52	6.95 – 8.12	
	7.41	7.26	

Table 6.4: Overlying water quality standards for metals.

	Water quality standard	
Fe	1 mgl^{-1} (annual mean)	'Good' standard for river. From WFD – The River Basins Districts Typology, Standards and Groundwater Threshold Values (WFD) (England and Wales) Directions 2010
Mn	0.3 mgl^{-1} (maximum acceptable concentration)	Proposed Aquatic Environmental Quality Standards for implementation of Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (Dangerous Substances Directive) – List II substances
Zn	0.075 mgl^{-1} (annual mean) (based on hardness – Table 6.5)	'Good' standard for river. From WFD – The River Basins Districts Typology, Standards and Groundwater Threshold Values (WFD) (England and Wales) Directions 2010
pH	6 - 9	Protection of fish life through the Freshwater Fish Directive.
Dissolved Oxygen	$\geq$ 7 mgl^{-1} (for Cyprinid waters)	Protection of fish life through the Freshwater Fish Directive.

Table 6.5: Range and median total hardness of overlying water (n = 8).

	Range and Median Total hardness (3 sf)
Macrophyte Species	**$CaCO_3$ mgl^{-1}**
S. erectum	156 – 173 162
T. latifolia	163 – 180 171
P. arundinacea	159 – 175 167

Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were used to identify significant differences in overlying water dissolved metal concentrations, pH and dissolved oxygen concentrations between the different macrophyte species. The only significant difference between the macrophyte species in terms of dissolved metal concentrations was for Fe (K-W, $p = 0.004$) with dissolved Fe concentrations in the overlying

water being significantly lower around *T. latifolia* compared to both *S. erectum* and *P. arundinacea* (Table 6.6). pH was significantly lower in the overlying water samples surrounding *S. erectum* as opposed to *T. latifolia* and *P. arundinacea* (Table 6.6).

Table 6.6: Statistically significant differences in dissolved metal concentrations, pH and dissolved oxygen of overlying water samples between species identified using Kruskal-Wallis (K-W) tests and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (n.s. = not significant, S = *S. erectum*, T = *T. latifolia* and P = *P. arundinacea*).

	K-W p-value	**S-D-C-F Significant differences ($p < 0.05$)**
Fe (mgl^{-1})	0.004	S, P > T
Mn (mgl^{-1})	0.114	n.s.
Zn (mgl^{-1})	0.652	n.s.
pH	0.003	T, P > S
Dissolved oxygen (mgl^{-1})	0.636	n.s.

Associations between the overlying water dissolved metal concentrations and the overlying water characteristics were explored by calculating Spearman's Rank correlation coefficients (Table 6.7). The only significant correlations were for dissolved Mn, which was significantly negatively correlated with pH (S-R, $p < 0.01$) and significantly positively correlated with dissolved oxygen (S-R, $p < 0.05$).

Table 6.7: Spearmans Rank correlations between overlying water dissolved metal concentrations and characteristics (n = 24). Correlation coefficients significant at $p < 0.01$ are shown in large and bold font, significant at $p < 0.05$ in large font and not significant ($p > 0.05$) in small font.

	Fe	**Mn**	**Zn**	**pH**	**Dissolved oxygen**
Fe					
Mn	0.299				
Zn	0.098	-0.233			
pH	-0.114	**-0.521**	0.242		
Dissolved oxygen	-0.349	0.508	0.007	-0.247	

6.4.2 Sediment

(i) Data preparation and description

All sediment samples had detectable concentrations of all of the metals of interest for pseudo-total metal concentrations apart from Cd, and detectable concentrations of Cu, Fe, Mn, Ni and Zn acetic acid extractable metals (full results are shown in Appendix VII). As 100% of the samples had concentrations of Pb_{acetic} that were <LoD this variable was removed from the data set. As <50% of samples were <LoD for Cd_{total}, Cd_{acetic} and Cr_{acetic} these samples were replaced with 0.5 LoD values (0.5 $mgkg^{-1}$ for Cd_{total}, 0.25 $mgkg^{-1}$ for Cd_{acetic} and 0.13 $mgkg^{-1}$ for Cr_{acetic}) to allow their inclusion in statistical analyses (Section 3.4.1 Chapter 3). Analysis therefore focussed on 20 variables. The data set is summarised in boxplots in Figure 6.7.

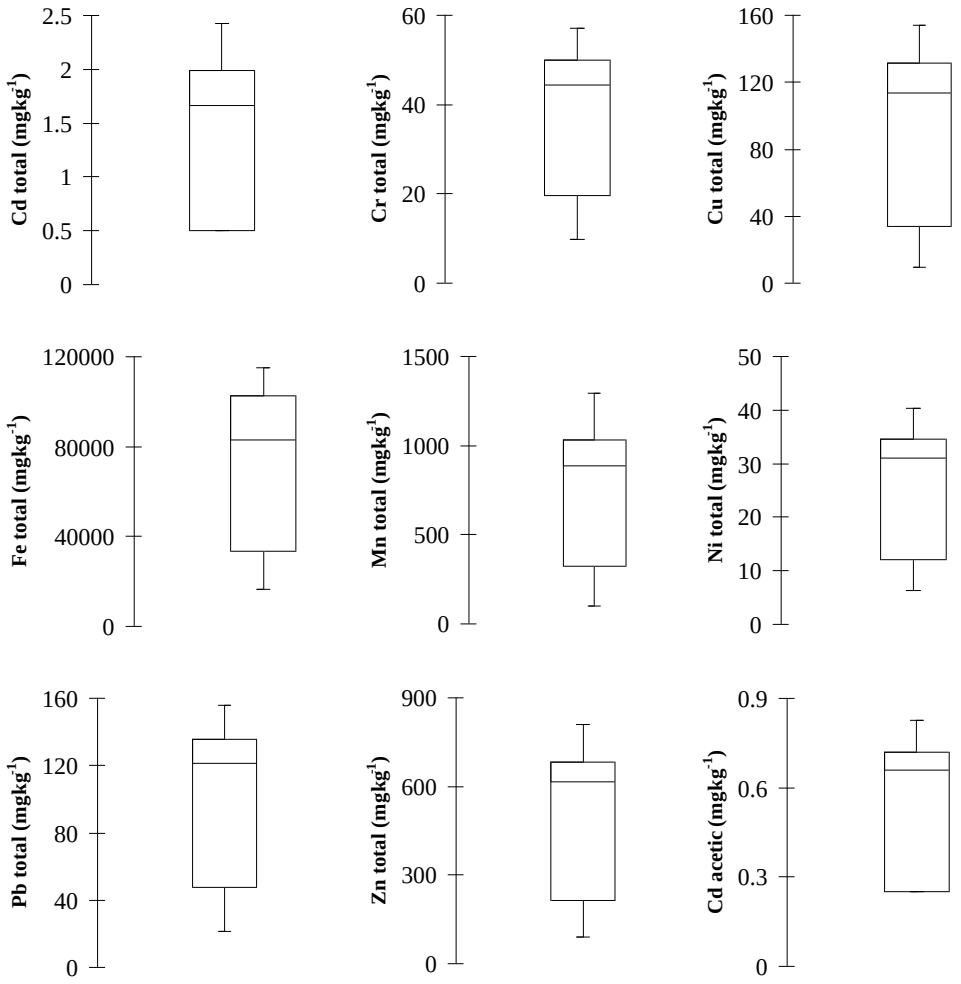


Figure 6.7: Boxplots of pseudo-total metals, acetic acid metals and sediment characteristics for the data set (*continued overleaf*).

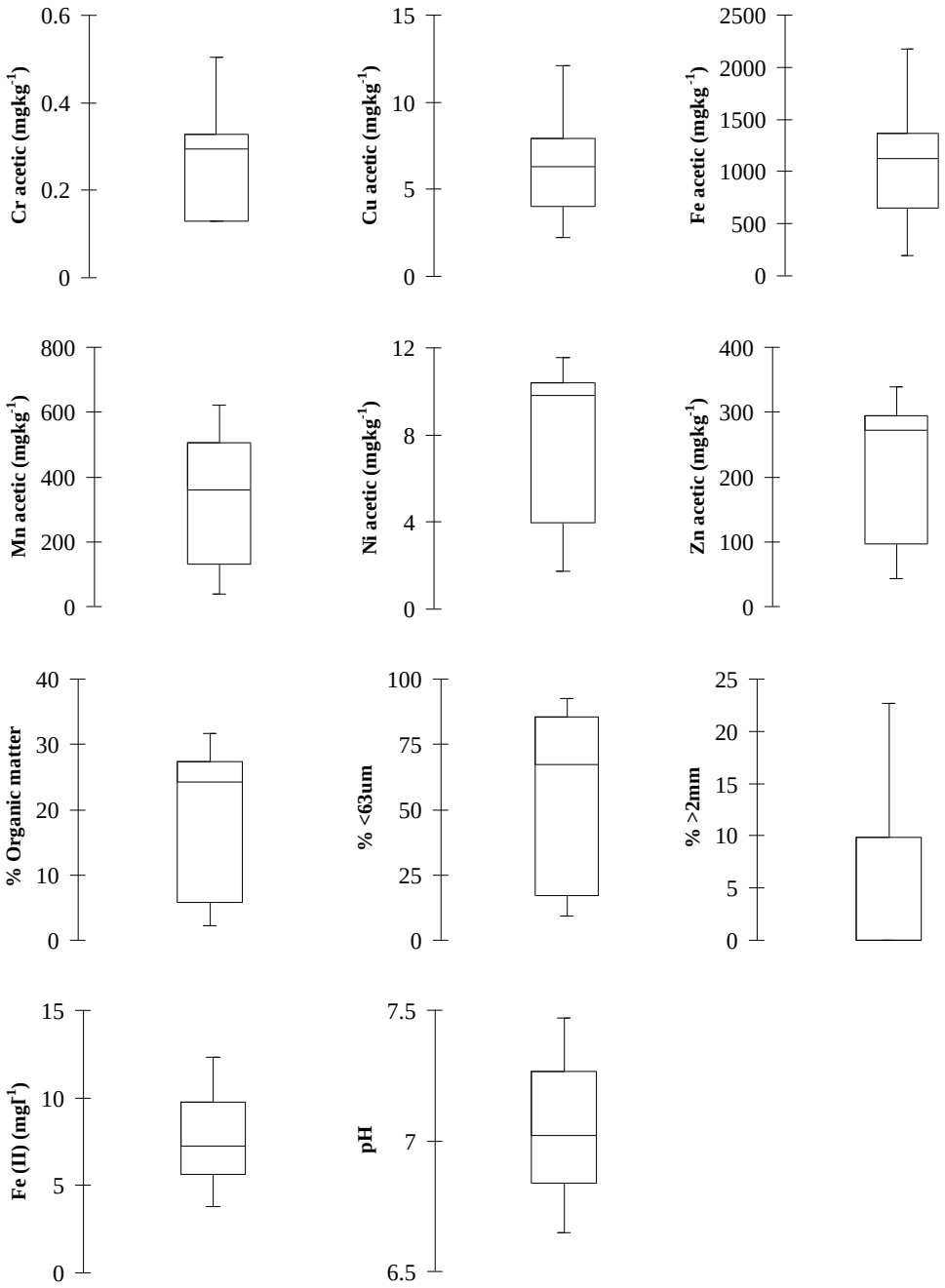


Figure 6.7: Boxplots of pseudo-total metals, acetic acid metals and sediment characteristics for the data set (*continued*).

(ii) Sediment metal concentrations and characteristics and differences between macrophyte species

The range and median values for sediment metal concentrations, % organic matter, % <63 µm, % >2 mm, Fe (II) concentrations and pH of the data set for each macrophyte species are presented in Table 6.8. There were large differences in concentrations of different metals. The highest pseudo-total metal median concentration was for Fe_{total} (105,000, 79,700 and 84,700

mgkg^{-1} for *S. erectum*, *T. latifolia* and *P. arundinacea* respectively) and the lowest for Cr_{total} (169, 1.66 and 1.69 mgkg^{-1} for *S. erectum*, *T. latifolia* and *P. arundinacea* respectively). The highest acetic acid metal median concentration was for Fe_{acetic} (1,290, 846 and 1,130 mgkg^{-1} for *S. erectum*, *T. latifolia* and *P. arundinacea* respectively) and the lowest for Cr_{acetic} 0.300, 0.284 and 0.306 mgkg^{-1} for *S. erectum*, *T. latifolia* and *P. arundinacea* respectively). Sediment pH values were all within the pH neutral range (range of medians pH 6.78 to 7.33). Median % >2 mm was 0.00% for all three macrophyte species due to all sediment samples having 0.00% >2 mm in the June 2012 sampling period. Based upon the whole data set, median sediment pseudo-total metal concentrations were in the order: Fe > Mn > Zn > Pb > Cu > Cr > Ni > Cd, and sediment acetic acid metal concentrations were in the order: Fe > Mn > Zn > Ni > Cu > Cd > Cr.

Table 6.8: Range and median metal concentrations and sediment characteristics of sediment samples for the data set (3 s.f.) (n = 8, apart from Fe (II) where n = 5 as only sampled in June 2012).

	S. erectum	***T. latifolia***	***P. arundinacea***
Cd_{total} ($mgkg^{-1}$)	0.500 – 2.17 1.69	0.500 – 2.00 1.66	0.500 – 2.43 1.69
Cr_{total} ($mgkg^{-1}$)	14.5 – 57.1 45.3	9.76 – 51.5 43.0	11.1 – 56.0 44.8
Cu_{total} ($mgkg^{-1}$)	20.5 – 153 118	9.69 – 137 111	16.4 – 154 113
Fe_{total} ($mgkg^{-1}$)	28,400 – 115,000 105,000	19,200 – 92,200 79,700	16,400 – 113,000 84,700
Mn_{total} ($mgkg^{-1}$)	202 – 1070 745	178 – 1300 937	98.2 – 1140 931
Ni_{total} ($mgkg^{-1}$)	9.47 – 37.7 31.3	6.36 – 38.4 31.0	7.30 – 40.3 31.6
Pb_{total} ($mgkg^{-1}$)	30.5 – 156 125	21.6 – 142 122	29.2 – 156 119
Zn_{total} ($mgkg^{-1}$)	143 – 789 639	89.8 – 740 622	98.9 – 810 604
Cd_{acetic} ($mgkg^{-1}$)	0.250 – 0.826 0.696	0.250 – 0.736 0.605	0.250 – 0.792 0.684
Cr_{acetic} ($mgkg^{-1}$)	0.130 – 0.399 0.300	0.130 – 0.503 0.284	0.130 – 0.354 0.306
Cu_{acetic} ($mgkg^{-1}$)	3.32 – 11.9 7.31	2.21 – 9.76 5.64	2.97 – 12.10 6.34
Fe_{acetic} ($mgkg^{-1}$)	411 – 2,180 1,290	194 – 1,370 846	526 – 1,520 1,130
Mn_{acetic} ($mgkg^{-1}$)	79.5 – 516 309	83.1 – 622 462	37.9 – 546 398
Ni_{acetic} ($mgkg^{-1}$)	2.96 – 10.9 9.07	1.76 – 11.3 9.80	2.50 – 11.6 10.4
Zn_{acetic} ($mgkg^{-1}$)	72.8 – 338 275	43.8 – 316 257	57.9 – 313 284
% Organic matter	4.55 – 29.67 24.69	2.30 – 31.7 25.6	4.00 – 28.11 22.82
% <63 µm	16.9 – 92.5 77.7	11.6 – 90.4 60.8	9.42 – 91.1 58.5
% >2 mm	0.0 – 11.2 0.00	0.0 – 22.7 0.00	0.0 – 19.14 0.00
Fe (II) (mgl^{-1})	7.19 – 12.3 10.3	3.77 – 7.24 4.04	6.72 – 10.4 8.70
pH	6.65 – 7.08 6.78	7.20 – 7.47 7.33	6.75 – 7.32 7.02

Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were used to identify significant differences in metal concentrations and characteristics of the sediment samples between the different macrophyte species (Table 6.9). There were no significant differences in metal concentrations, organic matter content or grain size indicators (% <63 µm and % >2 mm) between the species (K-W, $p > 0.05$, Table 6.9). Fe (II) concentrations (sampled only in June 2012) were significantly greater in the sediment samples surrounding *S. erectum* than *T. latifolia* (K-W, $p = 0.018$), and pH was significantly greater in the sediment samples surrounding *T. latifolia* and *P. arundinacea* than *S. erectum* ($p = 0.003$) (Table 6.9).

Table 6.9: Statistically significant differences in metal concentrations and characteristics of the sediment samples between the macrophyte species identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s. = not significant, S = *S. erectum*, T = *T. latifolia* and P = *P. arundinacea*. * = Fe (II) data set only for June 2012).

	K-W p-value	**S-D-C-F Significant differences ($p < 0.05$)**
Cd_{total} ($mgkg^{-1}$)	0.902	n.s.
Cr_{total} ($mgkg^{-1}$)	0.692	n.s.
Cu_{total} ($mgkg^{-1}$)	0.758	n.s.
Fe_{total} ($mgkg^{-1}$)	0.349	n.s.
Mn_{total} ($mgkg^{-1}$)	0.454	n.s.
Ni_{total} ($mgkg^{-1}$)	0.885	n.s.
Pb_{total} ($mgkg^{-1}$)	0.932	n.s.
Zn_{total} ($mgkg^{-1}$)	0.821	n.s.
Cd_{acetic} ($mgkg^{-1}$)	0.592	n.s.
Cr_{acetic} ($mgkg^{-1}$)	0.982	n.s.
Cu_{acetic} ($mgkg^{-1}$)	0.498	n.s.
Fe_{acetic} ($mgkg^{-1}$)	0.435	n.s.
Mn_{acetic} ($mgkg^{-1}$)	0.444	n.s.
Ni_{acetic} ($mgkg^{-1}$)	0.353	n.s.
Zn_{acetic} ($mgkg^{-1}$)	0.797	n.s.
% Organic matter	0.939	n.s.
% <63µm	0.797	n.s.
% >2mm	0.879	n.s.
Fe (II) (mgl^{-1})*	0.018	S > T
pH	0.003	T, P > S

Sediment pseudo-total metal concentrations were analysed using sediment quality guidelines to assess the potential impact upon the aquatic ecosystem (Environment Agency, 2008).

Draft freshwater quality guidelines were published by the Environment Agency in 2008 for As, Cd, Cr, Cu, Pb, Ni and Zn (Environment Agency, 2008). These draft guidelines define two levels of concentrations for metals: the 'Threshold Effect Level' (TEL) and the 'Predicted Effect Level' (PEL) (Table 6.10). The TEL is the concentration below which sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms. The PEL is the lower limit of the range of concentrations associated with adverse biological effects. However, these concentrations are just triggers for further investigation since other environmental conditions, such as pH and organic matter content, have an impact upon the potential bioavailability of these metals to aquatic organisms.

Table 6.10: Environment Agency draft freshwater sediment quality guidelines Threshold Effects Level (TEL) and Predicted Effects Level (PEL) concentrations for the metals of interest (Environment Agency, 2008).

	TEL	**PEL**
Metal	**($mgkg^{-1}$ dry weight)**	
Cr	37.3	90
Cu	36.7	197
Ni	18	35.9
Pb	35	91.3
Zn	123	315

Figure 6.8 shows the percentage of sediment samples which were below the TEL concentration, those that exceeded the TEL concentration (but were below the PEL concentration) and those that exceeded the PEL concentration for Cr, Cu, Ni, Pb and Zn. The TEL was exceeded for some samples for every metal. The PEL was not exceeded for any samples for Cr and Cu and a greater percentage of samples exceeded the PEL than just the TEL for Pb and Zn.

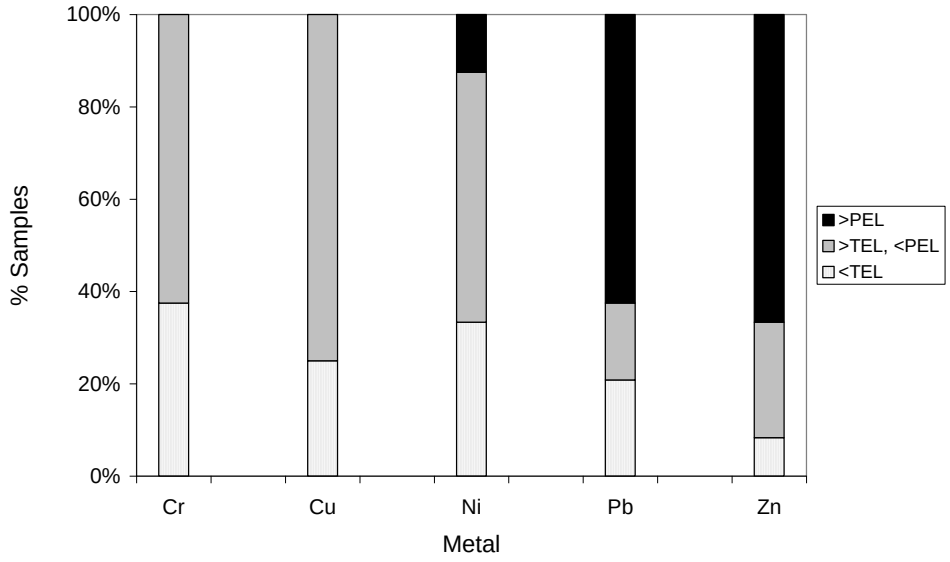


Figure 6.8: Percentage of sediment samples exceeding Environment Agency sediment quality guidelines.

The proportion of the acetic acid extractable metal concentration in the samples in relation to the pseudo-total metal concentration is presented in Table 6.11. Acetic acid extractable metal concentrations provide an indication of the concentration of metal which is more bioavailable, being only weakly sorbed and associated with carbonates (Trujillo-Cardenas *et al*., 2010; Filgueiras *et al.*, 2002; and, Gleyzes *et al*., 2002). Hence, greater proportions of acetic acid extractable metals indicate potentially greater bioavailability. The metals Cd, Mn and Zn had the greatest proportion in the acetic acid extractable form (> 40%) and Cr, Fe and Cu had the lowest proportion (< 10%) (Table 6.11). Ni had ca. 30% (Table 6.11) (note: the higher sediment drying temperature was found to increase Cr and Cu and decrease Fe acetic acid extractable concentrations Section 3.3.2, Chapter 3).

Table 6.11: Median percentage of total metals in sediment which are acetic acid extractable.

	Percentage of metals which are acetic acid extractable						
	Cd	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
S. erectum	46	0.7	9	1	46	29	45
T. latifolia	41	0.7	7	1	47	31	44
P. arundinacea	42	0.6	7	2	45	32	47

Associations between the sediment metal concentrations and sediment characteristics were explored by calculating Spearman's Rank correlation coefficients (Figure 6.9). As Fe (II) concentrations were only determined in the June 2012 sampling period, this subset of data was only used for Fe (II) concentration correlations.

The majority of sediment metal concentrations and sediment characteristics showed significant correlations with each other (S-R, $p < 0.05$). All metal concentrations (both pseudo-total and acetic acid) had significant positive correlations with each other (all at S-R, $p < 0.01$ apart from Mn_{total} and Fe_{acetic}, $p < 0.05$). Organic matter content and % <63 μm both were significantly positively correlated with all metal concentrations and each other (S-R, $p < 0.01$). All metal concentrations were significantly negatively correlated with % >2 mm (S-R, $p < 0.01$). There were no significant correlations between pH and the metal concentrations and other sediment characteristics (S-R, $p > 0.05$) for the whole data set. For the June 2012 data set similarly there were no significant correlations between Fe (II) concentrations and the sediment metal concentrations and other sediment characteristics (S-R, $p > 0.05$).

Full Data Set																				June 2012 Data Set
Cd total																			0.057	
0.940	**Cr total**																		0.146	
0.949	**0.990**	**Cu total**																	0.029	
0.797	**0.839**	**0.839**	**Fe total**																0.479	
0.741	**0.789**	**0.805**	**0.683**	**Mn total**															-0.350	
0.941	**0.961**	**0.967**	**0.788**	**0.856**	**Ni total**														-0.057	
0.924	**0.968**	**0.984**	**0.808**	**0.827**	**0.968**	**Pb total**													-0.121	
0.942	**0.984**	**0.990**	**0.841**	**0.797**	**0.968**	**0.981**	**Zn total**												0.021	
0.817	**0.857**	**0.844**	**0.872**	**0.715**	**0.837**	**0.839**	**0.853**	**Cd acetic**											0.343	
0.805	**0.820**	**0.820**	**0.715**	**0.600**	**0.805**	**0.826**	**0.842**	**0.804**	**Cr acetic**										-0.282	
0.555	**0.666**	**0.646**	**0.833**	**0.623**	**0.598**	**0.645**	**0.636**	**0.813**	**0.642**	**Cu acetic**									0.400	
0.669	**0.732**	**0.721**	**0.743**	0.460	**0.696**	**0.704**	**0.748**	**0.666**	**0.813**	**0.595**	**Fe acetic**								0.089	
0.684	**0.737**	**0.751**	**0.668**	**0.970**	**0.780**	**0.767**	**0.731**	**0.674**	**0.535**	**0.655**	**0.410**	**Mn acetic**							-0.332	
0.744	**0.830**	**0.822**	**0.617**	**0.768**	**0.859**	**0.822**	**0.829**	**0.681**	**0.745**	**0.534**	**0.789**	**0.711**	**Ni acetic**						-0.154	
0.884	**0.936**	**0.939**	**0.810**	**0.758**	**0.931**	**0.933**	**0.949**	**0.881**	**0.896**	**0.683**	**0.791**	**0.683**	**0.851**	**Zn acetic**					-0.061	
0.927	**0.940**	**0.951**	**0.804**	**0.849**	**0.952**	**0.953**	**0.954**	**0.823**	**0.790**	**0.615**	**0.675**	**0.793**	**0.789**	**0.918**	**OM**				-0.186	
0.787	**0.848**	**0.852**	**0.846**	**0.778**	**0.816**	**0.840**	**0.832**	**0.793**	**0.733**	**0.777**	**0.591**	**0.792**	**0.631**	**0.766**	**0.828**	**%<63 µm**			0.045	
-0.832	**-0.774**	**-0.777**	**-0.776**	**-0.688**	**-0.779**	**-0.780**	**-0.783**	**-0.832**	**-0.833**	**-0.768**	**-0.601**	**-0.677**	**-0.602**	**-0.773**	**-0.777**	**-0.809**	**% >2 mm**			
-0.044	-0.062	-0.040	-0.255	0.271	0.031	0.036	-0.039	-0.255	-0.056	-0.237	-0.167	0.270	0.108	-0.083	0.045	-0.035	0.152	**pH**	**-0.645**	
																			Fe (II)	

Figure 6.9: Spearmans Rank (r_s) correlations between sediment metal concentrations and characteristics (n = 24, n = 15 for Fe (II)). Correlation coefficients significant at $p<0.01$ in large and bold font, $p<0.05$ in large font and $p>0.05$ in small font. (no Fe (II) and >2mm correlation as all >2mm values were zero).

6.4.3 Macrophytes

(i) Data preparation and description

All macrophyte samples contained concentrations of Fe and Mn above the limit of determination (LoD) (full results are shown in Appendix VII). Since the majority of samples were <LoD for Cd (100%) and Pb (92%) these variables were removed. As <50% samples were <LoD for Cr, Cu, Ni and Zn these samples were replaced with 0.5 LoD values (0.1 $mgkg^{-1}$ for Cr, 1 $mgkg^{-1}$ for Cu, 2.1 $mgkg^{-1}$ for Ni and 7 $mgkg^{-1}$ for Zn) to allow their inclusion in statistical analyses (Section 3.4.1 Chapter 3). It should be noted that the Ni <LoD values were present in the leaf/stem and rhizome samples.

Analysis therefore focussed on six metals (Cr, Cu, Fe, Mn, Ni and Zn). As in the exploratory November 2011 sampling period *P. arundinacea* below-ground tissues could not be separated into roots and rhizomes due to low tissue weights these root/rhizome samples have been removed from analysis. The data set is summarised in boxplots in Figure 6.10.

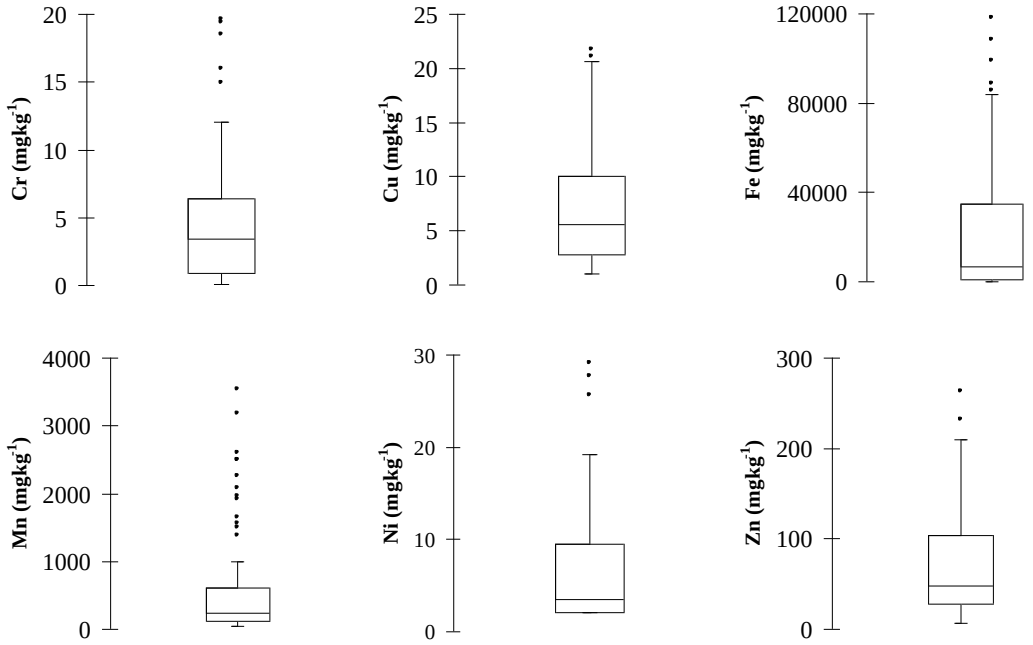


Figure 6.10: Boxplots of macrophyte metal concentrations.

(ii) Macrophyte metal concentrations and differences between tissues and species

Based upon the whole data set, median metal concentrations in macrophytes were in the order: Fe > Mn > Zn > Cu > Cr > Ni. Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were used to identify the differences in metal concentrations between the macrophyte species (Table 6.12). The only significant differences were for Cu and Zn with Cu concentrations in *S. erectum* being significantly greater than in *T. latifolia* (K-W, p = 0.015,

Table 6.12) and Zn concentrations in *P. arundinacea* being significantly greater than in *T. latifolia* (K-W, p = 0.012, Table 6.12).

Table 6.12: Statistically significant differences in metal concentrations between macrophyte species identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n.s. = not significant, S = *S. erectum*, T = *T. latifolia* and P = *P. arundinacea*).

	K-W p-value	**S-D-C-F Significant differences ($p < 0.05$)**
Cr ($mgkg^{-1}$)	0.451	n.s.
Cu ($mgkg^{-1}$)	0.015	S > T
Fe ($mgkg^{-1}$)	0.126	n.s.
Mn ($mgkg^{-1}$)	0.616	n.s.
Ni ($mgkg^{-1}$)	0.096	n.s.
Zn ($mgkg^{-1}$)	0.012	P > T

Differences in metal concentrations in the different tissues of each macrophyte species were explored by visually assessing boxplots and statistically tested using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (Figure 6.11 and Table 6.13).

Boxplots, with median values in brackets above, of metal concentrations in the different tissues of each macrophyte species are presented in Figure 6.11. Based upon the whole data set, root metal concentrations were in the order: Fe > Mn > Zn > Ni > Cu > Cr, rhizome metal concentrations were in the order: Fe > Mn > Zn > Cu > Cr > Ni and, leaf/stem metal concentrations were in the order: Fe > Mn > Zn > Cr > Cu > Ni. Overall, metal concentrations were greater in the below-ground tissues, particularly the roots. All three macrophyte species showed the same pattern for Cu, Fe, Ni and Zn concentrations. Cu, Ni and Zn concentrations were significantly greater in the roots than both the rhizomes and leaf/stems (K-W, $p < 0.05$, Table 6.13, root > rhizome, leaf/stem) and Fe concentrations were significantly greatest in the roots and significantly lowest in the leaf/stems, with rhizome concentrations in-between (K-W, $p < 0.05$, Table 6.13, root > rhizome > leaf/stem). For Mn, all three macrophytes species had significantly greater concentrations in the roots compared to the rhizomes, with *S. erectum* and *P. arundinacea* also having significantly greater concentrations in the leaf/stems compared to the rhizomes, and for *P. arundinacea* the root concentrations were also significantly greater than the leaf/stem concentrations (K-W, $p < 0.05$, Table 6.13). The only significant differences in Cr concentrations between the tissues were for *P. arundinacea* with concentrations in the roots significantly greater than concentrations in the rhizomes (K-W, p = 0.028, Table 6.13).

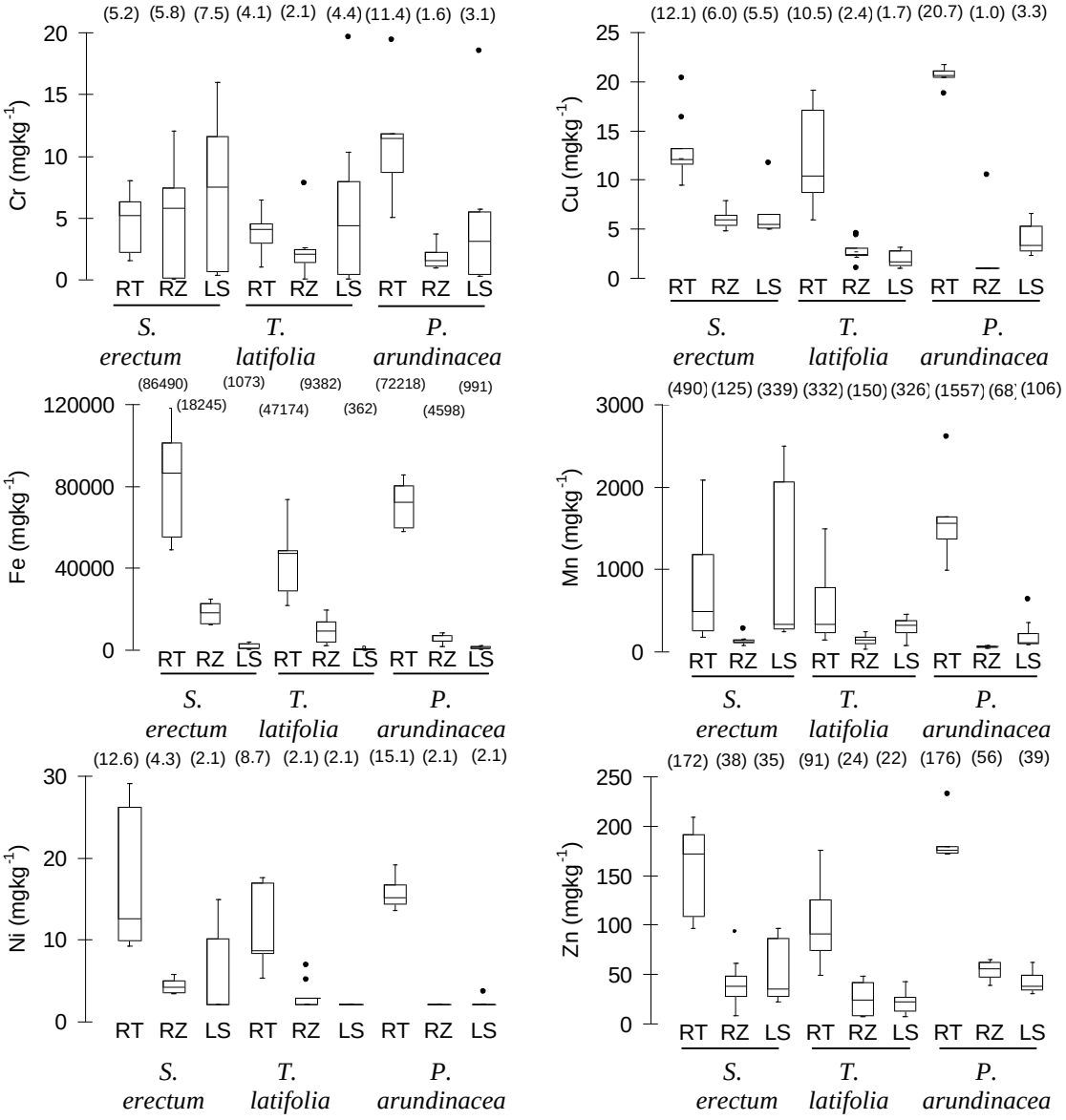


Figure 6.11: Boxplots of metal concentrations, with median values shown above in brackets, in different tissues of each macrophyte species (n = 8, apart from *P. arundinacea* root and rhizome n = 5, RT = root, RZ = rhizome, LS = leaf/stem).

Table 6.13: Statistically significant differences in metal concentrations between different tissues for each species identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (n = 8, apart from *P. arundinacea* root and rhizome n = 5, n.s = not significant, RT = root, RZ = rhizome, LS = leaf/stem).

	S. erectum		***T. latifolia***		***P. arundinacea***	
	K-W p-value	**S-D-C-F Significant differences ($p < 0.05$)**	**K-W p-value**	**S-D-C-F Significant differences ($p < 0.05$)**	**K-W p-value**	**S-D-C-F Significant differences ($p < 0.05$)**
Cr ($mgkg^{-1}$)	0.646	n.s.	0.434	n.s.	0.028	RT > RZ
Cu ($mgkg^{-1}$)	0.001	RT > RZ, LS	0.000	RT > RZ, LS	0.002	RT > RZ, LS
Fe ($mgkg^{-1}$)	<0.0001	RT > RZ > LS	<0.0001	RT > RZ > LS	0.001	RT > RZ > LS
Mn ($mgkg^{-1}$)	0.001	RT, LS > RZ	0.017	RT > RZ	0.001	RT > LS > RZ
Ni ($mgkg^{-1}$)	0.004	RT > RZ, LS	<0.0001	RT > RZ, LS	0.001	RT > RZ, LS
Zn ($mgkg^{-1}$)	0.003	RT > RZ, LS	0.000	RT > RZ, LS	0.003	RT > RZ, LS

Comparison of the median macrophyte metal concentrations recorded in this study to those cited in the literature as toxic indicates that only Fe concentrations appear to be within the range considered to be toxic for all macrophytes, with the median concentration of Cr in *S. erectum* just within the toxic concentration range (Table 6.14).

Table 6.14: Comparison of median macrophyte metal concentrations recorded in this study to toxic concentrations (from Kabata-Pendias & Pendias (1984) but Fe from Allen (1989)).

		Median (3 s.f. $mgkg^{-1}$)		
	Toxic concentration ($mgkg^{-1}$ dry weight)	***S. erectum***	***T. latifolia***	***P. arundinacea***
Cr	**5 – 30**	5.79	3.08	2.86
Cu	**20 – 100**	6.50	2.79	5.85
Fe	**40 – 500**	18,200	9,380	4,340
Mn	**300 – 500**	276	243	171
Ni	**10 – 100**	5.44	2.10	2.10
Zn	**100 - 400**	73.8	34.3	62.2

Although comparisons can be made between species and tissues based on metal concentrations within the macrophytes, the three macrophyte species are morphologically very different in terms of dry biomass of different tissues and density of growth within the river, which will result in differing storage of metals per plant and per m^2 of channel with macrophyte growth

(Table 6.15). Therefore, using macrophyte metal concentrations, dry biomass of the different tissues and a count of the number of plants per m^2 of channel the mass of metal stored in the different macrophyte species per plant and per m^2 of channel with macrophyte growth was calculated (see Section 6.3.3 in methods of this chapter, Figures 6.12 and 6.13). The three macrophyte species showed the same pattern of metal storage per plant for each metal, with *T. latifolia* > *S. erectum* > *P. arundinacea*. When calculated per m^2 of river channel with macrophyte growth, based on plant density, *P. arundinacea* consistently showed the lowest mass for all metals. *S. erectum* showed the greatest mass for Cr, Cu and Zn and *T. latifolia* showed the greatest mass for Fe and Mn.

Table 6.15: Dry biomass of different tissues and number of plants per m^2 for each macrophyte species.

		Median dry biomass per plant (g) (3 s.f.)	Number of plants per m^2
S. erectum	**Root**	0.770	76
	Rhizome	0.244	
	Leaf/stem	12.4	
T. latifolia	**Root**	5.64	24
	Rhizome	9.06	
	Leaf/stem	24.6	
P. arundinacea	**Root**	0.218	184
	Rhizome	0.690	
	Leaf/stem	1.35	

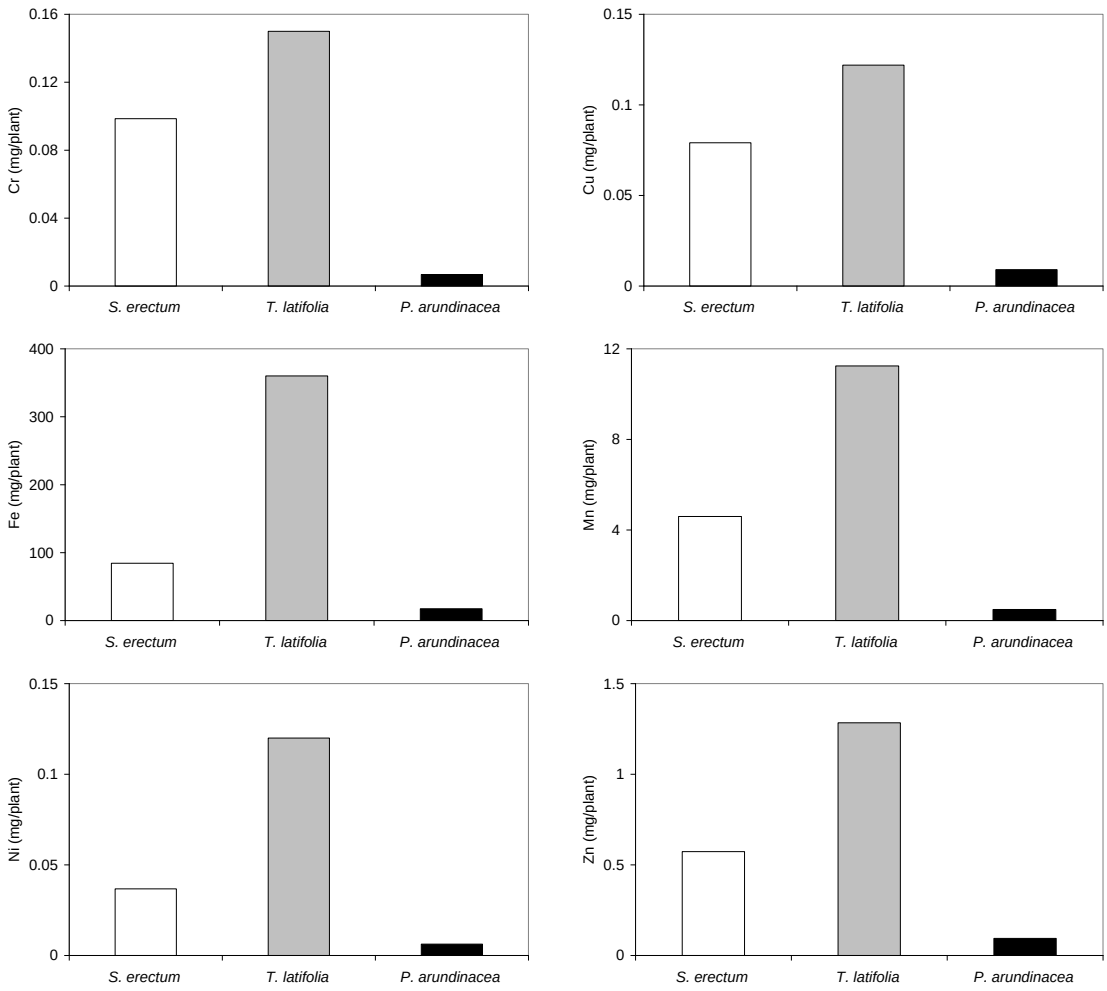


Figure 6.12: Calculated mass of metal per individual plant for each macrophyte species.

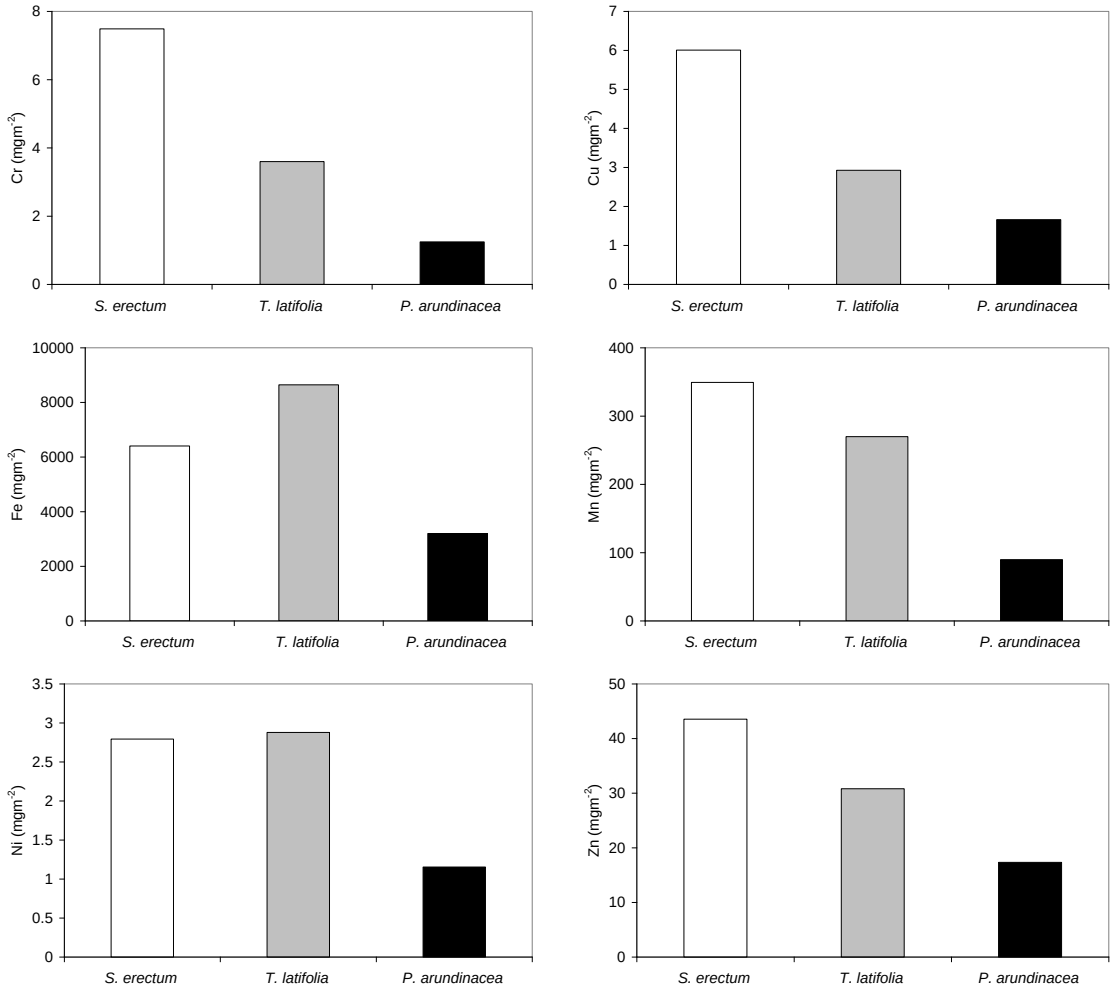


Figure 6.13: Calculated mass of metal per m^2 of river channel with macrophyte growth for each macrophyte species.

The mass of metals in the macrophytes per m^2 of river channel with macrophyte growth (Figure 6.13 above) was subdivided into above-ground (leaf/stem) and below-ground (roots and rhizomes) tissues for each macrophyte species and the proportion of storage in both the above-ground and below-ground tissues calculated (Figure 6.14, mass displayed (in mgm^{-2} of river channel) on the bar). For all three macrophyte species the vast majority of Fe storage was in the below-ground tissues (84% *S. erectum*, 98% *T. latifolia* and 92% *P. arundinacea*). *S. erectum* showed a clear pattern of the majority of storage of the remaining metals being in above-ground tissues (Figure 6.14). The majority of Cr was also stored in above-ground tissues for *T. latifolia* and *P. arundinacea* and Mn in above-ground tissues for *T. latifolia* and below-ground tissues for *P. arundinacea*. There was roughly equal storage of Cu, Ni and Zn in the above- and below-ground tissues for *T. latifolia* and *P. arundinacea*.

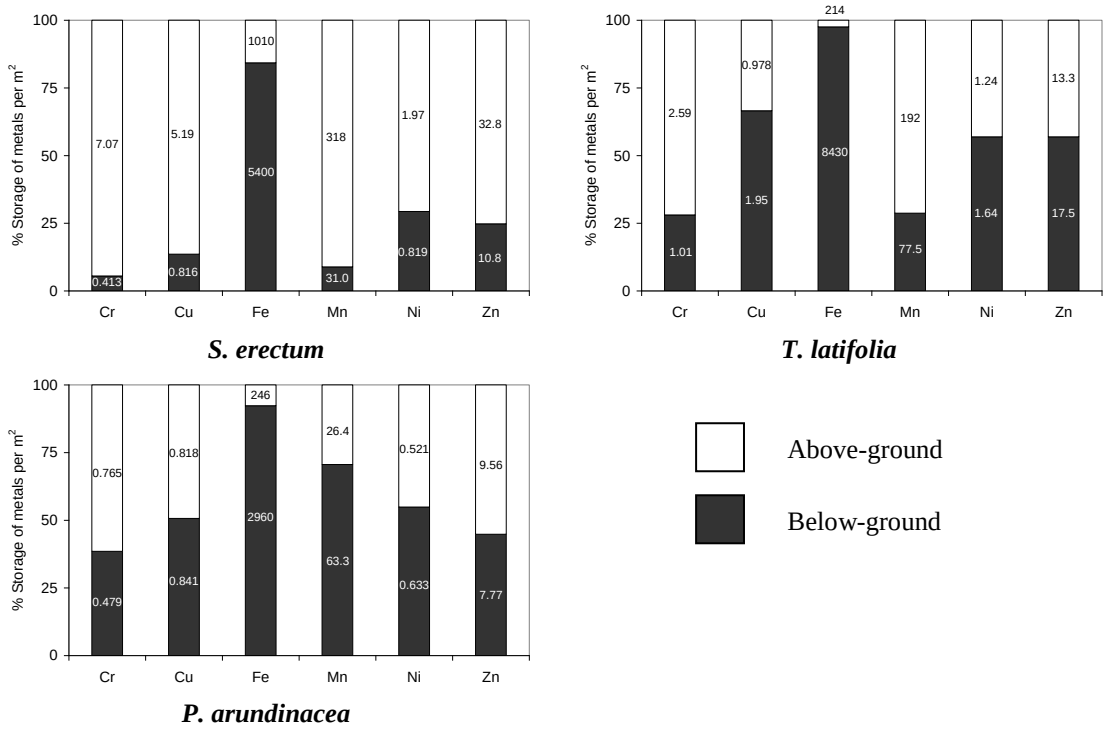


Figure 6.14: Percentage storage of metals in above-ground and below-ground tissues per m^2 of river channel with macrophyte growth and mass of metal in above-ground and below-ground tissues (shown in mgm^{-2} on bar) for each metal and each macrophyte species.

6.4.4 Associations between overlying water, sediment and macrophyte metal concentrations

Relationships between sediment characteristics and metal concentrations, overlying water characteristics and metal concentrations, and macrophyte metal concentrations were investigated by calculating Spearmans Rank (S-R) correlation coefficients (Table 6.16). There were few significant relationships.

There were significant positive correlations between pseudo-total and acetic acid Cr in sediment and Cr in roots and leaf/stems and pseudo-total and acetic Zn in sediment and rhizomes. Sediment acetic acid Cr and Cr in rhizomes and sediment acetic Cu and leaf/stems also showed significant positive correlations. Pseudo-total and acetic acid Fe in sediment was significantly negatively correlated with Fe in roots, rhizomes and leaf/stems. No overlying water metal concentrations were significantly correlated with macrophyte concentrations.

Sediment Fe (II) concentrations were significantly negatively correlated with Mn in roots and significantly positively correlated with Mn and Ni in rhizomes and Cu in leaf/stems. Sediment

pH was significantly negatively correlated with Fe in roots, rhizomes and leaf/stems, Cu in rhizomes and leaf/stems and Zn in roots and leaf/stems.

Overlying water pH was significantly negatively correlated with Ni in roots and rhizomes and Cu in rhizomes and leaf/stems. Overlying water dissolved oxygen was significantly positively correlated with Ni in roots and significantly negatively correlated with Cr in rhizomes and leaf/stems and Zn in rhizomes.

Table 6.16: Spearmans Rank correlation coefficients (r_s) between all sediment and overlying water metal concentrations and characteristics and macrophyte metal concentrations. Correlation coefficients significant at $p < 0.01$ shown in large and bold font, significant at $p < 0.05$ in large font and not significant ($p > 0.05$) in small font. (n = 21 apart from sediment Fe (II) concentrations where n= 15. No correlations for Ni in leaf/stem as all values identical as were <LoD and replaced).

		Sediment Fe (II)	Sediment pH	Sediment metal (total)	Sediment metal (acetic)	Overlying water pH	Overlying water DO	Overlying Water Metals
Root	**Cr**	-0.361	-0.171	**0.662**	0.499	0.261	-0.450	
	Cu	-0.421	-0.209	0.155	0.030	-0.033	0.168	
	Fe	-0.304	**-0.688**	0.123	-0.069	-0.332	-0.123	0.277
	Mn	-0.557	-0.265	0.144	0.095	0.135	0.060	-0.022
	Ni	-0.458	-0.280	**-0.600**	-0.480	-0.539	**0.653**	
	Zn	-0.293	-0.506	-0.139	-0.110	-0.327	0.223	-0.064
Rhizome	**Cr**	0.382	-0.236	0.360	0.449	-0.059	**-0.570**	
	Cu	0.509	**-0.572**	-0.129	0.025	**-0.591**	0.114	
	Fe	0.418	-0.444	0.274	0.151	-0.393	-0.358	0.016
	Mn	**0.711**	-0.060	-0.305	-0.218	-0.112	0.101	-0.219
	Ni	0.534	-0.359	-0.549	**-0.631**	**-0.739**	0.256	
	Zn	-0.143	-0.428	0.484	**0.556**	0.170	**-0.574**	-0.006
Leaf/ stem	**Cr**	0.357	-0.116	0.472	**0.569**	0.258	**-0.632**	
	Cu	0.515	**-0.842**	0.005	0.163	**-0.628**	-0.056	
	Fe	-0.257	**-0.772**	0.079	0.017	-0.380	0.033	0.295
	Mn	0.461	-0.232	-0.247	-0.207	-0.186	0.027	-0.293
	Ni		-0.405	-0.511	-0.538	-0.427	0.407	
	Zn	-0.339	**-0.573**	0.017	-0.018	-0.057	0.018	-0.110

Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were used to identify the significant differences in metal concentrations between the overlying water, sediment and macrophyte samples (Table 6.17). For all metals, the sediment pseudo-total metal concentrations were significantly greater than all other samples and the overlying water metal concentrations (where detected) the significantly lowest (K-W, $p < 0.0001$). For Cu, Mn and Ni the sediment acetic acid metal concentrations and macrophyte metal concentrations were not

significantly different, whereas for Cr and Fe the macrophyte metal concentrations were significantly greater than the sediment acetic acid metal concentrations (K-W, all $p < 0.0001$). For Zn the sediment acetic acid metal concentrations were significantly greater than the macrophyte metal concentrations (K-W, all $p < 0.0001$).

Table 6.17: Statistically significant differences in metal concentrations between overlying water, sediment and macrophyte samples identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests (W = overlying water, ST = pseudo-total metal sediment, SA = acetic acid metal sediment and M = macrophyte).

	K-W p-value	**S-D-C-F Significant differences ($p < 0.05$)**
Cr ($mgkg^{-1}$)	< 0.0001	ST > M > SA
Cu ($mgkg^{-1}$)	< 0.0001	ST > SA, M
Fe ($mgkg^{-1}$)	< 0.0001	ST > M > SA > W
Mn ($mgkg^{-1}$)	< 0.0001	ST > SA, M > W
Ni ($mgkg^{-1}$)	< 0.0001	ST > SA, M
Zn ($mgkg^{-1}$)	< 0.0001	ST > SA > M > W

Using the calculation of the storage of metal in *S. erectum* per m^2 of channel (as calculated above in Figure 6.13) and calculation of the storage of metal in the sediment underlying *S. erectum* per m^2 of channel (Section 6.3.3) the distribution of metal storage between the sediment and the *S. erectum* plants for each metal was calculated. These are presented in Figure 6.15 and give an indication of whether sediments or *S. erectum* plants provide the greatest metal storage per m^2 of river channel with *S. erectum* growth. The underlying sediments provided the main storage of Cr, Cu, Fe, Ni and Zn (> 55%), whereas the *S. erectum* plants provided the main storage of Mn (69%) (Figure 6.15).

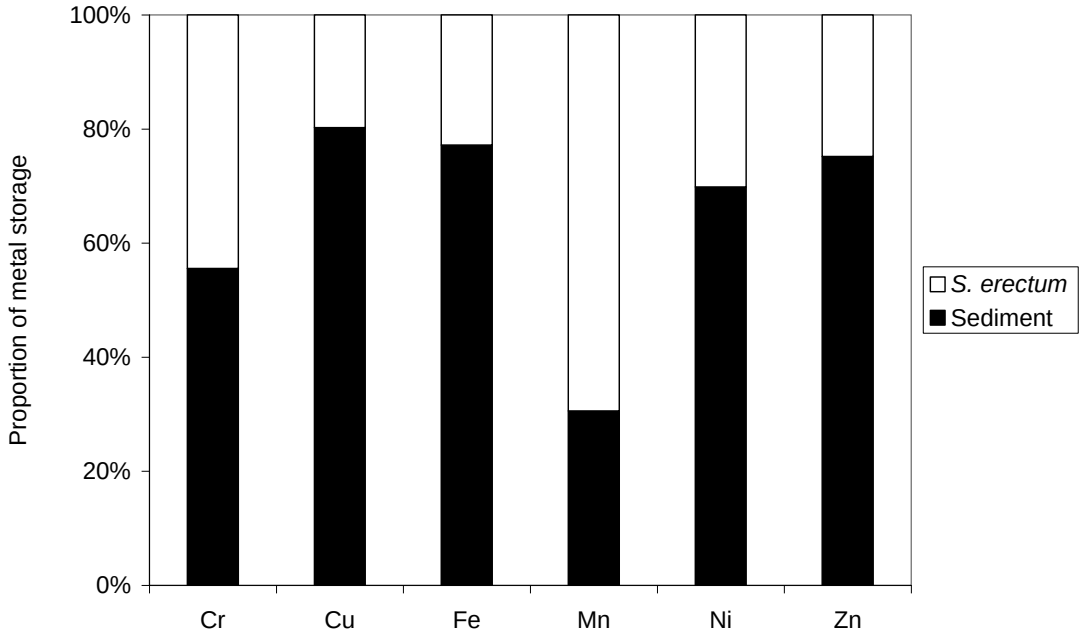


Figure 6.15: Proportion of metal storage in underlying sediment and *S. erectum* plants per m^2 of river channel with *S. erectum* growth.

6.4.5 Bioconcentration and translocation of metals by macrophytes

Root, rhizome and leaf/stem bioconcentration factors (BCF) were calculated using sediment pseudo-total metal concentrations and macrophyte metal concentrations for each macrophyte species (Section 6.3.3 in methods) to evaluate the ability of the macrophytes to concentrate metals within their tissues from the sediment and are displayed in Figure 6.16. BCFs over one indicate a net bioconcentration of the metal from the sediment to the macrophyte tissue.

All median BCF's, apart from Mn for *P. arundinacea* roots, were below one. Generally, all macrophyte species and metals showed greatest median BCF's for the roots and there was no discernable difference between the species. Overall, the highest BCF's were for Fe and Mn in the roots for all macrophyte species and Mn in the leaf/stems of *S. erectum* and *P. arundinacea*. Cr and Cu showed a very low level of bioconcentration.

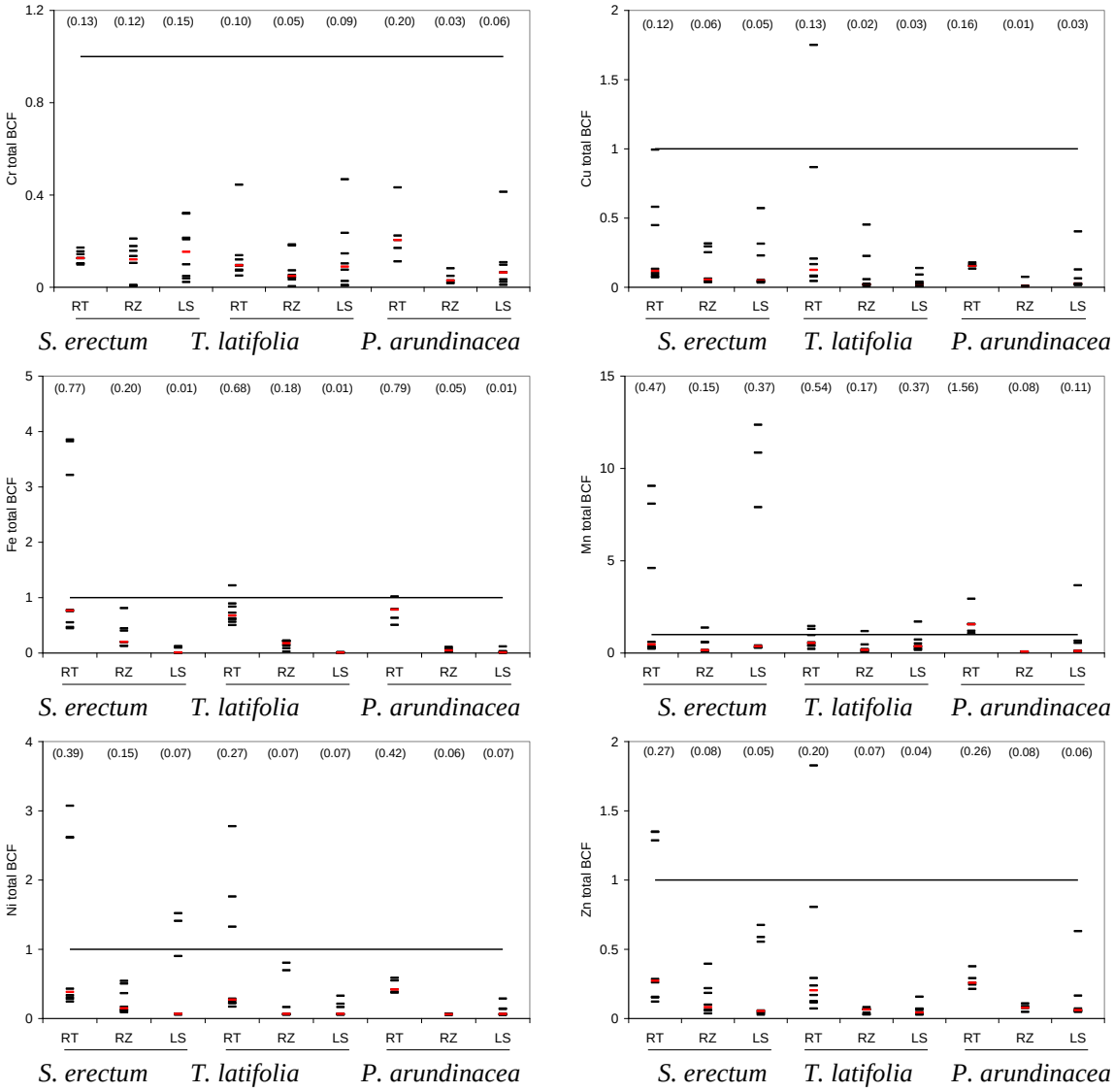


Figure 6.16: Root (RT), rhizome (RZ) and leaf/stem (LS) pseudo-total metal bioconcentration factors (BCF) for each macrophyte species, with median BCF represented by red dash and in brackets above. Horizontal line indicates BCF = one.

The ability of the macrophytes to translocate metals from below-ground to above-ground tissues was assessed through calculation of translocation factors (TF) (Figure 6.17). TFs over one indicate a net translocation of metals from below-ground to above-ground tissues. None of the metals or macrophytes had median TFs which were over one. For all macrophyte species there was a greater translocation of Cr to above-ground tissues and for *S. erectum* and *T. latifolia* there was also a greater translocation of Mn to above-ground tissues. For all macrophyte species the lowest translocation of metals to above-ground tissues was for Fe.

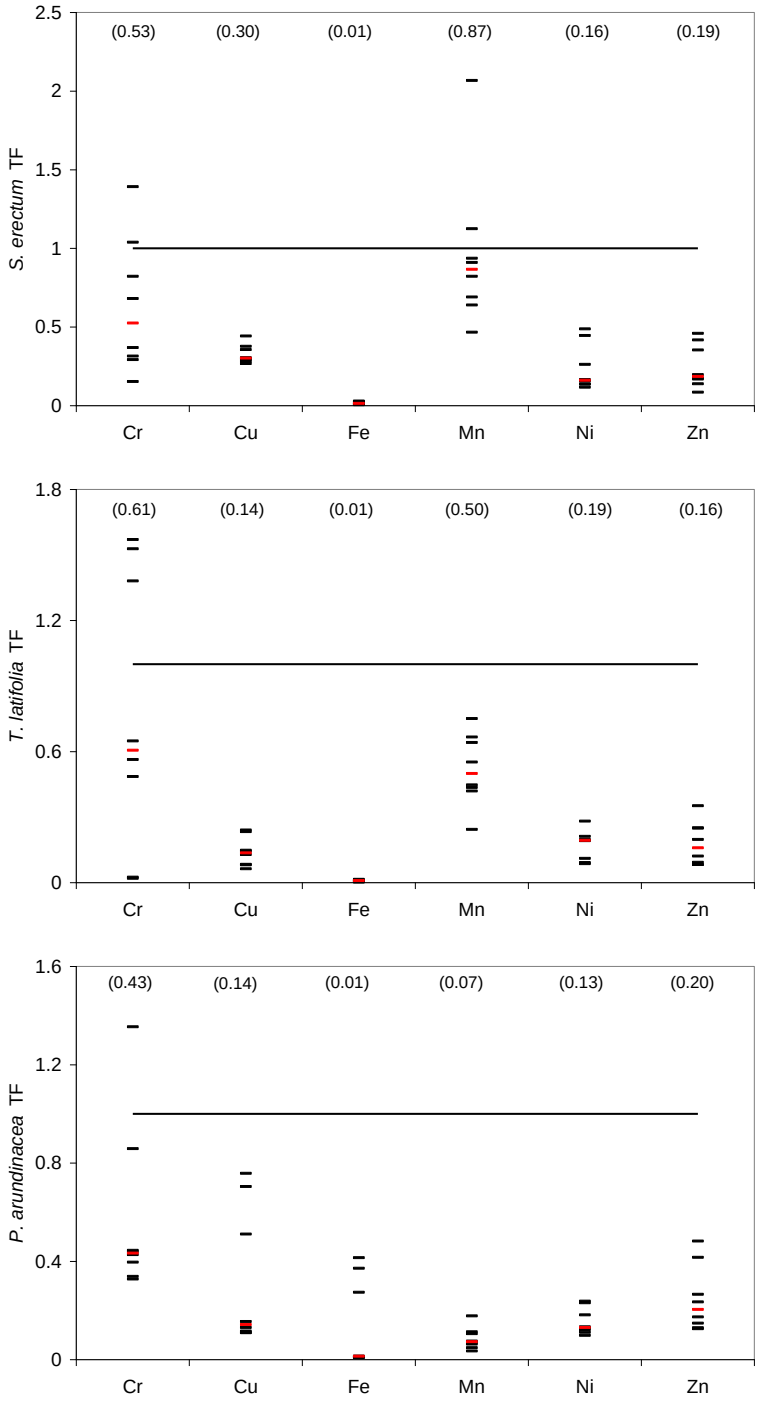


Figure 6.17: Translocation factors (TF) for each metal for the three macrophyte species, with median TF represented by red dash and in brackets above. Horizontal line indicates TF = one.

6.5 Discussion

In the following section the following research questions are discussed:

- What is the distribution of metals between three commonly occurring emergent macrophytes (*Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*) and associated overlying water and sediments?

- To what extent do the characteristics and metal concentrations of overlying water and sediment associated with these three commonly occurring emergent macrophytes vary between the species?

- How does the uptake and storage of metals in three commonly occurring emergent macrophyte species vary?

- To what extent do three commonly occurring emergent macrophyte species bioconcentrate and translocate metals?

6.5.1 Distribution of metals within the river environment

Pseudo-total sediment metal concentrations were significantly greater than sediment acetic acid metal concentrations, macrophyte metal concentrations and metal concentrations in overlying water (where detected) (Table 6.17). Where detected, metal concentrations in the overlying water samples were the significantly lowest (Table 6.17). Higher metal concentrations in sediment as opposed to overlying water have been reported in many studies (e.g. Fawzy *et al*., 2012; Ladislas *et al*., 2012; and, Sasmaz *et al*., 2008) as have higher metal concentrations in sediments as opposed to macrophytes (e.g. Romero Nunez *et al*., 2011 and Zhang *et al*., 2010). Sediments act as sinks for metals, accumulating particulate-phase metals from the overlying water through sedimentation and also providing many binding sites for dissolved metals in the overlying water (Luoma & Rainbow, 2008 and Foster & Charlesworth, 1996). Therefore sediments within rivers often have metal concentrations orders of magnitudes higher than concentrations found in the overlying water (Luoma & Rainbow, 2008 and Foster & Charlesworth, 1996).

The high concentrations of Pb and Zn were of greatest concern in the sediment, being found at concentrations which could potentially cause adverse biological effects (Figure 6.8). Studies undertaken on the Pearl River Delta, South China and Lake Macquarie, New South Wales,

Australia, also found high concentrations of Pb and Zn (among other metals) exceeding sediment quality guidelines (Roach, 2005 and Cheung *et al*., 2003).

Few significant correlations were found between sediment and overlying water metal concentrations and macrophyte metal concentrations (Table 6.16). There was no consistency of increasing metal concentrations in the water or sediment resulting in increasing metal concentrations in the macrophytes, with Spearmans Rank correlation coefficients (whether significant or not) showing a mix of positive and negative relationships. Many other similar studies have also shown a lack of significant correlations between metal concentrations in the sediment, overlying water and the macrophytes along with a mix of positive and negative relationships, which, given the temporal variability in water quality, is not surprising. For example, Cardwell *et al*., (2002) reported just Zn showing a clear pattern of increasing concentrations in roots with increasing concentrations in sediment for a range of 15 rooted macrophyte species and Romero Nunez *et al*., (2011), analysing for Hg, Cu, Cd, Pb and Zn, found only a few significant positive correlations between sediment concentrations and the roots and leaves of seven macrophyte species investigated. A mix of positive and negative significant correlations have been reported by Fawzy *et al*., (2012), Samecka-Cymerman & Kempers (2001) and Sparling & Lowe (1998) all investigating a range of metals in a range of macrophytes.

The lack of significant correlations between sediment and macrophyte metal concentrations has been suggested in some studies (e.g. Romero Nunez *et al*., 2011; Sundberg-Jones & Hassan, 2007; and, Cardwell *et al*., 2002) to be due to correlations being undertaken on total metal sediment concentrations, which are not indicative of the fraction of metals which are bioavailable to the macrophytes for uptake. The acetic acid extractable sediment metal concentrations analysed in this study are indicative of a more bioavailable form of metals (Section 3.3.2 in Chapter 3). However there were only two more significant correlations with acetic acid extractable metals compared to pseudo-total metals, and acetic acid extractable metals also showed a mix of positive and negative correlations (Table 6.16). Keller *et al*. (2008) found a similar lack of significant correlations between labile metals in sediments and metals in *Phragmites australis* roots, which they suggested may be related to the release of metals from root tissues during decay.

Calculations of metal storage in the sediment underlying *S. erectum* and in the *S. erectum* plants on a per m^2 of river channel with *S. erectum* growth basis showed that the underlying sediments provided the main storage of Cr, Cu, Fe, Ni and Zn (> 55%), whereas the *S. erectum* plants provided the main storage of Mn (69%) (Figure 6.15). Similar calculations undertaken by

Karathanasis & Johnson (2003), which defined the contribution of macrophytes and sediment to metal storage in a constructed wetland treating acid mine drainage, indicated that the macrophytes contributed a very small proportion to total metal storage across the whole wetland per year compared to the sediment (for example, 0.3% Al and 0.2% Mn for the macrophytes). They conclude that this suggests physiochemical processes which accumulate metals within underlying sediments are far more significant in terms of metal storage than macrophytes, a suggestion which has been made in other studies, although no actual calculations have been made (Romero Nunez *et al*., 2011 and Cardwell *et al*., 2002). The Karathanasis & Johnson (2003) study had a far more conservative estimate of plant density across the wetland as a whole compared to this study (their study 3.1 plants/m^2, this study *S. erectum* density 76 plants/m^2) which would have a significant effect upon calculation of metal storage by the macrophytes.

6.5.2 Effect of, and differences between, three common emergent macrophytes upon overlying water and sediment environmental conditions and metals

Redox and pH are two important environmental conditions which can have an effect upon metal mobility in overlying water and sediments (Foster & Charlesworth, 1996). In overlying waters, oxic and near-neutral waters favour low dissolved metal concentrations (Atkinson *et al*., 2007; Shiller, 1997; and, Brick & Moore, 1996). In sediments redox conditions and pH are important in determining the binding of metals to different ligands and thus metal mobility (Du Laing *et al*., 2009 and Jacob & Otte, 2003). Within reduced sediments, sulphides precipitate out and metals strongly adsorb or co-precipitate, however Fe and Mn (hydr)oxides are solubilised and bound metals are released (Du Laing *et al*., 2009 and Jacob & Otte, 2003). A change to a more oxidising environment can cause sulphides to be oxidised and metals which were adsorbed or co-precipitated to be released (Jacob & Otte, 2003). Conversely, the creation of an oxidising environment can cause the precipitation of Fe and Mn oxides to which metals co-precipitate and adsorb (Jacob & Otte, 2003). Decreases in sediment pH can increase the mobility of metals from the release of metals bound to carbonates and sulphides and a lowering of the cation exchange capacity of organic matter, clay and Fe and Mn (hydr)oxides (Du Laing *et al*., 2009).

There are various studies which have investigated the effect of macrophyte beds upon their immediate surrounding water quality in terms of dissolved oxygen and pH (e.g. Al-Kenzawi & Al-Rawi, 2009; Caraco & Cole, 2002; Miranda *et al*., 2000; Rose & Crumpton, 1996; and, Barko *et al*., 1988). Compared to areas of open water, water within macrophyte beds has been shown to have lower dissolved oxygen concentrations (Caraco & Cole, 2002; Miranda *et al*., 2000; and, Rose & Crumpton, 1996). These decreases in dissolved oxygen concentrations have been related to: (i) a decrease in atmospheric-water oxygen exchange from macrophyte growth reducing water surface area; (ii) respiring macrophyte tissues within the water column using up

oxygen; (iii) material accumulated within the macrophyte beds (which is often organic rich) and associated organisms respire and use up oxygen; (iv) during senescence, breakdown of macrophyte material uses up oxygen; (v) increased temperature in the macrophyte beds reduces dissolved oxygen concentration of water; and, (vi) little hydrologic exchange and therefore mixing of waters between the open water and the macrophyte beds (Al-Kenzawi & Al-Rawi, 2009; Caraco *et al*., 2006; Caraco & Cole, 2002; and, Miranda *et al*., 2000). Differences in the magnitudes of dissolved oxygen decreases have been related to: time (diurnal variations from photosynthesis/respiration cycle and growth and senescence of macrophytes); morphology of plant (floating-leaved and emergent species decrease dissolved oxygen more than submerged species); and, density of macrophyte growth (greater density decreases dissolved oxygen concentrations more) (Caraco *et al*., 2006; Caraco & Cole, 2002; and, Rose & Crumpton, 1996). Similar decreases in pH beneath macrophyte canopies have been reported and been related to the breakdown of organic matter which produces CO_2 and the lower rates of photosynthesis (Al-Kenzawi & Al-Rawi, 2009; and, Barko *et al*., 1988).

Although comparisons between the overlying water in the open channel and in the macrophyte beds were not made in this study, the lack of significant differences in dissolved oxygen concentrations between the overlying water samples from the three macrophyte species suggests that they are having similar effects upon dissolved oxygen concentrations, and at the time of sampling were all surrounded by oxic waters (Tables 6.3 and 6.6). This is to be expected since they are all emergent species, sampled at the same time during the day and although having different counts of plants per m^2 channel were all at the same stage of growth.

pH was significantly lower (although all were near-neutral) in the overlying water surrounding *S. erectum* as opposed to *T. latifolia* and *P. arundinacea* (Tables 6.3 and 6.6), which corresponds to the lower dissolved oxygen concentrations around this macrophyte species, although it was not statistically significant (Table 6.6).

Since very few significant differences in dissolved oxygen concentrations and pH were found between these macrophyte species, it follows that there were few significant differences in dissolved metal concentrations between the macrophyte species (Table 6.6). Fe concentrations were significantly greater in the samples from around *S. erectum* and *P. arundinacea* than from around *T. latifolia* (Table 6.6). This could be due to the samples from these two macrophytes being taken downstream of the Cove Brook entering the site (Figure 6.2).

The low dissolved metal concentrations in the overlying water samples surrounding all three macrophyte samples can be explained by all overlying waters being oxic and near-neutral,

environmental conditions which favour low dissolved metal concentrations (Atkinson *et al*., 2007; Shiller, 1997; and, Brick & Moore, 1996). The only detectable concentrations were of dissolved Fe, Mn and Zn (ranges 0.060 to 0.19, 0.032 to 0.048 and 0.019 to 0.090 mgl^{-1} respectively), which did not exceed any water quality standards, indicating low concentrations of these metals within the river (Tables 6.3 and 6.4). Since water quality varies continuously, it is important to note that the observed concentrations are only representative of the time of sampling. Low concentrations of dissolved metals in overlying water are to be expected (for example, similar concentrations are reported by Vardanyan *et al*., (2008) in rivers sampled around Lake Sevan (Armenia) and in natural wetlands sampled by Romero Nunez *et al*., (2011)) unless the overlying water samples are taken from a treatment facility (constructed wetland) or a highly contaminated setting (mine drainage). For example, higher metal concentrations are reported in lakes formed by coal mining (Samecka-Cymerman & Kempers, 2001), a wetland receiving acid main drainage (Karathanasis & Johnson, 2003) and a wetland receiving urban runoff (Scholes *et al*., 1998).

Though not all metals were at concentrations detectable in the overlying water, they were accumulated in the sediment (Table 6.8). The range of pseudo-total metal concentrations recorded within this study is summarised in Table 6.18 along with similar data from other studies on metal uptake by macrophytes. Data from the sediment accumulated around in-channel vegetation samples from Chapter 4 of this thesis is also presented. The range of sediment pseudo-total metal concentrations in this study is similar to those found in the other studies conducted on other rivers within the Thames catchment (Chapter 4 results), although the maximum concentration of Fe is higher than the other Fe concentrations recorded. The range of metal concentrations recorded in this study are within a similar range to most other studies, though some higher concentrations were recorded in a study looking at constructed wetlands which receive mine runoff (Deng *et a*l., 2004) and urban runoff (Scholes *et al*., 1998).

Table 6.18: Summary of sediment pseudo-total metal concentrations from this study and similar data from other studies looking at metal uptake by macrophytes including data from Chapter 4 of this thesis (*continued overleaf*).

	Range/mean	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mgkg^{-1} dry weight							
River Blackwater, Hawley Meadows, Hawley, UK (This study)	Range	0.500 – 2.43	9.76 – 57.1	9.69 - 154	16,400 – 115,000	98.2 – 1,300	6.36 – 40.3	21.6 - 156	89.8 - 810
River Wandle, Beddington Park, London, UK (Chapter 4)	Range		18.6 – 70.3	31.5 - 340	12,100 – 29,300	145 - 537	8.64 – 28.6	73.6 - 587	118 - 996
Pool River, Bell Green, London, UK (Chapter 4)	Range		8.97 – 48.0	24.1 - 216	10,700 – 31,100	170 - 738	7.34 – 30.0	35.0 - 287	108 - 669
River Quaggy, Chinbrook Meadows, London, UK (Chapter 4)	Range		14.1 – 40.4	11.7 - 150	13,200 – 45,100	259 – 1,510	10.1 – 32.9	43.1 - 245	69.9 - 462
River Quaggy, Sutcliffe Park, London, UK (Chapter 4)	Range		27.8 – 67.4	90.4 - 262	30,800 – 47,800	244 - 716	28.4 – 41.7	80.2 - 243	271 - 817
Wetlands by mines in China Deng *et al*., (2004)	Range of means	17 - 46		95 – 5,770				112 – 11,161	713 – 4,805
Kehli Stream, Turkey. Receives discharge from waste treatment plant Sasmaz *et al*., (2008)	Mean		60	45		450	50		70
Six urban streams, near Brisbane, Australia. Cardwell *et al*., (2002)	Range of means	0.00 – 16.1		4.1 – 263.3				0.20 – 431.5	13.3 – 1,568

Table 6.18: Summary of sediment pseudo-total metal concentrations from this study and similar data from other studies looking at metal uptake by macrophytes including data from Chapter 4 of this thesis (*continued*).

	Range/mean	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
		mgkg^{-1} dry weight							
Nine lakes in W Poland, from through coal mining Samecka-Cymerman & Kempers (2001)	Range of means	<0.08 – 3.3	20 - 165	0.4 – 18.6	1,160 – 21,500	3 - 158	0.3 - 31		10 - 131
Three natural wetlands, Colombia Romero Nunez *et al*. (2011)	Range	0.013 – 0.027		0.386 – 1.29				0.070 – 0.200	0.451 – 1.76
Detention pond receiving urban runoff, Nantes, France Ladislas *et al*., (2012)	Mean	1.3	59	70			76	44	410
Two wetlands receiving urban runoff. Scholes *et al*. (1998)	Range	3.0 – 9.6	3 - 167	17 - 178			17 - 187	38 - 350	21 - 830

There were no significant differences in pseudo-total metal concentrations between the sediments surrounding the three macrophyte species (Table 6.9). Organic matter and proportion of fine sediment (<63 µm), which are both important ligands within sediments for metal binding due to their high surface area and cation exchange capacity (Du Laing *et al*., 2009; Luoma & Rainbow, 2008; Horowitz, 1991; Fergusson, 1990; and, Forstner & Wittmann, 1981), similarly show no significant difference between the sediments surrounding the three macrophyte species (Table 6.9), and thus the similarity in pseudo-total metal concentrations could be explained by the similarity in these two sediment characteristics. This shows that there is no difference between the three macrophyte species in terms of their accumulation of pseudo-total metal sediment concentrations in their underlying sediments.

As mentioned earlier, sediment characteristics in terms of redox conditions and pH are important in determining the binding of metals to different ligands and thus metal mobility (Du Laing *et al*., 2009 and Jacob & Otte, 2003). Redox and pH conditions within sediments can be influenced and altered by macrophytes, and thus have an effect upon metal mobility.

Sediment redox conditions around macrophytes can be influenced by radial oxygen loss (ROL) from the roots, the breakdown of organic matter and the position of the macrophyte in the channel. Macrophytes have adapted to growth in anoxic sediments. They move oxygen from their shoots to roots and have developed aerenchyma tissues which aid this movement (Du Laing *et al*., 2009; Colmer, 2003; and, Jackson & Armstrong, 1999). The flux of oxygen from the roots/rhizomes to the rhizosphere through radial oxygen loss (ROL) aerates the sediments in the immediate vicinity and can create a thin zone of oxidation, and thus altering metal mobility (Cambrolle *et al*., 2008; Colmer, 2003; Keller *et al*., 1998; and, Lacerda *et al*., 1997). The breakdown of organic matter in sediment, which accumulates around macrophytes, uses oxygen and can result in lower redox conditions (Gudasz *et al*., 2010 and den Heyer & Kalff, 1998). The position of the macrophyte in the river channel can affect redox conditions, with macrophytes higher up the bank likely to experience more oxic conditions.

The presence of Fe (II) in the porewater samples from the sediments surrounding all three macrophyte species indicates that all sediments had low redox conditions (Table 6.8). However, comparison between the three macrophyte species in this study indicated that sediments were more anoxic around *S. erectum* than around *T. latifolia* (Table 6.9). As organic matter content was not significantly different in the sediments surrounding the three macrophyte species (Table 6.9), this suggests that other factors (ROL or position in channel) were important. *S. erectum*, *T. latifolia* and *P. arundinacea* are all able to transfer oxygen from their shoots to roots and have ROL (Calhoun & King, 1997 and Bedford *et al*., 1991). Differences between macrophyte species in their rates of ROL, and hence their potential for oxidising the sediments, have been shown in other studies (e.g. Aldridge & Ganf, 2003; Visser *et al*., 2000; Reddy *et al*., 1990; and, Michaud & Richardson, 1989). Direct comparison between the three macrophyte species in this study in terms of ROL was difficult due to no studies directly comparing all three macrophyte species and difficulties in finding ROL rates for all three macrophyte species. However, both Steinberg & Coonrod (1994) and Bedford *et al.* (1991) have shown that *T. latifolia* oxidises the rhizosphere more than *P. arundinacea* and Michaud & Richardson (1989) have shown that *T. latifolia* oxidises the rhizosphere more than *S. americanum*, suggesting that of the three macrophyte species in this study *T. latifolia* has the greatest ROL. No study was found comparing ROL between *S. erectum* and *P. arundinacea*, however Calhoun & King (1997) compared *Pontederia cordata* and *Sparganium eurycarpum* (burreed) and found that *S. eurycarpum* released very little oxygen. This suggests that *S. erectum* may have lower rates of ROL which may be causing the lower redox conditions. However, the low redox conditions in sediments surrounding all three macrophyte species suggests ROL may be confined to a small area immediately surrounding the root/rhizomes and not having an effect upon the wider accumulated sediments. The relative position of *S. erectum* in the low flow channel relative to

the other macrophyte species could also help explain the more anoxic sediments. *T. latifolia* and *P. arundinacea* tend to grow closer to the bank and at a higher relative elevation (often at or above the low flow water level), suggesting sediments surrounding *S. erectum* may be continuously saturated and thus anoxic. The lower redox conditions in the sediments surrounding *S. erectum* compared to *T. latifolia* suggests a greater dominance of sulphides for metal binding in these sediments.

Decreases in sediment pH in the vicinity of macrophytes can occur from the decomposition of the accumulated organic matter releasing organic acids, differences in ROL which affect the decomposition of organic matter and the exudation of a variety of substances, including organic acids, from roots (Du Laing *et al*., 2009; Ratushnyah, 2008; van der Welle, 2007; Mucha *et al*., 2005; Neori, 2000; and, Weis & Weis, 2000). Sediment pH was significantly lower in the sediments accumulating around *S. erectum* compared to the other two macrophyte species (Table 6.9). As organic matter content was not significantly different in the sediments surrounding the three macrophyte species (Table 6.9), this suggests that differences in organic matter breakdown were not the cause of differing pH. As was discussed above, rates of ROL from *S. erectum* may be lower than from *T. latifolia* and therefore not potentially causing a greater rate of organic matter breakdown and thus release of organic acids. Literature on the relative release of organic acids from roots of the three macrophyte species in this study was generally not available, apart from one study indicating *T. latifolia* releases a range of acids (including asparaginic acid and glutamic acid) (Ratushnyak, 2008). However, although the results suggest *S. erectum* may be releasing greater amounts of organic acids than the other two macrophyte species, this lower pH does not appear to be increasing metal mobility since there were no significant differences in acetic-acid extractable metal concentrations (a more mobile form of metals) between the macrophyte species (Table 6.9). This could be explained by sediment pH still being in the near-neutral region for *S. erectum*, despite a lowering in comparison to the other two macrophyte species, and could indicate a more localised effect of the organic acids close to the roots (Table 6.8).

This study has shown that although there were some differences between the macrophyte species in terms of environmental conditions in the overlying water and underlying sediment, these differences were not significant enough to cause variation in metal concentrations in the overlying water and underlying sediment between the macrophyte species, due to all overlying waters being oxic and near-neutral and underlying sediments being anoxic and near-neutral. This shows that none of the macrophyte species studied here were having a greater or lesser effect upon dissolved metal concentrations in the overlying water and pseudo-total and acetic acid extractable metal concentrations in the underlying sediment.

6.5.3 Uptake and storage of metals by three commonly occurring emergent macrophyte species

There were few significant differences in metal concentrations between the macrophyte species (Table 6.12), with only Cu and Zn concentrations in *T. latifolia* being significantly lower than in *S. erectum* and *P. arundinacea*, respectively. Concentrations of metals within the macrophytes were generally not at a toxic level (Table 6.14).

For all three macrophyte species metal concentrations were significantly highest in the roots for Cu, Fe, Ni and Zn (Table 6.13). There was not such a clear pattern for Cr and Mn (Table 6.13).

Numerous studies looking at the uptake of metals by macrophytes which have analysed macrophyte tissues separately have shown this very common pattern of below-ground tissues, particularly roots, having greater metal concentrations compared to the above-ground tissues. These have been reported for a great range of metals including Cd, Co, Cr, Cu, Ni, Pb, and Zn (Fawzy *et al*., 2012; Romero Nunez *et al*., 2011; Mazej & Germ, 2009; Yeh *et al*., 2009; Ebrahimpour & Mushrifah, 2008; Sasmaz *et al*., 2008; Liu *et al*., 2007; Deng *et al*., 2004; and, Cardwell *et al*., 2002). However, there are some exceptions to this general pattern which have been reported. Higher concentrations of Hg and Mn in the leaves and shoots as opposed to the roots have been reported by Romero Nunez *et al*., (2011) and Sasmaz *et al.*, (2008) respectively. Scholes *et al*., (1998) reported concentrations of Cd, Cr, Cu, Ni, Pb and Zn decreasing in the order root > leaf > rhizome, and Fawzy *et al*, (2012) report Cd showing a variable distribution within the tissues of macrophytes.

The high concentration of metals within roots of macrophytes suggests the high availability of metals in the sediment to the macrophytes (Romero Nunez *et al*., 2012; Soda *et al*., 2012; Bonanno & Giudice, 2010; and, Deng *et al*., 2004). As previously discussed above (Section 6.5.2), sediment redox and pH conditions have an effect upon metal mobility, which can influence metal uptake by macrophytes (Zhang *et al*., 2010 and van der Welle *et al*., 2007). As shown in the previous Section (6.5.2) although there were some significant differences in pH and redox conditions in the sediment between the macrophyte species, these were not large enough to change the overall environmental conditions with the underlying sediments being anoxic and pH neutral, which can explain the lack of differences in metal concentrations between the macrophyte species. The general negative correlations between sediment pH and macrophyte metal concentrations in this study (although not always significant) indicate increasing pH resulted in lower metal concentrations in macrophytes (Table 6.16). Fe (II) concentrations showed a less clear pattern, although all root metal concentrations were negatively correlated with Fe (II), though not all significantly (Table 6.16).

Acetic-acid extractable sediment metal concentrations are indicative of metals which are more bioavailable to the macrophytes (Table 3.9, Chapter 3). Therefore, the proportion of the pseudo-total metal sediment concentration which is acetic-acid extractable gives an indication of the availability of that metal in the sediment to the macrophytes. Table 6.11 shows that while there was no discernable difference between the proportion of pseudo-total metals in the sediment that were acetic acid extractable (i.e. more bioavailable) between the macrophyte species, there were differences between the metals themselves, suggesting a greater bioavailability of Cd, Mn, Ni and Zn than Cr, Cu and Fe to macrophytes.

Similarly high bioavailabilities of Cd, Ni and Zn have been reported in some studies (Aleksander- Kwaterczak & Helios-Rybicka, 2009; Sakan *et al*., 2009; Svete *et al.,* 2001; and, Yu *et al*., 2001). Mn shows a higher bioavailability, contrary to some studies which report its low bioavailability attributed to its natural occurrence in the environment, particularly as Mn (hydr)oxides (Li *et al*., 2009; Sakan *et al*., 2009; and, Akcay *et al*., 2003). Some studies have however found higher bioavailabilities of Mn (Sakan *et al*., 2009 and Tuzen 2003), with Sakan *et al.* (2009) noting that these more mobile fractions of Mn are unlikely to be from anthropogenic sources, and are more likely to be stable phases of Mn in carbonate minerals and ion-exchangeable forms (Table 3.9, Chapter 3). Low bioavailabilities of Cr, Cu and Fe have been reported in other studies, thought to be due to Fe being a constituent of clay and Fe (hydr)oxides, Cr co-precipitating with Fe (hydr)oxides and Cu associating with organic matter and sulphides, all of which are lower bioavailable fractions of metal binding (Li *et al*., 2009; Sakan *et al.*, 2009; Tuzen, 2003; and, Yu *et al*., 2001, Table 3.9, Chapter 3)

The greater bioavailability of Mn, Zn and Ni in the sediments explains Mn, Zn and Ni having the second, third and fourth highest concentrations, respectively, within the macrophyte roots (Figure 6.11). Conversely, the low bioavailability of Cr and Cu in the sediments explains the low concentrations of these within the macrophyte roots (Figure 6.11).

Although Fe had one of the lowest sediment bioavailabilities (Table 6.11) it had the highest concentration in the macrophyte roots (Figure 6.11). This could be explained by the formation of Fe plaques (Fe (hydr)oxides) on the roots of macrophytes in oxidising conditions which can contribute to the measured Fe concentrations in the roots despite thorough washing of the tissues (Romero Nunez *et al*., 2011; Karathanasis & Johnson, 2003; and, Cardwell *et al*., 2002). As has been discussed above in Section 6.5.2 all three macrophyte species transport oxygen from their shoots to roots and have ROL, and thus the formation of Fe plaques would be possible on all three macrophyte species.

Table 6.19 summarises the metal concentrations found in the different tissues of the three macrophyte species in this study compared to published values from the literature for the same species. Unfortunately no published values could be found for *S. erectum* or *Sparganium* sp.

The concentrations of metals found in the three macrophyte species are generally comparable to those reported in the literature. The concentrations reported by Sasmaz *et al*. (2008) appear to be somewhat higher, however the *T. latifolia* samples were taken from a stream which received wastewater from a sewage treatment plant, which could account for the greater concentrations found in the macrophytes.

Table 6.19: Summary of macrophyte metal concentrations from this study and other published studies (*continued overleaf*).

			Concentration ($mgkg^{-1}$)					
	Species	**Tissue**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
This study Median	*S. erectum*	Root	5.2	12.1	86,490	490	12.6	172
		Rhizome	5.8	6.0	18,245	125	4.3	38
		Leaf/stem	7.5	5.5	1,073	339	2.1	35
	T. latifolia	Root	4.1	10.5	47,174	332	8.7	91
		Rhizome	2.1	2.4	9,382	150	2.1	24
		Leaf/stem	4.4	1.7	362	326	2.1	22
	P. arundinacea	Root	11.4	20.7	72,218	1557	15.1	176
		Rhizome	1.6	1.0	4,598	68	2.1	56
		Leaf/stem	3.1	3.3	991	106	2.1	39
Cardwell *et al*., (2002) Range	*T. orientalis*	Root		4.1 – 47.1				13.3 – 764.2
		Shoot		2.37 – 4.93				20.2 – 74.7
	T. domingensis	Root		53.5 – 127.4				355.5 – 1,030
		Shoot		3.37 – 14.9				21.4 – 83.4
Ladislas *et al*., (2012) Mean	*Typha* sp	Root					6.8	47.3
		Shoot					3.1	23.9
Samecka-Cymerman & Kempers, (2001) Mean	*Phalaris arundinacea*	Leaves	4.3	7.0	1,410	95	3.8	13

Table 6.19: Summary of macrophyte metal concentrations from this study and other published studies (*continued*).

			Concentration ($mgkg^{-1}$)					
	Species	**Tissue**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
Ye *et al*., (1997) Range	*T. latifolia*	Root						46 - 946
		Rhizome						36 - 456
		Leaves						22 - 122
Ebrahimpour & Mushrifah (2008) Range	Range emergent macrophytes	Root		6.41 – 13.0				
		Stem		4.63 – 6.27				
		Leaves		6.14 – 6.94				
Sasmaz *et al*. (2008) Mean	*T. latifolia*	Root	44	50		860	55	340
		Leaves	21	30		990	40	215

Calculation of metal mass within individual plants for each macrophyte species based upon tissue dry biomass showed a consistent pattern for all metals of the greatest metal mass being in *T. latifolia* plants and the lowest in *P. arundinacea*, indicating greater storage of metals by *T. latifolia*, a clear reflection of differing dry biomasses from differing morphologies and sizes (Chapter 5) (Figure 6.12 and Table 6.15). However, when the individual plant calculations were multiplied up to mass per m^2 of river channel with macrophyte growth based upon density of macrophyte growth, different macrophyte species patterns occurred. *P. arundinacea* still showed the lowest mass of metals per m^2 of channel, but *S. erectum* had the greatest mass of Cr, Cu and Zn and *T. latifolia* the greatest mass of Fe and Ni per m^2 of channel, a reflection of the higher density growth of *S. erectum* compared to *T. latifolia* (Figure 6.13 and Table 6.15). This indicates that *S. erectum* and *T. latifolia* had the greatest storage of metals per m^2 of river channel with macrophyte growth. In terms of metals in above-ground tissues, *S. erectum* had the greatest mass of metals in above-ground tissues for all metals of the three macrophyte species (Figure 6.17) indicating greatest storage in the above-ground tissues for *S. erectum*.

A few other studies have used macrophyte concentration data with measurements of biomass to calculate actual metal storage in macrophytes. Kamal *et al*. (2004) undertook research looking at the uptake of Hg, Cu, Fe and Zn by three macrophytes (*Myriophylhum aquaticum* (parrot feather) *Ludwigna palustris* (creeping primrose) and *Mentha aquatic* (water mint)) in a controlled wetland experiment. Metal mass in the macrophytes was calculated for both a control and treatment wetland. The range of metal mass in the treatment wetland were higher

than those found in this study. However, the range found in the macrophytes in the control wetland were similar to those found in this study: Cu, control wetland 0.87 mg to 2.8 mg per plant, this study 0.009 to 0.12 mg per plant; Fe, control wetland 110 mg to 146.5 mg per plant, this study 17.4 mg to 84.3 mg per plant; Zn, control wetland 6 mg to 35 mg per plant, this study 0.09 mg to 1.3 mg per plant. Liu *et al*. (2007), looking at a range of 19 macrophytes in a wetland treating urban road runoff, recorded average accumulation across the species of 30 mg Zn per plant and Ellis *et al.* (1994) undertaking research in a similar wetland found that *T. latifolia* and *Sparganium* sp. accumulated approximately 450 mgm^{-2} and 150 mgm^{-2} Zn respectively. These values are considerably higher than those recorded in this study of 0.09 to 1.3 mg Zn per plant. However, the Liu *et al.* (2007) study had higher average plant metal concentrations for both above-ground and below-ground than this study and Ellis *et al*., (1994), although not stating macrophyte metal concentrations, the biomass of *T. latifolia* in particular was larger than the biomass used in this study.

Although all three macrophytes stored the majority of Fe in below-ground tissues there were differences between the species for the storage of the other metals (Figure 6.14). *S. erectum* stored the other metals in above-ground tissues, whereas *T. latifolia* stored the majority of Cr and Mn in above-ground tissues and Cu in below-ground tissues and *P. arundinacea* stored Cr in above-ground tissues and Mn in below-ground tissues. The other metals were roughly equally distributed between above-ground and below-ground tissues in *T. latifolia* and *P. arundinacea*. Ellis *et al*. (1994) recorded greater storage of Zn in the roots for *T. latifolia* and in the shoots for *Sparganium* sp., which is consistent with this study. Conversely, Liu *et al*. (2007) found across 19 wetland plants 66.5% of Cd, Pb and Zn was accumulated in the above-ground tissues, which is consistent with the findings for *S. erectum* in this study. Greater storage of metals in above-ground tissues can result in greater recycling of metals within the river due to the higher decomposition rates of above-ground tissues compared to below-ground tissues (Windham *et al*., 2003).

This study has shown that the greatest uptake of metals generally occurred in the roots of the three macrophyte species, with the greatest uptake generally being for the metals which were most bioavailable in the sediment. *S. erectum* and *T. latifolia* had the greatest storage of metals per m^2 of river channel with macrophyte growth, a reflection of their high biomass and density of growth. *S. erectum* stored the majority of metals in above-ground tissues, whereas the other two macrophyte species had no clear storage in either above-ground or below-ground tissues.

6.5.4 Bioconcentration and translocation of metals by three commonly occurring emergent macrophytes

This study showed that generally there was little discernable difference between the three common emergent macrophyte species in terms of their ability to bioconcentrate metals from the sediment into their above-ground and below-ground tissues.

The BCF's calculated in this study were always greater for the roots than the rhizomes or leaf/stems (Figure 6.16), which concurs with a study undertaken by Sasmaz *et al*. (2008) focussing on *T. latifolia* which found higher BCFs for roots as opposed to leaves for a range of metals (Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn). This finding is also consistent with the roots generally showing higher metal concentrations compared to the above-ground leaf/stems in this study (Table 6.13) and indicates that within the macrophytes the roots are the location of the greatest metal bioconcentration.

Generally, all BCFs for pseudo-total metals were below one indicating that there was not a net bioconcentration of metals from the sediment into the macrophyte tissues, apart from Mn in the roots of *P. arundinacea* (BCF 1.56) (Figure 6.16). However, there were differences between metals with Cr and Cu showing the smallest and Fe, Mn, Ni and Zn the greatest bioconcentration.

A range of root BCFs for macrophytes have been reported in the literature. Some studies have only reported a net bioconcentration of metals into macrophyte roots (e.g. Zhang *et al*., 2010 and Yeh *et al*., 2009), whereas others have reported varying BCFs depending on metals and macrophyte species. For example, Romero Nunez *et al.* (2011) reported BCFs for a range of macrophytes below one for Cu and Zn and above one for Hg and Cd. Similarly Ladislas *et al*. (2012), investigating three macrophyte species (*Typha* sp., *Juncus* sp. and *Oenanthe* sp.), reported BCFs below one for Ni for all three macrophyte species, below one for Cd for all species except *Typha* sp. and below one for Zn for just *Oenanthe* sp..

The difference in BCFs between the metals in this study could be related to the requirements of the metals by the macrophytes. Fe, Mn, Ni and Zn are all essential elements for macrophytes and therefore will be readily taken up by them (Fawzy *et al*., 2012; Ladislas *et al*., 2012; Sasmaz *et al*., 2008; Kapustka *et al*., 2004; and, Sparling & Lowe, 1998). Cr is not an essential element (Bonanno & Giudice, 2010) and thus would not actively be bioconcentrated by the macrophyte. Cu, although an essential element, does become toxic if accumulated in high concentrations, and thus may not be bioconcentrated as readily by macrophytes in comparison to other elements (Fawzy *et al*., 2012 and Deng *et al*., 2004).

The three common emergent macrophyte species generally showed no net translocation of metals from below-ground tissues (roots and rhizomes) to above-ground tissues (leaf/stem), with median TFs being below one for all metals and macrophyte species (Figure 6.17). Higher TFs were shown for Cr for all three macrophyte species and Mn for *S. erectum* and *T. latifolia*. The lowest TFs were shown for Fe for all three macrophyte species.

Deng *et al.* (2004) reported that lower T's occurred with higher metal concentrations in sediments, which concurs with this study with Cr having a high TF and low sediment concentration, and Fe a low TF and high sediment concentration (Table 6.8 and Figure 6.17).

The lack of translocation of metals to above-ground tissues in macrophytes has been shown in other studies. Deng *et al.* (2004) report TFs to above-ground tissues for 12 emergent wetland macrophytes, including *T. latifolia* and *P. arundinacea*, largely below one for Cd, Cu, Pb and Zn, similarly Yeh *et al*. (2009) report TFs to aboveground tissues below one for *T. latifolia* and *Phragmites australis* for Cu (0.41 and 0.36, respectively) and Zn (0.36 and 0.27 respectively). Similar to results in this study which showed greater translocation of Mn and Cr to above-ground tissues Sasmaz *et al*. (2008) studying *T. latifolia* reported Cr, Cu, Ni and Zn having a TF below one but Mn having a TF over one (1.18) and Zhang *et al*. (2010) report all TFs below one (for Cd, Cu, Ni, Pb and Zn) apart from Cr (1.09). Other studies have reported that essential elements are more readily translocated to above-ground tissues from below-ground (Mazej & Germ, 2009 and Cardwell *et al*., 2002), which is true of Mn in this study, although the other essential elements did not have high TFs and Cr, a non-essential, did.

It has been suggested that there are differences in metal translocation between dicotyledons and monocotyledons, with higher respiration rates in broad leaved dicotyledons, as opposed to narrow leaved monocotyledons, promoting greater metal translocation (Ladislas *et al*., 2012 and Deng *et al*., 2006). The three macrophyte species in this study are all monocotyledons, and thus the lack of metal translocation could be explained by this differentiation.

The lack of translocation of metals to above-ground tissues indicates limited mobility of metals once inside the macrophytes and classifies the macrophyte species as metal excluders (Romero Nunez *et al*., 2012; Sasmaz *et al*., 2008; Deng *et al*., 2004; and, Kapustka *et al*., 2004). This has been termed a metal tolerance strategy whereby some macrophyte species may have developed mechanisms to prevent the translocation of metals or have root cells which have the ability to absorb greater amounts of metals (Sundberg-Jones & Hasson, 2007 and Taylor & Crowder, 1983).

6.6 Conclusions

From this study, the potential use of the three common emergent macrophytes studied here for remediation of metal contaminated sediments in urban river restoration can be assessed. The highest metal concentrations were found in the surrounding sediment, and in the case of *S. erectum* the highest storage of metals per m^2 of channel too, indicating that although the macrophytes may be used for phytoremediation, the sediment is likely to still be the greatest store of metals. There was no evidence of differences between the macrophyte species in alteration of sediment and overlying water environmental conditions in terms of pH and redox, and hence no differences between metal concentrations and mobilities.

Although there generally was no net bioconcentration from the sediments in terms of pseudo-total metal concentrations (apart from Mn in the roots of *P. arundinacea*) or translocation of metals from below-ground to above-ground tissues, the macrophytes were found to bioconcentrate Fe and Mn to the greatest extent and Cr and Cu to the least extent, although Cr and Mn were translocated most to above-ground tissues (all species for Cr and not *P. arundinacea* for Mn) and Fe was not translocated much at all.

Far greater understanding of the phytoremediation potential of the three macrophyte species can be gained from looking at the mass of metals stored within the macrophytes as opposed to just the concentrations, since the macrophyte species themselves had very different morphologies and thus dry biomasses and also densities of growth. Overall, of the three common emergent macrophyte species investigated in this study, *S. erectum* and *T. latifolia* showed the greatest promise for phytoremediation having the greatest metal storage per plant and per m^2 of channel with macrophyte growth. Fe is predominantly stored in below-ground tissues for both of these macrophyte species, with *S. erectum* storing other metals in above-ground tissues and *T. latifolia* storing Cr and Mn in above-ground tissues, Cu in below-ground tissues and Ni and Zn equally distributed. Therefore, in terms of the management of phytoremediation, if these macrophyte species were to be used for phytoremediation then their above-ground tissues should be collected at the end of the growing season to prevent the release of metals, particularly Cu, Cr, Mn and Zn, back in to the river system during senescence.

At this particular study site, the high concentrations of Pb and Zn in the sediments were of greatest concern in terms of sediment quality guidelines. There was no evidence of phytoremediation in terms of metal uptake for Pb by the macrophytes, with Pb not detected in the majority of macrophyte tissues. The uptake of Zn by all three macrophyte species was shown, with 43.6 mgm^{-2}, 30.8 mgm^{-2} and 17.33 mgm^{-2} of channel for *S. erectum, T. latifolia* and *P. arundinacea* respectively, with the majority stored in the above-ground tissues for *S. erectum*

and *P. arundinacea* and equally distributed between the above-ground and below-ground tissues for *T. latifolia*.

However, the ability for common emergent macrophytes to reinforce, stabilise and phytoremediate metal contaminated sediments in urban rivers depends upon the ability of them to decrease flows and trap and accumulate sediments. The ability of the most common emergent macrophyte, *S. erectum*, to reduce flow velocities and trap and accumulate sediments is considered in Chapter 7.

Chapter 7

The Effect of *Sparganium erectum* Growth upon Flow and Sedimentation

7.1 Introduction

As macrophytes grow within a river channel they create a resistance to flow. This causes a slowing down of flow velocities within, and around, the macrophyte stands to the extent that significant quantities of sediment may settle and accumulate (Jones *et al*., 2011; Luhar *et al*., 2008; Haslam, 2006; Pluntke & Kozerski, 2003; and, Schulz, 2003). A great deal of research has already focussed on the hydraulic effects of macrophytes, both in the field and in the laboratory, and at the reach, stand and individual plant scale (*e.g.* Dijkstra & Uittenbogaard, 2010; Liu *et al*., 2010; Larsen *et al*., 2009; Naden *et al*. 2006; Green, 2005a and 2005b; Lee *et al*., 2004; Stephan & Gutknecht, 2002; Champion & Tanner, 2000; Sand-Jensen & Pedersen, 1999; and, Sand-Jensen & Mebus, 1996). However, there has been less research on the effect of macrophytes upon sedimentation, with much of this work focussed on submerged species (*e.g.* Kleeberg *et al*., 2010; Heppell *et al*., 2009; Cotton *et al*., 2006; Wharton *et al*., 2006; Horvath, 2004; Pluntke & Kozerski, 2003; Schulz *et al*., 2003; and, Sand-Jensen, 1998), although emergent plants have received some attention (*e.g.* Asaeda *et al*., 2010 and Koetsier & McArthur, 2000), particularly in laboratory flume experiments (*e.g.* Gorrick & Rodriguez, 2012; Zong & Nepf, 2010; Bennett *et al*., 2008; and, Sharpe & James, 2006).

As a result of these interactions between macrophytes, flows and sediments, macrophytes can create patches within river channels characterised by relatively low flow velocities and relatively fine sediment bed material separated by areas of higher velocity and coarser substrates, which has led to them being described as 'ecosystem engineers' due to their ability to "modify, maintain and/or create habitats" (Jones *et al*., 1994, p374) (Jones *et al*., 1994 and 1997 and Sand-Jensen & Madsen, 1992). This concept was further developed by Clarke (2002) who suggested that on the short- to medium-term macrophytes can have an impact upon geomorphology through significant sediment retention. In a reach scale study, Gurnell *et al*. (2006) suggested that where emergent and submerged plants co-existed in a reach, the emergent macrophytes, located along the bank toe appeared to retain the largest quantities of fine sediment.

The development of fluvial landforms through the interactions of river flows, riparian plants and sediments has been described by Corenblit *et al*. (2007) in the 'Fluvial Biogeomorphic Succession Concept' where pioneer species initially colonise the bare sediment surfaces of exposed bars, finer sediments then accumulate around the plants and become stabilised by their root systems to form new landforms. Recently this concept has been extended to a wider range of river types and to aquatic and wetland plants by Gurnell *et al.* (2012), who emphasise the importance of emergent plants, in particular, for landform building and river channel morphodynamics in low energy river environments.

The ability of macrophytes to induce changes in flow velocities and sediment retention depend upon the morphology of the macrophyte and its biomechanical growth traits. This Chapter reports on a study into the effect of the seasonal growth of the emergent macrophyte *S. erectum* upon flow velocity and sediment retention at the patch scale, with a focus on the following research questions:

- To what extent does the presence of *S. erectum* affect sedimentation and flow velocities?

- To what extent does sedimentation vary through the annual growth cycle of *S. erectum*?

7.2 Research Site

Research was undertaken at site two on the River Blackwater in Surrey, UK, a lowland urban river which has been heavily impacted by gravel extraction, transport infrastructure development and urbanisation (Figure 7.1 and Section 3.2.2 in Chapter 3). Research site two is approximately 11 km downstream from the river's source (centre of site SU 88230 54974). The site is bounded by the A331 to the right bank with lakes and residential areas beyond, and a railway line with residential areas beyond on the left bank (Figure 7.2). The site is located on private land, with no public access and no grazing cattle, resulting in a secure site with very little chance of the river bed being disturbed and affecting sedimentation measurements. Marginal areas of dense *S. erectum* growth with associated deep fine sediment depositions are present alongside the left bank of the channel, with minimal in-channel submerged vegetation growth within the rest of the channel.

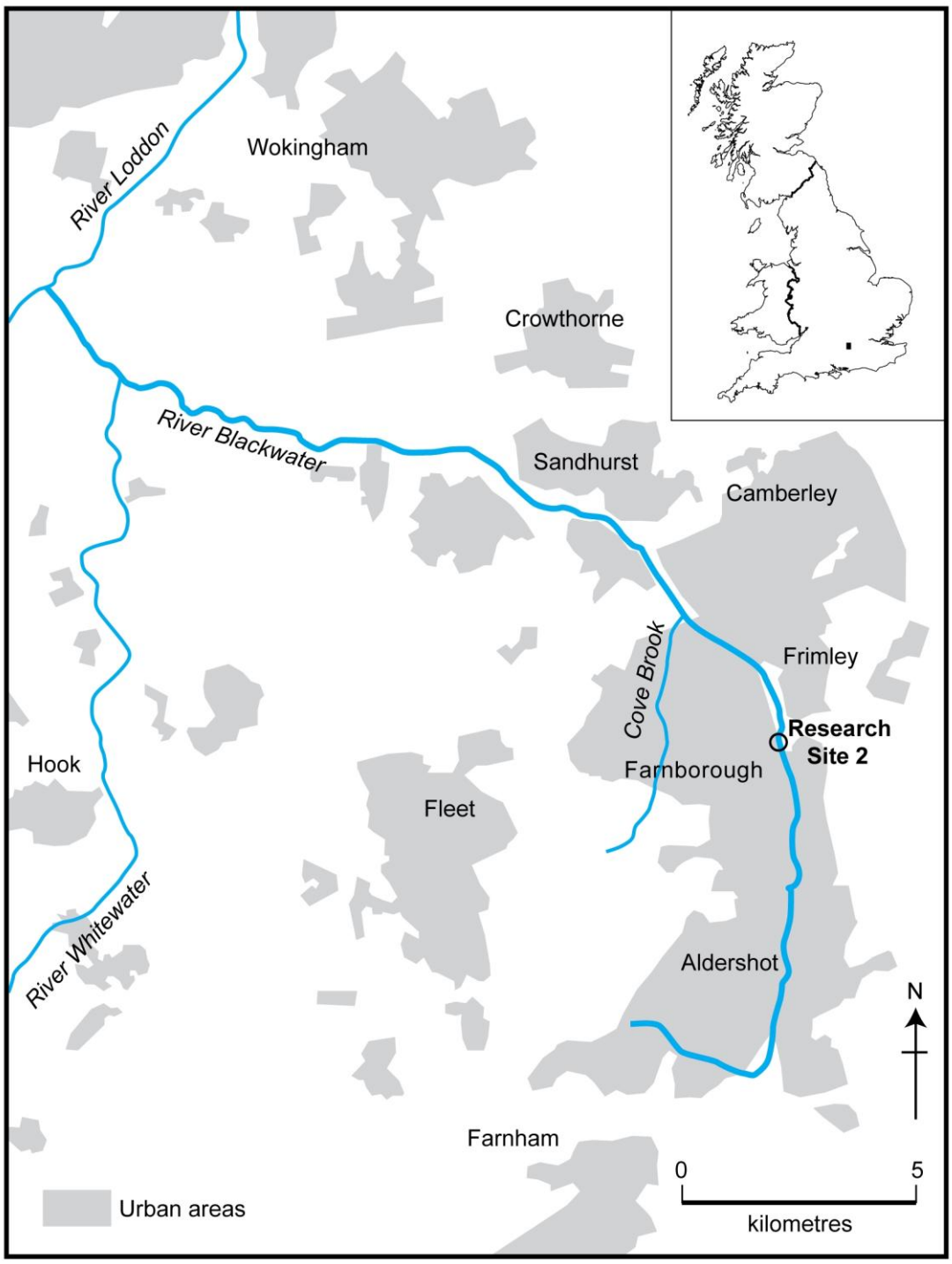


Figure 7.1: Location of research site two, Mytchett, on the River Blackwater.

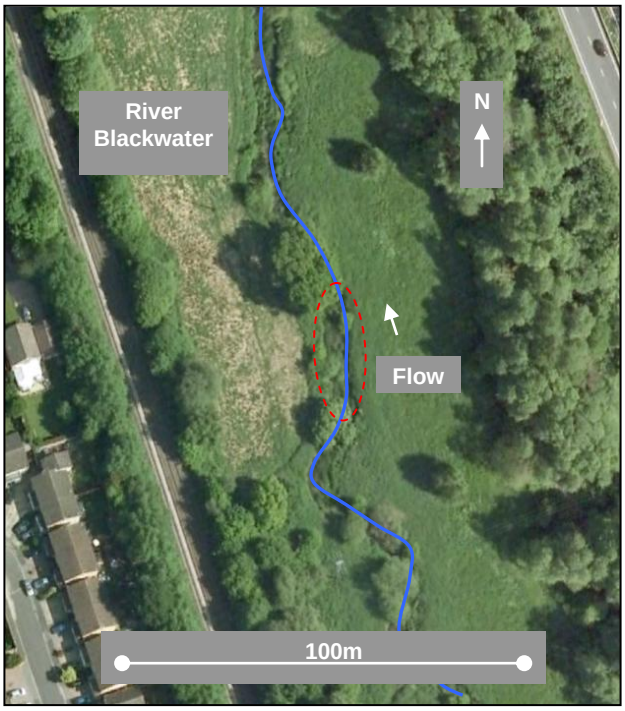


Figure 7.2: Detailed map of location of research site two, Mytchett, on the River Blackwater.

7.3 Methods

7.3.1 Fieldwork

Field measurements were undertaken on 11 occasions during the macrophyte growth season over two years (six measuring periods in 2010 and five measuring periods in 2011) in order to capture the full extent of the growing period of the macrophytes (Table 7.1). As far as possible measurements were taken during base flow conditions so that differences in discharge at monitoring times were minimised.

Table 7.1: Dates of the eleven measuring periods.

Measuring Period		Date
1	17/03/10	Mid-March 2010
2	30/04/10	End-April 2010
3	15/06/10	Mid-June 2010
4	05/08/10	Early-August 2010
5	13/09/10	Mid-September 2010
6	22/11/10	End-November 2010
7	31/05/11	End-May 2011
8	14/07/11	Mid-July 2011
9	22/08/11	End-Aug 2011
10	11/10/11	Mid-October 2011
11	22/11/11	End-November 2011

S. erectum was chosen for detailed flow and sediment accumulation investigation from the three species investigated in earlier chapters (Chapters 5 and 6) as it is the most frequently occurring linear emergent macrophyte species across the UK (Table 5.1, Chapter 5, Gurnell *et al*., 2010 and Haslam, 2006) and is known to have a significant influence upon flow velocities and sediment retention (Liffen, 2011; Asaeda *et al*., 2010; and, Naden *et al*., 2006).

A paired-quadrat approach was used, similar to that used by Asaeda *et al*. (2010) in their research on sediment retention by *S. erectum*. The locations of three paired-quadrats within the channel were identified in March 2010 using knowledge of the site gained during research conducted the previous year on the reach immediately downstream. Each pair consisted of a quadrat located in the centre of a stand of *S. erectum* (*S. erectum* quadrat 1, 2 and 3) and a quadrat in the adjacent open-channel area (channel quadrat 1, 2 and 3) (Figure 7.3a). Metal poles were inserted in to the river bed to mark the four corners of the six quadrat locations so that a moveable quadrat could be precisely relocated on each field visit. The moveable quadrat, measuring 1 m by 1 m, was divided into a 20 cm grid of 25 squares (Figure 7.3b). Care was taken during every field visit to avoid walking over the areas of river bed where the quadrats were located so that plant growth and sedimentation could proceed without human disturbance.

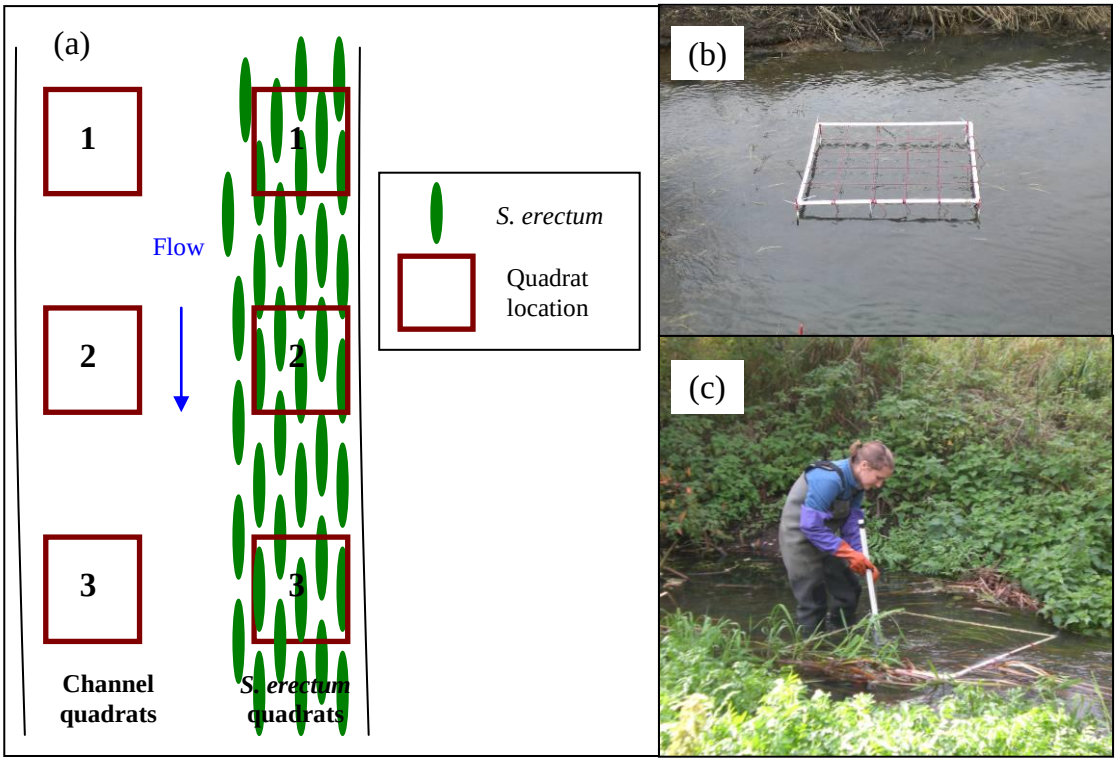


Figure 7.3: (a) Schematic diagram of the three paired-quadrats located in the river channel (b) the 1 m x 1 m moveable quadrat divided in to 20 cm grid (c) undertaking field measurements.

For two years the following measurements were undertaken: (i) fine sediment depth, using a thin metal pole (4 mm diameter) inserted into the sediment and measured against a metre ruler at the centre of each of the 25 squares within the moveable quadrat at all six quadrat locations (Figure 7.3), (ii) the coverage of the quadrat by macrophytes, and the species of macrophytes, and, (iii) the maximum leaf length of the *S. erectum* plant in the centre of the three biomass quadrats in 2010 and the centre of each *S. erectum* quadrat in 2011. During the 2010 measuring periods additional data was collected at the centre of each of the 25 squares within the moveable quadrat at all six quadrat locations in order to elucidate the relationships between flow, water depth and fine sediment accumulation: (i) flow velocity, averaged over 30 seconds, at 0.6 depth from the water surface (ms^{-1}), using a Valeport Model 801 electromagnetic flow meter, and (ii) water depth, using a metre ruler (Figure 7.3). Additionally, in another section of the river at the same site, three random 0.5 m x 0.5 m quadrats of *S. erectum* were selected in well-developed stands. The above-ground portions of the plants within the quadrats were collected and taken back to the laboratory for biomass measurements. Fine sediment depth measurements were undertaken first to minimise any effects of disturbance to the sediment from subsequent measurements. Whilst undertaking flow measurements, the base of the flow meter was placed very gently upon the sediment surface, with the weight of the meter being held by the fieldworker, to minimise compaction and disturbance to the fine sediment. Similarly, care was taken whilst undertaking water depth measurements to minimise disturbance to the fine sediment surface.

7.3.2 Laboratory analysis

The *S. erectum* plants collected during 2010 were thoroughly washed to remove all sediment and split into dead and living tissues. The plants were then dried at 85°C for at least 72 hours, until a constant weight was achieved and subsequently the dry weights recorded (Asaeda *et al*., 2010). The dead and living biomass as grams dry weight per m^2 (BM, gdw/m^2) was calculated as:

$$BM = DW \times 4$$

where DW was the dry weight (in grams) of the macrophytes in the 0.5 m x 0.5 m quadrat.

7.3.3 Data analysis

All data analysis was undertaken using Microsoft Excel 2003, XLSTAT Pro 2011 and 2012 and SPSS version 16.0. The frequency distributions of the measured variables were visually analysed using histograms and tested using Kolmogorov Smirnov (K-S) normality tests (full results in Appendix VIII). Although the observations of three variables (maximum leaf length,

total biomass and shoot density) did not differ significantly from a normal distribution (K-S test, $p > 0.05$), the remaining four variables were not normally distributed (K-S, $p < 0.05$). Although it might have been possible to transform observations of these latter variables to achieve a normal distribution (Section 3.4.3, Chapter 3) comparisons are not easily made between the results of analyses of transformed and non-transformed data, and it is difficult to directly compare the results from different (parametric and non-parametric) statistical tests. Therefore non-parametric statistical methods were used to analyse the data. Changes in macrophyte cover and biomass between the quadrats and over time were visually compared using bar charts. Differences in flow velocities, water depths and fine sediment depths between the quadrats and over time were visualised using boxplots and statistically tested using the non-parametric Mann-Whitney U test (M-W) when comparing observations between the two types of quadrats and the Kruskal-Wallis test (K-W) comparing measurements taken at different times. If the K-W test indicated there were significant differences then post-hoc Steel-Dwass-Critchlow-Fligner tests (S-D-C-F) tests were used to identify which measuring periods were significantly different. Non-parametric Spearman's Rank correlation coefficients were calculated to analyse the associations between flow velocity, water depth and fine sediment depth.

The volume of fine sediment (V, cm^3m^{-2}) beneath each quadrat on each monitoring occasion was calculated as:

$$V = \sum (D^* 400)$$

where D is the fine sediment depth recorded in each 20 cm^2 square (cm).

7.4 Results

7.4.1 Data description

Analysis focussed on seven variables: macrophyte coverage, biomass, shoot density, maximum leaf length, flow velocity, water depth and fine sediment depth. The full data set for each of these seven variables is summarised in boxplots in Figure 7.4.

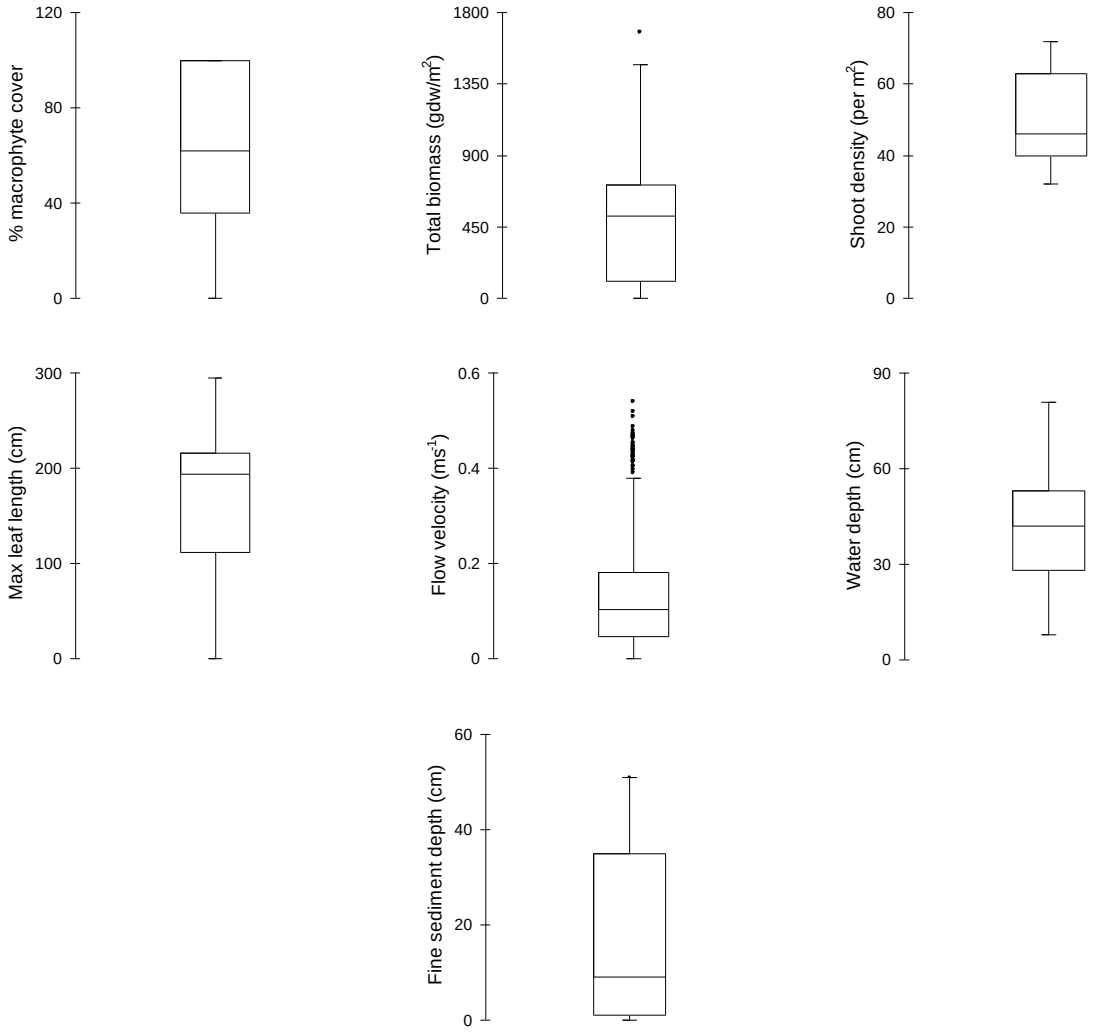


Figure 7.4: Boxplots of the seven variables.

7.4.2 Variations in macrophyte cover, species, biomass and condition between quadrats and over time

Percentage cover of the quadrats by macrophytes for each measuring period, and *S. erectum* plant growth measurements, are presented as bar charts in Figures 7.5 and 7.8 and were visually analysed to assess differences between the quadrats and over time.

Visual analysis of the bar charts shows that there were clear differences in macrophyte cover both between the *S. erectum* and channel quadrats and over time (Figure 7.5). The channel (Figure 7.5a) and *S. erectum* (Figure 7.5b) quadrats showed an increase in the percentage macrophyte coverage through the main annual growth cycle (from measuring periods 1 to 5 and 7 to 10) followed by a decrease in measuring periods 6 and 11. Minimum coverages were recorded at the first measuring period of each year for channel quadrats (0% and 40% median for measuring periods 1 and 7 respectively) and the first measuring period of 2010 for *S. erectum* quadrats (median 20%). Maximum coverages were recorded in measuring periods 4 and 10 for the channel quadrats (median 48% and 100% respectively) and in measuring periods 4, 5, 8, 9 and 10 for the *S. erectum* quadrats (all 100% coverage).

There was a greater percent macrophyte cover in the *S. erectum* quadrats compared to the channel quadrats at all measurement periods throughout the two years (Figure 7.5a and 7.5b) and, therefore, overall the *S. erectum* quadrats had statistically significant greater macrophyte coverage than the channel quadrats (M-W, $p < 0.0001$). Additionally, the *S. erectum* quadrats showed a less rapid decrease in percentage macrophyte coverage towards the end of the two annual growth cycles compared to the channel quadrats. Figure 7.6 illustrates the growth and senescence of the macrophytes within the channel through the two years of measurements at the same location.

None of the macrophytes recorded within the channel quadrats throughout the two years were *S. erectum*. The dominant species in the channel quadrats were *Sparganium emersum*, *Potamogeton natans* and *Zannichellia palustris*, all of which are submerged/floating-leaf species. Additionally, towards the end of 2011 (measuring periods 10 and 11) *Rorippa nasturtium-aquaticum* (watercress) was recorded, although it had not been observed in 2010 (Figure 7.7). In contrast, *S. erectum* was the only species recorded in *S. erectum* quadrats 2 and 3 in all measuring periods during 2010 (Figure 7.5c). However, in *S. erectum* quadrat 1 *P. natans* and *S. emersum* plants were also recorded in 2010 during measuring periods 2, 3 and 4. During 2011 there was a decrease in the proportion of *S. erectum* plants in the *S. erectum* quadrats towards the end of the year, with none recorded in measuring period 11. This was primarily due to *R. nasturtium-aquaticum* in measuring period 10 and *R. nasturtium-aquaticum* plus *P. natans* and *S. emersum* in measuring period 11 growing into these quadrats following the senescence and collapse of *S. erectum* (Figure 7.7). *S. erectum* was observed to be predominantly submerged during measuring periods 1 and 2, emergent from measuring periods 2 to 4 and 7 to 9 and collapsing in measuring periods 4 to 6 and 9 to 11 (Figure 7.5c).

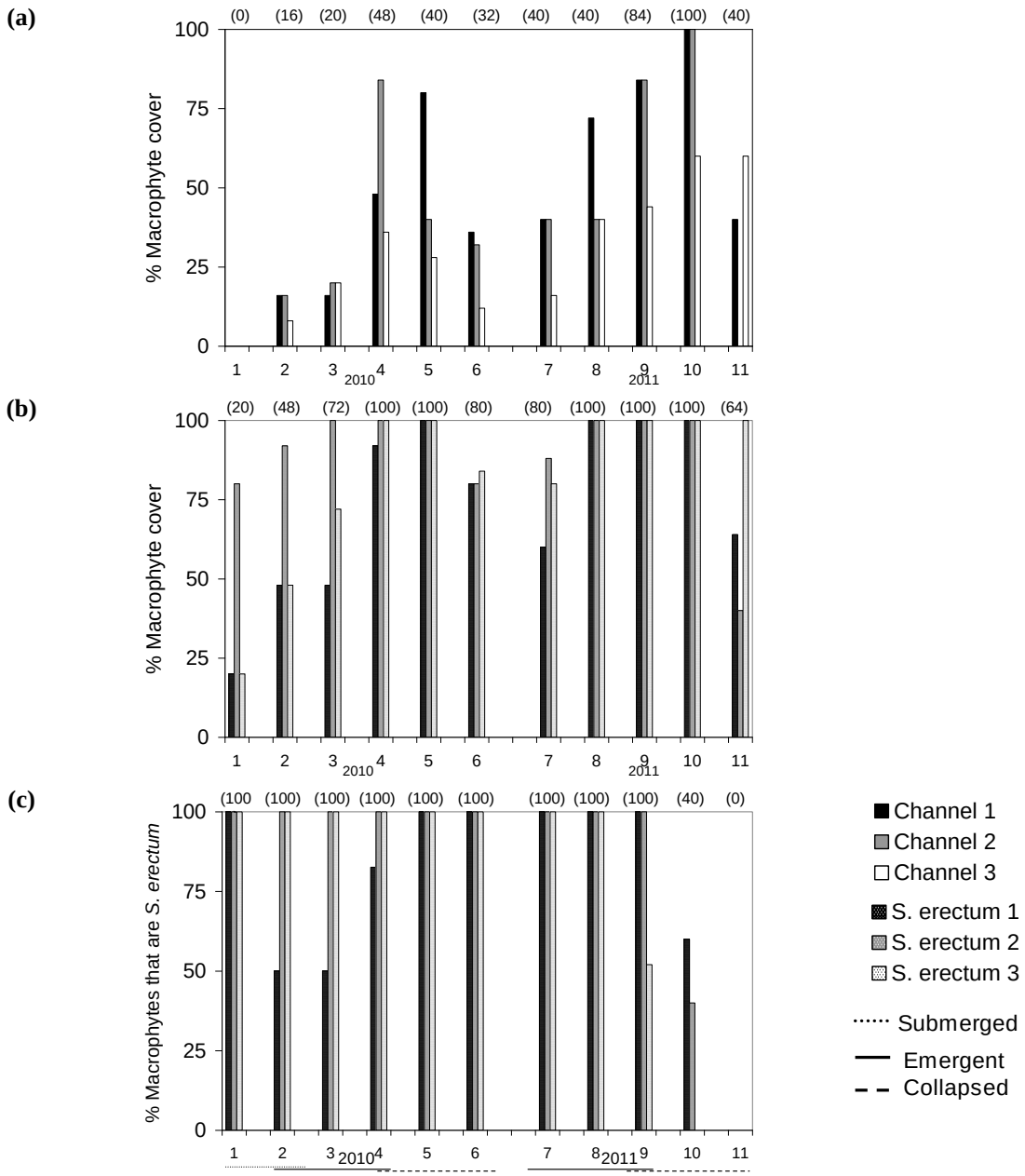


Figure 7.5: Percentage macrophyte cover of (a) channel quadrats and (b) *S. erectum* quadrats over time with median values in brackets. (c) Percentage of macrophytes within the *S. erectum* quadrats that are *S. erectum*, along with observation of submergent, emergent and collapsed form. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

Measuring Period 1 (17/3/2010)

Measuring Period 2 (30/04/2010)

Measuring Period 3 (15/06/2010)

Measuring Period 4 (05/08/2010)

Measuring Period 5 (13/09/2010)

Measuring Period 6 (22/11/2010)

Measuring Period 7 (31/05/2011)

Measuring Period 9 (22/08/2011)

Measuring Period 10 (11/10/2011)

Measuring Period 11 (22/11/2011)

Figure 7.6: Series of photographs showing temporal changes in macrophyte coverage at the same location (measuring period 8, 14/07/2011 photograph missing) through the two year study. (*S. erectum* is located in the background and *S. emersum* and other submerged species are in the foreground).

Channel quadrat 1
Measuring period 11 (22/11/2011)

***S. erectum* quadrat 3**
Measuring period 11 (22/11/2011)

Figure 7.7: Photographs of *R. nasturtium-aquaticum* growing in channel quadrat 1 and *S. erectum* quadrat 3 in measuring period 11 (22/11/2011).

Biomass measurements taken during the 2010 growth cycle showed a steady increase in total *S. erectum* biomass from a minimum in measuring period 1 (median 1.5 gdw/m^2) to maximum in measuring period 5 (median 1,474 gdw/m^2) (Figure 7.8a). The senescence and collapse of *S. erectum* is reflected in the increase in dead biomass proportions and lower total biomass observed in measuring period 6. Shoot density peaked in measuring period 4 (median 68/m^2) and then steadily decreased through the remaining monitoring in measuring periods 5 and 6 (Figure 7.8b). *S. erectum* maximum leaf lengths peaked in measuring period 5 in 2010 (median 267 cm) and measuring period 9 in 2011 (median 202 cm) (Figure 7.8c).

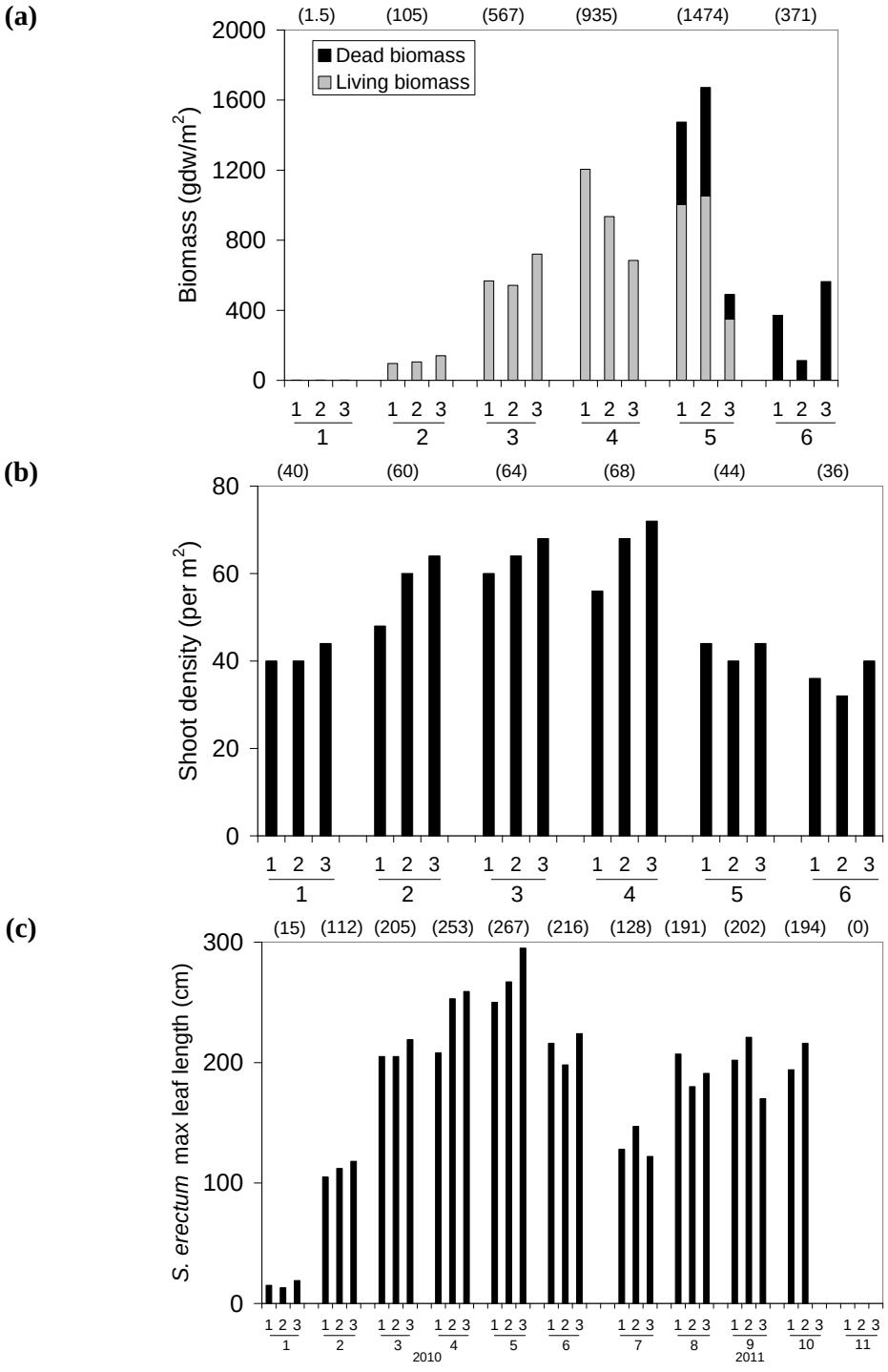


Figure 7.8: Bar charts of *S. erectum* (a) biomass, (b) shoot density and (c) maximum leaf length in each of the three quadrats on each of the monitoring occasions in 2010 and 2011 with median values in brackets (median total biomass). (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

7.4.3 Variations in flow velocity and water depth within and between quadrats and over time

Flow velocities and water depths for each quadrat type and for each measuring period were plotted as boxplots to visualise any differences in these variables between quadrats and over time (Figures 7.9, 7.10, 7.11 and 7.12). Mann-Whitney U (M-W) and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were then employed to identify significant differences in these variables between the quadrats and over time (Tables 7.2, 7.3, 7.4 and 7.5).

Flow velocities were measured during 2010 (measuring periods 1 to 6). Overall, flow velocities were significantly greater in the channel quadrats (median 0.18 ms^{-1}) than the *S. erectum* quadrats (median 0.05 ms^{-1}) (M-W, $p < 0.0001$, Table 7.2), and a greater range of flow velocities were also recorded in the channel quadrats than the *S. erectum* quadrats (Figure 7.9).

All of the channel quadrats showed a similar temporal pattern in the recorded median and range of flow velocities. The highest velocities were recorded early and late in the macrophyte growth cycle (measuring periods 1 and 6, medians 0.42 ms^{-1} and 0.32 ms^{-1}, 0.43 ms^{-1} and 0.33 ms^{-1}, 0.33 ms^{-1} and 0.26 ms^{-1}, for channel quadrats 1, 2 and 3 respectively) and the lowest flow velocities were recorded during measuring periods 2 to 5 (median range 0.09 to 0.12 ms^{-1}, 0.11 to 0.020 ms^{-1}, 0.11 to 0.20 ms^{-1}, channel quadrats 1, 2 and 3 respectively) (Figure 7.10). In channel quadrats 1 and 2 flow velocities during measuring periods 1 and 6 were both significantly greater than flow velocities in measuring periods 2 to 5 (K-W, $p < 0.0001$, Table 7.2) and in channel quadrat 3, flow velocities observed in measuring period 1 were significantly greater than recordings taken in all other measuring periods (K-W, $p < 0.0001$, Table 7.2).

The highest flow velocities in *S. erectum* quadrats 2 and 3 were recorded early and late in the macrophyte growth cycle (measuring periods 1 and 6, medians 0.07 ms^{-1} and 0.08 ms^{-1}, 0.10 ms^{-1} and 0.12 ms^{-1}, *S. erectum* quadrats 2 and 3 respectively) with notably lower flow velocities recorded between measuring periods 2 and 5 (median range 0.02 to 0.05 ms^{-1} and 0.02 to 0.08 ms^{-1}, *S. erectum* quadrats 2 and 3 respectively) (Figure 7.10). *S. erectum* quadrat 1 showed a different pattern with highest flow velocities recorded during measuring period 6 (median 0.11 ms^{-1}) and lowest flow velocities during the period between measuring periods 1 and 5 (median range 0.03 to 0.08 ms^{-1}) (Figure 7.10). This quadrat also showed a greater range of flow velocities at each monitoring occasion than the other two *S. erectum* quadrats. Flow velocities in *S. erectum* quadrats 2 and 3 in measuring periods 1 and 6 were both significantly greater than flow velocities in measuring periods 2 to 5 (K-W, $p < 0.0001$, Table 7.2) and flow velocities in

S. erectum quadrat 1 in measuring period 6 were significantly greater than in all of the other five measuring periods (K-W, $p < 0.0001$, Table 7.2).

When flow velocities were compared, for each pair of quadrats within each measuring period, the flow velocity in the channel quadrat was always significantly greater than in the *S. erectum* quadrat (all M-W, $p < 0.05$, Table 7.3).

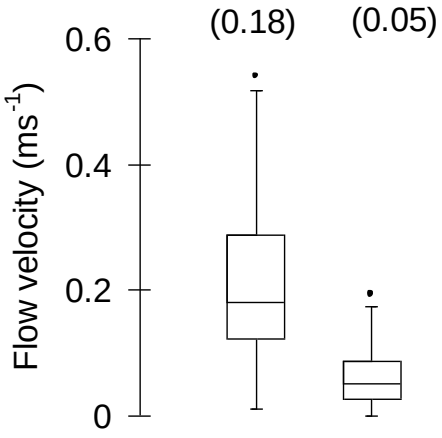


Figure 7.9: Boxplots of flow velocities in channel and *S. erectum* quadrats with median values shown in brackets.

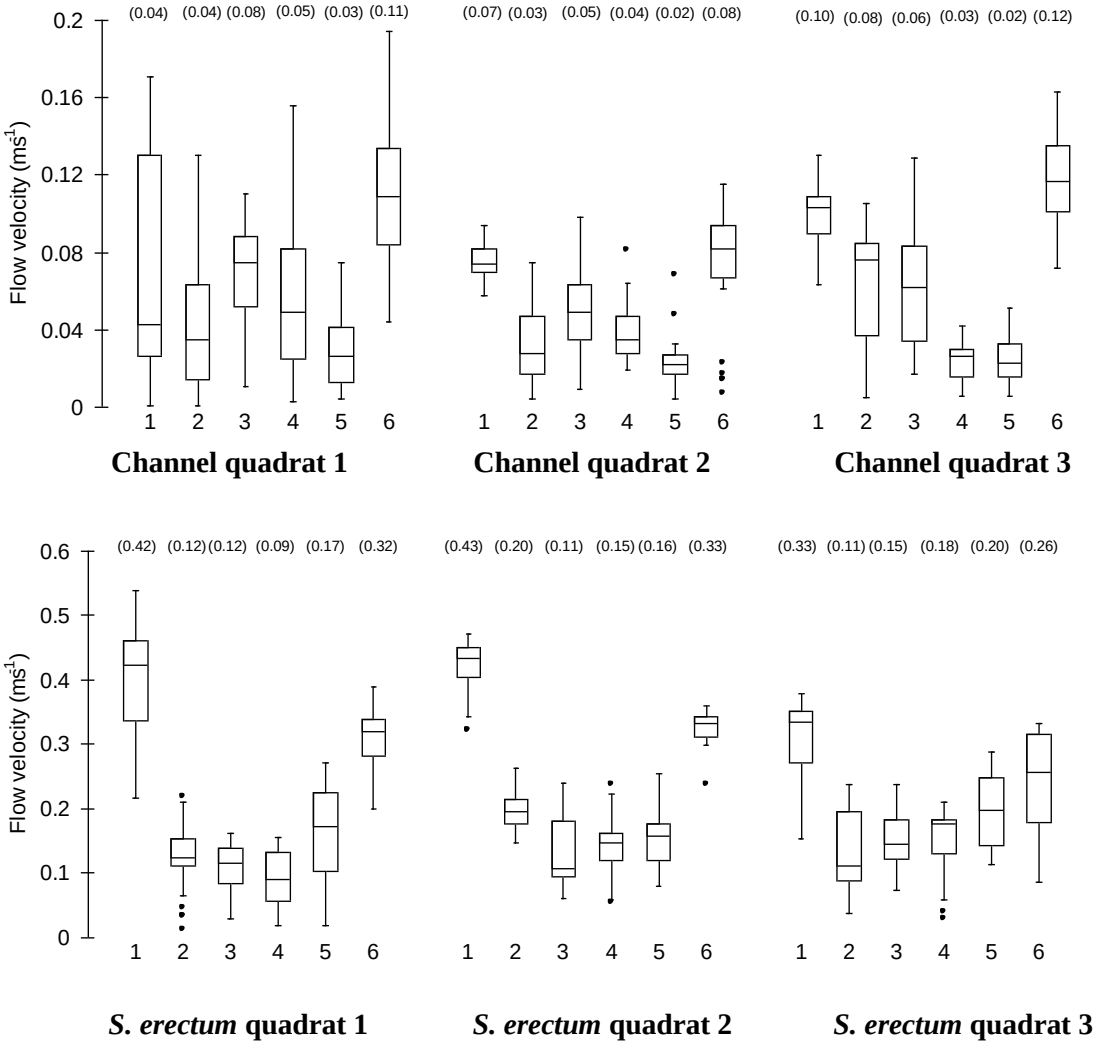


Figure 7.10: Boxplots of flow velocity at each quadrat and over time with median values shown in brackets. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010)).

Table 7.2: Statistically significant differences in flow velocities recorded in the channel in comparison with the *S. erectum* quadrats throughout 2010 identified using Mann-Whitney (M-W) U tests, and in each of the three channel quadrats and three *S. erectum* quadrats during the six measuring periods in 2010 identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010)).

	p value	Significant differences
Flow velocities	M-W $p < 0.0001$	Channel > *S. erectum*
Channel 1 quadrat flow velocities	K-W $p < 0.0001$	1 > 6 > 5 > 3, 4 1 > 6 > 2, 3, 4
Channel 2 quadrat flow velocities	K-W $p < 0.0001$	1 > 6 > 2 > 3, 4, 5
Channel 3 quadrat flow velocities	K-W $p < 0.0001$	1 > 6 > 3, 4 > 2 1 > 5 > 2
***S. erectum* 1 quadrat flow velocities**	K-W $p < 0.0001$	6 > 3 > 2, 5 6 > 1, 4
***S. erectum* 2 quadrat flow velocities**	K-W $p < 0.0001$	1, 6 > 3, 4 > 5 1, 6 > 2
***S. erectum* 3 quadrat flow velocities**	K-W $p < 0.0001$	1, 6 > 2, 3 > 4, 5

Table 7.3: Statistically significant differences in flow velocities recorded in the channel and *S. erectum* quadrat of each quadrat pair on each measuring period identified using Mann-Whitney U tests (M-W).

	M-W p values and significant differences		
Measuring Period	**Channel 1 and *S. erectum* 1 quadrats**	**Channel 2 and *S. erectum* 2 quadrats**	**Channel 3 and *S. erectum* 3 quadrats**
1	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
2	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p = 0.000$ Channel > *S. erectum*
3	$p = 0.001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
4	$p = 0.030$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
5	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
6	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*

Overall, water depths were significantly greater in the channel quadrats (median 47 cm) than the *S. erectum* quadrats (median 33 cm) (M-W, $p < 0.0001$, Table 7.4), with *S. erectum* quadrats recording a greater range of water depths than the channel quadrats (Figure 7.11).

Both the channel and *S. erectum* quadrats showed a similar general pattern of changing water depths through the growth cycle. Water depths were low at the beginning, increased through the growth cycle and then decreased again during plant senescence (Figure 7.12). Channel quadrats 1 and 3, and all *S. erectum* quadrats, showed a slight decrease in median water depths in measuring period 4 (Figure 7.12). All channel quadrats recorded minimum water depths during measuring period 1 (median 33 cm, 33 cm and 23 cm, channel quadrats 1, 2 and 3 respectively, Figure 7.12) and maximum water depths were recorded in measuring period 5 for channel quadrats 2 and 3 and in measuring period 3 for channel quadrat 1 (median 67 cm, 61 cm and 54 cm, channel quadrats 1, 2 and 3 respectively, Figure 7.12). For all channel quadrats, water depths in measuring period 1 were significantly lower than all other measuring periods (K-W, $p < 0.0001$, Table 7.4), and significantly higher in measuring periods 3 and 5 for channel quadrats 1 and 2 respectively (both K-W, $p < 0.0001$, Table 7.4).

All *S. erectum* quadrats recorded minimum water depths during measuring period 1 (median 11 cm, 12 cm and 15 cm *S. erectum* quadrats 1, 2 and 3 respectively, Figure 7.12) and maximum water depths were recorded in measuring period 5 for *S. erectum* quadrats 1 and 2 (median 60 cm and 48 cm respectively) and in measuring period 3 for *S. erectum* quadrat 3 (median 48 cm) (Figure 7.12). For all *S. erectum* quadrats, water depths in measuring period 1 were significantly lower than all other measuring periods (K-W, $p < 0.0001$, Table 7.4), and significantly higher in measuring period 5 for *S. erectum* quadrat 1 and 2 and in measuring period 3 for *S. erectum* quadrat 3 (all K-W, $p < 0.0001$, Table 7.4).

At each measuring period, for each pair of quadrats, the water depth in the channel quadrat was significantly greater than the *S. erectum* quadrat (all M-W, $p < 0.05$, Table 7.5), apart from between channel quadrat 1 and *S. erectum* quadrat 1 in measuring period 5 (M-W, $p = 0.430$, Table 7.5).

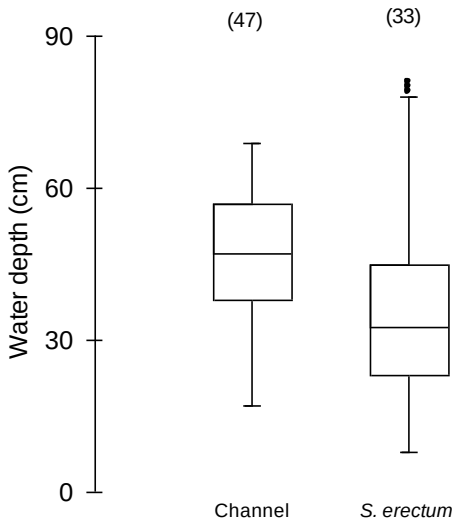


Figure 7.11: Boxplots of water depth measurements in channel and *S. erectum* quadrats with median values shown in brackets.

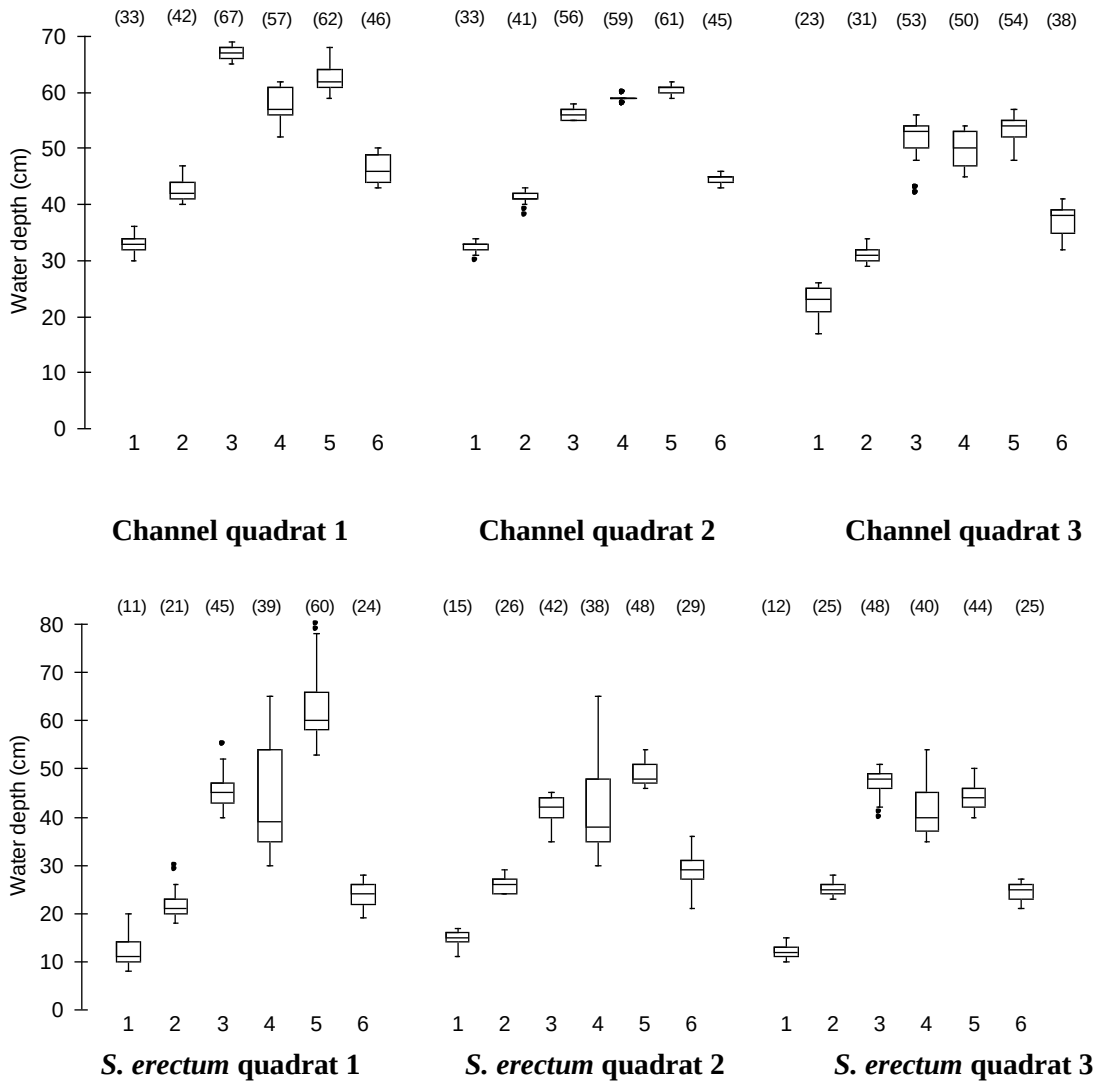


Figure 7.12: Boxplots of water depth measurements at each quadrat and over time with median values shown in brackets. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010)).

Table 7.4: Statistically significant differences in water depths recorded in the channel in comparison with the *S. erectum* quadrats throughout 2010 identified using Mann-Whitney U tests (M-W), and in each of the three channel quadrats and three *S. erectum* quadrats during the six measuring periods in 2010 identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010)).

	p-value	Significant differences
Water depth	M-W $p < 0.0001$	Channel > *S. erectum*
Channel 1 quadrat water depth	K- W $p < 0.0001$	3 > 5 > 4 > 6 > 2 > 1
Channel 2 quadrat water depth	K- W $p < 0.0001$	5 > 4 > 3 > 6 > 4 > 3
Channel 3 quadrat water depth	K- W $p < 0.0001$	5 > 4 > 6 > 2 > 1 3 > 6 > 2 > 1
***S. erectum* 1 quadrat water depth**	K- W $p < 0.0001$	5 > 3, 4 > 2, 6 > 1
***S. erectum* 2 quadrat water depth**	K- W $p < 0.0001$	5 > 3, 4 > 6 > 2 > 1
***S. erectum* 3 quadrat water depth**	K- W $p < 0.0001$	3 > 4, 5 > 2, 6 > 1

Table 7.5: Statistically significant differences in water depths recorded in the channel and *S. erectum* quadrat of each quadrat pair on each measuring period identified using Mann-Whitney U tests (M-W) (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) n.s = not significant).

	M-W p-value and significant differences		
Measuring Period	**Channel 1 and *S. erectum* 1 quadrat**	**Channel 2 and *S. erectum* 2 quadrat**	**Channel 3 and *S. erectum* 3 quadrat**
1	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
2	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
3	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p = 0.000$ Channel > *S. erectum*
4	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
5	$p = 0.430$ n.s.	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*
6	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*	$p < 0.0001$ Channel > *S. erectum*

7.4.4 Variations in fine sediment depths within and between quadrats and over time

Fine sediment depths for each quadrat type and for each measuring period were plotted as boxplots to visualise any differences in these variables between quadrats and over time (Figures 7.13 and 7.14). Mann-Whitney U (M-W) and Kruskal-Wallis tests (K-W) followed by post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests were then employed to identify significant differences in this variable between the quadrats and over time (Tables 7.6 and 7.7).

Overall, fine sediment depths were significantly greater in the *S. erectum* quadrats than the channel quadrats (median 35 cm and 1 cm for *S. erectum* and channel, respectively, Figure 7.13, M-W, $p < 0.0001$, Table 7.6) over the two years of monitoring.

There was no clear temporal pattern in fine sediment depths recorded in the channel quadrats. All quadrats recorded a range of depths at each measuring period and low median values through the two years (median range 0 cm to 8 cm, Figure 7.14). However, due to the

shallowness of the fine sediment there were greater difficulties in measuring them accurately. Channel quadrat 3 generally showed a greater range in sediment depths at each measuring period compared to channel quadrats 1 and 2 (Figure 7.14). In 2010, fine sediment depths in channel quadrat 1 were significantly greater in measuring period 1 than both measuring period 3 and 6 (K-W, $p = 0.006$, Table 7.6). In 2011 fine sediment depths in measuring period 10 were significantly lower than the other measuring periods (K-W, $p < 0.0001$, Table 7.6). For channel quadrat 2, fine sediment depths were significantly greater in measuring period 4 (for 2010) and both measuring periods 8 and 9 (for 2011) than the other measuring periods (both K-W, $p < 0.0001$, Table 7.6). Fine sediment depths in channel 3 quadrat in 2010 in measuring period 1 were significantly greater than the other measuring periods (K-W, $p < 0.0001$, Table 7.6) and in 2011 measuring period 7 was significantly greater than measuring period 10 and both measuring periods 7 and 9 were significantly greater than measuring period 8 (K-W, $p = 0.000$ and $p < 0.0001$ respectively, Table 7.6).

All *S. erectum* quadrats showed a clear temporal pattern in fine sediment depths in both years with greater fine sediment depths at the start of each growth cycle followed by a decrease to minimum depths in measuring periods 4 and 9 for the majority and measuring period 10 for *S. erectum* quadrat 3 in 2011, followed by an increase again (Figure 7.14). In 2010 fine sediment depths were significantly lowest in measuring period 4 for all *S. erectum* quadrats (all K-W, $p < 0.0001$, Table 7.6) and significantly greatest in measuring period 6 for *S. erectum* quadrats 1 and 2 and in measuring periods 1 and 6 for *S. erectum* quadrat 3 (all, K-W, $p < 0.0001$, Table 7.6). In 2011, all *S. erectum* quadrats had significantly greatest fine sediment depths in measuring period 7 (all K-W, $p < 0.0001$, Table 7.6) and significantly lowest depths in measuring periods 8 and 9 for *S. erectum* quadrat 2, measuring period 10 for *S. erectum* quadrat 3 and for *S. erectum* quadrat 1 there was no clear lowest with measuring periods 8, 9 and 11 all showing shallower depths than measuring periods 7 and 10, but measuring period 9 also being significantly lower than measuring period 8 (K-W, $p < 0.0001$, Table 7.6). The fine sediment depth in the *S. erectum* quadrat was significantly greater than the channel quadrat for every quadrat pair at every measuring period (all M-W, $p < 0.0001$, Table 7.7).

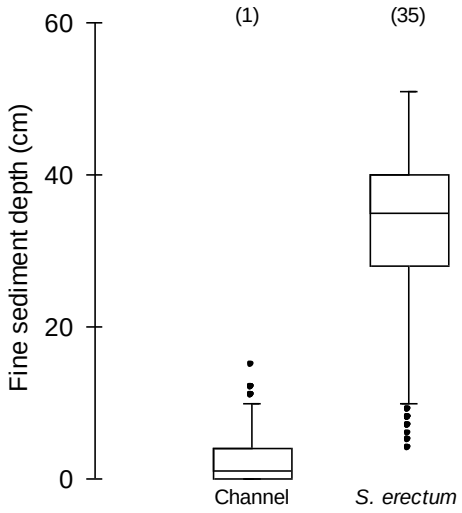


Figure 7.13: Boxplots of fine sediment depth measurements in the channel and *S. erectum* quadrats with median values shown in brackets.

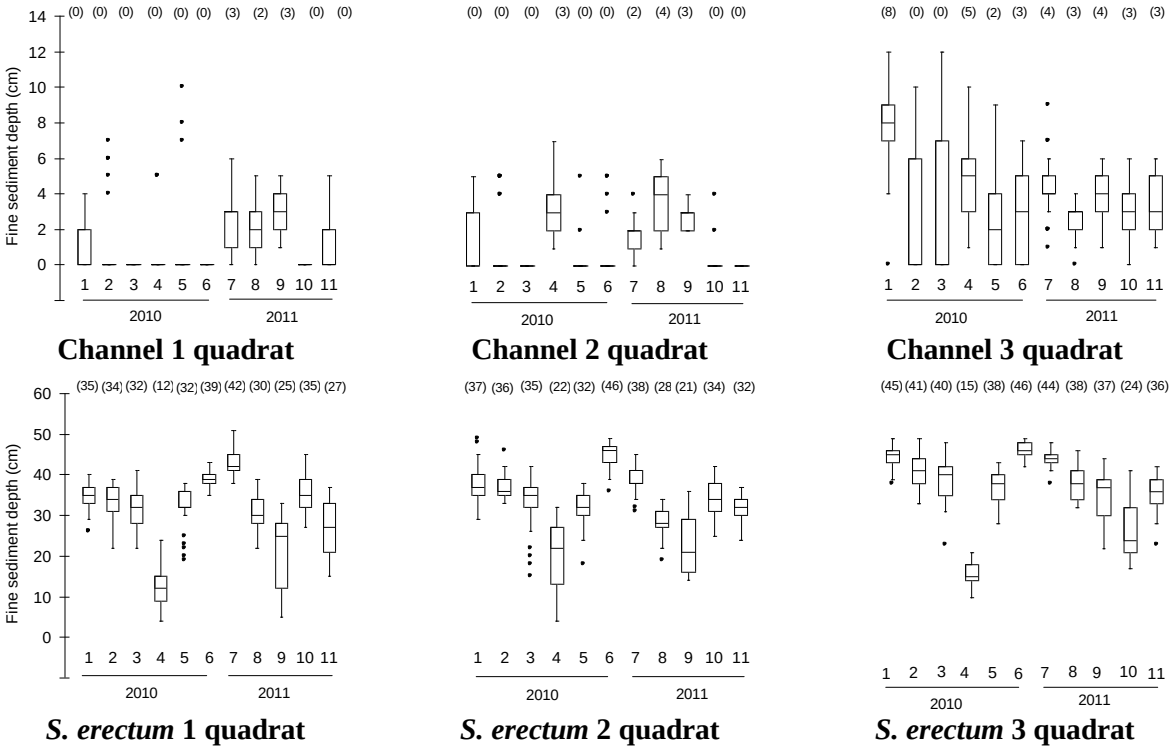


Figure 7.14: Boxplots of fine sediment depth measurements at each quadrat and over time with median values shown in brackets. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

Table 7.6: Statistically significant differences in fine sediment depths recorded in the channel in comparison with the *S. erectum* quadrats throughout 2010 and 2011 identified using Mann-Whitney U tests (M-W), and in each of the three channel quadrats and three *S. erectum* quadrats during the eleven measuring periods identified using Kruskal-Wallis (K-W) and post-hoc Steel-Dwass-Critchlow-Fligner (S-D-C-F) tests. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

	p-value	Significant differences
Fine sediment depth	M-W $p < 0.0001$	*S. erectum* > Channel
Channel 1 quadrat fine sediment depth	2010 K-W $p = 0.006$	2010 1 > 3, 6
	2011 K-W $p < 0.0001$	2011 9 > 11 > 10 7, 8 > 10
Channel 2 quadrat fine sediment depth	2010 K-W $p < 0.0001$	2010 4 > 1, 2, 3, 5, 6
	2011 K-W $p < 0.0001$	2011 8, 9 > 7 > 10, 11
Channel 3 quadrat fine sediment depth	2010 K-W $p < 0.0001$	2010 1 > 2, 3, 4, 5, 6
	2011 $p = 0.000$	2011 7, 9 > 8 7 > 10
***S. erectum* 1 quadrat fine sediment depth**	2010 K-W $p < 0.0001$	2010 6 > 1, 2, 3, 5 > 4
	2011 K-W $p < 0.0001$	2011 7 > 10 > 8 > 9 7 > 10 > 11
***S. erectum* 2 quadrat fine sediment depth**	2010 K-W $p < 0.0001$	2010 6 > 1, 2, 5 > 4 6 > 3 > 4
	2011 K-W $p < 0.0001$	2011 7 > 10, 11 > 8, 9
***S. erectum* 3 quadrat fine sediment depth**	2010 K-W $p < 0.0001$	2010 1, 6 > 2 > 5 > 4 6, 1 > 3 > 4
	2011 K-W $p < 0.0001$	2011 7 > 8, 9, 11 > 10

Table 7.7: Statistically significant differences in fine sediment depths recorded in the channel and *S. erectum* quadrat of each quadrat pair on each measuring period identified using Mann-Whitney U (M-W) tests. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

	M-W p-value and significant differences		
Measuring Period	**Channel 1 and *S. erectum* 1 quadrat**	**Channel 2 and *S. erectum* 2 quadrat**	**Channel 3 and *S. erectum* 3 quadrat**
1	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
2	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
3	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
4	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
5	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
6	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
7	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
8	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
9	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
10	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel
11	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel	$p < 0.0001$ *S. erectum* > Channel

Fine sediment volumes (cm^3m^{-2}) were calculated for each quadrat at each measuring period in order to compare sediment storage beneath the *S. erectum* and channel quadrats, and are displayed in Figure 7.15. The median sediment volume through the two years was 20,800 cm^3 of fine sediment per m^2 of channel for the channel quadrats and 344,000 cm^3 of fine sediment per m^2 of channel for the *S. erectum* quadrats. The difference between the channel and *S. erectum* lines represents the additional volume of fine sediment which is retained by the *S. erectum*. The mean of this through the year is represented by the dashed line, with the mean values for each year shown in the grey box, showing that areas of the river bed under *S. erectum* stands retain an additional ca. 310,000cm^3 of fine sediment per m^2 of channel in comparison with areas that are not supporting *S. erectum*.

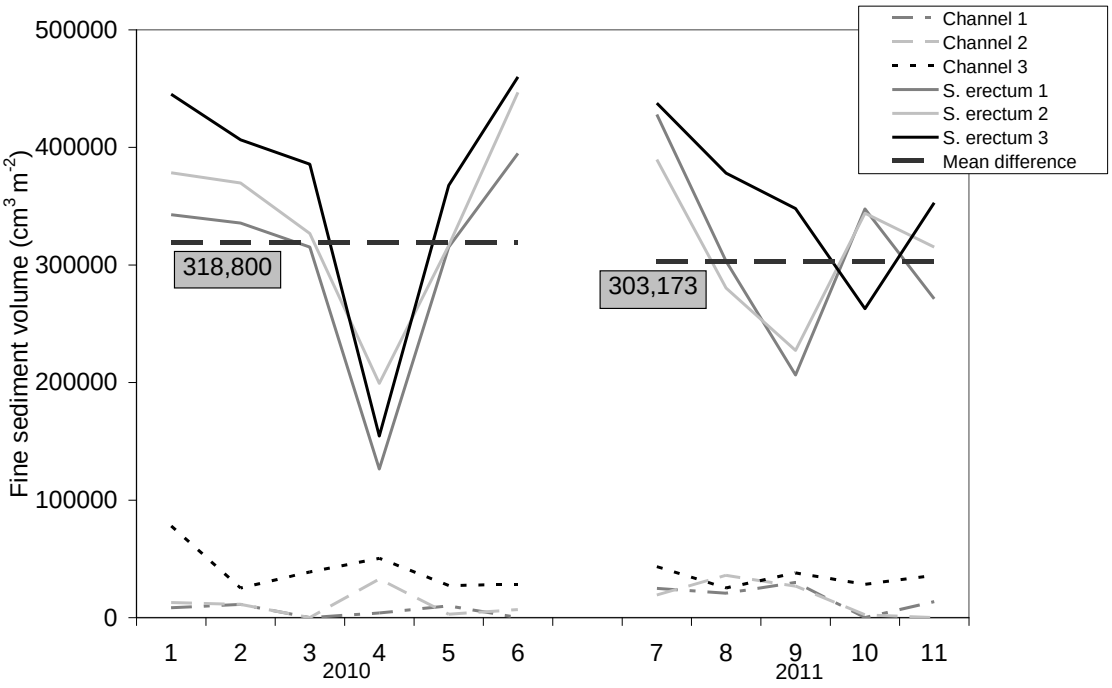


Figure 7.15: Calculated fine sediment volumes in the three channel and three *S. erectum* quadrats on the six measuring periods in 2010 (left) and five measuring periods in 2011 (right) . The mean difference in sediment volumes stored within the two quadrat types in each year is given in the grey boxes. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

7.4.5 Relationships between flow velocity, water depth, fine sediment depth and macrophyte growth

To explore the inter-relationships between flow velocity, water depth, fine sediment depth and macrophyte growth, these variables were plotted variously on scatterplots, bar and line graphs and Spearman's Rank (S-R) correlation coefficients were calculated for each quadrat type (Figures 7.16, 7.17 and 7.18).

Flow velocity and fine sediment depth were significantly positively correlated for the *S. erectum* quadrats, whereas the negative correlation was not significant for the channel quadrats (S-R, r_s = -0.018 (not significant) and r_s = 0.400 ($p < 0.01$) for channel and *S. erectum* quadrats respectively, Figure 7.16). For both channel and *S. erectum* quadrats, flow velocity and water depth were significantly negatively correlated (S-R, r_s = -0.498 and r_s = -0.363, both $p < 0.01$, channel and *S. erectum* quadrats respectively, Figure 7.16). Similarly, fine sediment depth and water depth were significantly negatively correlated for both quadrats (r_s = -0.269 and r_s = -0.468, $p < 0.01$, Figure 7.16).

The inter-relationships between macrophyte cover and flow velocity, water depth and fine sediment depth were explored for each quadrat through visual analysis of bar and line graphs (Figures 7.17 and 7.18).

For the channel and *S. erectum* quadrats, the lowest flow velocities generally coincided with the highest macrophyte covers of the quadrats in measuring periods 3, 4 and 5 (Figure 7.17a). Conversely, the highest water depths coincided with the highest macrophyte covers in measuring periods 3, 4 and 5 (Figure 7.17b).

The inter-relationship between macrophyte cover and fine sediment depth in the channel quadrats was more difficult to interpret, due to the low fine sediment depths recorded (Section 7.4.3), although generally greater fine sediment depths were recorded when greater macrophyte cover was recorded (Figure 7.18). In the *S. erectum* quadrats, generally the lowest fine sediment depths were recorded during the middle of the macrophyte growing season coinciding with near maximum macrophyte cover (measuring periods 4 and 9/10) (Figure 7.18).

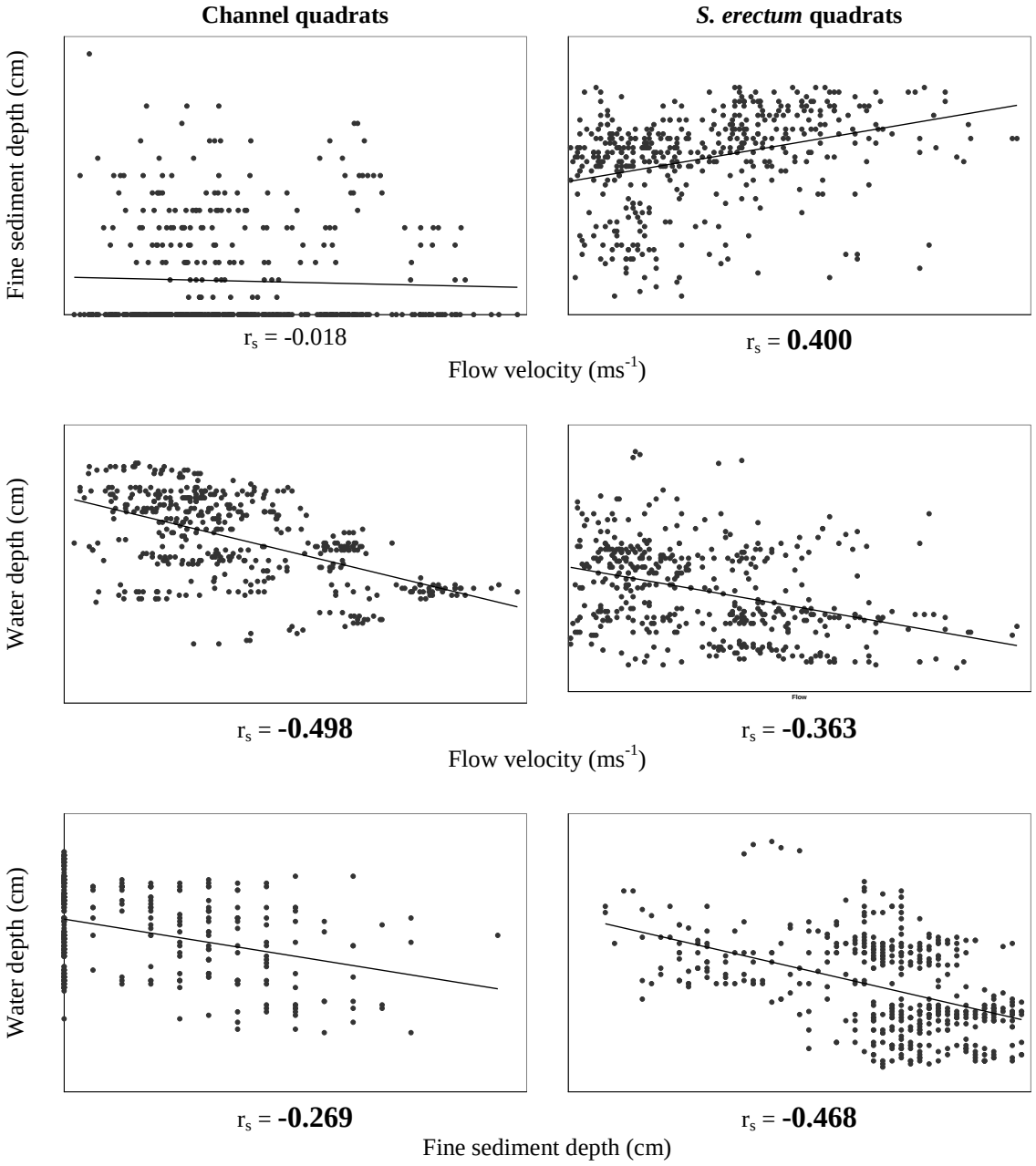
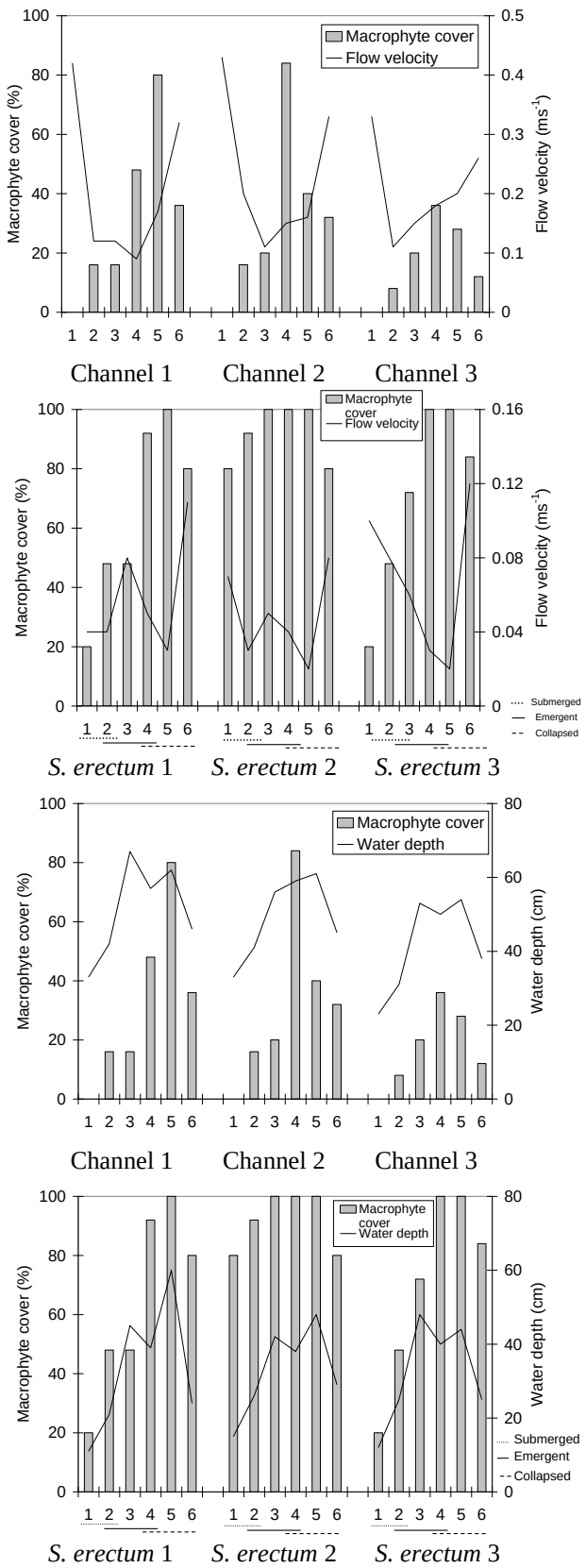


Figure 7.16: Scatterplots between flow velocities, water depth and fine sediment depth with Spearman's Rank correlation coefficients (r_s) beneath, those significant at $p < 0.01$ in bold and large font, those not significant ($p > 0.05$) in small font.

(a)



(b)

Figure 7.17: Relationship between macrophyte cover and (a) flow velocities and (b) water depths during the 2010 measuring periods at each channel and *S. erectum* quadrat. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010)).

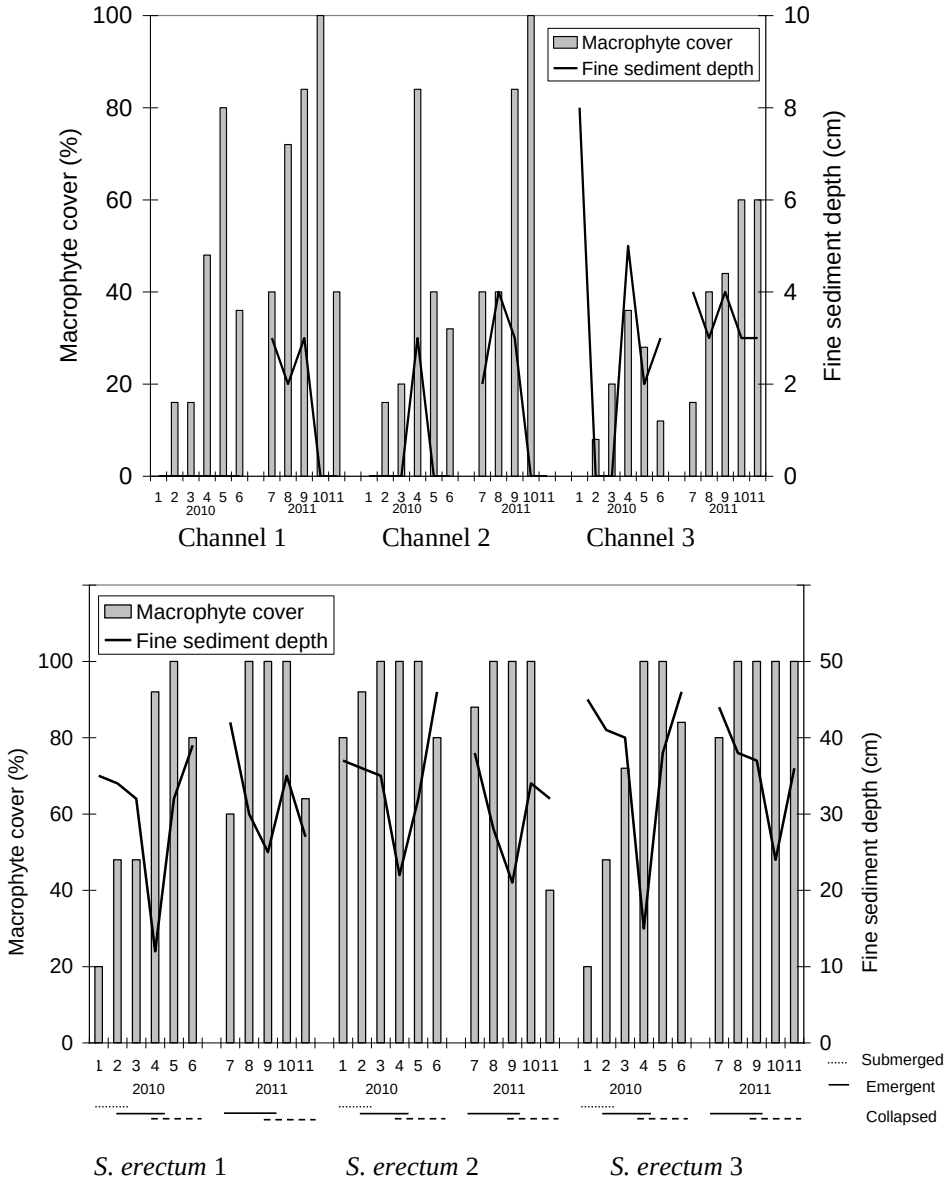


Figure 7.18: Relationship between macrophyte cover and fine sediment depths at each of the 2010 and 2011 measuring periods at each channel and *S. erectum* quadrat. (Measuring period 1 = mid-March, 2 = end-April, 3 = mid-June, 4 = early-August, 5 = mid-September, 6 = end-November (in 2010) 7 = end-May, 8 = mid-July, 9 = end-August, 10 = mid-October, 11 = end-November (in 2011)).

7.5 Discussion

The following section focuses on discussion of the following research questions:

- To what extent does the presence of *S. erectum* affect sedimentation and flow velocities?
- To what extent does sedimentation vary through the annual growth cycle of *S. erectum*?

7.5.1 Effect of *S. erectum* growth upon water depth, flow velocities and sedimentation

Comparison of the presence of macrophyte species growing within the quadrats showed that no *S. erectum* was recorded within the channel quadrats (Figure 7.5c). The macrophytes growing within the channel quadrats were a range of submerged/floating-leaf species, with watercress (*R. nasturtium-aquaticum*, an emergent) being recorded towards the end of 2011. The dominant species within the *S. erectum* quadrats was *S. erectum*, apart from towards the end of 2011 when *R. nasturtium-aquaticum*, *P. natans* and *S. emersum* began to encroach. The *S. erectum* quadrats also showed a very high proportion of macrophyte cover throughout the year in comparison to the channel quadrats (Figure 7.5a and b). These differences mean that indications of the local effect of *S. erectum* growth upon water depths, flow velocities and sedimentation can be gained by comparing the channel quadrats to the *S. erectum* quadrats. However, it is important to note that the presence of significant stands of *S. erectum* within this relatively small channel will have indirect effects on the channel quadrats by affecting flow patterns and associated sediment dynamics at the cross-section and reach scale.

Within the *S. erectum* quadrats (and the channel quadrats) decreasing flow velocities were significantly associated with increasing water depths (Figure 7.16), likely to be caused by the increased macrophyte biomass in the channel at times of low velocities resulting in an increase in water depths across the channel from the constriction of the water (Berger & Wells, 2008).

The *S. erectum* quadrats showed significantly lower flow velocities, lower water depths and greater fine sediment depths than the channel quadrats (Tables 7.2, 7.4 and 7.6). Median flow velocities in the *S. erectum* quadrats were 72% lower, median water depths were 30% lower and median fine sediment depths were 35 times greater than in the channel quadrats. Also *S. erectum* retained ca. 310,000 cm^3m^{-2} channel bed more fine sediment than the channel quadrats (Figure 7.15).

Other researchers have shown similar effects of macrophytes, especially for submerged macrophytes, and in particular *Ranunculus*. Wharton *et al*., (2006) undertook measurements at five sites across two rivers in Dorset and found that flow velocities recorded within vegetated

areas (dominated by the submerged macrophyte *Ranunculus*) were consistently lower than flow velocities recorded within the open channel. Sediment accumulations measured around the *Ranunculus* stands were in the range 0.0075 to 0.088 m^3m^{-2} (Wharton *et al*., 2006). Similar studies on *Ranunculus* have reported decreases of flow velocities within stands of *Ranunculus* of 88% (Cotton *et al*., 2006) and 68% (Trimmer *et al*., 2009) and average sediment accumulation depths in May at two sites of 6 cm and 16 cm (Cotton *et al*., 2006) and sediment accumulation rates of 3.1 kg/m^2/month (Trimmer *et al*., 2009). Schulz *et al.* (2003) investigated three macrophyte species (*Sparganium emersum*, *Potamogeton pectinatus* and *Sagittaria sagittifolia*) and found that flow velocities decreased 10-fold at all depths within the macrophyte stands as opposed to outside them. Mean net sediment accumulation during mid-summer for three macrophyte species (*Callitriche cophocarpa*, *Elodea canadensis* and *Sparganium emersum*) has been recorded as 5.64 cm, 2.42 cm and 0.80 cm depth, respectively (Sand-Jensen, 1998). In the context of emergent macrophytes, *S. erectum* stands have been reported to decrease flow velocities by 75% (Asaeda *et al*., 2010).

In the present study, the *S. erectum* quadrats showed a similar reduction in flow velocities compared to the channel quadrats (with less dense, mainly submerged macrophytes) as in the Asaeda *et al*. (2010) study. The depths and volumes of fine sediment recorded beneath the *S. erectum* in this study were greater than those found in the literature for other species, but within the same range for the channel quadrats.

The ability of a macrophyte to affect flow, and thus accumulate sediment, operates at two differing scales: the stem/leaf scale and the stand scale (Green, 2005b). Differing resistances to flow, and hence the effect upon flow modification and sediment accumulation, are a result of the differing morphologies of macrophytes in terms of branching, thickness and flexibility at the stem/leaf scale, and differing macrophyte density at the stand scale. The broad morphological groupings of macrophytes (emergent, floating-leaf and submerged) can be classified as showing a decreasing gradient in flow resistance and hence associated decrease in sediment accumulation (Jones *et al*., 2011). Similarly, at the stand scale, a greater density of macrophytes within the stand results in greater flow resistance and associated sediment accumulation (Jones *et al*., 2011 and Clarke, 2002).

The great ability for *S. erectum* to reduce flows and accumulate large quantities of fine sediment can be explained by its morphological characteristics. Being a rigid-emergent macrophyte which grows in dense stands it can significantly resist flows hence reducing flow velocities and allowing the settling and accumulation of fine sediments. The differences in flow velocities and sediment accumulation between submerged and emergent species has been shown in research

undertaken by Liffen (2011) focussing on *S. erectum* growth in the River Blackwater. Areas of the river with consistently low flow velocities were associated with *S. erectum* growth and fine sediment accumulation, whereas areas of the river with higher flow velocities were associated with coarser sediments, low *S. erectum* growth and greater submerged macrophyte growth. Similarly, Gurnell *et al*. (2006), in research on the River Frome, Dorset, found that greater fine sediment deposition and lower flow velocities occurred around emergent macrophytes (mainly *S. erectum*) rather than around submerged macrophytes (mainly *R. penicillatus*). Baattrup-Pedersen & Riis (1999), looking at the associations between macrophyte species and sediment calibre in 14 streams in Denmark, found that submerged species were associated with coarser sediments and other species (which grew in both submerged and emergent forms) were associated with finer sediments. Although flow velocity measurements were not undertaken the differences in sediment calibre were explained in relation to the different effects of the macrophytes upon flow velocities and sedimentation.

This study shows that growth of the emergent macrophyte *S. erectum* decreases water depth and flow velocities. *S. erectum* also has a greater ability to accumulate fine sediments compared to many submerged species, which is related to its rigid, emergent structure and its growth in high density significantly reducing flow velocities.

7.5.2 Associations between growth cycle of *S. erectum* and sedimentation

The seasonal pattern of the growth and senescence of *S. erectum* is reflected in the measures of cover, biomass, shoot density and leaf length which showed the highest values during the summer months, when plant development was at a maximum and before the plants started to senesce (Figures 7.5 and 7.8).

Flow velocities and water depths in the *S. erectum* quadrats generally reflected the seasonal growth and senescence cycle of *S. erectum* with lower flow velocities and greater water depths during mid- to late-summer when the *S. erectum* plants were at their maximum growth and were causing the greatest restriction to flow (Figure 7.17). This seasonal pattern was also shown in the channel quadrats, and has been identified in relation to macrophyte growth by other researchers. Champion & Tanner (2000) found an increase in the area of low flow velocities in the channel and increased water depths in the summer in New Zealand streams, which corresponded with an increase in the submerged macrophyte channel coverage. Naden *et al*., (2006) found an increase in macrophyte cover in the river channel from 18% to 27% between May and September in another section of the River Blackwater caused an increase in water depth of 20 cm for the same discharge. Additionally, the vertical depth flow velocity profiles in

September were significantly affected by the growth of submerged macrophytes compared to the profiles in May.

As the processes of deposition and accumulation of fine sediment within *S. erectum* stands are inter-related to the processes of macrophyte growth and flow velocities, it would be expected that the pattern of fine sediment depths would also reflect the annual growth cycle and related flow velocities, with greatest fine sediment depths at times of the greatest macrophyte development and lowest flow velocities (Jones, 2011 and Clarke, 2002). Research undertaken by Heppell *et al*., (2009) at a site on the River Frome and a site on the River Piddle, Dorset did find this correspondence between the seasonal pattern of sediment storage and macrophyte cover. Maximum sediment storage at the River Frome site coincided with maximum channel macrophyte cover (from *Ranunculus*) in May/June/July and at the River Piddle site maximum sediment storage coincided with maximum channel macrophyte cover (from *Ranunculus* and *Rorripa*) from August to October. Similarly, Kleeberg *et al*., (2010) found greater sediment accumulation within stands of *S. sagittifolia* on the River Spree, Germany, during peak biomass and entrainment of this sediment in autumn months at the time of the senescence of *S. sagittifolia*. In this study however, the *S. erectum* quadrats showed increasing fine sediment depths with increasing flow velocities and although the channel quadrats showed increasing fine sediment depths with decreasing flow velocities, this was not significant (Figure 7.16). In terms of macrophyte coverage and seasonality, the channel quadrats did show this seasonal pattern to some extent, but the *S. erectum* quadrats did not show a correspondence between maximum macrophyte growth and maximum fine sediment depths, instead showing an inverse pattern (Figure 7.18). Fine sediment depths decreased from mid-June to early-August 2010 and from late-May to late-August/early-October 2011 coinciding with the *S. erectum* plants being emergent and achieving peak biomass (Figure 7.18). An increase in fine sediment depths was then recorded through the rest of the measuring periods coinciding with the senescence and collapse of *S. erectum* (Figure 7.18). A similar pattern was seen by Asaeda *et al.*, (2010), who concluded that the different forms that *S. erectum* takes during its growth cycle (submerged, emergent and collapsed) has differing effects upon flow velocities, water depths and sediment accumulation, and so does not produce a clear seasonal pattern.

The decrease in fine sediment depths recorded during the middle of the growth cycle could be due to three main processes: (i) bioturbation and remobilisation of the upper layers of the retained sediment as a result of the sudden extensive growth of rhizomes and development of secondary plants at this point in the growth cycle (Liffen *et al*., 2011); (ii) the compaction of the loose organic-rich sediments retained by the developing *S. erectum* stand earlier in the growth cycle; and, (iii) the high density and large diameter of *S. erectum* shoots at this time (Liffen,

2011), which result in very low flow velocities within the centre of the *S. erectum* stands and thus a negligible supply of sediment into the stands for deposition.

Liffen (2011) studied changes in below-ground biomass (roots and rhizomes) of *S. erectum* through the growth season and found very clear differences in the seasonal growth traits of the roots and the rhizomes. Roots grew very vigorously at the start of the growth season, and then died back suddenly between August and September. Rhizomes however, although being constantly present in the top five cm of fine sediment throughout the year, showed notably vigorous growth between June and November, penetrating to 10 cm and even 15 cm depth. This vigorous rhizome growth is due to the vegetative reproduction of *S. erectum* which has been shown to produce two and sometimes three cohorts of plants within a single growth season, in the form of daughter plants from the below-ground rhizomes (Liffen, 2011 and Asaeda *et al*., 2010). *S. erectum* rhizomes are of a significant diameter (median 4 mm diameter Chapter 5) thus their growth in the top layers of the retained fine, organic rich sediment is likely to significantly disturb it through bioturbation causing its resuspension and the lowering of the surface of the retained fine sediment below. Fine sediment resuspension was observed during this research during mid growth cycle measurements (August measurements). Compaction of the fine sediment, whether or not in combination with resuspension, would also lower the surface of the accumulated fine sediment. Although no direct measurements were made of this process, the retained fine sediment was noted during fieldwork to become firmer as the growing season progressed. There is also the possibility that the resuspension of fine sediment caused some degree of error in measurements of fine sediment depths due to the difficulties in establishing the exact surface of the fine sediment during mid growth cycle measurements.

During the middle of the growth cycle the flow velocities within the *S. erectum* quadrats were extremely low (Figure 7.10), indicating the strong flow blockage effect of the *S. erectum* stand. These very low flow velocities indicate that *S. erectum* stands are effectively a dead flow zone at this growth stage, with no sediment transport into the stand. Additionally, the bioturbed fine sediments are likely to remain in suspension within the stand, rather than being transported away.

Once the *S. erectum* plants senesce and begin to collapse (from August onwards) flow velocities begin to increase slightly, increasing the potential for delivery of fine sediment in to the *S. erectum* stands but with the collapsed shoots providing protection for the accumulated fine sediments and an effective trap for newly delivered sediments (Figure 7.17).

Measurements from the *S. erectum* quadrats also indicate that accumulated fine sediments are retained from year to year with minimal loss over the winter (Figure 7.18). This occurs despite the complete loss of above ground biomass during the winter and can be attributed to the stabilisation effects of the substantial below-ground network of rhizomes which persist over winter and protect the fine sediment surface from erosion (Jones *et al*., 2011 and Liffen, 2011).

This study has shown that there is not a clear pattern between the growth cycle of *S. erectum* and the accumulation of fine sediments, with a decrease in fine sediment depths at time of maximum biomass. However, fine sediment depths increase again once *S. erectum* collapses and begins to senesce, and fine sediments were retained over the winter.

7.6 Conclusions

Although previous research has considered the effect of submerged macrophytes upon flow velocities and sediment accumulation, little research has previously been directed at emergent species. This study has shown that the morphology and growth traits of the emergent *S. erectum,* in terms of its rigid stem and its high stand density, enable it to significantly lower flow velocities during its growth season. This enables it to trap and accumulate large quantities of fine sediment which persist from year to year, probably due to the overwintering of its substantial below-ground root and rhizome network. Compared to some submerged species, the pattern of fine sediment accumulation does not show a simple seasonal positive correlation with plant growth. It appears that the association between the plants annual growth and senescence cycle and sediment retention is complex. Although there are no direct measurements to explain this, there are a number of mechanisms which may contribute to understanding this complexity. These mechanisms include: (i) very effective sediment trapping during the spring and early summer during the submerged and emergent growth phases of the plant; (ii) vigorous rhizome and secondary shoot growth disturbing the accumulated fine sediments and causing bioturbation and sediment resuspension in mid-summer; (iii) compaction of sediments retained from earlier in the growth cycle; (iv) the high density and large diameter of shoots in mid to late summer severely lowering flow velocity within the stands and restricting sediment supply into the stands; (v) the senescence and collapse of the plants in early autumn so that the thick layer of open decaying foliage protects and traps sediment; and, (vi) the rhizome network develops strongly from mid-summer and persists so protecting sediment from erosion during winter when there is no above ground biomass.

The interactions between sediments and macrophytes in urban river systems in terms of sediment trapping, stabilisation and metal uptake has been discussed in the preceding Chapters

(Chapters 4 to 7). Chapter 8 summarises the key research findings and discusses the implications of the research to the restoration and management of urban rivers.

Chapter 8

Summary, Implications, Future Research and Conclusions

8.1 Introduction

This Chapter summarises the results of the research reported in Chapters 4 to 7, discusses the implications of the research for urban river restoration and the Water Framework Directive, highlights some areas for future research and provides the overall conclusions of the research. The first section (Section 8.2) summarises each of the four studies undertaken in this thesis in terms of sites and methodologies and provides the key research findings as answers to the eleven initial research questions that were set out in Section 2.8, Chapter 2. Sections 8.3 and 8.4 then discusses the wider implications of the research findings in terms of the restoration and management of urban rivers and the Water Framework Directive. Section 8.5 outlines future research opportunities which have been revealed by the research and finally Section 8.6 details the overall conclusions of the research.

8.2 Summary of Research Findings

8.2.1 Sediment characteristics and metal concentrations of bed sediments in contrasting restored and unrestored London urban rivers (Chapter 4)

Four research sites with adjacent restored and unrestored stretches on three rivers within the Thames catchment in Greater London were chosen for the study of sedimentation patterns and sediment characteristics and metal concentrations. The Thames catchment was chosen for the study due to the historical management of rivers from urban development and the current drive for river restoration. The research sites were chosen based on: proximity of restored and unrestored stretches; contrasts in morphology between the stretches; and, safe access to the rivers.

Detailed bed sediment mapping was undertaken in July 2010 to map the presence and extent of four different bed sediment types: unvegetated gravel, sand and finer sediment and sediment accumulated around in-channel vegetation. The four bed sediment types were sampled in the restored and unrestored stretches at the four study sites in May, August and November 2010. The sediment samples were analysed for a range of characteristics (organic matter content and particle size) and pseudo-total metal concentrations (aqua regia extraction). Additionally at

Sutcliffe Park in August 2010 sediment pH and redox conditions and a more bioavailable form of metal concentrations (acetic acid extractable) were investigated.

1. Are there differences in the pattern and extent of sedimentation and in-channel vegetation growth between restored and unrestored stretches of urban rivers in London?

Analysis of the mapping of bed sediment types indicated that at all sites the presence and extent of finer sediment and that accumulated around in-channel vegetation was a reflection of both the availability of sediment (determined by the degree of bed and bank engineering and connection to the floodplain) and the hydraulic conditions prevalent within the channel (determined by the channel planform and cross-profile). At two sites, Chinbrook Meadows and Sutcliffe Park, there were very clear differences in the patterns and extents of the different bed sediment types between the restored and unrestored stretches. Greater sediment availability (from a lack of bed and bank protection and connection to the floodplain) and lower channel slopes (from greater channel sinuosity) in the restored stretches at both sites in comparison with the unrestored stretches resulted in greater deposition of finer sediment and accumulation of sediments around in-channel vegetation.

2. What are the characteristics of sediment (metal concentrations, grain size etc.) retained within restored and unrestored stretches of urban rivers in London and to what extent do these characteristics vary in space and time?

The results of the analysis of sediments sampled from different bed sediment types, in restored and unrestored stretches at four study sites at three sampling times, clearly showed that the greatest differences in sediment characteristics and metal concentrations were between different bed sediment types and study sites rather than between restored and unrestored stretches and sampling times. Three bed sediment types were important for high metal concentrations: finer sediment and that accumulated around in-channel vegetation due to their high organic matter content and high proportion of fine sediment (<63 μm), which are important ligands for metal binding in sediment; and, gravel sediment thought to be due to the precipitation of Fe and Mn (hydr)oxides and the presence of discrete anthropogenic particles. Finer sediment and that accumulated around in-channel vegetation were found to be more anoxic and have a lower pH, with metals also found to generally be more bioavailable in these sediments. Although the gravel sediments were important for high metal concentrations, when metal storage on a per m^2 of river channel was considered the gravel sediments proved less significant due to the high proportion of sediment >2 mm within this bed sediment type, hence reinforcing the importance of finer sediment and that accumulating around in-channel vegetation for both metal concentrations, metal storage and bioavailabilities of metals.

Sutcliffe Park was found to have the highest sediment metal concentrations, due to the high organic matter content and proportion of fine sediments (<63 μm) within the bed sediments at this site, which are important ligands for metal binding in sediments. After granulometric correction of metal concentrations, Beddington Park and Bell Green had the greatest normalised metal ratios indicating at these two sites factors other than grain size were important for metal concentrations, thought to be discrete anthropogenic particles from surface water discharges at Beddington Park and runoff from the adjacent railway and roads at Bell Green.

3. What factors explain the observed variations in metal concentrations and sediment characteristics in restored and unrestored urban rivers in London?

As discussed above, the main factor influencing the variations in metal concentrations and sediment characteristics was grain size. Finer sediments and those accumulating around in-channel vegetation had similarly high proportions of <63 μm and organic matter content, which resulted in high metal concentrations. Coarser, gravel sediments also had high metal concentrations thought to be from the precipitation of Fe and Mn (hydr)oxides and the presence of discrete anthropogenic particles. The strong influence of these two fractions of grain size throughout the data set was also shown in the results of the PCA. In the whole data set, 44% and 34% of the variance was explained by the finer and coarser sediment respectively, and in the Sutcliffe Park August data set 42% and 22% of the variance was explained by the organic rich and fine sediment respectively.

The Sutcliffe Park site provided a clear example of the connection between sedimentation patterns and metal storage. Restoration practices have resulted in a large increase in finer sediment deposition in the restored site, particularly accumulating around in-channel vegetation, which has resulted in greater metal storage and potentially high metal bioavailabilities at the restored site. Similarly at Chinbrook Meadows, restoration practices have resulted in a significant overall increase in sedimentation within the river channel and thus increased metal storage.

4. To what extent are the sediments in London urban rivers potentially harmful to humans and ecosystems?

Comparison of the sediment metal concentrations to sediment quality guidelines for both ecosystems and human health indicated that in the surveyed urban rivers in London the sediment metal concentrations were of a greater risk to ecosystems than to human health. This indicates that use of the rivers by humans for recreation was of low risk, at least in relation to metal contamination. However, there was no clear visual evidence of detrimental impacts upon

the ecosystems, with macrophyte growth appearing healthy, particularly at Sutcliffe Park which had abundant macrophyte growth.

8.2.2 Biomechanical properties of three common emergent macrophyte species: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea* (Chapter 5)

Three emergent macrophytes, *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea*, were chosen for the study of biomechanical properties. These three macrophyte species were chosen due to them being three of the most common linear emergent macrophytes in Great Britain and also displaying differences in physical characteristics, which suggested that their biomechanical properties may be different.

Hawley Meadows, a site on the River Blackwater, Surrey, was chosen for the study of the biomechanical properties of *S. erectum*, *T. latifolia* and *P. arundinacea*. Abundant growth of all three macrophyte species occurs at the site, so destructive research could be supported and the site was easily accessible to carry heavy equipment across a short distance.

Biomechanical measurements in terms of uprooting resistance and stem strength and above-ground and below-ground measures of plant size/biomass were undertaken on five occasions during the macrophyte growth season (April to October) in 2011 to capture the full extent of the growing period of the macrophytes. Biomechanical measurements were then interpreted to infer the ability of the macrophytes to reinforce and reduce erosion and resuspension of metal contaminated sediments, with consideration of differences both between the species and through the growth cycle.

5. How does the ability of three commonly occurring emergent macrophyte species (Sparganium erectum, Typha latifolia and Phalaris arundinacea) to retain and reinforce fine sediment and thus reduce sediment erosion and resuspension, vary between species and through their annual growth cycles?

Interpretation of the biomechanical measurements indicated that *T. latifolia* was the species most able to reinforce and protect underlying sediment due to its morphological characteristics of high stem cross-section and large roots and rhizomes. Conversely, the biomechanical measurements of *P. arundinacea* indicated that it was the species least able to reinforce and protect underlying sediment. The location of *P. arundinacea* however higher up the river bank suggests the macrophyte is likely to be subjected to lower flow stresses than the other two species.

Differences in biomechanical measurements through the growth cycle suggest that sediments underlying *S. erectum* and *T. latifolia* would be most at risk of releasing metals in the middle of the growth season (mid-July), whereas sediments underlying *P. arundinacea* would be most at risk of releasing metals at the beginning of the growth season (mid-April) and also during the winter when no above-ground biomass is present.

Comparison of published biomechanical measurements in the literature suggested that the studied emergent macrophytes had a greater ability to reinforce and protect underlying sediments than submerged macrophytes. Additionally, the well-developed below-ground biomass of all three species during winter (although achieved by different root and rhizome development) provides an ability to retain sediments when the above-ground biomass is negligible.

8.2.3 The uptake and translocation of metals by three common emergent macrophytes: *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea* (Chapter 6)

The three emergent macrophytes, *Sparganium erectum*, *Typha latifolia* and *Phalaris arundinacea* used in the biomechanical properties study (Chapter 5) were also investigated in the uptake and translocation of metals study to allow continuity between the studies. Additionally, the Hawley Meadows site on the River Blackwater, Surrey, which was used in the biomechanical properties study (Chapter 5) was used in this study, again due to the abundant growth of the three macrophytes which would support destructive research and the accessibility of the site for carrying equipment and samples.

Macrophyte and associated overlying water and underlying sediment samples were collected in November 2011 as an exploratory study, and then again in June 2012. The overlying water samples were analysed for dissolved metals, pH and dissolved oxygen. The underlying sediment samples were analysed for pH, organic matter content, particle size and metal concentrations (both pseudo-total through an aqua regia extraction and a more bioavailable form through an acetic acid extraction). Additionally in June 2012 sediment redox conditions were analysed. The macrophytes were separated into above-ground (leaf/stem) and below-ground tissues (roots and rhizomes) and analysed for metal concentrations. The results were interpreted in terms of the potential use of the three macrophyte species for phytoremediation.

6. What is the distribution of metals between three commonly occurring emergent macrophytes (Sparganium erectum, Typha latifolia and Phalaris arundinacea) and associated overlying water and sediments?

The underlying sediments had the highest metal concentrations compared to the overlying water and macrophytes. Calculations for *S. erectum* indicated the underlying sediments, as opposed to the *S. erectum* plants, had the greatest storage of metal per m^2 of river channel with *S. erectum* growth, thus indicating that although macrophytes may be used for phytoremediation, the sediment is likely to still be the greatest store of metals. There were no significant differences in metal concentrations between the three macrophyte species.

7. To what extent do the characteristics and metal concentrations of overlying water and sediment associated with these three commonly occurring emergent macrophytes vary between the species?

There were some differences in the characteristics of overlying water and underlying sediment in terms of pH and redox between the macrophyte species, with overlying water pH and sediment redox and pH being lower around *S. erectum*. The lower redox and pH in the sediments surrounding *S. erectum* were thought to be due to the position of the species in the low flow channel, lower rates of radial oxygen loss and greater exudation of acids from the roots. However, there was little evidence of these differences in redox and pH conditions altering metal concentrations and mobilities, with no differences in sediment pseudo-total and acetic acid extractable metal concentrations between the macrophyte species and only dissolved Fe concentrations in overlying water being significantly lower around *T. latifolia* than the other two macrophyte species. This lack of differences in metal concentrations is thought to be due to the redox and pH differences not being large enough to alter the fundamental environmental conditions, resulting in the overlying waters all being oxic and near-neutral and the underlying sediments being anoxic and near-neutral.

8. How does the uptake and storage of metals in three commonly occurring emergent macrophyte species vary?

Generally, the greatest uptake of metals was in to the root tissues of the macrophytes, with greater uptake of metals that were more bioavailable (acetic-acid extractable) in the sediment. Overall, *S. erectum* and *T. latifolia* stored the greatest metal mass per plant and per m^2 of river channel with macrophyte growth, indicating that these two species show the greatest promise of the three macrophytes in this study for phytoremediation. This was due to the high dry biomasses and plant density of these two species compared to *P. arundinacea*. The distribution of metal storage between above-ground and below-ground tissues indicated that if these two macrophyte species were to be used for phytoremediation then their above-ground tissues

should be collected at the end of the growing season to prevent the release of metals, particularly Cr, Cu, Mn and Zn, back in to the river system during senescence.

9. To what extent do three commonly occurring emergent macrophyte species bioconcentrate and translocate metals?

Generally there was no net bioconcentration of metals from the sediment or translocation of metals from below-ground to above-ground tissues for all of the three macrophyte species. There were also no clear differences between the macrophyte species in their ability to bioconcentrate or translocate metals. Greater differences were seen between the metals, with greater bioconcentration of essential metals (Fe, Mn, Ni and Zn) compared to non-essential metals (Cr) and those which become toxic at high concentrations (Cu). The general lack of metal translocation to above-ground tissues is thought to be due to lower respiration rates from monocots (which these three macrophyte species are) and classifies the three macrophyte species as metal excluders.

8.2.4 The effect of *Sparganium erectum* growth upon flow and sedimentation (Chapter 7)

Of the three emergent macrophytes used in the previous studies (Chapters 5 and 6) *Sparganium erectum* was chosen to be investigated in the study of the effect of macrophyte growth upon flow and sedimentation due to it being the most common linear emergent macrophyte in the UK.

A second site, Mytchett, on the River Blackwater, Surrey, was chosen for the study of the effect of *S. erectum* growth upon flow and sedimentation due to it having abundant *S. erectum* growth and being located on private land with no public access or grazing cattle, meaning there was a low chance of the river bed being disturbed by humans or cattle.

Measurements were taken in paired quadrats, located in the centre of *S. erectum* stands and in the adjacent open channel, on 11 occasions during the macrophyte growth season over two years (2010 and 2011) in order to capture the full extent of the macrophyte growing period. Two years of fine sediment depth, macrophyte coverage and maximum leaf length measurements were taken. Additional data in 2010 on flow velocity, water depth and macrophyte biomass was collected. The data was analysed to assess differences between the *S. erectum* and channel quadrats over time through the growth season and the relationships between flow, water depth, fine sediment depth and macrophyte growth.

10. To what extent does the presence of S. erectum affect sedimentation and flow velocities?
S. erectum quadrats showed significantly lower flow velocities (72% lower), water depths (30% lower) and greater fine sediment accumulation (35 times higher) compared to the channel quadrats. Compared to published literature on fine sediment accumulation around submerged macrophyte species, *S. erectum* appeared to accumulate greater depths attributed to its morphology and growth traits in terms of rigid stem and high stem density. The large quantities of fine sediment accumulated beneath *S. erectum* were also found to persist from year to year, probably due to the overwintering of its substantial below-ground root and rhizome network.

11. To what extent does sedimentation vary through the annual growth cycle of S. erectum?
Although flow velocities and water depths generally reflected the seasonal growth and senescence of *S. erectum*, with lower flow velocities and greater water depths at baseflow during periods of maximum macrophyte growth in summer, compared to some submerged species, the pattern of fine sediment accumulation was not simply correlated to macrophyte growth, with a more complex association between the macrophyte growth and senescence cycle and sediment retention. A number of mechanisms were proposed to contribute to understanding this complexity: (i) very effective sediment trapping during the spring and early summer during the submerged and emergent growth phases of the plant; (ii) vigorous rhizome and secondary shoot growth disturbing the accumulated fine sediments and causing bioturbation and sediment resuspension in mid-summer; (iii) compaction of sediments retained from earlier in the growth cycle; (iv) the high density and large diameter of shoots in mid to late summer severely lowering flow velocity within the stands and restricting sediment supply into the stands; (v) the senescence and collapse of the plants in early autumn so that the thick layer of open decaying foliage protects and traps sediment; and, (vi) the rhizome network develops strongly from mid-summer and persists to protecting sediment from erosion during winter when there is no above ground biomass.

8.3 Implications for Urban River Restoration

As has been discussed in this thesis, the restoration of urban rivers, many of which are polluted by metal contaminated sediments, is currently being driven by numerous environmental, legislative and social drivers. The results from the research undertaken in this thesis into the interactions between macrophytes and sediments in urban river systems have important implications for the restoration, and management, of these urban river systems, and are discussed below.

Within an urban river channel, finer sediment and that which accumulates around in-channel vegetation are of importance in terms of metal storage and increased metal bioavailability. The

presence and extent of these two bed sediment types are driven by the availability of sediment and the hydraulic conditions within the river channel, which can be altered during urban river restoration to the extent that greater finer sediment deposition and in-channel vegetation colonisation occurs, resulting in greater metal storage and metal bioavailability. Accumulations of metal contaminated sediments in rivers have frequently been managed through dredging, which is expensive and would cause damage in a newly restored river channel. This research has however shown the possibilities of using common emergent macrophytes in the management of metal contaminated sediments in restored urban rivers, through their ability to accumulate, retain and stabilise significant quantities of fine sediment. Macrophytes are commonly planted, or seeded, in restoration schemes and thus their implementation and use could be modified to help in the management of metal contaminated sediments. Although the emergent macrophytes did not significantly bioconcentrate metals from the sediment, other phytoremediation processes that are induced by macrophytes are of importance in terms of the management of metal contaminated sediments. These include: the accumulation, stabilisation and protection of sediments by both above-ground and below-ground tissues which reduce the erosion and resuspension of sediments and hence reduce the risk of metal remobilisation; the creation of predominantly anoxic sediment conditions which cause metals to be bound strongly to the sediments and therefore reduces the risk of metal remobilisation; and, the more localised oxidation of sediments in the rhizosphere around the roots and rhizomes which can increase metal availability to the macrophytes and hence increase macrophyte metal uptake. Additionally, over time macrophyte-associated pioneer landform development (as in Gurnell *et al*., 2012) will extend the river banks into the channel and bring the metal contaminated sediments into storage within the river bank. The removal of metal contaminated sediments from the active river channel and the potentially erosive forces of river flows will decrease the risk of remobilisation of metals from the sediments in the river channel. The storage of metals in the above-ground emergent macrophyte tissues suggests that the collection of macrophyte leaves and stems once collapsed would also help to reduce the cycling of metals back into the river during senescence.

A very useful framework for minimising the risk to human health from contaminated sediments in the restoration of urban rivers was presented by Scholes *et al*., (2008). However, there is no consideration within the framework for the use of emergent macrophytes to help minimise the risks from contaminated sediments. A summarised and updated version of this framework (with updates highlighted in grey), which incorporates the use of emergent macrophytes and focuses specifically upon metal contaminated sediments and considers best practice for minimising issues of sedimentation and sediment quality and associated ecological and human health issues, is shown in Figure 8.1 and discussed below.

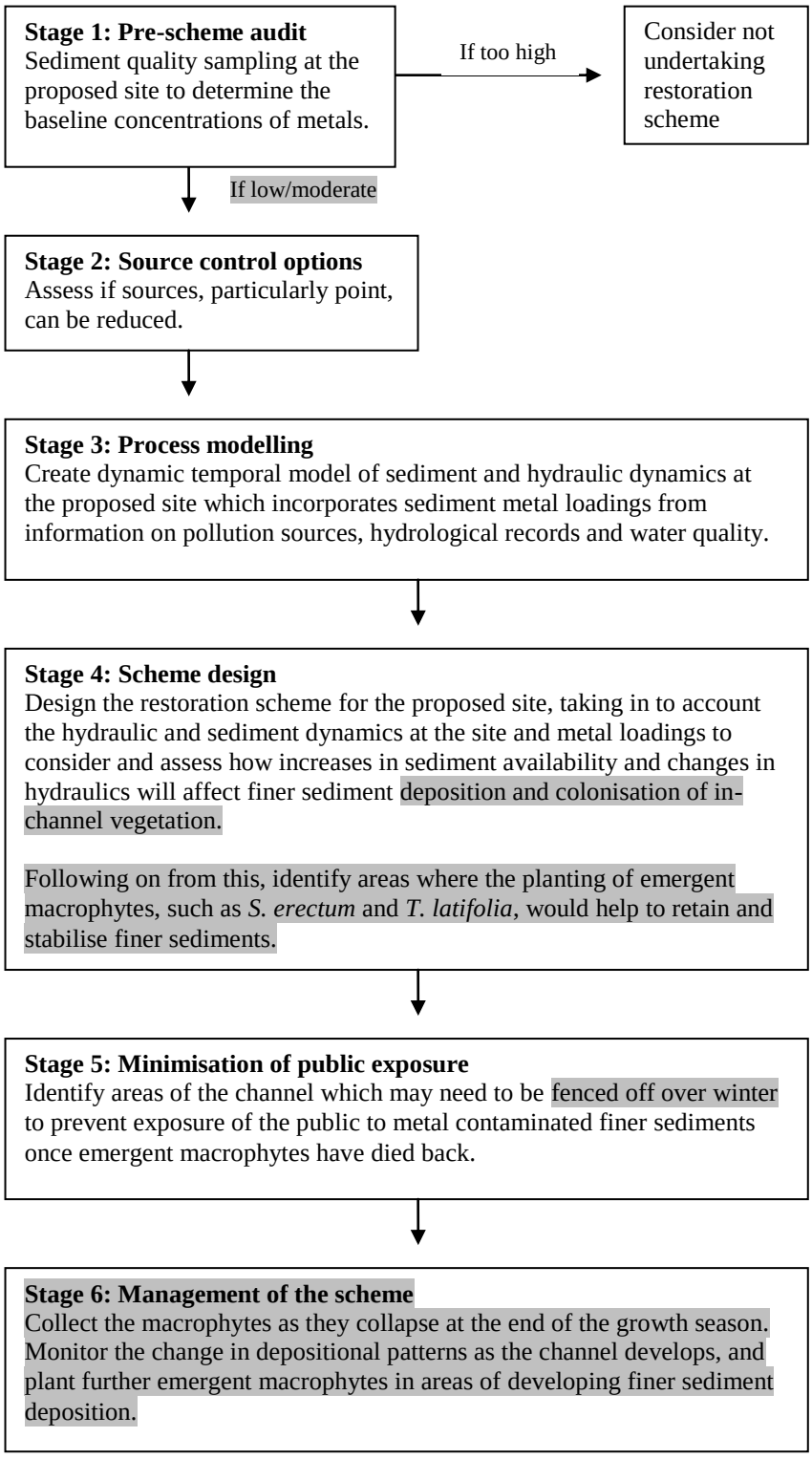


Figure 8.1: Framework for minimising risk of metal contaminated sediments in urban river restoration schemes (taken and updated from Scholes *et al*., 2008 with updates highlighted in grey).

Stage 1: prior to undertaking any restoration works, a baseline sediment quality survey of the proposed site should be undertaken in order to understand the current extent of metal contamination at the site. If the metal contamination is too high, then the possibility of not undertaking the restoration scheme should be considered. However, the decision not to undertake some form of restoration should only be a last resort since the use of emergent macrophytes and minimisation of public exposure (see below) can all be incorporated in to the scheme. Scholes *et al*. (2008) proposed that source control options should only be considered if the contamination was moderate. However, it is proposed here that consideration of sources for all proposed schemes should be undertaken, as they could be incorporated into the scheme (see below).

Stage 2: the sources of metal contamination to the site (identification of point sources will be easier than diffuse sources) should be identified and the possibilities for reducing them considered. This could include incorporation of reduction measures within the restoration scheme, e.g. a small wetland area in front of an outfall, or planting of some riparian vegetation if road runoff is immediately adjacent to the site.

Stage 3: it is important to understand the current hydraulics and sediment dynamics at the site prior to planning the restoration as changes to both processes (as has been shown in this thesis) can have an effect upon sediment metal loadings and bioavailability within river channels. Information on pollutant sources, hydrological records and water quality monitoring should be gathered to create a process model.

Stage 4: using knowledge from the process model, the scheme should be designed taking into account how changes in sediment sources and hydraulics will affect the deposition of finer sediments and the colonisation of in-channel vegetation (and further finer sediment accumulation). The areas where finer sediment deposition and accumulation are likely to occur should be highlighted, these could be backwater areas, the insides of meander bends and along banks. The design of the scheme should incorporate plans for emergent macrophyte species, such as *S. erectum* and *T. latifolia* which are able to withstand relatively high flows, to be planted in the newly restored urban river channel within the highlighted areas of finer sediment deposition in order to accumulate the finer sediments and stabilise them. It is also important that the hydraulics of the channel are not altered to the extent that flows are so low that the channel becomes filled with finer sediment and blocked by excessive growth of in-channel vegetation.

Stage 5: emergent macrophyte growth from spring to autumn in these areas will prevent people having contact with the metal contaminated sediments, therefore rather than permanently blocking areas of the channel which accumulate large areas of metal contaminated sediments from public access all year round (as was suggested by Scholes *et al*., 2008) fencing could be placed by these areas just in the winter once the emergent macrophytes have died back. Additionally, it is likely that over winter there will be far less interaction with the river channel by people.

Stage 6: at the end of the growth cycle as the macrophytes begin to collapse, the above-ground macrophyte tissues should be collected to prevent the cycling of the metals back in to the river system. This could occur at the same time as fencing off the river areas as suggested above. Also, as the channel develops over time and new areas of finer sediment accumulation develop, *S. erectum* and *T. latifolia* should be planted again, if they do not colonise naturally, for accumulation and stabilisation purposes.

It is recognised that many urban restoration schemes would not necessarily have the funding required to carry out such a detailed risk assessment, particularly in the pre-scheme audit and process modelling stages. However, the general concepts of being aware of the changes in sediment supply and hydraulics from the proposed restoration scheme and the planting of emergent macrophyte species in areas of finer sediment deposition can easily be incorporated in to urban river restoration schemes at minimal extra cost.

8.4 Implications for the Water Framework Directive

As was previously mentioned in Section 2.3.2, increased retention of metal contaminated sediments within urban rivers has the potential to negatively affect the implementation of, and compliance with, the WFD. The results from the research undertaken in this thesis has shown that there is the potential for increased retention of metal contaminated sediments in urban river restoration schemes where there is increased accumulation of finer sediments and those around in-channel vegetation, which could potentially have a negative impact upon the WFD status of that water body. However, as part of the implementation of the WFD within the UK there is a requirement for a WFD compliance assessment to be undertaken for works or modifications to water bodies (Environment Agency, 2010). The compliance assessment assesses whether the works or modifications will cause deterioration in the current ecological status and whether they will prevent good ecological status being met. This research has shown that an important aspect of a WFD compliance assessment for urban river restoration schemes would be to assess the potential increase in the accumulation of metal contaminated sediments, and the likely impacts of this upon the WFD status. As part of the planning process for large urban river restoration

schemes it is likely that a WFD compliance assessment would have to be undertaken. Although smaller projects may not necessarily require a WFD compliance assessment, it would be prudent to take into consideration the potential impact of the restoration works upon the WFD status of the water body.

8.5 Future Research

Although the four research studies in this thesis have developed knowledge on the interactions between macrophytes and sediments in urban river systems, the research has also highlighted areas for future research. These are outlined below.

1. What are the processes causing high metal concentrations in the gravel sediments in urban river systems?

Two possible processes were proposed for the high metal concentrations in the coarser gravel sediments: the precipitation of Fe and Mn (hydr)oxides and discrete anthropogenic particles. Analysis of gravel sediments under electron microscopes or through x-ray fluorescence (methods previously used by Taylor & Robertson, 2009; Taylor *et al*., 2003; and, Rees *et al*., 1999) could identify metalliferous discrete anthropogenic particles and whether these particles are hosts of other metals. Undertaking sequential extractions on the sediments would determine the binding mechanisms of metals within the sediments, and hence if Fe and Mn(hydr)oxides were a dominant binding phase in the sediments.

2. Do other sediment-associated contaminants show similar spatial and temporal variations in concentrations within urban river systems? What are the sediment quality risks from these?

Other sediment-associated contaminants, for example PAHs, hydrocarbons and nutrients, have been reported to be at elevated concentrations within urban river systems (Christensen *et al*., 2006; Wilson *et al*., 2005a; and, Owens *et al*., 2001). Undertaking similar research to investigate the spatial and temporal patterns of these contaminants in restored and unrestored urban river systems, and analysing the ecosystem and human health risks of the concentrations, would increase the knowledge on sediment-associated contaminants in restoration of urban rivers.

3. Are there any detrimental impacts upon ecosystems occurring in these urban river systems from the high sediment metal concentrations?

Analysis of the sediment metal concentrations with ecosystem based sediment quality guidelines (Environment Agency, 2008) indicated that metals were at concentrations that could be a hazard to aquatic ecosystems. Visually, there appeared to be no detrimental impacts upon

macrophyte growth, which appeared healthy and was particularly abundant at Sutcliffe Park which had the greatest sediment quality guideline exceedances. However, other indicators of metal toxicity on macrophytes include decreases in root length, root elongation, shoot elongation and biomass (Ayeni *et al*., 2010; Ait Ali *et al*., 2004; and, Ye *et al*., 2003). Therefore, further detailed surveys of macrophyte growth and morphology could provide greater information on any impacts on macrophytes from high metal concentrations. Similarly, macroinvertebrate and fish communities are affected by high metal concentrations, with reductions in their diversity, increases in pollution tolerant species, and increased tissue metal concentrations (Pyle *et al*., 2005; Beasley & Kneale, 2004; Sures, 2003; Burger *et al*., 2002; Rainbow, 2002; and, Clements *et al*., 2000). Surveys of macroinvertebrate and fish populations and analysis of their tissue metal concentrations would yield information on any detrimental effects from high metal concentrations.

4. How do people interact with and use restored urban rivers, and what are the risks of metal contaminated sediments from these uses?

Analysis of the sediment metal concentrations with human health based sediment quality guidelines (Dutch Ministry of Housing, Spatial Planning and Environment, 2009) indicated that there was a low risk to human health. However, more detailed models of human health risk assessments could indicate the risks from ingestion of, and dermal contact with, contaminated sediments and overlying water by calculating exposure levels and comparing them to tolerable daily intakes (Filipsson *et al*., 2009 and Albering *et al*., 1999). These models use data on site specific metal concentrations and exposure frequency, based on peoples use of the site. By undertaking visual observations and questionnaires relating to peoples use of restored urban rivers and detailed sampling of overlying water and sediment concentrations, then these more detailed exposure models could be used and the assessment of risks to humans improved.

5. What are the rates of radial oxygen loss and exudation of acids from the three commonly occurring emergent macrophyte species? How do they vary, and what are the effects upon the immediate rhizosphere and metal mobility?

The study on metal uptake and translocation indicated that the underlying sediments surrounding *S. erectum* were more anoxic and of a lower pH, with differences in radial oxygen loss (ROL) and exudation of acids from the roots suggested as the cause. Rates of ROL from the three macrophyte species could be measured in controlled laboratory experiments. Macrophytes could be grown in stagnated deoxygenated solution (Visser *et al*., 2000) or standardised sediment (Jespersen *et al*., 1998) and redox measured in-situ with a redox probe. Alternatively, macrophytes could be placed in nutrient solution with a known volume of an ion (for example, anthraquinone radical anion or Ti^{3+}citrate) which changes colour through

oxidation, and water samples taken and analysed on a spectrophotometer (Inoue & Tsuchiya, 2008 and Visser *et al.*, 2000). Macrophyte exudates can be collected by immersing clean roots in deionised water for a few hours and analysing the solution for a range of organic acids by chromatography (Mucha *et al*., 2008; Ratushnyak, 2008; and, Mucha *et al*., 2005). Additionally, careful sampling of the sediments from immediately around the root/rhizome area and those from further away, and sequential extraction of the metals in the sediment samples, would provide complementary information on the different mobilities of metals from these two different zones.

6. How does sediment cohesion vary and impact upon sediment stability between the macrophyte species?

Sediment cohesion is an additional key variable which is important in the ability of macrophytes to withstand uprooting forces and hence protect the underlying sediments from erosion and resuspension (Pollen-Bankhead *et al*., 2011; Schutten *et al*., 2005; and, Handley & David, 2002). Sediment properties which affect the cohesion of river sediments (as reviewed by Grabowski *et al*., 2011) include physical properties (particle size, bulk density, water content), geochemical properties (water geochemistry, pH, metals, organic content) and biological properties (disturbance by organisms, roots and rhizomes, feeding). Underlying sediment pH and root and rhizome structures have been shown to vary between the three macrophyte species in this thesis. Other variables, for example water content due to differing positions of growth along the river bed and bank, are likely to vary between the macrophyte species, which suggest sediment cohesion may vary between the three species. Sediment cohesion can be measured in-situ using field based equipment (Widdows *et al*., 2007; Yallop *et al*., 2000; and, Tolhurst *et al*., 1999) and the data collected would increase the understanding of the ability of the three macrophyte species to protect underlying metal-contaminated sediments.

7. What are the interactions between flow, sedimentation and growth for T. latifolia and P. arundinacea and other common emergent macrophytes? Are they complex as has been demonstrated for S. erectum? How much sediment do they trap compared to S. erectum?

S. erectum was found to have a more complex interaction between flow, sedimentation and growth compared to some submerged species. Undertaking similar measurements of flow, sedimentation and growth in patches of *T. latifolia* and *P. arundinacea*, or other common emergent macrophyte species, throughout the growth cycle would enable similar interactions to be understood. The fine sediment depth measurements would also allow calculations of the storage of metals in the macrophytes and the underlying sediments on a per m^2 of river channel with macrophyte growth basis, as was done for *S. erectum*. This would show the distribution of metal storage.

8. How does a newly restored stretch of urban river develop?

The implementation of a long-term monitoring project on a newly restored stretch of urban river would yield a wealth of data and information on the progressive development of, and interactions between, sediment and macrophytes and the effects upon sediment metal chemistry and metal storage. Pre-restoration surveys would provide a baseline for the monitoring. Regular surveys of: channel planform; extents of bed sediment types; extents and species of in-channel vegetation; sediment depths; and, sediment chemistry would elucidate information on: how sedimentation patterns develop and in-channel vegetation growth develops as the channel develops over time; the development of landforms within the river channel from the interactions between in-channel vegetation and sediment; how the development of landforms and changes in sedimentation patterns alter sediment chemistry and metal mobility; and, how this channel development over time alters metal storage and mobilities within the stretch.

8.6 Conclusions

From the research in this thesis three main conclusions can be drawn relating to sediments and macrophytes in urban river systems.

Firstly, within urban river systems there are three bed sediment types which are important in terms of high metal concentrations. These are finer sediment, sediments which accumulate around in-channel vegetation and gravel sediments. However, in terms of metal storage within urban river channels and metal bioavailability, finer sediment and sediment which accumulates around in-channel vegetation are the most important.

Secondly, urban river restoration practices can increase the supplies of sediment into a river channel and alter the hydraulics to the extent that greater deposition of finer sediments occurs and in-channel vegetation colonises which accumulates sediments. These can then have an effect upon increased metal storage within the channel and increased bioavailability of metals.

Thirdly, the interactions between emergent macrophytes and sediments within urban rivers are important and could be used in the management of metal contaminated sediments in the restoration of urban rivers. The most common emergent macrophyte species, *S. erectum*, traps and accumulates significant quantities of fine sediment, which persist from year to year. Although three common emergent macrophyte species (*S. erectum*, *T. latifolia* and *P. arundinacea*) do not phytoremediate metal contaminated sediments significantly through metal uptake or bioconcentration from the sediments, two other processes help to reduce the risk of metal mobilisation from the sediments and thus reduce the risk of the sediments turning from a sink into a source of metals. These are the reinforcement and stabilisation of these accumulated

sediments (particularly by *S. erectum* and *T. latifolia*), which was found to be greater than with submerged macrophytes, and the creation of anoxic sediment conditions which strongly bind metals.

This shows the great potential of using emergent macrophytes in the restoration and management of urban rivers contaminated by sediment-associated metals.

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Appendix I

Quality Control Results for Laboratory Analysis in Chapter 4

Aqua regia sediment extractions (pseudo-total metal concentrations)

	Recoveries (%) CRM LGC6187 (aqua regia)							
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	89	81	92	98	81	82	83	87
	88	80	91	98	80	81	82	88
AR2	98	84	103	119	87	87	91	94
	93	83	102	112	86	87	92	92
AR3	100	82	95	108	83	84	89	92
	104	81	94	118	83	85	90	91
AR4	92	80	99	104	84	79	91	92
	91	77	98	101	81	77	88	89
AR5	91	82	103	115	89	82	94	98
	91	81	99	108	89	82	89	96
AR6	91	84	97	112	88	90	89	94
	87	80	97	112	83	85	87	91
AR7	99	83	104	116	90	86	93	96
	102	85	104	120	89	85	95	96
AR8	88	81	98	108	86	82	94	95
	90	77	95	110	85	79	88	92
AR9	96	80	98	103	88	83	92	97
	106	80	101	104	89	85	96	98
AR10	93	81	92	118	93	80	84	93
	87	78	90	116	90	77	82	90
AR11	89	83	101	117	91	87	86	98
	94	83	100	115	90	85	86	98
AR12	99	79	99	107	90	81	92	93
	95	80	100	118	88	83	88	94
AR13	90	82	95	112	83	82	83	92
	86	84	96	114	83	85	86	93
AR14	94	75	95	110	80	76	83	90
	90	74	94	107	81	75	80	89
AR15	99	85	94	119	79	83	85	93
	93	84	90	117	78	82	85	91
AR16	87	80	95	113	78	80	87	92
	86	80	97	114	79	79	89	92
AR17	89	78	91	111	79	74	82	88
	87	77	92	109	78	76	84	87
AR18	87	72	93	106	83	85	85	96
	84	73	89	107	84	87	85	96

	% RSD of Triplicate Extractions (aqua regia)								
Batch	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	6.16	4.01	2.95	1.11	5.59	2.71	0.97	1.53	2.74
	5.30	1.33	1.83	4.26	3.96	2.24	2.53	6.93	2.45
AR2	14.15	<LoD	18.15	72.78	20.86	13.57	18.30	42.82	3.74
	18.10	<LoD	9.93	4.93	11.93	9.72	1.22	12.79	3.74
AR3	7.59	13.95	6.40	15.45	7.02	8.82	4.40	26.23	14.09
	6.62	<LoD	6.07	6.02	5.71	4.13	4.51	2.05	3.37
AR4	5.72	<LoD	5.83	2.35	6.31	4.59	6.58	19.82	7.38
	10.10	<LoD	4.07	10.65	2.64	16.55	2.71	22.29	3.02
AR5	8.65	<LoD	4.91	2.67	4.77	1.81	3.21	3.40	3.60
	7.52	7.55	1.21	2.40	2.46	3.14	1.95	2.61	2.09
AR6	16.09	<LoD	23.96	39.30	16.73	31.02	25.02	47.63	22.82
	3.42	<LoD	6.17	4.45	0.98	3.03	2.74	10.14	13.95
AR7	2.12	<LoD	4.32	5.00	2.29	7.99	1.51	7.96	4.61
	20.65	<LoD	14.16	45.13	4.39	8.47	26.83	22.09	22.53
AR8	19.97	<LoD	41.74	39.71	10.19	9.48	13.39	33.37	38.92
	14.38	<LoD	15.33	9.85	7.40	9.38	7.13	17.35	6.05
AR9	7.34	9.06	3.72	4.92	1.82	2.62	3.82	1.20	3.28
	6.31	<LoD	3.07	5.43	2.75	3.94	0.60	6.16	5.81

AR10	3.82	<LoD	26.57	9.65	8.54	6.24	7.87	9.61	2.83
	19.04	<LoD	25.70	16.95	2.51	10.10	4.88	7.58	6.70
AR11	4.45	<LoD	18.96	15.87	4.73	15.44	8.94	22.82	0.96
	6.84	<LoD	21.79	11.67	5.59	9.17	5.34	23.24	9.95
AR12	0.18	<LoD	0.84	0.17	0.05	0.89	0.51	4.00	0.82
	0.77	<LoD	1.88	1.61	1.55	0.51	2.09	2.88	1.20
AR13	3.95	<LoD	7.03	5.48	2.97	7.14	9.39	1.34	3.47
	3.48	<LoD	2.35	16.70	5.85	4.18	3.39	11.66	2.25
AR14	6.15	<LoD	4.22	2.18	1.91	4.79	3.75	4.05	3.19
	10.09	<LoD	8.47	14.58	8.80	12.58	6.75	16.21	5.46
AR15	10.96	<LoD	17.01	3.44	7.90	12.23	13.88	11.99	3.98
	7.89	<LoD	2.42	9.29	5.29	16.76	18.59	5.89	4.94
AR16	3.62	7.50	0.40	1.38	5.17	1.52	1.92	0.73	0.93
	8.12	<LoD	12.67	9.15	8.56	15.04	5.53	1.57	2.25
AR17	6.70	<LoD	16.76	15.27	19.73	15.57	11.28	7.82	5.02
	11.12	<LoD	10.76	9.57	5.21	9.11	15.54	16.22	5.24
AR18	14.64	<LoD	14.24	7.83	3.86	11.49	9.03	3.56	4.30
	11.45	<LoD	11.65	12.70	5.54	12.83	11.19	17.90	21.12

Analytical Blanks (mgl^{-1}) (aqua regia)

Batch	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
AR1	0.11	<LoD	<LoD	0.01	0.13	0.01	<LoD	<LoD	<LoD
	0.09	<LoD	0.00	0.01	0.05	<LoD	<LoD	0.03	0.01
AR2	0.13	<LoD	<LoD	0.01	0.11	0.01	<LoD	<LoD	0.08
	0.12	<LoD	<LoD	0.01	0.09	0.01	<LoD	<LoD	0.02
AR3	0.16	<LoD	<LoD	0.01	0.17	0.01	<LoD	<LoD	0.01
	0.07	<LoD	<LoD	0.01	0.07	0.01	<LoD	<LoD	0.03
AR4	0.07	<LoD	<LoD	0.02	0.09	0.01	<LoD	<LoD	0.01
	0.05	<LoD	<LoD	0.02	0.06	<LoD	<LoD	<LoD	0.01
AR5	0.14	<LoD	<LoD	<LoD	0.24	<LoD	<LoD	<LoD	0.02
	0.13	<LoD	<LoD	0.02	0.11	<LoD	0.04	<LoD	0.03
AR6	0.08	<LoD	<LoD	<LoD	0.05	<LoD	<LoD	<LoD	0.01
	0.09	<LoD	<LoD	<LoD	0.05	<LoD	<LoD	<LoD	0.01
AR7	0.05	<LoD	<LoD	<LoD	0.30	0.01	<LoD	<LoD	0.01
	0.15	<LoD	<LoD	<LoD	0.06	<LoD	<LoD	<LoD	0.01
AR8	0.10	<LoD	<LoD	0.01	0.22	0.01	<LoD	<LoD	0.02
	0.07	<LoD	<LoD	<LoD	0.09	<LoD	<LoD	<LoD	0.01
AR9	<LoD	<LoD	<LoD	<LoD	0.09	0.01	<LoD	<LoD	0.03
	<LoD	<LoD	<LoD	<LoD	0.04	<LoD	<LoD	<LoD	0.04
AR10	0.10	<LoD	<LoD	0.01	0.15	0.01	<LoD	<LoD	0.06
	0.04	<LoD	<LoD	0.01	0.05	<LoD	<LoD	<LoD	0.01
AR11	0.08	<LoD	<LoD	0.01	0.04	0.01	<LoD	<LoD	0.01
	0.03	<LoD	<LoD	0.01	<LoD	<LoD	<LoD	<LoD	0.02
AR12	0.05	<LoD	<LoD	<LoD	0.07	0.01	<LoD	<LoD	0.07
	0.03	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	0.05
AR13	0.12	<LoD	<LoD	<LoD	0.05	0.01	<LoD	<LoD	0.02
	0.08	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	0.01
AR14	0.03	<LoD	<LoD	<LoD	0.06	0.01	<LoD	<LoD	<LoD
	<LoD	<LoD	<LoD	0.01	<LoD	<LoD	<LoD	<LoD	<LoD
AR15	0.09	<LoD	<LoD	<LoD	0.05	<LoD	<LoD	<LoD	<LoD
	0.05	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
AR16	0.04	<LoD	<LoD	<LoD	0.04	<LoD	<LoD	<LoD	0.04
	0.06	<LoD	<LoD	0.01	0.10	<LoD	<LoD	0.03	0.05
AR17	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	0.01
	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
AR18	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	0.04
	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	0.01

% RSD of Analytical Triplicate on ICP-OES (aqua regia)

Batch	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
AR1	0.67	<LoD	1.67	1.04	2.87	1.01	0.87	0.78	0.82
	0.78	<LoD	1.31	2.00	4.93	0.85	1.46	1.48	1.27
AR2	1.68	1.96	2.29	1.23	0.78	1.16	2.10	1.27	1.14
	0.84	2.43	3.80	0.06	1.05	1.61	2.61	2.52	2.76
AR3	0.47	<LoD	2.11	2.19	2.94	1.24	2.19	0.79	2.07
	2.04	1.21	1.94	2.36	1.67	2.10	2.27	0.62	2.81
AR4	3.04	3.20	0.20	0.78	2.96	0.77	0.51	0.11	0.29
	0.39	6.55	0.62	0.49	1.21	0.55	0.93	0.68	0.66
AR5	1.40	12.93	2.18	0.63	1.55	0.90	2.25	1.09	0.52
	0.15	<LoD	0.48	0.31	0.71	0.33	0.66	0.85	0.27

AR6	0.35	<LoD	1.81	0.08	1.25	0.92	2.61	0.91	0.37
	0.34	2.77	0.34	0.57	1.34	0.53	1.23	0.31	0.12
AR7	2.94	<LoD	0.90	1.32	2.42	0.70	0.60	3.31	0.93
	0.60	<LoD	0.26	0.35	1.29	0.58	1.84	3.69	0.62
AR8	0.59	<LoD	1.46	0.87	1.81	0.82	2.23	0.29	0.23
	0.77	2.70	0.52	0.62	0.78	8.54	2.32	1.50	0.57
AR9	0.89	6.15	1.29	1.07	1.57	1.32	0.73	1.30	1.35
	0.44	1.64	0.42	0.85	1.13	1.23	0.80	0.58	0.31
AR10	0.63	<LoD	0.34	0.11	0.63	0.14	2.23	3.18	1.14
	0.46	<LoD	0.56	0.47	1.53	0.35	1.90	0.88	0.42
AR11	0.21	<LoD	1.22	0.22	0.79	0.47	4.98	0.34	0.28
	1.05	<LoD	0.68	0.66	0.34	0.37	0.42	0.75	0.96
AR12	0.18	<LoD	0.84	0.17	0.05	0.89	0.51	4.00	0.82
	0.77	<LoD	1.88	1.61	1.55	0.51	2.09	2.88	1.20
AR13	0.14	<LoD	0.32	0.12	1.64	0.54	0.31	0.13	0.57
	0.34	4.65	0.45	0.11	1.38	0.71	0.87	0.82	0.13
AR14	0.12	<LoD	0.73	0.40	1.86	0.40	3.79	1.19	0.04
	0.59	<LoD	0.94	0.33	5.16	0.70	1.67	2.24	1.49
AR15	0.12	<LoD	0.49	0.14	4.39	0.50	0.64	0.26	0.52
	0.21	<LoD	1.92	0.79	0.96	2.14	1.63	3.29	1.59
AR16	0.36	<LoD	1.39	0.40	4.02	0.80	2.81	0.84	4.34
	0.32	2.39	0.13	0.30	0.73	0.49	2.23	0.57	0.40
AR17	0.23	<LoD	1.93	0.67	0.62	0.75	1.14	0.53	0.54
	0.57	<LoD	0.16	0.28	1.79	0.26	4.46	1.12	0.14
AR18	0.07	<LoD	0.28	0.55	0.83	0.58	2.06	2.00	0.88
	0.89	<LoD	0.58	0.10	1.47	0.86	1.93	0.69	0.24

Acetic acid sediment extractions

% Recovery BCR701 (acetic acid)						
Batch	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
AA1	93	85	84	86	97	92
	92	79	81	85	90	91
AA2	94	80	85	80	79	93
	93	76	83	81	84	93

% RSD of Triplicate Extractions (acetic acid)									
Batch	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	6.25	<LoD	<LoD	9.21	10.96	5.36	<LoD	<LoD	5.59
	3.10	8.25	1.42	5.68	12.21	4.22	4.75	<LoD	8.23
AA2	5.36	<LoD	<LoD	6.06	4.07	9.92	5.89	<LoD	5.52
	3.37	<LoD	<LoD	17.68	2.34	1.12	<LoD	33.20	3.46

Analytical blanks (mgl^{-1}) (acetic acid)									
Batch	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
	<LoD	<LoD	<LoD	<LoD	0.02	<LoD	<LoD	<LoD	<LoD
AA2	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD
	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD	<LoD

% RSD of Analytical Triplicates on ICP-OES (acetic acid)									
Batch	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	0.43	6.65	<LoD	11.53	0.10	0.92	9.72	10.38	0.41
	1.12	<LoD	4.95	0.95	0.49	1.75	5.18	<LoD	1.11
AA2	0.12	<LoD	<LoD	1.82	0.60	0.08	7.66	1.11	0.15
	0.05	<LoD	<LoD	0.21	0.04	0.46	4.01	9.74	0.25

Particle Size Analyser
Bold figure indicates CRM outside acceptable range.

	Median % <63 µm Micrometrics CRM	
Batch	**CRM 1**	**CRM 2**
PSA1	**4.06**	**3.94**
PSA2	**3.05**	**3.05**
PSA3	3.65	3.73
PSA4	3.87	3.65
PSA5	3.73	3.90
PSA6	3.63	3.82
PSA7	3.70	3.82
PSA8	3.69	3.78
PSA9	3.88	3.71
PSA10	3.68	3.81
PSA11	3.90	3.67
PSA12	**3.11**	**2.91**
PSA13	3.65	**3.08**
PSA14	3.81	3.92
PSA15	**3.24**	**3.07**
PSA16	3.70	3.89
PSA17	3.73	3.86
PSA18	3.68	3.70
PSA19	3.66	3.92
PSA20	3.64	3.77
PSA21	3.90	3.68
PSA22	3.76	3.85
PSA23	3.73	3.72

Appendix II

Full Data Set from Chapter 4

BP = Beddington Park
BG = Bell Green
SP = Sutcliffe Park
CM = Chinbrook Meadows
R = Restored stretch
U = Unrestored stretch
G = Gravel
S = Sand
F = Finer
V = In-channel vegetation
1 – 5 = samples 1 to 5

May 2010

	Pseudo-total metal concentration (aqua regia extractable) $mgkg^{-1}$											
Sample	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**% organic matter**	**% <63 µm**	**% >2 mm**
BP.R.G.1	5157.91	<LoD	11.38	82.89	8662.11	195.70	6.41	38.48	94.48	2.40	12.5	75
BP.R.G.2	3849.57	<LoD	10.39	49.57	11641.88	165.61	7.77	34.84	92.22	2.00	14.9	93
BP.R.G.3	3513.83	<LoD	11.42	54.11	9324.46	123.48	8.75	79.61	88.94	2.90	17.5	94
BP.R.G.4	2827.53	<LoD	13.15	29.22	8739.53	235.10	8.27	64.56	78.65	1.60	11.8	80
BP.R.G.5	4690.45	<LoD	30.69	46.55	27731.84	298.64	20.51	49.40	97.94	1.60	13	90
BP.R.S.1	3060.61	<LoD	20.69	17.46	9827.07	162.99	8.10	66.55	85.50	1.10	5.21	21
BP.R.S.2	5263.59	<LoD	31.23	30.07	11345.62	182.26	10.08	80.44	194.53	2.20	6.26	27
BP.R.S.3	3215.39	<LoD	7.83	40.76	7210.61	151.34	6.58	49.70	99.90	1.80	6.59	3
BP.R.S.4	3138.85	<LoD	10.57	16.18	8592.02	224.10	7.06	64.48	74.72	2.11	4.13	25
BP.R.S.5	2649.08	<LoD	6.63	15.44	6827.23	122.43	4.79	50.44	66.78	1.78	8.52	14
BP.R.F.1	7104.41	2.02	45.71	207.72	20578.74	188.90	17.40	224.83	543.69	26.84	31.3	9
BP.R.F.2	3596.13	<LoD	19.31	58.90	9300.27	142.77	8.80	99.35	192.56	10.13	23.5	4
BP.R.F.3	4949.24	<LoD	11.43	28.59	9425.39	196.49	9.49	575.05	221.49	2.78	24.6	48
BP.R.F.4	4413.42	1.32	24.70	88.68	11173.99	123.25	10.90	137.42	294.76	8.86	26.9	10
BP.R.F.5	3705.82	<LoD	19.12	83.02	9338.74	103.71	9.77	175.01	246.30	14.13	22.6	21
BP.R.V.1	12568.97	<LoD	56.77	270.09	27782.90	499.19	26.47	313.10	884.41	45.68	77.3	45
BP.R.V.2	9522.04	<LoD	41.43	174.71	16630.82	148.10	18.24	232.03	549.59	26.45	75.3	15
BP.R.V.3	9269.50	4.07	57.04	287.85	23075.78	426.69	25.87	587.21	854.42	18.03	57.6	5
BP.R.V.4	8405.55	2.59	47.20	205.26	19107.31	322.61	19.62	311.73	624.40	17.28	30.6	5
BP.R.V.5	6973.11	<LoD	20.51	71.06	15627.48	280.52	12.90	91.99	190.37	7.26	12.9	29
BP.U.G.1	2707.08	<LoD	13.56	51.74	8665.66	127.22	8.29	90.65	92.92	2.59	12.6	93
BP.U.G.2	5167.82	<LoD	22.45	43.67	12050.35	271.54	10.86	69.35	114.51	3.29	17.8	81
BP.U.G.3	6256.07	<LoD	15.41	78.49	11704.77	369.25	9.60	45.56	146.73	4.00	13.5	90
BP.U.G.4	5550.87	<LoD	16.59	93.04	14424.96	207.75	10.77	70.03	152.88	2.11	11.4	81
BP.U.G.5	3166.69	<LoD	10.70	70.68	7229.75	273.35	6.93	46.16	131.10	3.71	1.97	84
BP.U.S.1	3672.80	<LoD	16.18	73.47	9416.44	122.66	8.06	72.23	132.83	2.81	11.8	8
BP.U.S.2	2902.70	<LoD	11.50	26.00	8151.65	135.38	12.35	58.23	104.67	2.11	2.08	6
BP.U.S.3	2993.68	<LoD	22.49	26.13	7812.05	102.20	8.50	162.03	105.81	3.78	7.83	3

BP.U.S.4	3307.87	<LoD	14.74	32.01	8992.77	129.83	7.66	68.01	115.58	3.08	15.9	9
BP.U.S.5	3592.90	<LoD	14.24	47.44	11904.43	144.55	9.55	74.22	137.57	4.51	19.2	63
BP.U.F.1	4390.14	1.21	25.03	81.14	11458.45	124.10	11.24	137.46	277.10	10.16	28.6	6
BP.U.F.2	8121.82	2.27	49.55	222.93	19834.88	196.21	20.16	250.59	613.03	19.18	31.8	8
BP.U.F.3	7203.14	2.32	53.08	205.96	19267.08	184.24	22.17	238.39	613.15	23.32	66.4	13
BP.U.F.4	8995.69	2.75	43.84	196.69	19579.80	203.27	19.30	279.60	587.65	23.63	40.9	17
BP.U.F.5	4999.42	1.28	26.64	109.48	13647.88	166.13	14.48	167.16	456.44	15.40	34.1	9
BP.U.V.1	5608.98	2.54	33.93	293.89	13585.84	177.15	14.69	262.25	383.00	10.75	25.1	4
BP.U.V.2	8871.04	3.00	54.30	259.99	22195.50	380.87	22.88	274.78	774.78	30.23	22.5	13
BP.U.V.3	9784.06	3.36	60.50	299.46	24539.36	408.78	24.78	344.20	853.79	24.98	63.2	3
BP.U.V.4	12970.46	3.73	70.25	340.34	28035.92	521.27	28.59	383.59	996.40	24.27	51.9	6
BP.U.V.5	8321.28	2.71	55.87	255.74	21082.28	387.43	21.55	279.11	761.99	24.80	40.1	10
BG.R.G.1	3587.79	<LoD	12.72	53.37	14183.35	261.19	10.96	39.62	138.14	1.79	10.2	94
BG.R.G.2	8645.51	<LoD	56.47	382.82	34990.74	1007.88	33.32	43.56	254.57	5.03	10.9	95
BG.R.G.3	4280.07	<LoD	10.61	56.71	16258.60	240.06	12.17	166.90	133.20	1.31	2.95	79
BG.R.G.4	5906.62	<LoD	15.62	105.58	16996.37	419.30	23.33	89.51	414.07	1.39	24.2	83
BG.R.G.5	5392.10	<LoD	13.81	70.32	15899.72	315.96	14.78	48.76	201.29	3.59	10.3	72
BG.R.V.1	6208.82	<LoD	12.14	28.17	15372.14	297.32	11.60	76.08	280.62	4.12	40.1	19
BG.R.V.2	7365.63	<LoD	17.68	79.63	18234.91	502.77	15.87	137.12	395.51	8.35	33.5	7
BG.R.V.3	5990.99	<LoD	27.43	79.11	14397.84	432.10	14.25	116.82	225.21	7.75	38.8	13
BG.R.V.4	8933.17	<LoD	30.52	126.48	20054.82	737.96	21.30	287.11	414.37	10.32	46.9	5
BG.R.V.5	11804.48	<LoD	37.74	181.21	26329.60	606.75	25.60	232.06	529.14	12.29	36.9	27
BG.U.G.1	5002.64	<LoD	15.32	50.65	16467.08	291.76	14.15	89.73	238.06	6.23	27.4	59
BG.U.G.2	5695.51	<LoD	19.46	93.96	32411.69	499.59	35.47	308.48	245.57	2.91	4.67	83
BG.U.G.3	4203.46	<LoD	147.31	145.66	56232.91	569.85	72.26	43.88	246.20	3.53	23.1	86
BG.U.G.4	4676.59	<LoD	15.07	31.27	18566.63	305.99	17.11	179.00	132.47	1.89	9.69	55
BG.U.G.5	5951.43	<LoD	40.98	49.46	23447.49	529.04	14.91	55.74	155.25	1.60	7.27	78
BG.U.V.1	18158.54	<LoD	31.87	27.49	31119.15	371.34	18.22	38.64	143.37	6.11	25.1	5
BG.U.V.2	6916.53	<LoD	24.23	90.52	16580.32	536.93	17.60	150.08	335.91	14.40	22.5	9
BG.U.V.3	12794.48	<LoD	42.75	216.08	27549.02	684.87	29.99	246.66	669.21	22.67	63.2	5
BG.U.V.4	5718.50	<LoD	21.08	89.07	17776.28	333.66	17.98	247.15	343.64	18.68	51.9	6
BG.U.V.5	3883.28	<LoD	10.78	27.90	14747.32	229.35	10.88	269.90	142.40	4.21	40.1	6
SP.R.G.1	4640.12	<LoD	28.29	110.00	64625.20	521.10	48.87	116.14	353.04	6.65	53.1	90
SP.R.G.2	8909.07	<LoD	41.41	85.67	84520.87	487.10	17.65	116.73	344.85	3.27	54.3	92
SP.R.G.3	7835.24	<LoD	35.37	90.16	51679.20	286.43	31.64	115.25	378.16	5.58	48.1	90
SP.R.G.4	8899.25	<LoD	33.17	92.09	81311.88	196.91	26.79	105.20	312.82	4.91	68.1	95
SP.R.G.5	12749.55	<LoD	15.95	43.89	16802.57	369.03	23.99	103.90	331.86	5.81	74.5	94
SP.R.F.1	17952.01	<LoD	38.23	146.73	36944.87	381.23	34.69	136.46	418.90	23.19	100	18
SP.R.F.2	28907.06	3.05	59.89	234.37	40901.41	677.51	37.18	246.54	738.34	31.99	92.5	15
SP.R.F.3	20612.85	3.32	56.58	237.20	42102.77	796.64	36.95	246.54	786.43	29.33	100	7
SP.R.F.4	25801.65	3.10	57.68	222.25	36090.40	548.17	34.84	216.49	726.01	30.26	94.3	10
SP.R.F.5	31365.38	3.26	63.12	247.16	45452.14	552.31	39.74	233.82	781.97	27.60	100	10
SP.R.V.1	23499.80	2.80	53.22	221.37	31716.23	702.64	33.01	262.69	675.41	39.29	84.1	27
SP.R.V.2	19784.25	3.29	53.00	216.91	32649.10	619.54	34.37	216.34	718.95	30.31	92.5	32
SP.R.V.3	18658.87	3.16	51.98	237.88	39614.31	757.07	36.57	242.87	774.45	37.43	88.5	9
SP.R.V.4	24032.47	2.89	56.51	217.76	35595.22	596.06	35.36	206.17	673.00	28.54	99.1	14
SP.R.V.5	35599.21	2.10	62.70	188.23	45266.53	501.54	40.86	170.22	562.30	22.50	100	12
SP.U.G.1	10152.61	<LoD	24.29	56.36	37261.19	794.50	24.29	60.88	242.76	3.49	52	90
SP.U.G.2	6939.57	<LoD	14.71	93.01	23399.61	236.65	17.70	72.20	188.94	3.69	20.3	93
SP.U.G.3	11546.91	<LoD	27.81	91.59	69975.70	876.63	27.78	99.96	394.93	8.06	100	98
SP.U.G.4	13803.05	5.36	35.16	283.74	89670.50	1045.88	35.14	139.83	530.85	13.86	62.7	98
SP.U.G.5	7040.04	<LoD	47.03	154.63	77982.39	732.60	50.06	64.40	385.10	5.09	41.2	98
SP.U.F.1	8549.66	<LoD	23.32	42.36	25599.80	250.87	15.90	57.67	183.14	2.61	9.39	33
SP.U.F.2	7579.34	<LoD	13.90	34.10	22034.27	211.53	14.79	63.56	183.19	2.97	8.13	20

SP.U.F.3	6772.67	<LoD	26.37	73.85	34109.02	410.81	19.16	60.39	258.09	3.02	22.9	31
SP.U.F.4	4880.83	<LoD	14.76	55.22	10540.70	109.84	9.61	76.78	166.49	3.18	37.8	2
SP.U.F.5	5952.09	<LoD	12.70	33.58	21461.88	278.79	13.93	65.39	140.63	1.80	18.9	16
CM.R.G.1	6017.62	<LoD	14.02	53.18	25488.55	1985.83	25.86	33.90	122.19	3.41	17	79
CM.R.G.2	4089.72	<LoD	20.95	54.64	20560.29	1088.89	15.43	28.64	88.36	3.50	8.52	87
CM.R.G.3	6996.07	<LoD	14.71	28.64	19041.95	667.41	13.19	31.32	75.12	3.42	15.4	93
CM.R.G.4	4714.41	<LoD	14.11	26.30	25758.43	403.29	18.89	55.55	90.88	2.39	20.5	65
CM.R.G.5	6590.40	<LoD	12.70	62.26	19068.10	1190.49	21.29	41.76	132.40	4.17	1.91	94
CM.R.F.1	3218.84	<LoD	14.92	14.03	11425.86	331.57	9.18	33.69	83.77	1.30	15.3	5
CM.R.F.2	3856.01	<LoD	11.06	20.46	15714.09	347.71	8.55	33.83	93.88	3.27	12.7	18
CM.R.F.3	2446.65	<LoD	12.73	10.93	22525.34	893.84	14.75	21.73	104.05	1.10	8.37	4
CM.R.F.4	4365.94	<LoD	13.42	46.42	13562.06	413.01	11.89	42.10	116.13	3.40	17.1	15
CM.R.F.5	5098.19	<LoD	15.78	37.56	13803.52	196.92	11.03	70.49	151.98	6.89	21.9	4
CM.R.V.1	8069.32	<LoD	20.62	63.31	18341.61	333.81	14.61	87.02	204.70	12.91	22.2	9
CM.R.V.2	6751.48	<LoD	25.13	46.42	23147.33	899.86	16.74	81.30	165.91	9.22	23.7	29
CM.R.V.3	12573.29	2.96	28.21	64.93	22568.44	322.67	19.53	115.61	394.14	8.66	49.7	14
CM.R.V.4	11970.99	<LoD	28.80	98.40	20856.45	508.71	18.61	132.10	287.89	21.97	74.6	4
CM.R.V.5	4422.13	<LoD	14.11	36.08	15643.25	282.28	12.69	80.19	130.39	6.08	20.6	9
CM.U.G.1	6350.10	<LoD	18.16	72.56	16424.07	209.20	11.29	69.86	191.82	8.22	16.8	98
CM.U.G.2	4012.27	<LoD	21.23	34.59	24829.96	833.21	12.51	48.18	132.28	3.19	25.7	87
CM.U.G.3	3775.09	<LoD	9.99	34.07	21621.24	422.35	9.46	137.61	145.02	3.40	15.3	85
CM.U.G.4	3448.98	<LoD	12.02	35.96	21417.26	602.99	14.53	49.57	78.25	5.00	25.8	89
CM.U.G.5	7188.16	<LoD	15.47	67.52	28519.24	1533.08	17.19	107.75	161.85	5.05	26.3	76
CM.U.F.1	4373.53	<LoD	15.12	25.17	13450.50	301.58	9.35	97.91	115.72	2.29	22.5	20
CM.U.F.2	3792.00	<LoD	9.23	11.45	13059.40	346.86	10.01	36.51	130.21	2.41	9.08	2
CM.U.F.3	9323.63	1.60	31.45	133.16	22810.39	390.67	20.72	159.71	420.07	22.65	44.9	6
CM.U.F.4	7926.54	1.39	19.74	91.30	16273.20	164.32	13.70	155.39	220.67	9.39	47.7	6
CM.U.F.5	3882.71	<LoD	10.74	17.62	11245.73	456.65	8.70	30.33	80.75	3.81	23.6	35
CM.U.V.1	15500.81	<LoD	40.41	140.80	25711.47	864.08	24.61	173.80	461.64	26.94	76.1	5
CM.U.V.2	12484.10	<LoD	33.43	108.50	23280.13	863.58	22.65	151.70	360.29	14.07	78.3	3
CM.U.V.3	10508.14	<LoD	29.86	114.17	22187.27	791.83	21.37	146.44	364.88	22.39	69.6	10
CM.U.V.4	7152.45	<LoD	17.63	88.84	18305.76	282.38	16.67	245.16	204.20	7.29	23.4	26
CM.U.V.5	14379.02	<LoD	33.87	109.77	26383.39	720.86	21.35	143.34	352.06	23.16	44.5	5

August 2010

	Pseudo-total metal concentration (aqua regia extractable) mgkg^{-1}											
Sample	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**% organic matter**	**% <63 µm**	**% >2 mm**
BP.R.G.1	5360.92	<LoD	9.56	19.46	11011.72	173.31	12.56	34.00	85.74	1.96	1.18	88
BP.R.G.2	4766.01	<LoD	13.21	16.07	11192.83	251.48	9.90	42.64	99.77	4.79	1.72	81
BP.R.G.3	3859.99	<LoD	38.71	61.12	11153.89	168.27	23.53	65.55	89.83	3.31	6.65	81
BP.R.G.4	3965.68	<LoD	10.20	18.38	11015.14	257.98	10.68	104.78	81.92	2.62	1.89	89
BP.R.G.5	3329.24	<LoD	12.58	23.69	11825.06	166.78	10.88	48.56	83.25	1.18	3.13	89
BP.R.S.1	3533.58	<LoD	9.71	26.86	9921.39	159.40	10.54	71.74	107.87	3.20	6.24	22
BP.R.S.2	2633.48	<LoD	8.20	16.65	7532.42	137.40	7.87	34.88	82.52	1.51	4.95	19
BP.R.S.3	2597.30	<LoD	15.95	17.80	8735.15	124.18	8.17	43.51	89.85	2.36	2.68	42
BP.R.S.4	4375.63	<LoD	12.47	50.98	11921.78	160.12	9.00	50.75	119.79	5.83	9.6	6
BP.R.S.5	5973.37	<LoD	25.41	43.20	14765.45	185.69	11.79	88.75	176.79	2.93	16	14
BP.R.F.1	8894.51	5.95	39.47	166.67	18261.86	169.61	16.77	199.64	457.30	17.44	44.6	14
BP.R.F.2	3396.71	<LoD	19.05	51.09	8819.67	106.97	9.32	176.59	156.15	6.19	20.8	5
BP.R.F.3	4292.54	1.68	26.73	91.26	11210.93	139.92	10.75	161.64	290.66	6.82	30	7

BP.R.F.4	5233.79	<LoD	19.79	73.07	10757.39	124.34	10.48	147.00	212.27	21.89	33.1	13
BP.R.F.5	5250.67	<LoD	23.04	85.38	13692.59	153.50	14.15	129.91	253.74	11.00	32.3	48
BP.R.V.1	8778.09	2.04	39.52	212.63	22677.03	238.95	19.33	285.65	634.67	25.30	62.7	12
BP.R.V.2	9812.92	2.80	54.42	306.40	29255.67	536.69	24.64	279.36	919.07	27.65	38.7	27
BP.R.V.3	6943.16	<LoD	26.80	71.52	14791.97	219.51	13.06	139.70	229.64	39.34	83	21
BP.R.V.4	5393.52	<LoD	23.54	81.80	14644.27	224.62	12.89	145.70	263.07	14.17	31.6	33
BP.R.V.5	7072.17	1.32	34.67	178.28	18273.01	154.13	17.14	233.35	550.54	10.50	26	10
BP.U.G.1	3292.15	<LoD	10.91	25.52	8737.21	106.21	10.57	47.25	88.72	3.01	5.03	91
BP.U.G.2	5009.30	<LoD	19.12	38.12	11555.41	223.80	15.13	70.02	95.74	1.83	4.65	83
BP.U.G.3	5859.62	<LoD	18.37	18.65	10815.64	432.62	9.09	61.42	94.97	1.72	10.2	94
BP.U.G.4	5733.20	<LoD	14.45	24.80	8899.04	192.66	11.93	58.00	91.11	2.46	15.8	90
BP.U.G.5	3545.01	<LoD	4.89	17.03	7302.88	145.99	6.30	42.04	72.67	2.30	18.6	95
BP.U.S.1	3369.26	<LoD	12.78	54.20	7659.02	182.97	7.57	92.40	97.25	1.73	5.4	14
BP.U.S.2	2209.09	<LoD	8.14	12.31	5971.28	134.79	4.86	69.82	66.62	1.91	4.84	1
BP.U.S.3	3208.04	<LoD	7.82	18.81	6524.66	103.91	6.60	50.99	84.57	2.12	3.1	1
BP.U.S.4	3938.20	<LoD	26.71	41.26	8727.94	133.10	13.88	81.97	149.61	2.85	6.09	2
BP.U.S.5	2969.34	<LoD	5.65	12.95	6538.99	120.10	6.47	39.78	62.59	0.95	8.67	56
BP.U.F.1	3557.24	<LoD	16.90	60.23	8852.07	115.89	9.59	114.72	215.46	8.34	35	6
BP.U.F.2	3683.64	1.22	31.36	85.17	12468.27	120.11	9.93	162.55	277.70	8.29	56.1	6
BP.U.F.3	5964.49	1.64	22.90	83.09	12555.51	150.30	11.04	133.78	291.53	29.80	42.7	4
BP.U.F.4	4955.04	1.54	32.80	115.39	14388.30	180.72	13.66	167.55	404.44	14.50	39.5	25
BP.U.F.5	5041.80	<LoD	23.53	62.87	10855.11	129.58	10.13	132.26	221.53	7.50	30	5
BP.U.V.1	5532.32	1.86	39.86	171.29	17093.71	242.72	15.50	203.06	484.14	24.06	29.8	10
BP.U.V.2	8829.18	2.16	43.13	191.09	18393.69	199.47	19.53	228.53	620.99	40.54	21.2	14
BP.U.V.3	4545.92	1.24	29.43	123.09	14403.36	183.07	13.37	191.32	388.31	14.27	23.2	5
BP.U.V.4	5789.04	1.56	32.51	123.18	12933.47	145.20	14.08	159.80	369.43	15.01	12.7	6
BP.U.V.5	9232.17	2.30	48.33	213.84	20947.46	281.44	18.71	241.45	602.68	29.25	11.2	16
BG.R.G.1	6172.55	<LoD	39.99	44.26	33727.70	607.97	33.56	34.46	167.39	1.43	19.7	86
BG.R.G.2	4770.13	<LoD	21.77	121.60	50984.68	527.92	19.76	46.15	186.63	2.04	15.1	92
BG.R.G.3	4406.29	<LoD	9.10	16.51	16420.73	223.21	12.20	33.96	117.20	1.81	14.4	87
BG.R.G.4	7485.14	<LoD	21.03	97.16	33706.90	341.51	28.15	89.63	262.89	1.52	24.8	91
BG.R.G.5	6636.01	<LoD	91.69	108.04	25751.58	542.77	62.24	114.41	196.11	2.69	27.3	88
BG.R.V.1	3477.73	<LoD	11.07	24.59	11294.15	185.71	8.61	41.54	142.37	1.34	17.2	7
BG.R.V.2	3971.51	<LoD	21.23	24.06	15205.75	184.60	13.41	70.88	154.13	0.67	9.25	20
BG.R.V.3	3855.62	<LoD	12.56	42.18	14137.01	293.40	13.77	93.45	227.85	3.54	42.6	14
BG.R.V.4	5383.65	<LoD	47.95	77.74	19663.63	500.30	22.43	182.06	258.99	5.39	29.2	29
BG.R.V.5	6899.21	1.61	17.45	74.11	19031.42	315.11	16.36	94.12	230.23	6.05	5.38	20
BG.U.G.1	5168.69	<LoD	12.51	17.20	37741.89	326.02	21.38	39.26	142.69	2.81	13.7	93
BG.U.G.2	6173.81	<LoD	24.07	1974.71	56972.54	609.46	35.01	185.87	424.43	3.28	7.21	81
BG.U.G.3	6949.30	<LoD	10.95	1110.05	30218.81	436.65	16.99	50.55	144.00	1.39	26.6	78
BG.U.G.4	11007.27	<LoD	21.61	58.60	43631.50	377.08	27.49	157.54	482.93	2.11	28.9	83
BG.U.G.5	4475.74	<LoD	32.89	82.97	60863.13	324.44	56.77	419.46	135.51	1.86	13.7	89
BG.U.V.1	2710.37	<LoD	8.97	26.55	10918.68	193.54	8.44	90.71	118.57	2.89	29.8	4
BG.U.V.2	5159.38	<LoD	21.70	78.12	18665.93	487.33	15.66	137.19	285.01	9.34	27.4	4
BG.U.V.3	4139.22	<LoD	14.20	55.76	16021.01	336.86	12.28	108.76	209.33	7.32	23.2	4
BG.U.V.4	7307.87	<LoD	26.51	85.46	21007.99	356.98	15.94	124.80	244.30	4.38	12.7	14
BG.U.V.5	2322.94	<LoD	13.06	25.79	10698.53	176.64	7.34	86.35	107.68	2.60	11.2	1
SP.R.G.1	11511.25	<LoD	26.23	29.49	28663.71	378.75	28.65	19.67	76.12	3.08	48.7	91
SP.R.G.2	9543.66	<LoD	38.15	53.10	33700.06	285.56	39.96	28.47	95.55	2.91	68.2	96
SP.R.G.3	6953.36	<LoD	23.10	39.06	33243.97	514.93	31.09	28.49	111.20	4.41	58.6	93
SP.R.G.4	7464.93	<LoD	15.66	13.82	29190.98	181.26	20.55	18.17	63.73	2.56	50.4	96
SP.R.G.5	19563.43	<LoD	34.33	34.44	41945.28	223.62	33.76	21.07	100.29	4.04	85.9	94
SP.R.F.1	16279.77	2.59	42.11	194.58	32578.95	677.91	29.61	186.42	617.00	38.29	100	56
SP.R.F.2	27499.80	2.30	54.15	181.78	38020.08	444.24	34.33	172.94	581.50	24.70	74.6	11

SP.R.F.3	26422.02	2.80	57.16	207.73	40924.37	481.08	34.86	214.83	688.28	30.26	85.3	18
SP.R.F.4	13193.31	1.88	35.50	161.52	31528.64	344.49	32.96	141.71	451.52	17.84	88.3	37
SP.R.F.5	13581.38	2.97	46.01	235.86	32840.96	472.50	33.39	221.40	711.67	27.70	93.5	7
SP.R.V.1	11976.87	2.97	42.00	222.62	30775.43	649.83	28.38	216.66	671.80	31.13	89.7	20
SP.R.V.2	15954.18	2.31	44.02	195.99	33826.03	362.69	34.06	185.65	594.61	29.17	86.4	24
SP.R.V.3	33100.13	3.14	67.43	261.76	43797.14	658.70	41.38	242.61	798.65	27.87	96	0
SP.R.V.4	28908.52	<LoD	47.15	102.98	36643.98	316.30	38.39	82.30	276.93	11.22	83.6	22
SP.R.V.5	26783.41	<LoD	46.95	108.11	47754.38	271.59	38.47	93.85	335.24	13.24	87.1	20
SP.U.G.1	7973.92	<LoD	40.03	94.73	54561.67	1041.09	40.92	70.04	324.07	3.54	10.5	94
SP.U.G.2	7153.38	2.78	45.01	83.78	98561.09	3987.11	63.51	65.86	534.16	6.38	38.2	99
SP.U.G.3	7298.67	1.53	25.62	77.16	39379.06	2176.36	45.63	65.54	280.99	6.01	99.7	99
SP.U.G.4	14974.90	<LoD	34.38	52.47	37414.86	771.50	34.48	80.94	262.10	5.11	28.4	95
SP.U.G.5	5154.26	<LoD	26.31	160.92	60719.88	659.16	29.48	107.21	383.79	4.37	6.94	96
SP.U.F.1	10449.73	1.23	26.82	59.76	20880.26	287.32	17.68	112.24	254.75	5.23	22.9	3
SP.U.F.2	6373.69	<LoD	14.48	35.72	17857.63	210.65	15.36	205.99	180.51	4.42	38.3	3
SP.U.F.3	17122.93	1.04	32.58	52.73	37730.03	640.88	28.34	107.87	339.63	6.26	32.9	10
SP.U.F.4	5573.89	<LoD	14.51	26.54	14889.76	189.97	11.91	52.70	144.68	3.68	4.65	1
SP.U.F.5	5340.26	<LoD	16.45	54.85	17652.13	255.15	14.74	119.57	213.46	6.74	23.7	10
CM.R.G.1	4720.75	<LoD	9.03	15.38	21580.60	205.51	12.41	31.59	65.04	1.70	15.1	84
CM.R.G.2	3953.08	<LoD	15.25	18.33	18696.34	508.07	15.12	34.31	99.17	2.23	21.9	96
CM.R.G.3	4198.74	<LoD	42.00	81.75	22059.62	665.47	32.58	23.78	101.85	1.97	18	96
CM.R.G.4	2414.32	<LoD	25.25	28.60	28405.68	1752.30	26.02	51.65	62.75	3.01	13.6	95
CM.R.G.5	9241.16	<LoD	43.84	685.34	28805.37	937.87	38.05	44.02	130.22	3.41	32.5	88
CM.R.F.1	3671.67	<LoD	13.06	22.49	13155.14	343.73	10.20	43.68	89.52	10.66	12.1	15
CM.R.F.2	5477.63	<LoD	15.97	70.39	15675.05	418.62	12.72	94.61	210.88	13.22	19.5	2
CM.R.F.3	2924.11	<LoD	5.22	9.99	9250.30	255.03	7.32	26.69	65.99	2.54	17.1	2
CM.R.F.4	2831.58	<LoD	13.20	19.74	10638.94	229.33	8.69	111.30	95.12	7.80	6.43	8
CM.R.F.5	11226.45	<LoD	26.42	89.32	20559.42	519.70	17.34	129.49	287.44	12.30	28.6	1
CM.R.V.1	5206.81	<LoD	28.55	63.30	15568.61	397.86	13.93	92.59	203.65	11.62	25.6	13
CM.R.V.2	8925.65	<LoD	26.90	108.45	22072.67	662.24	18.78	149.23	331.75	18.57	50.7	2
CM.R.V.3	7686.60	<LoD	24.16	149.55	20299.68	604.84	18.77	139.27	301.77	14.69	46.6	0
CM.R.V.4	9293.80	<LoD	31.05	130.73	23711.98	711.07	20.26	184.77	390.61	18.58	41.4	3
CM.R.V.5	4647.65	<LoD	15.55	53.91	15087.17	316.76	12.87	91.87	201.68	10.30	16.2	16
CM.U.G.1	5464.12	<LoD	36.95	24.86	90922.03	1119.51	42.84	29.64	103.98	3.33	5.65	99
CM.U.G.2	4345.25	<LoD	21.94	18.00	26106.65	968.30	17.59	29.30	59.82	1.61	15	94
CM.U.G.3	2969.56	<LoD	14.61	14.96	33466.10	464.87	15.24	16.11	50.86	0.91	11.1	85
CM.U.G.4	4511.74	<LoD	15.91	17.44	27340.06	2080.85	27.70	22.30	79.55	2.01	32.8	93
CM.U.G.5	3965.82	<LoD	6.16	14.31	26599.40	436.80	12.31	329.57	48.96	1.75	1.27	91
CM.U.F.1	2439.08	<LoD	9.79	19.74	9520.03	180.45	8.32	33.50	82.25	2.66	14.3	4
CM.U.F.2	3151.00	<LoD	13.41	37.84	10482.84	182.72	8.56	43.59	109.41	2.99	24.1	19
CM.U.F.3	11535.06	4.33	34.08	92.58	20655.32	525.00	18.63	113.71	319.20	17.68	23.9	20
CM.U.F.4	8089.25	1.86	21.86	72.67	16552.73	391.41	14.28	87.25	223.55	8.38	25.8	10
CM.U.F.5	4261.57	1.29	16.63	50.43	13919.16	377.73	10.95	89.61	176.55	7.27	33.7	51
CM.U.V.1	3905.42	<LoD	15.14	28.57	22049.05	349.40	10.76	50.97	108.08	4.50	18.2	12
CM.U.V.2	5204.26	<LoD	22.56	31.53	45103.62	1512.45	32.94	43.23	99.91	3.13	24.9	4
CM.U.V.3	6621.74	<LoD	21.21	89.96	20738.92	551.48	15.44	118.00	269.46	15.56	34.6	5
CM.U.V.4	9533.90	1.52	30.31	119.97	23836.56	677.51	20.66	149.98	389.56	19.73	50.8	5
CM.U.V.5	4923.64	1.73	18.50	59.96	14989.13	432.78	13.66	85.87	221.88	12.78	57.2	6

November 2010

Sample	Pseudo-total metal concentration (aqua regia extractable) ($mgkg^{-1}$)									% organic matter	% <63 µm	% >2 mm
	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn			
BP.R.G.1	3723.52	<LoD	11.54	19.95	11155.34	205.71	12.02	36.80	79.47	1.36	5.57	89
BP.R.G.2	4523.76	<LoD	14.72	21.82	11303.34	236.23	9.65	42.95	78.84	1.29	8.08	82
BP.R.G.3	3048.56	<LoD	11.70	19.27	7752.37	228.84	7.45	42.29	79.62	1.56	1.25	23
BP.R.G.4	2858.61	<LoD	9.37	17.91	7592.10	203.67	6.14	33.44	76.45	1.37	1.66	93
BP.R.G.5	5931.06	<LoD	12.77	140.95	33695.89	400.57	29.75	108.44	404.33	1.87	8.91	87
BP.R.S.1	3425.10	<LoD	10.15	161.94	9175.73	223.96	7.71	28.55	74.55	1.56	14.7	27
BP.R.S.2	3209.31	<LoD	53.72	15.05	7256.06	131.98	5.39	33.72	66.56	1.06	2.26	2
BP.R.S.3	2673.46	<LoD	7.17	14.26	6271.38	156.21	5.95	35.39	75.81	1.23	1.22	2
BP.R.S.4	6556.83	<LoD	24.13	37.46	12955.61	246.96	16.67	59.37	144.40	3.88	3.3	5
BP.R.S.5	5703.03	<LoD	13.03	26.35	14960.98	261.70	10.02	57.37	115.07	3.13	15.4	7
BP.R.F.1	3542.62	<LoD	14.15	35.15	8605.56	142.20	7.52	63.34	134.66	3.58	29.6	4
BP.R.F.2	8807.92	2.16	48.47	193.13	20207.31	190.79	20.05	242.71	555.10	16.82	25.6	9
BP.R.F.3	3253.69	<LoD	18.42	53.62	9672.61	142.93	8.82	106.99	175.36	6.13	21.1	5
BP.R.F.4	3110.45	<LoD	15.60	32.71	7620.96	120.45	6.90	64.39	138.69	3.16	10.7	2
BP.R.F.5	3040.77	<LoD	12.61	25.95	8890.21	103.08	7.35	53.59	103.53	4.85	8.61	5
BP.R.V.1	10394.43	2.86	54.04	271.82	25094.86	397.87	24.15	443.10	768.21	21.64	49.9	1
BP.R.V.2	3782.77	3.35	19.04	43.33	13247.65	152.06	12.24	153.59	177.46	3.84	5.88	3
BP.R.V.3	10097.13	1.01	46.92	204.62	20057.17	202.57	22.17	259.90	679.54	7.89	43.7	19
BP.R.V.4	6741.16	<LoD	27.92	71.89	14615.78	231.69	15.43	129.56	228.29	7.49	29.1	12
BP.R.V.5	3566.92	<LoD	18.65	31.45	12127.31	200.90	8.64	73.56	117.78	2.82	22.8	2
BP.U.G.1	2571.63	<LoD	8.81	64.08	8055.86	98.67	5.51	63.91	643.90	1.65	17.3	87
BP.U.G.2	5244.79	<LoD	10.01	21.21	9163.78	241.00	7.97	50.26	76.89	1.73	22.9	67
BP.U.G.3	5809.24	<LoD	14.54	18.33	13522.94	263.51	12.37	37.99	107.14	1.42	14.5	18
BP.U.G.4	5432.00	<LoD	9.49	24.99	10616.42	214.79	9.57	84.20	98.63	1.47	20.4	89
BP.U.G.5	5286.45	<LoD	13.45	17.20	8988.84	282.38	11.61	40.83	87.09	2.59	12.4	88
BP.U.S.1	2950.32	<LoD	11.48	17.10	7145.48	146.84	5.81	44.80	74.53	3.32	1.87	2
BP.U.S.2	3004.98	<LoD	16.45	16.07	9729.55	145.74	10.12	75.09	113.25	1.61	13.5	1
BP.U.S.3	2366.06	<LoD	14.36	15.93	5853.15	180.61	5.82	35.36	63.86	1.37	2.79	8
BP.U.S.4	3681.77	<LoD	6.13	24.21	7522.15	244.17	7.32	37.91	149.07	1.19	10.4	45
BP.U.S.5	3031.93	<LoD	7.59	16.47	4878.53	153.18	4.82	41.52	64.86	1.29	16.7	6
BP.U.F.1	6377.51	1.70	30.51	165.03	13238.36	136.34	14.50	198.77	406.43	12.50	32.6	17
BP.U.F.2	4956.08	2.28	30.74	131.60	14242.26	173.63	13.97	210.45	415.07	15.08	30.6	9
BP.U.F.3	3943.20	1.43	30.36	122.66	12109.60	155.82	12.47	157.68	360.21	9.90	16.3	14
BP.U.F.4	3553.15	1.02	20.06	71.08	9377.59	162.74	9.88	143.30	243.62	9.51	18	10
BP.U.F.5	5315.29	1.41	33.27	95.22	12520.49	141.96	13.87	158.24	314.01	9.13	34.6	3
BP.U.V.1	4266.73	1.22	27.12	107.31	12748.35	190.77	13.50	189.76	332.50	11.90	21.7	15
BP.U.V.2	7353.50	2.77	48.40	229.90	21528.52	258.39	21.65	282.29	709.63	20.42	36.7	12
BP.U.V.3	8036.75	2.54	44.28	183.43	18021.53	196.95	18.97	261.65	581.64	17.29	33.8	8
BP.U.V.4	7432.47	1.73	40.92	158.80	16617.81	208.85	16.61	219.58	528.19	14.82	31.6	12
BP.U.V.5	4361.96	1.03	22.78	89.10	12119.51	205.96	11.35	178.59	307.24	6.38	28.6	9
BG.R.G.1	4003.71	<LoD	10.08	102.09	22769.24	379.98	14.87	37.24	294.98	1.58	21.8	84
BG.R.G.2	4800.98	<LoD	13.80	33.18	21891.07	255.28	16.88	121.09	134.75	1.99	31.5	92
BG.R.G.3	4848.37	<LoD	20.34	41.03	26906.59	235.78	13.95	52.32	116.28	1.71	33	85
BG.R.G.4	5712.58	<LoD	10.70	56.57	30448.79	397.94	21.82	60.44	486.27	1.15	6.98	89
BG.R.G.5	3746.77	<LoD	19.29	68.53	29847.28	336.35	20.95	59.49	266.09	1.32	43.3	91
BG.R.V.1	5268.41	<LoD	38.86	43.21	18627.57	309.25	13.64	218.47	204.02	2.03	28.4	2
BG.R.V.2	4232.29	<LoD	17.51	49.28	13893.41	170.02	9.82	35.00	147.28	0.49	28	7
BG.R.V.3	4125.53	<LoD	16.01	62.44	14277.37	221.90	11.59	121.57	190.51	5.13	21.1	6
BG.R.V.4	3801.65	<LoD	23.63	60.06	17842.36	419.12	17.24	171.16	246.40	5.93	33.7	13
BG.R.V.5	3341.79	<LoD	14.74	52.66	16330.98	386.58	12.96	94.85	211.23	7.69	24.7	11

BG.U.G.1	7158.67	<LoD	25.89	20.38	43316.92	480.35	18.94	155.96	142.44	2.34	17.7	94
BG.U.G.2	5330.72	<LoD	8.47	18.23	14115.37	417.76	9.56	45.87	136.21	1.83	15.8	89
BG.U.G.3	4762.05	<LoD	14.55	53.00	40024.51	418.36	16.63	46.02	212.77	1.19	11.1	94
BG.U.G.4	5361.06	<LoD	12.24	22.72	28597.93	304.95	16.97	48.88	147.09	1.85	14.3	87
BG.U.G.5	3175.98	<LoD	7.98	16.48	16454.48	203.44	9.78	87.84	114.51	1.46	20.2	79
BG.U.V.1	4181.85	<LoD	26.06	58.00	17453.61	692.06	16.97	193.94	305.21	5.83	14.2	10
BG.U.V.2	6785.53	<LoD	19.59	68.24	19002.38	538.85	15.52	177.90	300.16	7.73	21.7	20
BG.U.V.3	3642.09	<LoD	10.19	33.67	18786.08	239.93	10.63	64.09	155.56	4.40	22.2	46
BG.U.V.4	3415.27	<LoD	11.08	47.65	15165.21	254.14	11.12	89.29	198.17	4.69	24.4	4
BG.U.V.5	4476.66	<LoD	21.18	31.93	17012.31	321.86	11.72	127.42	220.56	1.76	27.6	3
SP.R.G.1	19826.57	<LoD	31.97	42.34	40159.01	343.17	29.56	33.81	152.38	7.11	85.2	96
SP.R.G.2	19327.44	<LoD	31.54	43.83	40574.13	374.01	34.10	38.48	157.68	5.90	83.3	95
SP.R.G.3	4735.04	<LoD	15.05	27.57	37704.21	283.21	23.66	28.81	101.31	4.81	43	94
SP.R.G.4	12980.18	<LoD	22.50	26.08	25795.35	258.21	22.46	26.06	92.45	4.14	39.4	91
SP.R.G.5	27436.91	<LoD	41.34	33.92	37122.75	451.41	30.04	24.94	123.99	5.20	59	91
SP.R.F.1	23292.78	2.60	53.41	195.86	36362.58	538.09	36.54	196.96	619.39	25.85	89.9	17
SP.R.F.2	11439.49	2.57	39.50	201.42	31039.23	649.16	30.76	200.25	602.04	25.16	85.7	22
SP.R.F.3	21112.66	1.41	42.80	123.02	38248.30	327.46	39.91	112.75	380.42	12.38	79.7	38
SP.R.F.4	25815.81	3.74	64.10	277.45	42376.47	770.48	38.02	255.63	823.92	27.56	96.6	0
SP.R.F.5	26404.48	2.63	56.54	211.10	41979.42	580.75	36.86	198.58	660.89	23.61	77.8	2
SP.R.V.1	25278.39	3.10	57.44	236.91	40182.57	716.42	35.85	229.82	741.74	34.02	90.3	4
SP.R.V.2	11816.00	<LoD	27.76	92.62	37106.51	243.74	38.39	80.21	270.82	10.81	94	21
SP.R.V.3	24928.74	<LoD	45.47	90.35	45260.73	392.37	41.74	81.73	278.03	11.37	78.2	14
SP.R.V.4	23225.63	3.26	58.99	247.37	41109.67	702.38	37.25	241.39	816.52	33.28	100	31
SP.R.V.5	20276.55	2.39	49.85	189.49	40845.03	447.22	40.02	181.65	614.05	18.62	79.8	48
SP.U.G.1	3934.38	<LoD	14.11	56.91	19584.64	371.02	13.16	69.09	229.81	2.80	39	89
SP.U.G.2	7076.97	<LoD	19.18	90.88	30896.22	328.00	23.53	86.40	323.38	3.91	23.8	97
SP.U.G.3	7525.16	<LoD	69.61	87.07	36585.22	436.51	25.35	69.70	279.16	2.56	25.4	90
SP.U.G.4	5070.33	2.07	16.85	57.71	32117.38	533.16	23.88	89.05	231.43	7.21	63.5	98
SP.U.G.5	6283.98	<LoD	15.69	52.72	37289.17	298.90	24.94	61.17	321.27	1.89	27.6	89
SP.U.F.1	2929.51	1.57	13.66	22.78	12246.94	111.92	9.75	42.80	138.38	2.52	6.88	3
SP.U.F.2	7841.22	<LoD	18.44	40.92	25789.47	310.23	18.17	108.76	210.52	4.95	9.04	29
SP.U.F.3	5024.38	<LoD	14.37	31.80	19015.39	320.13	13.62	60.51	206.05	6.19	29.4	1
SP.U.F.4	4405.70	<LoD	11.29	23.70	16375.66	207.68	11.77	61.23	132.52	2.94	18.3	7
SP.U.F.5	4183.29	1.07	14.31	35.79	17524.09	238.60	15.01	65.40	166.99	3.56	30.3	3
CM.R.G.1	3758.65	<LoD	14.09	24.91	27162.06	462.03	16.41	34.10	112.94	1.59	15.1	78
CM.R.G.2	2750.35	<LoD	14.08	15.15	15647.81	289.07	8.24	33.65	69.37	1.60	1.56	25
CM.R.G.3	4107.20	<LoD	30.93	17.96	21467.02	269.22	11.56	25.82	68.31	1.71	20.5	83
CM.R.G.4	5005.65	<LoD	11.51	16.59	16373.07	285.78	11.44	34.79	70.50	2.27	14.4	88
CM.R.G.5	4043.59	<LoD	26.41	14.79	35641.06	488.64	15.00	21.76	73.64	1.53	11.9	84
CM.R.F.1	4922.15	<LoD	14.54	30.55	12296.57	182.32	10.60	62.05	131.62	4.61	10.9	11
CM.R.F.2	2618.83	<LoD	11.33	11.70	9446.04	147.79	6.00	27.97	59.14	1.57	17	12
CM.R.F.3	2791.05	<LoD	7.96	114.14	13593.51	169.77	12.01	25.23	80.44	3.12	6.73	7
CM.R.F.4	2326.56	<LoD	14.82	15.30	13148.08	164.97	8.20	33.87	73.65	2.08	14.8	32
CM.R.F.5	4578.24	<LoD	13.71	18.73	15462.12	335.83	9.98	43.77	89.74	1.90	21	16
CM.R.V.1	6775.49	<LoD	19.12	33.00	15754.71	378.30	12.05	66.65	133.93	5.11	26.1	6
CM.R.V.2	3717.50	<LoD	18.77	36.11	13861.61	259.40	11.29	99.46	134.63	4.78	24	3
CM.R.V.3	3634.27	<LoD	16.39	51.67	13198.62	284.41	11.88	70.27	157.69	6.41	17.5	6
CM.R.V.4	4861.46	<LoD	19.13	74.22	14931.78	453.06	13.75	134.65	238.85	9.92	44.9	2
CM.R.V.5	5530.09	<LoD	26.63	42.65	15217.18	299.23	12.04	74.97	171.37	4.77	19.6	9
CM.U.G.1	4868.83	<LoD	11.70	21.52	23698.18	356.73	11.93	33.95	96.96	3.27	5.51	87
CM.U.G.2	3432.50	<LoD	10.55	10.91	14824.81	299.35	9.27	16.37	48.07	1.57	4.65	90
CM.U.G.3	2032.54	<LoD	8.10	11.62	17339.46	206.94	9.44	23.41	64.28	1.72	17.3	78
CM.U.G.4	3796.24	<LoD	13.31	19.09	21483.46	393.75	9.83	36.73	83.25	2.83	9.34	91
CM.U.G.5	5980.05	<LoD	11.02	101.59	28995.97	269.99	10.70	45.32	193.39	2.19	15.5	81
CM.U.F.1	15911.45	3.25	45.31	165.66	29443.06	556.11	27.69	222.20	572.50	24.65	100.0	11

CM.U.F.2	9886.51	3.72	37.06	169.11	25821.08	538.76	24.34	217.88	545.25	27.53	95.8	13
CM.U.F.3	16264.44	2.37	42.26	144.22	27031.64	539.27	25.29	197.91	472.60	23.04	70.7	9
CM.U.F.4	13278.21	1.86	34.65	149.11	24906.02	588.89	22.33	174.49	441.39	15.75	54.5	29
CM.U.F.5	6789.65	1.09	23.02	91.99	18541.89	416.43	17.12	139.74	312.42	11.71	68.6	9
CM.U.V.1	5079.09	<LoD	18.29	58.01	17693.11	556.36	13.43	69.00	163.46	7.17	23.4	18
CM.U.V.2	3389.40	<LoD	19.11	11.65	14751.90	266.30	10.07	43.09	69.87	1.47	11.5	30
CM.U.V.3	10163.46	2.49	30.04	121.87	24197.24	689.36	21.00	160.00	384.79	20.44	41.3	7
CM.U.V.4	12177.56	1.42	34.01	114.35	24401.38	832.33	21.94	154.04	399.02	21.11	58.6	0
CM.U.V.5	10349.66	1.60	33.82	76.37	19628.35	396.31	16.94	99.29	267.80	11.32	34.9	10

Appendix III

Full data set for Chapter 4, Sutcliffe Park August data set

SP = Sutcliffe Park
R = Restored
U = Unrestored
G = Gravel
F = Finer
V = In-channel vegetation
1 – 5 = samples 1 to 5

August 2010

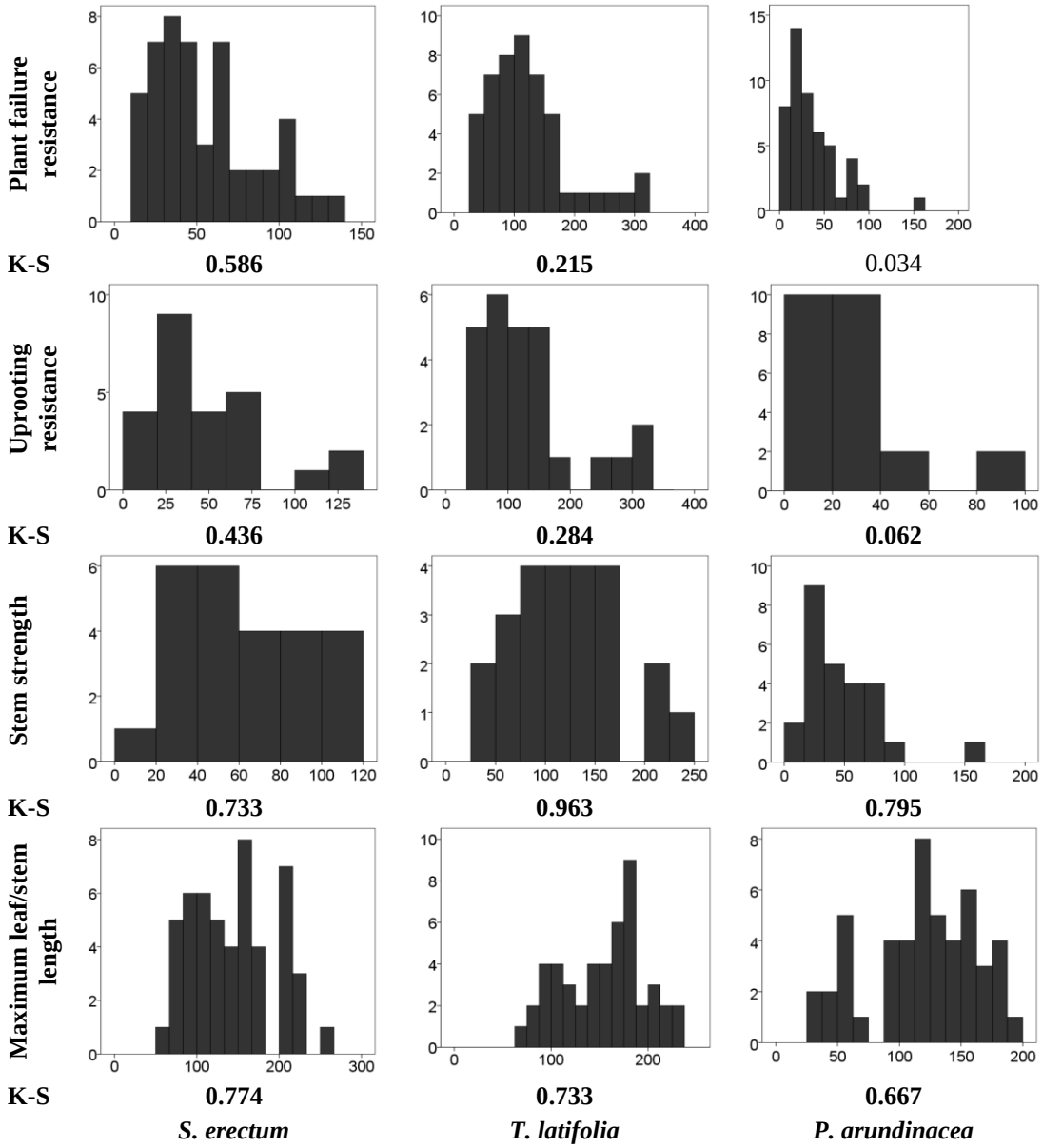
Sample	Pseudo-total metal concentration (aqua regia extractable) $mgkg^{-1}$									% organic matter	% <63 µm	% >2 mm
	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn			
SP.R.G.1	11511.25	<LoD	26.23	29.49	28663.71	378.75	28.65	19.67	76.12	3.08	48.7	91
SP.R.G.2	9543.66	<LoD	38.15	53.10	33700.06	285.56	39.96	28.47	95.55	2.91	68.2	96
SP.R.G.3	6953.36	<LoD	23.10	39.06	33243.97	514.93	31.09	28.49	111.20	4.41	58.6	93
SP.R.G.4	7464.93	<LoD	15.66	13.82	29190.98	181.26	20.55	18.17	63.73	2.56	50.4	96
SP.R.G.5	19563.43	<LoD	34.33	34.44	41945.28	223.62	33.76	21.07	100.29	4.04	85.9	94
SP.R.F.1	16279.77	2.59	42.11	194.58	32578.95	677.91	29.61	186.42	617.00	38.29	100	56
SP.R.F.2	27499.80	2.30	54.15	181.78	38020.08	444.24	34.33	172.94	581.50	24.70	74.6	11
SP.R.F.3	26422.02	2.80	57.16	207.73	40924.37	481.08	34.86	214.83	688.28	30.26	85.3	18
SP.R.F.4	13193.31	1.88	35.50	161.52	31528.64	344.49	32.96	141.71	451.52	17.84	88.3	37
SP.R.F.5	13581.38	2.97	46.01	235.86	32840.96	472.50	33.39	221.40	711.67	27.70	93.5	7
SP.R.V.1	11976.87	2.97	42.00	222.62	30775.43	649.83	28.38	216.66	671.80	31.13	89.7	20
SP.R.V.2	15954.18	2.31	44.02	195.99	33826.03	362.69	34.06	185.65	594.61	29.17	86.4	24
SP.R.V.3	33100.13	3.14	67.43	261.76	43797.14	658.70	41.38	242.61	798.65	27.87	96	0
SP.R.V.4	28908.52	<LoD	47.15	102.98	36643.98	316.30	38.39	82.30	276.93	11.22	83.6	22
SP.R.V.5	26783.41	<LoD	46.95	108.11	47754.38	271.59	38.47	93.85	335.24	13.24	87.1	20
SP.U.G.1	7973.92	<LoD	40.03	94.73	54561.67	1041.09	40.92	70.04	324.07	3.54	10.5	94
SP.U.G.2	7153.38	2.78	45.01	83.78	98561.09	3987.11	63.51	65.86	534.16	6.38	38.2	99
SP.U.G.3	7298.67	1.53	25.62	77.16	39379.06	2176.36	45.63	65.54	280.99	6.01	99.7	99
SP.U.G.4	14974.90	<LoD	34.38	52.47	37414.86	771.50	34.48	80.94	262.10	5.11	28.4	95
SP.U.G.5	5154.26	<LoD	26.31	160.92	60719.88	659.16	29.48	107.21	383.79	4.37	6.94	96
SP.U.F.1	10449.73	1.23	26.82	59.76	20880.26	287.32	17.68	112.24	254.75	5.23	22.9	3
SP.U.F.2	6373.69	<LoD	14.48	35.72	17857.63	210.65	15.36	205.99	180.51	4.42	38.3	3
SP.U.F.3	17122.93	1.04	32.58	52.73	37730.03	640.88	28.34	107.87	339.63	6.26	32.9	10
SP.U.F.4	5573.89	<LoD	14.51	26.54	14889.76	189.97	11.91	52.70	144.68	3.68	4.65	1
SP.U.F.5	5340.26	<LoD	16.45	54.85	17652.13	255.15	14.74	119.57	213.46	6.74	23.7	10

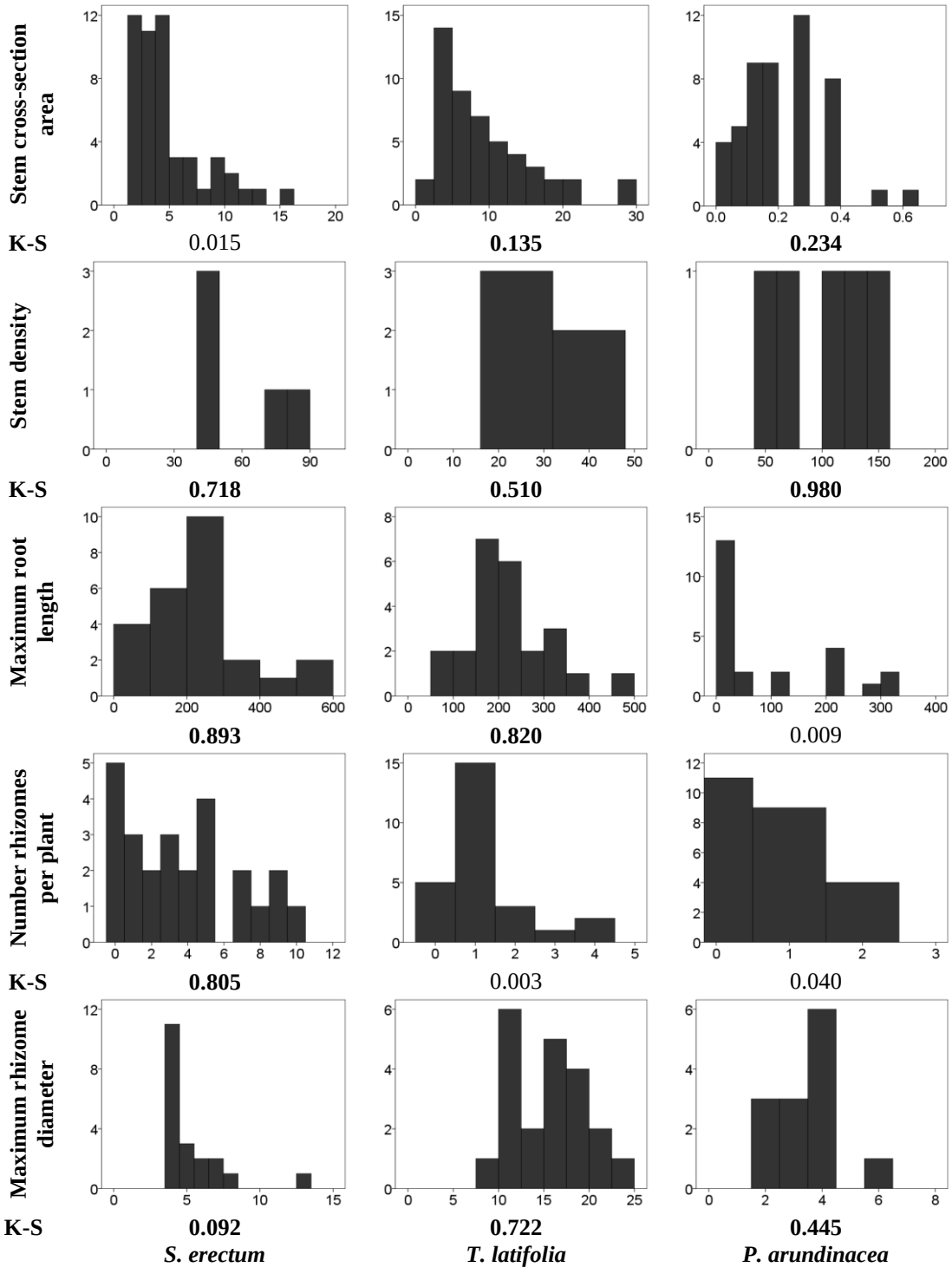
Sample	Acetic acid extractable metal concentration ($mgkg^{-1}$)									Fe (II) concen (mgl^{-1})	pH
	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn		
SP.R.G.1	50.36	<LoD	<LoD	7.01	137.98	84.33	1.68	<LoD	29.79	0.60	7.95
SP.R.G.2	37.35	<LoD	<LoD	8.02	156.68	216.00	2.90	<LoD	33.96	0.43	7.58
SP.R.G.3	26.02	<LoD	<LoD	3.95	193.23	124.52	2.34	<LoD	37.48	0.19	7.80
SP.R.G.4	27.06	<LoD	<LoD	2.27	120.42	67.41	<LoD	<LoD	23.20	0.68	7.75
SP.R.G.5	28.35	<LoD	<LoD	4.22	116.98	60.27	<LoD	<LoD	21.58	0.18	7.75
SP.R.F.1	88.78	0.74	0.36	5.82	239.34	333.29	4.74	2.29	214.53	1.09	6.92
SP.R.F.2	92.05	0.75	0.29	5.45	446.62	197.84	5.55	2.38	205.92	0.81	7.11
SP.R.F.3	110.86	0.82	0.36	5.90	524.67	224.17	5.44	3.64	240.08	4.99	7.04
SP.R.F.4	76.82	0.74	<LoD	7.86	512.55	121.39	5.16	2.15	171.92	1.30	6.94
SP.R.F.5	91.07	1.05	0.37	6.54	518.65	184.68	7.20	2.78	265.82	0.97	7.09
SP.R.V.1	84.72	0.89	0.34	6.38	416.08	395.08	5.26	2.09	254.96	1.01	6.88
SP.R.V.2	123.29	0.77	0.41	7.41	595.41	164.84	6.11	4.54	204.30	0.94	7.11
SP.R.V.3	109.60	1.06	0.39	8.21	606.44	308.14	7.16	4.56	275.93	0.95	7.01
SP.R.V.4	66.79	<LoD	<LoD	8.46	336.61	105.81	3.47	<LoD	82.90	0.29	6.91
SP.R.V.5	75.73	<LoD	<LoD	6.64	503.56	86.02	4.52	<LoD	115.61	0.72	7.22
SP.U.G.1	66.11	<LoD	<LoD	5.96	19.94	253.07	2.78	<LoD	67.53	0.14	7.54
SP.U.G.2	43.93	0.84	<LoD	7.61	49.29	406.56	3.78	<LoD	95.64	0.19	7.57
SP.U.G.3	44.24	0.84	<LoD	3.81	41.19	925.03	5.18	<LoD	81.97	0.30	7.62
SP.U.G.4	58.30	<LoD	<LoD	3.89	120.82	236.36	2.55	<LoD	110.10	0.16	7.65
SP.U.G.5	61.25	<LoD	<LoD	12.88	92.49	293.44	2.06	2.18	73.10	0.47	7.52
SP.U.F.1	83.40	0.98	<LoD	4.50	310.11	158.43	2.52	3.76	129.88	0.80	7.16
SP.U.F.2	66.04	<LoD	<LoD	2.51	174.06	81.60	1.64	3.29	97.02	0.77	7.23
SP.U.F.3	49.03	<LoD	<LoD	3.86	120.69	224.39	2.27	2.19	118.07	1.06	7.34
SP.U.F.4	60.79	<LoD	<LoD	2.15	371.78	88.35	<LoD	2.93	66.64	6.34	7.16
SP.U.F.5	76.46	<LoD	<LoD	4.03	227.11	148.29	2.24	3.19	89.01	5.14	7.40

Appendix IV

Frequency Histograms and Kolmogorov-Smirnov (K-S) Normality Test results for Chapter 5 data

Kolmogorov-Smirnov (K-S) normality test p-values below frequency histograms. Those normally distributed ($p > 0.05$) shown in bold font, those non-normally distributed ($p < 0.05$) shown in regular font.




Stem cross-section area
K-S
0.015
0.135
0.234
Stem density
K-S
0.718
0.510
0.980
Maximum root length
0.893
0.820
0.009
Number rhizomes per plant
K-S
0.805
0.003
0.040
Maximum rhizome diameter
K-S
0.092
0.722
0.445
S. erectum
T. latifolia
P. arundinacea

Appendix V

Quality Control Results for Laboratory Analysis in Chapter 6

Aqua regia sediment extractions (pseudo-total metal concentrations)

Recoveries (%) CRM LGC6187 (aqua regia)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	90	84	94	108	84	80	87	91
AR2	93	89	99	105	86	91	89	95
	94	89	99	105	88	92	92	96

% RSD of Triplicate Extractions (aqua regia)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	<LoD	3.85	10.06	9.00	8.42	9.59	12.71	9.31
AR2	6.26	1.27	4.27	3.83	2.32	2.81	1.81	4.04
	3.75	2.74	4.47	6.89	2.95	3.59	2.68	4.24

Analytical Blanks (mgl^{-1}) (aqua regia)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	<LoD	0.004	0.002	0.183	0.002	<LoD	<LoD	<LoD
AR2	<LoD	0.004	0.003	0.102	0.003	<LoD	<LoD	<LoD
	<LoD	0.002	<LoD	0.901	0.001	<LoD	<LoD	<LoD

% RSD of Analytical Triplicate on ICP-OES (aqua regia)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AR1	<LoD	0.58	0.43	1.77	0.88	1.64	1.59	0.47
AR2	7.59	0.48	0.01	1.15	0.98	0.30	0.31	0.29
	5.41	0.47	0.10	1.39	0.39	0.61	0.40	0.32

Acetic acid sediment extractions

% Recovery BCR701 (acetic acid)						
Batch	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
AA1	87	84	84	76	83	81
AA2	88	90	102	86	74	104
	84	80	94	76	75	87

% RSD of Triplicate Extractions (acetic acid)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	<LoD	<LoD	3.52	2.34	1.07	2.09	<LoD	1.00
AA2	2.77	14.48	13.27	1.23	1.88	0.35	<LoD	3.63
	5.13	7.11	10.1	2.82	1.57	1.52	<LoD	1.22

Analytical blanks (mgl^{-1}) (acetic acid)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	<LoD	<LoD	<LoD	0.016	<LoD	<LoD	<LoD	0.012
AA2	<LoD	<LoD	0.130	0.003	0.001	<LoD	<LoD	0.092
	<LoD	<LoD	0.005	0.082	0.004	<LoD	<LoD	<LoD

% RSD of Analytical Triplicates on ICP-OES (acetic acid)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
AA1	<LoD	<LoD	2.35	1.02	0.95	3.52	<LoD	0.31
AA2	3.58	3.35	34.48	0.44	0.49	1.71	<LoD	2.45
	3.62	2.51	10.76	0.25	0.16	0.32	<LoD	0.35

Particle Size Analyser

Bold figure indicates CRM outside of acceptable range.

Median % <63 µm Micrometrics CRM		
Batch	**CRM1**	**CRM2**
PSA1	**3.21**	3.71
PSA2	3.70	3.86
PSA3	**3.59**	**4.01**
PSA4	3.68	3.87
PSA5	3.79	3.65

Macrophyte metals

% Recovery BCR060 (macrophyte)					
Batch	**Cd**	**Cu**	**Mn**	**Pb**	**Zn**
M1	99	92	87	87	92
M2	103	105	96	101	103
	98	97	89	90	95

% RSD of Triplicate Extractions (macrophyte)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
M1	<LoD	<LoD	4.33	3.42	0.32	<LoD	<LoD	2.87
M2	<LoD	<LoD	11.88	5.36	0.87	<LoD	<LoD	<LoD
	<LoD	<LoD	9.40	6.59	5.39	2.93	<LoD	6.29

Analytical blanks (mgl^{-1}) (macrophyte)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
M1	<LoD	<LoD	<LoD	0.14	<LoD	<LoD	<LoD	<LoD
M2	<LoD	<LoD	<LoD	0.07	<LoD	<LoD	<LoD	<LoD
	<LoD	<LoD	0.01	0.17	0.01	<LoD	<LoD	<LoD

% RSD of Analytical Triplicates on ICP-OES (macrophyte)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
M1	<LoD	16.89	1.07	1.83	1.50	2.88	9.08	1.14
M2	<LoD	39.58	20.01	3.25	4.23	<LoD	<LoD	<LoD
	<LoD	7.66	5.41	0.46	2.64	3.77	9.95	3.49

Overlying water dissolved metals

% RSD of Analytical Triplicates on ICP-OES (overlying water)								
Batch	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
M1	<LoD	<LoD	<LoD	11.25	0.67	<LoD	<LoD	11.71
M2	<LoD	<LoD	<LoD	8.23	2.34	<LoD	<LoD	9.65
	<LoD	<LoD	<LoD	10.43	5.95	<LoD	<LoD	8.37

Overlying water total hardness

Batch	% Recovery Hach Lange CRM
M1	100
M2	105
	99.5

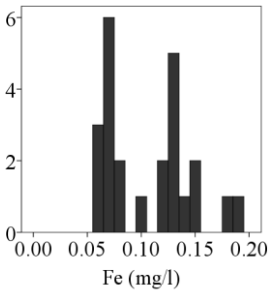
Batch	% RSD of Triplicate Determinations (overlying water hardness)
M1	1.47
M2	1.54
	0.35

Appendix VI

Frequency Histograms and Kolmogorov-Smirnov (K-S) Normality Test results for Chapter 6 data

Kolmogorov-Smirnov (K-S) normality test p-values below frequency histograms. Those normally distributed ($p > 0.05$) shown in bold font, those non-normally distributed ($p < 0.05$) shown in regular font.

Overlying Water



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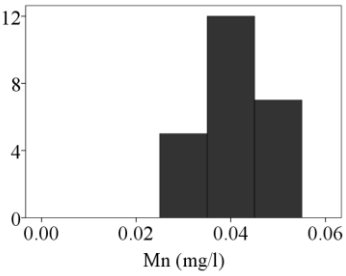

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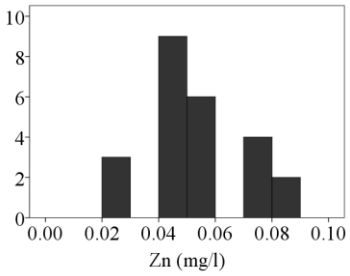

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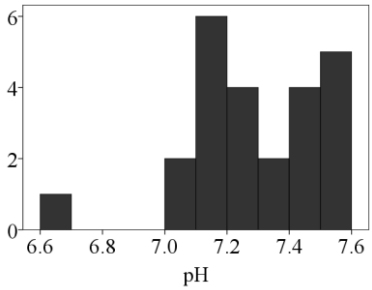

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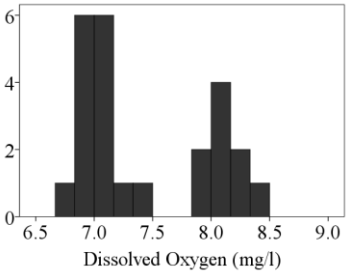

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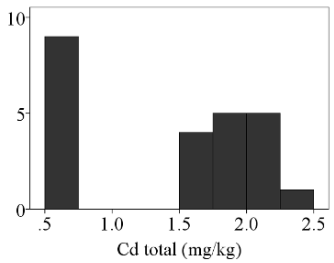
Sediment



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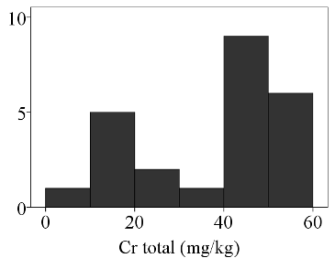

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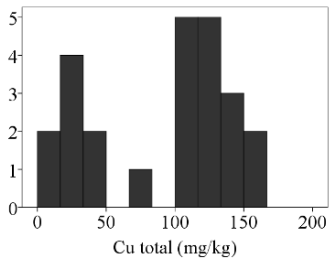

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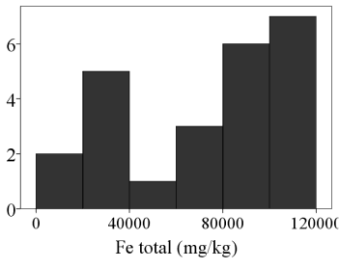

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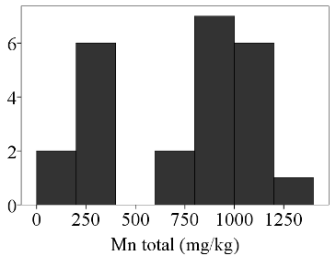

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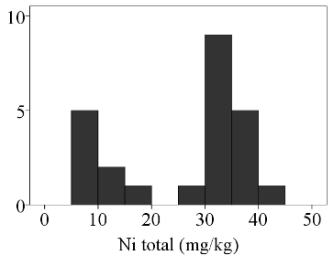

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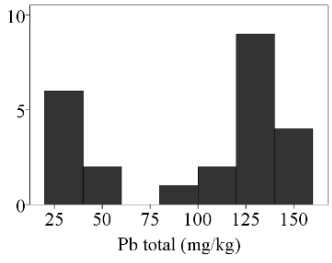

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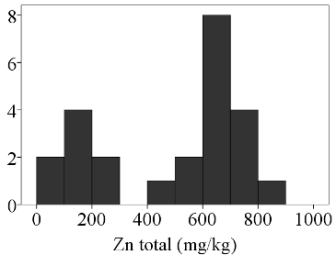

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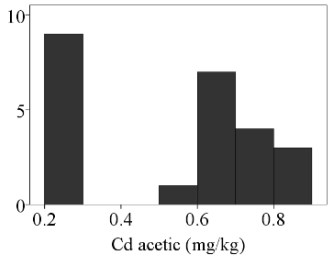

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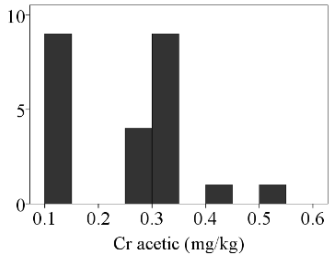

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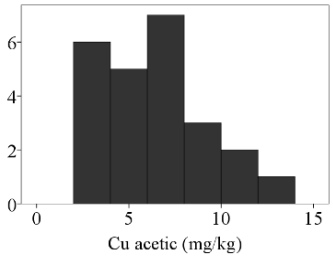

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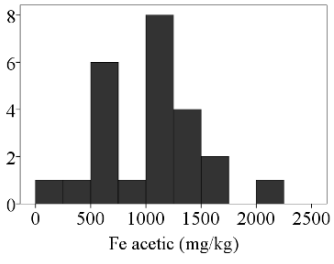

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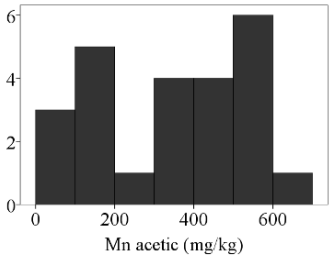

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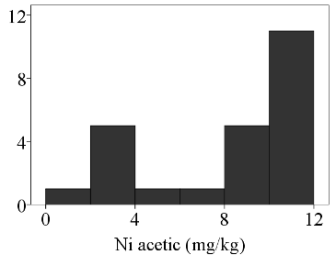

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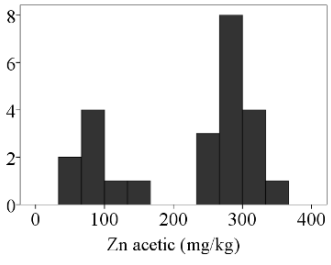

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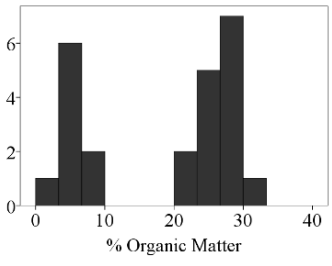

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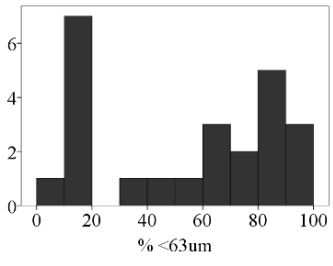

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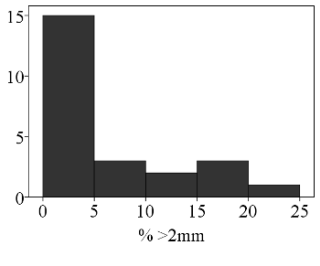

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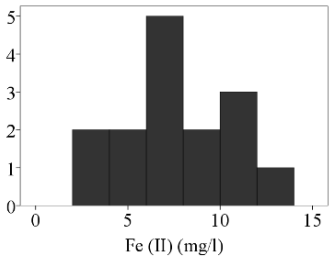

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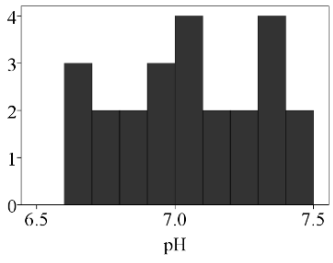

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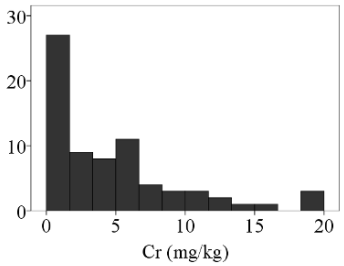
Macrophytes



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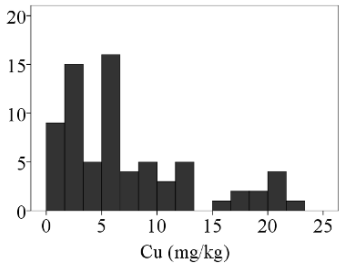

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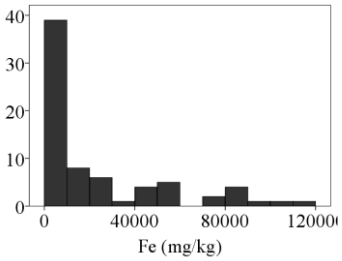

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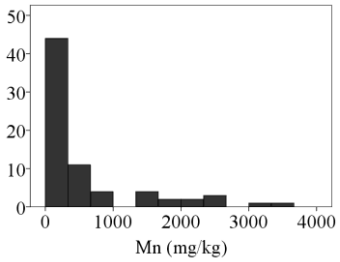

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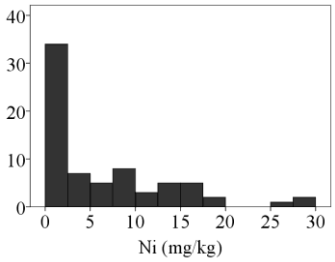

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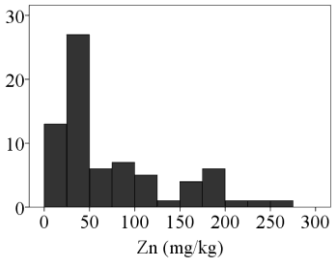

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Appendix VII

Full data set from Chapter 6

S = *S. erectum*
T = *T. latifolia*
P = *P. arundinacea*

November 2011

Overlying Water

	Dissolved metal concentration (mgl^{-1})									
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**pH**	**DO mgl^{-1}**
S1	<LoD	<LoD	<LoD	0.0958	0.0470	<LoD	<LoD	0.0540	6.68	7.96
S2	<LoD	<LoD	<LoD	0.0701	0.0448	<LoD	<LoD	0.0382	7.28	8.04
S3	<LoD	<LoD	<LoD	0.0744	0.0443	<LoD	<LoD	0.0317	7.09	8.1
T1	<LoD	<LoD	<LoD	0.0601	0.0392	<LoD	<LoD	0.0471	7.14	8.35
T2	<LoD	<LoD	<LoD	0.0680	0.0471	<LoD	<LoD	0.0703	7.28	8.3
T3	<LoD	<LoD	<LoD	0.1260	0.0481	<LoD	<LoD	0.0186	7.35	8.26
P1	<LoD	<LoD	<LoD	0.0819	0.0453	<LoD	0.0583	0.0513	7.13	7.99
P2	<LoD	<LoD	<LoD	0.0735	0.0469	<LoD	<LoD	0.0354	7.23	8.12
P3	<LoD	<LoD	0.01	0.1200	0.0464	<LoD	<LoD	0.0320	7.26	8.00

Sediment

	Pseudo-total metal concentration (aqua regia extractable) ($mgkg^{-1}$)							
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	<LoD	16.13	20.73	28356.21	242.06	9.47	30.48	146.78
S2	<LoD	15.07	24.81	30651.49	201.84	9.82	33.88	143.37
S3	<LoD	14.51	20.45	30796.53	230.04	10.58	35.50	155.29
T1	<LoD	14.55	20.18	29851.18	329.70	9.854	31.66	139.79
T2	<LoD	20.90	37.08	34172.74	358.97	12.69	51.44	233.08
T3	<LoD	9.75	9.68	19194.13	177.58	6.36	21.59	89.76
P1	<LoD	11.07	16.42	16399.16	98.22	7.29	29.17	98.88
P2	<LoD	21.39	45.54	45365.86	310.44	15.11	56.68	296.32
P3	<LoD	31.81	78.09	73099.78	946.06	25.29	85.53	455.23

	Acetic acid extractable metal concentration ($mgkg^{-1}$)							
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	<LoD	<LoD	3.31	411.06	123.24	3.57	<LoD	72.75
S2	<LoD	<LoD	4.31	588.93	119.70	3.76	<LoD	82.51
S3	<LoD	<LoD	4.05	532.12	79.47	2.95	<LoD	74.22
T1	<LoD	<LoD	3.99	533.92	152.43	3.91	<LoD	78.29
T2	<LoD	<LoD	3.96	680.90	122.56	4.01	<LoD	101.99
T3	<LoD	<LoD	2.20	193.78	83.07	1.76	<LoD	43.83
P1	<LoD	<LoD	2.96	525.95	37.92	2.49	<LoD	57.87
P2	<LoD	<LoD	3.43	1034.87	134.97	6.12	<LoD	147.14
P3	<LoD	<LoD	5.74	1238.20	461.05	10.95	<LoD	237.07

Sample	% organic matter	% <63 µm	% >2 mm	pH
S1	4.72	17.5	9	6.84
S2	6.02	17.0	11	6.65
S3	4.54	16.9	6	6.98
T1	5.42	14.0	12	7.25
T2	8.31	14.6	23	7.4
T3	2.29	11.6	16	7.47
P1	4.01	9.4	7	6.75
P2	4.87	16.2	19	7.00
P3	8.81	37.4	18	7.32

Macrophytes

Sample		Metal concentration ($mgkg^{-1}$ dry weight)							
		Cd	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	**Leaf/Stem**	<LoD	0.62	6.52	3233.44	1912.72	8.55	<LoD	86.37
	Rhizome	<LoD	0.10	5.25	12647.66	141.18	3.47	<LoD	8.47
	Root	<LoD	1.59	12.05	108463.62	1958.69	29.11	20.40	198.08
S2	**Leaf/Stem**	<LoD	0.35	5.69	3800.24	2496.77	14.94	<LoD	96.89
	Rhizome	<LoD	<LoD	7.85	12451.30	277.66	4.95	<LoD	26.48
	Root	<LoD	2.16	11.14	118176.84	929.85	25.66	22.70	184.41
S3	**Leaf/Stem**	<LoD	0.70	11.69	2978.84	2496.77	14.94	<LoD	86.15
	Rhizome	<LoD	0.15	6.05	24966.14	137.36	5.75	<LoD	34.00
	Root	<LoD	2.26	20.33	99061.35	2082.94	27.75	22.59	209.16
T1	**Leaf/Stem**	<LoD	<LoD	1.86	423.45	241.63	<LoD	<LoD	10.02
	Rhizome	<LoD	2.63	4.57	6511.46	153.86	6.87	<LoD	9.09
	Root	<LoD	1.36	17.51	21695.24	167.84	17.37	15.15	112.61
T2	**Leaf/Stem**	<LoD	0.57	1.46	325.47	78.00	<LoD	<LoD	<LoD
	Rhizome	<LoD	<LoD	2.15	2962.64	37.47	<LoD	<LoD	<LoD
	Root	<LoD	1.06	7.66	30605.91	141.56	16.84	14.03	68.15
T3	**Leaf/Stem**	<LoD	<LoD	1.35	272.12	302.60	<LoD	<LoD	14.16
	Rhizome	<LoD	0.72	4.38	4274.41	211.25	5.12	<LoD	7.36
	Root	<LoD	4.34	16.95	23442.88	260.35	17.67	21.55	164.01
P1	**Leaf/Stem**	<LoD	0.38	6.62	1965.21	360.56	<LoD	<LoD	62.40
	Root&Rhizome	<LoD	0.86	9.40	5287.01	3186.81	11.55	<LoD	129.33
P2	**Leaf/Stem**	<LoD	0.49	5.85	1502.53	170.53	<LoD	<LoD	49.13
	Root&Rhizome	<LoD	0.37	7.72	3624.81	2255.65	9.09	<LoD	118.08
P3	**Leaf/Stem**	<LoD	0.33	5.06	2165.22	631.41	3.63	<LoD	33.09
	Root&Rhizome	<LoD	0.83	9.91	7902.47	3546.18	15.26	<LoD	124.40

June 2012

Overlying Water

	Dissolved metal concentration (mgl^{-1})									
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**	**pH**	**DO mgl^{-1}**
S1	<LoD	<LoD	<LoD	0.15	0.036	<LoD	<LoD	0.090	7.04	7.13
S2	<LoD	<LoD	<LoD	0.14	0.036	<LoD	<LoD	0.044	7.2	6.75
S3	<LoD	<LoD	<LoD	0.12	0.036	<LoD	<LoD	0.035	7.15	6.87
S4	<LoD	<LoD	<LoD	0.11	0.036	<LoD	<LoD	0.043	7.12	7.05
S5	<LoD	<LoD	<LoD	0.12	0.037	<LoD	<LoD	0.036	7.19	6.94
T1	<LoD	<LoD	<LoD	0.07	0.031	<LoD	<LoD	0.040	7.48	6.93
T2	<LoD	<LoD	<LoD	0.06	0.032	<LoD	<LoD	0.051	7.52	7.01
T3	<LoD	<LoD	<LoD	0.07	0.031	<LoD	<LoD	0.065	7.54	7.22
T4	<LoD	<LoD	<LoD	0.06	0.031	<LoD	<LoD	0.036	7.52	6.97
T5	<LoD	<LoD	<LoD	0.06	0.033	<LoD	<LoD	0.068	7.51	6.96
P1	<LoD	<LoD	<LoD	0.19	0.040	<LoD	<LoD	0.068	7.4	7.04
P2	<LoD	<LoD	<LoD	0.14	0.038	<LoD	<LoD	0.080	7.52	7.38
P3	<LoD	<LoD	<LoD	0.12	0.038	<LoD	<LoD	0.060	7.47	7.13
P4	<LoD	<LoD	<LoD	0.12	0.037	<LoD	<LoD	0.060	7.44	7.06
P5	<LoD	<LoD	<LoD	0.17	0.049	<LoD	<LoD	0.041	7.41	6.95

Sediment

	Pseudo-total metal concentration (aqua regia extractable) ($mgkg^{-1}$)							
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	2.17	57.14	152.99	100422.24	858.48	37.71	155.58	789.00
S2	1.95	49.77	130.44	109361.33	781.95	32.47	131.35	666.23
S3	2.12	50.24	132.42	114359.95	1067.49	35.48	135.28	713.90
S4	1.75	46.89	122.83	111014.60	1028.36	33.50	129.80	664.74
S5	1.62	43.75	112.72	115185.52	707.86	30.19	120.81	614.23
T1	1.98	46.85	124.53	87905.56	1295.67	35.17	131.45	656.42
T2	1.67	48.67	131.20	85482.39	1150.38	33.53	141.89	679.06
T3	1.64	42.01	107.32	78653.92	883.83	30.75	117.09	588.05
T4	1.91	43.91	114.62	80790.09	989.99	31.16	126.15	659.34
T5	2.00	51.49	137.33	92183.05	1146.77	38.35	139.45	739.78
P1	1.82	44.80	114.21	78471.34	886.00	32.77	122.26	616.79
P2	2.42	55.99	153.86	93880.15	999.42	40.26	155.84	810.09
P3	2.09	52.67	139.53	113397.33	1040.22	34.282	140.60	717.98
P4	2.01	51.10	137.73	109254.76	1137.65	35.87	136.69	696.81
P5	1.54	44.74	112.05	91012.65	916.17	30.51	116.70	591.02

	Acetic acid extractable metal concentration ($mgkg^{-1}$)							
Sample	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	0.81	0.39	7.39	2175.41	326.15	10.89	<LoD	338.37
S2	0.67	0.31	7.75	1370.77	351.22	9.25	<LoD	268.45
S3	0.79	0.28	7.22	1210.54	502.11	10.07	<LoD	302.07
S4	0.82	0.31	10.28	1362.93	516.28	10.31	<LoD	281.65
S5	0.71	0.33	11.86	1725.36	292.17	8.87	<LoD	283.83
T1	0.64	0.27	6.11	665.58	622.06	9.78	<LoD	249.33
T2	0.73	0.32	9.75	1011.60	558.94	10.12	<LoD	295.18
T3	0.63	0.28	6.61	1168.68	451.74	10.09	<LoD	265.55
T4	0.57	0.33	5.16	1222.64	472.91	9.81	<LoD	283.13
T5	0.71	0.50	6.51	1367.33	517.85	11.32	<LoD	316.66

P1	0.68	0.34	6.94	1524.81	339.16	11.08	<LoD	290.57
P2	0.69	0.35	4.30	1372.03	370.63	11.55	<LoD	312.54
P3	0.69	0.31	9.24	1176.29	530.84	10.20	<LoD	294.92
P4	0.79	0.32	8.48	1083.75	545.74	10.63	<LoD	309.72
P5	0.68	0.29	12.10	958.82	426.29	8.98	<LoD	276.76

Sample	% organic matter	% <63 µm	% >2 mm	Fe (II) concen (mgl^{-1})	pH
S1	29.19	84.5	0.00	7.47	6.71
S2	26.16	92.5	0.00	12.33	7.08
S3	29.66	77.0	0.00	10.74	6.84
S4	25.84	78.3	0.00	10.34	6.7
S5	23.53	85.1	0.00	7.19	6.65
T1	27.36	89.6	0.00	4.03	7.33
T2	27.43	86.6	0.00	4.57	7.42
T3	24.84	65.8	0.00	7.24	7.2
T4	26.27	55.8	0.00	3.76	7.32
T5	31.69	90.4	0.00	3.89	7.23
P1	22.94	48.1	0.00	7.19	7.12
P2	28.10	69.9	0.00	8.69	7.02
P3	27.48	86.6	0.00	6.71	7.02
P4	26.87	91.1	0.00	9.13	7.01
P5	22.68	68.8	0.00	10.42	6.95

Macrophytes

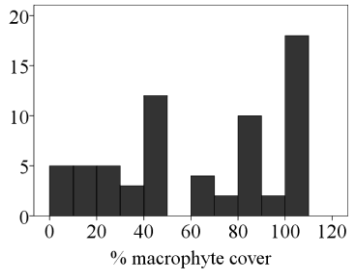
		Metal concentration ($mgkg^{-1}$ dry weight)							
Sample		**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
S1	**Leaf/Stem**	<LoD	5.67	5.14	610.03	246.33	<LoD	<LoD	21.88
	Rhizome	<LoD	12.06	6.25	13209.73	81.93	3.43	<LoD	28.82
	Root	<LoD	5.91	12.07	55644.10	274.55	9.24	<LoD	96.57
S2	**Leaf/Stem**	<LoD	16.02	5.08	933.74	239.81	<LoD	<LoD	28.27
	Rhizome	<LoD	5.25	4.81	14121.63	109.57	4.13	<LoD	42.55
	Root	<LoD	6.25	9.45	48985.64	181.96	9.24	<LoD	101.04
S3	**Leaf/Stem**	<LoD	10.45	5.35	665.87	339.66	<LoD	<LoD	26.38
	Rhizome	<LoD	8.96	5.42	22779.92	161.21	4.45	<LoD	44.24
	Root	<LoD	6.38	12.14	88979.17	369.67	10.86	<LoD	111.89
S4	**Leaf/Stem**	<LoD	14.97	6.47	1045.69	337.85	<LoD	<LoD	38.87
	Rhizome	<LoD	6.36	5.88	22368.63	111.86	3.56	<LoD	263.13
	Root	<LoD	8.05	16.33	84002.03	611.25	14.42	<LoD	189.31
S5	**Leaf/Stem**	<LoD	9.39	5.03	1100.59	291.95	<LoD	<LoD	30.85
	Rhizome	<LoD	6.91	7.07	22907.03	110.83	5.12	<LoD	61.50
	Root	<LoD	4.51	11.74	54101.99	200.57	10.19	<LoD	160.14
T1	**Leaf/Stem**	<LoD	4.83	<LoD	285.96	349.00	<LoD	<LoD	25.59
	Rhizome	<LoD	2.06	2.36	19733.39	80.69	<LoD	<LoD	19.69
	Root	<LoD	6.50	9.93	73767.95	750.91	7.81	<LoD	82.27
T2	**Leaf/Stem**	<LoD	7.14	<LoD	511.72	197.61	<LoD	<LoD	19.38
	Rhizome	<LoD	1.63	<LoD	13094.83	103.67	<LoD	<LoD	28.23
	Root	<LoD	3.54	5.95	48148.55	254.32	8.62	<LoD	49.38
T3	**Leaf/Stem**	<LoD	19.66	2.82	794.91	461.27	<LoD	<LoD	27.66
	Rhizome	<LoD	7.81	2.67	16027.87	169.47	<LoD	<LoD	40.28
	Root	<LoD	5.05	9.04	47749.90	860.98	8.84	<LoD	99.66
T4	**Leaf/Stem**	<LoD	10.35	2.77	398.61	365.61	<LoD	<LoD	42.99

	Rhizome	<LoD	2.35	2.34	2251.43	145.62	<LoD	<LoD	45.38
	Root	<LoD	4.24	19.14	50745.41	402.96	5.36	<LoD	76.77
T5	**Leaf/Stem**	<LoD	3.94	3.15	199.78	425.35	<LoD	<LoD	27.30
	Rhizome	<LoD	2.14	2.53	12252.91	245.85	<LoD	<LoD	48.67
	Root	<LoD	3.93	10.98	46599.88	1498.44	8.61	<LoD	175.88
P1	**Leaf/Stem**	<LoD	18.54	2.35	777.48	93.49	<LoD	<LoD	35.10
	Rhizome	<LoD	2.20	<LoD	8653.89	67.59	<LoD	<LoD	47.34
	Root	<LoD	19.40	20.42	80108.39	2607.79	19.22	<LoD	232.47
P2	**Leaf/Stem**	<LoD	5.47	2.52	907.38	101.06	<LoD	<LoD	49.83
	Rhizome	<LoD	0.98	<LoD	4597.94	39.43	<LoD	<LoD	38.92
	Root	<LoD	11.47	20.65	59630.18	1556.96	15.12	<LoD	173.17
P3	**Leaf/Stem**	<LoD	5.72	3.54	668.10	83.67	<LoD	<LoD	34.45
	Rhizome	<LoD	1.56	10.46	4336.98	83.37	<LoD	<LoD	55.73
	Root	<LoD	11.82	21.74	57793.65	1644.15	14.35	<LoD	176.06
P4	**Leaf/Stem**	<LoD	3.32	2.90	666.50	100.32	<LoD	<LoD	42.01
	Rhizome	<LoD	1.09	<LoD	1954.56	56.21	<LoD	<LoD	62.15
	Root	<LoD	8.71	21.13	85786.81	1376.00	13.62	<LoD	179.59
P5	**Leaf/Stem**	<LoD	2.86	3.07	1076.21	111.57	<LoD	<LoD	30.75
	Rhizome	<LoD	3.68	<LoD	7295.32	69.16	<LoD	<LoD	64.61
	Root	<LoD	5.02	18.78	72218.84	990.67	16.78	<LoD	172.36

Appendix VIII

Frequency Histograms and Kolmogorov-Smirnov (K-S) Normality Test results for Chapter 7 data

Kolmogorov-Smirnov (K-S) normality test p-values below frequency histograms. Those normally distributed ($p > 0.05$) shown in bold font, those non-normally distributed ($p < 0.05$) shown in regular font.



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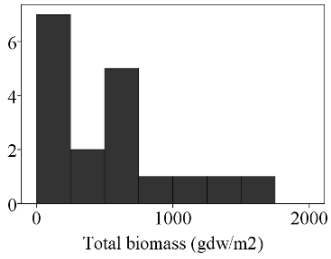

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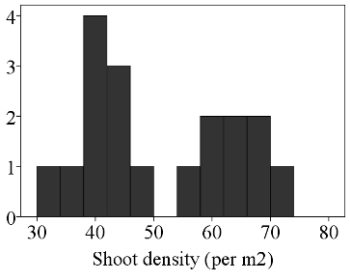

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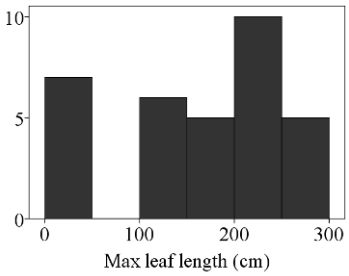

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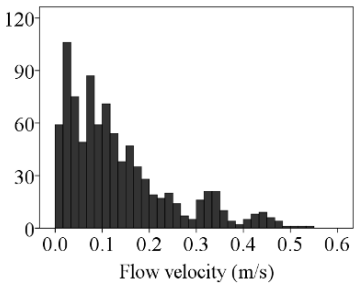

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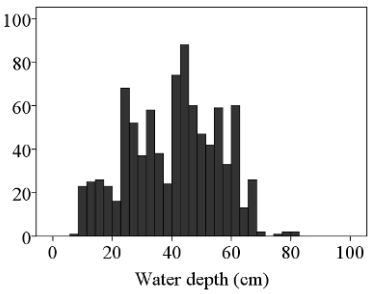

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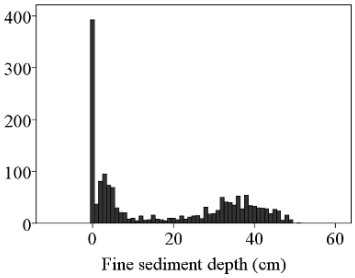

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