Physicochemical changes to soil and sediment in managed realignment sites following tidal inundation

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Declaration

I, **Margaret Kadiri**, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

The recognition of the value of salt marshes and concerns over salt marsh loss has led to the adoption of managed realignment in coastal areas. Managed realignment involves the landward relocation of the seawall, allowing an area of agricultural land to be tidally inundated. It is believed that managed realignment sites can act as a sink for contaminants. However, these sites may also act as a contaminant source and pose a risk to estuarine biota.

In this thesis, the potential for metal and herbicide release from agricultural soil and dredged sediment in managed realignment sites was investigated by laboratory microcosm experiments. The agricultural soil and dredged sediment were subjected to two different salinities and drying-rewetting treatments. Results indicate the release of metals (Cu, Ni and Zn) and herbicides (simazine, atrazine and diuron) was dependent on their strength of binding to the soil and sediment, and complexation and competition reactions between seawater anions, cations and the sorbed metals. The release patterns indicated that metal and herbicide release into overlying water may continue for extended periods of time after an initial rapid release. The total metal and herbicide loads released into the overlying water followed the order: Cu < Zn < Ni and diuron < atrazine < simazine with a greater release from the soil than sediment. The increase in CO_2 release, mineralisation rates, total metal and herbicide loads after drying and rewetting the soil suggested an increase in the mineralisation of organic matter and the release of organic matter associated metals and herbicides. Results of linear regression analyses provided evidence that the release of the metals and herbicides as DOC-complexes was important for soil but not for sediment. These findings indicate that there is a lower potential for contaminant release from managed realignment sites where dredged sediments are beneficially re-used.

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Chapter 1: Introduction

1.1 General Introduction

In recent years, there has been a paradigm shift in the management of coastal areas from the maintenance of seawalls to the restoration of coastal habitats (Crooks et al., 2002). Integral to this shift is the recognition of salt marshes as an important part of the coastal system and its significance relative to other global ecosystems. Costanza et al. (1997) estimated the average annual global value of different ecosystems and attributed a value of \$ 1,648 yr^{-1} x 10^{9} to salt marshes and mangroves (the tropical equivalent of salt marshes). The annual global value of salt marshes was equivalent to that of lakes and rivers. Salt marshes provide several economic and environmental benefits such as coastal flood defence enhancement (Tiner et al., 1987). However, salt marshes are under threat from rising sea levels and associated salt marsh loss. In the UK, the area of salt marshes along the Colne, Blackwater and Stour estuaries in Essex reduced by 42 % between 1988 and 1997/8 due to salt marsh erosion (Hughes and Paramor, 2004). The loss of salt marshes coupled with the high cost of maintaining and upgrading seawalls has resulted in salt marsh restoration through managed realignment (Andrews et al., 2006). Managed realignment aims to restore salt marsh to coastal areas by the landward relocation of seawalls, allowing the tidal inundation of low-lying agricultural land. It is intended that the reintroduction of tidal inundation will promote salt marsh development which in turn will serve as a natural coastal flood defence in front of the seawall. Apart from salt marsh restoration and the enhancement of coastal defence, managed realignment may provide other potential benefits, one of which includes providing a sink for metals and other particle reactive contaminants (NRA, 1994, Andrews et al., 2006; Cave et al., 2005). Andrews et al. (2006) indicated that managed realignment sites can serve as a sink for metals because it provides space for the accumulation of sediments. However, physical and chemical changes in sediments such as salinity changes can affect the binding of contaminants to sediments and result in contaminant release (Calmano et al., 1992; Gambrell et al., 1991). Consequently, changes in the physical and chemical conditions in the soil and sediment in managed realignment sites following tidal inundation can result in the release of contaminants into estuarine waters. The release of these contaminants may affect estuarine water quality and have adverse effects on living organisms in the food chain (Call et al., 1987; Moriarty, 1999) leading to man.

In this thesis, a series of investigations (a field study, laboratory experiments and modelling investigation) were conducted which were aimed at assessing the potential for contaminant release from agricultural soil and dredged sediment following tidal inundation in managed realignment sites. Both inorganic and organic contaminants (i.e. metals and herbicides) were considered. The following sections provide background information on salt marshes and managed realignment, describe the sorption-desorption of metals and herbicides and the changes to agricultural soil and dredged sediment in managed realignment sites which can result in the potential release of metals and herbicides into estuarine waters.

1.2 Nature of salt marshes

There are several definitions of salt marshes. Beeftink (1977) defined a salt marsh as a "natural or semi-natural halophytic grassland and dwarf brushwood on the alluvial sediment bordering seawater bodies whose water table fluctuates either tidally or non-tidally". Bates and Jackson (1980) defined a salt marsh as a flat, poorly drained land which is subject to periodic flooding by seawater and is usually covered by a thick mat of grassy halophytic (salt-tolerant) plants. Adam (1990) defined a salt marsh as an area vegetated by herbs, grasses or low shrubs bordering seawater bodies. Allen and Pye (1992) defined a salt marsh as an area of land covered by halophytic vegetation which is frequently inundated by seawater.

Salt marshes are found in the middle and high latitudes along intertidal shores throughout the world (Mitsch and Gosselink, 2000). They develop in sheltered low energy areas with medium to large tidal ranges (< 3 m) where alluvial sediment become deposited on intertidal mudflat. The alluvial sediments are derived from upland run-off, reworked marine deposits, coastal erosion and fluvial transport (William et al., 1994; Pethick, 1984; Mitsch and Gosselink, 2000). In the UK, approximately 45,300 ha (4.53 x 10^8 m^2) of salt marshes are found along the coastline with one fifth of the total area of salt marshes in England found along the coast of Norfolk, Suffolk and Essex (Burd, 1989, 2003).

Salt marshes develop between Mean High Water Neap (MHWN) and Mean High Water Spring (MHWS) (French, 2006; Legget and Dixon 1994; Pye and French, 1993). They are periodically inundated by sea water which infiltrates the saltmarsh sediment during high tide and drains at low tide (Boorman and Hazelden, 2002; Williams et al., 1994). While the frequency and duration of tidal inundation depends on the elevation of the marsh surface relative to the sea-level and the tidal regime which varies temporally at several timescales, the ease with which the marsh drains depends on the topography of the salt marsh (Rozas, 1995; Mitsch and Gosselink, 2000; Pethick, 1980; ABP, 1998),

Salt marshes are situated in a buffer zone between marine and terrestrial habitats and are usually fronted by mudflats (Boorman, 2003; Adam, 1990). They are often divided by muddy creeks of characteristic dendritic patterns which serve as important conduits for material such as particulate organic matter between the marsh and the adjacent estuary (Pye, 2000; Mitsch and Gosselink, 2000). Higher seawater velocities are experienced in the creeks compared to the salt marsh surface because the velocities are reduced at the marsh surface by the surface roughness of the salt marsh plants (Boorman et al., 1998). The lowest limit of the distribution of individual salt marsh plants species depends on several factors such as tolerance to tidal inundation, salinity and water movement whilst the upper limit is determined by factors such as interspecific competition, with those plants species less tolerant of tidal inundation occurring at higher elevation (Shunway and Bertness, 1992; Sanchez et al., 1996; Davy et al., 2000, Pennings and Callaway, 1992). The plants established at lower elevation impede the water flow and enables suspended sediments to settle, thereby promoting sediment deposition. This increases the height of the area and creates a suitable environment for the establishment of plant species less tolerant of tidal inundation (Boorman et al., 1998). The different responses by different salt marsh plant species produce a zonation pattern or a successional sequence from low to high elevation as shown in Figure 1.1 (Boorman, 2003).

Salt marshes act as transformers of nutrients by importing dissolved oxidized inorganic forms (nitrite, nitrate, phosphate) and exporting dissolved and particulate reduced forms (ammonium, organic nitrogen and phosphorus compounds) (Odum, 1988). They function either as sinks or sources of nutrients depending on a variety of factors such as the successional age of the marsh, salinity, presence of upland sources of nutrients, tidal range, presence of litter layer, and the magnitude and stability of nutrient flux in the estuary to which the marsh is coupled (Stevenson et al., 1977; Osgood, 2000). Typically, older salt marshes with well developed inorganic and organic nutrient pools are likely to be exporters of nutrients while younger systems are expected to import nutrients (Childers, 1994).

Salt marsh sediments are mainly made up of silt and clay sized particles and they are rich in organic matter deposited from coastal waters and trapped into the salt marsh or from organic production within the marsh (Mitsch and Gosselink, 2000; Nixon, 1980). Generally, salt marsh sediments have reducing conditions which is reflected by their low redox potential (Howes, 1981). The redox potential decreases with increasing sediment depth due to the utilization of a sequence of terminal electron acceptors (O^2, NO_3^-; Mn^{4+}; Fe^{3+}; $SO4^{2-}$, CO_2) by a vertical succession of microbes with different tendencies to oxidise organic matter as a carbon source (Froelich et al., 1979). Consequently, salt marsh sediments are redox-stratified and exhibit a vertical succession of oxic and anoxic zones (Koretsky et al., 2003). The depth of the oxic zone can range from a few mm to tens of cm (Zwolsman et al., 1993). The transition between the oxic and anoxic zones is called the redoxcline and is identified by a visual change in colour from reddish-brown at the surface to dark greyish-black at depth which is synonymous with the presence of ferric oxide precipitates at the surface and insoluble pyrite at depth (Williams et al., 2004).

1.3 Value of salt marshes

Salt marshes have several values which are summarised in Table 1.1. However, the main values of salt marshes to the UK Environment Agency (EA) which has a statutory duty to promote the conservation of coastal areas are the value to conservation and the enhancement of coastal flood defence (NRA, 1992).

The value of salt marshes to conservation has been recognised for many years. Salt marshes provide habitats, food sources and breeding areas for a wide range of organisms which are vital to the coastal ecosystem as a whole (Beeftink and Rozema, 1988). Salt marshes also provide suitable habitats for a range of invertebrates, birds and fishes. The dense invertebrate fauna are an important food source for mussels, cockles, birds and fishes (Boorman, 1992) and they also play a significant role in sedimentary processes by secreting binding mucus which stabilises deposited sediments (Legget and Dixon, 1994; Daborn et al., 1993).

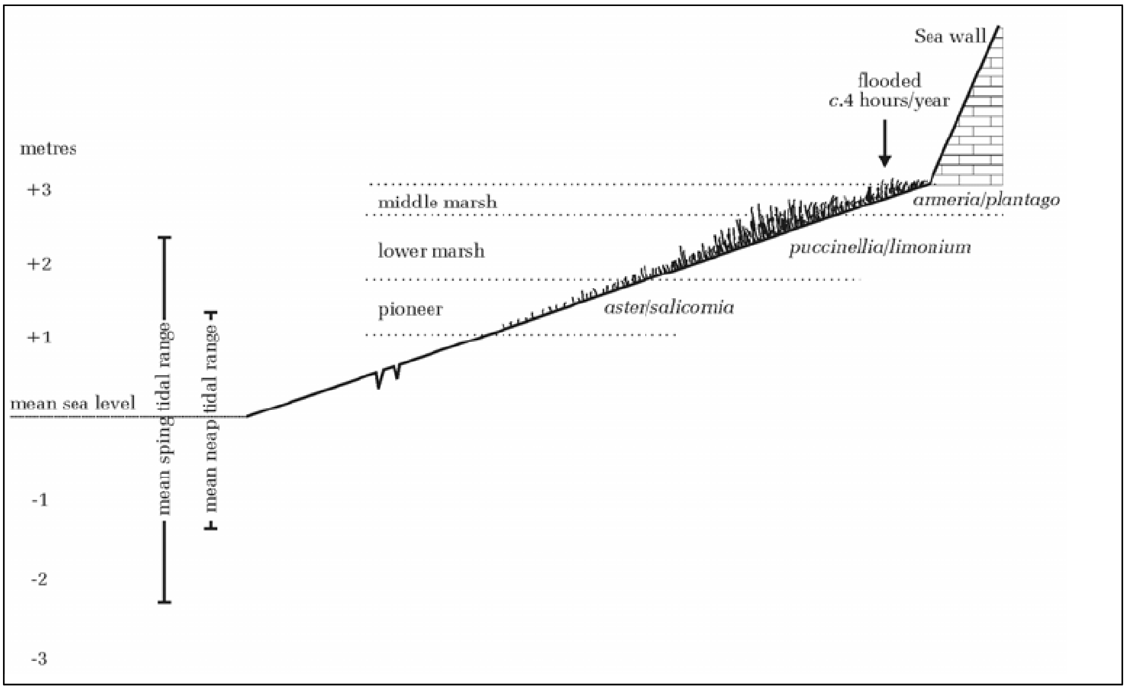

Figure 1.1 Diagrammatic representation of the vegetation zones and tidal changes in the water level at a typical salt marsh (after Boorman, 2003).

Salt marshes serve as a feeding, roosting and nesting areas to a large number of birds including migratory and over-wintering birds. For example, the salt marshes in south-east England provide suitable feeding, breeding and roosting areas for up to 250,000 waterfowls and waders (Dixon, 1998). While birds utilise the exposed surface of the salt marsh, the creeks provide a transitory habitat for fishes. These creeks serve as sheltered spawning and nursery sites (King and Lester, 1995; Boorman, 1992). King and Lester (1995) indicated that salt marshes increase the fishery potential of coastal waters. The creeks also serve as feeding sites for fishes. Fishes such as grey mullet feed on algae on the creek banks, bass feeds on invertebrate fauna and flat fish such as plaice move into creeks at high tides (King and Lester, 1995). Due to the importance of the salt marshes in supporting these habitats, most of the salt marshes in England have several national and international conservation designations (Hughes and Paramor, 2004). More than 80 % of the salt marshes in south-east England are Sites of Special Scientific Interest (SSSI), Environmentally Sensitive Areas (ESA), Special Protected Areas (SPA), Special Areas of Conservation (SAC) and Ramsar sites (Paramor and Hughes, 2004).

Table 1.1 Major values of wetlands (modified from Tiner, 1987)

Values	Uses
Socio-economic	Fishing, wildfowling, recreation, aesthetics
	Education and scientific research
	Livestock grazing, flood control, erosion control
	Protection from the wave damage
	Ground water recharge and water supply
Environmental quality	Nutrient recycling, water quality maintenance
	Pollution filters, aquatic productivity
	Oxygen production, microclimate regulator

Salt marshes play a significant role in enhancing coastal flood defence by dissipating wave energy so that little energy remains on the landward limit (Pethick, 1992; Toft and Maddrell, 1995; Moller et al., 2001). Moller et al. (1999) indicated that salt marshes dissipate wave energy through the reduction in water depth over the marsh and the increased friction of the vegetated surface reducing wave height. However, the effectiveness of salt marshes in enhancing coastal flood defence depends on the width of the salt marsh that is in front of the seawall. For example, a 3 m high seawall with an 80 m wide salt marsh in front of it will give adequate protection. If there is a 30 m wide salt marsh, a 5 m seawall is needed. However, a 12 m wide salt marsh is needed if there is no seawall (NRA, 1992; Boorman, 2003). Salt marshes also reduce the impact of wave action on the seawall thereby offering protection to the seawall and reducing its maintenance cost (Dixon and Weight, 1996; King and Lester, 1995, Leggett and Dixon, 1994). King and Lester (1995) estimated that the loss of saltmarsh from Essex would cost £ 600 million for the increased maintenance of the seawall.

1.4 Loss of salt marshes

Historically, there has been a significant loss of coastal wetlands globally as a result of human activities. Over the last century, more than 70% of California's coastal wetlands in the USA and approximately 40 % of the coastal wetlands in France have been lost (ABP, 1998). This is mainly because salt marshes were not considered to be important and as a result many salt marshes were drained and reclaimed for agricultural, industrial and recreational purposes (Moy and Levin, 1991). However, in recent years, loss of salt marshes has been extensively reported and they are now seen as a threatened ecosystem (Harmsworth and Long, 1986; Nuttle et al., 1997). Some of the causes of these losses include drought, hurricanes, subsidence due to relative sea level rise, discharges of materials (e.g. nutrient loadings from domestic sewage and agricultural run-off) and erosion (Tiner, 1987). In the UK, significant areas of salt marsh have been lost to reclamation extensively practiced historically. However, there are current concerns over the erosional loss of salt marshes particularly in south-east England (Table 1.2). These losses have great implications for both conservation and coastal flood defence. The recent salt marsh erosion has been attributed to the prevention of the landward migration of salt marshes, by seawalls, in response to rising sea levels (Boorman, 1992; Turner, 1995; Burd, 1992). As the outer marsh zones move landward, the inner marsh zones are unable to migrate due to the presence of the sea wall. The salt marshes become squeezed between the static sea wall and the rising sea level leading to the progressive loss of salt marshes. This process has been termed 'coastal squeeze' (Boorman, 1992; Turner, 1995; Burd, 1992). However, Hughes and Paramor (2004) have argued that an increase in bioturbation and herbivory by the rag worm *Nereis diversicolor* as opposed to coastal squeeze, may be responsible for the salt marsh erosion in south-east England. Salt marsh erosion is expected to continue as sea level rise in south-east England has been estimated to range from 1 – 4 mm year^{-1} (Boorman, 1992; Turner, 1995; Underwood, 1997; Hughes, 2001).

Table 1.2 Proportions (%) of saltmarsh lost from Essex and the Orwell in Suffolk, from 1973 – 1988 and from 1988 – 1997/8. (modified from Hughes and Paramor, 2004)

	1973 - 1988		1988 – 1997/8
	Total lost	Pioneer zone	Total
Orwell	40	74	23
Stour	44	60	28
Colne	12	53	7
Blackwater	23	74	7

1.5. Salt marsh restoration through managed realignment

Salt marshes are at a great risk of erosion due to climate change and sea level rise. The continuing rate of salt marsh erosion in south-east England due to sea level rise has been estimated to be 40 ha year^{-1} (Coastal Geomorphological Partnership, 2000). Balcombe (1992) indicated that salt marshes could disappear in 50 years except deliberate measures are taken to protect them. The concerns over salt marsh erosion due to rising sea levels as well as the high cost of maintaining and upgrading seawalls has led to considerations for a more cost-effective and sustainable coastal management strategy (Andrews et al., 2006; Shepherd et al 2007). Most of the seawalls in south-east England have reached the end of their design life as they were constructed after the North sea storm surge of 1953 and they now need expensive upgrading and maintenance (Moller et al., 1999). However, the maintenance and upgrading of the seawalls are deemed uneconomical particularly when it is more expensive than the value of the land protected (Dixon and Weight, 1996). This is the case for 25 % of the seawalls on the Essex coast where the cost of maintenance is more than the value of the land protected (Hughes and Paramor, 2004). In addition, the biological diversity in salt marshes has been recognized in law under the European Union Habitat Directive 92/43/EEC. The directive maintains a ‘no-net-loss’ policy in total habitat area and the UK has an obligation, under this directive, to maintain and restore salt marshes to the total area present in 1992 (UK Biodiversity Group, 1999). Hence, the UK is committed under the EU Habitat Directive and the UK Biodiversity Action Plan, to develop strategies to conserve and enhance biodiversity in salt marshes. As a result of the need to comply with the Habitat directive as well as the concerns about salt marsh erosion due to rising sea levels and the high cost of maintenance and upgrading of seawalls, coastal managers and policy makers have now adopted the soft engineering technique known as managed realignment over the hard engineering option (i.e. seawalls). This soft engineering technique aims to achieve a dynamic equilibrium in coastal environments and hence regard salt marshes as an important part of the coastal environment (MAFF, 1993).

Managed realignment (also known as managed retreat or set back) involves constructing a new sea wall further inland on higher ground and deliberately breaching the existing seawall, allowing for the tidal inundation of the area between the existing and new seawall. Salt marsh plants colonise the inundated area and dissipate wave energy, thus offering coastal flood protection. Managed realignment also reduces the effect of coastal squeeze by allowing the landward migration of salt marshes with rising sea levels, creates a more sustainable seawall and meets conservation objectives. Managed realignment is a cheaper alternative to maintaining and upgrading existing seawalls (French, 2006). The cost of implementing a managed realignment scheme at Northey Island on the Blackwater Estuary in Essex in 1992 was approximately £22,000 while the estimated cost of upgrading and maintaining the existing seawall was between £30,000 and £55,000 (Leafe, 1992). Given that realignment reduces the impact of wave action, the new seawall need not be constructed to the same specifications as the existing wall, thus reducing implementation costs (Brampton, 1992). In addition to the fulfillment of the flood defence and conservation objectives, an additional proposed benefit of managed realignment is that the site may act as a sink for contaminants such as metals and organic contaminants from estuarine waters (NRA, 1994; MacLeod et al., 1999).

Managed realignment sites are periodically inundated by seawater during high tide and drained at low tide. The extent of the tidal inundation and drainage depends on the site elevation relative to the tide, the topography of the site and the ease with which the site drains (ABP, 1998). Areas at low elevation relative to the tide are regularly inundated by the tides twice daily. Conversely, areas at higher elevation relative to the tide are irregularly inundated, mainly by spring tides (Scott pers. comm., 2006) making these areas susceptible to wetting and drying cycles.

Typically, managed realignment is implemented on reclaimed agricultural land partly because the land had originally been salt marsh and therefore has a proven ability to support such an environment (French, 2006). After the seawall is breached, the soil is inundated and estuarine sediments start to accumulate. The accretion of sediment in a managed realignment site is required for the restoration of salt marsh plants. This is because, over time, there is a drop in elevation in reclaimed areas relative to the tide due to dewatering and compaction and the accretion of sediment raises the land elevation to a suitable level (between MHWN and MHWS) for salt marsh plants to develop (French, 2006; Crooks and Pye, 2000). As a result, managed realignment has also been implemented by importing dredged estuarine sediments into the site in order to raise the elevation of the site. The sediments used are usually from maintenance dredging of navigation routes in estuaries (ABPmer, 2004). Since estuaries are sinks for contaminants, these estuarine sediments can have significant contaminant levels (Cave et al., 2005; Spencer et al., 2002) which can be incorporated into the managed realignment site. Andrews et al. (2006) has highlighted that managed realignment provides accommodation space for sediment accumulation, therefore they act as a sink for metal and other particle reactive contaminants. However, the binding of contaminants to sediments is not permanent and these contaminants may be released due to physical and chemical changes in the sediment (Gambrell et al., 1991; Ip et al., 2007). In addition, contaminants may be present in the pre-inundated agricultural land due to land use practices such as herbicide usage for crop production. Herbicides are widely used in agriculture in the UK to control the spread of weeds during crop production (CABI, 2003). In 2004, approximately 10, 600 tonnes of herbicides were applied to agricultural land for UK crop production (DEFRA, 2006). The application of herbicides may cause herbicide enrichment in agricultural soil. These herbicides may be released from the soil due to physical and chemical changes in the soil environment following tidal inundation in a managed realignment site.

Metals are of environmental concern because of their wide spread use, potential toxic effect on organisms and long residence time in the environment as they cannot be degraded to innocuous by-products. Certain metals are essential for living organisms in trace amounts such as Cu, Zn, Co and Mo but exposure to high concentrations can have toxic biological effects (Forstner and Wittmann, 1981; Kaputska et al., 2004). The toxicity of these metals depends on several factors such as the form of the metals (i.e. dissolved metals or metals associated with particulate matter), presence of other metals, the conditions and behavioral response of the organisms (Forstner and Wittmann, 1981). Other metals such as Pb, Hg, Cd, Ni and As that have no metabolic role can also have adverse effects on organisms once exposure to a certain threshold and uptake are exceeded (Moriarty, 1999). In contrast to metals, organic contaminants such as herbicides are synthesized compounds which are designed to have adverse effects on weeds in order to control their spread during crop production (CABI, 2003). Several herbicides are used in agriculture in the UK with simazine and atrazine being the two most widely used triazine herbicides accounting for 28 % and 33 % respectively of the total triazine herbicides used for crop production in 2004 (DEFRA, 2006). In addition to their usage for crop production, some phenylurea herbicides such as diuron are also used as biocides in antifoulant paints for boats and ships to protect their hull from colonization by bacteria and algae (Voulvoulis et al., 1999). Herbicides can be inherently harmful to non-target organisms which make them an environmental concern. Laboratory experiments have shown that diuron at a concentration greater than 78 µg L^{-1} can result in the death of the fish *Pimephales promelas* (Call et al., 1987). These contaminants can also enter into the food chain and potentially result in bioaccumulation in higher organisms such as oysters and ultimately affect human health. For example, simazine and atrazine are known to be potential endocrine disruptors (a range of substances which can interfere with the hormone systems of humans) (COM, 2001).

Managed realignment schemes have been implemented in other countries such as Germany, United States, Japan and The Netherlands since the 1970’s (ABP, 1998). The drivers for the implementation of the scheme vary geographically but generally include salt marsh restoration and creation, recovery of threatened species, improvement of landscape integrity and flood defence (Spencer et al., 2008). In the UK, the main drivers for the implementation of managed realignment are salt marsh restoration in order to comply with the no-net loss policy of the EU Habitat Directive and the enhancemant of coastal flood defence (Andrews et al., 2006). In the UK, several managed realignment schemes have been commissioned, mainly in south-east England where there is considerable salt marsh erosion. Some of these include the managed realignment scheme at Tollesbury fleet and Orplands Farm which were commissioned in 1995, the scheme at Abbott Hall which was commissioned in 1996 and the scheme at Wallasea Island which was commissioned in 2006. Due to concerns over the eventual fate of dredged sediments and their ecological consequences, only a few managed realignment schemes have been implemented by flooding sites where dredged sediment have been beneficially re-used to raise the elevation of the site for salt marsh plant establishment in the UK (ABP, 1998; Bolam et al., 2005). The restoration of coastal habitats in these managed realignment sites partly depends on the sediment properties. For example, macrofaunal colonisation depends upon the bulk density and particle size of the sediments and changes in these parameters (Bolam et al., 2005; Bolam et al., 2004). Organic matter is essential for the growth of aerial tissue and rhizomes in salt marsh cordgrass (Padgett and Brown, 1999). Nutrient uptake by salt marsh plants which is necessary for their development can be affected by sediment pH (ABP, 1998). Callaway (2001) indicated that drainage and compaction can impede root development in salt marsh plants. In the UK, sediment parameters are the least considered in monitoring assessments which are conducted to evaluation the success of these sites despite their importance for habitat restoration (Spencer et al., 2008). The monitoring that is carried out in managed realignment sites usually includes measurement of sediment accretion and/or erosion, water level, current flow and wave characteristics, species diversity and abundance of the saltmarsh and invertebrate habitats (Leggett et al., 2005; ABP, 1998).

More habitat restoration/creation schemes have been implemented using dredged sediments in the United States compared to the UK (ABP, 1998). Hence, several studies have monitored the changes in the sediment parameters in restored and created salt marshes in the United States (Lindau and Hossner, 1981; Moy and Levin, 1991, Streever, 2000; Shafer and Streever, 2000; Craft et al., 1999, Edward and Proffitt, 2003). These studies were designed to compare the physical and chemical parameters of the sediment in restored and created salt marshes with those in nearby natural salt marshes which served as developmental targets. This comparison is based on an assumption that over time, the sediment parameters in a created salt marsh become similar to those in the natural salt marsh and the created salt marsh may function in a similar manner to the natural salt marsh (Stolt et al., 2000). The parameters that are often monitored include organic matter content, sediment texture, bulk density and particle size (Moy and Levin, 1991; Shafer and Streever, 2000; Edward and Proffitt, 2003; Craft et al., 1999). Craft et al. (1999) observed that the organic matter content in a created saltmarsh in North Carolina was significantly lower compared to a nearby natural saltmarsh. However, Shafer and Streever (2000) found slight differences in the organic carbon content between created and natural saltmarshes along the Texas coast. Similar studies on salt marshes restored on sites where dredged sediments have been beneficially re-used in the UK (ABP, 1998), and as a result, there is insufficient understanding of sediment maturation in these sites and the effect of changes in these sediments on habitat development.

1.6 Sorption-desorption of metals and herbicides

1.6.1. Sorption-desorption of metals

In soil and sediment, some metals are incorporated into the crystalline sillicates by irreversible adsorption reactions. However, majority of metals are precipitated with carbonates, precipitated with or sorbed by ion exchange to Fe and Mn oxides and hydroxides, complexed with organic matter and adsorbed by ion-exchange to clay minerals (Eggleton and Thomas, 2004; Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Alloway, 1995). In the majority of anoxic sediments, metals are primarily bound to the sulphide phase (Jenne, 1976; Simpson et al., 1998; Eggleton and Thomas, 2004). Although these metals may precipitate as sulphides directly, given the high concentration of Fe and Mn in sediments, they are more likely to co-precipitate with FeS and MnS (Eggleton and Thomas, 2004). Changes in the physicochemical conditions in soil and sediment such as salinity, redox and pH have been observed to affect these metal particulate interactions, leading to metal desorption (Bauske and Goetz, 1993; Calmano et al., 1992; Millward and Liu, 2003; Gambrel et al., 1991). Therefore, metals which sorb to Fe and Mn oxides and hydroxides, carbonates, organic matter, sulphides and clay minerals are the metals that can potentially be affected by physical and chemical changes in the soil and sediment environment in managed realignment sites following tidal inundation.

Metal sorption has been shown to be a two stage process with an initial rapid sorption of metals onto particle surfaces, followed by a much slower sorption which is related to the diffusion of the metals into micropores and Fe oxides in particles (Millward and Turner, 1995; Mustafa et al; 2004, Liu et al., 1998; Selim and Amacher, 2001). The diffusion can lead to the formation of strongly bound metals over time (Millward and Liu, 2003) which can limit metal desorption into the porewater.

1.6.2. Sorption-desorption of herbicides

Herbicides sorb mainly to organic matter and clay particles, with organic matter being the most important sorption site (Chiou, 1989; Gao et al., 1998; Voulvoulis et al., 2002). Clay particles become important for the sorption of herbicides if the herbicide molecules are ionically charged (Laird et al., 1994; Spark and Swift, 2002). Herbicides such as simazine and atrazine can either be ionically charged or neutral. The distribution of these herbicides into the ionic and neutral forms depends on their respective dissociation constants (pKa) and the pH of the system. At pKa > pH, these herbicides exist as cations and sorb by cation exchange to clay particles while at pKa < pH, neutral forms become dominant and sorb by hydrophobic partitioning to organic matter (Seol and Lee, 2001). Other herbicides such as diuron (which is a phenylurea herbicide) are neutral with no surface charge and sorb by hydrophobic partitioning to organic matter. Hydrophobic partitioning is analogous to the partitioning of a hydrophobic compound between an aqueous phase and organic solvent phase. Partitioning refers to the homogenous distribution of the sorbed organic contaminant throughout the entire volume of the organic phase (Chiou et a., 1989; Warren et al., 2003). There are other sorption mechanisms which can occur instantaneously upon contact of herbicides and soil/sediment which include hydrogen bonding, Van der Waal forces and electrostatic interactions such as dipole-dipole interactions (Gevao et al., 2002).

The sorption of organic contaminants is often regarded as biphasic with an initial rapid sorption phase followed by a slow sorption phase (Ball and Roberts, 1991; Wu and Gschwend, 1986; Brusseau and Rao, 1989; Pignatello et al., 1993). The slow sorption has been attributed to the diffusion of organic contaminants into pores within particles (intraparticle diffusion or sorption retarded particle diffusion) (Ball and Roberts, 1991; Wu and Gschwend, 1986) and diffusion into the organic matter matrix (intra-sorbent diffusion or retarded organic matter diffusion) (Brusseau and Rao, 1989; Pignatello and Xing, 1996; Brusseau et al., 1991). Slow sorption can lead to the formation of strongly bound contaminant residues over time which is resistant to desorption (Pignatello and Xing, 1996). Therefore, sorbed organic contaminants may be easily desorbed, desorbed with varying degree of difficulty or not desorbed at all. In general, the desorption of organic contaminants decreases with increasing contaminant n-octanol-water partition coefficient (K_{ow}) (Karickhoff and Morris, 1985). The n-octanol-water partition coefficient (K_{ow}) is used to assess the contaminant hydrophobicity and it reflects the affinity of the organic contaminant to sorb to organic matter (Hassett and Banwart, 1989; Chiou and Kile, 1994).

1.7. Changes to sediment and soil in managed realignment sites

Maintenance-dredged estuarine sediments are usually anoxic and changes can occur in the physicochemical conditions in these sediments following their importation into a managed realignment site to raise the elevation of the site for salt marsh plant establishment. After dredging, the sediments are transported through pipelines to the site and they usually have high moisture content (ABPmer, 2004). The moisture content in dredged sediment can be greater than 60 % of the total weight of the sediments (Vermeulen et al., 2003). Hence, the sediments require dewatering. Dewatering can occur either through evaporation, run-off or drainage. Sedimentation and consolidation also occur during dewatering. As sediment particles start to settle, those less than 2 µm in diameter (clay minerals) may flocculate and form floc (Vermeulen et al., 2003). Floc formation occurs when negative charges on the particles are neutralised by seawater cations (Open University, 1999). The flocs then start to form bonds and this is the beginning of the self-weight consolidation of the sediment particles. The pressure resulting from the weight of the sediments forces out pore water and causes further consolidation (Vermeulen et al., 2003). These processes (dewatering, sedimentation and consolidation) transform the sediment from a soft to a hard consistency, improve aeration, increase permeability and lead to subsidence of the surface of the sediment and the formation of prisms separated by shrinkage cracks (Vermeulen et al., 2003). The improved sediment aeration can result in an increase in redox potential, an increase in microbial activity and a decrease in pH primarily due to the oxidation of metal sulphides formed under the anoxic conditions (Petersen et al., 1997; Simpson et al., 1998; 2000). The oxidation of metal sulphides can result in the release of sulphide bound metals into the porewater (Eggleton and Thomas, 2004). Metals co-precipitated with or adsorbed to FeS and MnS are rapidly oxidised due to their relative solubility in oxic conditions while more stable sulphide bound metals such as CuS and FeS_2 take longer to be oxidised due to their slower oxidation kinetics (Caetano et al., 2003; Eggleton and Thomas, 2004).

Flooding of agricultural soil in a managed realignment site can lead to physical and chemical changes in the soil environment. The influx of seawater into the soil results in an increase in salinity as the fresh water in the soil pores is replaced by seawater (Blackwell et al., 2004; Boorman and Hazelden, 2002). The increase in salinity can affect the organisation of the clay particles and increase their susceptibility to dispersion. These changes can lead to water-logging of the soil, loss of soil structure and a reduction in hydraulic conductivity (Crooks and Pye, 2000; Blackwell et al., 2004; Emmerson, 2000). As the soil becomes water-logged, O_2 is depleted in the soil due to the continued microbial utilization of O_2 for organic matter oxidation and the low solubility of O_2 in water (McBride, 1994). When the dissolved O_2 reduces to trace levels (about 10^{-6}M), anaerobic conditions develop and this is reflected in a decrease in redox potential accompanied by an increase in pH towards neutrality (pH 6.7 to pH 7.2) (McBride, 1994; Mitsch and Gosselink, 2000). Anaerobic microbial communities that are capable of utilizing alternative terminal electron acceptors for the oxidation of organic matter develop (Mitsch and Gosselink, 2000; Williams et al., 2004; Corstanje and Reddy, 2004). The alternative terminal electron acceptors are utilized in the following sequence: NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-} and CO_2 (Salomon and Forstner, 1984; Mitsch and Gosselink, 2000). The reduction of Fe^{3+} and Mn^{4+} can lead to the release of co-precipitated and sorbed metals into the porewater (Williams et al., 1994; Spencer et al., 2002). These reduction reactions require continued soil flooding to saturate the pore spaces in order to create anaerobic conditions and organic matter in order to support microbial activity. Once the soil drains and O_2 re-enters the soil, many of the reduction reactions are reversed and the redox potential is increased, the reduced Fe and Mn are oxidised, and pH is decreased (McBride, 1994).

An increase in the salinity of soil and sediment can result in metal desorption from the soil and sediment particles (Millward and Turner, 1995; Millward and Liu, 2003; Paalman et al., 1994; Gambrell et al., 1991; Calmano et al., 1992). This is due to competition between seawater cations (Na^+, Mg^{2+}, K^+ and Ca^{2+}) and the sorbed metals for binding sites on the soil and sediment particles leading to metal desorption into the porewater. The metals that are readily desorbed are those sorbed by cation exchange reactions onto the particle surface (Warren and Haack, 2001). Furthermore, seawater is enriched with high concentrations of seawater anions (Cl and SO_4^{2-}) which can form soluble complexes with sorbed metals (Turner and Millward, 2002; Millward and Liu, 2003; Paalman et al., 1994). The formation of these soluble complexes can also result in metal desorption from the soil and sediment particles into the porewater. Organic contaminants exhibit different behaviours in response to changes in salinity depending on whether they are ionically charged or neutral. In general, the solubility of uncharged neutral organic contaminants such as diuron show an inverse relationship with the concentration of dissolved salts in solution due to salting out effect. Salting out refers to the reduction in the aqueous solubility of neutral organic contaminants due to the more ordered and compressible nature of water in the presence of dissolved ions (Turner and Millward, 2002; Turner and Rawling, 2001). The water-ion interactions and the compression of water molecules in hydration spheres act to salt out the organic solute from solution (Turner and Millward, 2002). Therefore, as salinity increases, the sorption of these contaminants is expected to increase as the dissolved contaminant concentration in the porewater decreases. For organic contaminants which carry a charge and bind to particles by cation exchange, an increase in salinity can lead to a decrease in the sorption of these contaminants to particle surfaces due to competition reactions with seawater cations (Burton et al., 2004) leading to desorption into the porewater.

As previously described in Section 1.5, managed realignment sites are periodically inundated and drained which makes them susceptible to wetting and drying cycles particularly in areas of high elevation. Several studies have found that such drying and rewetting can enhance the mineralisation of soil organic matter which is reflected in the increased formation of CO_2 (Van Gestel et al., 1993; Degens and Sparkling, 1995; Miller et al., 2005; Fierer and Schimel, 2003, Haney et al., 2004; Bottner, 1985; Magid et al., 1999; Kieft et al., 1987; Lundquist et al., 1999; Appel, 1998). This is due to the disruption of soil aggregates following drying and rewetting which exposes organic matter previously trapped within the soil. The exposure of organic matter stimulates microbial activity which results in enhanced organic matter mineralisation and CO_2 release (Kieft et al., 1987; Lundquist et al., 1999; Appel, 1998). The increase in the mineralisation of organic matter due to drying and rewetting can also lead to an increase in the release of dissolved organic matter (DOC) (Fierer and Schimel, 2003; Miller et al., 2005; Reemtsma et al., 2000). Unlike soil, studies on the effect of drying and rewetting on organic matter mineralisation in sediments are limited and have focussed on changes in microbial metabolism and nutrient cycling (Amalfitano et al., 2008; Baldwin and Mitchell, 2000). The enhanced mineralisation of soil organic matter following drying and rewetting can have implications for the release of metals and herbicides from soil and sediment into the porewater given that organic matter is an important binding site for metals (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Alloway, 1995) and herbicides (Gao et al., 1998; Voulvoulis et al., 2002, Chiou et al., 1989) The enhanced mineralisation of soil organic matter due to drying and rewetting may affect the binding of the metals and herbicides to the soil organic matter and result in the increased solubility and release of organic matter associated metals and herbicides into the porewater. This potential for metal and herbicide release from soil and sediment in managed realignment sites due to the effect of drying and rewetting cycles on the mineralisation of organic matter has not been previously considered.

1.8 Modelling contaminant release

Contaminant release is mainly controlled by physical transport (diffusion and advection), chemical (sorption and desorption) and biological processes (bioturbation) (Vandenberg et al., 2001). Diffusion is often the dominant transport mechanism in fine-grained sediments with high clay and silt content, low permeability and low hydraulic conductivity (Grathwohl, 1998; Huettel et al., 2003; Berner, 1980). Diffusion describes mass transport due to the random motion of solute molecules (Grathwohl, 1998). Solute molecules are constantly in random motion, colliding with water molecules in the process. This results in the net movement of molecules from a region of high concentration to a region of low concentration. Transport by advection can be caused hydrological flows (Boudreau, 1997). Hydrological flows can cause pressure gradients that force porewater across the sediment-water interface (Huettel et al., 1998). The intensity of the advective porewater exchange is dependent on intrinsic permeability, occurring mainly in coarse sandy sediment with permeability greater than 10^{-12} m^2 (Huettel and Rusch, 2000; Huettel et al., 2003). Bioturbation refers to the daily activities of benthic organisms such as sediment ingestion/defecation, burrowing, excavation and tube construction which can result in enhanced particle, dissolved and sorbed solute transport (Reible et al., 1996; Aller and Aller, 1992; Aller and Aller, 1998). Bioturbation usually occurs in the upper few centimetres of sediments and it can increase fluxes from/into the overlying water (Warren et al., 2003; Reible et al., 1996). The principal agents include macro-invertebrates such as polychaetes, oligochaetes, chironomides and crustaceans. Bioturbation is a significant transport mechanism in aquatic environments comprising organic rich sediments with high biological productivity and where sediment resuspension by erosive forces is negligible (Reible et al., 1996; Warren et al., 2003).

Models based on the physical transport processes have been developed to predict contaminant transport and fate in aquatic systems (Valsaraj et al., 1998; Qaisi et al., 1996; Valsaraj and Sojitra, 1997; Allan et al., 2004; Daniels et al., 1998, Bekhit and Hassan, 2005). In the development of contaminant transport models, it is necessary to represent the operating process in the model as mathematical differential equations.

There are two general ways of solving these resulting equations: analytically or numerically. Based on this, models can be described as analytical or numerical. Analytical models are based on simplified assumptions and they are only applicable to simple systems due to the need to produce exact solutions (Go et al., 2008; Grathwohl, 1998). However, most environmental systems are often described by functions for which there are no analytical solutions due to the complexity of these systems (Wainwright and Mulligan, 2004). For example, in modelling contaminant transport, the contaminant concentration may constantly be altered in a way that is not regular, and analytical solutions may not be possible in these situations. In these cases, numerical solutions are frequently the only option. Numerical models can accommodate temporal and spatial variability inherent in environmental systems. For example, Allan et al. (2004) investigated the spatially explicit diffusive transport of organic contaminants in river sediments using numerical modelling. The sorption and desorption kinetics of organic contaminants have also been examined using numerical modelling (Wu and Gschwend, 1986).

1.9 Aim and objectives

One of the justifications for the implementation of managed realignment offered by the UK Environment Agency is that these sites can serve as a sink for contaminants from estuarine waters (NRA, 1994). Andrews et al. (2006) and Cave et al. (2005) have also indicated that managed realignment sites can be important stores for metals and other particle reactive contaminants. However, these sites may also serve as a source of contaminants to estuarine waters due to changes in the physical and chemical conditions in the soil and sediment environment following tidal inundation.

In the UK, there are only a few managed realignment sites where dredged sediments have been beneficially re-used to raise the elevation of the site for salt marsh establishment (ABP, 1998). In order to comply with the EU Habitat Directive, the requirement of the Biodiversity Action Plan is for an annual rate of habitat restoration of 60 ha year^{-1}, with an additional 40 ha year^{-1} for 15 years (UK Biodiversity Group, 1999). With this scale of habitat restoration, the implementation of managed realignment by flooding of agricultural soil or sites where dredged sediments have been beneficially re-used is likely to increase in the future. Estuarine sediments can have significant metal levels due to anthropogenic contamination of the estuarine environment and the strong affinity of metals for particulate matter (Spencer et al., 2002; Cave et al., 2005). Herbicide application during crop production may also result in herbicide enrichment in agricultural soils. In managed realignment sites, salinity changes in agricultural soil and dredged sediment following tidal inundation may lead to the release of these metals and herbicides into estuarine waters. In addition, drying and rewetting cycles can increase the mineralisation of soil organic matter (Van Gestel et al., 1993; Degens and Sparkling, 1995; Miller et al., 2005; Fierer and Schimel, 2003**)**. Such increased organic matter mineralisation due to drying and wetting cycles in managed realignment sites following tidal inundation may result in the release of organic matter associated metals and herbicides. While several studies have examined the biological and ecological development of managed realignment sites (Garbutt et al., 2006**;** Wolters et al., 2005; Bolam and Whomersley, 2005; Hughes and Paramor, 2004), only a few studies have examined geochemical changes in agricultural soil in these sites (Emmerson et al., 2000; MacLeod et al., 1999). These studies have indicated that there is a release of metals following tidal inundation of agricultural soil in managed realignment sites. Darby et al. (1986) also observed the release of metals from the dredged sediments in created salt marshes. However, there have been no studies on the fate of soil and sediment associated organic contaminants such as herbicides in managed realignment sites. Given that our current understanding of the fate of contaminants in managed realignment sites is limited, this thesis sets out to address this by considering the following aim and objectives.

The overall aim of this thesis was to examine the potential for metal and herbicide release from agricultural soil and dredged sediment in managed realignment sites following tidal inundation. In order to achieve this aim, a series of investigations were conducted which included a field study, laboratory experiments and a modelling investigation. The specific research objectives were:

- To examine the physical and chemical changes in sediment exposed to drying-wetting cycles and salinity changes in the Wallasea Island Managed realignment site in order to inform the laboratory experiments, and to examine by comparison, whether the sediment parameters in the restored salt marsh and mudflat were approaching those in a natural salt marsh and mudflat.
- To examine the effect of salinity on the release of metals and herbicides from agricultural soil and dredged sediment

- To examine the effect of drying and rewetting on the release of metals and herbicides from agricultural soil and dredged sediment
- To investigate, using a diffusion model, the mechanisms of metal and herbicide release from agricultural soil and dredged sediment under the experimental conditions in this study.

Chapter 2 Physical and chemical changes in sediments at Wallasea Island managed realignment site.

2.1 Introduction

The main goals of managed realignment in the UK are habitat restoration and the enhancement of coastal flood defence. The restored salt marsh compensates for salt marsh loss due to coastal squeeze and provides an area over which wave energy is dissipated thereby enhancing coastal flood defence (Shepherd et al., 2007; Boorman, 2003). Typically, managed realignment is implemented on low-lying reclaimed agricultural land and the restoration of salt marsh plants requires the accretion of sediments to raise the land to an elevation suitable for salt marsh plant development (French, 2006; Crooks and Pye, 2000). As a result, managed realignment has also been implemented by importing dredged estuarine sediments into the site to raise the elevation of the site. Estuarine sediments can be a sink for contaminants and they can have significant contaminant levels (Cave et al., 2005; Spencer et al., 2002; Comber et al., 2002). However, these sediments are not permanent sinks and changes in the physical and chemical conditions in the sediment can result in a release of the contaminants. Changes in sediment parameters such as pH and salinity have been shown to result in the release of metals (Gambrell et al., 1991; Calmano et al., 1993; Emmerson et al., 2001). The extent of these changes in sediments in managed realignment sites and hence the potential for contaminant release will depend on the frequency and duration of sediment tidal inundation and drainage which in turn depends on the elevation of the sites. As earlier described in Chapter 1, drying and wetting cycles, and salinity changes to agricultural soil and dredged sediment in managed realignment sites can lead to the potential release of contaminants from the soil and sediment into estuarine water and this is examined through laboratory experiments described in Chapter 3. A field study will be beneficial in identifying the salinity conditions in the sediment and the periodicity of sediment inundation and drainage at a managed realignment in order that the conditions can be simulated for the purposes of the laboratory experiments.

A number of studies have monitored the changes in the physical and chemical parameters of sediments in habitat restoration/creation schemes where dredged sediments have been beneficially re-used in the United States (Lindau and Hossner, 1981; Moy and Levin, 1991; Streever, 2000; Shafer and Streever, 2000). These studies compared the physical and chemical parameters of the sediment in restored and created salt marshes with those of nearby natural salt marshes. The use of this approach is based on an assumption that over time, the sediment parameters in a restored or created salt marsh become similar to those in the natural salt marsh, hence the restored or created salt marsh is likely to function in a similar manner to the natural salt marsh over time (Stolt et al., 2000). Similar studies on salt marshes restored on sites where dredged sediments have been beneficially re-used are limited in the UK (ABP, 1998), hence sediment maturation in these sites are poorly understood.

This chapter presents the findings of a field study which assessed the physical and chemical changes in sediments exposed to drying-wetting cycles and salinity changes at Wallasea Island managed realignment site in order to inform the laboratory column microcosm experiments which examined the effect of drying-rewetting and salinity on the release of metals and herbicides from soil and sediment in managed realignment sites and to examine, by comparison, whether the sediments parameters of the restored salt marsh and mudflat were approaching those of a natural salt marsh and mudflat adjacent to the managed realignment site. This was achieved by using a multi-parameter monitoring approach to track the changes in the sediment at the Wallasea Island managed realignment site over a 12-month period. Wallasea Island managed realignment site is the largest managed realignment site in the UK where dredged sediment have been beneficially re-used to raise the elevation of the site for salt marsh plant establishment. The sediment parameters which were measured include moisture content, organic matter content, bulk density and porosity, pH, porewater DOC and porewater Cl content. Cl content was used as a proxy for sediment salinity; organic matter content and porewater dissolved organic carbon were measured to evaluate changes in organic matter; changes in sediment compaction were evaluated by measuring bulk density and estimating porosity and pH gave a measure of the sediment alkalinity. In addition, the on-site conditions (e.g. atmospheric temperature) were used to design the laboratory experiments (Chapter 3, Section 3.3.2 and 3.3.4) in order to ensure that the experiments simulated practical conditions at a managed realignment site. This study provides valuable insight on the changes to beneficially re-used sediments in managed realignment schemes. Such information will be valuable in evaluating the status of similar schemes.

2.2 Materials and methods

2.2.1 Site Description

Wallasea Island (51^0 36.999N; 00^0 49.299E) is located in Essex, south-east England (Figure 2.1). It is bordered to the north and south by the Crouch and Roach estuaries respectively. The Crouch estuary converges with the Roach estuary on the north east corner of Wallasea Island and forms a single system that drains into the sea between the Thames and the Blackwater estuaries. From the confluence, the Crouch and the Roach estuaries extend for approximately 30 km and 15 km before reaching their tidal limits at Battlesbridge Mill and Rochford respectively (ABPmer, 2004). The Crouch estuary is a micro-tidal coastal plain system with low volumes of fresh water input relative to the volume of the estuary (Waldock, 1999; ABPmer, 2004). For most of the year, the estuary is dominated by flows of high-salinity waters along much of its length (approximately 25 - 31 ‰) (Bolam et al., 2004; ABPmer, 2004).

The estuary system is a relatively shallow and narrow channel that is entirely defended by seawalls. The system is ebb dominated and suffers from poor 'flushing' on the low ebb tides (Bolam et al., 2004; ABPmer, 2004). This results in the deposition of sediment and a decrease in channel depth. With rising sea levels, and as tidal velocities increase, erosion has become a dominant feature of the estuary channel, placing considerable stress on existing seawalls (ABPmer, 2004).

The estuary has limited intertidal margins which consist mainly of mudflats with narrow fringes of salt marsh (ABPmer, 2004). Much of the intertidal area has been reclaimed and the salt marshes have been subjected to excessive erosion. These two factors have resulted in approximately 50 % reduction in the inter-tidal area along the Crouch estuary (Cottle et al., 2002). Despite its greatly diminished extent, the remaining salt marshes continue to support a significant number of birds, particularly the wintering water birds such as the brent goose and up to 20,000 waterfowls (Cottle et al., 2002; Chesman et al., 2006). The salt marshes are also important for the assemblage of several species of rare invertebrates such as the scarce emerald damselfly and an assemblage of nationally scarce plants such as shrubby sea-blite (Cottle et al., 2002). By virtue of the species diversity of the plants and invertebrates and the abundance of the bird population, the area is deemed important for conservation. It has several national and international designations. It is a Special Protection Area (SPA) for wild birds (designated under the

European Commission Directive on the conservation of wild birds), a Special Area of Conservation (SAC) (designated under the EU Habitat directive) and a Ramsar site (designated as a wetland of international importance under the Ramsar Convention) (Cottle et al., 2002).

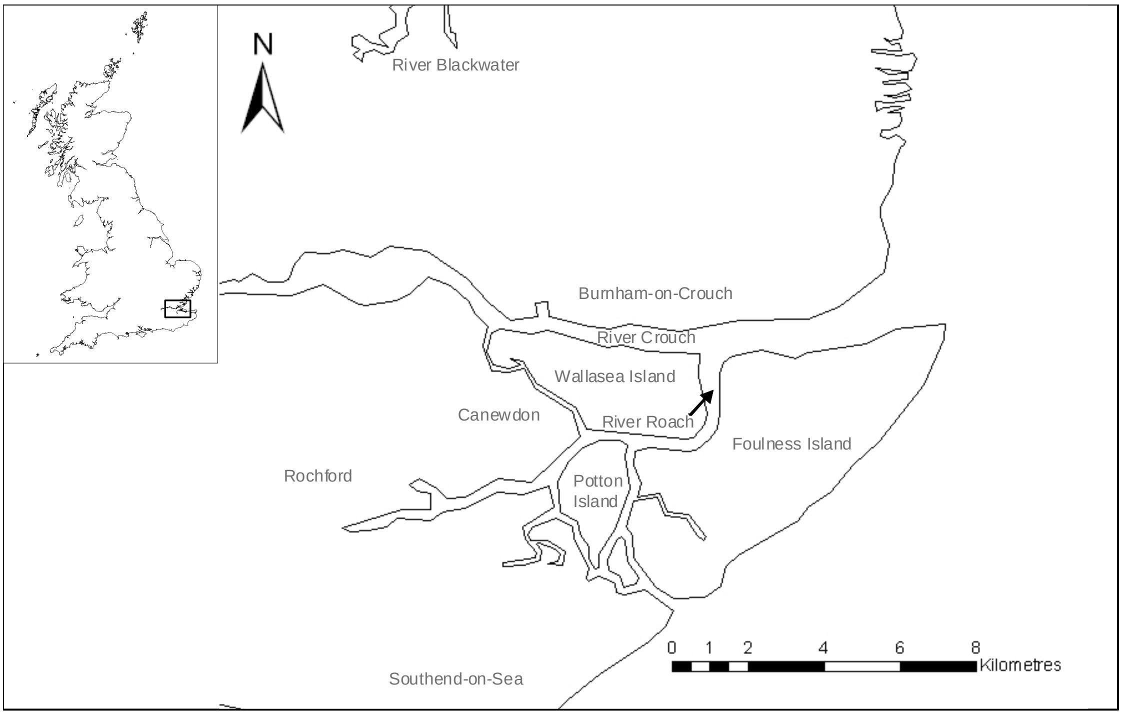

Figure 2.1 Map of the South East coast of England showing the location of Wallasea Island. The insert map shows the UK with a box denoting the location of the detailed section.

Wallasea Island was a salt marsh prior to reclamation and it is hydrologically isolated from direct tidal influence by seawalls, typically clay embankments, constructed over 100 years ago (ABPmer, 2004). The seawall has been subject to several episodes of breaching. The most significant to date is the great flood of 1953 which overtopped and breached the seawall leaving most of the Island under water (ABPmer, 2004). The Island is primarily rural in character with 820 ha (8.2 x 10^6 m^2) of farmed arable agricultural land owned by Wallasea Farms Limited and about 50 ha (0.5 x 10^6 m^2) of residential areas with a few cottages to the west of the island (ABPmer, 2004). In addition, there is the Essex Yacht Marina located to the western end of Wallasea Island and the Stambridge Mill which are the main areas of commercial activity. There is also a nearby timber yard, a hotel and Ministry of Defence estates at Foulness, Havengore and Baltic Terminals respectively to the north western end of the Island. The closest built up area is Burnham-On-Crouch which is 3 km north of Wallasea Island, on the north bank of the Crouch estuary. The Crouch estuary is extensively used for recreational activities such as water skiing, sailing, canoeing and wind surfing. The harbour is one of the leading sailing and power boating centres in the UK (ABPmer, 2004)

The managed realignment site is located on the north eastern bank of Wallasea Island, south shore of the Crouch estuary (Figure 2.2). Before May 2005, the seawall in this area of the Island (north eastern bank) was in a deplorable condition because it was steadily eroded by repeated tidal force and wave energy (ABPmer, 2004). There was a high risk of the seawall breaching in an unmanaged way which could result in the flooding of the Island and other significant potential effects on the estuary. As a result, a new seawall was constructed on the north eastern bank of the Island in 2005, with the new seawall set back 400 m from the original seawall (ABPmer, 2004). The area between the original and the new seawall formed the managed realignment site which is approximately 108 ha (1.08×10^6 m^2) in size and 4 km in length. Before construction, the site was a part of the 820 ha (8.2×10^6 m^2) arable agricultural land owned by Wallasea Farms Limited. The primary objective of the managed realignment scheme was to compensate for the loss of habitats that occurred following port developments at Lappel Bank in the Medway and at Fagbury Flats in the Orwell Estuary. The objective overlapped with providing a robust defence against flooding from the sea (ABPmer, 2004).

Several studies have indicated that the elevation most suitable for salt marsh plant establishment in the UK lies between Mean High Water Neap and Mean High Water Spring (French, 2006; Legget and Dixon 1994; Pye and French, 1993). The Mean Low Water and Mean High Water Neap tide levels in the Crouch estuary are at 0.65 and 1.85 m ODN respectively while the Mean Low Water and Mean High Water Spring tide levels are at 1.65 and 2.85 m ODN respectively (ABPmer, 2004). Since the land at Wallasea Island is at a relatively low elevation, the land surface had to be raised to an intertidal threshold elevation relative to the tidal level suitable for salt marsh establishment (ABPmer, 2004). To achieve this, the managed realignment site was raised by importing into the site, approximately 700,000 tonnes of dredged sediment sourced from maintenance dredging at the Port of Harwich (ABPmer, 2004).

Figure 2.2 Aerial photo of Wallasea Island Managed Realignment site showing the River Crouch and the arable agricultural land. Courtesy of Colin Scott, ABPmer Limited, Southampton.

Discharge pipelines connected to a trailer suction dredger were used to pump the dredged sediment ashore between the pre-constructed containment bunds and the new seawall (Figure 2.3). The bunds, designed such that they erode over a period of 5 – 10 years, ensured the retention of the fine grained sediment, allowing it to settle, dewater and consolidate. The sediment was pumped as a thick slurry with a bulk density of approximately 1.25 g cm^{-3} (ABPmer, 2004). The original seawall was breached at six locations to facilitate the restoration of intertidal habitats in the managed realignment site following tidal inundation. The site was divided into three hydrodynamically separate restored areas namely Area A west, Area A east and Area B, with each area exchanging water with the adjacent estuary but no flows between neighbouring areas of the wider realignment site (ABPmer, 2004) .

Figure 2.3 Sediment discharge into a containment bund at Wallasea Island Managed realignment site. Looking north across the River Crouch to Burnham-On-Crouch. Courtesy of Colin Scott, ABPmer Limited, Southampton.

The physical and chemical changes in the sediment were measured at four different locations: two within the managed realignment site, with one in the restored salt marsh (RMS) and the other in the restored mudflat (RMF), one within the nearby natural salt marsh (NSM), and one within the nearby natural mudflat (NMF) (Figure 2.4). These sampling locations will be hereafter referred to as RSM, RMF, NSM and NMF. The NSM and NMF served as reference sites. The sampling locations within the managed realignment site were restricted to Area A east (Figure 2.4) because most of the site was not accessible due to the relatively unconsolidated nature of the sediment and it was in close proximity to the natural salt marsh and mud flat. The NSM and RSM had elevations between 2.5 – 3.0 m ODN and 2.3 – 2.5 m ODN respectively while NMF and RMF had an elevation between 1.3 – 1.5 m ODN (ABPmer, 2004). These elevations, provided by ABPmer Limited, are based on a Digital Terrain Model (DTM) of Wallasea Island developed by ABPmer Limited using Geographical Information System (GIS) software. The model used Environment Agency Light Detection and Ranging (LiDAR) images and results of bathymetric surveys to describe the vertical elevation of the site with a vertical accuracy ± 30 cm. Figure 2.5 shows the surface elevation profile of the sampling locations incorporating the variation in elevation, with the seawall showing up in the profile as higher grounds.

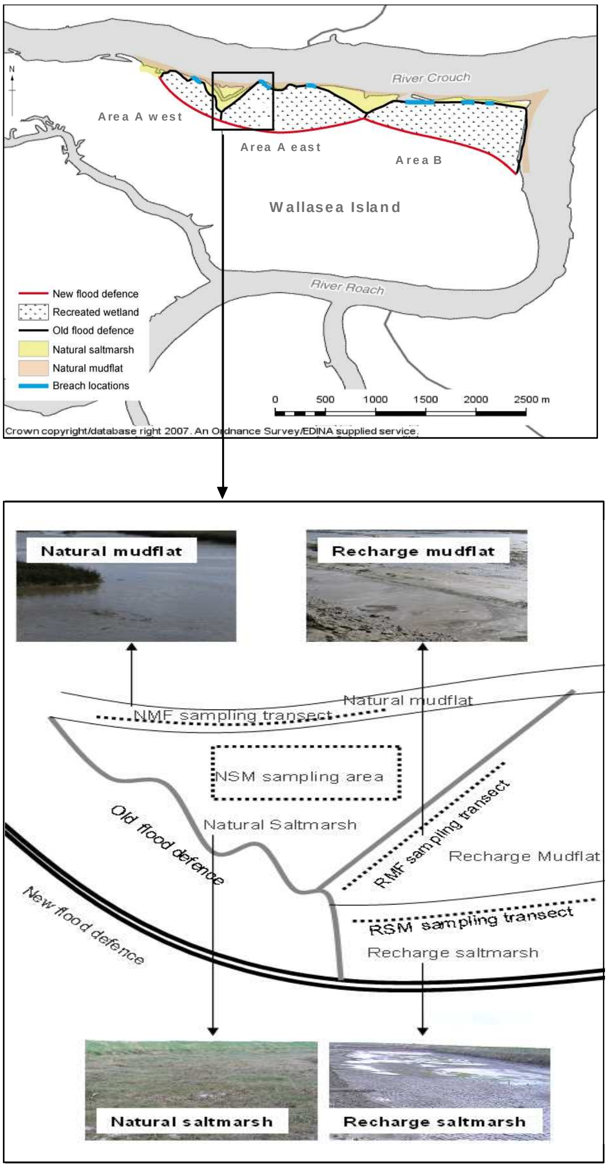

Figure 2.4. Map of Wallasea Island showing the three locations of the managed realignment site. The insert box denotes the location of the detailed section showing the four sampling locations.

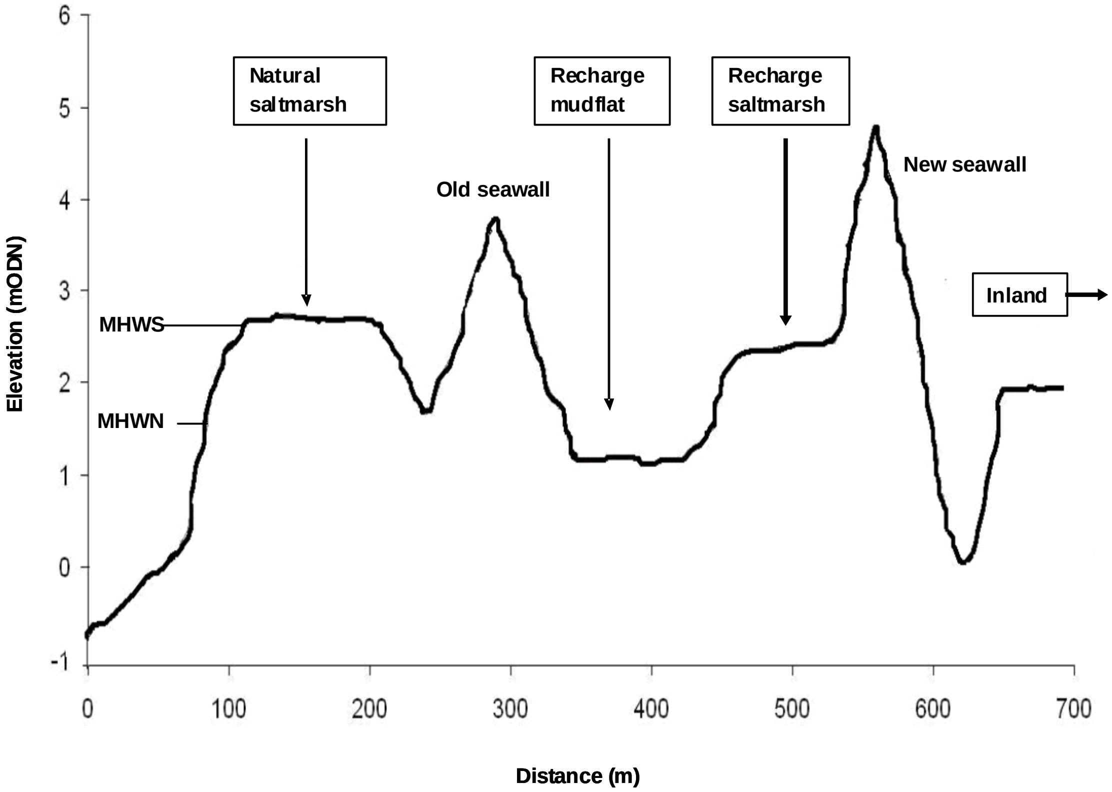

Figure 2.5 Surface elevation profile across the managed realignment site. The profile show vertical elevation (mODN) and distance from the sea (m). MHWS and MHWN represent Mean High Water Spring and Mean High Water Neap. Courtesy of Colin Scott, ABPmer Limited, Southampton.

Due to the similar elevations of the restored sites and the respective natural reference sites, the frequency and duration of tidal inundation of the sites were also similar (Figure 2.6). The frequency of tidal inundation was estimated based on the relationship between the site surface elevation and the water level. The frequency of inundation at the RMF and NMF were estimated to be approximately 43 %, covered by neap and spring tides indicating that these sampling locations were regularly flooded. In contrast, the RSM and NSM were not regularly flooded by tides. While the estimated frequency of inundation at the RSM was approximately 15 %, the frequency of inundation at the NSM was estimated to be approximately 10 %. These estimates were based on the site elevation (provided by ABPmer Limited) and predicted water level data (Crouch Harbour Authority tide timetable). Hence, the above percentages may be underestimated.

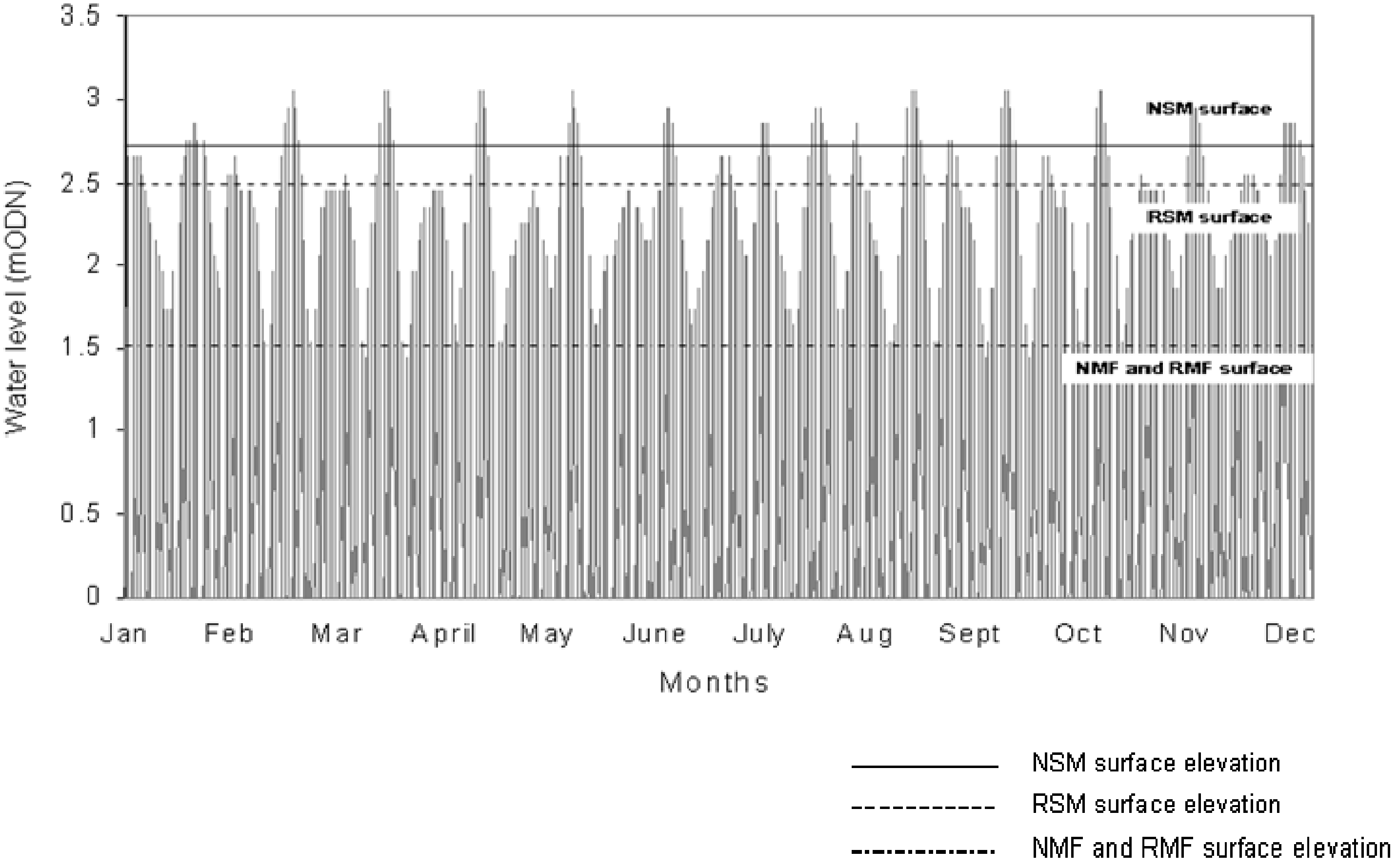

Figure 2.6 Water level and site elevation at NSM, RSM, NMF and RMF. The water levels were tidal predictions (mODN) from the Crouch Harbour Authority tide timetable.

2.2.2. Sediment sampling

As stated earlier, samples were collected from four sampling locations: RSM, RMF, NSM and NMF. Random sampling is preferred because every part of the sampling area has an equal probability of being sampled thereby reducing bias in the generated data set. However, random sampling was not possible at the four sampling locations because the relatively unconsolidated sediment within the managed realignment site and the natural mudflat presented a safety hazard which limited accessibility. Therefore, systematic sampling was employed in the RSM, RMF and NMF. Even though systematic sampling was the only option, the selected sampling locations and the sample size were deemed appropriate to give a good representation of the changes in the sediment over the study period.

Due to the limited accessibility, sampling was carried out along three permanent transects marked at each end with wooden stacks in the RSM, RMF and NMF (Figure 2.4). At each sampling location, sediment samples were collected monthly at 10 sampling points, each 5 m apart over the 12-month study period from January to December 2007. However, samples were collected for only 9-months in the NMF from April to December 2007. The 10 samples collected for each month served as replicates.

Random sampling rather than systematic sampling was employed in the NSM because of the easy access of the entire salt marsh. Within the NSM, a 169 m^2 rectangular sampling area was chosen and marked with wooden stacks. This area had distinct pioneer, lower and middle salt marsh vegetation that was representative of a well established salt marsh. Within the marked area, samples were collected each month from 10 randomly selected sampling points determined by a random number generator and these samples served as replicates. Care was taken not to re-sample a previous sample point.

At each sampling point, a stainless steel hand-held trowel was used to collect surface samples from the top 2 cm of the sediment. The samples were placed in a waterproof polyethylene bags, clearly labeled. The samples were analysed immediately after collection.

In the RSM and NSM, hollow bulk density rings (5.2 cm in diameter, 2.5 cm in height) were used to collect undisturbed sediment samples. Samples were collected at each sampling point, sealed with water tight end-caps and transferred to appropriately labelled polythene bags. Bulk density samples were not collected at the RMF and NMF for health and safety reasons.

Core samples were also collected from the NSM and RSM to determine organic matter content at 8 - 10 cm depth. For health and safety reasons, the core samples were not collected from RMF and NMF. Five cores, each 10 cm in length and 5 cm in diameter, were collected from five of the sampling points in the RSM and NSM. At the time of coring, the 8 – 10 cm subsurface layer was sectioned and placed in a labelled polyethylene bag. All samples were collected at low tide.

Summary

Table 2.1 summarises the samples collected and measurements taken in the four sampling locations during the study period. The particle size distribution analysis was conducted once. Samples were collected from the top 0 – 2 cm surface sediment and the 8 – 10 subsurface sediment.

Table 2.1 List of samples collected and measurements taken at each sampling location.

Sample		Moisture content %	Organic matter %	Bulk density g m^{-3}	Porosity (cm^3 cm^{-3})	pH	Chloride mg L^{-1}	Particle size	DOC mg L^{-1}
RSM	Surface (0 - 2 cm)	√	√	√	√	√	√	√	√
	Subsurface (8 – 10 cm)	√	√						
NSM	Surface (0 - 2 cm)	√	√	√	√	√	√	√	√
	Subsurface (8 – 10 cm)	√	√						
RMF	Surface (0 - 2 cm)	√	√			√	√	√	√
	Subsurface (8 – 10 cm)								
NMF	Surface (0 - 2 cm)	√	√			√	√	√	√
	Subsurface (8 – 10 cm)								

2.2.3 Sample preparation and analysis

2.2.3.1 Organic matter and moisture content

Different methods have been developed for the determination of organic matter content in soil and sediment such as loss-on-ignition (LOI), wet oxidation using hydrogen peroxide or potassium dichromate (Rowell, 1994). In this study, organic matter content was determined by loss-on-ignition because it is rapid, inexpensive and safer compared to the other methods. LOI is used as an approximate measure of the organic matter content, following ignition of the soil or sediment at 500 – 550 ^{O}C. When soil or sediment is ignited, the organic portion oxidizes to CO_2, H_2O and a small amount of ash. Thus, the measurement of the mass lost during ignition can be used as an estimate of the organic matter content. Given that LOI is a mass loss based method, it is important to recognize that the loss of other components of the soil or sediment during ignition can affect the estimates. Structural water adsorbed to clay particles or present as part of the mineral lattice can be lost during ignition along with volatile salts and inorganic carbon leading to an over-estimation of organic matter content (Rowell, 1994).

In this study, approximately 10 g (± 0.01) sub-sample was weighed into a crucible. The sub-sample was oven-dried at 105 ^{0}C overnight, cooled in a desiccator and reweighed. The percentage moisture content was calculated. The oven-dried sample was then placed in a muffle furnace at 550 ^{0}C for 4 hours. The ignited sub-sample was cooled in a desiccator and re-weighed to estimate the organic matter content.

2.2.3.2 Dry bulk density and porosity

Bulk density samples were placed in an oven at 105 ^{0}C over night, cooled in a desiccator and weighed to give the mass of the oven-dried sample. Bulk density was determined by dividing the mass of the oven-dried sample by the volume of the sample.

The sample porosity was calculated using the bulk density and particle density as:

$$\text{Porosity} = \frac{1 - \text{bulk density (g cm}^{-3})}{\text{Particle density (g cm}^{-3})}$$

where the particle density was assumed to be 2.65 g cm^{-3} (Rowell, 1994).

2.2.3.3. Particle size analysis

The particle size distribution (i.e. clay, silt and sand fractions) of the sediment samples were analysed using a Laser Diffraction Particle Size Analyser (Beckmann). Laser diffraction is a rapid technique which covers a wide range of particle sizes (from 0 to 2000 µm) and therefore covers the whole range likely to be encountered in these sediments. The sizes of the clay fraction (< 4 µm), the silt fraction (4 - 63 µm) and the sand fraction (63 - 2000 µm) are equivalent to the Wentworth scale. Prior to the analysis, the organic matter was removed to allow for the analysis of the particle size of the mineral fraction (clay, silt and sand), as organic matter can bind the particles together (Rowell, 1994). The removal of organic matter can also lead to the disaggregation of large aggregates. Organic matter can be removed through ignition or through wet oxidation using hydrogen peroxide. While ignition is a rapid method of removing organic matter, loss of structural water from clay particles during ignition may result in changes in the size of the clay particles. Thus, in this study, hydrogen peroxide was used to remove organic matter.

Prior to the analysis, hydrogen peroxide was added to the samples and the samples were heated at around 80 ^{o}C on a hotplate until no further reaction occurred. The samples were then resuspended using sodium hexametaphosphate dissolved in deionised water which served as a dispersant.

2.2.3.4. pH

The sample pH was determined by using a sample suspension made with deionised water. 100 g (± 0.01) sub-sample was carefully weighed into a conical flask. 100ml of deionised water was added and the flask was sealed with parafilm. The pH of the deionised water was pH 5.9. The suspension was shaken for 30 minutes on a flat bed shaker to disperse the sediment in the water. This sample preparation ensured that adequate water was available in the sample to make liquid contact with the pH electrode (Craft et al., 2002). The pH of the sediment suspension was determined using a HANNA pH electrode and a HANNA HI 83140 pH meter. The pH meter was calibrated prior to use with two calibration solutions at pH 4 and 7. The pH electrode was rinsed with deionised water and wiped dry between sample readings.

2.2.3.5. Porewater dissolved organic carbon (DOC) and chloride (Cl)

The measurements of DOC and Cl were made from extracts of sample suspensions. Sample suspensions were used because the samples contained small volumes of porewater which were not adequate for the techniques used for the analysis of DOC and Cl. As a result, sample suspensions were prepared by adding deionised water to the samples and the added deionised water was accounted for after the analysis in order to determine the porewater concentrations. To determine the porewater concentration after the analysis, the sample oven-dry weight was subtracted from the sample wet weight (i.e. before the addition of deionised water) to get the actual mass of the porewater in the sample. Assuming that the density of the porewater was one, the volume of the porewater in the sample was determined. The total mass of DOC and Cl in the sample (i.e. added deionised water plus porewater) was calculated by multiplying the measured concentration of DOC and Cl by the volume of the sample. The total mass was divided by the volume of porewater to obtain the concentration of DOC and Cl in the porewater.

100 g (± 0.01) sub-sample was weighed into a 250 ml plastic beaker and 100 ml of deionised water was added, hence the solid-to-water ratio was 1:1. The beaker was sealed with parafilm and shaken on a flat bed shaker for 10 minutes. The sample suspension was transferred to plastic centrifuge tubes and centrifuged for 30 minutes at 2500 rpm. The supernatant was filtered through pre-rinsed (10 mL rinse with deionised water) 0.45 µm hydrophilic polyethersulphone membrane filter paper (Supor®) discarding the first 10 mL of the extract. The extract was split into two sub-samples for DOC and Cl analysis and stored at 4 ^{0}C prior to analysis. Filtration was carried out using a filter paper with a 0.45 µm pore size hydrophilic polyethersulphone membrane filter paper (Supor®) in order to separate the DOC fraction from the particulate organic carbon fraction and to remove particulates that can contaminate the analytical equipment. Filter papers were changed between samples to avoid contamination.

2.2.3.6. Analysis of DOC

Dissolved organic carbon analysis was carried out on a HyperToc Carbon analyser with a non-dispersive infrared detector (NDIR) using the UV-persulphate non-purgeable organic carbon (NPOC) method. This method is one of the three commonly used methods for the analysis of DOC in seawater (Aminot et al., 2004; Packard et al., 2000). Unlike the high temperature catalytic oxidation and the wet chemical oxidation methods, the UV-persulphate method ensured the fast and complete oxidation of organic carbon in the difficult salt matrix. It involves the oxidation of organic carbon to CO_2 by persulphate in the presence of UV light. Prior to analysis, HCl acid was added to the sample and it was sparged with O_2 gas at a flow rate of 10 ml min^{-1} to remove the inorganic carbon before the addition of persulphate. The O_2 gas was used as a carrier gas to lead the CO_2 produced through to the infra-red detector for quantification. The system had an automated autosampler which injected the sample into the UV reactor, two infra-red detectors and was supported by the ThEuS software. The generated peaks were integrated in order to calculate the concentration of DOC. The reagents used were 1.5 M sodium persulphate solution and 5% v/v HCl. Standards of known concentrations prepared from potassium hydrogen phthalate were used for calibration before each analytical run. One quality control standard and a duplicate sample were incorporated in each analytical run to assess repeatability and precision within each run.

2.2.3.7. Analysis of Cl

Cl was analysed using a Dionex ICS-2500 chromatographic system with a Dionex ED-50 conductivity detector. A 2 x 250 mm RFIC™ IonPac® AS18 analytical column with an IonPac AS18 guard column was used. The system had an AS50 autosampler for automated sample injection and Chromeleon software for system control and data processing. The eluent used was 100 mM KOH pumped by a GP-50 gradient pump at a flow rate of 0.25 ml min^{-1} in a gradient mode. A set of four calibration standards at varying concentrations were made up and used for calibration before each run. One standard and a duplicate sample were analysed in each analytical run in order to assess repeatability and precision.

2.2.4. Statistical Analysis

Statistical analysis was conducted using SPSS statistical package (Version 16). A Levene test of homogeneity of variance was carried out to test for equal variances in the data and several dataset had unequal variances. In addition, the datasets were not symmetrical and normally distributed and the assumptions of the parametric t-test could not be met. Hence, a Mann-Whitney test was employed to test for differences in the datasets between the sediment parameters in the reference sites (NSM and NMF) and in the managed realignment site (RSM and RMF). Mann-Whitney test is a non-parametric test which tests for significant differences between groups of samples. Although this test is less powerful than the equivalent parametric t-test, the Mann-Whitney test does not make any assumptions about the dataset.

2.3. Results and Discussion

2.3.1. Meteorological conditions

The monthly average atmospheric temperature and monthly total precipitation conditions during the sampling period are presented in Table 2.2. The precipitation and temperature data were obtained from ABPmer Limited on-site weather station. Table 2.2 shows that there were higher temperatures in the spring and summer than in the winter and autumn. The highest monthly total precipitation and monthly average temperature recorded on-site were in May and August respectively.

Table 2.2 Monthly average temperature and monthly total precipitation in Wallasea Island from January to December 2007. Data presented courtesy of Colin Scott, ABPmer Limited, Southampton.

Months	**Monthly average temperature (^{0}C)**	**Monthly total precipitation (mm)**
January *	n/a	n/a
February	6	86.8
March	8	63.2
April	12	1.2
May	13	88.8
June	16	52.2
July *	n/a	n/a
August	17	47.6
September	15	23.4
October	12	39.2
November	0	22.8
December	6	82.0

* Data for January and July were not available (n/a) due to a fault in the weather station during this period.

2.3.2. Changes in sediment parameters

Moisture content

The monthly average moisture content measurements at the sediment surface are presented in Figure 2.7 and the ranges recorded are presented in Table 2.3. The complete data are available in Appendix 1. The lowest moisture contents were in the RSM and the highest moisture contents were observed in the NSM. The moisture content values recorded in the NMF and RMF were intermediate between those in the NSM and RSM. The range of sediment moisture content values in the NSM, RMF and NMF indicate that these sediments were water-saturated (Table 2.3). Seasonal fluctuations were observed at the four sampling locations with lower moisture contents during the summer months (Figure 2.7). However, the seasonal variability in the sediment moisture contents were least evident in the RMF and NMF where the sediments were continuously wet by more frequent tidal inundation compared to the RSM and NSM.

Infiltration of the sediment with seawater during tidal inundation and precipitation can lead to high sediment moisture content while evaporation and drainage can lead to low sediment moisture content. Hence, changes in the sediment moisture content are mainly due to a combination of tidal inundation, precipitation, evaporation and drainage. The lower moisture contents at all the sampling locations observed during the summer is likely due to higher atmospheric temperatures in the summer compared to the other seasons (Table 2.2) and therefore, higher evaporation from the sediments. However, the months with the highest average moisture content did not coincide with the months with the highest monthly total precipitation (Table 2.2). This is probably due to the contributing effect of the other factors that control sediment moisture content.

Sediment texture and organic matter content can also affect the sediment moisture content (Crooks et al., 2002). The NSM had a sandy silt texture with a higher sand and lower clay and silt content than the RSM (Table 2.3). Given that sand particles have lower water holding capacity and are more easily drained than clay and silt particles (Brady and Weil, 2002), the NSM was expected to have a lower moisture content than the RSM. However, the results obtained were contrary, suggesting that the higher moisture content in the NSM may be due to the higher organic matter content in the NSM compared to the RSM (Table 2.3) which increased the residence time of water in the NSM. Therefore, organic matter seems to play a more dominant role than the sediment texture in affecting the sediment moisture content at the NSM. Crooks and Pye (2000) observed high moisture content and poor drainage in established salt marsh sediments in Essex, south-east England due to a deficiency in calcium carbonate. The deficiency reduced the dissolution of calcium carbonate particles and hence calcium ions which enhance the close particle interactions between constituent clay minerals. This resulted in poorly drained sediments. Although the calcium carbonate content of the sediment in this study was not evaluated, the higher sediment moisture content in the NSM may also be due to calcium carbonate deficiency. Crack formation was observed in the RSM which is likely to have improved permeability and resulted in the low moisture content at the sediment surface. As sediments with high clay content dry-out, the clay particles are re-orientated as a result of the retreating water film around the particles and this can lead to formation of cracks and increased permeability (Vermeulen, 2003). Crack formation was not observed in the RMF because the sediments at this sampling location were continuously wet by regular tidal inundation compared to those in the RSM. The regular inundation in the RMF due to its lower elevation is likely to have resulted in the higher sediment moisture content in the RMF compared to the RSM. The comparable organic matter content and the sand, silt and clay content in the RMF and NMF, in addition to their similar frequency and duration of tidal inundation due to their elevation may explain the comparable moisture contents at these sampling locations.

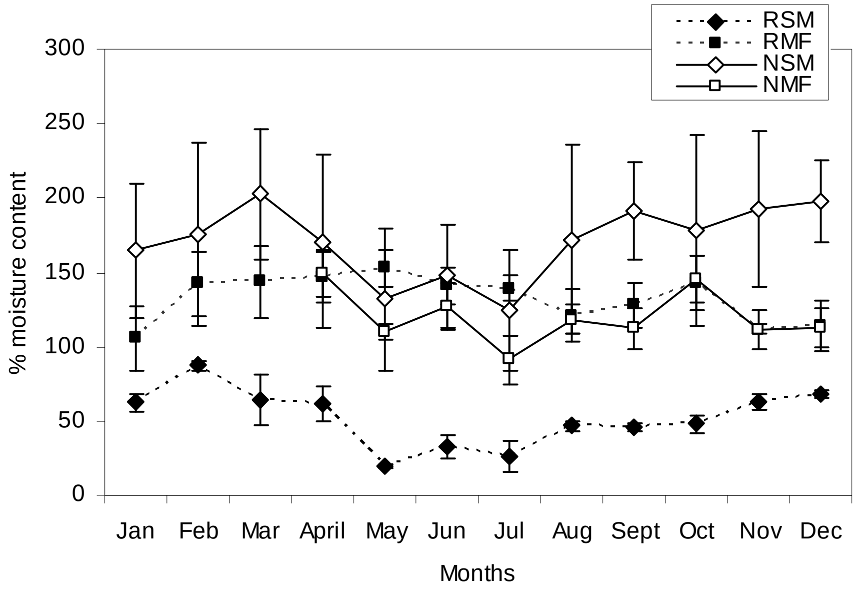

Figure 2.7 Monthly average moisture content in surface sediment layer at the RSM, RMF, NSM and NMF (bars = standard deviation (SD), n = 10).

Table 2.3. Range of sediment parameters in the surface sediment at the RSM, NSM, RMF and NMF.

	RSM	NSM	RMF	NMF
Moisture (%)	11 – 107[a]	67 – 280[a]	79 – 183[b]	63 – 170[b]
Organic matter (%)	6 – 14[a]	12 – 26[a]	7 – 16[b]	9 – 13[b]
Bulk density (gcm^{-1})	0.8 – 1.6[a]	0.4 – 0.7[a]		
Porosity (cm^3 cm^{-3})	0.3 – 0.7[a]	0.6 – 0.9[a]		
pH	7.2 – 8.2[a]	6.8 – 7.7 [a]	6.6 – 7.4[b]	7.0 – 7.5[b]
Cl (mgL^{-1})	1,760 – 28,852[a]	164 – 18,525[a]	1,379 – 13,165[b]	3,149 – 19,537[b]
DOC (mgL^{-1})	13 – 237[b]	7 – 266[b]	11 – 191[b]	10 – 156[b]
Clay (%)	37	28	37	36
Silt (%)	49	32	47	51
Sand (%)	14	40	16	14

[a] denotes significant difference between sampling locations (i.e. RSM and NSM; RMF and NMF) at $p < 0.05$ significance level, [b] denotes no significant difference. The clay fraction was < 4 µm, the silt fraction was 4 - 63 µm and the sand fraction was 63 - 2000 µm.

Sediment moisture content in the surface and the 8 – 10 cm subsurface sediment in the RSM and NSM were compared in Figure 2.8. The complete data in the 8 – 10 cm subsurface sediment are presented in Appendix 1. Unlike the moisture content at the sediment surface, there were fewer changes between the monthly averages in the subsurface sediment in the RSM and no seasonal trends were observed. The moisture contents in the subsurface sediments were approximately three times higher than those in the surface sediments in the summer months in the RSM. These findings suggest that the surface sediments are more exposed to wetting and drying than the subsurface sediments. High evaporation from the RSM during the hot summer months is likely to be the main factor responsible for the lower moisture content in the surface sediment compared to the subsurface sediment. In the NSM, the temporal changes in the moisture content in the subsurface sediments were relatively similar to those observed in the surface sediments with the surface sediments having slightly higher moisture contents (Figure 2.8). Evaporation from the surface sediment and uptake of water by salt marsh plant roots from the subsurface sediment in the NSM are likely to have resulted in the slight differences in the moisture content between the surface and subsurface sediments. Crooks et al. (2002) also observed minimal changes in the moisture content of salt marsh sediment over a 0 – 60 cm depth profile.

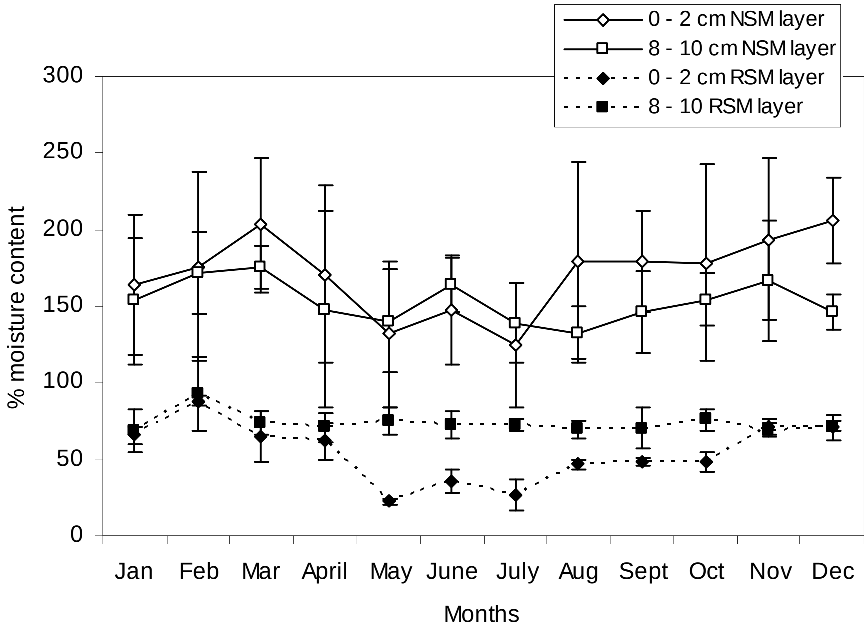

Figure 2.8 Monthly average moisture content in the surface (0 – 2 cm) and subsurface (8 – 10 cm) sediment in the NSM and RSM (bars = standard deviation (SD), n = 5).

Organic matter content

The monthly average organic matter content data in the surface sediment are presented in Figure 2.9. The complete data are presented in Appendix 2. The organic matter content in the RSM, RMF and NMF were comparable with ranges from 6 % to 14 %, 7 % to 16 % and 9 % to 13 % respectively (Table 2.3). The organic matter content in the NSM was approximately twice as high as those in the RSM with a range from 12 to 26 %. Whilst slight variations were observed in the RSM, RMF and NMF, a progressive increase in the organic matter content was observed in the NSM.

Organic matter content is generally a balance between inputs and outputs (Kentula, 2000). Whilst inputs of salt marsh plant litter and organic-rich sediment from the water column are sources of organic matter, output is due to decomposition by microbes and other organisms (Mitsch and Gosselink, 2000). Hence the higher organic matter content in the vegetated NSM compared to the unvegetated RSM is likely due to the presence of established saltmarsh plants which provide a source of plant litter that contributes to the organic matter content in the NSM. The vegetation in the NSM is also likely to trap detrital organic matter, leading to higher organic matter content compared to the RSM. The activities of various burrowing invertebrates present in salt marsh such as *Nereis diversicolor* incorporates the organic-rich plant litter into the sediment. Furthermore, the high moisture content in the NSM reduces sediment aeration, providing suitable conditions for anaerobiosis. This in turn may have led to the microbial utilization of alternative electron sinks such as NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2 in the absence of O_2 for organic matter decomposition and such anaerobic processes proceed at a slower rate than aerobic decomposition (Williams et al., 1994; Bishel-Machung et al., 1996; Craft et al., 2002; Portnoy and Giblin, 1997; Sun et al., 2002) leading to organic matter accumulation in the NSM. The progressive increase in the sediment organic matter content observed in the NSM (Figure 2.9) further suggests organic matter accumulation at the sediment surface in the NSM. Slight variations were observed in the organic matter content in the RSM and RMF but no progressive increase was found (Figure 2.9). An increase in the organic matter content may not be evident at these sampling locations because the rate at which organic matter accumulates due to organic-rich sediment accretion equals the rate at which organic matter is lost due to decomposition given that these sampling locations were unvegetated. However, as salt marsh plants colonise the managed realignment site and organic matter starts to accumulate, an increase in the organic matter content is likely to become evident. The sediment organic matter contents observed in the RMF and NMF were comparable and this is probably due to the lack of vegetation at both sampling locations.

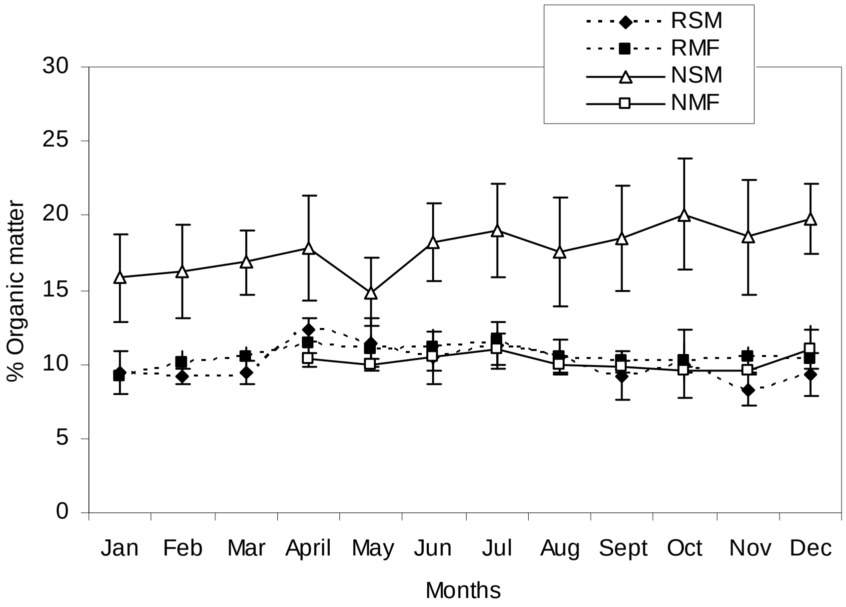

Figure 2.9 Monthly average organic matter content at sediment surface in the RSM, RMF, NSM and NMF (bars = standard deviation (SD), n = 10).

The monthly average organic matter content data in the surface and the 8 – 10 cm subsurface sediment in the RSM and NSM were compared in Figure 2.10 (see Appendix 2 for the complete subsurface sediment organic matter content data). In the NSM, the organic matter content in the subsurface sediments with a range from 10 % – 20 % was lower than those at the surface sediments. However, the organic matter in the subsurface sediment in the RSM ranged from 6 % – 11 % and was comparable to those in the surface sediment. The lower organic matter content in subsurface sediment compared to the surface sediment in the NSM agrees with the study of Bishel-Machung et al. (1996) where decreasing organic matter content was observed with depth. The lower subsurface sediment organic matter content in the NSM is likely due to organic matter accumulation at the sediment surface. In the RSM, no change was observed in the organic matter content with depth, further suggesting that there was no organic matter accumulation in the surface sediment at this sampling location.

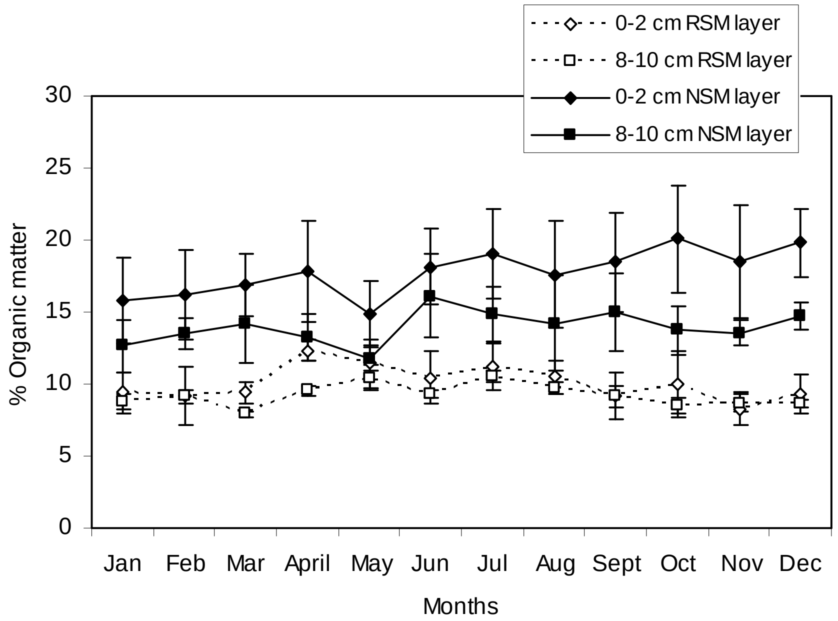

Figure 2.10. Monthly average organic matter content at the sediment surface and 8 – 10 cm subsurface layers at the RSM and NSM (bars = standard deviation (SD), n = 5).

Bulk density and porosity

Figure 2.11 and 2.12 shows the monthly average bulk density and porosity data for the RSM and NSM. The complete data is presented in Appendix 3. It should be noted that there are no bulk density or porosity data for the RMF and NMF because the relatively unconsolidated sediment within the restored and natural mudflat presented a safety hazard. The bulk density values in the RSM ranged from 0.8 - 1.6 g cm^{-3} whilst the range in the NSM was from 0.4 – 0.7 g cm^{-3} (Table 2.3). These ranges show that the bulk density values in the RSM were approximately twice as high as those in the NSM (Table 2.5). The porosity values in the RSM were lower compared to the NSM with ranges from 0.3 - 0.7 cm^{3} cm^{-3} and 0.6 - 0.9 cm^{3} cm^{-3} respectively (Table 2.3). The sediment bulk density and porosity values remained relatively constant in both the RSM and NSM over the study period with slight variations observed (Figure 2.11 and 2.12).

Bulk density and porosity depend on the proportion of the total pore spaces occupied by air and the density of the particles (Rowell, 1994). Sediment bulk density and porosity can be affected by the sand, silt and clay content, organic matter content, the presence of plant roots and bioturbation by invertebrates. The relatively stable sediment bulk density and porosity values in the RSM (Figure 2.11 and Figure 2.12) suggest that there was no progressive increase in sediment compaction during the study period. The higher bulk density and lower porosity values in the RSM compared to the NSM (Table 2.3) may be due to the nature of the sediment in the RSM. The sediment in the RSM was sourced from dredged material at Harwich Port with a high in-situ density and was imported into the managed realignment site with a bulk density of approximately 1.25 g cm^{-3} (ABPmer, 2004). The high bulk density was sustained over the study period, probably due to the low organic matter content in the RSM (Table 2.3). Several studies have observed a negative relationship between sediment organic matter content and bulk density (Bishel-Machung et al., 1996; Craft et al., 2002). In addition, surface sediment compaction due to sedimentation and consolidation following the importation of the sediment into the managed realignment site may also have contributed to the high bulk density and low porosity values in the RSM. The high organic matter content, bioturbation and the associated sediment mixing by invertebrates in the NSM are also likely to have contributed to the lower bulk density and higher porosity in the NSM compared to the RSM.

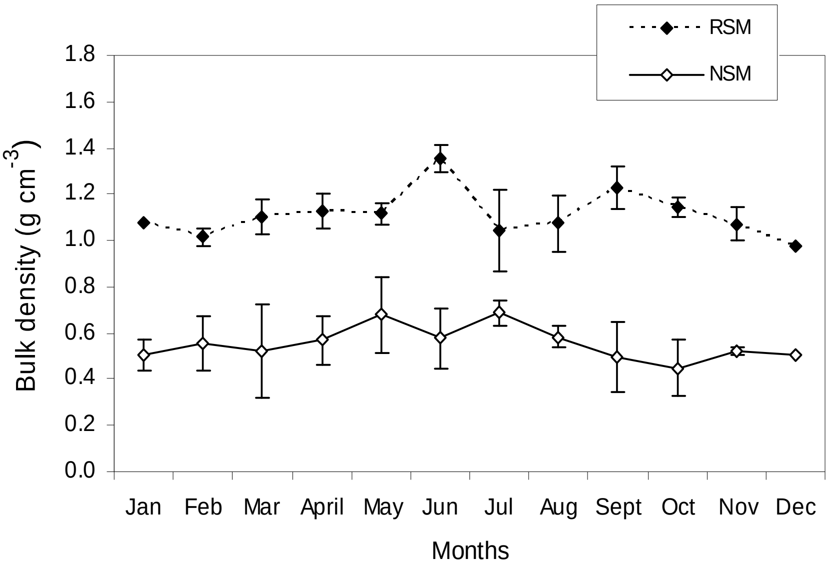

Figure 2.11 Monthly average bulk density data in the RSM and NSM (bars = standard deviation (SD), n = 10).

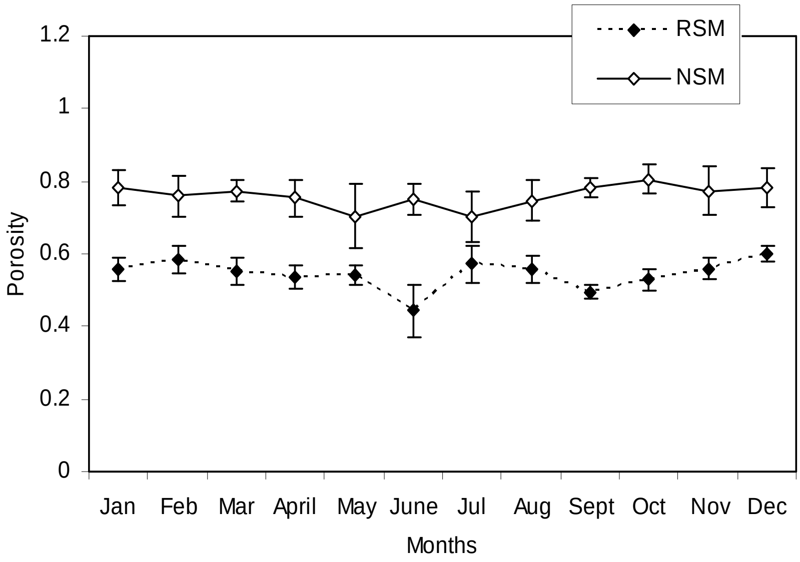

Figure 2.12 Monthly average porosity data in the RSM and NSM during the study period (bars = standard deviation (SD), n = 10).

Sediment pH

The monthly average sediment pH data are presented in Figure 2.13 with the complete data in Appendix 4. The pH values observed in the RSM and NSM ranged from pH 7.2 to pH 8.2 and pH 6.8 to pH 7.7 respectively (Table 2.3). In the RMF and NMF, the pH values had a range from pH 6.6 to pH 7.4 and pH 7.0 to pH 7.5 respectively (Table 2.3). The pH values in each of the sampling locations were relatively constant over the study period with no progressive trend observed (Figure 2.13). However, the pH values in the NSM, RMF and NMF were lower than those in the RSM (Figure 2.13).

Generally, sediments in wetlands often have stable neutral to alkaline pH conditions (Mitsch and Gosselink, 2000). The relatively constant pH values observed in this study indicate that stable pH conditions exist in the sediments probably due to tidal flushing of the sediments in each of the sampling locations. Approximately 90 % of all the sediment pH values at the four sampling locations were between pH 7.1 and pH 8.2. This indicates that majority of the sediments were alkaline given that neutral pH is generally in the range of pH 6.7 to pH 7.2 (Mitsch and Gosselink, 2000). The lower pH values in the NSM, RMF and NMF compared to the RSM may be due to the higher sediment moisture content in the NSM, RMF and NMF. The high moisture content at these sampling locations is likely to have resulted in reduced sediment aeration and the development of reducing conditions in the sediment. Most reducing reactions which occur under these conditions consume hydrogen ions which can lead to an increase in pH (McBride, 1994). However, at alkaline pHs, the reducing conditions can lower pH when metal ions such as Fe^{2+} and Mn^{2+}, made soluble by reduction, precipitate as carbonates. The precipitation reaction can generate H^+ which can counter those consumed by reduction (McBride, 1994). Consequently, the precipitation of metal ions as carbonates in the alkaline, water-saturated sediments in the NSM, RMF and NMF may have led to the generation of H^+ and hence, a decrease in pH at the NSM, RMF and NMF compared to the RSM.

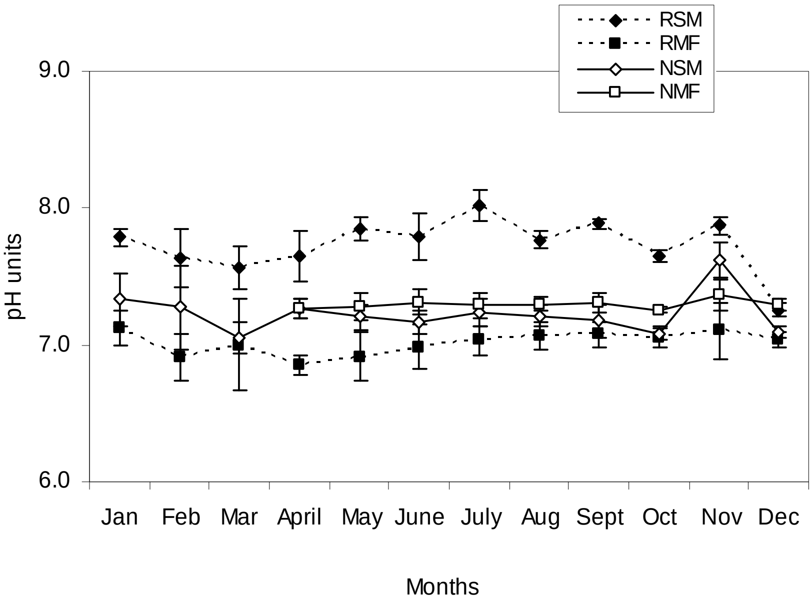

Figure 2.13 Monthly average pH values in the RSM, RMF, NSM and NMF (bars = standard deviation (SD), n = 10).

Sediment porewater Cl

The monthly average sediment porewater Cl concentration data are shown in Figure 2.14 and the range at each sampling location presented in Table 2.3. The complete data are presented in Appendix 5. Seasonal variability in the sediment porewater Cl concentrations were observed in the RSM, NSM, RMF and NMF with higher concentrations measured in the summer months and lower concentrations in the winter months (Figure 2.14). While the sediment porewater Cl concentration in the RSM was higher than that in the NSM particularly in June and July, the sediment porewater Cl concentrations in the RMF and NMF were relatively similar and both sampling locations showed the same temporal trend (Figure 2.14).

Sediment porewater salinity is controlled by a variety of factors including the frequency and duration of tidal inundation, precipitation, evaporation, freshwater inflow, sediment texture and presence of salt marsh vegetation (Otero and Macias, 2002; Mitsch and Gosselink, 2000). In this study, the sediment porewater Cl concentration was used as a proxy for salinity. The increase in the porewater salinity in the summer compared to the winter at all the sampling locations is likely due to the higher summer temperatures (Table 2.2) which led to higher evaporation, leaving behind high salt concentrations at the sediment surface. The higher salinity at the sediment surface in the RSM compared to the NSM during the summer (Figure 2.15) is attributed to higher evaporation from the RSM due to the lack of salt marsh plants and the lower moisture content in the RSM (Figure 2.7). Likewise, the salinity at the sediment surface in the RSM was higher compared to the RMF and this is likely due to less tidal flushing in the RSM which leads to a greater accumulation of salts in the RSM compared to the RMF (Figure 2.7). In the winter, precipitation is likely to have resulted in the dilution of the high salt concentrations at the sediment surface, thereby leading to a decrease in the porewater salinity at the sampling locations (Figure 2.15). A similar pattern of seasonal variation in the salinity of salt marsh sediments has been reported by Otero and Macias (2002) with high salinities during the summer and low salinities in the winter. The similar observations at the RMF and NMF may be due to both sampling locations having the same surface elevation. Hence they experience similar frequencies and durations of flooding, and associated salt inputs.

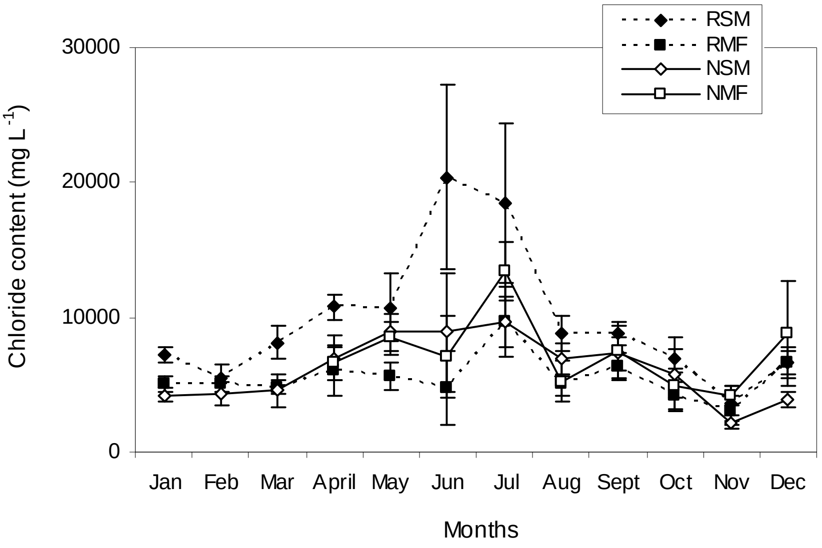

Figure 2.14 Monthly average Cl content in the RSM, RMF, NSM and NMF (bars = standard deviation (SD), n = 10).

Porewater dissolved organic carbon (DOC)

The monthly average porewater DOC concentrations measured in the RSM, RMF, NSM and NMF are presented in Figure 2.15 with the complete data in Appendix 6. The range of porewater DOC concentrations at the four sampling locations are shown in Table 2.3. Temporal variations were observed at all the sampling locations during the study period.

DOC concentrations in sediment porewater reflects the balance between inputs from plant root exudates, decomposition of plant litter, particulate organic matter, dead microbial biomass and losses from sediment fluxes to the estuary, adsorption to particles, uptake by heterotrophic bacteria and other organisms (Koepfler et al., 1993). In this study, higher porewater DOC concentrations were expected in the NSM compared to RSM because of the higher organic matter content in the NSM sediment. However, the DOC concentrations at these sampling locations were similar (Table 2.4). In the RMF and NMF, the porewater DOC concentrations were also comparable (Table 2.4). Higher DOC concentrations were observed in the summer at the RSM and NSM. The sediment porewater DOC concentration measured in the RSM in July was approximately three times higher than that measured in June (51.3 mg L^{-1} to 139.7 mg L^{-1}) (Figure 2.15). Similarly, a fivefold increase was observed in the porewater DOC concentration in the

NSM between June and July (29.3 mg L^{-1} to 140.2 mg L^{-1}) (Figure 2.15). Several field studies have observed higher porewater DOC concentrations in sediments in the summer (Herndl et al., 1987; Hargrave and Phillips, 1989; Koepfler et al., 1993). The increase in porewater DOC was due to an increase in microbial biomass activity in the summer and hence, an increase in the rate of decomposition of particulate organic matter. The higher porewater DOC concentrations observed in the summer in this study may be due to an increase in the microbial biomass activity and decomposition of organic matter at the sampling locations. The presence of the filamentous green alga *Enteromorpha* sp. in the RSM in the summer is also likely to have provided an additional carbon source for decomposition into DOC in the RSM. The higher porewater DOC concentrations were not observed in the RMF and NMF in the summer probably due to greater tidal flushing of DOC from the RMF and NMF into the estuary due to more frequent tidal inundation at these sampling locations compared to the RSM and NSM.

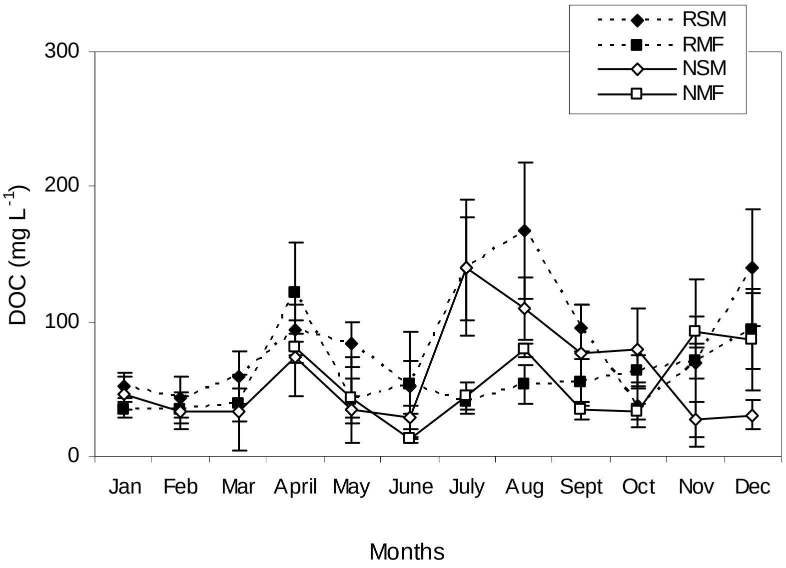

Figure 2.15 Monthly average DOC porewater concentrations in the RSM, RMF, NSM and NMF (bars = standard deviation (SD), n = 10).

2.4. Summary and conclusion

This chapter has identified little or no change in the organic matter content, bulk density, porosity and pH values in the sediment at the restored salt marsh and mudflat within the Wallasea Island managed realignment site during the 12-months study period. However, lower moisture contents and higher porewater Cl concentrations were observed in the sediment in the hotter summer months due to higher atmospheric temperatures and hence, higher evaporation in the summer. The porewater Cl concentration was used as a proxy for salinity and the seasonal range in the porewater salinity (i.e. maximum and minimum monthly average porewater Cl concentrations in the summer and winter respectively) was used as the two different salinity treatments in the laboratory column microcosm experiments so that the experiments simulated the field conditions. In addition, the sediment porewater DOC concentration in the restored salt marsh was higher in the summer, probably due to increased microbial biomass activity, higher decomposition rate and the presence of the filamentous green alga *Enteromorpha* sp. in the restored salt marsh in the summer which is likely to have provided an additional carbon source for decomposition.

This chapter has also shown that the sediment parameters (i.e. moisture content, organic matter content, pH, porewater Cl and porewater DOC) in the natural and restored mudflat were similar. However, the same cannot be said for the salt marsh pair as most of the sediment parameters were different and far from approaching those in the natural salt marsh. The organic matter content was higher in the natural salt marsh compared to the restored salt marsh due to the presence of an additional source of organic matter from plant litter and organic matter accumulation in the natural salt marsh. The organic matter content in the restored saltmarsh should begin to accumulate and approach that in the natural saltmarsh as saltmarsh plants start to colonise the site. The sediment moisture content was also higher in the natural salt marsh compared to the restored salt marsh probably due to calcium carbonate deficiency and higher organic matter content in the natural salt marsh and crack formation in the restored salt marsh. Higher sediment bulk density and lower porosity were observed in the restored salt marsh compared to the natural saltmarsh which was likely due to the lower organic matter content and higher bulk density of the imported sediment, and the surface sediment compaction due to sedimentation and consolidation following the importation of the sediment into the managed realignment site. The sediment pH values were lower in the natural salt marsh compared to the restored salt marsh probably due to the generation of H^+ following the precipitation of metal ions as carbonates in the water-saturated alkaline sediments in the natural salt marsh. Higher Cl concentrations were observed in the restored salt marsh compared to the natural salt marsh in the summer which was likely due to the lack of salt marsh plants and hence higher evaporation from the restored salt marsh. These findings indicate that further years are required before the sediments in the restored salt marsh become similar to those in the natural salt marsh.

Chapter 3 Laboratory Experiments: Methodology

3.1. Introduction

This chapter describes the laboratory experiments that were conducted to examine the effects of salinity and drying and rewetting on the release of metals and herbicides from agricultural soil and dredged sediment in managed realignment sites following tidal inundation. The experiments were designed to simulate conditions in a managed realignment site. This was done by using field observations obtained from the study at Wallasea Island managed realignment site described in Chapter 2. The chapter begins with details of the collection and storage of the soil and sediment used for the experiments. It then describes the experiments that were performed which include the column microcosm experiments, conducted under two different salinity and drying-rewetting treatments, carbon mineralisation experiments and batch sorption experiments. The carbon mineralisation experiments were conducted to test the hypothesis that organic matter mineralisation will be enhanced during drying and rewetting of the soil and sediment leading to the release of organic matter associated metals and herbicides into the overlying water. The batch sorption experiments were conducted to calculate the partition coefficients (K_d) of the metals and herbicides in order to evaluate the changes in contaminant binding to the soil and sediment with changes in salinity.

3.2. Sediment and soil collection

The sediment was collected from Wallasea Island managed realignment site. The soil was collected from Wallasea Farms, the arable agricultural land adjacent to the managed realignment site (Chapter 2, Figure 2.2). Surface soil and sediment samples were collected randomly from the managed realignment site and the arable agricultural land and mixed into composite soil and sediment samples. Following collection, the soil and sediment samples were returned to the laboratory, sieved to < 4 mm and stored in water tight plastic buckets at 4 ^{0}C for the six months duration of the entire experiments. It is important to recognise the potential changes that can occur in soil and sediment during storage. These include changes in microbial activity which can cause changes to the concentrations of ammonia, sulphides and biologically-active components in the porewater; changes in redox properties; changes in speciation and partitioning of baseline metals and loss of baseline organic contaminants due to microbial degradation. Prior to the start of the experiments, the soil and sediment properties (pH, organic matter content, sand, silt and clay content) were determined using standard methods described in Chapter 2 (Section 2.2.3).

3.3. Laboratory microcosm experiments

3.3.1. Column microcosm

Experimental systems such as mesocosms and microcosms have frequently been used in toxicological, ecological and biogeochemical studies of aquatic and terrestrial ecosystems (Johnson et al., 1986; Wielder et al., 1990; Horne 1991, Ahn et al., 2001; Tueben and Verhoef, 1992; Van Wensem, 1989). Microcosm experiments have been performed in the laboratory to examine the release fluxes of DOC and organic contaminants from sediments (Valsaraj et al., 1996; Ortiz et al., 2004), microbial activity in soils by measuring CO_2 production and the availability of macronutrients in soil (Lundquist et al., 1999; Tueben and Verhoef, 1992) and the effect of herbicides on the productivity and biogeochemical functions of wetland plants and invertebrates (Johnson, 1986). Microcosms have been frequently used because they are considered analogous to the natural system (Tueben and Verhoef, 1992). These microcosms provide a means of conducting field-level experiments under controlled, replicated and repeatable conditions which are difficult to achieve in the field (Ahn and Mitsch, 2002; Verhoef, 1996). Although the complex array of interactions found in the field may not always be simulated by microcosms, they are still considered models of natural systems (Ahn and Mitsch, 2002; Tueben and Verhoef, 1992). In this study, the experiments were conducted in simple column microcosms which allowed for the control of the experimental conditions, the simulation of tidal inundation in a managed realignment site and replication of the experiments.

In the column microcosms, artificial sea water flowed over the surface of the soil and sediment, simulating natural tidal inundation at a managed realignment site. A schematic diagram of the column microcosm is shown in Figure 3.1. The design of the columns was adapted from Ortiz et al. (2004). Each microcosm was 60 cm in length and 10 cm in diameter. The microcosms were made of glass with an air inlet and a sampling outlet. The lid was fitted with a water inlet connected by flexible tubing to a reservoir containing artificial seawater, allowing water supply to be initiated at the soil and sediment surface. However, the water inlet was designed such that the artificial seawater flow into the column was not directly against the soil and sediment surface (Figure 3.1). This was done in order to minimise turbulence and particle resuspension due to direct water flow against the soil and sediment surface, thereby reducing the transport of contaminants into the overlying water column by re-suspended particles.

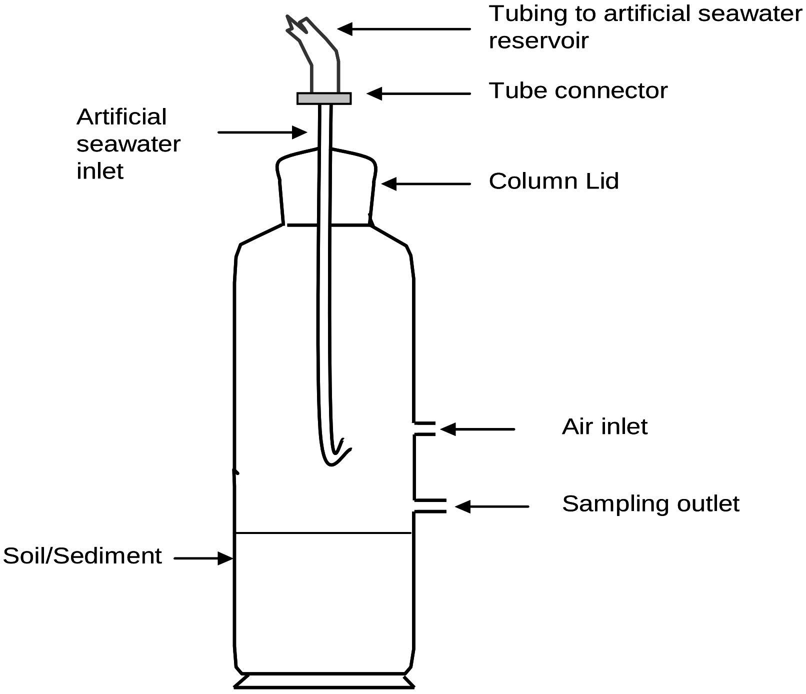

Figure 3.1 Schematic diagram of the laboratory column microcosm

3.3.2 Experimental procedure

Each microcosm was packed gently with approximately 800g (wet weight) of either soil or sediment slurry spiked with the studied metals and herbicides. Both the soil and sediment were spiked according to the procedure described in Section 3.3.3. After packing the microcosms with the soil and sediment under the same conditions, they were left to dewater and consolidate. This was done in order to simulate the Wallasea Island managed realignment site where the sediment used to raise the elevation of the site was allowed to dewater and consolidate before the seawall was breached (Chapter 2, Section 2.2.1). In these experiments, 4 days were chosen for dewatering and consolidation because of the high clay and silt content in the soil and sediment (Chapter 4, Table 4.1). Following dewatering and consolidation, the overlying supernatant at the soil and sediment surface was removed. The microcosms were then kept in a temperature control cabinet maintained at 10 ^{0}C. This temperature which was within the range of the atmospheric temperature observed in the field site where the monthly average atmospheric temperature recorded ranged from 6 – 17 ^{0}C (Chapter 2, Table 2.3).

Artificial seawater was delivered by a peristaltic pump (Watson-Marlow Bredel Pumps Ltd, UK) to the microcosms in the temperature control cabinet with the water flowing laterally over the soil and sediment surface. Artificial seawater, made from deionised water and sea salt (Sigma Aldrich, UK) was used instead of the natural seawater to ensure that dissolved organic carbon was not present in the seawater introduced into the microcosms. The presence of dissolved organic carbon in the seawater can facilitate contaminant release (Kalbitz and Wenrich, 1998; Gao et al., 1998) which may mask release due to salinity effects and drying-rewetting cycles. Table 3.1 shows the composition of the sea salt. The artificial seawater was delivered at a flow rate of 1.6 ml min^{-1} in order to minimise particle resuspension from the soil/sediment surface. Samples were then collected from the overlying water (Section 3.3.4.1 and 3.3.4.2). The first sample was collected one hour after the initial delivery of artificial seawater to allow sufficient water flow into the microcosms. Each sample was collected over a one hour period to collect adequate sample volume for analysis.

Table 3.1 Composition of sea salt (Sigma Aldrich)

Components	Concentration (mg l^{-1})
Chloride	19,290
Sodium	10,780
Sulphate	2,660
Magnesium	1,320
Potassium	420
Calcium	400
Carbonate	200
Boron	5.6
Bromide	56
Iodide	0.24
Fluoride	1.0

3.3.3. Sediment and soil spiking procedure

The soil and sediment used in these experiments were spiked with three metals; Cu, Ni and Zn and three herbicides; simazine, atrazine and diuron. Cu, Ni and Zn were chosen because of their strong association with organic matter (Millward and Liu, 2003; Sokolowski *et al*., 2001; McBride, 1994), their affinity to form soluble complexes with DOC (Gerringa et al., 1990; Kalbitz and Wennrich, 1998; Sauve et al., 1997; Turner et al., 1998) and their tendency to form soluble chlorocomplexes (Millward and Liu, 2003; Salomon and Forstner, 1984; Millward and Turner, 1995). Cu shows a higher affinity for organic matter than Ni and Zn (Forstner and Wittmann, 1981; McBride, 1994). Ni forms relatively strong complexes with DOC (Turner et al., 1998) and so is likely to be relatively mobile. Similarly, Zn has a strong capacity to form chlorocomplexes (Millward and Moore, 1982) and is also likely to be relatively mobile. In addition, these metals are common anthropogenic contaminants in estuarine sediments (Cave et al., 2005; Spencer et al., 2002; Williams et al., 1994). Simazine, atrazine and diuron were chosen because of their different physico-chemical properties (Table 3.2) and their usage on agricultural land for crop production. Furthermore, these herbicides have also been detected in coastal and estuarine sediments (Meakins et al., 1995; Voulvoulis et al., 2002; Comber et al., 2002).

Table 3.2 Physico-chemical properties of simazine, atrazine and diuron. [a]Margoum et al. (2001); [b]HSE, 1993; [c]Lewis and Gardiner, 1996; [d]Pacakova et al. (1996); [e]Moreau-Kervevan and Mouver, 1998.

Pesticides	Group	Aqueous solubility (mg l^{-1})	log K_{ow}	pKa
Simazine	Triazine	6.2[a]	2.18[a]	1.65[d]
Atrazine	Triazine	33[b]	2.68[b]	1.71[e]
Diuron	Phenylurea	42[c]	2.85[c]	

The baseline contaminant concentrations in the soil and sediment were determined before spiking by extracting the metals and herbicides from the soil and sediment using a microwave assisted Aqua regia digest (3:1 HCl:HNO_3) and solvent extraction (9:1 acetonitrile:water) respectively (Bettinelli et al., 2002; Eskilsoon and Bjorklund, 2000). A certified reference material (CRM) (PACS2) was included only in the metal extraction because no CRM was available for the herbicide extraction. An aliquot of the metal and herbicide extracts were then filtered through a 0.45 µm hydrophilic polyethersulphone membrane filter (Supor®, Germany) filter paper before analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) and high performance liquid chromatography (HPLC) with UV detection.

In the soil and sediment, the baseline Cu, Ni and Zn concentrations ranged from 12 - 23 mg kg^{-1}, 25 - 33 mg kg^{-1} and 65 - 80 mg kg^{-1} respectively while the baseline simazine, atrazine and diuron concentrations ranged from 0.02 - 0.05 mg kg^{-1}, 0.01 - 0.03 mg kg^{-1} and 0.008 - 0.01 mg kg^{-1} respectively. The recovery of Cu, Ni and Zn based on the comparison with the CRM were very high (81 - 90 % for Cu; 83 - 92 % for Ni and 91 - 92 % for Zn) indicating that the extraction method was efficient in extracting the metals.

The soil and sediment were made into slurries before the addition of the metals and herbicides. This was done to aid the even distribution of the added metals and herbicides within the soil and sediment in order to produce homogenously contaminated soil and sediment (Northcott and Jones, 2000). The slurries were made by adding 400ml of deionised water to 1600g of soil and sediment giving a 4:1 solid-liquid ratio. Prior to spiking with the metals and herbicides, the sediment was fully oxidised in order to eliminate sulphides such as FeS_2, thereby avoiding metal release due to sulphide oxidation during the column microcosm experiments. Metal release due to sulphide oxidation can mask the release due to salinity effects and drying-rewetting cycles and may result in higher metal concentrations in the overlying water column during the experiments. The sediment was oxidised by shaking in large Nalgene bottles open to the atmosphere (Buykx et al., 2000). It was mixed with a whisk periodically until a stable positive redox potential (greater than 120 mV) was measured which took 7 days.

The soil and sediment were spiked to attain 1000 mg kg^{-1} Cu, Ni and Zn concentrations and 7.5 mg kg^{-1} simazine, atrazine and diuron concentrations, assumed from mass balance. The metal concentration in the spiked soil and sediment were within the range observed in sites with moderately to heavily contaminated sediments (200 – 7600 mg kg^{-1}) (Burton et al., 2006). The herbicide concentration in the spiked soil and sediment were expected to be lower than those applied to agricultural land for crop production. Given that the baseline metal and herbicide concentrations in the samples were negligible compared to the metal and herbicide concentrations following spiking, the metals and herbicides released from the samples into the overlying water during the column experiments were not expected to be significantly confounded by the release of the baseline contaminants.

The spiking concentrations ensured that the metal and herbicide concentrations released from the soil and sediment into the overlying water during the column microcosm experiments exceeded the limit of detection of the analytical techniques used for analysis.

A composite herbicide spike solution was made up from simazine, atrazine and diuron standards (powder form) (Fluka, analytical grade) in acetonitrile to a concentration of 60 mg l^{-1}. The high concentration of the herbicide spike solution and the low solubility of the herbicides in water (Table 3.2) necessitated the use of acetonitrile to ensure all the herbicides were soluble and they did not precipitate out of solution. 100 ml of the herbicide spike solution was added to 800 g (wet weight) of the soil and sediment slurries. After adding the spike solution, the slurries were vigorously agitated on a flat bed shaker at 300 rpm for 1 hour. The spiked soil and sediment were then placed in a fume cupboard for 6 hours to allow the residual acetonitrile to evaporate thereby minimising its effect in the soil and sediment. Following evaporation, 200 ml of the spike solution of Cu, Ni and Zn at a concentration of 4000 mg l^{-1} was added to the herbicide-spiked soil and sediment. The spike solution was made up from metals' nitrate salts (Aldrich, analytical grade with 99% purity) dissolved in ultra-pure water (Milli-Q^{TM}). Following the metal addition, the spiked soil and sediment were agitated for 1 hour and allowed to equilibrate at 10 ^{0}C for 21 days. Simpson et al. (2004) suggested that sediments spiked with metals should be equilibrated between 18 – 25 ^{0}C because the metals bind more strongly to the sediment particles due to faster kinetic reactions at this temperature range. However, within this temperature range, organic contaminants are likely to undergo considerable degradation. Therefore, the spiked soil and sediment were kept at 10 ^{0}C during the equilibration period.

Several studies have observed that metal and herbicide sorption to soil and sediment is biphasic with an initial rapid phase followed by a slow phase (Millward and Turner, 1995; Mustafa et al; 2004, Liu et al., 1998; Selim and Amacher, 2001; Ball and Roberts, 1991; Wu and Gschwend, 1986; Brusseau and Rao, 1989). Slow sorption is related to the diffusion of the metals and herbicides into particle matrices which can take days to months. Hence, it was important to allow enough time period for the reactions to be completed after spiking. This also prevented abnormally high metal and herbicide porewater concentrations which can lead to high fluxes into the overlying water. The recommended time for equilibration vary from 10 – 70 days for Cu, Ni and Zn and organic contaminants depending on the properties of the contaminant, the available binding sites and particle size distribution of the soil and sediment (Simpson et al., 2004; Northcott and Jones, 2000). In this study, an equilibration period of 21 days was chosen after a preliminary experiment was conducted to determine a sufficient time period for equilibration due to the differences in the properties of the soil and sediment (Chapter 4, Table 4.1). In the preliminary experiment, the soil and sediment were spiked with the metals and herbicides at the concentrations stated above. After spiking the soil and sediment, the metal and herbicide porewater concentrations were measured during equilibration on day 1, 5, 7, 9, 12, 14, 16, 19 and 21. Contaminant porewater concentrations were measured because they are indicative of contaminant partitioning between the solid and liquid phase (Northcott and Jones, 2000). 10 g soil and sediment samples were weighed into non-reactive PTFE tubes (Nalgene) in duplicates. The samples were centrifuged at 3000 rpm for 15 minutes. The porewater was decanted, filtered using a 0.45 µm PTFE filter (Nalgene) and analysed for the metals by inductively coupled plasma optical emission spectrometry (ICP-OES) (Section 3.6.1) and for herbicides by high performance liquid chromatography (HPLC) in direct injection mode (Section 3.6.2). The metal and herbicide porewater concentrations in the soil and sediment were within 10 % of the average concentrations. The average metal and herbicide porewater concentrations in the soil and sediment indicated that 21 days was sufficient length of time for bulk of the contaminants to bind to the soil and sediment at the spiking concentrations (Figure 3.2 and 3.3).

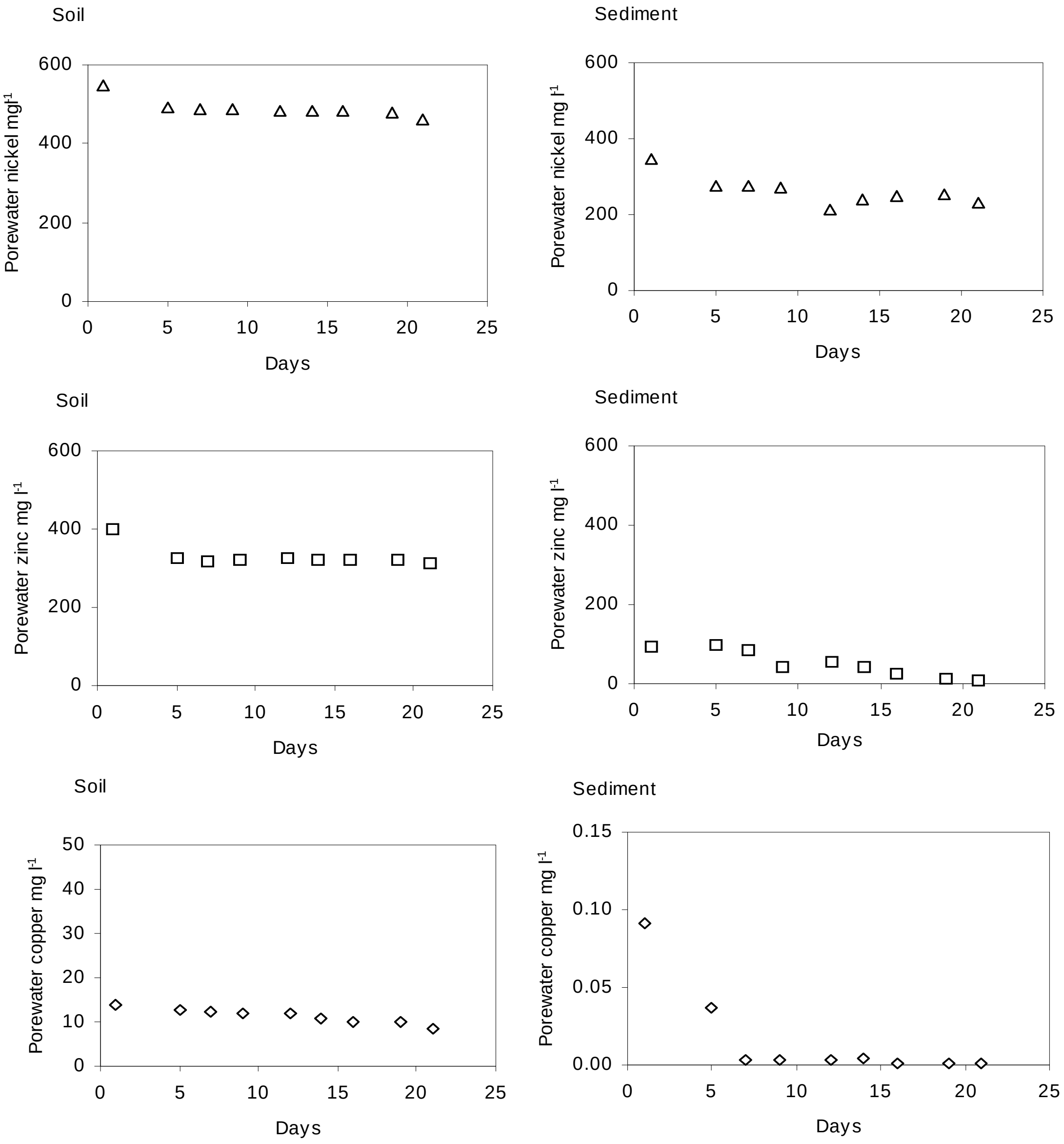

Figure 3.2 Average porewater concentrations of Ni, Zn and Cu in the soil and sediment over 21 days (n = 2).

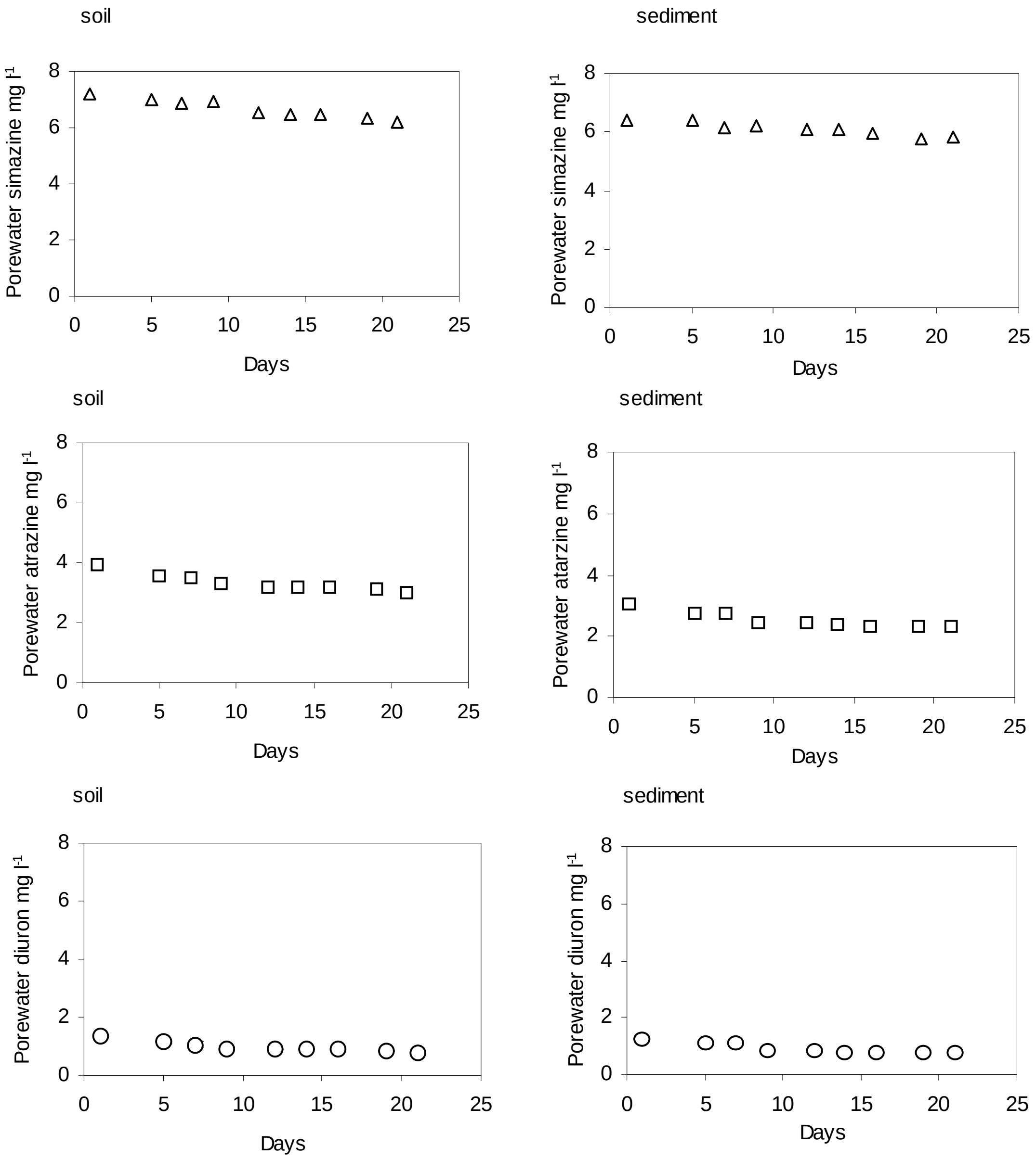

Figure 3.3 Average porewater concentrations of simazine, atrazine and diuron in the soil and sediment over 21 days (n = 2).

3.3.4. Experimental designs

3.3.4.1. Experimental design: effect of salinity on metals and herbicides release from soil and sediment (salinity treatment)

To investigate the effect of salinity on the release of metals and herbicides from soil and sediment, the microcosms were continuously flooded with artificial seawater throughout the duration of these experiments. The experiments were performed in triplicate. During the experiments, the metals, herbicides and DOC concentrations released into the overlying water column were measured. The salinity of the artificial seawater delivered to the microcosms was 5 and 20 representing low and high salinity treatments respectively in these experiments. These two different salinity treatments reflect the seasonal range (minimum and maximum) in the salinity of the sediment porewater observed in the field study (Chapter 2, Figure 2.14). Although the salinity of the natural sea water which inundates the field site was not measured directly during the field study, the sediment porewater Cl concentrations were measured and were used as a proxy for salinity.

The experiments were carried out over 21 days. There was no observation of anoxia in the soil and sediment in the microcosms throughout the duration of the experiment. Samples from the overlying water were collected twice daily, with a 6-hour interval between sampling for the first 12 days and then a 3-day interval for the remainder of the experiment. This was done in order to assess the release pattern of the metals, herbicides and DOC over time. Immediately after collection, the sample pH was measured using a HANNA HI 83140 pH meter. The samples were then filtered through a 0.45 µm pre-rinsed (10 ml rinse with deionised water) hydrophilic polyethersulphone membrane filter (Supor®, Germany). The 0.45 µm hydrophilic membrane filter separated out the DOC fraction from particulate organic matter and prevented the sorption of the herbicides or metals to the filter. Aliquots of the filtrate were then analysed for the metals by ICP-OES (Section 3.6.1); herbicides by the on-line solid phase extraction-high performance liquid chromatography (on-line SPE-HPLC) (Section 3.6.2) and DOC using a HyperToc carbon analyser with a non-dispersive infrared detector (Chapter 2, Section 2.2.3.6). Due to analytical and time constraints, herbicides were analysed in only one of the two samples collected daily for the first 12 days, in addition to those collected during the remaining 9 days of the experiment.

A control experiment was performed under the conditions described above with unspiked soil and sediment. While the initial Ni and Zn concentrations released from the soil into the overlying water ranged from 0.04 – 0.06 mg l^{-1} and 0.05 – 0.09 mg l^{-1} respectively, the initial Cu, simazine, atrazine and diuron concentrations were below the limit of detection of the analytical techniques used for the analyses. In the case of the sediment, the initial Cu, Ni, Zn, simazine, atrazine and diuron concentrations released into the overlying water were below the limit of detection of the analytical techniques used for the metal and herbicide analyses. This indicates that the baseline metals and herbicides released from the soil and sediment into the overlying during the column experiment were negligible and hence was not significantly confounding or contributing to contaminant release.

3.3.4.2 Experimental design: effect of drying and rewetting on metals and herbicides release from soil and sediment (drying-rewetting treatment)

To investigate the effect of drying and rewetting on the release of metals and herbicides, the soil and sediment were dried at 25 ^{0}C for 7 days and then continuously rewet at 10 ^{0}C for 5 days with artificial seawater at a salinity of 20. This was repeated resulting in two dry-rewet cycles over a 24-day period. The duration of the drying and rewetting periods were based on an estimated 43 % frequency of tidal inundation in the Wallasea Island managed realignment site (Chapter 2, Section 2.2.1). This estimate was based on the site elevation data (provided by ABPmer Limited, Southampton) and water level data (Crouch Harbour Authority tide timetable). These experiments were performed in triplicate.

Sampling was carried out only during both cycles of continuous rewetting and the aqueous samples were collected from the overlying water twice daily with a 6-hour interval between sampling. The samples were filtered through a 0.45 µm pre-rinsed (10 ml rinse with deionised water) hydrophilic polyethersulphone membrane filter paper (Supor®, Germany). Aliquots of the filtrate were then analysed for metals by ICP-OES (Section 3.6.1), herbicides by the on-line SPE-HPLC (Section 3.6.2) and DOC using a HyperToc carbon analyser with a non-dispersive infrared detector (Chapter 2, Section 2.2.3.6). Similar to the experimental design described in Section 3.3.4.1, only one of the two samples collected daily was analysed for the herbicides due to analytical and time constraints.

3.4 Carbon mineralisation experiments

Drying and rewetting of soil can lead to the disruption of aggregates which exposes organic matter trapped within the soil. The exposure of organic matter stimulates microbial activity which leads to enhanced organic matter mineralisation, DOC release and CO_2 release (Degens and Sparkling, 1995; Van Gestel et al., 1993; Fierer and Schimel, 2003). The mineralisation of soil microbial biomass-derived substrates resulting from the death of part of the microbial population during drying can also lead to an increase in CO_2 release following rewetting of dried soil (Bottner et al., 1985; Van Gestel et al., 1993; Haney et al., 2004). Since organic matter is an important binding site for metals (Salomons and Forstner, 1984; Alloway, 1995) and herbicides (Gao et al., 1998; Voulvoulis et al., 2002), the enhanced mineralisation of organic matter due to drying and rewetting may result in the release of organic matter associated metals and herbicides. In order to test the hypothesis that organic matter mineralisation will be enhanced during drying and rewetting of the soil and sediment and lead to the release of organic matter associated contaminants, carbon mineralisation experiments were conducted. Carbon mineralisation can be determined by measuring CO_2 accumulation in the headspace of incubated soil and sediment (Fierer and Schimel, 2002; Lundquist et al., 1999; Canfield et al., 1993; Dauwe et al., 2001). In this study, carbon mineralisation was determined by measuring CO_2 in the headspace of microcosms containing fully wet and dried-rewet soil/sediment.

The experiments were set up to run simultaneously with those described in Section 3.3.4.2 and were carried out in triplicate, using the same column microcosms as those described in Section 3.3.1. The air inlet, water inlet and sampling outlet were fitted with Suba-seal gas impermeable rubber septa in order to create an air-tight chamber (Figure 3.1). Spiked soil and sediment were packed into the column microcosms following the procedures of Section 3.3.3. The microcosms were then divided into two groups. In group one, the microcosms were kept in a temperature control cabinet maintained at 10 ^{0}C and artificial seawater at a salinity of 20 was delivered to the microcosms by a peristaltic pump at a flow rate of 1.6 ml min^{-1} for one hour so as to fully wet the soil and sediment. The water inlet was then sealed with a gas impermeable rubber septum. The microcosms were left for one hour to allow the gases within the headspace to equilibrate before sampling. The headspace was then sampled once daily over the 15 days duration of the experiment. In group two, microcosms containing the soil and sediment were dried in the temperature control cabinet for 7 days at 25 ^{0}C. After drying, the temperature was reduced to 10 ^{0}C and artificial seawater at a salinity of 20 was supplied to the microcosms at a flow rate of 1.6 ml min^{-1} for one hour. The water inlet was then sealed with a gas impermeable rubber septum in order to create an air-tight chamber and the gases within the headspace were left to equilibrate for one hour before sampling. Headspace samples were collected once daily for 6 days. An additional set of microcosms containing soil and sediment which were used for microbial biomass determination were included in group two. The soil and sediment microbial biomass were determined in order to assess the changes in microbial biomass due to drying and rewetting.

Gas samples (2 ml) were withdrawn from the headspace via the sampling septum using a gas tight syringe (Hamilton, Switzerland). The collected gas samples were then injected into gas tight exetainer vials (Labco, UK) and filled with deionised water using a two way valve. The vials were inverted and stored at room temperature until analysis. The inverted position kept the gas samples above water and hence prevented atmospheric gas exchange. The analysis was carried out using gas chromatography (GC) with a flame ionisation detector described in Section 3.6.3. The storage of CO_2 gas above water may lead to CO_2 dissolution in the deionised water. As a result, the concentration of CO_2 dissolved in the deionised water during storage was calculated using Henry's law and the CO_2 solubility coefficient (Stumm and Morgan, 1981). The calculated CO_2 concentration was added to the measured CO_2 concentration in the headspace of the vial to get the total CO_2 concentration (headspace plus water).

The mineralisation rate was calculated as the rate of change of CO_2 concentration per unit mass of the soil/sediment per day using the formula:

$$\text{Mineralisation rate } (\mu g CO_2 kg^{-1} d^{-1}) = \frac{[CO_2]_i - [CO_2]_{i-1}}{t} \qquad (3.1)$$

where $[CO_2]$ is CO_2 concentration in headspace (µg CO_2 kg^{-1}), i is sample number and t (day) is time between sampling.

The mineralisation rate on day 1 could not be calculated because two samples were needed to calculate the mineralisation rate.

The soil and sediment microbial biomass were determined using the substrate induced respiration method. The most commonly used methods for the determination of microbial biomass are substrate induced respiration (Anderson and Domsch, 1978; West and Sparkling, 1986; Lin and Brookes, 1999; Degens and Harris, 1997) and chloroform fumigation-extraction (Franzleubbers et al., 2000; Magid et al., 1999). In this study, the substrate induced respiration method was used because it determines the active living microbial biomass (Hoper, 2006; Lin and Brookes, 1999) hence the changes due to microbial death during drying could be estimated. The microbial biomass in the soil and sediment were determined just before drying, after drying and 6 days after rewetting the soil and sediment. On the specified days, the additional microcosms containing the soil and sediment were removed from the temperature control cabinet and samples equivalent to 1 g dry weight were placed in 10 mL gas-tight exetainer vials (Labco, UK). 2 ml of glucose solution was added to each exetainer vial (West and Sparkling, 1986). Glucose was used because most microbes can easily utilize it as a carbon source (Lin and Brookes, 1999). After glucose addition, the vials were sealed and then shaken for 5 minutes on a wrist action shaker at 100 oscillations per minute to ensure the even distribution of glucose within the soil and sediment samples. The vials were then incubated at 22 ^{0}C in a temperature control cabinet for 4 hours before sampling (Degens and Harris, 1997). The incubation period allowed for measurable CO_2 levels in the headspace of the vials. A 2ml gas sample was withdrawn from the headspace of the vial using a gas tight syringe (Hamilton, Switzerland). The collected gas samples were then injected, using a two-way valve, into gas tight exetainer vials (Labco, UK) filled with deionised water. The vials were then inverted and stored at room temperature until analysis. The analysis was carried out using gas chromatography (Section 3.7.2). The concentration of CO_2 dissolved in the deionised water during storage was accounted for using Henry's law and the solubility coefficient of CO_2 (Stumm and Morgan, 1981). The microbial biomass was calculated according to Anderson and Domsch (1978):

$$\text{Microbial biomass } (\mu gCg^{-1}) = \mu lCO_2g^{-1}hr^{-1} \times 40.04 + 0.37 \qquad (3.2)$$

where 40.04 and 0.37 are constants.

3.5 Batch sorption experiments

Batch sorption experiments were conducted to determine the partition coefficients of the metals and herbicides at two different salinities (5 and 20) in order to evaluate the changes in contaminant binding to the soil and sediment with changes in salinity. The concentrations of the metals and herbicides associated with the solid and liquid phase were fitted to a linear sorption isotherm to calculate the partition coefficients (K_d). The coefficients reflect the relative distributions of the metals and the herbicides between the solid and liquid phase. The partition coefficient was calculated as follows:

$$K_d = \frac{C_s}{C_{aq}} \tag{3.3}$$

where K_d (l kg^{-1}) is the partition coefficient, C_s (mg kg^{-1}) is the contaminant concentration in the solid phase and C_{aq}(mg l^{-1}) is the contaminant concentration in the liquid phase.

In this study, the partition coefficients were derived from mass balance calculations. As a result, other processes such as contaminant loss either due to degradation or adsorption to container walls during batch sorption experiments can affect the coefficients. Particle concentration can also affect partition coefficients. Turner and Millward (2002) notes that K_d has an inverse dependence on particle concentration as suspended particles are an important control on contaminant partitioning. The dependence of K_d on particle concentrations can compromise the extrapolation of the coefficients to different environmental conditions.

3.5.1 Metal sorption experiments

4 g of air-dried soil and sediment samples were weighed into clean centrifuge tubes. Artificial seawater at salinities of 5 and 20 were spiked with nitrate salts of Cu, Ni and Zn (Aldrich, analytical grade) to achieve composite solutions with three final spiking concentrations: 200, 500 and 1000 µg l^{-1}. 20ml of the spiked solutions were then added to the soil and sediment samples to give a solid-liquid ratio of 1:5. The tubes were placed on a flat bed shaker and agitated at 300 oscillations per minute for 24 hours after which the

samples were filtered through a 0.45 µm cellulose nitrate membrane filter paper (Whatman). 10 ml aliquots of the filtrate were acidified with 2 % nitric and stored at 4 ^{0}C until analysis by ICP-OES (Section 3.6.1). The experiments were conducted with triplicates for each spiking concentration at room temperature with two blank and two control samples included. All the plastic and glassware used were cleaned by soaking for 24 hours in Decon solution, rinsing in deionised water three times, followed by soaking again in 10 % nitric solution overnight and then rinsing three times in deionised water. The control samples did not indicate any significant loss of metals to the walls of the centrifuge tubes.

3.6.2 Herbicide sorption experiments

4 g of air-dried soil and sediment samples were weighed into clean non-reactive PTFE tubes. Similar to the metals sorption experiments, artificial seawater at salinities of 5 and 20 were spiked with Cu, Ni and Zn (powder form) (Fluka, analytical grade) to achieve composite solutions with three final spiking concentrations: 200, 500 and 1000 µg l^{-1}. 20 ml of the spiked solutions were added to the soil and sediment samples. The tubes were sealed and agitated, at room temperature, on a flatbed shaker for 24 hours at 300 oscillations per minute. After 24 hours, the samples were filtered using a 0.45 µm disposable PTFE membrane syringe filter (Nalgene). 1 ml aliquots of the sample filtrates were transferred to amber vials and stored at 4 ^{0}C until analysis by HPLC technique in direct injection mode (Section 3.6.2). The experiments were conducted at room temperature with duplicate for each spiking concentration, two blank and two control samples. The PTFE tubes used were cleaned by soaking for 24 hours in Decon solution, rinsing three times in deionised water and then in HPLC grade acetonitrile to remove any traces of herbicides. The control samples did not indicate any sorption of the herbicides onto the PTFE tubes.

3.6 Analytical techniques

3.6.1 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The overlying water samples collected from the microcosm experiments and samples from the metal batch sorption experiments were analysed for Cu, Ni and Zn using ICP-OES (Varian Vista-PRO^{TM}). The instrument was equipped with a one-piece low flow extended high dissolved solids torch with a quartz injector tube (2.3 mm diameter), a two channel peristaltic pump, a glass cyclonic spray chamber and a concentric glass slurry nebulizer. The axially viewed torch system improved sensitivity and lowered detection limits by increasing the analyte signal and reducing the background intensity (Brenner et al., 1997). The instrument was programmed by the ICP Expert software. The operating conditions were optimized using the Varian's Automax^{TM} function designed to obtain the optimum measurement conditions for any combination of metals (Table 3.3).

Table 3.3 Operating conditions of the Varian Vista-PRO spectrometer

Radio frequency power (W)	1200
Plasma gas flow (l min^{-1})	15
Auxiliary gas flow (l min^{-1})	1.5
Pump rate (rev. min^{-1})	15
Nebuliser gas flow (l min^{-1})	0.9

The ICP-OES was calibrated at the beginning of each run with standards at concentrations which covered the range of sample concentrations analysed. The calibration standards made up from a multi-elemental standard solution were matrix matched to the composition of the samples in order to minimise interferences on the analyte signal. One quality control standard was incorporated after every ten samples in each analytical run. This monitored drift in the analyte signal over time. The most sensitive analyte wavelengths without spectral interferences were used. A blank sample and a duplicate sample were also included in each analytical run to evaluate precision The blank values were constantly below the limits of detection for Cu, Ni and Zn which were calculated as three standard deviations of the mean of ten replicate readings of a blank sample and are shown in Table 3.4.

Table 3.4 ICP-OES detection limits of Cu, Ni and Zn in mg l^{-1}

Element	LoD (3σ)
Cu	0.001
Ni	0.10
Zn	0.03

3.6.2 On-line solid phase extraction-high performance liquid chromatography (on-line SPE-HPLC)

The samples collected from the overlying water in the microcosm experiments and samples from the herbicide sorption experiment were analysed for simazine, atrazine and diuron by HPLC. The technique has been recommended for the analysis of non-volatile and thermolabile pesticides such as those considered in this study due to the low temperature conditions associated with the technique (Field, 1997; Pico, 2000). In addition, HPLC allows for the direct analysis of aqueous samples (Hernandez et al., 2001). However, sample pre-concentration by solid phase extraction (SPE) prior to the HPLC analysis was necessary for the analysis of the overlying water samples collected from the microcosm experiments. This was because the concentrations of the herbicides contained in some of the samples were below the detection levels by direct injection into the HPLC.

SPE is used for the extraction of organic contaminants in aqueous samples with a wide range of polarities by passing the aqueous samples through a sorbent material which retains the organic contaminants (Hennion, 1999). The on-line SPE procedure was automated using a MIDAS autosampler and Prospekt-2^{TM} solid-phase extraction unit consisting of an Accelerated Cartridge Exchanger (ACE) and High Pressure Dispenser (HDP) (Spark Holland, The Netherlands). The MIDAS autosampler loaded the samples on to SPE cartridges on the ACE and the HPD delivered the solvent for extraction. The procedure was programmed by the SparkLink (v 2.3) software operated on a Hewlett-Packard L1720. PLRP-S cartridges (10 x 2 mm i.d.) (Spark Holland, The Netherlands) containing styrene-divinylbenzene polymeric sorbent material were used because of their stability over the entire pH range (1 – 14) and their large specific surface area which enables them to effectively retain analytes such as the herbicides considered in this study (Hennion, 1999). The SPE procedure required only a small amount of solvent, making it very economical and cost effective. The automation allowed for multiple sample extractions, minimised sample handling resulting in more reproducible results and decreased the risk of sample contamination (Hernandez et al., 2001). Prior to sample loading, the SPE cartridges were preconditioned with 2 ml of acetonitrile and equilibrated with 14 ml of ultra-pure water both delivered at 5 ml min^{-1}. 1 ml of the sample was loaded on to the preconditioned cartridge at 4 ml min^{-1}. The sample volume was kept to a minimum in order to avoid clogging up the sorbent in the cartridges with particulate material and to maintain satisfactory detection levels for all the studied herbicides with good recoveries. Following sample loading, the cartridge was first washed with 1 ml of ultra-pure water at 4 ml min^{-1} and then backwashed with another 1 ml of ultra-pure water at 2 ml min^{-1}. Finally, the herbicides retained on the cartridges were eluted with acetonitrile directly into the LC column by valve switching.

The HPLC unit (Agilent 1100 Series) comprised of a quaternary pump, a solvent degasser, a temperature controlled Wellplate autosampler and ultra-violet photodiode array detector (UV-DAD). The unit was controlled by the ChemStation software (v 4.1) operated on a Hewlett-Packard L1720 lab based computer. The LC analytical column used for separating the herbicides was a Supelcosil^{TM} ABZ+ (25 cm in length, 4.6 mm in diameter, 5 µm particle size) (Supelco, Belfonte, USA) and it was maintained at a temperature of 40 ^{0}C. Disposable guard columns were used to protect the column from the build up of particulates that could contaminate the column and interfere with its performance. The sample was injected into the column at a flow rate of 1 ml min^{-1} and a gradient elution was carried out using acetonitrile (LC solvent A) and ultra-pure water (LC solvent B) according to the following programme: from LC solvent A-B (35 %:65 %) to LC solvent A-B (60 %:40 %) in 15 minutes and then returned to LC solvent A-B (35 %:65 %) in 5 minutes. After 5 minutes of stabilisation, the next sample was injected. The detection wavelength for quantification on the UV-DAD was set at 240 nm because the chromatographic peaks were effectively resolved with good peak shapes which were maintained at this wavelength. The chromatographic peak areas were automatically integrated. However, the integration was adjusted manually using the ChemStation software on occasions when the integration algorithm did not adequately integrate the peaks.

At the beginning of each run, the system was calibrated with standards (concentrations range from 0.01 – 500 µg l^{-1}) which were subjected to the complete online SPE-HPLC technique to ensure that the standards and samples passed through the same process. One quality control standard was analysed after every ten samples. This monitored drift in the analyte signal intensity and the performance of the HPLC between the analyses of samples over time. A blank sample and a duplicate sample were also included in each analytical run.

The % recovery and detection limits are presented in Table 3.5 and 3.6 respectively. The % recovery was determined by analysing triplicate composite herbicide solutions at 3 initial concentrations (50, 100 and 500 µg l^{-1}) and calculating the ratio between the initial concentration of the herbicide and the measured concentration after solid phase extraction and analysis, expressed as a percentage. The % recoveries indicate that the method was satisfactory for the analysis of the herbicides. The blank samples were below the limit of detection for each of the herbicides which were calculated by using the lowest calibration standard with a signal:noise ratio ≥ 3 (i.e. the ratio between the peak intensity and the noise) (Ferrer and Barcelo et al., 1999).

Table 3.5. Recoveries of simazine, atrazine and diuron (average ± standard deviation (SD), n = 3).

Herbicides	Spiked level (µg l^{-1})	% recovery
Simazine	50	85 ± 2.2
	100	89 ± 8.2
	500	86 ± 6.2
Atrazine	50	93 ± 4.5
	100	89 ± 4.7
	500	96 ± 3.9
Diuron	50	90 ± 7.9
	100	91 ± 6.9
	500	95 ± 4.9

Table 3.6. Limit of detection (SN ≥ 3) of simazine, atrazine and diuron

	Simazine	Atrazine	Diuron
LOD (µg l^{-1})	0.1	0.1	0.05

3.6.3. Gas chromatography (GC)

The headspace samples collected from the organic matter mineralisation experiments and the microbial biomass incubations were analysed for CO_2 using gas chromatograph (GC). The GC unit (Agilent Technologies, Cheshire) was equipped with a flame ionisation detector (FID), an electronic integrator and an autosampler (Gerstel, GmbH, Germany). A stainless steel column (1.8 m length, 12mm diameter) packed with Porapak Q (80/100 mesh, particle size 0.13 – 0.15 mm) (Alltech Ltd) was used for analysis. The column and FID detector were maintained at a constant temperature of 30 ^{0}C and 385 ^{0}C respectively. The analysis was conducted with hydrogen gas and zero grade air at a flow rate of 430 ml min^{-1}. The GC was programmed by the Agilent ChemStation software operated on a Hewlett-Packard L1720 lab based computer. The system was calibrated with standards prepared from 99.99 % CO_2 gas (1, 5, 20, 100, 200, 500 µl) at the beginning of each run. . A 100 µl sample was withdrawn from the headspace gas sample by the autosampler using a gas-tight syringe and injected into the GC. The headspace CO_2 concentration was calculated from the peak area using the electronic integrator and calibrated against the standards. One standard sample and a duplicate sample were included in each analytical run to monitor drift during the analysis and to evaluate precision.

3.7. Statistical Analysis

Statistical analysis was carried out using SPSS statistical package (Version 16). Linear regression analysis was conducted on the DOC, metal and herbicide concentrations measured in the overlying water under the drying-rewetting treatment to determine the relationship between DOC, the metals and herbicides. Linear regression is a powerful parametric test which determines the strength of the relationship between two variables and describes how much of the variation in one variable (dependent variable) is explained by the relationship with the other variable (independent variable) (Quinn and Keough, 2002). The coefficients of determination from the regression analysis were interpreted as the proportion of variance in the metal and herbicide concentrations attributable to the variance in the DOC concentrations. The concentration data that had unequal variances and asymmetric distributions were log-transformed in order to meet the assumptions of the test.

A two-way ANOVA was used to test for significant differences between the partition coefficients (log K_d) for soil and sediment at salinities of 5 and 20 calculated from the batch sorption experiments; between the total contaminant loads and between the total DOC loads released into the overlying water from the soil and sediment under the treatments in the column experiments. Two-way ANOVA is a parametric test which tests for significant differences between the effects of two different factors simultaneously and interactions between the factors. The total metal, herbicide and DOC loads were determined by multiplying the average measured metal, herbicide and DOC concentrations between sampling periods by the time interval between sampling and dividing by the flow rate at which artificial seawater was delivered to the microcosm. The loads at each sampling period were then summed to get the total load. Due to the small sample size for the two-way ANOVA, emphasis was placed in Chapter 5, on discussing the trends observed for the total metal and herbicide loads released into the overlying water from the soil and sediment. Instances where significant differences were observed are highlighted. The dataset that had unequal variances and asymmetric distributions were log-transformed to meet the assumptions of the test.

Chapter 4: Experimental Results

4.1. Introduction

This chapter presents the laboratory experimental data obtained from the batch sorption, column microcosm and carbon mineralisation experiments which examine the effect of salinity and drying and rewetting on the release of metals and herbicides from agricultural soil and dredged sediment in managed realignment sites following tidal inundation. Batch sorption experiments were conducted to calculate partition coefficients (K_d) of the contaminants at two different salinities (5 and 20) in order to evaluate the changes in contaminant binding with changes in salinity. Column microcosm experiments gave rise to two datasets, one to investigate the effect of two different salinities (5 and 20), and one to investigate the effect of drying-rewetting conditions on contaminant release from the soil and sediment. The two sets of experimental data were obtained by measuring the contaminants released from the soil and sediment into overlying water and the observed patterns of release will be described. pH and DOC are important controls on both metal and herbicide release and hence these data are also presented. Soil and sediment microbial biomass data and headspace CO_2 data measured during the carbon mineralisation experiments will be presented in order to test the hypothesis that organic matter mineralisation will be enhanced during drying and rewetting of the soil and sediment leading to the release of organic matter associated contaminants into the overlying water. These experimental data will be discussed in Chapter 5.

4.2. Soil and sediment properties

Properties of the soil and sediment used in this study are presented in Table 4.1. The soil and sediment comprised predominantly silt and clay sized particles. The organic matter content in the sediment was higher than the soil. These soil and sediment properties were within the range reported for salt marsh soil (Edwards and Proffitt, 2003; Shafer and Streever, 2000; Craft et al., 1999; MacLeod et al., 1999), hence the soil and sediment used were representative of salt marsh soils.

Table 4.1 Properties of the soil and sediment used in this study (average ± SD, n = 5).

Properties	Soil	Sediment
pH	7.1 ± 0.2	7.0 ± 0.3
Organic matter (%)	7.4 ± 0.1	8.7 ± 0.1
Clay (%)	28 ± 0.9	40 ± 1.2
Silt (%)	38 ± 0.7	47 ± 0.8
Sand (%)	34 ± 0.4	13 ± 0.7

4.3. The effect of salinity on contaminant release from managed realignment soil and sediment: results

4.3.1. Partition coefficient data under two different salinity treatments

Tables 4.2 and 4.3 present the average partition coefficients (log K_d) of the metals and herbicides respectively at 5 and 20 salinities. The complete data are presented in Appendix 8. The batch sorption experiments were conducted with a metal concentration range from 0.2 to 1 mg L^{-1} and the partition coefficients were calculated as described in Chapter 3 (Section 3.5). The concentrations of the metals and herbicides associated with the solid and liquid phase were fitted to a linear sorption isotherm to calculate the partition coefficients. The coefficients reflect the relative distributions of the metals and the herbicides between the solid and liquid phase. The r^2 values (at $p < 0.05$) indicated that the partition coefficient sufficiently describes the distribution of the metals ($r^2 = 0.83 – 0.99$) and the herbicides ($r^2 = 0.94 – 0.99$) in the soil and sediment (Table 4.2 and 4.3).

In both the soil and sediment in the 5 salinity treatment, Cu had the highest log K_d values, followed by Zn and then Ni (Table 4.2). With the exception of Zn in the sediment, the log K_d generally decreased as salinity increased, indicating that the sorption of the metals to the soil and sediment decreased with higher salt concentration in the liquid phase under the high salinity treatment. However, a significant difference in the partition coefficients between the 5 and 20 salinity treatments was only observed for Cu (Two-way ANOVA: F = 14.76, $p < 0.05$) (Table 4.2). Table 4.2 also shows that the log K_d of Cu, Ni and Zn were consistently higher in the sediment compared to the soil. The differences were significant for Cu (Two-way ANOVA: F = 13.04, $p < 0.05$) and Ni (Two-way ANOVA: F = 30.73, $p < 0.05$) at both salinities and Zn (Two-way ANOVA: F = 15.29, $p < 0.05$) at 20 salinity.

Table 4.2 Average partition coefficients of Cu, Ni and Zn for soil and sediment at 5 and 20 salinity (average ± standard deviation (SD), n = 9)

Metal	Soil				Sediment			
	5 ‰		20 ‰		5 ‰		20 ‰	
	log K_d	r^2	log K_d	r^2	log K_d	r^2	log K_d	r^2
Cu	2.76 ± 0.04^{a}	0.85	2.54 ± 0.07^{b}	0.97	2.97 ± 0.05^{b}	0.83	2.74 ± 0.07^{ac}	0.89
Ni	2.33 ± 0.07^{a}	0.98	2.28 ± 0.03^{a}	0.95	2.52 ± 0.01^{b}	0.99	2.44 ± 0.05^{b}	0.94
Zn	2.61 ± 0.02^{a}	0.99	2.55 ± 0.05^{ab}	0.86	2.68 ± 0.01^{a}	0.99	2.75 ± 0.04^{ac}	0.92

The same letter (a, b, c) denotes no significant difference between the 5 and 20 salinity treatments and between the soil and sediment under the respective salinity treatments at 95 % significance level.

Log K_d values for the herbicides were considerably higher than those of the metals (Table 4.3) suggesting that the herbicides sorb more strongly to the soil and sediment than the metals. The log K_d values were highest for diuron, followed by atrazine and then simazine in both the soil and sediment at 5 and 20 salinities (Table 4.3). No significant differences between the log K_d at 5 and 20 salinities were observed for atrazine and diuron. Simazine was an exception with the log K_d value significantly higher in the soil at 5 salinity compared to 20 salinity (Two-way ANOVA: $F = 7.16$, $p < 0.05$). The log K_d values were higher in the sediment than the soil except for simazine. A significant difference was only observed between the soil and sediment log K_d values for simazine at 5 salinity (Two-way ANOVA: $F = 5.53$, $p < 0.05$).

Table 4.3 Average partition coefficients of simazine, atrazine and diuron for soil and sediment at 5 and 20 salinity (average ± standard deviation (SD), n = 6)

Herbicides	Soil				Sediment			
	5 ‰		20 ‰		5 ‰		20 ‰	
	log K_d	r^2	log K_d	r^2	log K_d	r^2	log K_d	r^2
Simazine	3.76 ± 0.03^{a}	0.98	3.63 ± 0.02^{b}	0.99	3.67 ± 0.04^{b}	0.99	3.67 ± 0.02^{b}	0.99
Atrazine	3.87 ± 0.02^{a}	0.99	3.87 ± 0.01^{a}	0.99	3.94 ± 0.03^{a}	0.99	3.93 ± 0.01^{a}	0.99
Diuron	4.22 ± 0.05^{a}	0.94	4.24 ± 0.06^{a}	0.95	4.33 ± 0.08^{a}	0.94	4.39 ± 0.06^{a}	0.90

The same letter (a, b) denotes no significant difference between the 5 and 20 salinity treatments and between the soil and sediment under the respective salinity treatments at 95 % significance level.

4.3.2. Column microcosm experimental data under two different salinity treatments

This section presents the average metal and herbicide concentrations and total loads measured in the overlying water during the column microcosm experiments examining the effect of salinity on the release of the metals and herbicides from the soil and sediment. The experiments were carried out in triplicate and the soil and sediment were continuously flooded with artificial seawater at two different salinities, 5 and 20 (referred to in the text as low and high salinity treatments respectively). pH and DOC data are also presented here as they are important parameters that control metal and herbicide release. The total contaminant and DOC load were calculated by multiplying the average contaminant and DOC concentrations between sampling periods by the time interval between the sampling and dividing by the flow rate at which artificial seawater was delivered to the microcosm. The loads for each time period were then summed to get the total load.

4.3.2.1 Release of metals into the overlying water under the low and high salinity treatments

Figure 4.1 presents the average concentrations of Cu, Ni and Zn released from the soil and sediment to the overlying water under low and high salinity treatments (see Appendix 9 for the complete data set). For both the soil and sediment, there were high concentrations of Cu, Ni and Zn in the overlying water in the first 24 hours which declined rapidly and remained relatively constant for the remainder of the experiment. This release pattern suggests an initial phase of rapid release followed by a phase of slow release.

Table 4.4 shows the total metal loads released into the overlying water from the soil and sediment over the course of the experiments under the low and high salinity treatments. With the exception of Cu released from the sediment, the total metal loads released from the soil and sediment into the overlying water were higher under the high salinity treatment compared to the low salinity treatment. However, the results of the two-way ANOVA showed that there was no significant difference in the total metal loads released into the overlying water from the soil and sediment under the high salinity treatment in comparison to the low salinity treatment except for Ni. The total Ni load released from the sediment under the high salinity treatment was significantly higher than that released under the low salinity treatment (Two-way ANOVA: $F = 5.51$, $p < 0.05$). The total Cu, Ni and Zn loads released into the overlying water from the sediment were lower than those released from the soil (Table 4.4). However, the differences in the total loads between the soil and sediment were only significant for Ni and Zn under the low salinity treatment (Two-way ANOVA: $F = 3.42$, $p < 0.05$ for Ni and $F = 7.51$, $p < 0.05$ for Zn) and for Cu under both treatments (Two-way ANOVA: $F = 17.37$, $p < 0.05$). Although the soil and sediment were spiked with all three metals at the same concentration, the total load of the individual metals released into the overlying water from the soil and sediment were in the order: Ni > Zn > Cu with the Cu loads two orders of magnitude lower than those of Ni and Zn under both salinity treatments.

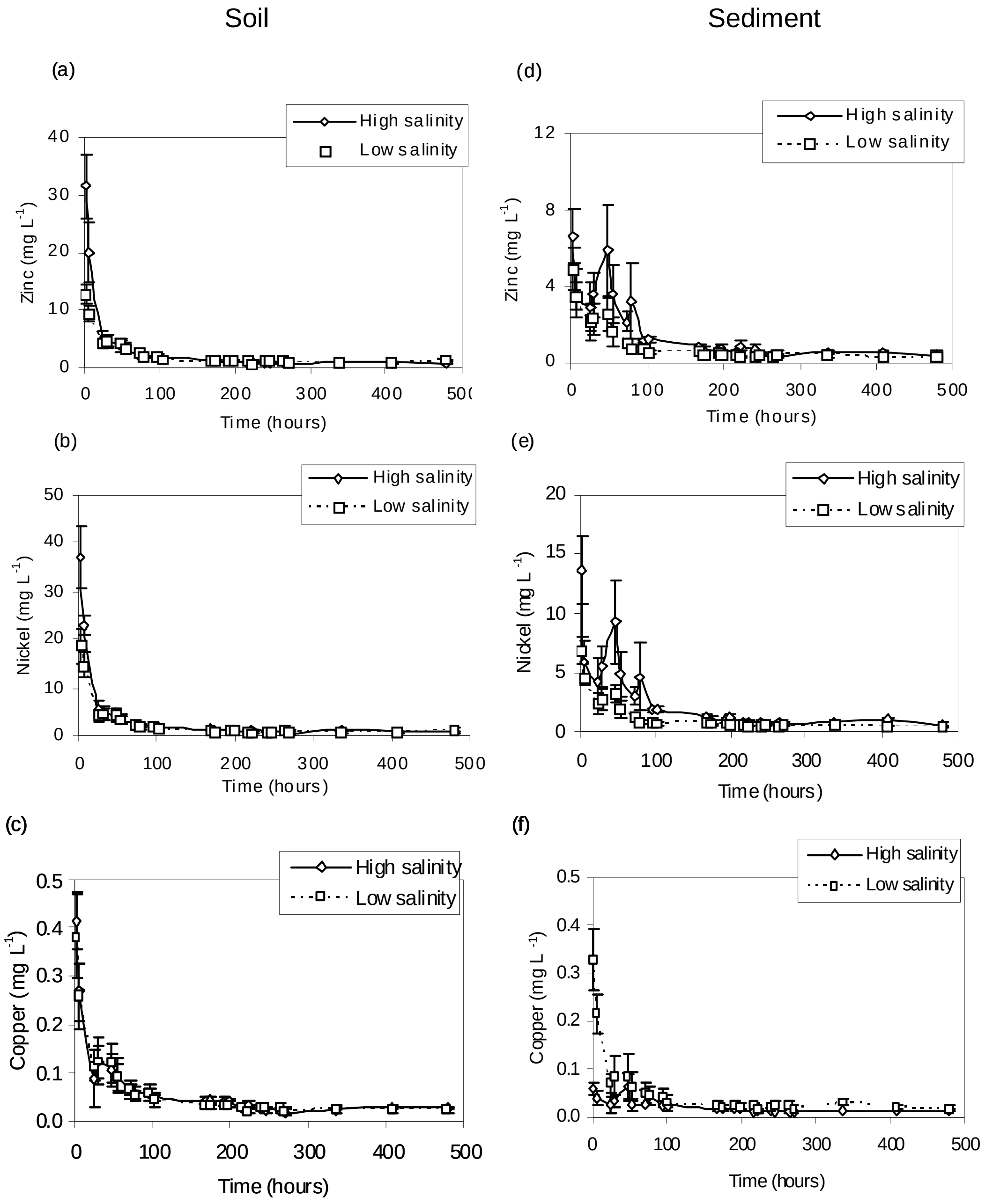

Figure 4.1 Concentrations of (a) Zn, (b) Ni and (c) Cu released from soil and (d) Zn, (e) Ni and (f) Cu released from sediment under the low and high salinity treatments (bars = standard deviation (SD), n = 3).

Table 4.4 Total metal loads (mg) released into the overlying water from the soil and sediment under the low and high salinity treatments (average ± SD, n = 3).

Metals	Soil		Sediment	
	Low salinity	High salinity	Low salinity	High salinity
Cu (mg)	0.6 ± 0.2^{a}	0.7 ± 0.2^{a}	0.3 ± 0.1^{b}	0.3 ± 0.04^{b}
Ni (mg)	25 ± 4.3^{bc}	28 ± 4.8^{b}	13 ± 2.3^{a}	27 ± 4.6^{b}
Zn (mg)	23 ± 2.3^{a}	24 ± 4.6^{a}	11 ± 2.2^{b}	18 ± 2.9^{ab}

The same letter (a, b, c) denotes no significant difference between the low and high salinity treatments and between the soil and sediment under the respective salinity treatments at 95 % significance level.

4.3.2.2. Release of herbicides into the overlying water under low and high salinity treatments

The average concentrations of simazine, atrazine and diuron released from the soil and sediment into the overlying water under the low and high salinity treatments are presented in Figure 4.2, with the complete data in Appendix 10. The simazine, atrazine and diuron concentrations in the overlying water were high in the first 24 hours, followed by a rapid decrease to relatively constant concentrations indicating an initial rapid release phase followed by a slow release phase.

Table 4.5 presents the total herbicide load (µg) released into the overlying water from the soil and sediment under the low and high salinity treatments. The total simazine, atrazine and diuron loads released into the overlying water from the soil were higher than those released from the sediment under both salinity treatments. However, the differences were not significant (Table 4.5). Similarly, the total simazine, atrazine and diuron loads released under the low salinity treatment were not significantly different from those released under the high salinity treatment. Table 4.5 also highlights differences in the individual herbicide load released into the overlying water from the soil and sediment. Simazine had the highest load in the overlying water, followed by atrazine and then diuron despite the soil and sediment having been spiked with all three herbicides at the same concentration.

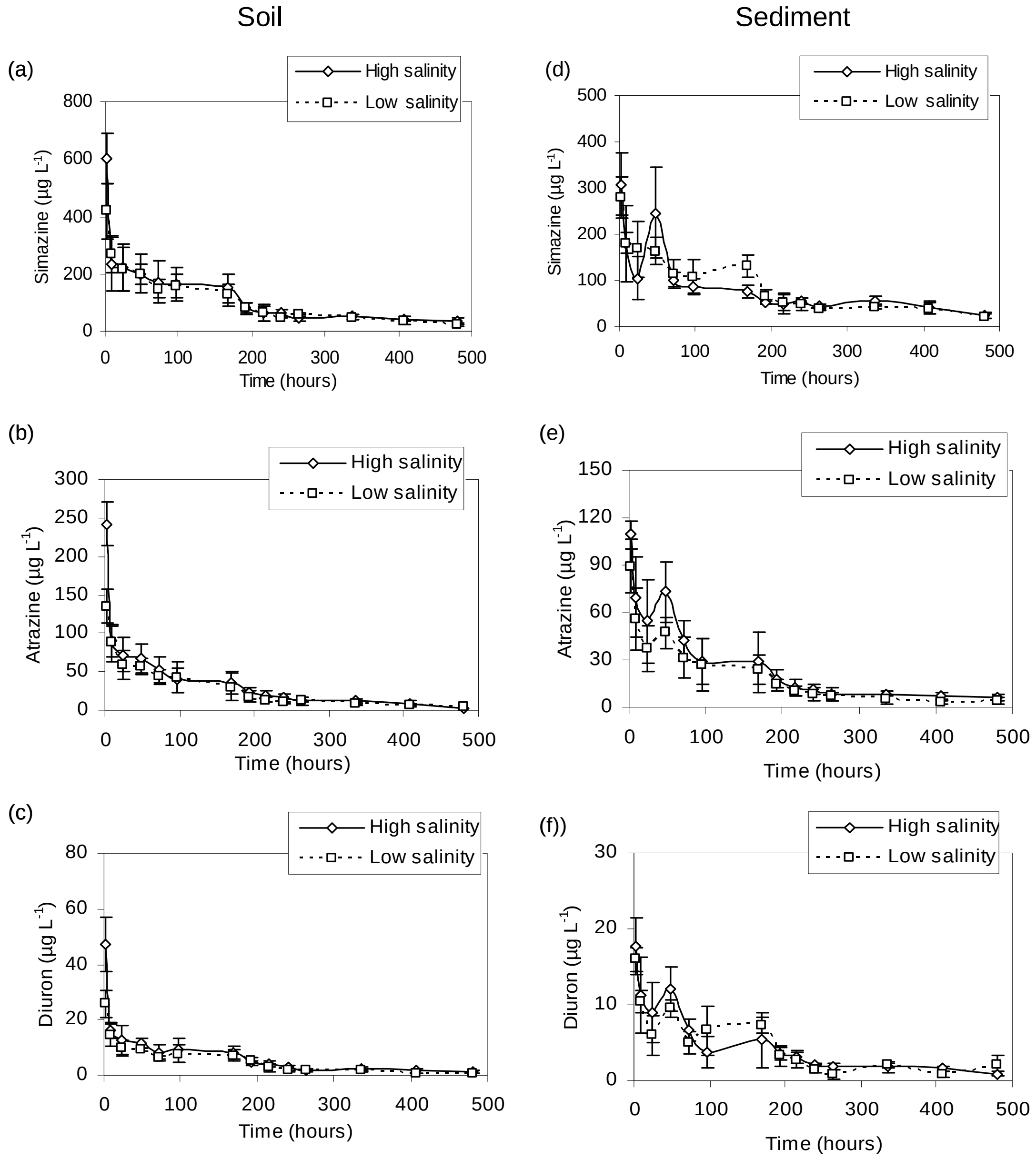

Figure 4.2 Concentrations of (a) simazine, (b) atrazine and (c) diuron released from the soil and (d) simazine, (e) atrazine and (f) diuron released from sediment under low and high salinity treatments (bars = standard deviation (SD), n = 3).

Table 4.5 Total herbicide loads (µg) released into the overlying water from soil and sediment under low and high salinity treatment (average ± standard deviation SD, n = 3)

Herbicides	Soil		Sediment	
	Low salinity	High salinity	Low salinity	High salinity
Simazine (µg)	1303 ± 259.2[a]	1423 ± 429.5[a]	1117 ± 206.1[a]	1045 ± 51.40[a]
Atrazine (µg)	318 ± 93.1[a]	381 ± 117[a]	231 ± 78.9[a]	311 ± 108[a]
Diuron (µg)	59 ± 8.6[a]	74 ± 21[a]	54 ± 9.1[a]	56 ± 15[a]

The same letter (a) denotes no significant difference between the 5 and 20 salinity treatments and between the soil and sediment under the respective salinity treatments at 95 % significance level.

4.3.2.3. The release of DOC into the overlying water under low and high salinity treatment

The average DOC concentrations released into the overlying water from the soil and sediment under the low and high salinity treatments are presented in Figure 4.3. The complete results can be found in Appendix 11. The release patterns of DOC were similar to those of the metals (Figure 4.1) and herbicides (Figure 4.2) with high DOC concentrations in the overlying water in the first 24 hours which rapidly decreased to relatively constant levels indicating rapid and slow release phases.

Table 4.6 shows the total DOC loads released into the overlying water from the soil and sediment. The total DOC loads released from the soil and sediment were higher under the low salinity compared to the high salinity treatment. Whilst a higher total DOC load was released into the overlying water from the soil than the sediment under the low salinity treatment, a lower total DOC load was released from the soil than the sediment under the high salinity treatment. However, the differences were not statistically significant.

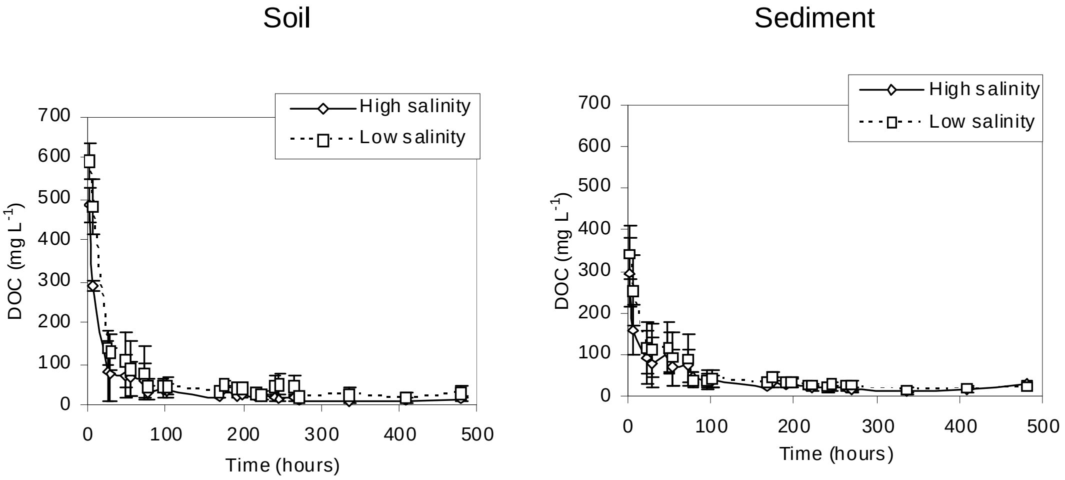

Figure 4.3 Concentrations of (a) DOC released from the soil and (b) DOC released from the sediment under the low and high salinity treatments (bars = standard deviation (SD), n = 3).

Table 4.6 Total DOC loads (mg) released into the overlying water from the soil and sediment under the low and high salinity treatments (average ± standard deviation (SD), n = 3).

	Soil		Sediment	
	Low salinity	High salinity	Low salinity	High salinity
DOC (mg)	787 ± 83[a]	476 ± 101[a]	642 ± 155[a]	531 ± 98[a]

The same letter (a) denotes no significant difference between the 5 and 20 salinity treatments and between the soil and sediment under the respective salinity treatments at 95 % significance level.

4.3.2.4. pH values in the overlying water under low and high salinity treatments

Figure 4.4 shows the average pH values in the overlying water under the low and high salinity treatments. The complete data are presented in Appendix 12. The pH values of the overlying water ranged from weakly alkaline to alkaline (pH 7.3 – pH 8.1) under the low and high salinity treatments with the pH values lower under the low salinity than high salinity treatment. During the first 24 hours, the pH values increased rapidly (Figure 4.3) before becoming relatively stable in the experiments with the soil, although pH values in the sediment continued to fluctuate.

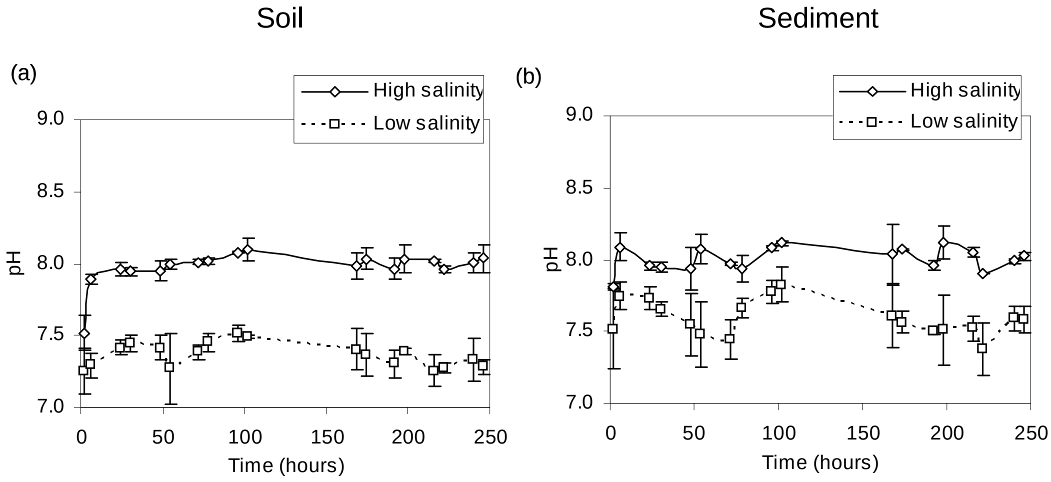

Figure 4.4 pH values of the overlying water for the soil (a) and pH values of the overlying water for the sediment (b) under low and high salinity treatments (bars = standard deviation (SD), n = 3).

4.4. The effect of drying and rewetting on contaminant release from managed realignment soil and sediment: results

4.4.1 Column microcosm experimental data under drying-rewetting treatment

The effect of drying and rewetting on the release of metals and herbicides from the soil and sediment into the overlying water was investigated using column microcosm experiments. The experiments were designed to have two drying-rewetting treatments with the soil and sediment dried for 7 days and then continuously rewet for 5 days with artificial seawater at a salinity of 20 in each treatment as described in Chapter 3, Section 3.3.4.2. The average metal, herbicide and DOC concentrations measured in the overlying water are presented in this section, with the complete data available in Appendices 13, 14 and 15 respectively. Comparisons were made between the experimental data under the first drying-rewetting treatment and data described in Section 4.3.2.1 where the soil and sediment were continuously flooded under high salinity treatment (referred to as ‘fully wet’ treatment in this section) in order to highlight any differences between the total loads.

4.4.1.1 Release of metals into the overlying water under the drying-rewetting treatment

Figure 4.5 shows the average metal concentrations released from the soil and sediment into the overlying water under the first drying-rewetting and the fully wet treatment over the same time period. The complete data for the metal concentrations released into the overlying water under the drying-rewetting treatment are presented in Appendix 13. Under the drying-rewetting treatment, high metal concentrations in the overlying water were observed in the first 24 hours following wetting, followed by a decrease which reaches a plateau with little or no change in the concentrations. The release pattern indicates an initial rapid release phase followed by a slow release phase.

Table 4.7 shows the total metal loads released into the overlying water from the soil and sediment under the first drying-rewetting treatment and for comparison the fully wet treatment over the same time period. Despite the soil and sediment having been spiked with all three metals at the same concentration, the total Cu, Ni and Zn loads released into the overlying water from the soil under the drying-rewetting treatment were significantly higher than those released from the sediment (Two-way ANOVA: $F = 40.13$, $p < 0.05$ for Cu; $F = 15.80$, $p < 0.05$ for Ni and $F = 14.37$, $p < 0.05$ for Zn). In addition, the Cu load released into the overlying water from the soil and sediment were two orders of magnitudes lower than the Ni and Zn load released.

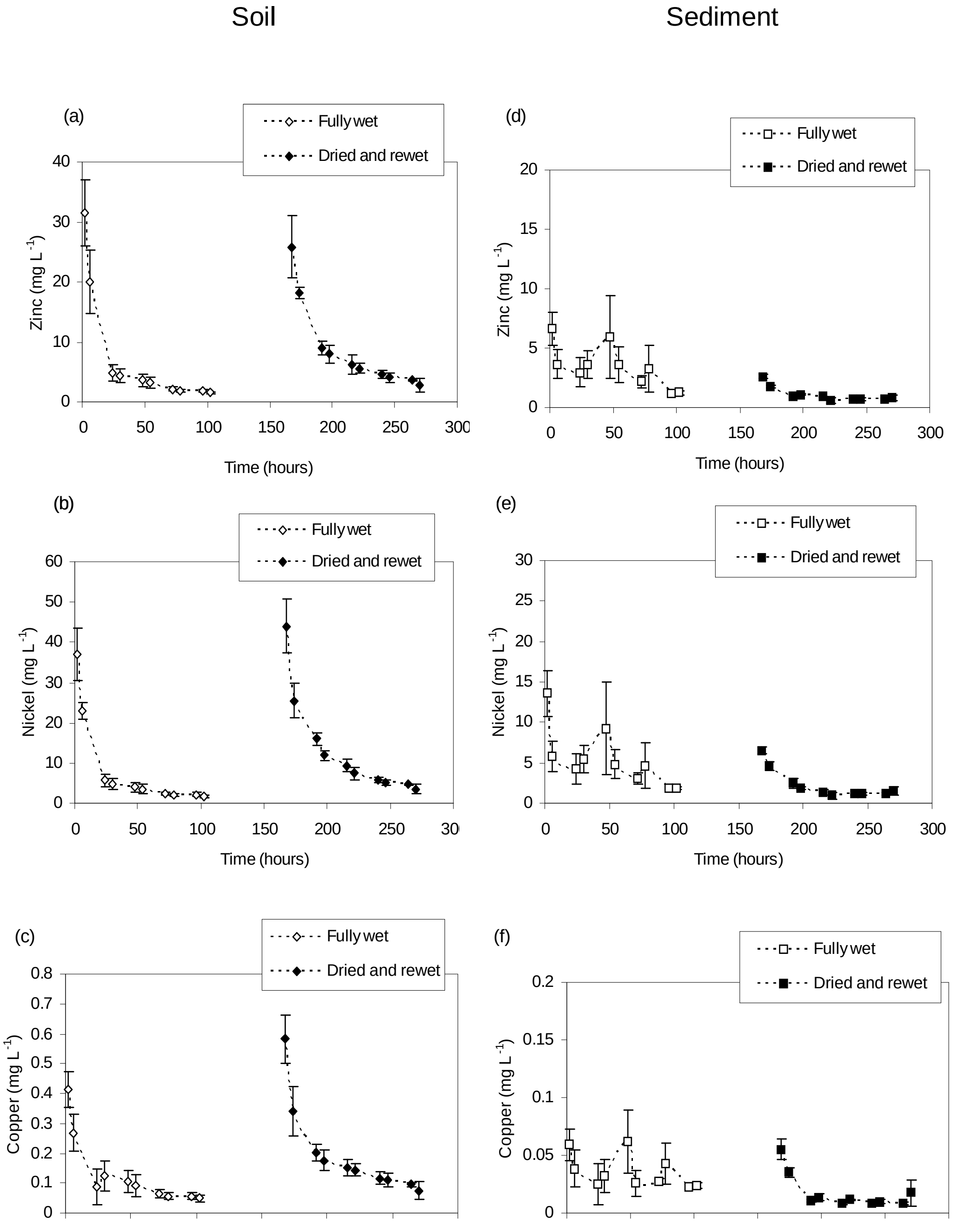

Figure 4.5 Concentrations of (a) Zn, (b) Ni and (c) Cu released from soil and (d) Zn, (e) Ni and (f) Cu release from sediment under the first drying-rewetting and fully wet treatments (bars = standard deviation (SD), n = 3).

The total Cu, Ni and Zn loads released into the overlying water from the soil were 66 %, 110 % and 61 % higher under the drying-rewetting treatment compared to the fully wet treatment. A significant difference in the total loads between the two treatments was only observed for Ni (Two-way ANOVA: F = 19.01, $p < 0.05$). Conversely, the total Cu, Ni and Zn loads released from the sediment into the overlying water under the drying-rewetting treatment were 67 %, 65 % and 73 % lower than those released under the fully wet treatment. A significant difference in the total loads between the two treatments was observed for Cu (Two-way ANOVA: F = 8.15, $p < 0.05$) and Ni (Two-way ANOVA: F = 19.01, $p < 0.05$) but not for Zn (Two-way ANOVA: F = 8.50, $p = 0.08$).

Table 4.7 Total metal loads (mg) released into the overlying water under the fully wet and the first drying-rewetting treatment over the same time period (average ± standard deviation (SD), n = 3)

Metals	Soil		Sediment	
	Fully wet	Drying-rewetting	Fully wet	Drying-rewetting
Cu (mg)	0.32 ± 0.09^{a}	0.53 ± 0.10^{a}	0.12 ± 0.03^{a}	0.04 ± 0.01^{b}
Ni (mg)	15.4 ± 2.81^{a}	32.3 ± 3.09^{b}	16.6 ± 4.75^{a}	5.77 ± 0.72^{c}
Zn (mg)	13.6 ± 3.17^{a}	21.95 ± 3.17^{a}	11.2 ± 3.38^{b}	3.08 ± 0.32^{b}

The same letter (a, b, c) denotes no significant difference between the drying-rewetting and fully wet treatments and between soil and sediment under the drying-rewetting treatment at 95 % significance level.

Figure 4.6 presents the average metal concentrations released into the overlying water from the soil and sediment over two drying-rewetting treatments. The complete data are presented in Appendix 13. Figure 4.6 shows that the release patterns of Cu, Ni and Zn under the second drying rewetting treatment were similar to the first drying-rewetting treatment with a rapid release observed initially, followed by a slow release until a plateau is reached.

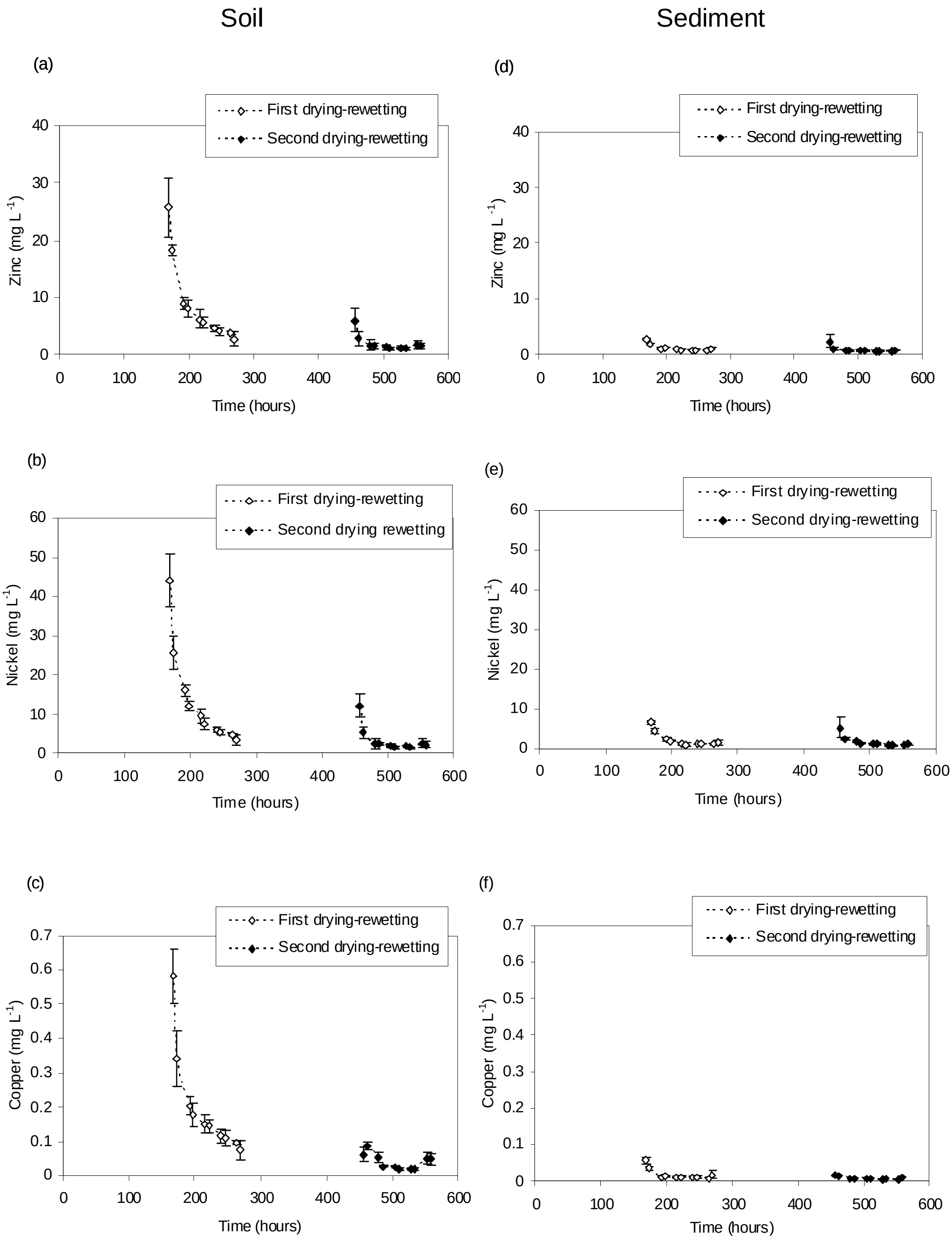

Figure 4.6 Concentrations of (a) Zn, (b) Ni and (c) Cu released from soil and (d) Zn, (e) Ni and (f) Cu released from sediment under the two drying-rewetting treatments (bars = standard deviation (SD), n = 3). The delay between the origin and the first drying-rewetting defines the 7 days of drying.

Table 4.8 shows the total Cu, Ni and Zn loads released into the overlying water from the soil and sediment under the two drying-rewetting treatments. The total Cu, Ni and Zn loads released into the overlying water from the soil under the second drying-rewetting treatment were significantly higher than those released from the sediment (Two-way ANOVA: F = 61.15, $p < 0.05$ for Cu, F = 74.25, $p < 0.05$ for Ni and F = 58.23, $p < 0.05$ for Zn). In addition, the total metal loads released into the overlying water from the soil were significantly lower under the second drying-rewetting treatment compared to the first drying-rewetting treatment (Two-way ANOVA: F = 17.32, $p < 0.05$ for Cu, F = 38.41, $p < 0.05$ for Ni and F = 27.52, $p < 0.05$ for Zn). The total Cu, Ni and Zn loads released from the soil into the overlying water under the second drying-rewetting treatment as a proportion of the total loads released under the first drying-rewetting treatment were approximately 77 %, 74% and 77% lower. In the case of the sediment, the total Cu, Ni and Zn loads released from the sediment under the second drying-rewetting treatment as a proportion of the total loads released under the first drying-rewetting treatment were approximately 50 %, 25 % and 28 % lower. However, the total metal loads released from the sediment under the two drying-rewetting treatments were not significantly different (Table 4.8).

Table 4.8 Total metal loads (mg) released into the overlying water under the two drying-rewetting treatments (average ± standard deviation (SD), n = 3)

Metals	Soil		Sediment	
	First drying-rewetting	Second drying-rewetting	First drying-rewetting	Second drying-rewetting
Cu (mg)	0.53 ± 0.10^a	0.12 ± 0.03^b	0.04 ± 0.01^a	0.02 ± 0.01^a
Ni (mg)	32.3 ± 3.09^a	8.15 ± 1.44^b	5.77 ± 0.72^a	4.35 ± 0.40^a
Zn (mg)	21.95 ± 3.17^a	5.02 ± 1.35^b	3.08 ± 0.32^a	2.21 ± 0.27^a

The same letter (a, b) denotes no significant difference between the first and second drying-rewetting treatments and between soil and sediment under the second drying-rewetting treatment at 95 % significance level.

4.4.1.2 Release of herbicides into the overlying water under the drying-rewetting treatment

The average concentrations of simazine, atrazine and diuron released into the overlying water from the soil and sediment under the first drying-rewetting and fully wet treatment over the same period are presented in Figure 4.7, with the complete data for the herbicide concentrations released under the drying-rewetting treatment in Appendix 14. Similar to the fully wet treatment, an initial rapid release from the soil and sediment was observed in the first 24 hours, followed by a slow release reaching relatively constant concentrations.

Table 4.9 shows the total herbicide loads released into the overlying water from the soil and sediment under the first drying-rewetting and fully wet treatment over the same time period. Although the soil and sediment were spiked with all three herbicides at the same concentration, the total simazine, atrazine and diuron loads released into the overlying water from the soil were higher than those released from the sediment. However, the difference was only significant for diuron (Two-way ANOVA: $F = 5.11$, $p < 0.05$) (Table 4.9). In addition, the total diuron load in the overlying water was one order of magnitude lower than those of atrazine and simazine.

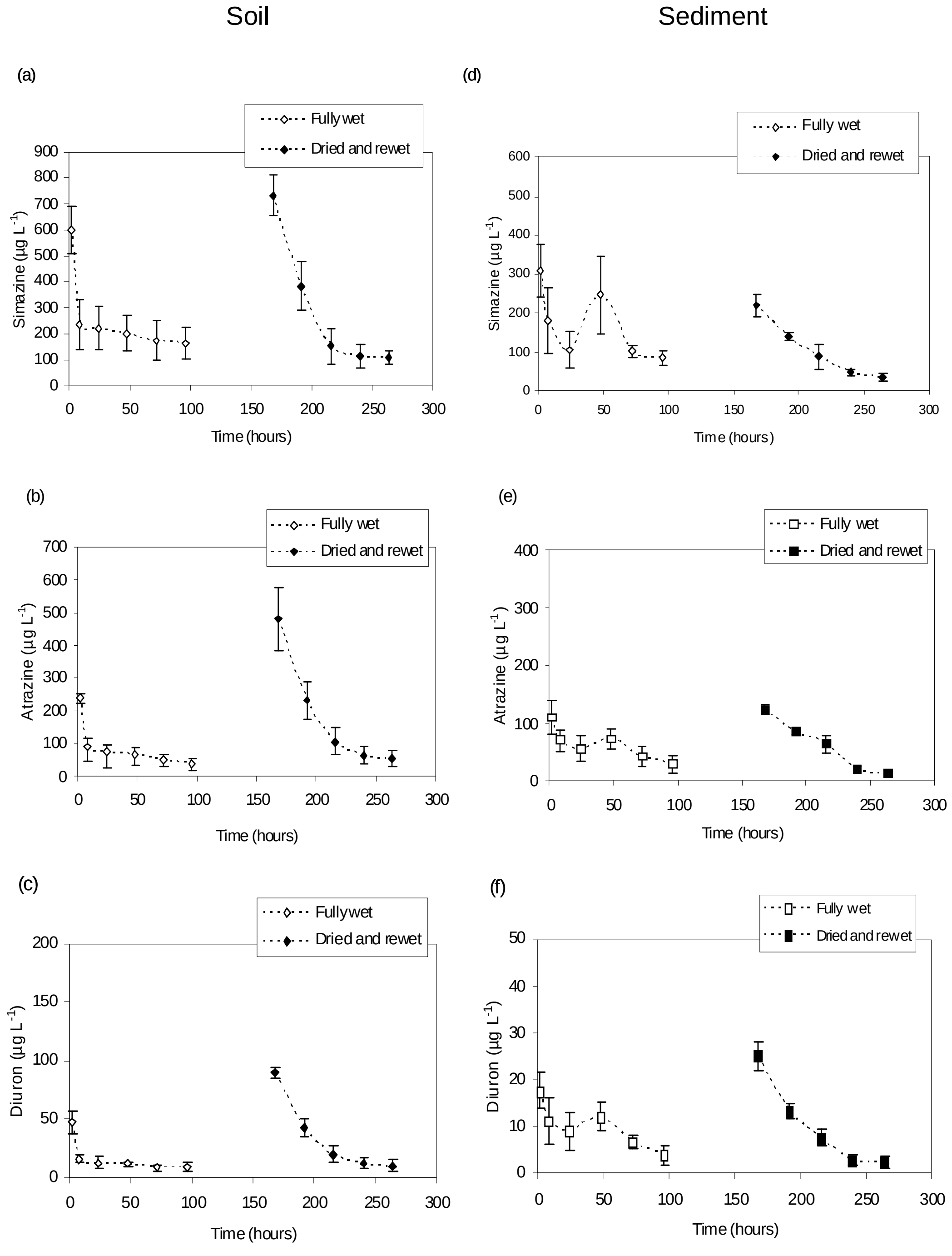

Figure 4.7 Concentrations of (a) simazine, (b) atrazine and (c) diuron released from soil and (d) simazine, (e) atrazine and (f) diuron released from sediment under the drying-rewetting and fully wet treatments (bars = standard deviation (SD), n = 3).

Whilst the total atrazine and diuron loads released into the overlying water from the soil were approximately 29 % and 42 % higher under the drying-rewetting than the fully wet treatment, the simazine load was approximately 28 % lower under the drying rewetting treatment. For the sediment, the total loads of simazine, atrazine and diuron released under the drying-rewetting treatment were approximately 64 %, 44 % and 50 % lower than those released under the fully wet treatment. No significant differences in the herbicide loads between the fully wet and drying-rewetting treatments were observed for either the soil or sediment (Table 4.9).

Table 4.9 Total herbicide loads (µg) released into the overlying water under the fully wet and the first drying-rewetting treatments over the same time period (average ± standard deviation (SD), n = 3)

Herbicides	Soil		Sediment	
	Fully wet	Drying-rewetting	Fully wet	Drying-rewetting
Simazine (µg)	375.4 ± 135.8[a]	270.4 ± 87.9[a]	314.4 ± 52.9[a]	112.6 ± 19.1[a]
Atrazine (µg)	125.1 ± 31.6[a]	162.0 ± 55.8[a]	110.9 ± 22.9[a]	62.1 ± 6.1[a]
Diuron (µg)	21.5 ± 4.8[a]	30.7 ± 9.6[a]	18.1 ± 2.6[b]	9.0 ± 1.1[b]

The same letter (a, b) denotes no significant difference between the drying-rewetting and fully wet treatments and between soil and sediment under the drying-rewetting treatment at 95 % significance level.

Figure 4.8 shows the average concentrations of simazine, atrazine and diuron released into the overlying water from the soil and sediment under the two drying-rewetting treatments with the complete data in Appendix 14. The release patterns under the second drying-rewetting treatment were similar to the first drying-rewetting treatment with an initial rapid release observed, followed by a slow release.

Table 4.10 shows the total simazine, atrazine and diuron loads released into the overlying water from the soil and sediment under the two drying-rewetting treatments. The total simazine, atrazine and diuron loads released into the overlying water from the soil were higher but not significantly different from those released from the sediment (Table 4.10). The total simazine, atrazine and diuron loads released into the overlying water from the soil under the second drying-rewetting treatment as a proportion of the total metal load released under the first drying-rewetting treatment reduced by approximately 50 %, 61 % and 71 % respectively. Significant differences in the total herbicide loads between the first and second drying-rewetting treatments were only observed for atrazine (Two-way

ANOVA: F = 4.82, $p < 0.05$) and diuron (Two-way ANOVA: F = 12.08, $p < 0.05$) (Table 4.10). In the sediment, the total simazine, atrazine and diuron loads released into the overlying water under the second drying-rewetting treatment as a proportion of the total load released under the first drying-rewetting treatment reduced by approximately 4 %, 31 % and 14 %. No significant differences were observed in the total loads between the first and second drying-rewetting treatments for simazine, atrazine and diuron.

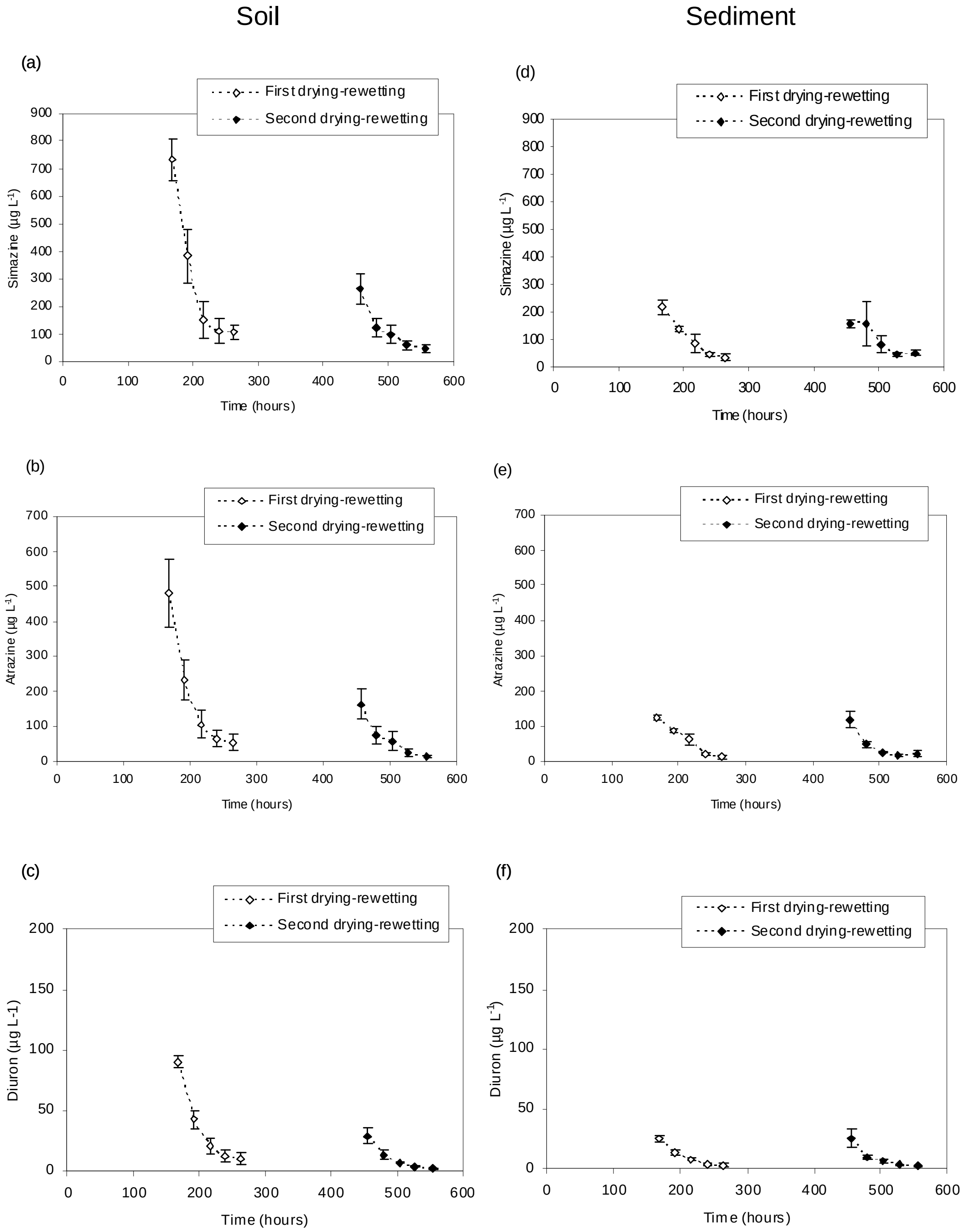

Figure 4.8 Concentrations of (a) simazine, (b) atrazine and (c) diuron released from soil and (d) simazine, (e) atrazine and (f) diuron released from sediment under the two drying-rewetting treatments (bars = standard deviation (SD), n = 3). The delay between the origin and the first drying-rewetting defines the 7 days of drying.

Table 4.10 Total herbicide loads (µg) released into the overlying water under the two drying-rewetting treatments (average ± standard deviation (SD), n = 3)

Herbicides	Soil		Sediment	
	First drying-rewetting cycle	Second drying-rewetting cycle	First drying-rewetting cycle	Second drying-rewetting cycle
Simazine (µg)	270.4 ± 87.9^a	134.7 ± 36.5^a	112.6 ± 19.1^a	107.7 ± 27.0^a
Atrazine (µg)	162.0 ± 55.8^a	63.1 ± 23.1^b	62.1 ± 6.1^b	42.9 ± 2.6^b
Diuron (µg)	30.7 ± 9.6^a	8.8 ± 1.1^b	9.0 ± 1.1^b	7.7 ± 0.9^b

The same letter (a, b) denotes no significant difference between the first and second drying-rewetting treatments and between soil and sediment under the second drying-rewetting treatment at 95 % significance level.

4.4.1.3 Release of DOC into the overlying water under the drying-rewetting treatment

The average DOC concentrations released from the soil and sediment under the fully wet and first drying-rewetting treatment over the same period are illustrated in Figure 4.9 with the complete data for the DOC concentrations released under the drying-rewetting treatment in Appendix 15. Similar to the release pattern under the fully wet treatment, high DOC concentrations were observed under the drying-rewetting treatment within the first 24 hours following wetting which decreased rapidly to relatively constant values.

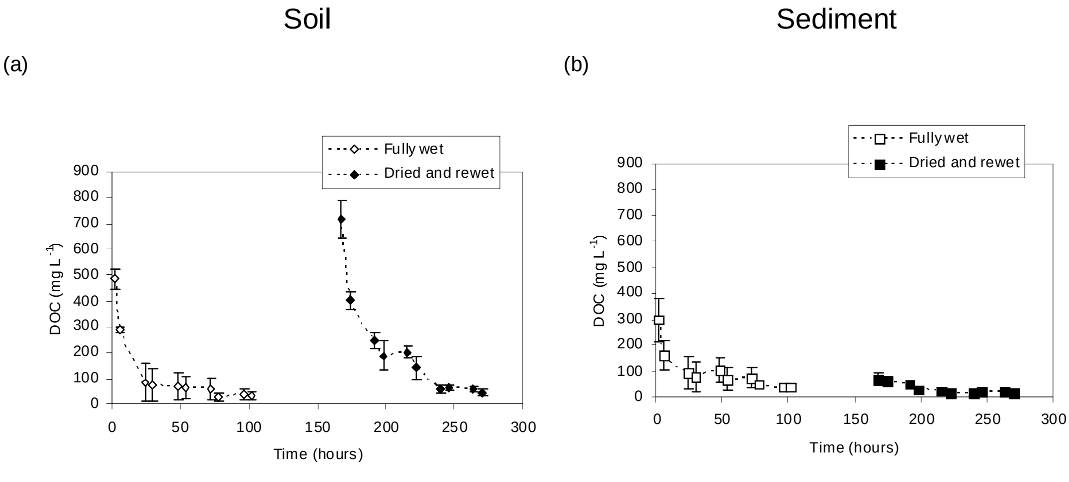

Figure 4.9 Concentrations of (a) DOC released from soil and (b) DOC released from sediment under the drying-rewetting and fully wet treatments (bars = standard deviation (SD), n = 3).

Table 4.11 shows the total DOC loads released into the overlying water from the soil and sediment under the first drying-rewetting and fully wet treatments over the same time period. The total DOC load released from the soil into the overlying water under the drying-rewetting treatment was significantly higher than that released from the sediment (Two-way ANOVA: F = 4.55, $p < 0.05$). The total DOC load released from the soil under the drying-rewetting treatment was approximately twice as high as the load released under the fully wet treatment. Conversely, the total DOC load released from the sediment was three times lower under the drying-rewetting than the fully wet treatment. However, these differences between the total DOC loads released under the drying-rewetting and fully wet treatments for both the soil and sediment were not statistically significant.

Table 4.11 Total DOC loads (mg) released into the overlying water from the soil and sediment under the fully wet and first drying-rewetting treatment (average ± standard deviation (SD), n = 3)

	Soil		Sediment	
	Fully wet	Drying-rewetting	Fully wet	Drying-rewetting
DOC (mg)	250.5 ± 138.8^a	510.7 ± 50.0^a	267.5 ± 130.0^a	88.4 ± 6.3^b

The same letter (a, b) denotes no significant difference between the drying-rewetting and fully wet treatments and between soil and sediment under the drying-rewetting treatment at 95 % significance level.

Figure 4.10 shows the average DOC concentrations released into the overlying water under the two drying-rewetting treatments with the complete data in Appendix 15. The release patterns of DOC under the second drying-rewetting treatment were similar to the first drying-rewetting treatment. Table 4.12 shows the total DOC loads released into the overlying water from the soil and sediment under the two drying-rewetting treatments. The total DOC load released from the soil under the second drying-rewetting treatment were significantly lower than those released under the first drying-rewetting treatment (Two-way ANOVA: F = 33.20, $p < 0.05$). However, no significant difference was observed between the total DOC loads released from the sediment under the two drying-rewetting treatments (Table 4.11). Furthermore, the total DOC load released into the overlying water from the soil under the second drying-rewetting treatment was significantly higher than that released from the sediment (Two-way ANOVA: F = 80.72, $p < 0.05$).

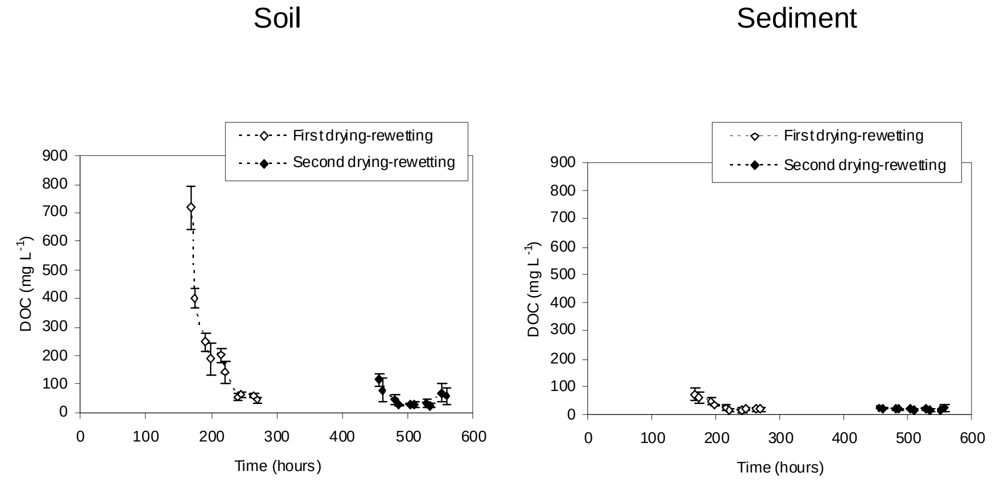

Figure 4.10 Concentrations of (a) DOC released from soil and (b) DOC released from sediment under the two drying-rewetting treatments (bars = standard deviation (SD), n = 3). The delay between the origin and the first drying-rewetting defines the 7 days of drying.

Table 4.12 Total DOC loads (mg) released into the overlying water from the soil and sediment under the first and second drying-rewetting treatment (average ± standard deviation (SD), n = 3)

	Soil		Sediment	
	First drying-rewetting cycle	Second drying-rewetting cycle	First drying rewetting cycle	Second drying-rewetting cycle
DOC (mg)	510.7 ± 50.0^{a}	144.7 ± 24.9^{b}	88.4 ± 6.3^{a}	62.6 ± 10.1^{a}

The same letter (a, b) denotes no significant difference between the drying-rewetting and fully wet treatments and between soil and sediment under the drying-rewetting treatment at 95 % significance level.

4.5 Carbon mineralisation, CO_2 release and microbial biomass

The average headspace CO_2, soil and sediment microbial biomass data measured during the carbon mineralisation experiments are presented below with the full data in Appendix 16. These data test the hypothesis that microbial activity and organic matter mineralisation will be stimulated during the drying-rewetting of the soil and sediment which will lead to the release of metals and herbicides associated with organic matter. The experiments were conducted with fully wet soil and sediment and dried-rewet soil and sediment which were dried for 7 days and then rewet with artificial seawater at 20 ‰

for 1 hour. The CO_2 released into the headspace from the fully wet and dried-rewet soil and sediment were measured for 15 days (i.e. from the beginning of the experiment) and 6 days (i.e. after rewetting the soil/sediment) respectively. The soil and sediment microbial biomass were measured before drying, after drying and six days after rewetting by substrate induced respiration method described in Chapter 3, Section 3.4. The carbon mineralisation rate in the soil and sediment were determined from the CO_2 data as described in Chapter 3, Section 3.4. The carbon mineralisation rates were used as a measure of soil and sediment organic matter mineralisation.

4.5.1. CO_2 released from fully wet soil and sediment

Average cumulative CO_2 released from the fully wet soil and sediment and mineralisation rates are given in Figure 4.11 and 4.12 with the full data in Appendix 16. The cumulative CO_2 released ranged from 8 - 26 µg CO_2 kg^{-1} soil (wet weight) and 11 - 33 µg CO_2 kg^{-1} sediment (wet weight) for the soil and sediment respectively. The increase in the cumulative CO_2 released for the soil and sediment suggest the production of CO_2 as organic matter in the soil and sediment is mineralised. The cumulative CO_2 released from the sediment was higher than that released from the soil. In contrast, the carbon mineralisation rates generally decreased in the soil and sediment (Figure 4.12).

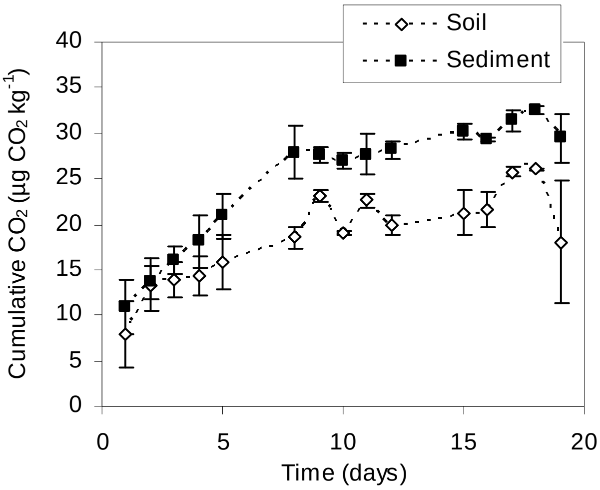

Figure 4.11 Cumulative CO_2 release from the fully wet soil and sediment (bars = standard deviation (SD), n = 3).

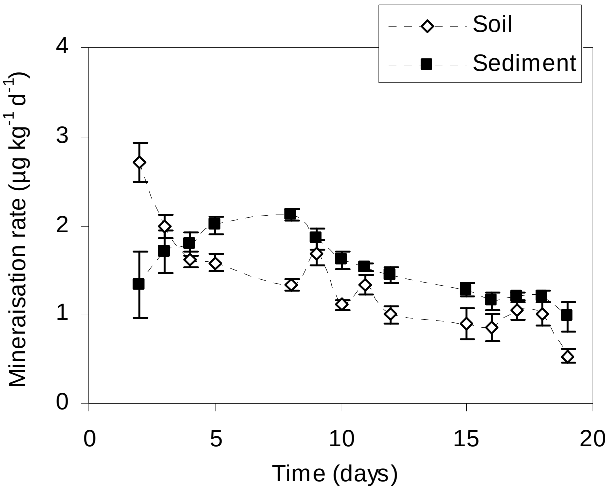

Figure 4.12 Carbon mineralisation rates under fully wet soil and sediment treatment (bars = standard deviation (SD), n = 3).

4.5.2. CO_2 released from dried-rewet soil and sediment

Figures 4.13 and 4.14 show the cumulative CO_2 released from the dried-rewet soil and sediment and the mineralisation rates respectively. An increase was observed in the cumulative CO_2 released from the soil and sediment with ranges from 1613 - 7458 µg CO_2 kg^{-1} soil and 2619 - 4803 µg CO_2 kg^{-1} sediment indicating greater cumulative CO_2 release from the soil. The ranges of CO_2 release for these dried-rewet soil and sediment were two orders of magnitude higher than those released from the fully wet soil and sediment. The mineralisation rate in the soil and sediment decreased and became relatively constant for the remainder of the experiment (Figure 4.14) with the mineralisation rates in the soil higher than those in the sediment. Mineralisation rates in the dried-rewet soil and sediment were two to three orders of magnitude higher than those in the fully wet soil and sediment suggesting that drying and rewetting led to an increase in carbon mineralisation in the soil and sediment.

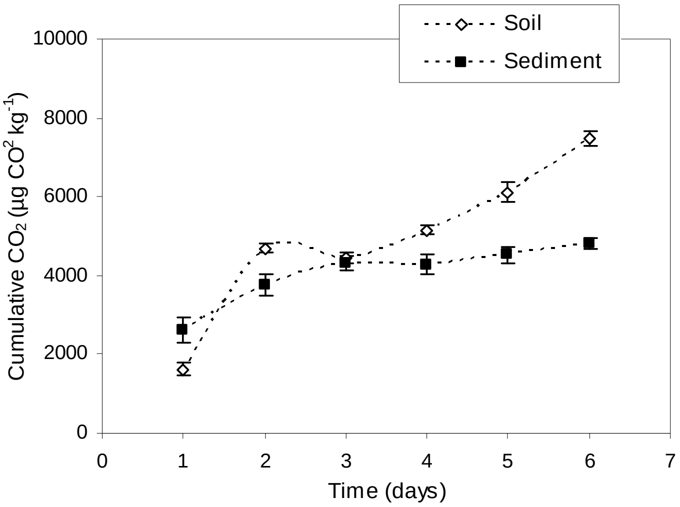

Figure 4.13 Cumulative CO_2 released from the dried-wet soil and sediment (bars = standard deviation (SD), n = 3).

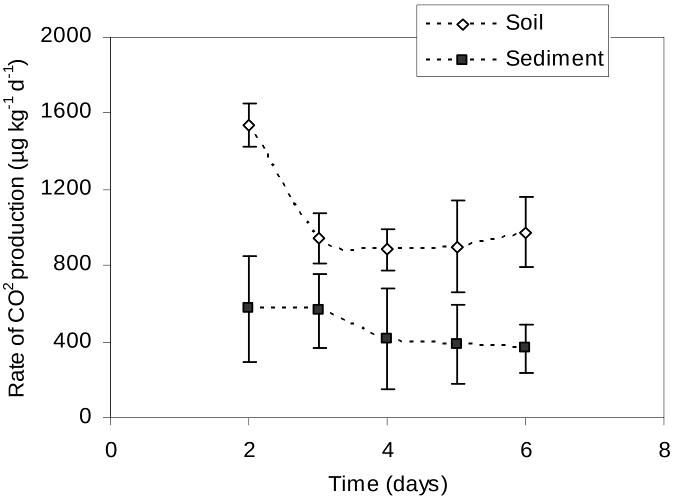

Figure 4.14 Carbon mineralisation rates under dried-rewet soil and sediment treatment (bars = standard deviation (SD), n = 3).

4.5.3. Soil and sediment microbial biomass data

Figure 4.15 presents the soil and sediment microbial biomass data measured by substrate induced respiration method before drying, after drying and 6 days after rewetting. Differences were observed between the sediment and soil microbial biomass before drying, after drying and 6 days after rewetting. The microbial biomass varied during the experiment with the sediment microbial biomass decreasing and the soil microbial biomass increasing. However, before drying, the microbial biomass was higher in the sediment than the soil but after drying, the microbial biomass became lower in the sediment than the soil.

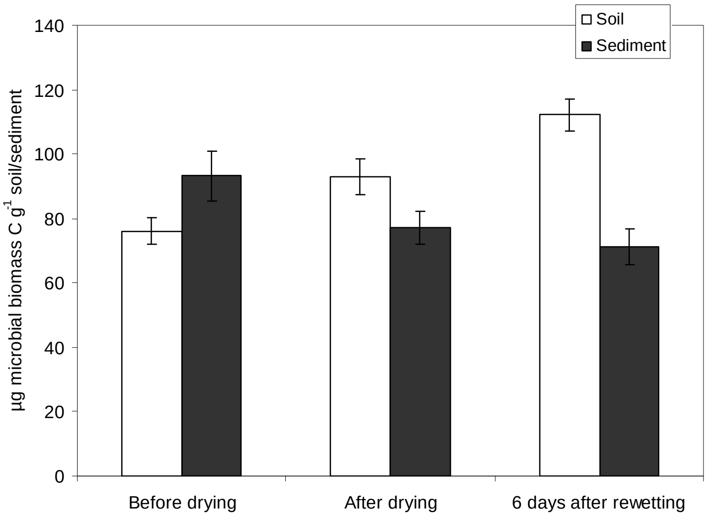

Figure 4.15 Soil and sediment microbial biomass before drying, immediately after drying and 6 days after rewetting (bars = standard deviation (SD), n = 3).

Chapter 5 The release of metals and herbicides from managed realignment soil and sediment

5.1. Introduction

Tidal inundation of soil and sediment by seawater in managed realignment sites is accompanied by several changes in the soil and sediment chemistry. For example, as seawater inundates the soil, the fresh water in the soil pores is replaced by saline solution, and the salinity of the porewater increases (Blackwell et al., 2004; Boorman and Hazelden, 2002). An increase in pH can also occur following the inundation of soil and sediment by seawater (Mitsch and Gosselink, 2000). These changes can affect the binding of contaminants to the soil and sediment leading to contaminant release into the overlying water during tidal inundation. In addition, the periodic tidal inundation and drainage in these environments exposes the soil and sediment to drying-rewetting cycles which may lead to increased organic matter mineralisation, increased DOC release and the potential release of organic matter associated contaminants into the overlying water.

In this thesis, the effect of salinity and drying-rewetting cycles on the release of metals (Cu, Ni and Zn) and herbicides (simazine, atrazine and diuron) from soil and sediment in managed realignment sites was investigated by laboratory simulation experiments. This chapter discusses the results of the laboratory experiments presented in Chapter 4. Total contaminant loads released into the overlying water from the soil and sediment were measured under two different salinities and drying-rewetting cycles which gave an indication of the nature of the likely processes affecting the potential release of metal and herbicide from soil and sediment in managed realignment sites.

5.2. Effect of salinity on the release of metals and herbicides from soil and sediment

Flooding soil and sediment with seawater can lead to an increase in the salinity of the soil and sediment porewater. This increase in salinity can in turn lead to an increase in porewater metal concentrations through the influence of seawater cations (i.e. Na^+, Ca^{2+}, Mg^{2+}, K^+) which compete with the sorbed metals for cation exchange binding sites and, seawater anions (Cl and SO_4^{2-}) which form soluble complexes with metals (Turner and Millward, 2002; Phillips et al., 2004; Riba *et al*., 2003). An increase in salinity can also be accompanied by changes in pH (Turner and Millward, 2002) which can also affect metal sorption to soil and sediment. An increase in pH can lead to an increase in the sorption of metals through less competition from H^+ ions for cation exchange sorption sites; the increased formation of metal binding sites on Fe and Mn oxides; hydrolysis of metals leading to the formation of hydroxyl cations which are more likely to bind to the solid phase; and more negatively charged pH dependent sorption sites (Forstner and Wittmann, 1981; Alloway, 1995; Jackson, 1998; Rate et al., 2000; Standring et al., 2002; Peng et al., 2003). Conversely, a decrease in pH can lead to more positively charged particle surfaces through association with additional H^+ ions (Brady and Weil, 2002; Zwolsman et al., 1993). The concentration of dissolved metals in solution, therefore, increases under low pH conditions.

Metals take part in a number of interactions in soil and sediment. Metals can be incorporated into crystalline silicates (Jenne, 1976). They can also be precipitated with carbonates or sulphides, co-precipitated or sorbed to Fe and Mn oxides and hydroxides, sorbed or incorporated into clay minerals and complexed with organic matter (Eggleton and Thomas, 2004; Simpson et al., 1998; Salomons and Forstner, 1984; Alloway, 1995). Changes in salinity have been observed to affect the latter metal particulate interactions, resulting in metal desorption (Bauske and Goetz, 1993; Millward and Liu, 2003; Gambrel et al., 1991).

Charge distribution, polarity, hydrophobicity, basicity and acidity are some properties of herbicides which control their binding to soil and sediment (Khan, 1978, Gevao et al., 2000). Triazine herbicides such as simazine and atrazine are weakly basic herbicides hence they can undergo ionisation and become positively charged depending on the pH of the system and their respective acid dissociation constants (pKa) (Seol and Lee, 2001; McBride, 1994). Changes in solution pH can change the charge distribution and binding of the triazine herbicides to the soil and sediment and lead to desorption into solution. Seawater cations may also displace charged triazine herbicides binding by cation exchange on soil and sediment particles and lead to higher herbicide concentrations in solution. Phenyl urea herbicides such as diuron are neutral molecules and do not undergo ionisation, hence their sorption and desorption is not affected by pH. However, an increase in salinity can lead to an increase in the sorption of these neutral organic contaminants due to salting out effect (Turner and Millward, 2002; Turner and Rawling, 2001).

Herbicides bind mainly to organic matter and clay particles in soil and sediment, with organic matter being the primary binding component (Chiou, 1989; Gao et al., 1998; Voulvoulis et al., 2002). Clay particles become important for the sorption of triazine herbicides if their molecules are charged (Laird et al., 1994; Spark and Swift, 2002). At pKa < pH, organic bases such as triazines exist as neutral species particularly when the primary sorption domain is organic matter while at pKa > pH, a considerable amount of the herbicides exist as cations and undergo cation exchange (Weber et al., 1969; Seol and Lee, 2001).

The effect of salinity on the release of metals (Zn, Ni and Cu) and herbicides (simazine, atrazine and diuron) was examined under two different salinities; 5 and 20 referred to as low and high salinity treatments respectively. The effect of salinity on the release of the metals from the soil and from the sediment following the inundation with artificial seawater will be considered together in Section 5.2.1, followed by the effect of salinity on the release of the herbicides from the soil and from the sediment in Section 5.2.2.

5.2.1. Effect of salinity on the release of metals from soil and sediment

The log K_d values of Cu, Ni and Zn calculated in the batch sorption experiments ranged from 2.54 to 2.97 L kg $^{-1}$, 2.28 to 2.52 L kg $^{-1}$ and 2.55 to 2.75 L kg $^{-1}$ respectively in both the soil and sediment (Chapter 4, Table 4.2). These log K_d values are within the ranges reported in the literature. Phillips et al (2004) reported log K_d values of 2.02 L kg $^{-1}$ to 4.22 L kg $^{-1}$ for Zn and 3.41 – 4.19 L kg $^{-1}$ for Cu in sediments. The K_d (expressed on a $\log_{10}$ basis) for Ni, Zn and Cu was found to range from 0.48 to 3.86 L kg $^{-1}$, 0.86 to 3.26 L kg $^{-1}$ and 2.31 to 3.36 L kg $^{-1}$ respectively in sandy aquifer material (Christensen et al., 1996; 2000). Usman et al. (2008) reported K_d (expressed on a $\log_{10}$ basis) for Ni, Zn and Cu of 2.2 L kg^{-1}, 2.08 L kg $^{-1}$ and 2.9 L kg^{-1} in soil. In this study, the log K_d values of Cu, Ni and Zn were consistently higher in the sediment than the soil (Chapter 4, Table 4.2) indicating that the metals were binding more strongly to the sediment than the soil and/or there was a greater availability of binding sites in the sediment at both 5 and 20 salinities. The differences between the partition coefficients were significant for Cu (Two-way ANOVA: F = 13.04, $p < 0.05$) and Ni (Two-way ANOVA: F = 30.73, $p < 0.05$) at both salinities and Zn (Two-way ANOVA: F = 15.29, $p < 0.05$) at a salinity of 20. The greater availability of binding sites for the metals in the sediment is due to the higher clay and organic matter content in the sediment compared to the soil (Chapter 4, Table 4.1). In addition, oxic estuarine sediments such as those used in this study often comprise Fe and Mn oxides and carbonates which are important binding sites for metals (Eggleton and Thomas, 2004; Forstner and Wittmann, 1981; Filguieras et al., 2002). Although the Fe and Mn oxides and carbonate content in the soil and sediment were not evaluated in this study, the sediment is likely to have a greater amount of these solid phases than the soil which may also be contributing to the higher partition coefficients in the sediment. Several mechanisms such as complexation, precipitation and cation exchange interactions are likely to have contributed simultaneously to the binding of Cu, Ni and Zn to the soil and sediment solid phases in this study.

At a salinity of 5, log K_d values of the metals were in the order Cu > Zn > Ni in both the soil and sediment (Chapter 4, Table 4.2) with Cu the most strongly bound and Ni the least strongly bound. Cu is known to be strongly associated with organic matter and often shows the greatest affinity for Fe oxides compared to Ni and Zn (Millward and Liu, 2003; Forstner and Wittmann, 1981; Stephens et al., 2001; Alloway, 1995; McBride, 1994). The trend in the log K_d values corresponds with the reported binding strength of Cu, Ni and Zn to organic matter which is in the order Cu > Zn > Ni (Filgueiras et al., 2002; Forstner and Wittmann, 1981; Alloway, 1995). This suggests that the relative differences in the log K_d values among the metals may in part be due to the differences in the strength of binding of Cu, Ni and Zn to organic matter with Cu being the most strongly bound, followed by Zn and then Ni. In addition, Cu, Ni and Zn can form soluble chlorocomplexes in seawater (Turner, 1998**;** Phillips et al., 2004**;** Riba et al., 2003) which keeps the metals in solution and reduces sorption. The complexation of Cu, Ni and Zn with Cl is generally in the preferential order Zn > Ni > Cu (Forstner and Wittmann, 1981) indicating that Zn has the greatest tendency to form soluble chlorocomplexes and hence the least likely to bind to the soil and sediment. However, in this study, Ni was the least bound to the soil and sediment suggesting that the conditions at the salinity of 5 was more favourable for the formation of soluble Ni chlorocomplexes compared to Zn.

The sorption of Cu, Ni and Zn to soil and sediment has been reported to decrease with increasing salinity due to competitive adsorption by seawater cations (i.e. Na^+, Mg^{2+}, K^+ and Ca^{2+}) and the formation of stable soluble complexes with seawater anions (i.e. Cl and SO_4^{2-}) (Millward and Turner, 1995; Phillips et al. 2004; Comber et al., 1996). Accordingly, in this study, lower log K_d values were observed for the metals at the salinity of 20 compared to those at the salinity of 5 except for Zn in the sediment (Chapter 4, Table 4.2). The difference between the log K_d values at the salinities of 5 and 20 were statistically significant for Cu (Two-way ANOVA: $F = 14.76$, $p < 0.05$). At the salinity of 20, the log K_d values were in the order Cu/Zn > Ni suggesting that at the higher salinity, Cu formed more soluble chlorocomplexes compared to Zn which lowered Cu sorption to the soil and sediment in this study. Bourg (1987) also found that an increase in chlorinity suppressed Cu sorption more than that of Zn.

Metal release from the soil and sediment into the overlying water in the column experiments is controlled by a combination of processes within the soil and sediment, and at the soil/sediment-water interface. Following the introduction of artificial seawater, an initial rapid release phase of Cu, Ni and Zn was observed followed by a slow release phase from the soil and sediment for the remainder of the experiments (Chapter 4, Figure 4.1). The initial rapid release is attributed to the release of readily available metals present in the porewater and weakly sorbed to the soil and sediment following the exchange and mixing of the artificial seawater with the porewater. Thereafter, desorption and diffusion is likely to have transported the metals from the interior of the soil and sediment column towards the surface from where they are released into the overlying water during the slow release phase. Several kinetic and transport studies with soil and sediment have observed an initial rapid release, followed by a slow and continued release for extended periods of time (Millward and Liu, 2003, Mustafa et al; 2004, Liu et al., 1998). The latter phase is due to the slow release of metals which have become more strongly bound over time due to migration from weak to strong binding sites on the particle surface and diffusion into Fe oxides and micropores within particles (Millward and Liu, 2003; Selim and Amacher, 2001; Wang and Xing, 2002; Mustafa et al., 2004; Almas et al., 2000). In this study, portions of the metals may have become strongly bound to the soil and sediment during the 21 days equilibration period of the spiked soil and sediment due to transfer to strong binding sites and diffusion into micropores and Fe oxides, limiting metal desorption during the slow release phase.

Several studies have observed that seawater cations and anions are effective in mobilizing metals sorbed to soil and sediment through competition and complexation reactions respectively (Calmano et al., 1992; Paalman et al., 1994; Millward and Liu, 2003). This suggests that in these column experiments, competition between seawater cations and the sorbed metals for cation exchange binding sites is likely to have resulted in the displacement of the metal ions into the overlying water. The formation of soluble metal complexes with the seawater anions is also likely to have led to metal desorption from the soil and sediment into the overlying water. The total metal loads released into the overlying water from the soil and sediment under the low salinity treatment was in the order Ni > Zn > Cu with the Cu load two orders of magnitude lower than those of Zn and Ni despite the soil and sediment having been spiked at the same concentration (Chapter 4, Table 4.4). This relative order among the metals had an inverse relationship with the log K_d values of the metals at the salinity of 5 as depicted in Figure 5.1a suggesting that the total metal loads released into the overlying water were dependent on the log K_d values. Therefore, the strength of binding of Cu, Ni and Zn to the soil and sediment was also important for metal release from the soil and sediment at low salinity. Cu, being the most strongly bound, was the most resistant to desorption and therefore had the lowest load released into the overlying water compared to Zn and Ni. Millward and Liu (2003) also observed a similar order for the desorption of Cu, Ni and Zn from sediment.

At high salinity, the total loads of Zn and Ni released into the overlying water from the soil and sediment were higher than those released at low salinity (Chapter 4, Table 4.4). The differences were statistically significant for the total Ni load released from the sediment (Two-way ANOVA: $F = 5.51$, $p < 0.05$). The increase in pH (from pH 7.25 to pH 8.1) observed during the experiments is unlikely to have increased metal desorption and release into the overlying water. Metals become more strongly associated with soil and sediment as pH increases (Alloway, 1995; Jackson, 1998; Standring et al., 2002; Peng et al., 2003). Therefore, lower total metal loads would be expected to be released into the overlying water with an increase in pH. The increase in the competitive and complexation effects of seawater cations and anions under the high salinity treatment is likely to have led to greater desorption of Zn and Ni bound to cation exchange binding sites and hence higher total loads in the overlying water. In addition, the total Ni loads released from the soil and sediment into the overlying water was higher than those of Zn (Chapter 4, Table 4.4). The inverse relationship between the log K_d values and total loads for Ni and Zn at high salinity (Figure 5.1b) suggests that the relative differences between the total Ni and Zn loads is partly due to their binding strength to the soil and sediment.

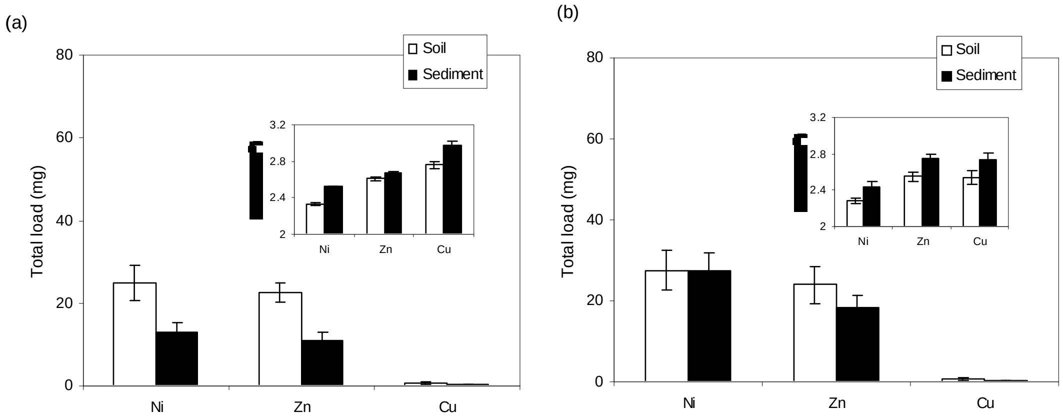

Figure 5.1 Total loads of Ni, Zn and Cu released from the soil and sediment under (a) low and (b) high salinity treatments (bars = standard deviation (SD), n = 3). The inset graphs are the log K_d of Ni, Zn and Cu for the soil and sediment at the respective salinities.

At the salinity of 20, Zn and Cu had similar log K_d values in the batch sorption experiments, yet the total Cu loads released into the overlying water from the soil and sediment during the column experiments were much lower (Figure 5.1b). The different behaviour of Cu compared to Zn suggests that Cu was more strongly bound to the soil and sediment during the 21 days equilibration period of the spiked soil and sediment used in the column experiments relative to the 24 hours equilibration in the batch sorption experiments. This is probably because Cu tends to bind more strongly to soil and sediment than Zn over time. Several studies have indicated that metals are more strongly bound to particles over time due to their transfer from surface to interior binding sites and diffusion into Fe oxides and micropores within particles with Cu having a greater ease of transfer than Zn (Riewerts et al., 2000; Griscom et al., 2000; Almas et al., 2000; Burton et al., 2006; Lu et al., 2005). In order to evaluate if Cu was binding more strongly than Ni and Zn to the soil and sediment used in the column microcosm experiments, the theoretical initial concentrations of Cu, Ni and Zn in the first sample collected from the column microcosm experiments were calculated using an instantaneous equilibrium approach (Heppell et al., 2000) and compared to the measured initial concentration from the column experiments.

The equation used is represented by:

$$C_{aq} = T/ \{(K_d \times M) + V\} \tag{5.1}$$

where T is the total mass of metal in metal spike solution (mg), M is the mass of the soil or sediment in the column (0.8 kg), C_{aq} is the dissolved metal concentration in the first sample (mg L^{-1}) and V is the volume of overlying water plus the porewater in the soil or sediment (0.59 L and 0.63 L for soil and sediment respectively). The K_d values from the batch sorption experiments were used in the calculation. The theoretical initial metal concentrations in the overlying water under the low and high salinity treatments are shown in Table 5.1. The measured initial Cu concentrations were lower than the theoretical initial Cu concentrations while the measured initial Ni and Zn concentrations were higher than the theoretical initial Ni and Zn concentrations. This suggests that Ni and Zn were not as strongly bound as Cu over the 21 days equilibration period of the spiked soil and sediment used in the column experiment hence the different behaviour of Cu. In addition, Cu may be approaching saturation and precipitating out of solution given that the Cu concentration released into the overlying water during the column experiments exceeded the solubility of Cu in seawater (i.e. 0.1 mg l^{-1}). This may also be contributing to the difference in the behaviour of Cu compared to Ni and Zn.

Table 5.1 Theoretical initial metal concentrations (assuming instantaneous equilibrium) and measured initial metal concentrations in the overlying water

Metals (mg L^{-1})	Soil				Sediment			
	Low salinity		High salinity		Low salinity		High salinity	
	Measured	Theoretical	Measured	Theoretical	Measured	Theoretical	Measured	Theoretical
Zn	12.6	2.3	31.6	2.5	4.9	2.0	6.6	1.7
Ni	18.8	4.2	37.1	4.6	6.8	2.8	13.6	3.2
Cu	0.4	1.7	0.4	2.6	0.3	1.0	0.1	1.7

The Cu, Ni and Zn loads released into the overlying water from the sediment were lower than those released from the soil (Chapter 4, Table 4.4). These differences are likely due to the greater availability of binding sites in the sediment than the soil. The sediment had a higher organic matter and clay content than the soil (Chapter 4, Table 4.1). Other metal binding sites such as Fe and Mn oxides and carbonates are also likely to be higher in the sediment than the soil. Therefore, the sediment has a greater tendency to sorb and retain the metals more strongly resulting in lower metal loads released into the overlying water. This is reflected in the higher Cu, Ni and Zn partition coefficients in the sediment than the soil (Chapter 4, Table 4.2). The differences in the total loads released from the soil and sediment were statistically significant for Ni (Two-way ANOVA: $F = 3.42$, $p < 0.05$) and Zn (Two-way ANOVA: $F = 7.51$, $p < 0.05$) under low salinity and for Cu (Two-way ANOVA: $F = 17.37$, $p < 0.05$) under both salinities.

5.2.2. Effect of salinity on the release of herbicides from the soil and sediment

At pKa < pH, organic bases such as triazines (i.e. simazine and atrazine) exist as neutral species particularly when the primary sorption domain is organic matter while at pKa > pH, a considerable amount of the herbicides exist as cations and undergo cation exchange (Weber et al., 1969; Seol and Lee, 2001). In these experiments, the simazine and atrazine molecules sorbed to the soil and sediment are likely to be primarily uncharged because the soil pH (pH 7.1) and sediment pH (pH 7.0) were much larger than the reported pKa values of simazine (pKa 1.65) (Pacakova et al., 1996) and atrazine (pKa 1.71) (Moreau-Kervevan and Mouvet, 1998). Diuron exists only as a neutral molecule and hence is not influenced by pH.

The log K_d values of simazine, atrazine and diuron ranged from 3.63 to 3.76 L kg $^{-1}$, 3.87 to 3.94 L kg^{-1} and 4.22 to 4.39 L kg $^{-1}$ respectively in both the soil and sediment (Chapter 4, Table 4.3). Except for simazine, the log K_d values of the herbicides for the sediment were higher than those for the soil at both 5 and 20 salinities (Chapter 4, Table 4.3) suggesting that the herbicides were more strongly associated with the sediment than the soil. To determine if the differences were due to the influence of the herbicide sorption to organic matter or the clay particles, the organic carbon normalised partition coefficient (K_{oc}) (i.e. the soil and sediment partition coefficient normalised to the organic carbon fraction) of the soil and sediment was calculated as:

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{5.2}$$

where f_{oc} is the organic carbon fraction. The equation assumes that all the herbicide sorption is due to the organic carbon in the soil and sediment and it is commonly used for describing the extent of herbicide sorption to soil and sediment (Leake and Gatweiler, 1995; Heppell et al., 2009). Since organic matter is made up of approximately 50 % to 58 % organic carbon (Weber et al., 2000; vanLoon and Duffy, 2000), the organic carbon fraction in this study was assumed to be 54 % of the organic matter content (i.e. average of 50 % and 58 % organic carbon). Weber et al. (2000) also assumed that organic matter comprised 54 % organic carbon. The K_{oc} values (expressed on a $\log_{10}$ basis) of simazine, atrazine and diuron ranged from 3.04 to 3.30 L kg $^{-1}$, 3.29 to 3.48 L kg $^{-1}$ and 3.54 to 4.02 L kg $^{-1}$ respectively. These log K_{oc} values are within the range reported in the literature. Gawlik et al. (1998) reported K_{oc} values (expressed on a $\log_{10}$ basis) for simazine of 3.07 L kg $^{-1}$ in soil. Moreau and Mouvet (1997) reported a K_{oc} value (expressed on a $\log_{10}$ basis) of 2.67 L kg $^{-1}$ for atrazine in soil. The log K_{oc} value for diuron was found to range from 2.28 to 5.20 L kg $^{-1}$ in sediment (Comber et al., 2002). Figure 5.2 illustrates that the K_{oc} values of simazine, atrazine and diuron for the sediment were comparable to those for the soil suggesting that organic matter was responsible for the differences in binding between the soil and sediment and organic matter was the controlling factor by which simazine, atrazine and diuron were bound to the soil and sediment. Since the simazine and atrazine molecules were primarily uncharged within the soil and sediment pH range used in this study, the herbicides are likely to be binding to organic matter either by hydrogen bonding, van der Waal forces, dipole-dipole interaction, hydrophobic partitioning or a combination of these mechanisms. The precise nature of the binding mechanisms of these herbicides to the soil and sediment could not be determined from the data collected.

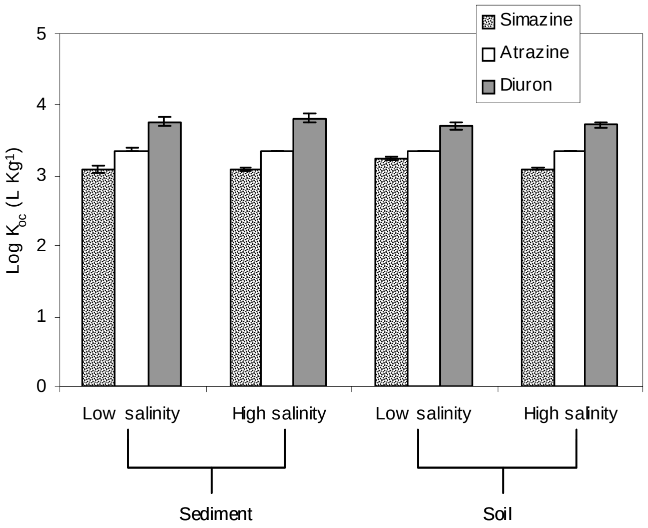

Figure 5.2 Comparison of organic carbon partition coefficients (K_{oc}) for simazine, atrazine and diuron in the soil and sediment (bars = standard deviation (SD), n = 6).

At the salinity of 5, differences were observed among the log K_d of the individual herbicides with diuron having the highest log K_d, followed by atrazine and then simazine in both the soil and sediment (Chapter 4, Table 4.3). These differences indicate that diuron was most strongly sorbed to the soil and sediment while simazine was the least sorbed of the three herbicides. The strength of atrazine sorption was intermediate between that of diuron and simazine. The differences in the hydrophobicity (i.e. n-octanol-water partition coefficient (log K_{ow})) of the herbicides may account for these differences in the binding strength observed among the herbicides. The n-octanol-water partition coefficient reflects the affinity of an organic compound to bind to natural organic matter. The higher the log K_{ow} of an organic compound, the more strongly bound the compound is to organic matter (Hassett and Banwart, 1989; Chiou and Kile, 1994). The experimentally derived log K_{ow} reported for diuron (2.85) was highest, followed by that of atrazine (2.68) and then simazine (2.17) (Lewis and Gardiner, 1996; HSE, 1993; Margoum et al., 2001) indicating that diuron was more hydrophobic compared to atrazine and simazine. These data support the observation in this present study with diuron being most strongly associated with the soil and sediment organic matter, followed by atrazine and then simazine.

Solution ionic strength and salt concentration can affect the binding of charged organic compounds to clay particles (Schwarzenbach, Gschwend and Imboden, 2003). In this study, the log K_d at 5 and 20 salinities were comparable with no significant differences observed except for simazine in the soil (Chapter 4, Table 4.3). Given that the increase in salinity had no effect on the sorption of the herbicides further implies that the herbicides were primarily uncharged and hence, were not binding predominantly by ion exchange interactions with the negative surface charges on the clay particles. No significant salting out effect was observed for any of the herbicides as their log K_d values at the salinity of 20 were not significantly higher than those at the salinity of 5 (Chapter 4, Table 4.3). At the salinity of 20, diuron had the highest log K_d, followed by atrazine and then simazine (Chapter 4, Table 4.3). This suggests that at the salinity of 20, the relative differences among the log K_d values of the herbicides is likely due to the binding strength of the herbicides to organic matter given that the log K_d values and the reported log K_{ow} of the herbicides were in the same order (i.e. diuron > atrazine > simazine). Several studies have indicated that the sorption of weakly polar organic compounds such as the studied herbicides are unaffected by changes in solution ionic strength and salt concentrations (Schwarzenbach, Gschwend and Imboden, 2003; Voulvoulis et al., 2002). The reason for the anomalous behaviour of simazine in the soil remains unclear.

The temporal release patterns of simazine, atrazine and diuron from the soil and sediment into the overlying water in the column experiments showed an initial rapid release phase with the influx of artificial seawater, followed by a slow release phase for the remainder of the experiment (Chapter 4, Figure 4.2). The initial rapid release phase is likely due to the exchange and mixing of the porewater and the artificial seawater leading to the release of readily available herbicides present in the porewater and weakly sorbed to the soil and sediment. Thereafter, desorption and diffusion is likely to have transported the herbicides from the interior of the soil and sediment column towards the surface from where they are released into the overlying water during the latter slow release phase. Several studies on the uptake and release of organic contaminants from soil and sediment have also observed that the release of organic contaminants is biphasic with an initial rapid release phase and a slow release phase (McCall and Agin, 1985; Kan et al., 1994; Carroll et al., 1994; Lee et al., 2000). A readily available labile fraction is released during the initial rapid phase (Carroll et al., 1994; Lee et al., 2000). The latter phase has been attributed to the slow release of the contaminants due to diffusion into pores within particles (intra-particle diffusion or sorption retarded particle diffusion) (Ball and Roberts, 1991; Wu and Gschwend, 1986) and diffusion into the organic matter matrix (intra-sorbent diffusion or retarded organic matter diffusion) (Brusseau and Rao, 1989; Pignatello and Xing, 1996; Brusseau et al., 1991). In these experiments, portions of simazine, atrazine and diuron may have diffused into the organic matter matrix and the pores in the soil and sediment particles during the 21 days equilibration period of the spiked soil and sediment which limited herbicide desorption during the slow release phase.

The total herbicide loads released into the overlying water from the soil and sediment under the low salinity treatment were in the order simazine > atrazine > diuron. The total atrazine and diuron loads were one and two orders of magnitude lower than that of simazine despite the soil and sediment having been spiked at the same concentration (Chapter 4, Table 4.5). The order of the partition coefficients (log K_d) of simazine, atrazine and diuron contrasts with the order of the total load of the individual herbicides released into the overlying water as shown in Figure 5.3a. This suggests that the relative difference among the total herbicide loads is due to the strength of binding of the individual herbicides to the soil and sediment organic matter. Diuron with the highest log K_d values was most strongly sorbed to the soil and sediment, hence least likely to be desorbed, followed by atrazine and then simazine. Consistent with these differences in the binding strength of the herbicides, diuron had the lowest total load while simazine had the highest total load and the total atrazine load was intermediate between that of simazine and diuron.

The total simazine, atrazine and diuron loads released into the overlying water from the soil and sediment at high salinity were not significantly higher than those released into the overlying water at low salinity (Chapter 4, Table 4.5) suggesting that the increase in salinity did not significantly increase the release of any of the herbicides from the soil and sediment. This is probably because the herbicide molecules remained predominantly uncharged at both salinities as indicated by the observed pH range (pH 7.3 to pH 8.1) under the low and high salinity treatments during the experiments which were considerably higher than the pKa values of the herbicides (pKa 1.65 for simazine (Pacakova et al., 1996) and pKa 1.71 for atrazine (Moreau-Kervevan and Mouvet, 1998)). The increase in salinity, therefore, did not significantly increase herbicide release into the overlying water under these experimental conditions. Similar to the low salinity treatment, an inverse relationship was observed between the simazine, atrazine and diuron log K_d values and the total herbicide loads released from the soil and sediment. These findings suggest that the strength of binding of the herbicides to organic matter is likely to control the release of these herbicides at high salinity.

Higher total simazine, atrazine and diuron loads were released into the overlying water from the soil than the sediment during the column experiments (Chapter 4, Table 4.5) suggesting that the herbicides are more easily desorbed from the soil than the sediment. This is likely due to the higher organic matter content in the sediment than the soil which led to stronger binding of the herbicides to the sediment with a lower tendency for desorption (Chapter 4, Table 4.1) hence, the lower herbicide loads released into the overlying water.

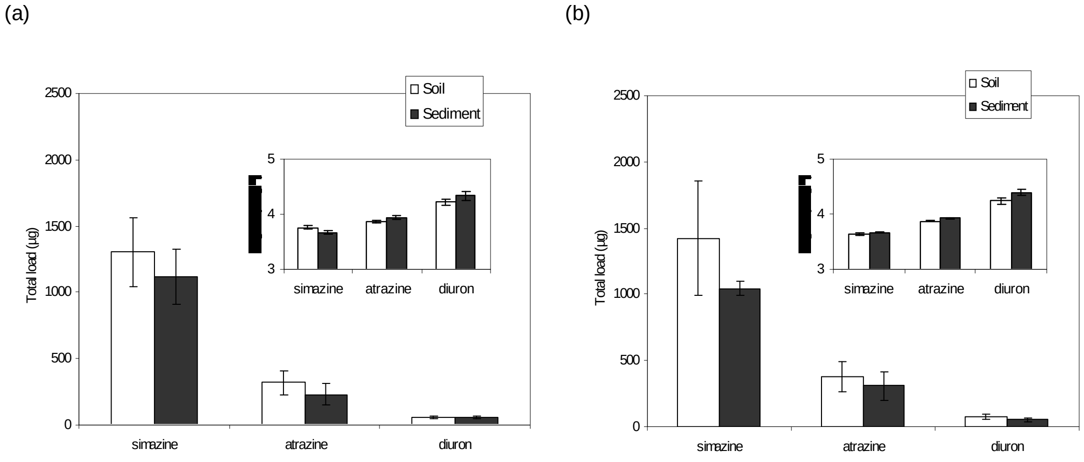

Figure 5.3 Total loads of simazine, atrazine and diuron released from the soil and sediment under (a) low and (b) high salinity treatments (bars = standard deviation (SD), N = 3). The inset graphs are the log K_d of simazine, atrazine and diuron for the soil and sediment at the respective salinities.

5.3. Effect of drying and rewetting on the release of metals and herbicides from soil and sediment

Several studies have examined the effect of drying and rewetting on microbial activity, CO_2 release and organic matter mineralisation in soils (Degens and Sparkling, 1995; Van Gestel et al., 1993; Kieft et al., 1987, Fierer and Schimel, 2003; Bottner, 1985; Haney et al., 2004, Franzluebbers et al., 1990; Miller et al., 2005; Pulleman and Tietema, 1999). These studies have observed that drying and rewetting of soil can lead to the disruption of aggregates which exposes organic matter trapped within the soil. The exposure of the organic matter stimulates microbial activity which leads to enhanced organic matter mineralisation and CO_2 release (Degens and Sparkling, 1995; Van Gestel et al., 1993; Fierer and Schimel, 2003). An increase in organic matter mineralisation in soil can also result in an increase in the release of DOC (Fierer and Schimel, 2003; Miller et al., 2005; Reemtsma et al., 2000). Unlike the soil, studies on the effect of drying and rewetting on microbial activity, CO_2 release and organic matter mineralisation in sediment are limited and have focussed on changes in microbial metabolism and nutrient cycling (Amalfitano et al., 2008; Baldwin and Mitchell, 2000). The mineralisation of organic matter due to drying and rewetting has potential implications for the release of metals and herbicides from the soil and sediment. Cu, Ni and Zn can bind to organic matter with Cu having the highest binding affinity for organic matter among these metals (Forstner and Wittmann, 1981; McBride, 1994). Organic contaminants such as simazine, atrazine and diuron bind to organic matter (Gevao et al, 2000; Pignatello and Xing, 1996). Therefore, an increase in organic matter mineralisation due to drying and rewetting can result in the release of the organic matter associated metals and herbicides.

In these experiments, the soil and sediment were inundated with artificial seawater at a salinity of 20 and subjected to two drying-rewetting treatments in order to test the hypothesis that organic matter mineralisation will be increased during drying and rewetting of the soil and sediment leading to the release of organic matter associated metals and herbicides into the overlying water. In addition to the concentration of the metals, herbicides and DOC released into the overlying water, CO_2 release from the fully wet and dried-rewet soil and sediment were measured and the carbon mineralisation rates were determined to reflect organic matter mineralisation. The changes in soil and sediment microbial biomass before drying, after drying and after rewetting were also measured. The changes in CO_2 release, carbon mineralisation rates and microbial biomass will first be discussed, followed by the contaminant release from the soil and sediment into the overlying water after drying and rewetting.

5.3.1 CO_2 release, carbon mineralisation rate and microbial biomass of soil and sediment

The cumulative CO_2 release and the carbon mineralisation rates were higher in the fully wet sediment compared to the fully wet soil (Chapter 4, Figure 4.11 and 4.12). The microbial biomass was also higher in the sediment compared to the soil before drying (Chapter 4, Figure 4.15). Unlike soil where the organic matter is derived mainly from the decomposition of plant debris and roots (Hedges and Kile, 1995), the major input of organic matter in estuarine sediment is rapidly sinking particles of terrestrial and marine origin which have undergone extensive mineralisation of the labile organic matter fraction in the water column before accumulating in the sediment (Cotano and Villate, 2006; Hedges and Kiel, 1995). Therefore, organic matter in these sediments comprises highly degraded and refractory organic material (Baldock et al., 2004; Hedges and Oades, 1997; Gallizia et al., 2004). Although the proportion of the labile and refractory organic matter pools in the soil and sediment used in this study were not evaluated, the sediment organic matter is likely to be more refractory and hence less mineralisable than the soil organic matter. Hence, the higher carbon mineralisation rates and CO_2 release from the sediment compared to the soil were probably due the higher sediment microbial biomass which in turn led to higher microbial activity and mineralisation in the sediment compared to the soil.

The cumulative CO_2 release and the carbon mineralisation rates in the soil and sediment subjected to the dry-rewet treatment were two to three orders of magnitude higher than those observed in the fully wet soil and sediment (Chapter 4, Section 4.5.1 and 4.5.2). This suggests that the drying-rewetting treatment of the soil and sediment enhanced carbon mineralisation and the release of CO_2. The higher CO_2 release may be due to the mineralisation of carbon exposed to microbial activity by drying and rewetting. Dead microbes in the soil due to drying can serve as a carbon source for mineralisation by the surviving microbes following rewetting and lead to an increase in CO_2 release (Bottner, 1985; Haney et al., 2004). In this study, no reduction in the soil microbial biomass pool was observed after drying the soil (Chapter 4, Figure 4.15) suggesting that the soil microbes survived the drying period. Hence, it is unlikely that dead microbial biomass was the organic carbon source responsible for the higher mineralisation and CO_2 release from the soil in these experiments. This is possibly because the microbes in the soil were resistant to the imposed drying temperature of 25 ^{0}C. Since the organic carbon source cannot be explained by dead microbial biomass during drying, the other possible carbon source is the soil organic matter. Hence, the higher mineralisation and CO_2 release from the soil is likely due to increased microbial activity on the soil organic matter previously protected in aggregates but rendered more available to the heat resistant microbes as a result of drying and rewetting. In addition, the increase in the soil microbial biomass after drying and rewetting (Chapter 4, Figure 4.15), which indicates microbial population growth, may have also contributed to the higher mineralisation of organic matter and CO_2 release from the soil. In the natural soil environment, the soil microbial population is exposed to external stresses such as temperature changes and drying-rewetting cycles, hence they were rapidly adaptable to the experimental conditions which probably resulted in their growth. In the sediment, a reduction in the microbial biomass was observed after drying (Chapter 4, Figure 4.15) indicating the death of part of the microbial population during the drying period, probably because the microbes were less resistant to drying since they are adapted to living in more stable environmental conditions under seawater. However, the surviving microbes effectively mineralised the available carbon source, which resulted in the increased CO_2 release from the sediment. The mineralised carbon source is likely to have been the dead microbial cells because the total carbon from the dead microbes after drying was 16 µg C g^{-1} sediment and the total carbon that was released as CO_2 over the course of the experiment was 1.31 µg C g^{-1} sediment indicating that the CO_2 released may have resulted mainly from the mineralisation of the dead microbes. It is also possible that the mineralisation of sediment organic matter exposed to microbial activity due to drying and rewetting led to the higher CO_2 release. However, this is unlikely because recently accumulated labile organic material are more readily mineralised during drying and rewetting (Degens and Sparkling, 1995; Marumoto et al., 1977) and the labile fraction of sediment organic matter are extensively mineralised in the water column resulting in highly degraded and refractory organic matter in sediments (Baldock et al., 2004; Hedges and Kile, 1995; Cotano and Villate, 2006; Hedges and Oades, 1997; Gallizia et al., 2004; Keil et al., 1994) which tends to be less mineralisable. Therefore, the dead microbes are likely to have been the carbon source that was mineralised in the sediment which led to the higher mineralisation rates and CO_2 release from the sediment.

5.3.2. Effect of drying and rewetting on the release of metals and herbicides from soil and sediment

Comparisons were made between the total Cu, Ni and Zn loads released into the overlying water under the drying-rewetting treatment and those released under the high salinity treatment described in Section 5.2.1 (referred to in this section as fully wet treatment). Differences between the total contaminant loads released under these two treatments were attributed to the effect of drying and rewetting on metal and herbicide release. The release pattern of the metals and herbicides from the soil and sediment were described in Section 5.3.2.1, the effect of drying and rewetting on the release of Cu, Ni and Zn from the soil was discussed in Section 5.3.2.2 and Sections 5.3.2.3 goes on to discuss the effect of drying and rewetting on metal release from the sediment. The effect of a second drying-rewetting treatment was also discussed relative to the first drying-rewetting treatment in the respective sections. The effect of drying and rewetting on herbicide release from the soil and sediment were discussed in a similar manner as the metals in Sections 5.3.2.4 and 5.3.2.5.

5.3.2.1. Release patterns of the metals and herbicides from the soil and sediment under the drying-rewetting treatment

Under the drying-rewetting treatment, there was an initial rapid release of the metals and herbicides from the soil and sediment with the influx of artificial seawater, followed by a slow release into the overlying water (Chapter 4, Figure 4.5 and 4.7). These release patterns were similar to those observed under the fully wet treatment. The initial rapid release was likely due to the exchange and mixing of the soil/sediment porewater and the artificial seawater which led to the release of the readily available metals and herbicides present in the porewater and weakly sorbed to the soil and sediment. Afterwards, desorption and diffusion is likely to have transported the metals and herbicides from the interior of the soil and sediment column towards the surface for release into the overlying water. Several studies have described metals and herbicides release as a two phase process with an initial rapid release phase, followed by a slow release phase (Mustafa et al., 2004; Millward and Liu, 2003; Kan et al., 1994; Carroll et al., 1994) which have been attributed to various mechanisms described in Section 5.2.1 and 5.2.2 for metals and herbicides respectively. In this study, portions of the metals and herbicides may have become strongly bound to the soil and sediment during the 21-days equilibration period of the spiked soil and sediment which were slowly desorbed and released into the overlying water after the initial rapid release. The various mechanisms described in Section 5.2.1 and 5.2.2 may also account for the metals and herbicides becoming strongly bound in this study.

5.3.2.2. Effect of drying and rewetting on the release of metals from soil

The higher CO_2 release and mineralisation rates in the dried-rewet soil compared to the fully wet soil and the increase in the soil microbial biomass after drying and rewetting indicate higher soil organic matter mineralisation due to drying and rewetting. In addition, the total DOC load released from the soil into the overlying water under the drying-rewetting treatment was higher than that released under the fully wet treatment (Chapter 4, Table 4.11) further suggesting that drying and rewetting led to higher mineralisation of soil organic matter. The total DOC load released into the overlying water was approximately 104 % higher under the drying-rewetting treatment relative to the fully wet treatment. Cu, Ni and Zn bind to organic matter, Fe and Mn oxides, carbonates and clay minerals in soil (Alloway, 1995; McBride, 1994). Therefore, it was expected that the Cu, Ni and Zn associated with the soil organic matter will be released into the overlying water and result in higher total metal loads in the overlying water under the drying-rewetting treatment relative to the fully wet treatment. In addition, the increase in the total metal loads under the drying-rewetting treatment relative to the fully wet treatment was also expected to be in the order Cu > Zn > Ni due to their affinity to bind to organic matter (Filgueiras et al., 2002; Forstner and Wittmann, 1981; Alloway, 1995). In agreement with the expectations, the total Cu, Ni and Zn loads released into the overlying water under the drying-rewetting treatment were higher than those released under the fully wet treatment (Chapter 4, Table 4.7) indicating that drying and rewetting led to the release of organic matter associated Cu, Ni and Zn into the overlying water. The total Ni load was significantly higher (Two-way ANOVA: $F = 19.01$, $p < 0.05$). The total Ni, Cu and Zn loads released into the overlying water under the drying-rewetting treatment relative to the fully wet treatment increased by approximately 110 %, 66 % and 61 % respectively. Hence, the relative percentage increase among the metals was in the order Ni > Cu > Zn which was different from the expected order, probably due to the association of the metals with DOC.

Several studies have observed that DOC forms soluble complexes with Cu, Ni and Zn which can facilitate their release from soils (Gerringa et al., 1990; Kalbitz and Wennrich, 1998; Sauve et al., 1997). In this study, in order to determine if DOC complexation with the metals under the drying-rewetting treatment was important for the release of Cu, Ni and Zn, the concentrations of Cu, Ni, Zn and DOC in the overlying water were analysed by linear regression. The results of the linear regression indicated that there were significant relationships between the metals and DOC with 50 %, 79 % and 55 % of the variations in the Cu, Ni, Zn concentrations explained by the variation in the DOC concentrations ($p < 0.05$). These results indicate that significant proportions of Cu, Ni and Zn in the overlying water were released from the soil as DOC-complexes. This was treated as evidence for suggesting that the formation of DOC-metal complexes was contributing to the release of these metals under the drying-rewetting treatment. Given that 79 % of the variation in Ni concentrations was explained by DOC and Ni had the highest relative increase in the total load released compared to the Cu and Zn (i.e. 110 %) suggests that Ni formed complexes with DOC more readily than Zn and Cu. Tuner et al. (1998) demonstrated that Ni has a relatively low particle affinity due to its strong association with DOC. The release of the metals as DOC complexes into the overlying water is likely to account for why the increase in the total metal loads under the drying-rewetting treatment relative to the fully wet treatment did not follow the expected order (i. e. Cu > Zn > Ni).

The total DOC load released into the overlying water decreased significantly under the second drying-rewetting treatment compared to the first treatment (Two-way ANOVA: F = 33.20, $p < 0.05$) (Chapter 4, Table 4.12) suggesting lower organic matter mineralisation. This is likely due to less organic matter available after the mineralisation under the first drying-rewetting treatment. Fierer and Schimel (2002) also observed a decrease in DOC as a result of a decrease in organic matter mineralisation with subsequent drying and rewetting of soil. The total DOC load released into the overlying water under the second drying-rewetting treatment as a proportion of the total DOC load released under the first drying-rewetting treatment reduced by approximately 72 %. Similar to the total DOC load, the total Cu, Ni and Zn loads released into the overlying water under the second drying-rewetting treatment were significantly lower than those released under the first treatment (Two-way ANOVA: F = 17.32, $p < 0.05$ for Cu; F = 38.41, $p < 0.05$ for Ni and F = 27.5 , $p < 0.05$ for Zn) (Chapter 4, Table 4.8). The total Cu, Ni and Zn loads released into the overlying water under the second drying-rewetting treatment as a proportion of the total metal loads released under the first drying-rewetting treatment reduced by approximately

77 %, 74% and 77% respectively. This suggests that, after the first drying-rewetting treatment, there was less organic matter for mineralisation which in turn led to reduced release of organic matter associated metals as well as DOC associated metals hence the lower total metal loads observed in the overlying water under the second drying-rewetting treatment. Less metals in the soil after the metal release under the first drying-rewetting treatment is also likely to have contributed to the lower total metal loads released into the overlying water under the second drying-rewetting treatment.

5.3.2.3. Effect of drying and rewetting on the release of metals from sediment

In the sediment, drying and rewetting led to an increase in mineralisation hence the higher CO_2 release and mineralisation rates observed in the dried-rewet sediment compared to the fully wet sediment. As previously discussed in Section 5.3.1, the higher CO_2 release and mineralisation rates in the sediment are likely due to the mineralisation of dead microbes resulting from the death of part of the microbial population during drying rather than the mineralisation of sediment organic matter. Therefore, organic matter associated metals were unlikely to be released into the overlying water. The total Cu, Ni and Zn loads released into the overlying water from the sediment under the drying-rewetting treatment were lower than those released under the fully wet treatment (Chapter 4, Table 4.7). The total Cu, Ni and Zn loads released into the overlying water were approximately 67 %, 65 % and 73 % lower under the drying-rewetting treatment relative to the fully wet treatment. Significant differences between the total loads released under the drying-rewetting and fully wet treatment were observed for Cu (Two-way ANOVA: $F = 8.15$, $p < 0.05$) and Ni (Two-way ANOVA: $F = 8.50$, $p < 0.05$). The lower total metal loads released under the drying-rewetting treatment compared to the fully wet treatment was probably due to the adsorption of the metals to Fe and Mn oxides formed during the drying period. Bordas and Bourg (1998) and Thomson et al. (1980) reported that drying of oxic sediments at 25 ^{O}C resulted in the formation of Fe and Mn oxides which led to decreased Cu and Zn extractability, with the effect increasing with an increase in drying temperature. Rapin et al. (1996) also observed that air-drying led to a decrease in the extractability of Zn. This was attributed to changes in the chemistry of Fe and Mn oxides caused by exposure to air. These studies indicate that drying of oxic sediments leads to a change in the distribution of metals to more strongly bound forms. Accordingly, the adsorption of the metals to Fe and Mn oxides formed as the sediments were exposed to air during the 7 days drying period in these experiments may account for the lower total Cu, Ni and Zn loads released into the overlying water under the drying-rewetting treatment compared to the fully wet treatment (Chapter 4, Table 4.7).

Similar to the metals, the total DOC load released into the overlying water under the drying-rewetting treatment was lower compared to that released under the fully wet treatment (Chapter 4, Table 4.11). The total DOC load was approximately 67 % lower under the drying-rewetting treatment relative to the fully wet treatment. In order to determine if the formation of DOC-metal complexes was contributing to the release of Cu, Ni and Zn from the sediment, a linear regression analysis of the DOC, Cu, Ni and Zn concentrations in the overlying water was conducted. The results of the regression analysis indicate that the relationships between DOC and the metals were not significant ($p > 0.05$). The variation in the DOC concentrations could account for only 8 %, 28 % and 13 % of the observed variation in the Cu, Ni and Zn concentrations in the overlying water. This suggests that significant proportions of the metals were not released into the overlying water as DOC-metal complexes under these experimental conditions. It is notable that the variation in the Ni concentrations explained by DOC was highest compared to that of Cu and Zn suggesting that Ni had the greatest affinity to form complexes with DOC compared to the other metals.

The total Cu, Ni and Zn loads released into the overlying water under the second drying-rewetting treatment were lower than those released under the first drying-rewetting treatment. The total Cu, Ni and Zn loads released into the overlying water under the second drying-rewetting treatment as a proportion of the total metal loads released under the first drying-rewetting treatment reduced by approximately 50 %, 25 % and 28 % respectively. The lower total metal loads in the overlying water suggests further adsorption of the metals to the Fe and Mn oxides formed when the sediments were exposed to air during the drying period hence the lower total metal loads in the overlying water under the second drying-rewetting treatment.

5.3.2.4 Effect of drying and rewetting on the release of herbicides from soil

The higher total DOC load released from the soil under the drying-rewetting treatment compared to the fully wet treatment, the higher CO_2 release and mineralisation rates in the dried-rewet soil compared to the fully wet soil and the increase in soil microbial biomass after drying and rewetting all suggest that drying and rewetting led to a higher mineralisation of soil organic matter. As a result, higher total herbicide loads were expected to be released into the overlying water under the drying-rewetting treatment compared to the fully wet treatment given that the herbicides were binding primarily to organic matter. Also, the percentage increase in the total herbicide loads released under the drying-rewetting treatment relative to the fully wet treatment were expected to be in the order: diuron > atrazine > simazine due to their strength of binding to organic matter. Diuron is the most hydrophobic (log K_{ow} of 2.85) of the studied herbicides and thus the most strongly bound to organic matter, followed by atrazine (log K_{ow} of 2.68) and then simazine (log K_{ow} of 2.17) (Lewis and Gardiner, 2006; HSE, 1993; Margoum et al., 2001). In agreement with the expectations, the increase in the total herbicide loads released into the overlying water followed the expected order with diuron > atrazine > simazine. The total atrazine and diuron loads in the overlying water under the drying-rewetting treatment relative to the fully wet treatment increased by approximately 29 % and 42% respectively while the simazine load decreased by approximately 28 %. The relative percentage increase of diuron was greater than that of atrazine and simazine which is consistent with the hydrophobicity of the herbicide and hence its strength of binding to organic matter. The percentage decrease in the total simazine load under the drying-rewetting treatment relative to the fully wet treatment may be due to simazine degradation under the drying-rewetting treatment.

Several studies have observed that the mobility of herbicides such as those considered in this study can be enhanced due to their complexation with DOC (Graber et al., 1995; Gao et al., 1998). In this study, the higher total DOC load and the higher total herbicide loads released into the overlying water under the drying-rewetting treatment compared to the fully wet treatment suggests that the herbicides may be released from the soil as DOC-complexes. In order to determine if the release of the herbicides as DOC-complexes was important in these experiments, the DOC, simazine, atrazine and diuron concentrations in the overlying water were analysed by linear regression. The results of the analysis indicates that there were significant relationships between DOC and the herbicides with the variations in the DOC concentrations accounting for 65%, 68% and 76% of the variations in the atrazine, diuron and simazine concentrations respectively ($p < 0.05$). These results suggest that significant proportions of the herbicides were released as DOC-complexes from soil into the overlying water.

The total DOC load released into the overlying water was significantly lower under the second drying-rewetting treatment compared to the first drying-rewetting treatment (Two-way ANOVA: F = 33.20, $p < 0.05$) (Chapter 4, Table 4.12) suggesting lower organic matter mineralisation under the second drying-rewetting treatment. The total DOC load released into the overlying water under the second drying-rewetting treatment as a proportion of the total load released under the first drying-rewetting treatment reduced by approximately 72 %. This is probably due to less organic matter available for mineralisation after the first drying-rewetting treatment. Similar to the total DOC load, the total simazine, atrazine and diuron loads released into the overlying water under the second drying-rewetting treatment were lower than those released under the first treatment. Significant differences in the total loads between the first and second drying-rewetting treatments were observed for atrazine (Two-way ANOVA: F = 4.82, $p < 0.05$) and diuron (Two-way ANOVA: F = 12.08, $p < 0.05$) (Chapter 4, Table 4.10). These findings suggest that there was less organic matter mineralisation under the second drying-rewetting treatment which in turn resulted in less release of organic matter associated and DOC associated herbicides hence the lower herbicide loads released under the second drying-rewetting treatment. In addition, the lower total herbicide loads released into the overlying water is also likely due to less herbicides in the sediment for release at the start of the second drying-rewetting treatment. The total simazine, atrazine and diuron loads released under the second drying-rewetting treatment as a proportion of the total load released under the first drying-rewetting treatment reduced by approximately 50%, 61% and 71% respectively. The relative differences among the herbicides was consistent with the hydrophobicity (log K_{ow}) of the herbicides suggesting that the strength of binding of the herbicides to organic matter also contributed to the release of the herbicides under the second drying-rewetting treatment.

Microbial population, oxygen availability and temperature are important factors facilitating the degradation of herbicides (Alexander, 1981; Meakins et al., 1995; Larsen et al., 2001) The degradation of simazine, atrazine and diuron into their degradation products, which are hydroxysimazine, desethylsimazine, hydroxyatrazine, desethylatrazine and 3,4-dichloroaniline, directly results in a decrease in the herbicide loads in the soil and hence, lower concentrations are released into the overlying water during the column experiments.

A study by White et al. (1998) on the effect of wetting and drying cycles on the bioavailability of aged organic contaminants in soil found that subjecting soil to drying and wetting cycles enhanced the degradation of phenanthrene. Accordingly, the decrease in the total simazine, atrazine and diuron loads in the overlying water in these experiments may also be due to degradation. Degradation due to the experimental drying temperature is unlikely because the temperature under the first and second drying-rewetting treatments were the same. However, herbicide degradation due to increased microbial activity as a result of the microbial population growth within the soil column may have contributed to the decrease in the total simazine, atrazine and diuron loads in the overlying water under the second drying-rewetting treatment. Microbial degradation may also account for the decrease in the total simazine load released under the first drying-rewetting treatment relative to the fully wet treatment. Given the data collected in this study, it is difficult to determine the relative importance of degradation under these experimental conditions.

5.3.2.5. Effect of drying and rewetting on the release of herbicide from sediment

Higher CO_2 release and mineralisation rates were observed under the drying-rewetting treatment compared to the fully wet treatment (Chapter 4, Section 4.5.2). As previously discussed in Section 5.3.1., dead microbes due to drying rather than sediment organic matter is the likely carbon source that was mineralised to CO_2 by the microbes that survived the drying period. This suggests that the herbicides associated with the sediment organic matter were unlikely to be released into the overlying water under the drying-rewetting treatment. The total simazine, atrazine and diuron loads released into the overlying water under the drying-rewetting treatment were approximately 64 %, 44 % and 50 % lower relative to the fully wet treatment. These lower total herbicide loads in the overlying water under the drying-rewetting treatment compared to the fully wet treatment is likely to be a consequence of simazine, atrazine and diuron degradation within the sediment column under the drying-rewetting treatment. Several studies have reported that high temperatures and adequate oxygen supply favours the microbial degradation of herbicides (Seol and Lee, 2001; Larsen et al., 2001; Warren et al., 2003). Topp et al. (1995) observed atrazine degradation under aerobic conditions but not under anaerobic conditions in sediments. This suggests that herbicides can be more readily degraded in aerated sediments than in water-saturated sediments. In this study, the exposure of the sediment to air and the drying temperature (i.e. 25 ^{0}C) during the 7-days drying period is likely to have provided more suitable conditions for the microbial degradation of simazine, atrazine and diuron under the drying-rewetting treatment compared to the fully wet treatment leading to the lower herbicide loads under the drying-rewetting treatment. Several studies have indicated that atrazine and simazine are moderately persistent herbicides with degradation rates in sediments ranging from 15 – 30 days half-life for atrazine (Jones et al., 1982), 29 - 57 days half-life for atrazine and 26 - 44 days half-life for simazine (Labbs et al., 2007). Howard et al. (1991) reported a degradation rate of 120 days half-life for diuron. In this study, the degradation rate of the herbicides could not be evaluated given the data collected.

The total DOC load released into the overlying water was approximately 67 % lower under the drying rewetting treatment compared to the fully wet treatment. This lower total DOC load and the lower total herbicide loads released under the drying-rewetting treatment compared to the fully wet treatment suggest that there was a relationship between the release of the herbicides and DOC. A linear regression analysis was conducted with the DOC, simazine, atrazine and diuron concentrations released into the overlying water to determine if the herbicides release as DOC-complexes was important in these experiments. The result of the analysis indicates that the relationships between the herbicides and DOC were not significant ($p > 0.05$). Only 41%, 31% and 22% of the variation in simazine, atrazine and diuron concentrations in the overlying water could be explained by the variation in the DOC concentrations. This suggests that the release of the herbicides as DOC-complexes was not significantly contributing to the release of atrazine, diuron and simazine from the sediment into the overlying water.

The total simazine, atrazine and diuron loads released into the overlying water under the second drying-rewetting treatment were slightly lower than those released under the first drying-rewetting treatment (Chapter 4; Table 4.10). The total simazine, atrazine and diuron loads released under the second drying-rewetting treatment as a proportion of the total load released under the first drying-rewetting treatment reduced by approximately 4 %, 31 % and 14 % respectively. These slightly lower herbicide loads released under the second drying-rewetting treatment are likely due to further degradation occurring within the sediment column during the second drying period. In addition, less herbicides in the sediment for release after degradation under the first drying-rewetting treatment is also likely to have contributed to the lower total herbicide loads released into the overlying water under the second drying-rewetting treatment.

5.4. Summary and conclusion

This chapter has identified that the release of metals (Cu, Ni and Zn) from the soil and sediment into the overlying water at low and high salinities (i.e. 5 and 20 respectively) was dependent on the strength of binding of the metals to the soil and sediment, competition between seawater cations and the sorbed metals for binding sites on the soil and sediment particles and the formation of soluble complexes between the sorbed metals and seawater anions. The importance of the strength of binding of the metals for release was revealed by the inverse relationship between the total metal loads (which followed the order Ni > Zn > Cu) and their log K_d values (which was in the order Cu > Zn > Ni). Higher total Zn and Ni loads were released into the overlying water at high salinity than at low salinity which was likely due to an increase in the competition and complexation reactions between the seawater cations, anions and the sorbed metals. Cu was more strongly bound to the soil and sediment than Ni and Zn which limited its release compared to the release of Ni and Zn. The metal release was lower from the sediment than the soil due to greater availability of binding sites and hence greater metal retention in the sediment. The release of the herbicides from the soil and sediment into the overlying water at low and high salinity was mainly dependent on the strength of binding of the herbicides to the soil and sediment organic matter which was in the order diuron > atrazine > simazine. The total herbicide loads released into the overlying water followed the order simazine > atrazine > diuron, with higher total loads released from the soil than the sediment due to the higher organic matter content in the sediment. The increase in salinity did not significantly increase the release of any of the herbicides from the soil and sediment probably because the herbicides molecules were primarily uncharged at both low and high salinity.

Drying and rewetting resulted in an increase in the mineralisation of soil organic matter and the total DOC load released into the overlying water due to increased microbial activity on the soil organic matter previously protected within the soil aggregates but made available by drying and rewetting. This in turn led to the release of organic matter associated metals and herbicides into the overlying water which was indicated by the higher total metal and herbicide loads in the overlying water under the drying-rewetting compared to the fully wet experimental conditions. The significant relationships between DOC, the metals and herbicides which were demonstrated by the results of the linear regression analysis provided evidence that the release of the metals and herbicides as DOC-complexes from the soil was important. The total metal and herbicide loads released into the overlying water were significantly lower after the second drying and rewetting of the soil compared to the first drying and rewetting which was probably due to less release of organic matter associated and DOC-associated metals and herbicides and less metals and herbicides in the soil for release at the start of the second drying and rewetting.

Drying and rewetting led to the mineralisation of dead microbes in the sediment which resulted from the death of part of the microbial population during drying, indicated by the observed decrease in the sediment microbial biomass after drying the sediment. The organic matter associated metals and herbicides were unlikely to be released into the overlying water since the sediment organic matter was not the carbon source that was mineralised. In comparison with the fully wet treatment, lower total Cu, Ni and Zn loads were released into the overlying water from the sediment after drying and rewetting probably due to the adsorption of the metals to Fe and Mn oxides formed when the sediments were exposed to air during the 7-days drying period. Similarly, the exposure of the sediment to air and the drying temperature during the drying period may have led to the degradation of the herbicides in the sediment column and the lower total simazine, atrazine and diuron total loads released into the overlying water after drying and rewetting relative to the fully wet experimental conditions. The results of a linear regression analysis showed that there were no significant relationships between DOC, the metals and herbicides indicating that DOC-complexation was unlikely to be important for metal and herbicide release from the sediment. The lower total metal and herbicide loads released into the overlying water after the second drying and rewetting of the sediment compared to the first drying and rewetting was likely a consequence of further metal adsorption to Fe and Mn oxides and further herbicide degradation during the second drying period as well as less herbicides in the sediment for release after their degradation under the first drying-rewetting treatment.

Similar temporal release patterns were observed under the low salinity, high salinity and drying-rewetting experimental conditions with an initial rapid release of the metals and herbicides, followed by a slow release into the overlying water. The initial rapid release was attributed to the release of readily available metals and herbicides present in the porewater and weakly sorbed to the soil and sediment, followed by the slow release of strongly bound metals and herbicides.

Chapter 6: Mechanisms of metal and herbicide release from soil and sediment

6.1. Introduction

One justification for the implementation of managed realignment is that they provide a sink for contaminants from estuarine waters (NRA, 1994). Andrews et al. (2006) indicated that managed realignment would increase sediment storage capacity and provide an effective sink for metals and other particle reactive contaminants and increase the burial of organic carbon. This is further supported by Shepherd et al. (2007) who indicated that organic carbon, nitrate and phosphorus storage would be enhanced in managed realignment schemes. These studies suggest that managed realignment provides biogeochemical benefits for the environment. However, the periodic tidal inundation of the soil and sediment by seawater in managed realignment sites may cause changes in the physicochemical conditions in the soil and sediment which can affect the binding of the metals and herbicides to the soil and sediment. Changes in salinity, pH and redox potential can affect the binding of contaminants to soil and sediment and lead to their release (Gambrell et al., 1991; Calmano et al., 1992). This occurrence of these changes in the soil and sediment in managed realignment sites following tidal inundation can lead to the release of contaminants such as metals and herbicides present in the pre-inundated soil and sediment into the overlying water. In addition, the periodic inundation of the soil and sediment can lead to drying-rewetting cycles which can enhance the mineralisation of organic matter and consequently the release of DOC and organic matter associated metals and herbicides. Although the effects of such mobilisation are difficult to assess, it has implications for water quality and can pose a risk to higher organisms. The connection with water quality is of concern in relation to the EU Water Framework Directive (222/60/EC) which requires that good ecological status of surface, transitional and coastal waters be maintained.

In this study, laboratory column microcosm experiments were conducted with the aim of examining the potential release of metals (Cu, Ni and Zn) and herbicides (simazine, atrazine and diuron) from soil and sediment in managed realignment sites following tidal inundation. The experiments focused on the effect of salinity and drying-rewetting cycles on the release of these contaminants from the soil and sediment into overlying water. The metal and herbicide concentrations released into the overlying water under two salinity treatments (5 and 20 referred to as low and high salinity) and drying-rewetting treatment were measured during the experiments. The observations from these experiments discussed in Chapter 5 indicated that there was an initial rapid release of Cu, Ni, Zn, simazine, atrazine and diuron from the soil and sediment, followed by a slow continued release for the remainder of the experiments. These release patterns were indicative of the diffusion of the metals and herbicides from the soil and sediment into the overlying water**.** The objective of this chapter was to investigate, using a diffusion model, the mechanisms of metal and herbicide release from the soil and sediment under the experimental conditions in this study. This was achieved by:

- using the diffusion model to predict the metal and herbicide concentrations released into the overlying water from the soil and sediment and
- assessing the agreement between the model predictions and the experimental metal and herbicide concentration data using several assessment methods. Disagreements between the model predictions and the experimental data were attributed to other mechanisms contributing to the metals and herbicides release from the soil and sediment in the column microcosm experiments but not accounted for in the model.

The model simulations were based on the metal and herbicide porewater concentrations in the soil and sediment at the start of the column microcosm experiments, the properties of contaminants and the soil/sediment properties. Statistical goodness-of-fit measures were used to evaluate the performance of the model. The following sections examine the modelling of diffusive contaminant transport, the various statistical goodness of fit criteria used for assessing the performance of models, describes the model developed in this study and the model parameters used for the model simulations.

6.2. Diffusive contaminant transport

Diffusion is an important contaminant transport mechanism in natural porous media such as soil and sediment (Grathwohl, 1998). Diffusion describes mass transport due to the random thermal motion of solute molecules (Grathwohl, 1998). It involves the net transfer of solute molecules from regions of high concentration to regions of low concentration. Several studies have examined contaminant diffusion in water-saturated soil and sediment environments. For example, dissolved metal fluxes have been determined by using porewater gradients of the dissolved metals to estimate the diffusive flux of the metals at the sediment water interface (Sawlan and Murray, 1983; Caetano et al., 2007). Monterroso et al. (2007) estimated the diffusive fluxes of Cu, Pb, Zn, Cd, Fe and Mn from the top 2.5 cm of a sediment core using Fick's Law and found that the sediment-water exchange of the metals were hindered by sulphide formation. Several studies have also examined the diffusive transport of organic contaminants in soil and sediment (Valsaraj et al., 1998; Qaisi et al., 1996; Valsaraj and Sojitra, 1997; Allan et al., 2004; Daniels et al., 1998, Bekhit and Hassan, 2005). In addition, diffusion based models have also been used to examine the sorption/desorption kinetics of organic contaminants in soil and sediment particles in several studies (Pignatello et al., 1993; Ball and Roberts, 1991, Brusseau et al., 1991).

In the modelling context, the main advantage of a simple model, such as the one developed in this study, concerns parsimony (i.e. using no more complex a model than is absolutely necessary) (Wainright and Mulligan, 2004). A parsimonious model is usually the one with the greatest predictive power and the least parameters and process complexity (Wainright and Mulligan, 2004). Thomann (1998) emphasised that there is a real danger that model complexity will be equated to a greater level of model success in representing the actual system. Simple models can achieve as high a level of performance as more complex models in terms of simulating the target variables (Perrin et al., 2001). Complex models usually need more input parameters for more detailed process descriptions and this has advantages from a theoretical point of view (Wainright and Mulligan, 2004; Wania and Mackay, 1999). However, the greater the number of input parameters, the more likely they are to be cross-correlated with each extra parameter adding relatively little to model predictive capability (Wainright and Mulligan, 2004). Moreover, the relatively large observational data sets needed for the evaluation of the performance of complex models are usually not available, thereby increasing the degree of uncertainty associated with the model predictions (Wania and Mackay, 1999). Another reason for keeping a model simple is that high model complexity may lead to users losing mental contact with the model due to the limitation of the human mind to grasp the significance of large quantities of data (Wania and Mackay, 1999). Wainwright and Mulligan (2004) pointed out that when developing a model, simplicity must be strived for but not at the expense of model performance.

In numerical modelling, several numerical solution methods are available to solve the differential equations such as the finite difference, finite element or finite volume methods (Smith, 1985; Anlauf and Liu, 1990; Versteeg and Malalasekera, 1995; Smith and Griffiths, 1998). However, the finite difference methods are the most commonly-used, with simplicity and easy implementation as their main advantages (Zheng and Bennett, 1995). In the finite difference methods, the transport equations are approximated using grids representing the change in property values that describe the model system. The finite difference method was used in this study.

Numerical models can be developed in a Microsoft Excel spreadsheet (Hardisty et al., 1993; Grathwohl, 1998). It is also possible to develop a model using codes which require high level computer programming languages such as FOTRAN, BASIC, Pascal, C++ and Java. Microsoft Excel offers a simple modelling environment and allows for rapid analysis of model sensitivity to changes in input parameters. Compared to the high level programming languages, Microsoft Excel is much easier to learn as it is not a specialist software and does not have steep learning curves (Mulligan and Wainwright, 2004). Microsoft Excel is also particularly useful at the early stage of model development (Mulligan and Wainwright, 2004) and hence was adopted in this study.

Models require input parameters in order to run the model simulations, and the model input parameters have some degree of uncertainty associated with them (Wainwright and Mulligan, 2004). In addition, assumptions such as those which define the model boundary conditions are also needed for model simulations. These uncertainties and assumptions can affect the performance of the model in representing the actual system. Hence, contaminant transport models need to be tested; such model testing shows the capability of the model in predicting contaminant fate and behaviour. Model testing also indicates the accuracy of the model predictions, thereby providing evidence which increases confidence in the model and promotes its acceptance and usage (Sterman, 2002, Tedeschi, 2006). Hence, the evaluation of the performance of a model is an important step in the development of a model (Tedeschi, 2006). In chemistry, analytical bias is estimated by the use of certified reference materials or by comparing a given method with another method. This general evaluation approach has been used in modelling studies to evaluate the performance of a numerical model by comparing its predictions against those of an analytical model which serves as a reference (Go et al., 2008). However, this approach is limited to simple systems because analytical models are unable to make satisfactory predictions in complicated environmental systems. Usually, model performance is evaluated by using one or more statistical goodness-of-fit criteria between the model predictions and measured field data or measured data from experiments set-up to simulate field conditions (Wainwright and Mulligan, 2004).

6.3. Measures for the evaluation of model performance

The goodness-of-fit measures usually used in describing a model's performance relative to the measured data include coefficients of determination, Nash-Sutcliffe efficiency coefficient, the root mean square error and mean absolute error (Tedeschi, 2006). Cichota et al. (2004) suggested that it is important to calculate the root mean square and mean absolute errors in order to improve understanding of the model's predictive power. It also provides information about the quality of the model and conclusions can be made about its validity (Ljung, 1987).

The coefficient of determination (r^2) is the most frequently used goodness-of-fit criteria. The coefficient of determination r^2, represents the proportion of variance in the observed data explained by the model predictions. The coefficient of determination, r^2, is defined as

$$r^2 = \left(\frac{\sum_{i=1}^{N} \left(X_{pred} - \overline{X_{pred}} \right) \cdot \left(X_{obs} - \overline{X_{obs}} \right)}{\sqrt{\sum_{i=1}^{N} \left(X_{pred} - \overline{X_{pred}} \right)^2} \cdot \sqrt{\sum_{i=1}^{N} \left(X_{obs} - \overline{X_{obs}} \right)^2}} \right)^2 \tag{6.1}$$

where X_{pred} is the predicted data value, X_{obs} is the observed data value, $\overline{X_{pred}}$ and $\overline{X_{obs}}$ are the means of the predicted and observed data values respectively.

The value of r^2 varies from 1, which indicates a perfect relationship between the predicted and observed data, to 0, which indicates no relationship. However, the coefficient may be oversensitive to extreme values (i.e. outliers) and insensitive to proportional deviations between predicted and observed values (Legates and McCabe, 1999). Because the coefficient of determination is not a robust statistical measure, it is prudent to use it in conjunction with other measures of goodness-of-fit such as measures of model error.

The Nash-Sutcliffe efficiency coefficient (NS) represents the deviation of the predicted data from the observed data in relation to the scattering of the observed data. It is a measure of the mean squared error to the observed variance given by:

$$NS = 1 - \frac{\sum_{i=1}^{N} \left(X_{obs} - X_{pred} \right)^2}{\sum_{i=1}^{N} \left(X_{obs} - \overline{X_{obs}} \right)^2} \tag{6.2}$$

If the NS efficiency coefficient is equal to 1, then the error is zero. This is indicative of an explained variance of 100 % which means the predicted and observed data fit perfectly. Unlike the correlation coefficient, the NS efficiency coefficient does not suffer from proportionality effects but it is still sensitive to extreme values (i.e. outliers) (Legate and McCabe, 1999).

The root mean squared error ($RMSE$) is a generalised measure of standard deviation and often considered the most valid indicator of relative model quality (Cichota et al., 2004; Willmott, 1981). $RMSE$ is defined as:

$$RMSE = \left[\frac{1}{N} \sum \left(X_{obs} - X_{pred} \right)^2 \right]^{1/2} \tag{6.3}$$

Although the $RMSE$ is more sensitive than the other measures, the squared term may give disproportionate weight to large errors (Go et al., 2008).

The mean absolute error (MAE) is an absolute indicator of the agreement between model predictions and measured data. It is given by:

$$MAE = \frac{1}{N}\sum_{i=1}^{N}\left(X_{obs-}X_{pred}\right) \qquad (6.4)$$

where N is the total number of observed data values. The MAE is less sensitive to outliers than the NS efficiency coefficient and the $RMSE$ (Wainright and Mulligan, 2004). A MAE of zero suggests an absolute agreement between the predicted and observed data.

6.4. Model Description

A time dependent, one-dimensional diffusion model was used to predict the Zn, Cu, Ni, simazine, atrazine and diuron concentrations released from the soil and sediment into the overlying water in the column microcosm experiments. The system was assumed to consist of a water column overlying a soil/sediment column and the volume of the water column was constant. The model was based on the diffusion of metal cations and herbicide molecules from a region of high concentration to a region of low concentration. Hence, the diffusive contaminant flux was driven by a concentration gradient. The contaminant flux was quantified using Fick's first law (Crank, 1975) given by

$$J = -D_{eff}\frac{\partial C}{\partial z} \qquad (6.5)$$

where J is the magnitude of contaminant flux (g m^{-2} s^{-1}), D_{eff} is the effective diffusion coefficient of the contaminant (m^{2} s^{-1}), C is the contaminant concentration (g m^{-3}) and z is soil and sediment depth (m). The model equation was solved using the finite difference numerical method by assuming that the overlying water column and the soil/sediment column are divided into thin notional layers with a constant depth called cells as depicted in Figure 6.1. Thin layers were required to obtain a good representation of the system, especially vertical variability in contaminant concentrations through the soil and sediment profile.

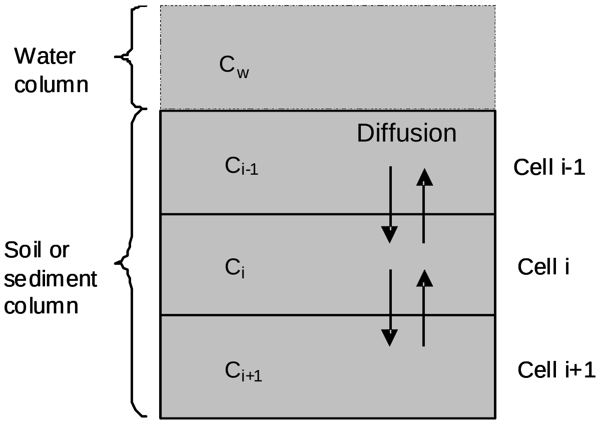

Figure 6.1. An illustration of the finite difference model arrangement in the soil and sediment experimental column

The contaminant mass transferred into cell i in a given time can be written in the finite difference form as:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{C_{i-1} - C_i}{\Delta z} \Delta t \qquad (6.6)$$

where Δz is the distance between the mid-point of adjacent cells (m) and Δt is timestep (sec).

The magnitude of contaminants in a particular cell depends on the contaminant concentration coming into the particular cell and that going out. The mass of the contaminant entering and leaving cell i (Figure 6.1) during a timestep, assuming that the flow rate is constant during the timestep is given by:

$$\Delta M_i = D_{eff} \frac{(C_{i-1} - C_i)}{\Delta z} A \Delta t - \left(D_{eff} \frac{(C_i - C_{i+1})}{\Delta z} A \Delta t \right) \qquad (6.7)$$

where M_i is the mass of contaminant in cell i, A is the area of sediment through which diffusion occurs.

Equation 6.7 can be rearranged as follows:

$$\Delta M_i = \frac{\left(C_{i-1} - 2C_i + C_{i+1}\right)}{\Delta z} AD_{eff}\Delta t \qquad (6.8)$$

Converting the change in mass to change in concentration, Equation 6.8 was divided by the volume of porewater and rewritten as

$$\Delta C_i = \frac{(C_{i-1} - 2C_i + C_{i+1})}{\Delta z} D_{eff}\Delta t \Big/ \varphi\Delta z \qquad (6.9)$$

where φ is the soil or sediment porosity (m^3 m^{-3}). The volume of porewater was given by $A\times\varphi\times\Delta z$.

Boundary conditions at the top and bottom of the model calculation domain were chosen to reflect what transpires at the upper and lower boundaries of the system being modelled. They can be concentration (Dirichlet), flux (Neumann) or mixed (Robin) conditions depending on the nature of the system and the assumptions that have been made (Hassanizadeh and Gray, 1989). In this study, the upper boundary condition was defined by the contaminant flux at the soil or sediment-water interface. The contaminants can diffuse to or from the overlying water column and to or from the soil or sediment surface (i.e. cell 1) depending on the concentration gradient. Assuming the diffusion across the soil or sediment-water interface is occurring across a half cell's depth and that between the cells 1 and 2 is occurring across a full cell's depth, the change in contaminant concentration in the porewater in cell 1 (i.e. the upper boundary) is defined by:

$$\Delta C_1 = \frac{2C_w - 3C_1 + C_2}{\Delta z} D_{eff}\Delta t \Big/ \varphi\Delta z \qquad (6.10)$$

where C_w is the concentration in the overlying water column.

To calculate the change in contaminant concentration released into the overlying water column (C_w) over time, the contaminant lost to water flowing over the soil and sediment and the exchange of contaminant between the water column and the first layer of the soil or sediment (cell 1) were determined. Since the water flowing over the soil or sediment initially contained no contaminant, this was not accounted for in the calculation. Assuming that the volume of the overlying water column above the soil or sediment was constant, the change in the contaminant concentration was given by:

$$\Delta C_w = \left(-V_t C_w - \left(AD_{eff} \Delta t \frac{C_w - C_1}{0.5\Delta z} \right) \right) \Big/ V \qquad (6.11)$$

where V_t is the volume of water (m^3) above the soil or sediment during a particular timestep, V is the volume of the column above the soil or sediment.

The lower boundary specifies the bottom of the soil or sediment column (i.e. cell *n*). The condition at this boundary was defined by a concentration gradient of zero because no diffusive flux was expected to take place across this boundary layer. This allowed contaminant concentrations in the soil or sediment column to adjust to changes in the contaminant concentration in the overlying water column. The governing equation for cell *n* was:

$$\Delta C_n = \frac{(C_{n-1} - C_n)}{\Delta z} D_p \Delta t \Big/ \varphi \Delta z \qquad (6.12)$$

6.5. Model parameters

The model input parameters are summarised in Table 6.1. The water flow rate, water column depth, area over which diffusion occurred and the simulation time were all obtained from the laboratory column microcosm experiments described in Chapter 3. A suitable time step and cell thickness were also chosen and inputted into the model. A timestep of 300 seconds and cell thickness of 0.05 m were chosen so that any changes in the contaminant concentration could be captured by the model. Whilst the soil and sediment porosities were measured, the effective diffusion coefficients of the metal cations and herbicide molecules were estimated using an empirical equation. Empirically estimated effective diffusion coefficients have been used in several studies (Go, 2008; Cussler, 1997). The effective diffusion coefficients were estimated using the equation proposed by Berner (1980):

$$D_{eff} = \frac{D}{\theta^2} \tag{6.13}$$

where D_{eff} is the effective diffusion coefficient of each contaminant in soil or sediment (m^2 s^{-1}), D is the diffusion coefficient of each contaminant in water (m^2 s^{-1}) and θ^2 is the tortuosity factor.

Table 6.1. Model parameters used in predicting the column experimental data for Zn, Cu, Ni, simazine, atrazine and diuron

Parameters	
Flow rate, ml min^{-1}	1.6
Water column depth, m	0.02
Diffusion area, m^2	0.01
Soil porosity, m^{3}m^{-3}	0.79
Sediment porosity, m^{3}m^{-3}	0.82
Cell thickness, m	0.05
Time step, sec	300
Simulation time, days	24

The diffusion coefficients of the herbicide molecules were estimated using empirical equations. There are several empirical equations available for estimating the molecular diffusion coefficient of compounds in liquid, some of which include the Stokes-Einstein equation (McClung and Kivelson, 1968) and molar volume based equations such as the Scheibel equation (Scheibel, 1954), the Wilke-Chang equation (Wilke and Chang, 1955) and the Hayduk-Laurie equation (Hayduk and Laurie, 1974). The Stokes-Einstein equation can only be used if the solute molecules are spherical with a radius that is five times greater than that of the solvent molecules (Cussler, 1997). Given that the size and shape of the herbicide molecules were not determined in this study, the Wilke-Chang equation was used in this study to estimate the molecular diffusion coefficients of the herbicide molecules. The use of this equation is not limited by the shape and radius of the solute molecules. The Wilke-Change equation has been widely used in many studies (van der Wielen et al., 1997; Niesner and Heintz, 2000, Li and Carr, 1997; Allan et al., 2004). The Wilke-Change equation is:

$$D = \frac{7.4x10^{-8}(\phi M)^{0.5}T}{\mu V^{0.6}} \tag{6.14}$$

where ϕ is the association parameter (which is 2.6 for water), M is the molecular mass of water (g mol^{-1}), T is absolute temperature (K), μ is the viscosity of water (cP), V is the molar volume of each herbicide at boiling point (cm^3 mol^{-1}).

Published molar volumes calculated with the le Bas method were used (Mackay et al., 1997). This was because a study by Sastri et al. (1996) suggested that the le Bas method was the most accurate for calculating molar volumes of compounds in liquids. The viscosity of water was calculated using the empirical formula (Yaws, 1999):

$$\log_{10}\mu = -10.2158 + \frac{1.7925x10^{-3}}{T} + 1.773x10^{-2} - 1.2631x10^{-5}T^2 \tag{6.15}$$

where T is absolute temperature (K).

The estimated diffusion coefficients of simazine, atrazine and diuron were 4.23 x 10^{-10} m^2 s^{-1}, 4.00 x 10^{-10} m^2 s^{-1} and 4.29 x 10^{-10} m^2 s^{-1}. In contrast to the herbicides, the diffusion coefficients of the metal cations were obtained from published literature (Li and Gregory, 1974) but corrected to the temperature at which the column experiments were performed (12 ^{o}C). The diffusion coefficient of Zn, Ni and Cu were 4.87 x 10^{-10}, 4.94 x 10^{-10} and 4.59 x 10^{-10} m^2 s^{-1}.

The diffusion coefficient of metal cations and herbicide molecules in water is about one order of magnitude higher than their effective diffusion coefficient in soil or sediment. This is due to the presence of the soil or sediment particles which reduce the area through which diffusion takes place. In addition, the pore spaces in soil or sediment through which the diffusing contaminant ions and molecules travel are convoluted due to the different particle sizes and the packing arrangement. Hence diffusion takes place over a longer distance and this is accounted for in Equation 6.13 by the tortuosity factor. Tortuosity is defined as the ratio of the distance traveled by diffusing ions and molecules in a porous medium to the linear distance traveled in a particle free-medium (Sweerts et al., 1991). Tortuosity has been estimated indirectly by measuring electrical resistivity (McDuff and Ellis, 1979), however, in this study it was estimated using the Modified Weissberg equation. The tortuosity values estimated using this equation had the best fit to data from lacustrine and marine sediment (Boudreau, 1996).

Based on the Modified Weissberg equation, tortuosity is given by:

$$\theta^2 = 1 - \ln\left(\varphi^2\right) \tag{6.16}$$

where φ is the porosity of soil or sediment ($m^3\ m^{-3}$).

6.6. Results

Table 6.2 presents the results of the goodness-of-fit criteria used to evaluate the performance of the model. The model runs were based on the average metal and herbicide concentrations in the soil and sediment porewater at the start of column experiments. The coefficients of determination (r^2) (at $p < 0.05$ significance level) indicated that the variance in the predicted metal and herbicide concentrations accounted for 97 % - 98 % of the variance in the measured Cu, Ni and Zn concentrations and 87 % - 92 % of the variance in the measured simazine, atrazine and diuron concentrations released from the soil into the overlying water under the low and high salinity treatments. In the case of the sediment, 52 – 97 % of the variance in the measured Cu, Ni and Zn concentrations and 72 % - 87 % of the variance in the measured simazine, atrazine and diuron concentrations released into the overlying water under the low and high salinity treatments were accounted for by the variation in the predicted metal and herbicide concentrations. The relatively high r^2 values indicated that the model performed reasonably well in predicting the measured concentrations in the overlying water in the column microcosm experiments. It is notable that the coefficients of determination for the predicted and measured metal concentrations released from the sediment into the overlying water were lower under the high salinity treatment compared to the low salinity treatment (Table 6.2).

No standard range of values for Nash-Sutcliffe (NS) efficiency coefficient is available to judge a model's performance as acceptable (Engel *et al.,* 2007). Ramanarayanan et al. (1997) judged the performance of the Agricultural Policy Environmental Extender (APEX) model as satisfactory when the correlation coefficient was greater than 0.5 and the NS coefficient was greater than 0.4. Santhi et al. (2001) used an NS efficiency coefficient of 0.5 as a criterion to evaluate if the Streamtube Model for Advective and Reactive Transport (SWAT) water quality model's performance was satisfactory. In this study, an NS efficiency coefficient of 0.4 was used as a threshold to judge the performance of the model. Not all the NS coefficients were greater than or equal to 0.5 (Table 6.2) suggesting that there were some measure of error associated with the model predictions. These errors which were reflected in the mean absolute error (MAE) and the root mean squared error (RMSE) shown in Table 6.2, were very close to zero with the exception of Zn and Ni. The low MAE and RMSE indicated that the model performed well in predicting the metal and herbicide release from the soil and sediment into the overlying water in the column microcosm experiments. The high MAE and RMSE for Zn and Ni may be due to the high initial Zn and Ni concentrations released from the soil and sediment into the overlying water during the column experiments which appear as outliers in the experimental dataset. The limitation of MAE and RMSE is their sensitivity to outliers. Although the different goodness-of-fit criteria have limitations, obtaining relatively reasonable values for some of the model simulation runs indicated that the model performed relatively well in predicting the metal and herbicide concentrations released from the soil and sediment into the overlying water in the column microcosm experiments.

Table 6.2 Goodness of fit criteria for the evaluation of the model performance

	r^2	MAE	RMSE	NS
Soil **High salinity**				
Zn	0.97	1.02	3.32	0.3
Cu	0.98	0.04	0.07	0.5
Ni	0.97	1.02	3.47	0.4
Low salinity				
Zn	0.97	1.26	1.76	0.6
Cu	0.98	0.04	0.06	0.5
Ni	0.97	0.89	2.40	0.7
Sediment **High salinity**				
Zn	0.62	1.15	1.73	0.1
Cu	0.52	0.01	0.01	0.8
Ni	0.74	1.10	2.18	0.5
Low salinity				
Zn	0.89	0.43	0.70	0.6
Cu	0.97	0.02	0.06	0.9
Ni	0.93	0.38	0.63	0.8
Soil **High salinity**				
Simazine	0.87	0.11	0.001	0.1
Atrazine	0.90	0.02	0.05	0.3
Diuron	0.89	0.01	0.01	0.2
Low salinity				
Simazine	0.89	0.09	0.002	0.1
Atrazine	0.92	0.02	0.02	0.6
Diuron	0.91	0.004	0.01	0.4
Sediment **High salinity**				
Simazine	0.72	0.06	0.08	0.1
Atrazine	0.81	0.02	0.03	0.3
Diuron	0.80	0.003	0.004	0.5
Low salinity				
Simazine	0.79	0.07	0.08	0.1
Atrazine	0.87	0.01	0.02	0.6
Diuron	0.78	0.003	0.004	0.2

The data plots of the measured metal and herbicide concentrations released from the soil and sediment into the overlying water under the low salinity, high salinity and drying-rewetting treatments in the column experiments and the predicted concentrations are shown in Figures 6.2 to 6.5 respectively. With the exception of the initial release of Cu and atrazine from the sediment under the low salinity and Ni from the sediment under the low salinity treatment, Figure 6.2 and 6.3 showed that the model under-estimated the initial metals and herbicides release into the overlying water from the soil and sediment under both the low and high salinity treatments. The model under-estimations were observed to be greater for the soil than the sediment particularly for metal release from the soil under the high salinity treatment. Figure 6.4 showed that under the drying-rewetting treatment, the model also under-estimated the initial release of the metals from the soil but not from the sediment. In the case of the herbicides, the model under-estimated the initial release from both the soil and sediment with the under-estimations greater for the soil than the sediment (Figure 6.5). Given that the model assumes that diffusion was the only mechanism controlling contaminant release, the observed model under-estimations suggest that other mechanisms in addition to diffusion were contributing to contaminant release during the initial phase of the column microcosm experiments.

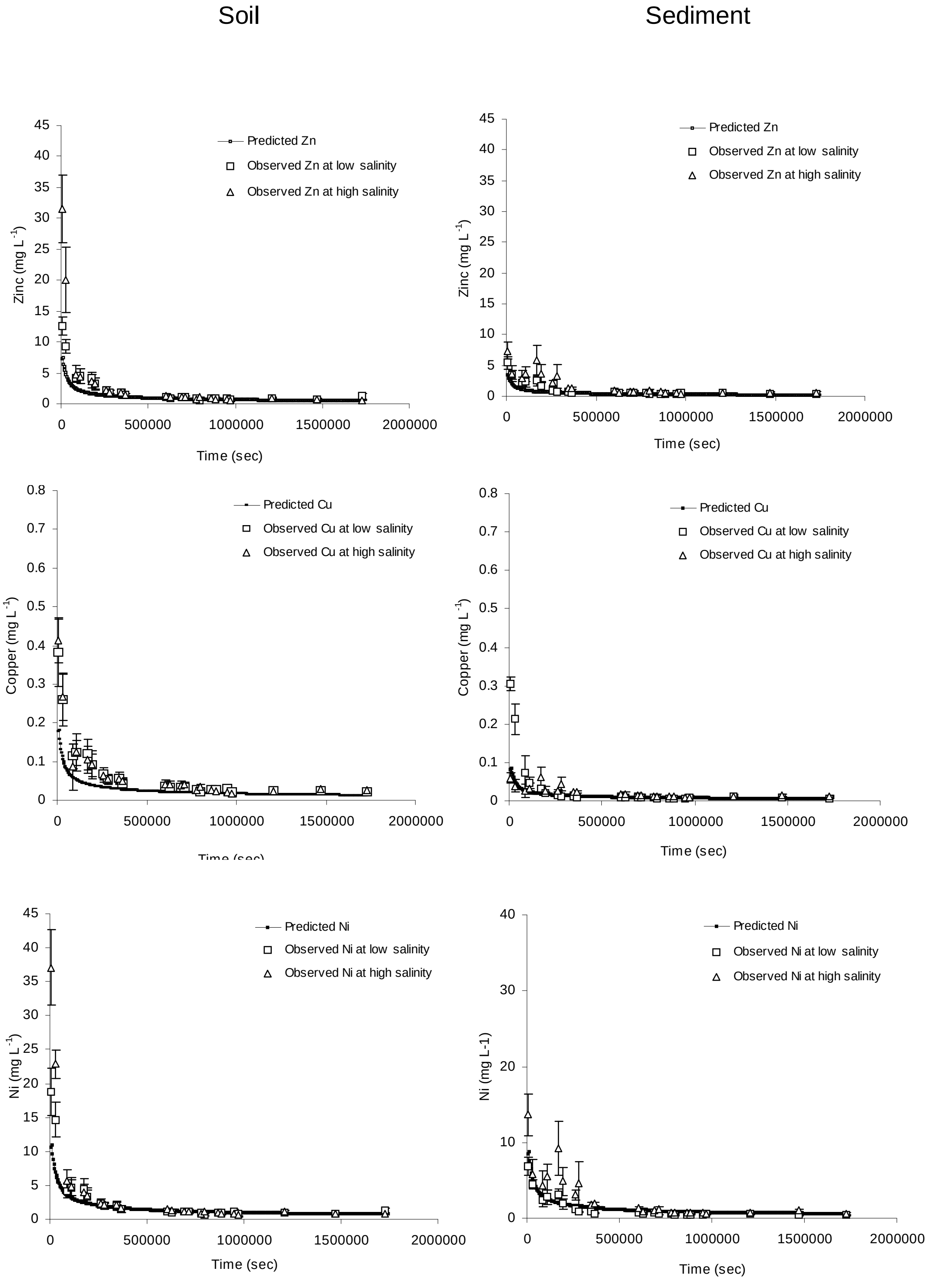

Figure 6.2 Predicted and measured concentration data for (a, d) Zn, (b, e) Cu and (c, f) Ni released into the overlying water column from the soil and sediment respectively under the low and high salinity treatments (bars = standard deviation (SD), n = 3).

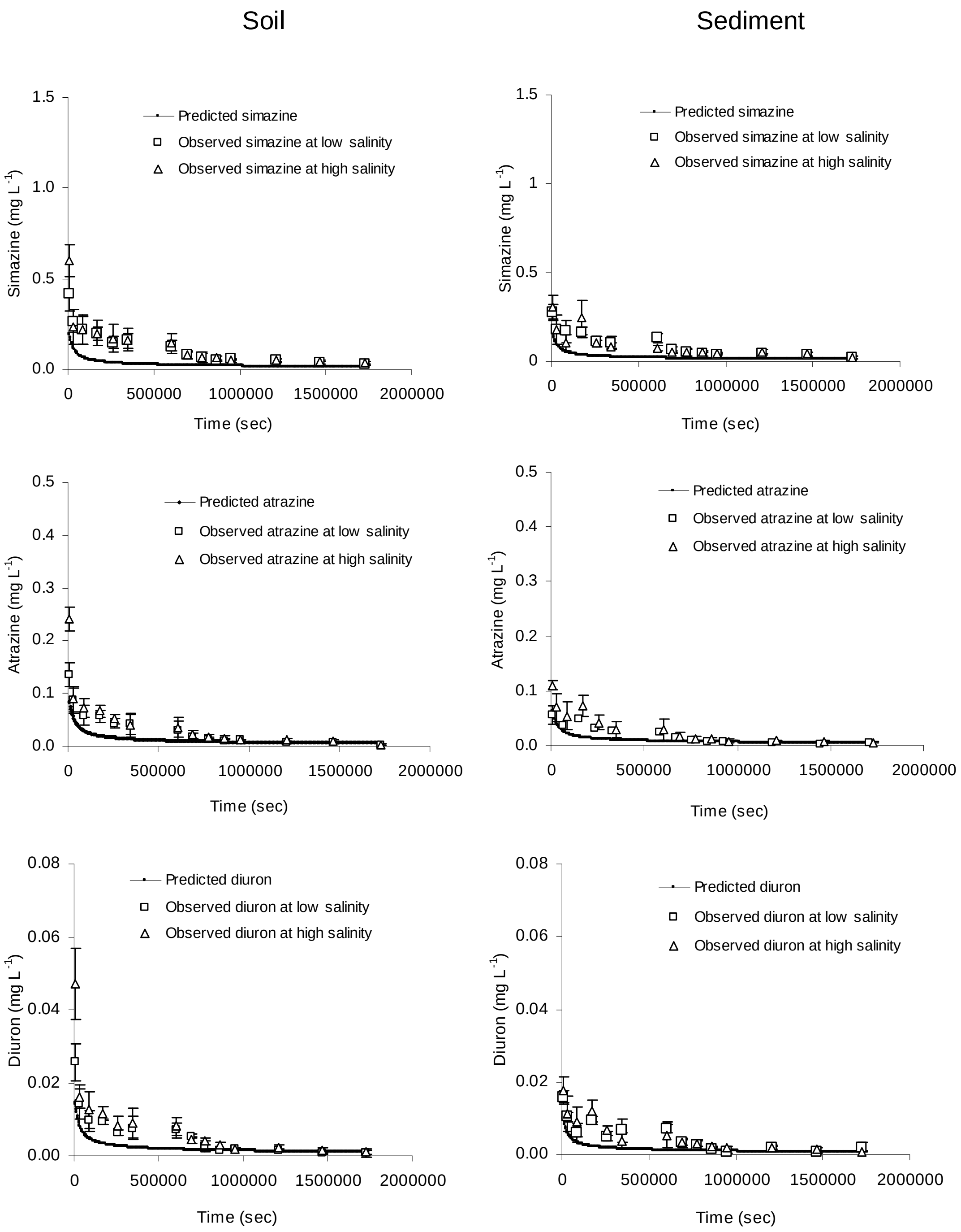

Figure 6.3 Predicted and measured concentration data for (a, d) simazine, (b, e) atrazine and (c, f) diuron released into the overlying water column from the soil and sediment respectively under the low and high salinity treatments (bars = standard deviation (SD), n = 3).

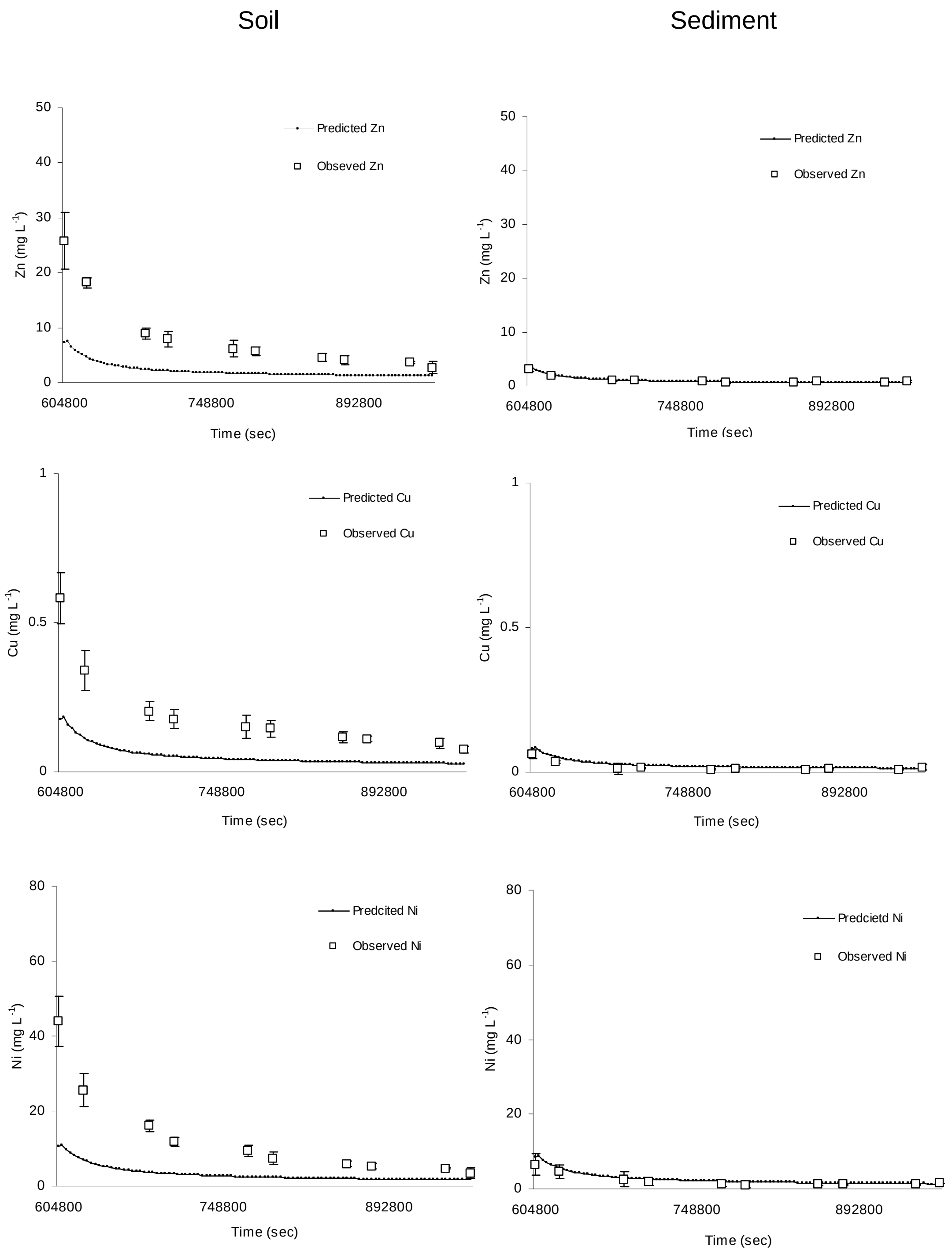

Figure 6.4 Predicted and measured concentration data for (a, d) Zn, (b, e) Cu and (c, f) Ni released into the overlying water column from the soil and sediment respectively under the drying-rewetting treatment (bars = standard deviation (SD), n = 3).

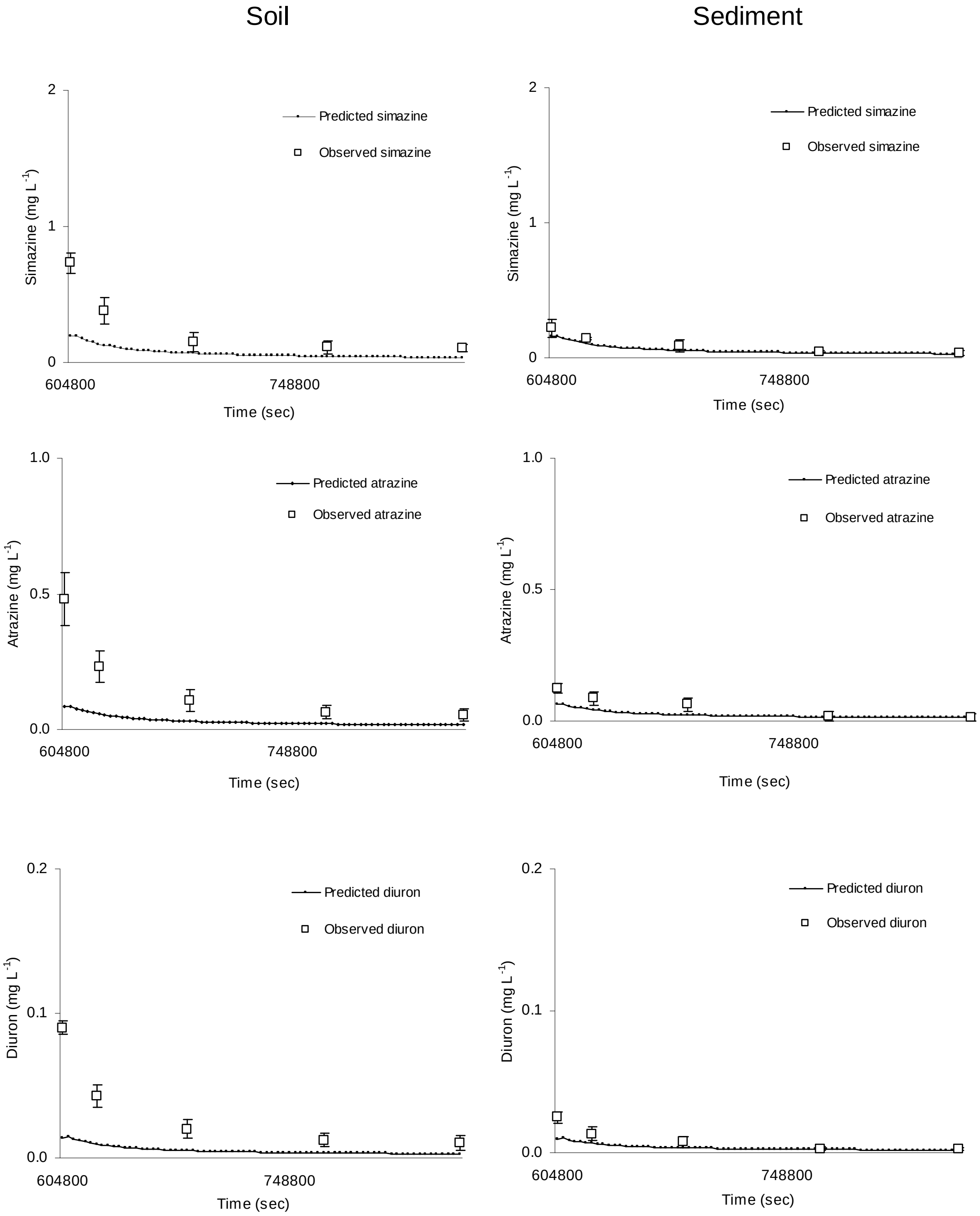

Figure 6.5 Predicted and measured concentration data for (a, d) simazine, (b, e) atrazine and (c, f) diuron released into the overlying water column from the soil and sediment respectively under the drying-rewetting treatment (bars = standard deviation (SD), n = 3).

The normal probability plots of the residuals between the predicted and measured metal and herbicide concentrations under the low salinity, high salinity and the drying-rewetting treatments are shown in Figures 6.6 to 6.11 respectively. The normal probability plots were used to analyse the distribution of the residuals. This was done by plotting the sorted residual values against theoretical values from the standard normal distribution (Go et al., 2008). If the plotted values are linear and in a uniform band around zero, this indicates that the residuals are normally distributed and the model adequately represents the actual system. However, departure from linearity or “tailings” indicates that the residuals are not normally distributed (Go et al., 2008). Such asymmetric distribution of residuals is indicative of an inadequate representation of the actual system by the model (Ljung, 1987; Soderstrom and Stoica, 1989) probably due to mechanisms which were not accounted for in the model.

The distribution of the residuals between the predicted and measured metal and herbicide concentrations under the low and high salinity treatments for the soil and sediment showed distinct tailings at one end of each of the plots (Figure 6.6 to 6.9). Under the drying-rewetting treatment, the residual plots for the metal concentrations showed distinct tailings at one end of each of the plots for the soil but not for the sediment (Figure 6.10). Similarly, the plots of the residuals between the predicted and measured herbicide concentrations under the drying-rewetting treatment showed distinct tailings at one end of each of the plots for the soil but very slight tailings on the plots for the sediment (Figure 6.11). The tailings were in the positive range of residual values on the plots (Figure 6.6 to 6.11) suggesting that the model was under-estimating metal and herbicide release and hence agreeing with the visual observations of the data plots in Figures 6.2 to 6.5 described above. The asymmetric distribution of the residuals is likely due to other mechanisms contributing to the release of the metals and herbicides into the overlying water during the column experiments which were not accounted for in the model.

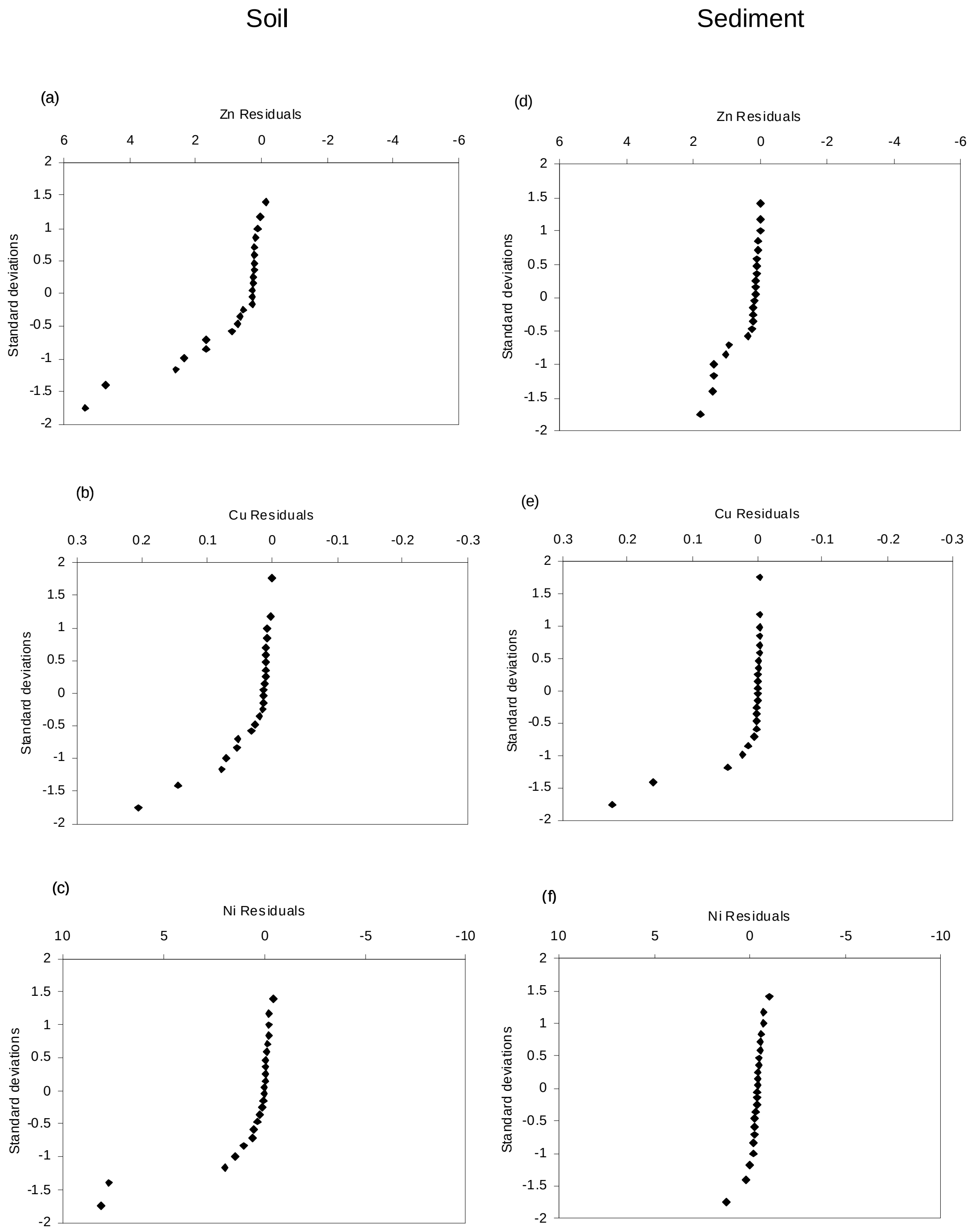

Figure 6.6 Analysis of residuals between the predicted and measured concentration data for (a, d) Zn, (b, e) Cu and (c, f) Ni released into the overlying water from the soil and sediment respectively under the low salinity treatment.

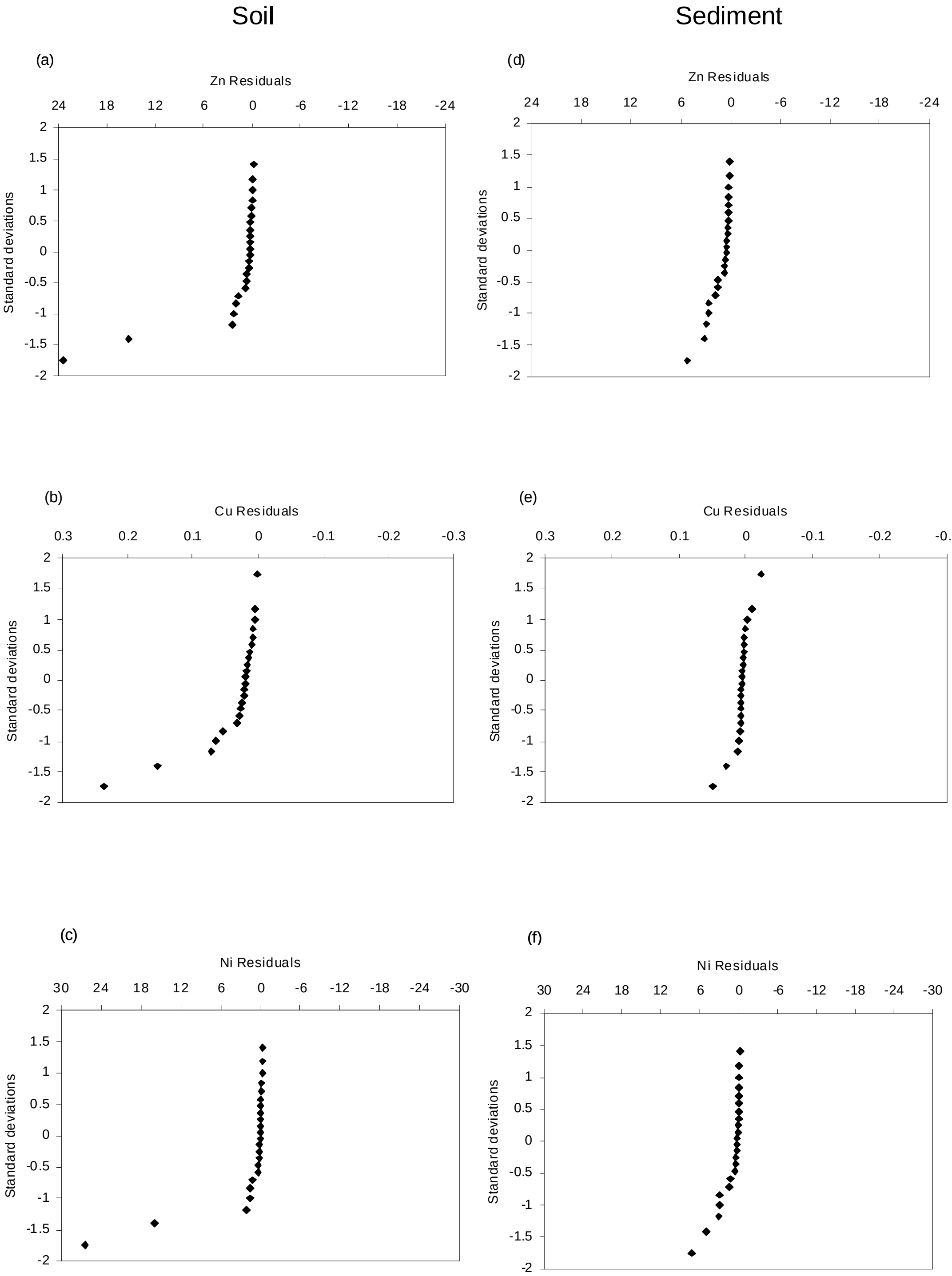

Figure 6.7 Analysis of residuals between the predicted and measured concentration data for (a, d) Zn, (b, e) Cu and (c, f) Ni released from the soil and sediment respectively under the high salinity treatment.

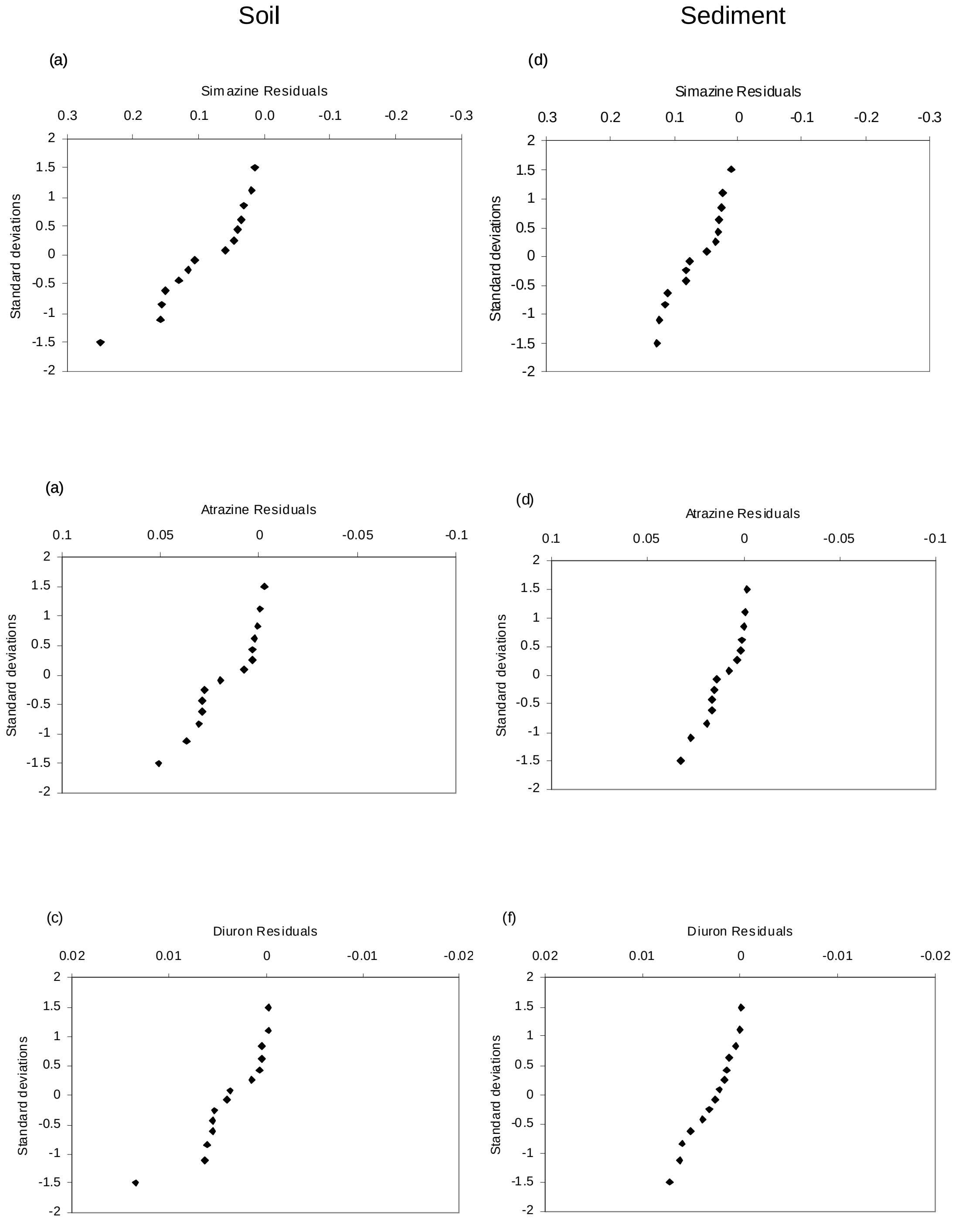

Figure 6.8 Analysis of residuals between the predicted and measured concentration data for (a, d) simazine, (b, e) atrazine and (c, f) diuron released into the overlying water column from the soil and sediment respectively under the low salinity treatment.

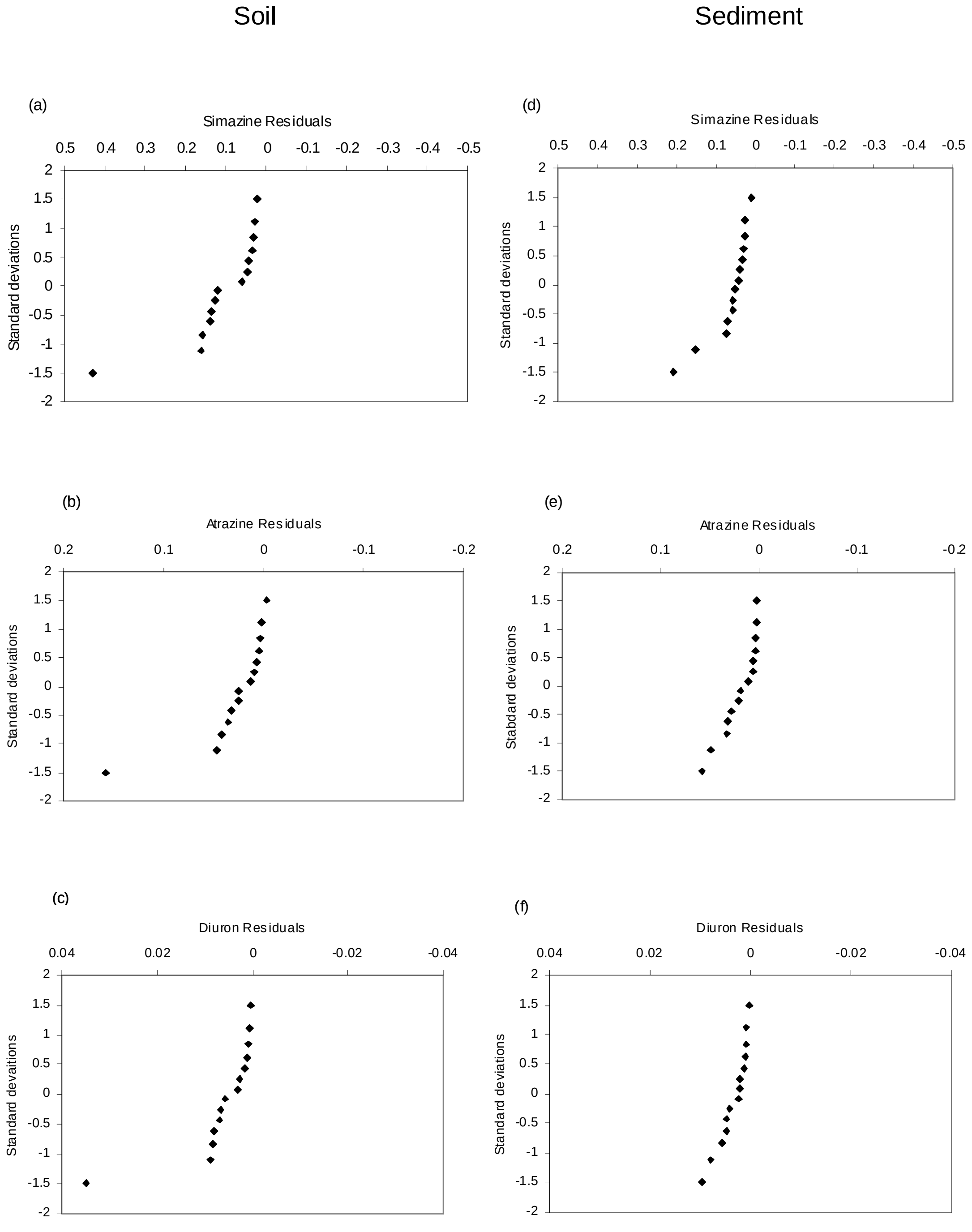

Figure 6.9 Analysis of residuals between the predicted and measured concentration data for (a, d) simazine, (b, e) atrazine and (c, f) diuron released into the overlying water column from the soil and sediment respectively under the high salinity treatment.

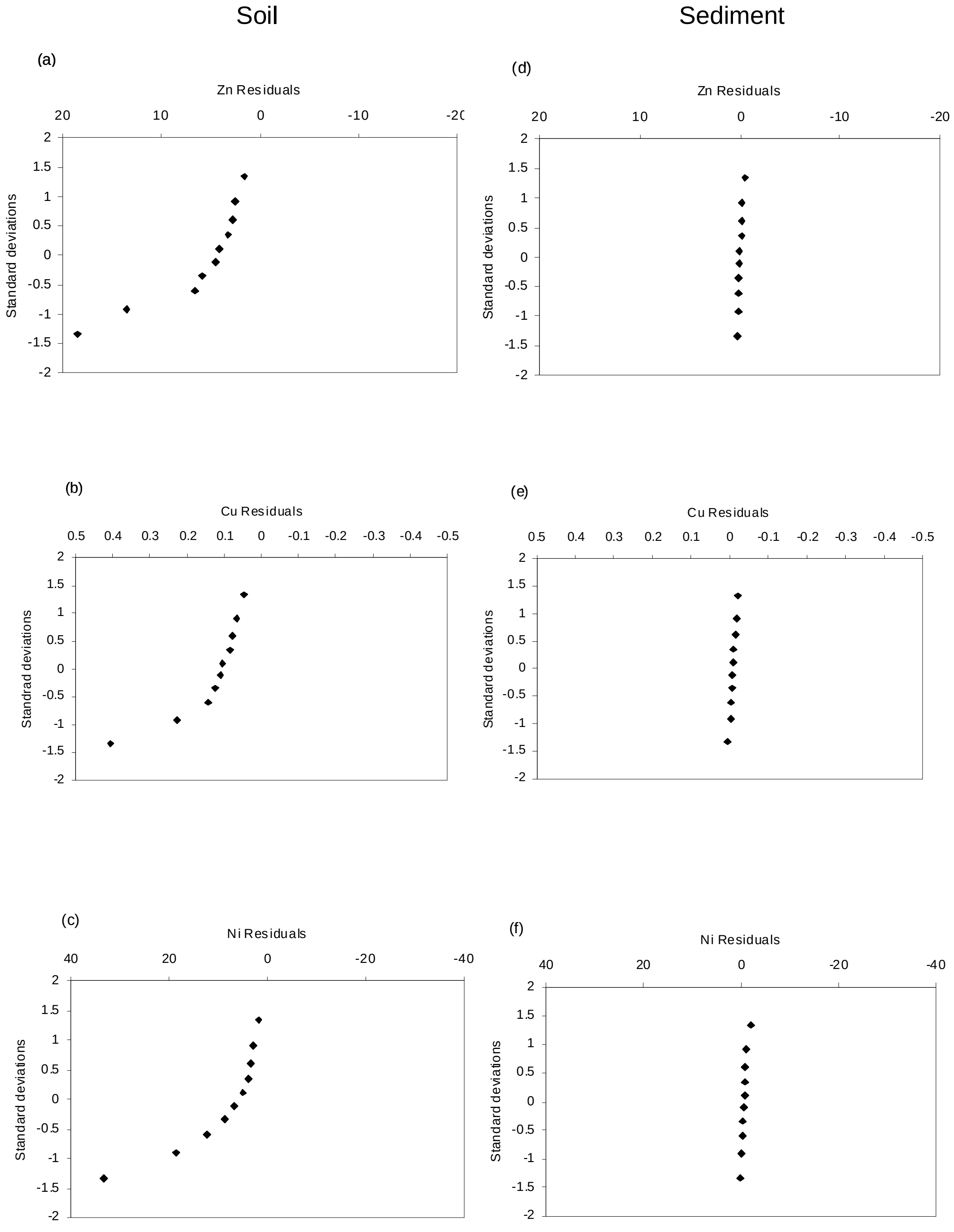

Figure 6.10 Analysis of residuals between the predicted and measured concentration data for (a, d) Zn, (b, e) Cu and (c, f) Ni released from the soil and sediment respectively under the drying-rewetting treatment.

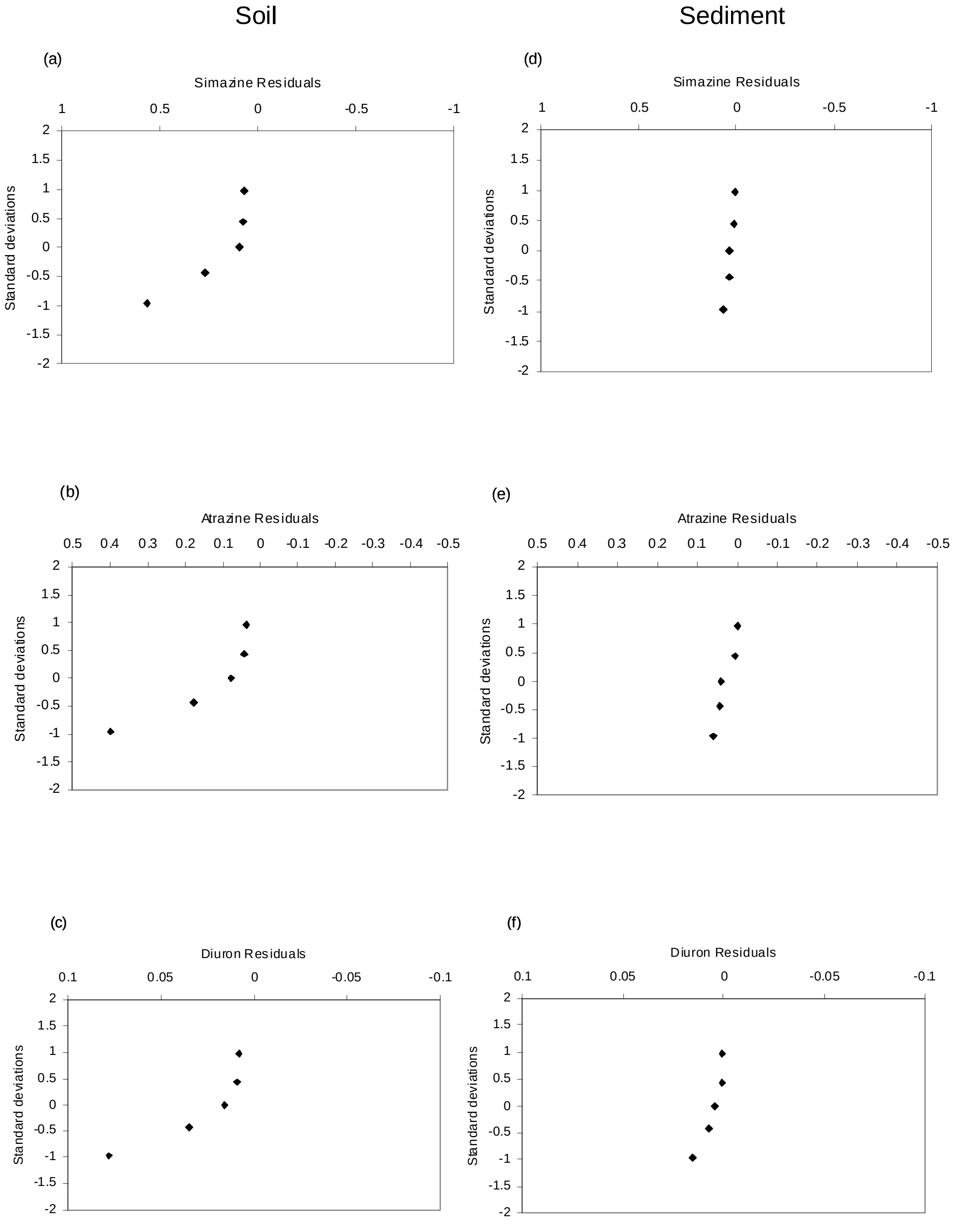

Figure 6.11 Analysis of residuals between the predicted and measured concentration data for (a, d) simazine, (b, e) atrazine and (c, f) diuron released from the soil and sediment respectively under the drying-rewetting treatment.

In order to estimate the rate of release of the predicted and measured metals and herbicides, exponential curves were fitted to the predicted and measured contaminant concentrations under both salinity treatments and the drying-rewetting treatment. The slopes of the fitted curves reflect the rate of the metals and herbicides release under the low and high salinity treatments and the drying-rewetting treatment and are shown in Table 6.3 and Table 6.4 respectively. The rate of release for the measured metal and herbicide concentrations for both the soil and sediment under the low and high salinity treatments were higher than those for the predicted metal and herbicide concentrations under the low and high salinity treatments (Table 6.3). With the exception of Cu and Zn in the sediment, higher rates of release were also observed for the measured metal and herbicide concentrations released from the soil and sediment under the drying-rewetting treatment compared to the predicted concentrations (Table 6.4). The disagreements between the rates of release for the measured and predicted metal and herbicide concentrations further suggests that the model under-estimated the release of the metals and herbicides from the soil and sediment in the column microcosm experiments.

Table 6.3 Slope of the exponential curves fitted to the predicted and measured contaminant concentrations under the low and high salinity treatments

	Soil	Sediment
	Slope (mg L^{-1} sec^{-1})	Slope (mg L^{-1} sec^{-1})
Measured Zn Low salinity	**5.0 x 10^{-3}**	**5.1 x 10^{-3}**
Measured Zn High salinity	**6.5 x 10^{-3}**	**6.0 x 10^{-3}**
Predicted Zn	**3.0 x 10^{-3}**	**3.0 x 10^{-3}**
Measured Cu Low salinity	**5.4 x 10^{-3}**	**5.9 x 10^{-3}**
Measured Cu High salinity	**5.1 x 10^{-3}**	**3.4 x 10^{-3}**
Predicted Cu	**3.1 x 10^{-3}**	**3.1 x 10^{-3}**
Measured Ni Low salinity	**9.0 x 10^{-3}**	**5.2 x 10^{-3}**
Measured Ni High salinity	**10.4 x 10^{-3}**	**6.3 x 10^{-3}**
Predicted Ni	**5.7 x 10^{-3}**	**3.1 x 10^{-3}**
Measured simazine Low salinity	**5.0 x 10^{-3}**	**4.7 x 10^{-3}**
Measured simazine High salinity	**5.0 x 10^{-3}**	**4.0 x 10^{-3}**
Predicted simazine	**3.0 x 10^{-3}**	**3.0 x 10^{-3}**
Measured atrazine Low salinity	**6.9 x 10^{-3}**	**6.7 x 10^{-3}**
Measured atrazine High salinity	**7.0 x 10^{-3}**	**6.0 x 10^{-3}**
Predicted atrazine	**3.1 x 10^{-3}**	**3.1 x 10^{-3}**
Measured diuron Low salinity	**7.2 x 10^{-3}**	**5.2 x 10^{-3}**
Measured diuron High salinity	**6.5 x 10^{-3}**	**5.5 x 10^{-3}**
Predicted diuron	**3.1 x 10^{-3}**	**3.0 x 10^{-3}**

Table 6.4 Slope of the exponential curves fitted to the predicted and measured contaminant concentrations under the drying-rewetting treatment

	Slope mg L^{-1}sec^{-1}	Slope mg L^{-1}sec^{-1}
Measured Zn	**19.3 x 10^{-3}**	**11.0 x 10^{-3}**
Predicted Zn	**12.2 x 10^{-3}**	**12.2 x 10^{-3}**
Measured Cu	**16.3 x 10^{-3}**	**12.2 x 10 $^{-3}$**
Predicted Cu	**12.2 x 10^{-3}**	**12.2 x 10 $^{-3}$**
Measured Ni	**22.0 x 10^{-3}**	**14.5 x 10^{-3}**
Predicted Ni	**12.3 x 10^{-3}**	**12.2 x 10^{-3}**
Measured simazine	**25.4 x 10^{-3}**	**25.3 x 10^{-3}**
Predicted simazine	**20.1 x 10^{-3}**	**20.1 x 10^{-3}**
Measured atrazine	**29.0 x 10^{-3}**	**33.0 x 10^{-3}**
Predicted atrazine	**20.1 x 10^{-3}**	**20.1 x 10 $^{-3}$**
Measured diuron	**28.5 x 10^{-3}**	**32.2 x 10^{-3}**
Predicted diuron	**20.1 x 10^{-3}**	**20.1 x 10^{-3}**

In order to improve the agreement between the model predictions and the observed data, the performance of the model was optimised by adjusting model parameters (i.e. le Bas molar volumes and diffusion coefficients of the herbicides and metals) used for the simulation runs. Table 6.5 shows the goodness-of-fit criteria used to assess the performance of the model after adjusting the model parameters. The coefficients of determination (r^2) increased from 97 % - 98 % to 98 % - 99 % for the metals and from 87 % - 92 % to 91 – 95 % for the herbicides in the soil. In the case of the sediment, the r^2 values increased from 52 % - 97 % to 79 % - 98 % for the metals and from 72 % - 87 % to 83 % – 93 % for the herbicides. The coefficients of determination (r^2) were all significant at the 0.01 probability level. The higher r^2 values indicates that the model performed better in predicting the measured metal and herbicide concentrations in the overlying water in the column experiments after adjusting the model parameters. All the NS coefficients were greater than or equal to 0.4 which was the threshold used in this study to judge the performance of the model (Table 6.5). Ramanarayanan et al. (1997) also used NS coefficient of 0.4 to judge the performance of the Agricultural Policy Environmental Extender (APEX) model as satisfactory. Compared to the mean absolute error (MAE) and the root mean squared error (RMSE) obtained before adjusting the model parameters (Table 6.2), the MAE and RMSE shown in Table 6.5 were closer to zero. Obtaining higher r^2 and NS values and lower MAE and RMSE values after adjusting the model parameters shows a considerable improvement in the agreement between the model predictions and the observed metal and herbicide concentrations released from the soil and sediment into the overlying water in the column microcosm experiments. This increases confidence in the predictive capability of the model.

Table 6.5 Goodness of fit criteria for the evaluation of performance of the refined model

	r^2	MAE	RMSE	NS
Soil **High salinity**				
Zn	0.98	0.52	0.82	0.8
Cu	0.99	0.02	0.05	0.7
Ni	0.98	0.63	0.90	0.6
Low salinity				
Zn	0.98	0.76	0.92	0.7
Cu	0.99	0.03	0.04	0.6
Ni	0.98	0.67	0.80	0.8
Sediment **High salinity**				
Zn	0.85	0.53	0.37	0.5
Cu	0.79	0.01	0.01	0.9
Ni	0.83	0.72	0.94	0.7
Low salinity				
Zn	0.95	0.16	0.21	0.8
Cu	0.98	0.01	0.05	0.9
Ni	0.96	0.25	0.41	0.9
Soil **High salinity**				
Simazine	0.91	0.09	0.001	0.4
Atrazine	0.95	0.01	0.03	0.6
Diuron	0.92	0.009	0.009	0.5
Low salinity				
Simazine	0.92	0.07	0.001	0.4
Atrazine	0.95	0.01	0.01	0.7
Diuron	0.94	0.002	0.01	0.5
Sediment **High salinity**				
Simazine	0.83	0.04	0.05	0.4
Atrazine	0.90	0.01	0.01	0.5
Diuron	0.89	0.001	0.002	0.6
Low salinity				
Simazine	0.91	0.02	0.05	0.5
Atrazine	0.93	0.009	0.01	0.7
Diuron	0.90	0.001	0.002	0.5

6.7. Discussion

Under both the low and high salinity treatment, the data plots showed that the model under-estimated the initial metal and herbicide release into the overlying water from the soil and sediment in the column microcosm experiments with the exception of the initial release of Cu, Ni and atrazine from the sediment (Figure 6.2 and 6.3); the model under-estimation was greater for the soil than the sediment particularly under the high salinity treatment; the normal probability plots of the residuals between the measured and predicted metal and herbicide concentrations showed tailings at one end of each of the plots in Figure 6.6 to 6.9 and the rates of release of the measured metal and herbicide concentrations from the soil and sediment were higher compared to those of the predicted concentrations (Table 6.3). These observations suggest that the model under-predicted the metals and herbicides release into the overlying water from the soil and sediment in the column microcosm experiments. This is likely due to other mechanisms in addition to diffusion contributing to the release of the metals and herbicides under the experimental conditions.

Competition and complexation between the seawater cations (Na^+, Ca^{2+}, K^+ and Mg^{2+}), anions (Cl and SO_4^{2-}) and the sorbed metals are likely mechanisms which occurred during the column experiments in addition to diffusion. Several studies have observed that seawater cations and anions are effective in mobilizing sorbed metals such as those considered in this study from soil and sediment into solution through competition and complexation reactions respectively (Emmerson et al., 2001; Paalman et al., 1994; Millward and Liu, 2003). The lower coefficients of determination (r^2) for the predicted and measured metal concentrations released from the sediment under high salinity treatment (Zn (0.62); Cu (0.52) and Ni (0,74)) compared to the low salinity treatment (Zn (0.89); Cu (0.97) and Ni (0.93)) (Table 6.2) and the greater model under-estimation of metal release from the soil under the high salinity treatment compared to low salinity treatment (Figure 6.2) suggests a greater formation of complexes between the seawater anions and the sorbed metals and the greater displacement of sorbed metals by seawater cations for cation exchange binding sites at high salinity compared to low salinity.

Resuspended particles can lead to contaminant transport into the water column when sufficient energy from advecting water is available to raise particles into the water column (Calamari, 1993). In this study, particles from the soil/sediment-water interface may have been re-suspended into the water column due to the influx of artificial seawater into the column microcosm during the experiments which in turn may have led to higher measured metal and herbicide concentrations in the overlying water compared to the predicted concentrations. The lower model under-estimations for the sediment compared to the soil suggests that particle resuspension likely occurred during the column microcosm experiments and contributed to the release of metals and herbicides into the overlying water. Fine-grained sediments such as those used in the column experiments are readily compacted and cohesive due to strong electrostatic forces which bind the particles together to form a cohesive mass, making them resistant to entrainment and resuspension (Masselink and Hughes, 2003; Pethick, 1984). Therefore, the sediments are likely to be more resistant to resuspension than the soil. In addition, fine particles with diameters less than 10 µm are more difficult to entrain than particles with diameters greater than 10 µm, with the degree of difficulty increasing as the particle diameter decreases (Masselink and Hughes, 2003),. In this study, 50 % of the particles in the sediment had a diameter less than 10 µm while only 25 % of the particles in the soil had a diameter less than 10 µm. This suggests that the sediment particles were less resuspendible than the soil particles which in turn resulted in less metals and herbicides release from the sediment into the overlying water compared to the soil.

Under the drying-rewetting treatment, the data plots showed that the model under-estimated the initial metal release from the soil but not from the sediment (Figures 6.4); the normal probability residual plots for the metals showed distinct tailings at one end of each of the plots for the soil but not for the sediment (Figure 6.10) and the rate of release were higher for the measured metal concentrations compared to the predicted concentrations for the soil but not for the sediment except for Ni (Table 6.4). For the herbicides, the data plots showed that the model under-estimated the initial herbicide release from both the soil and sediment but the under-estimation was greater for the soil than the sediment (Figures 6.5); the normal probability residual plots for the herbicides showed tailings at one end of each of the plots for the soil but only very slight tailings were observed for the sediment (Figure 6.11) and the rates of release of the measured herbicide concentrations from the soil and sediment were higher compared to those of the predicted concentrations (Table 6.3). These observations suggest that diffusion is likely the dominant mechanism controlling the release of the metals from the sediment after drying and rewetting except for Ni. Other mechanisms were contributing to the release of the metals and herbicides from the soil and herbicides from the sediments hence the observed model under-estimations. DOC can form complexes with metals and herbicides such as those considered in this study which can facilitate their mobility in soils and sediments (Weng et al., 2002; Sauve et al., 2000; Kalbitz and Wennrich, 1998; Garber et al., 1995; Nelson et al., 2001; Williams et al., 2000). Accordingly, DOC complexation with the metals and herbicides is likely to be contributing to the release of the metals and herbicides from the soil and the release of herbicides from the sediments in the column experiments in addition to diffusion. Reemtsma et al. (2000) and Miller et al. (2005) observed an increase in DOC concentrations in soil as a result of an increase in organic matter mineralisation with drying and rewetting of soil. The difference between the soil and sediment is likely a consequence of higher DOC-contaminant associated release from the soil than the sediment under the experimental conditions. The strong association of Ni with DOC which results in its low particle affinity (Turner et al., 1998) may account for the higher rates of release of Ni from the sediment compared to the other metals. The visual observations are consistent with the results of the linear regression analysis of the DOC, metal and herbicide concentrations discussed in Chapter 5 (Chapter 5, Section 5.3.2.2 to 5.3.2.5). For the soil, the results of the linear regression showed that there were strong significant relationships between the DOC and the metals released into the overlying water with 50 %, 79 % and 55 % of the variations in the Cu, Ni, Zn concentrations explained by the variation in the DOC concentrations ($p < 0.05$). Similarly, there were significant relationships between the DOC and the herbicides released into the overlying water with the variations in the DOC concentrations accounting for 65%, 68% and 76% of the variations in the atrazine, diuron and simazine concentrations respectively ($p < 0.05$). But for the sediment, the relationship between DOC, the metals and herbicides released into the overlying water were not significant ($p > 0.05$). Only 41%, 31% and 22% of the variations in simazine, atrazine and diuron concentrations and 13 %, 28 % and 8 % of the variations in the Zn, Ni and Cu concentrations in the overlying water could be explained by the variation in the DOC concentrations. The variation in the Ni concentrations explained by the DOC concentrations was higher compared to the other metals. These results suggested that significant proportions of the metals and herbicides were released as DOC-complexes from the soil but not from the sediment hence agreeing with the visual observations from the normal probability residual and data plots for the metals and herbicides release under the drying-rewetting treatment.

6.8 Summary and conclusion

By using a diffusion model, this chapter has shown that other mechanisms, in addition to diffusion, contributed to metal and herbicide release from the soil and sediment into the overlying water in the column experiments under the experimental conditions in this study. The goodness-of-fit criteria showed that the model performed reasonably well in simulating the metal and herbicide release from the soil and sediment into the overlying water column in the column experiments. Visual observations of the data plots, the normal probability residual plots and the rates of release for the measured and predicted metal and herbicide concentrations indicated that the model under-predicted the metals and herbicides release from the soil and sediment into the overlying water column in the column experiments. This was attributed to other mechanisms occurring during the column experiments but not accounted for in the model. The lower coefficients of determination and, the greater model under-estimation under the high salinity treatment compared to the low salinity treatment suggested that salinity effects due complexation and competition reactions contributed to the release of the metals into the overlying water in the column experiments. The observed difference in the model under-estimations for the soil and sediment under the salinity treatments indicated that particle resuspension is also likely to have contributed to the metals and herbicides release into the overlying water in the column experiments. Under the drying-rewetting treatment, DOC association with the metals and herbicides is likely to have contributed to the metals and herbicides release in the experiments particularly from the soil.

Chapter 7: Synthesis and conclusion

7.1. Introduction

The recognition of the intrinsic value of salt marshes as part of the coastal ecosystem and the threat to salt marshes due to rising sea levels has led to the current strategy of managed realignment. The main goals of managed realignment in the UK are habitat restoration and the enhancement of coastal flood defence. The restored salt marsh compensates for salt marsh loss due to coastal squeeze and provides a cost effective and sustainable seawall for coastal areas by dissipating wave energy (Shepherd et al., 2007; Moller et al., 1999). Managed realignment is usually implemented on reclaimed agricultural land. However, in low-lying areas, dredged sediments are beneficially re-used to raise the elevation of land for salt marsh plant development. One of the subsidiary justifications for the implementation of managed realignment is that they can be important sinks for metals and other particle reactive contaminants from estuarine waters (NRA, 1994; Macleod et al; 1999; Andrew et al., 2006; Cave et al., 2005). However, managed realignment sites may serve as a source of contaminants to the estuarine waters due to changes in the physical and chemical conditions in the soil and sediment following tidal inundation.

The overall aim of this thesis was to examine the potential for metal and herbicide release from agricultural soil and dredged sediment in managed realignment sites following tidal inundation. In order to achieve this aim, a series of investigations were conducted which include a field study, laboratory experiments and a model investigation. The field study examined the physical and chemical changes in sediments exposed to drying-wetting cycles and salinity changes in the Wallasea Island managed realignment site in order to inform the laboratory experiments, and examined by comparison, whether the sediments parameters in the restored salt marsh and mudflat were approaching those in a natural salt marsh and mudflat (Chapter 2). Wallasea Island managed realignment site is the largest managed realignment site in the UK where dredged sediments have been beneficially re-used to raise the elevation of the site for salt marsh plant development. The laboratory experiments examined the effect of salinity and, drying and rewetting on the release of metals and herbicides from agricultural soil and dredged sediments (Chapter 5). A diffusion model was used to investigate the mechanisms of metal and herbicide release from the soil and sediment in the column experiments under the experimental conditions in this study (Chapter 6).

7.2 Summary of findings

The field study (Chapter 2) showed that the sediment organic matter content, bulk density, porosity and pH values in the restored salt marsh and mudflat were maintained during the 12-month study period at Wallasea Island managed realignment site with little or no changes observed. However, considerable seasonal changes were observed in the moisture content, porewater Cl and DOC concentrations. Lower moisture contents and higher porewater Cl concentrations were observed in the sediment in the summer compared to the winter due to higher atmospheric temperatures and hence, higher evaporation in the summer. Higher porewater DOC concentrations in the restored salt marsh were also observed in the summer, probably due to increased microbial biomass activity, higher decomposition rates and the presence of the filamentous green alga *Enteromorpha* sp. which is likely to have provided an additional carbon source for decomposition. The comparison of the sediment parameters in the restored salt marsh and mudflat within the managed realignment site and a nearby natural salt marsh and mudflat showed that while the sediment parameters in the restored and natural mudflats were similar, most of the sediment parameters in the restored and natural salt marshes (i.e. organic matter content, moisture content, bulk density, porosity, pH and porewater Cl) were different. The lack of an additional source of organic matter from plant litter and organic matter accumulation is likely to have resulted in the significantly lower organic matter content in the restored salt marsh compared to the natural salt marsh. The lower sediment organic matter content contributed to the lower moisture content, higher bulk density and lower porosity in the restored salt marsh compared to the natural salt marsh. The sediment pH values were lower in the natural salt marsh compared to the restored salt marsh probably due to the precipitation of metal ions as carbonates which generated H^+ that countered those consumed by reduction in the alkaline, water-saturated sediments in the natural salt marsh. These findings indicated that the sediment parameters in the restored salt marsh were far from approaching those in the natural salt marsh and further years may be required before they become similar.

The sediment porewater Cl concentrations were used as a proxy for salinity and the seasonal range (i. e. the maximum and minimum monthly average concentrations in the summer and winter respectively) were used as the two different salinity treatments (i.e. 5 and 20 referred to as low and high salinity) in the laboratory column microcosm experiments (Chapter 5) which examined the effect of salinity on the release of metals and herbicides from agricultural soil and dredged sediment in managed realignment sites. Higher total metal loads (Ni and Zn) were released from the soil and sediment into the overlying water at high salinity compared to low salinity due to an increase in the competition and complexation reactions between the seawater cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), anions (Cl and SO_4^{2-}) and the sorbed metals (Chapter 5). This observation agrees with those from other studies which have also observed metal desorption and release into saline water due to complexation and competition effects (Paalman et al., 1994; Millward and Liu, 2003). The model predictions in Chapter 6 supports this finding from the laboratory experiments that salinity effect due to complexation and competition reactions contributed to metal release. This was indicated by the greater model under-estimations, lower coefficients of determination for metal release into the overlying water at high salinity compared to low salinity (Chapter 6). In addition, the strength of binding of the metals to the soil and sediment was also important for metal release into the overlying water at low and high salinity (Chapter 5). The total metal loads released into the overlying water followed the order Cu < Zn < Ni due to the strength of binding of the metals to the soil and sediment (which was in the order Cu > Zn > Ni) with the metal release higher from the soil than the sediment. In the case of the herbicides, the release from the soil and sediment into the overlying water at low and high salinity was primarily dependent on the strength of binding of the herbicides to the soil and sediment organic matter and followed the order simazine < atrazine < diuron (Chapter 5). The model predictions also indicated that particle resuspension was likely to have contributed to metal and herbicide release from the soil and sediment into the overlying water at low and high salinity (Chapter 6). This was indicated by the observed difference in the model under-estimations for the soil and sediment.

As earlier described in Chapter 1, drying and rewetting can result in the disruption of soil aggregates which exposes organic matter previously trapped within the soil. The exposure of the organic matter increases microbial activity which can result in an increase in the mineralisation of soil organic matter (Lundquist et al., 1999; Appel, 1998;

Fierer and Schimel, 2003). The increased mineralisation of organic matter may result in contaminant release given that organic matter is an important binding site for metals and herbicides. The experiments which examined the effect of drying and rewetting on the release of metals and herbicides from soil and sediment tested the hypothesis that organic matter mineralisation will be increased during drying and rewetting of the soil and sediment leading to the release of organic matter associated metals and herbicides into the overlying water (Chapter 5). The experimental conditions were based on the frequency of tidal inundation in the Wallasea Island managed realignment site (Chapter 2). Drying and rewetting resulted in an increase in the mineralisation of soil organic matter and an increase in the release of DOC from the soil. This was due to increased microbial activity on the soil organic matter previously protected within the soil aggregates but made available to the microbes by drying and rewetting. This in turn led to the release of organic matter associated metals and herbicides from the soil into the overlying water reflected in the higher total metal and herbicide loads released into the overlying water after drying and rewetting compared to the fully wet experimental conditions. The results of a linear regression analysis provided evidence that the release of the metals and herbicides as DOC-complexes contributed significantly to metal and herbicide release from the soil into the overlying water particularly for Ni which is likely due to its known strong association with DOC (Turner et al., 1998).

In the sediment, increased mineralisation was also observed due to drying and rewetting. But unlike the soil, the increased mineralisation in the sediment was due to increased microbial activity on dead microbes which resulted from the death of part of the microbial population during drying rather than the sediment organic matter. This was indicated by the observed decrease in the sediment microbial biomass after drying the sediment which is likely to have provided a readily mineralisable labile organic carbon source. Estuarine sediments such as those used in this study, generally have organic matter that are highly degraded and refractory with their labile organic matter fraction extensively mineralised (Baldock et al., 2004; Cotano and Villate, 2006; Hedges and Oades, 1997; Gallizia et al., 2004). This may also have contributed to the difference in the source of carbon that was mineralised in the soil and sediment. No reduction in the sediment organic matter content was observed during the field study (Chapter 2), further suggesting that the sediment organic matter was not the carbon source that was responsible for the increased mineralisation observed after drying and rewetting during the laboratory microcosm experiments. Hence, organic matter associated metals and herbicides were unlikely to be released into the overlying water in these experiments. The total herbicide and metal loads released from the sediment into the overlying water were lower under the drying and rewetting compared to the fully wet experimental conditions probably due to the microbial degradation of the herbicides and the adsorption of the metals to Fe and Mn oxides formed during the 7-days drying period. The results of a linear regression analysis provided evidence that the release of the metals and herbicides as DOC-complexes was not significantly contributing to metal and herbicide release from the sediment into the overlying water (Chapter 5). These findings indicate that there is a greater potential for the release of organic matter associated and DOC associated metals and herbicides from the soil than sediment due to the effect of drying and rewetting on the mineralisation of organic matter.

The total metal and herbicide loads released from the soil into the overlying water were significantly lower after the second drying and rewetting of the soil compared to the first drying and rewetting. This is probably due to less release of organic matter associated and DOC associated metals and herbicides into the overlying water after organic matter mineralisation in the first drying and rewetting of the soil and less metals and herbicides in the soil for release at the start of the second drying and rewetting. Similarly, lower total metal and herbicide loads were released into the overlying water after the second drying and rewetting of the sediment compared to the first drying and rewetting. This suggests further metal adsorption to Fe and Mn oxides and herbicide degradation during the 7-days drying period. Less herbicides in the sediment for release after their degradation under the first drying-rewetting treatment may also have contributed to the lower total herbicide loads released into the overlying water under the second drying-rewetting treatment.

Regarding the temporal metals and herbicides release patterns, the column experiments identified an initial rapid metal and herbicide release phase followed by a much slower continuous release phase (Chapter 5). The metals and herbicides readily available in the porewater and weakly sorbed to the soil and sediment particles are likely to have been released during the initial rapid phase while the metals and herbicides strongly bound to the soil and sediment due to transfer from weak to strong binding sites on particle surfaces and diffusion into pores, Fe oxides and organic matter matrix were slowly released during the latter phase. The slow continuous release indicates that metals and herbicides release from agricultural soil and dredged sediment from managed realignment sites following tidal inundation may continue for extended periods of time after the initial rapid release.

This study has provided valuable insight into the changes in sediments beneficially re-used to raise the elevation of low-lying agricultural land for salt marsh development in managed realignment sites. Such information will be beneficial in evaluating the status of similar schemes. This research has identified important processes which influence metal and herbicide release from agricultural soil and dredged sediment following tidal inundation in managed realignment sites which have been previously overlooked. These include the complexation of DOC with metals and herbicides which facilitates their release into estuarine waters, the mineralisation of organic matter due to increased microbial activity and the subsequent release of organic matter associated contaminants and the complexation and competition reaction between sorbed metals, seawater anions and cations following tidal inundation leading to the release of metals. This research has also highlighted that metals and herbicides release from agricultural soil and dredged sediment in managed realignment sites may persist for weeks and even months after an initial rapid release. These findings improve our current understanding of the processes controlling contaminant release from managed realignment sites. In addition, with climate change and global sea levels expected to rise by 44 ± 23 cm by 2070, the frequency of storminess and the occurrence of catastrophic events are predicted to increase (IPCC, 1990). This suggests that low-lying countries such as Bangladesh and Thailand are likely to be flooded over the next 60 years and this study gives some indication of what the fate of agricultural soil associated contaminants in these countries might be.

7.3 Limitation of study

Microcosm experiments have been performed in the laboratory to study processes in aquatic and terrestrial systems (Johnson et al., 1986; Ortiz et al., 2004; Valsaraj et al., 1996). This is mainly because microcosms are considered analogous to natural systems (Tueben and Verhoef, 1992). However, the degree to which the microcosm experimental conditions simulate the natural system is an important criterion for extrapolation of the microcosm experimental results to the field situation (Tueben and Verhoef, 1992). In this study, laboratory column microcosm experiments were conducted to examine the potential for metal and herbicide release from agricultural soil and dredged sediment following tidal inundation in managed realignment sites. These experimental conditions were based on the salinity conditions and the drying-wetting cycles (through the estimated frequency of tidal inundation) at the Wallasea Island managed realignment site. In addition, on-site field conditions were used to design the laboratory microcosm experiments (Chapter 3, Section 3.3.2). This ensured that the experiments simulated conditions at Wallasea Island managed realignment site and similar sites so that the findings from the microcosm experiments could be extrapolated to these sites. However, the soil and sediment used in the microcosm experiments were spiked with relatively high herbicide concentrations and with metal concentrations that were within the range expected in moderately to heavily contaminated sediments (Simpson et al., 2004; Burton et al., 2006). The spiking concentrations ensured that the metal and herbicide concentrations released from the soil and sediment into the overlying water during the column microcosm experiments exceeded the limit of detection of the analytical techniques used. In the UK, managed realignment schemes are unlikely to be implemented on agricultural land or by using dredged sediments with this level of contamination. The licensing process for the Wallasea Island managed realignment site included an evaluation of the sediment quality before they were beneficially re-used. This involved the analysis of metals and organic contaminants in the sediment to determine if their concentrations were below the threshold levels in the CEFAS (Centre for Environment, Fisheries and Aquaculture Science) sediment quality guidelines as there are currently no European Union sediment quality guidelines (Birchenough pers comm., 2006). The concentrations of the spiked soil and sediment used for the microcosm experiments exceeded the threshold levels in the sediment quality guidelines. As a result, it was not possible to estimate, using the concentrations measured in the overlying water in the column microcosm experiments, the metal and herbicide concentrations that can potentially be released into estuarine waters in managed realignment sites in the UK. Hence, the potential ecotoxicological risks to estuarine biota in these environments could not be estimated. However, this study has improved our current understanding of the processes controlling the release of soil/sediment-associated contaminants in managed realignment sites following tidal inundation. Furthermore, in countries where there are no sediment quality guidelines, dredged sediments with the level of contaminants used in this study could be beneficially re-used during managed realignment. The contaminant concentrations released into the overlying water in this study can be useful in estimating the contaminant loads that may potentially be released into overlying water in such managed realignment schemes.

7.4 Recommendations

Based on the findings in this study (Section 7.2), several recommendations are made below which are likely to minimise the potential for metal and herbicide release from managed realignment sites following tidal inundation.

(1) This study has shown that there is a greater potential for the release of metals and herbicides into overlying water from agricultural soil than dredged sediment. Based on this, consideration should be given to implementing managed realignment schemes on sites where dredged sediments can be beneficially re-used rather than agricultural land. Presently in the UK, more managed realignment sites have been implemented by flooding agricultural land and only a few schemes exist where dredged sediments are beneficially re-used. This recommendation is also relevant for the management of coastal areas in other countries such as the low-lying Baltic Sea coast in Germany where there are plans for the implementation of several managed realignment schemes (Rupp and Nicholls, 2002).

(2) This study has revealed that the release of metals and herbicides into the overlying water was lower from dried-rewet sediment compared to fully wet sediment. Therefore, sediments should be completely dried-out before tidal inundation in sites where dredged sediment are beneficially re-used as this can reduce the potential release of contaminants following tidal inundation.

(3) This study also indicated that particle resuspension contributed to metal and herbicide release from the soil and sediment into the overlying water. Hence, measures that minimise particle resuspension in managed realignment sites are likely to also minimise contaminant release and these should be considered. This may be achieved by planting salt marsh vegetation in these sites as this improves sediment stability and minimises particle resuspension.

7.5. Scope for future work

- Field scale mesocosms experiments which examine contaminant release should be carried out. This will aid in assessing the risk posed by the release of contaminants from managed realignment sites on estuarine water quality and biota. This will also provide the opportunity to examine the effect of biological processes such as bioturbation on contaminant release (which was not investigated in this study) in these environments. It is unknown how this process would affect contaminant release or the observations from the laboratory microcosm experiments conducted in this study.
- Additional experiments should be carried out to examine the microbial degradation of herbicides in the soil and sediment under field conditions. This will identify the importance of microbial degradation relative to the herbicide release mechanisms.
- A contaminant reaction and transport model which provides quantitative estimates of contaminant concentrations that could potentially be released from agricultural soil and dredged sediment following tidal inundation in managed realignment sites would be beneficial for informing management decisions. Such a model could be useful for estimating contaminant release from potential managed realignment sites. In addition, the model could also assist site managers in assessing site specific risks in the short-, medium- and long-term. This could inform risk-based decision making and assist in developing comprehensive site management strategies. Hence, further work on refining the contaminant diffusion model developed in this study should be carried out to enable its usage as a management tool for managed realignment sites.

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Appendix 1 Sediment moisture content (%) data in the restored saltmarsh (RSM), restored mudflat (RMF), natural saltmarsh (NSM), natural mudflat (NMF) and moisture content (%) data in the restored and natural saltmarshes at 8 – 10 cm depth.

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	51.2	86.8	41.9	52.0	19.0	22.4	11.0	43.1	47.1	36.3	60.0	70.6
RSM2	60.6	86.7	49.5	47.0	20.4	33.7	17.9	46.4	45.1	50.9	71.2	71.0
RSM3	59.3	88.2	68.9	42.3	18.8	20.8	40.1	43.5	46.2	44.8	60.3	71.8
RSM4	69.8	83.5	64.7	66.0	19.4	33.6	25.0	50.5	48.1	53.1	58.9	66.0
RSM5	73.4	89.2	73.8	44.2	19.7	46.8	19.7	49.0	43.5	46.0	61.5	69.1
RSM6	65.4	92.1	87.7	68.9	21.7	33.0	40.4	44.9	45.6	52.3	58.0	67.9
RSM7	58.8	84.2	72.4	56.0	18.7	32.0	32.9	47.7	49.6	42.4	70.7	66.3
RSM8	62.2	92.5	54.3	73.9	17.7	31.6	25.2	52.6	46.1	55.9	66.1	69.9
RSM9	64.2	83.7	52.2	106.8	22.3	33.7	16.1	46.7	43.6	50.0	57.8	61.3
RSM10	59.7	90.2	56.6	55.3	22.3	42.9	36.4	43.9	40.8	51.4	67.7	68.7

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JUY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RMF1	113.7	160.6	98.6	173.3	143.4	166.2	144.5	139.4	149.4	157.7	118.8	141.8
RMF2	91.1	155.5	153.7	126.9	155.7	147.4	146.6	101.5	142.3	111.6	104.3	138.0
RMF3	91.6	120.5	140.8	158.4	152.2	141.0	148.0	128.5	135.4	172.3	126.0	129.7
RMF4	150.4	119.5	155.5	151.6	158.3	142.3	133.9	108.8	112.7	143.2	109.1	107.8
RMF5	98.4	148.9	112.1	134.4	142.1	139.6	143.4	142.0	120.7	142.7	129.0	120.1
RMF6	103.4	106.0	163.7	148.0	152.9	127.8	145.6	127.0	110.6	131.8	124.5	113.2
RMF7	79.1	167.8	172.7	127.6	134.8	152.6	123.6	82.6	103.2	140.7	116.0	86.5
RMF8	128.6	163.1	151.7	127.0	182.7	132.3	139.0	119.2	130.3	168.8	104.6	104.8
RMF9	94.5	146.7	128.1	156.6	152.0	120.4	141.0	131.1	127.0	134.3	101.8	104.6
RMF10	119.4	133.9	158.5	167.7	153.6	140.4	124.1	128.9	146.4	125.6	83.8	93.6

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1	151.0	265.9	247.7	205.5	176.3	171.6	205.9	213.7	211.3	133.2	168.6	196.9
NSM2	222.3	224.4	160.9	239.7	90.0	167.1	151.7	198.8	168.0	197.5	164.5	183.1
NSM3	131.2	197.8	227.1	256.4	175.6	190.3	148.5	113.4	212.4	67.4	191.7	140.2
NSM4	219.3	119.6	218.8	232.1	177.1	175.6	157.3	108.2	221.4	144.9	216.8	194.9
NSM5	108.9	144.0	279.6	144.4	110.3	179.6	122.4	184.5	132.2	246.3	278.9	219.2
NSM6	141.8	162.6	140.3	125.2	95.1	111.1	86.9	162.2	169.7	257.1	178.0	243.9
NSM7	118.7	115.4	196.4	127.1	100.4	146.3	100.5	256.2	190.7	207.7	100.1	205.2
NSM8	132.0	274.3	168.0	165.0	89.5	136.4	106.1	274.9	241.1	218.0	149.3	215.0
NSM9	196.8	110.4	221.5	98.9	90.9	107.3	91.3	104.0	205.6	217.1	221.3	180.2
NSM10	222.7	145.2	168.2	112.6	212.4	88.8	72.8	106.7	159.6	96.0	255.3	193.7

	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NMF1	147.4	112.5	115.8	84.7	104.7	90.6	161.2	111.0	100.8
NMF2	126.6	109.7	102.6	61.6	107.5	104.1	151.4	109.2	118.3
NMF3	146.4	97.7	122.3	86.2	113.6	101.2	128.2	109.0	127.9
NMF4	136.9	104.6	110.1	79.7	133.8	111.2	166.7	109.3	121.9
NMF5	135.5	109.6	120.6	100.6	107.4	111.5	138.1	107.8	132.0
NMF6	164.7	107.4	139.5	97.6	122.4	115.8	152.0	114.7	117.9
NMF7	148.8	113.6	131.4	97.4	121.2	139.3	160.6	115.9	106.5
NMF8	164.6	116.4	128.2	111.7	128.1	120.4	120.8	117.9	93.9
NMF9	169.6	110.1	139.8	114.4	119.6	103.8	138.5	112.8	107.7
NMF10	148.0	115.1	157.1	78.8	123.8	125.3	136.1	110.0	100.6

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1 (8-10cm)	70.8	61.5	67.6	61.0	80.7	66.3	75.5	76.0	49.4	81.4	63.5	83.5
RSM2 (8-10cm)	45.0	73.0	64.9	65.8	60.6	67.4	66.7	64.7	79.5	78.2	67.6	64.4
RSM3 (8-10cm)	72.8	103.8	76.8	64.4	76.9	64.8	72.0	69.7	71.5	72.8	72.4	73.2
RSM4 (8-10cm)	80.0	98.6	78.4	77.3	74.6	80.8	71.8	62.4	83.3	81.6	73.5	68.4
RSM5 (8-10cm)	76.0	127.7	82.5	84.9	82.9	84.0	75.1	74.6	66.5	64.7	68.9	63.4

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1 (8-10cm)	208.4	207.4	170.7	101.3	116.4	153.1	181.8	159.4	137.9	165.6	175.2	150.8
NSM2 (8-10cm)	127.3	161.0	163.5	87.4	96.7	194.1	143.1	140.1	105.0	171.1	112.2	146.1
NSM3 (8-10cm)	170.0	183.7	198.7	124.9	155.7	154.9	128.7	126.4	165.2	131.4	203.5	135.5
NSM4 (8-10cm)	100.5	171.5	172.9	186.9	182.2	165.4	126.8	113.4	151.5	142.5	200.5	162.8
NSM5 (8-10cm)	161.1	134.0	170.5	239.5	150.2	152.2	113.4	118.6	171.9	161.0	141.1	135.5

Appendix 2 Sediment organic matter content (%) data in the restored saltmarsh (RSM), restored mudflat (RMF), natural saltmarsh (NSM), natural mudflat (NMF) and organic matter content (%) data in the restored and natural saltmarshes at 8 – 10 cm depth.

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	7.3	9.4	9.6	11.5	9.4	7.9	7.6	8.7	10.4	7.9	6.7	6.9
RSM2	8.1	9.6	8.2	11.4	9.8	8.4	10.4	9.2	10.3	12.8	8.6	9.3
RSM3	9.5	9.4	9.5	11.9	10.6	9.3	11.0	9.4	11.3	7.7	8.8	8.6
RSM4	11.4	8.6	9.4	12.5	9.3	9.9	11.0	10.9	10.2	11.2	9.1	8.9
RSM5	10.8	8.9	9.6	12.1	12.3	10.0	12.0	10.5	9.6	10.5	9.1	11.6
RSM6	8.7	8.6	10.5	12.2	11.2	9.6	10.5	10.2	9.4	10.4	8.6	7.8
RSM7	9.2	9.2	9.0	12.2	12.6	12.7	11.4	11.5	9.5	5.5	6.2	10.2
RSM8	11.8	8.8	9.4	13.3	11.9	12.2	12.8	10.7	8.3	10.4	8.3	10.9
RSM9	8.6	9.4	9.9	13.8	13.6	12.3	12.5	12.3	7.7	12.3	7.8	8.9
RSM10	8.8	10.0	9.6	12.1	13.6	12.2	13.0	11.6	5.6	11.5	9.8	10.1

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RMF1	9.3	10.8	11.8	12.3	11.3	11.7	12.4	11.6	11.1	9.4	9.8	10.0
RMF2	8.9	10.8	9.6	10.6	10.2	11.5	12.1	8.9	10.7	8.6	9.3	10.2
RMF3	9.7	9.2	10.4	10.9	11.1	13.9	11.4	10.7	10.8	9.8	11.6	9.1
RMF4	9.9	11.3	9.7	12.6	11.1	11.2	11.7	9.8	9.7	10.1	9.7	11.9
RMF5	10.5	9.4	10.3	11.2	9.5	10.7	12.5	11.3	9.9	10.0	9.9	9.5
RMF6	9.4	8.9	10.4	11.5	10.4	10.0	11.0	11.2	9.3	10.0	10.0	9.3
RMF7	7.1	10.1	10.7	10.9	10.6	11.0	11.7	10.1	10.0	13.4	10.0	8.3
RMF8	9.7	9.9	10.2	10.2	11.2	10.7	10.5	9.9	10.4	9.7	9.8	16.2
RMF9	8.3	10.3	11.1	12.6	12.9	10.0	11.3	11.3	10.0	11.0	9.2	9.7
RMF10	8.7	10.1	10.0	11.3	11.5	10.1	11.2	10.7	10.8	9.7	9.1	8.9

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	14.3	19.5	18.4	21.3	20.0	22.2	23.7	22.7	23.5	18.1	19.5	22.1
RSM2	19.8	21.0	15.0	24.6	14.9	14.9	23.6	19.6	17.6	19.2	14.1	17.4
RSM3	15.4	16.1	17.0	20.5	16.5	20.4	19.3	15.5	20.9	21.2	22.0	16.3
RSM4	17.0	13.3	16.4	19.1	15.7	20.0	19.8	16.0	18.7	17.0	19.6	19.1
RSM5	12.7	14.7	21.6	18.0	15.0	16.6	18.7	17.1	17.0	26.1	25.1	21.4
RSM6	14.1	14.3	15.6	15.7	13.9	16.7	15.0	12.7	14.4	23.3	15.8	24.1
RSM7	12.8	12.9	14.7	14.9	15.0	21.1	15.0	20.0	13.2	23.6	12.7	18.1
RSM8	13.0	20.8	14.4	16.6	12.4	16.5	20.9	23.5	23.3	20.1	15.4	20.8
RSM9	17.9	13.4	17.3	14.2	12.9	18.1	17.2	13.8	19.9	19.5	20.7	20.2
RSM10	20.8	16.2	18.1	13.5	12.2	15.0	16.8	15.0	16.0	12.9	20.7	18.6

	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NMF1	9.8	10.0	8.9	9.7	9.4	9.4	9.5	9.3	12.2
NMF2	9.6	10.2	9.2	12.8	9.9	9.8	9.6	9.4	10.2
NMF3	10.7	9.6	10.3	11.3	9.3	9.6	9.9	9.4	9.7
NMF4	10.1	10.2	10.1	12.0	10.5	9.6	9.4	9.4	12.9
NMF5	10.2	9.5	10.5	11.0	9.2	10.3	9.6	9.5	10.7
NMF6	10.1	9.6	10.7	10.5	10.7	10.0	9.7	9.6	11.2
NMF7	10.6	9.9	11.0	10.3	10.1	10.5	9.5	9.6	12.6
NMF8	10.7	9.8	11.2	11.0	10.4	9.4	9.6	9.4	8.9
NMF9	10.9	10.3	11.2	11.7	9.7	9.6	9.9	9.7	11.3
NMF10	10.2	10.6	11.2	9.5	10.3	9.5	9.3	9.7	10.1

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1 (8-10cm)	8.0	6.2	7.6	9.0	11.2	9.3	10.8	9.7	10.3	8.1	7.9	8.4
RSM2 (8-10cm)	9.3	8.4	7.9	9.4	9.4	9.1	10.7	9.2	8.2	8.5	8.8	8.4
RSM3 (8-10cm)	8.5	9.8	7.8	9.9	10.3	9.9	10.7	9.9	8.8	8.6	9.5	8.7
RSM4 (8-10cm)	9.0	10.2	8.1	9.6	9.8	9.0	10.5	10.3	9.4	9.4	8.4	8.5
RSM5 (8-10cm)	9.3	11.4	8.1	9.8	11.5	9.4	9.9	9.6	9.0	7.9	8.9	9.1

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1 (8 - 10cm)	14.9	14.5	19.1	13.9	10.7	15.5	17.2	20.1	15.7	13.1	14.2	15.5
NSM2 (8 - 10cm)	12.4	13.0	12.7	10.8	11.5	20.2	16.4	13.7	11.2	14.5	14.7	14.2
NSM3 (8 - 10cm)	11.2	13.9	13.3	15.0	11.9	13.0	12.3	13.1	13.7	12.9	12.5	13.6
NSM4 (8 - 10cm)	10.7	14.2	12.9	12.4	13.2	17.8	14.2	12.6	15.8	11.8	13.3	15.9
NSM5 (8 - 10cm)	14.1	11.9	12.9	14.0	11.6	14.1	14.2	11.7	18.7	16.3	13.2	14.5

Appendix 3 Sediment bulk density (g cm^{-1}) and porosity (cm^{3} cm^{-3}) data in the RSM and NSM

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	1.1	1.1	1.1	1.1	1.2	1.3	1.1	1.3	1.2	1.2	1.1	1.0
RSM2	1.1	1.0	1.2	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.1	0.9
RSM3	1.1	1.1	1.1	1.1	1.1	1.2	1.1	1.2	1.3	1.1	1.1	1.0
RSM4	1.1	0.9	1.2	1.1	1.1	1.2	1.1	1.0	1.3	1.1	1.0	1.1
RSM5	1.1	1.1	1.2	1.2	1.1	1.3	1.1	1.1	1.2	1.2	1.1	0.9
RSM6	1.1	1.0	0.9	1.1	1.0	1.2	0.9	1.0	1.3	1.1	1.0	1.0
RSM7	1.0	1.0	1.1	1.1	1.1	1.5	1.0	1.1	1.3	1.1	1.0	1.0
RSM8	1.0	1.1	1.1	1.1	1.2	1.6	1.2	1.0	1.2	1.1	1.1	1.0
RSM9	1.0	0.8	1.1	1.1	1.1	1.5	0.9	1.0	1.2	1.3	1.1	0.9
RSM10	1.1	1.1	1.1	1.2	1.0	1.6	0.9	1.1	1.3	1.1	1.0	1.0

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.5	0.4	0.5
NSM2	0.3	0.4	0.6	0.5	0.5	0.5	0.8	0.4	0.5	0.4	0.4	0.5
NSM3	0.6	0.4	0.5	0.4	0.5	0.5	0.5	0.7	0.6	0.4	0.4	0.5
NSM4	0.4	0.5	0.6	0.5	0.5	0.5	0.6	0.6	0.4	0.5	0.4	0.4
NSM5	0.6	0.7	0.5	0.6	0.7	0.5	0.7	0.6	0.6	0.4	0.6	0.7
NSM6	0.5	0.7	0.6	0.7	0.7	0.7	0.8	0.7	0.5	0.5	0.4	0.4
NSM7	0.6	0.5	0.5	0.6	0.7	0.5	0.7	0.4	0.5	0.5	0.5	0.6
NSM8	0.6	0.5	0.4	0.5	0.8	0.6	0.8	0.5	0.5	0.4	0.7	0.4
NSM9	0.4	0.7	0.5	0.8	0.9	0.7	0.8	0.7	0.6	0.4	0.6	0.4
NSM10	0.4	0.7	0.6	0.7	1.0	0.7	0.9	0.7	0.5	0.4	0.8	0.7

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JUNE	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6
RSM2	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.6
RSM3	0.6	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6
RSM4	0.5	0.6	0.5	0.5	0.6	0.5	0.6	0.6	0.5	0.6	0.6	0.6
RSM5	0.5	0.5	0.6	0.5	0.5	0.5	0.5	0.6	0.5	0.5	0.5	0.6
RSM6	0.6	0.6	0.6	0.6	0.6	0.5	0.6	0.6	0.5	0.5	0.6	0.6
RSM7	0.5	0.6	0.6	0.6	0.5	0.4	0.6	0.6	0.5	0.5	0.5	0.6
RSM8	0.6	0.6	0.6	0.5	0.5	0.4	0.5	0.6	0.5	0.6	0.6	0.6
RSM9	0.6	0.7	0.6	0.6	0.6	0.4	0.6	0.6	0.5	0.5	0.6	0.6
RSM10	0.6	0.6	0.6	0.5	0.6	0.3	0.6	0.6	0.5	0.6	0.6	0.6

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
NSM2	0.8	0.8	0.7	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8	0.8
NSM3	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8
NSM4	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8
NSM5	0.8	0.7	0.8	0.7	0.7	0.8	0.7	0.7	0.7	0.8	0.7	0.7
NSM6	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.8	0.8	0.8
NSM7	0.7	0.8	0.8	0.7	0.7	0.8	0.7	0.8	0.8	0.8	0.8	0.7
NSM8	0.7	0.8	0.8	0.8	0.6	0.7	0.7	0.8	0.8	0.8	0.7	0.8
NSM9	0.8	0.7	0.8	0.7	0.6	0.7	0.7	0.7	0.8	0.8	0.7	0.8
NSM10	0.8	0.7	0.7	0.7	0.6	0.7	0.6	0.7	0.8	0.7	0.6	0.7

Appendix 4 Sediment pH data in the restored saltmarsh (RSM), restored mudflat (RMF), natural saltmarsh (NSM) and natural mudflat (NMF)

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSM1	7.7	7.8	7.8	7.8	7.7	7.9	8.2	7.9	7.9	7.7	8.0	7.3
RSM2	7.7	7.9	7.8	7.8	7.9	8.1	8.0	7.8	7.9	7.6	7.8	7.3
RSM3	7.7	7.6	7.6	7.9	7.8	7.8	8.1	7.8	7.9	7.7	7.8	7.3
RSM4	7.8	7.5	7.5	7.5	7.8	8.0	8.1	7.8	7.8	7.7	7.9	7.3
RSM5	7.8	7.5	7.7	7.7	8.0	7.7	8.0	7.8	8.0	7.7	7.9	7.3
RSM6	7.9	7.4	7.4	7.6	7.8	7.6	8.0	7.8	7.9	7.6	7.9	7.3
RSM7	7.9	7.2	7.7	7.4	8.0	7.8	7.9	7.7	7.9	7.6	7.9	7.3
RSM8	7.8	7.7	7.2	7.5	7.9	7.6	8.2	7.7	7.9	7.7	7.9	7.2
RSM9	7.8	7.9	7.5	7.5	7.9	7.6	7.9	7.7	7.8	7.6	7.9	7.2
RSM10	7.8	7.8	7.5	7.8	7.9	7.8	7.9	7.7	7.9	7.6	7.9	7.2

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SPETEMBER	OCTOBER	NOVEMBER	DECEMBER
RMF1	7.0	6.8	7.1	6.9	6.6	6.9	7.0	6.9	7.0	6.9	7.1	6.9
RMF2	7.1	7.0	7.0	7.0	6.9	6.8	7.0	7.1	7.0	7.1	6.7	7.1
RMF3	7.2	6.8	7.3	6.9	7.2	7.0	7.2	7.0	7.0	6.9	7.2	7.0
RMF4	7.2	6.8	6.9	6.9	6.9	7.0	7.1	7.1	7.2	7.0	7.2	7.1
RMF5	7.0	7.0	6.8	6.8	6.6	7.0	7.1	7.0	7.1	7.1	7.1	7.0
RMF6	7.1	7.3	7.1	6.8	7.1	7.4	7.1	7.0	7.2	7.1	6.9	7.0
RMF7	7.3	6.7	7.1	6.8	7.0	6.9	6.8	7.3	7.0	7.1	7.1	7.0
RMF8	7.4	7.0	6.1	6.7	7.1	7.1	7.0	7.0	7.2	7.1	7.4	7.1
RMF9	6.9	6.9	7.1	6.8	6.9	6.9	7.1	7.0	7.2	7.1	7.4	7.1
RMF10	7.0	6.8	7.2	6.9	7.0	6.8	6.9	7.1	7.0	7.1	7.1	7.0

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NSM1	7.2	6.8	7.0	7.3	7.2	7.3	7.1	7.1	7.1	7.1	7.3	7.1
NSM2	7.1	7.0	7.2	7.2	7.2	7.0	7.2	7.2	7.2	7.0	7.7	7.1
NSM3	7.4	6.9	7.2	7.3	7.1	7.2	7.2	7.3	7.2	7.2	7.5	7.1
NSM4	7.2	7.1	7.0	7.2	7.1	7.1	7.4	7.3	7.1	7.1	7.5	7.1
NSM5	7.8	7.3	6.9	7.3	7.2	7.3	7.4	7.1	7.4	7.1	7.5	7.2
NSM6	7.3	7.6	7.1	7.3	7.1	7.1	7.2	7.3	7.1	7.0	7.6	7.1
NSM7	7.5	7.6	7.1	7.4	7.3	7.1	7.2	7.1	7.4	7.0	7.6	7.1
NSM8	7.5	7.6	6.9	7.3	7.3	7.2	7.2	7.2	7.2	7.0	7.6	7.1
NSM9	7.2	7.4	7.1	7.3	7.3	7.1	7.3	7.3	7.1	7.1	7.7	7.1
NSM10	7.3	7.5	7.1	7.2	7.3	7.2	7.3	7.3	7.1	7.1	7.7	7.0

	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
NMF1	7.2	7.0	7.4	7.4	7.4	7.3	7.3	7.4	7.3
NMF2	7.3	7.3	7.4	7.3	7.3	7.3	7.2	7.5	7.3
NMF3	7.2	7.3	7.1	7.1	7.3	7.3	7.3	7.2	7.2
NMF4	7.2	7.2	7.3	7.2	7.3	7.5	7.3	7.3	7.3
NMF5	7.2	7.4	7.3	7.4	7.3	7.2	7.2	7.3	7.3
NMF6	7.4	7.3	7.4	7.4	7.3	7.3	7.3	7.4	7.3
NMF7	7.3	7.4	7.4	7.3	7.2	7.3	7.3	7.5	7.4
NMF8	7.3	7.3	7.3	7.3	7.2	7.2	7.3	7.3	7.3
NMF9	7.4	7.3	7.3	7.2	7.3	7.3	7.3	7.5	7.3
NMF10	7.4	7.3	7.3	7.3	7.3	7.4	7.2	7.3	7.3

Appendix 5 Sediment porewater Cl concentration (mg L^{-1}) data in the restored saltmarsh (RSM), restored mudflat (RMF), natural saltmarsh (NSM) and natural mudflat (NMF)

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	3.3	9.1	2.3	3.6	5.1	8.2	5.5	1.2	9.8	5.6	2.6	3.9
RSM1	7210.07	5289.02	9461.14	11799.27	16269.12	22365.13	11687.64	9065.97	8155.74	5790.91	4547.99	6904.09
RSM2	7168.22	3541.38	9770.22	11533.77	8799.88	16332.07	25873.71	9334.52	8651.13	7168.22	2224.12	6710.73
RSM3	7533.04	4278.72	7550.71	10918.47	12725.79	24823.91	15701.70	8967.05	8686.77	7533.04	5513.37	7667.71
RSM4	6727.89	5494.87	7443.23	10348.96	8508.16	14238.23	13290.49	8695.96	8577.09	6727.89	4872.81	6561.32
RSM5	7026.79	6340.46	8197.27	10877.85	9895.00	24640.57	22350.29	8907.46	9859.51	7026.79	1760.20	7388.17
RSM6	7037.76	5681.46	6428.57	9669.72	7858.27	11210.91	11877.95	7564.84	7319.29	7037.76	3315.91	5307.09
RSM7	7542.32	6283.70	7425.81	12380.64	11381.60	28851.75	17504.81	7597.92	8335.72	7542.32	2482.98	6866.70
RSM8	5874.45	7002.78	7001.95	9896.08	12495.47	22030.09	26451.01	7152.13	8804.48	5874.45	3052.10	6792.38
RSM9	7947.06	6085.10	8731.65	9464.95	9917.92	28796.23	25205.40	11540.26	9259.34	7947.06	3595.18	7720.08
RSM10	8054.88	4849.58	9459.18	10760.02	9498.81	10487.70	14511.89	9158.95	10308.62	6960.85	5106.40	3949.44

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SPETEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	6.5	2.3	2.5	1.2	1.6	0.8	3.9	6.6	5.2	2.7	1.5	1.1
RMF1	4932.05	4105.52	4133.86	5299.43	6557.33	1378.45	13164.66	3991.85	8446.71	2959.86	2362.73	4835.31
RMF2	5389.53	4652.00	4919.04	3879.86	5430.69	1753.45	7044.67	4991.51	5304.55	5305.89	2731.15	6241.69
RMF3	5053.72	5051.87	4714.22	7215.70	4623.25	4199.10	11211.87	4929.29	7094.07	3108.35	2633.72	6229.78
RMF4	3815.69	5540.18	4381.22	4537.67	4338.76	7405.92	7856.01	4398.52	5648.82	4570.16	3089.01	7062.52
RMF5	4814.72	5162.05	5297.52	7406.84	6207.49	6948.58	7781.49	4657.16	6412.82	3201.32	5881.74	7062.53
RMF6	4784.51	5160.10	4842.65	6916.03	4021.16	3334.02	9754.47	4964.37	6043.31	5388.25	2290.63	6068.43
RMF7	5378.07	5552.25	4728.28	3907.53	6224.22	3738.18	9476.63	6926.57	6140.60	4070.71	2205.76	8347.38
RMF8	5533.53	4094.51	4153.74	8864.80	6435.17	5596.71	10086.48	5695.70	5401.31	3121.67	3370.29	7079.34
RMF9	4369.47	5562.87	5112.26	4354.95	5336.07	9917.44	9370.35	4131.18	7346.50	5418.34	2971.37	6539.69
RMF10	5809.48	5785.95	5871.85	8165.60	7193.71	2937.20	11110.24	5095.02	5392.36	4125.98	3054.74	6689.68

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	1.8	3.2	4.6	0.7	0.4	1.1	1.7	3.6	4.1	5.1	1.6	3.1
NSM1	4433.31	3319.16	3986.74	6731.52	8171.90	4084.47	8058.27	6999.99	6707.32	4221.61	1977.81	4476.79
NSM2	3651.38	4348.72	6479.47	6276.42	7521.88	11816.19	8200.36	7133.77	7110.23	4254.62	1752.46	2973.31
NSM3	4351.47	4577.09	5589.10	6625.62	10111.60	7017.01	7923.97	5843.36	6101.75	13151.25	2999.55	3299.96
NSM4	3354.54	6166.18	3027.10	5913.82	8359.28	5514.15	10754.80	6894.82	5723.28	5224.05	2602.05	3695.15
NSM5	4463.69	4245.02	3145.36	5980.25	11949.89	6215.79	12345.82	6161.63	9747.00	4198.47	2812.18	3333.98
NSM6	4673.17	4035.02	3064.46	7338.62	9441.01	12484.56	7516.89	4752.06	6872.38	4217.22	2500.42	4411.87
NSM7	5007.77	3983.10	5776.79	8462.86	8559.76	8494.36	8157.45	6991.27	9131.18	4855.81	1783.99	4489.04
NSM8	4298.01	3104.60	5102.02	5664.63	8924.62	10949.24	13638.60	7640.09	6779.93	6091.81	1788.43	4511.17
NSM9	4012.66	4209.53	5213.67	9718.00	7222.26	13539.30	10095.22	9570.58	7386.75	5854.64	1479.41	4224.38
NSM10	4001.30	5402.38	4614.04	10369.32	8918.02	18525.28	14686.27	6757.60	7382.87	6056.89	1968.19	3443.23

	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	0.5	3.1	4.4	1.8	1.6	0.6	2.2	2.5	0.9
NMF1	6948.66	6841.47	5008.88	11625.16	6027.23	6354.26	3925.19	4566.95	7643.42
NMF2	5436.88	8165.76	5646.21	12355.92	5373.27	6752.77	4415.96	4035.65	7109.51
NMF3	4888.65	9664.16	5269.31	18017.59	8161.57	7029.16	5519.21	5693.92	8951.92
NMF4	4989.14	8443.83	14740.14	14529.61	4063.25	12904.17	4042.51	4063.79	7301.52
NMF5	8563.20	7444.00	6562.92	11907.72	5308.66	7276.45	5357.50	4639.60	6948.38
NMF6	7489.49	9062.89	7320.09	11079.91	3542.14	6618.37	4990.67	4153.84	8602.26
NMF7	5640.67	9988.00	6397.55	13413.07	7062.32	7542.63	3690.76	4609.51	7773.55
NMF8	6547.29	8412.06	9570.63	13706.78	4128.91	6503.74	6339.18	3149.31	19537.44
NMF9	7713.71	9674.94	5200.73	12123.93	4985.01	7158.21	4668.07	3593.81	6850.59
NMF10	7446.12	6722.73	5078.18	15648.02	3480.75	6334.13	6449.25	3756.84	7050.32

Appendix 6 Sediment porewater DOC (mg L^{-1}) concentration data in the restored saltmarsh (RSM), restored mudflat (RMF), natural saltmarsh (NSM) and natural mudflat (NMF)

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	4.6	0.7	1.2	5.1	1.7	1.2	4.5	1.4	1.1	0.3	2.8	1.9
RSM1	44.91	27.76	65.99	117.76	75.57	66.57	135.06	180.63	67.21	12.70	24.92	137.14
RSM2	38.90	17.04	75.77	104.42	66.57	34.62	129.00	91.50	123.18	60.41	40.59	146.19
RSM3	51.89	37.82	79.65	53.25	99.95	80.54	73.95	130.64	101.85	48.92	45.95	184.16
RSM4	57.40	60.34	45.07	94.55	74.96	26.08	152.85	164.23	90.17	29.84	77.88	110.75
RSM5	72.16	55.74	25.80	87.03	110.29	33.11	197.51	164.49	88.51	32.99	62.00	142.97
RSM6	45.82	51.68	75.08	81.19	77.68	30.88	88.26	204.47	71.66	19.82	58.69	112.07
RSM7	51.49	40.26	72.20	116.48	82.85	72.69	129.34	200.89	111.58	45.37	22.87	196.31
RSM8	46.91	60.30	66.14	96.91	73.97	56.89	155.34	139.94	102.53	62.61	58.75	132.91
RSM9	62.81	55.70	31.27	83.63	63.96	61.32	149.14	269.93	102.65	28.55	236.94	187.40
RSM10	52.57	32.64	48.75	99.76	106.05	50.27	185.96	125.97	93.60	38.11	62.96	52.88

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	3.4	3.1	1.2	5.7	4.1	1.5	1.3	1.1	0.8	2.7	1.1	0.6
RMF1	33.43	46.44	35.33	74.12	28.84	143.03	43.37	77.17	71.79	55.02	96.97	95.41
RMF2	44.75	45.48	34.72	71.07	30.47	84.75	33.84	70.79	41.20	62.11	68.22	75.90
RMF3	36.82	28.11	27.61	136.97	17.86	64.42	50.45	49.67	51.05	69.32	64.01	78.04
RMF4	27.60	42.21	31.28	124.44	29.98	61.45	35.72	34.37	61.45	55.63	61.44	103.65
RMF5	32.76	30.90	46.63	97.10	39.32	45.40	40.26	39.43	78.26	61.96	59.17	77.54
RMF6	35.26	31.98	67.31	126.06	10.90	20.37	60.20	51.27	42.88	83.66	83.29	69.87
RMF7	28.27	17.46	47.63	106.16	83.79	17.80	35.54	65.92	76.59	43.51	59.17	161.42
RMF8	38.62	26.84	33.85	119.24	106.74	28.87	41.26	55.28	35.06	69.34	75.10	77.28
RMF9	40.09	40.26	36.12	191.26	32.00	31.96	34.37	48.38	33.59	75.60	77.96	90.88
RMF10	29.26	34.99	27.25	172.25	36.72	28.67	32.74	38.82	54.96	56.56	65.72	101.60

	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	1.1	0.8	5.5	4.7	3.4	2.30	0.7	3.3	0.8	5.6	3.3	1.5
NSM1	57.76	26.48	82.12	63.02	33.49	32.41	104.05	79.89	46.57	101.58	12.18	20.96
NSM2	63.76	20.93	17.02	49.20	25.05	20.82	80.61	81.89	72.36	86.12	46.55	37.28
NSM3	44.39	33.63	25.35	87.10	49.78	17.86	139.50	103.43	144.18	35.49	22.01	21.23
NSM4	60.38	16.65	87.18	145.42	29.57	18.79	117.06	127.84	66.79	43.50	38.55	46.22
NSM5	29.01	32.49	30.94	74.46	50.72	27.96	126.89	139.54	115.04	69.65	26.89	20.27
NSM6	33.16	32.60	11.64	59.09	41.04	32.22	134.14	93.00	39.15	61.96	6.70	18.02
NSM7	35.29	34.94	18.18	71.27	27.31	29.09	120.54	115.16	109.45	75.07	38.66	38.97
NSM8	39.09	26.53	18.44	46.37	40.56	28.67	139.81	129.78	33.18	120.66	19.03	32.16
NSM9	47.33	62.18	30.47	62.99	22.33	44.74	173.49	85.94	75.20	125.51	24.94	41.31
NSM10	53.37	52.29	7.70	76.05	26.66	40.90	266.41	136.12	62.08	79.71	39.92	33.50

	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
RSD %	4.2	1.6	0.6	2.9	1.8	1.1	1.8	3.6	2.7
NMF1	82.50	12.82	11.85	39.21	80.72	41.97	32.53	88.55	156.01
NMF2	68.33	34.97	10.82	45.70	83.06	30.38	27.92	73.95	45.33
NMF3	69.64	39.89	13.07	62.87	73.13	34.11	41.84	78.93	98.69
NMF4	91.99	62.81	15.94	58.83	79.01	27.89	23.58	100.18	78.43
NMF5	93.42	51.31	12.46	48.98	84.00	41.91	37.79	102.27	136.00
NMF6	71.46	38.10	12.97	30.80	77.57	36.79	32.44	81.62	68.62
NMF7	83.90	47.39	10.62	46.00	72.31	42.15	40.20	92.71	44.48
NMF8	72.15	41.54	10.11	37.47	73.90	33.65	33.65	106.68	67.42
NMF9	71.56	64.20	13.27	36.60	78.77	29.08	25.89	99.54	58.87
NMF10	97.38	38.33	11.49	42.13	84.26	24.65	32.15	103.72	107.57

Appendix 7 Properties of agricultural soil and dredged sediment

	pH	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)
Soil	7.2	7.6	26.6	38.8	34.6
	7.1	7.4	29.1	36.3	33.6
	7.1	7.2	26.1	35.5	33.5
	7.1	7.3	30.8	38.9	35.4
	7.1	7.5	28.9	37.9	34.1
Sediment	6.9	9.0	39.7	47.2	13.6
	7.0	8.4	45.2	43.6	10.1
	6.9	8.6	39.4	47.5	14.5
	7.0	8.6	38.5	47.6	13.4
	7.0	8.8	39.2	47.7	12.8

Appendix 8 Partition coefficients (log K_d) of the metals and herbicides for agricultural soil and dredged sediment at 5 ‰ and 20 ‰ salinity.

Samples	Cu	Ni	Zn
soil1_5	2.68	2.29	2.58
soil2_5	2.60	2.26	2.56
soil3_5	2.64	2.27	2.53
soil4_5	2.68	2.28	2.68
soil5_5	2.73	2.36	2.59
soil6_5	2.79	2.34	2.63
soil7_5	2.87	2.38	2.67
soil8_5	2.89	2.39	2.57
soil9_5	2.93	2.37	2.69
soil1_20	2.28	2.15	2.42
soil2_20	2.28	2.16	2.35
soil3_20	2.29	2.19	2.33
soil4_20	2.56	2.29	2.62
soil5_20	2.56	2.31	2.57
soil6_20	2.57	2.49	2.53
soil7_20	2.79	2.32	2.71
soil8_20	2.78	2.32	2.71
soil9_20	2.81	2.32	2.73
sediment1_5	2.80	2.53	2.67
sediment2_5	2.81	2.58	2.67
sediment3_5	2.78	2.54	2.73
sediment4_5	2.99	2.50	2.69
sediment5_5	2.99	2.53	2.65
sediment6_5	2.98	2.51	2.69
sediment7_5	3.14	2.45	2.69
sediment8_5	3.12	2.50	2.67
sediment9_5	3.12	2.58	2.68
sediment1_20	2.54	2.63	2.58
sediment2_20	2.52	2.71	2.78
sediment3_20	2.52	2.41	2.58
sediment4_20	2.71	2.37	2.76
sediment5_20	2.74	2.32	2.74
sediment6_20	2.73	2.29	2.85
sediment7_20	2.98	2.33	2.78
sediment8_20	2.98	2.46	2.93
sediment9_20	2.97	2.41	2.71

Samples	Simazine	Atrazine	Diuron
soil1_5	3.84	3.92	4.39
soil2_5	3.82	3.94	4.34
soil3_5	3.75	3.88	4.21
soil4_5	3.74	3.86	4.21
soil5_5	3.71	3.82	4.09
soil6_5	3.67`	3.83	4.09
soil1_20	3.52	3.85	4.46
soil2_20	2.69	3.94	4.38
soil3_20	2.61	3.85	4.19
soil4_20	3.63	3.88	4.21
soil5_20	3.63	3.88	4.16
soil6_20	3.57	3.84	4.07
sediment1_5	3.70	4.02	4.57
sediment2_5	3.85	4.05	4.58
sediment3_5	3.62	3.90	4.21
sediment4_5	3.64	3.86	4.29
sediment5_5	3.61	3.89	4.16
sediment6_5	3.63	3.89	4.20
sediment1_20	3.68	3.93	4.55
sediment2_20	3.74	3.99	4.59
sediment3_20	3.68	3.91	4.41
sediment4_20	3.65	3.93	4.35
sediment5_20	3.61	3.81	4.19
sediment6_20	3.64	3.91	4.25

Appendix 9 Concentrations of Cu, Ni and Zn (mg L^{-1}) released from the soil and sediment to the overlying water under low and high salinity treatments

Soil	High salinity			Low salinity			
Sample	Cu	Ni	Zn	Sample	Cu	Ni	Zn
HW 1	0.30	30.15	36.80	LW 1	0.56	24.68	15.20
HW 2	0.15	21.81	28.51	LW 2	0.39	17.99	11.20
HW 3	0.03	2.95	7.24	LW 3	0.10	3.72	3.36
HW 4	0.03	2.44	6.13	LW 4	0.16	6.41	5.95
HW 5	0.04	2.13	5.44	LW 5	0.18	6.90	5.34
HW 6	0.03	1.98	5.03	LW 6	0.12	4.30	3.92
HW 7	0.04	1.85	2.65	LW 7	0.09	3.66	3.23
HW 8	0.03	1.63	2.27	LW 8	0.07	2.71	2.39
HW 9	0.03	1.30	2.30	LW 9	0.08	3.09	2.69
HW 10	0.03	1.28	1.71	LW 10	0.06	2.30	1.97
HW 11	0.02	1.04	1.50	LW 11	0.04	1.60	1.34
HW 12	0.03	0.92	1.55	LW 12	0.03	1.33	1.08
HW 13	0.02	0.84	1.36	LW 13	0.04	1.55	1.27
HW 14	0.02	0.80	1.39	LW 14	0.03	1.56	1.27
HW 15	0.01	0.72	0.96	LW 15	0.03	1.12	0.90
HW 16	0.02	0.80	0.99	LW 16	0.02	0.93	0.72
HW 17	0.02	0.77	0.81	LW 17	0.03	1.21	0.94
HW 18	0.02	0.68	0.85	LW 18	0.03	1.09	0.82
HW 19	0.01	0.69	0.92	LW 19	0.04	1.86	1.42
HW 20	0.02	0.66	0.90	LW 20	0.04	1.51	1.19
HW 21	0.02	0.70	0.83	LW 21	0.04	1.65	1.32
HW 22	0.02	0.68	0.92	LW 22	0.03	1.19	0.95
HW 23	0.03	0.69	0.88	LW 23	0.03	0.98	0.75
HW 24	0.46	30.90	20.60	LW 24	0.27	12.50	12.50
HW 25	0.31	20.00	10.30	LW 25	0.21	9.52	9.52
HW 26	0.21	8.45	2.53	LW 26	0.07	2.60	3.60
HW 27	0.18	7.11	2.15	LW 27	0.06	2.27	2.27
HW 28	0.17	6.21	1.90	LW 28	0.04	1.57	2.57
HW 29	0.16	5.70	1.79	LW 29	0.03	1.35	1.35
HW 30	0.08	3.01	1.69	LW 30	0.03	1.33	1.33
HW 31	0.07	2.61	1.45	LW 31	0.04	1.84	1.84
HW 32	0.07	2.94	1.20	LW 32	0.03	1.01	1.01
HW 33	0.05	2.13	1.06	LW 33	0.02	0.73	0.73
HW 34	0.06	1.85	0.86	LW 34	0.02	0.92	0.92
HW 35	0.05	1.86	0.79	LW 35	0.02	0.69	0.69
HW 36	0.05	1.70	0.72	LW 36	0.03	0.88	0.88
HW 37	0.05	1.71	0.70	LW 37	0.02	0.69	0.69
HW 38	0.04	1.19	0.62	LW 38	0.03	1.32	1.32
HW 39	0.04	1.20	0.72	LW 39	0.01	0.44	0.44
HW 40	0.03	1.00	0.65	LW 40	0.03	1.20	1.20
HW 41	0.03	1.06	0.61	LW 41	0.04	1.31	1.31
HW 42	0.03	1.14	0.61	LW 42	0.02	0.91	0.91
HW 43	0.03	1.07	0.57	LW 43	0.01	0.34	0.34
HW 44	0.02	1.47	0.64	LW 44	0.02	0.86	0.86
HW 45	0.03	1.10	0.63	LW 45	0.02	0.75	0.75
HW 46	0.03	1.05	0.40	LW 46	0.01	2.16	2.16
HW 47	0.48	50.18	37.30	LW 47	0.32	19.11	10.11
HW 48	0.35	26.85	21.10	LW 48	0.17	16.42	7.42
HW 49	0.03	5.60	4.63	LW 49	0.17	6.37	5.37
HW 50	0.16	4.85	4.90	LW 50	0.15	5.23	5.23
HW 51	0.11	3.67	3.60	LW 51	0.14	4.86	4.86
HW 52	0.09	2.88	2.86	LW 52	0.12	4.42	4.42
HW 53	0.07	2.15	2.07	LW 53	0.07	2.10	2.10
HW 54	0.06	2.16	1.94	LW 54	0.04	1.25	1.25
HW 55	0.06	2.17	1.99	LW 55	0.06	1.71	1.71
HW 56	0.06	1.81	1.73	LW 56	0.05	1.40	1.40
HW 57	0.04	1.34	1.30	LW 57	0.04	1.15	1.15
HW 58	0.05	1.04	0.97	LW 58	0.04	1.10	1.10
HW 59	0.04	1.10	1.06	LW 59	0.03	0.92	0.92
HW 60	0.04	1.22	1.12	LW 60	0.05	1.18	1.18
HW 61	0.03	0.70	0.63	LW 61	0.02	0.56	0.56
HW 62	0.04	1.46	1.32	LW 62	0.03	0.72	0.72
HW 63	0.04	1.18	1.11	LW 63	0.02	0.69	0.75
HW 64	0.02	0.55	0.50	LW 64	0.02	0.68	0.69
HW 65	0.02	0.58	0.54	LW 65	0.02	0.58	0.68
HW 66	0.01	0.19	0.17	LW 66	0.02	0.62	0.58
HW 67	0.04	1.08	1.03	LW 67	0.01	0.51	0.62
HW 68	0.03	0.95	0.85	LW 68	0.02	0.54	0.51
HW 69	0.02	0.71	0.59	LW 69	0.02	0.75	0.54

Sediment	High salinity			Low salinity			
Sample	Cu	Ni	Zn	Sample	Cu	Ni	Zn
HS1	0.06	10.64	5.02	LS1	0.31	8.03	3.20
HS2	0.02	3.38	2.62	LS2	0.28	5.18	2.28
HS3	0.01	1.73	2.41	LS3	0.16	2.01	1.30
HS4	0.01	2.00	4.97	LS4	0.03	3.80	2.56
HS5	0.02	5.48	10.60	LS5	0.05	4.36	3.41
HS6	0.02	1.49	6.17	LS6	0.02	1.93	1.23
HS7	0.02	2.01	3.06	LS7	0.01	1.59	0.97
HS8	0.02	1.64	7.14	LS8	0.01	0.91	0.58
HS9	0.02	1.51	1.30	LS9	0.01	0.70	0.40
HS10	0.02	1.49	1.50	LS10	0.01	0.53	0.32
HS11	0.01	1.02	0.95	LS11	0.01	0.94	0.55
HS12	0.02	0.97	0.24	LS12	0.01	0.73	0.42
HS13	0.02	1.07	0.55	LS13	0.01	1.10	0.63
HS14	0.02	0.88	1.11	LS14	0.01	0.79	0.47
HS15	0.01	1.05	0.33	LS15	0.01	0.55	0.31
HS16	0.02	0.93	1.44	LS16	0.01	0.47	0.26
HS17	0.02	0.89	1.08	LS17	0.01	0.41	0.21
HS18	0.01	0.76	0.34	LS18	0.01	0.69	0.36
HS19	0.01	0.71	0.34	LS19	0.01	0.47	0.24
HS20	0.01	0.60	0.27	LS20	0.01	0.64	0.35
HS21	0.01	0.71	0.67	LS21	0.01	0.52	0.26
HS22	0.02	1.09	0.42	LS22	0.01	0.63	0.34
HS23	0.02	0.93	0.35	LS23	0.01	0.41	0.18
HS24	0.08	19.21	9.40	LS24	0.33	4.52	4.52
HS25	0.07	9.50	6.06	LS25	0.21	3.34	3.34
HS26	0.06	8.03	5.31	LS26	0.02	1.05	1.05
HS27	0.06	6.65	4.53	LS27	0.08	0.82	0.82
HS28	0.05	5.81	4.09	LS28	0.02	1.92	0.92
HS29	0.05	5.14	3.66	LS29	0.01	0.61	0.61
HS30	0.03	2.77	2.04	LS30	0.01	0.69	0.69
HS31	0.03	1.96	1.40	LS31	0.01	0.56	0.56
HS32	0.03	2.06	1.29	LS32	0.01	0.59	0.59
HS33	0.02	1.94	1.26	LS33	0.01	0.64	0.64
HS34	0.02	1.51	0.96	LS34	0.01	0.48	0.48
HS35	0.03	1.50	1.00	LS35	0.01	0.37	0.37
HS36	0.02	1.21	0.76	LS36	0.01	0.43	0.43
HS37	0.02	1.16	0.74	LS37	0.01	0.38	0.38
HS38	0.01	0.87	0.56	LS38	0.01	0.69	0.69
HS39	0.02	0.95	0.62	LS39	0.01	0.33	0.33
HS40	0.01	0.85	0.54	LS40	0.01	0.38	0.38
HS41	0.01	0.82	0.53	LS41	0.01	0.40	0.40
HS42	0.02	0.92	0.56	LS42	0.01	0.38	0.38
HS43	0.01	0.88	0.58	LS43	0.02	0.71	0.71
HS44	0.01	0.72	0.45	LS44	0.01	0.39	0.39
HS45	0.02	0.79	0.53	LS45	0.01	0.35	0.35
HS46	0.02	0.10	0.10	LS46	0.01	0.48	0.48
HS47	0.04	10.99	5.51	LS47	0.27	7.93	6.93
HS48	0.03	4.65	2.27	LS48	0.15	4.87	4.87
HS49	0.00	2.98	1.10	LS49	0.04	4.12	4.12
HS50	0.03	7.67	1.30	LS50	0.03	3.67	3.67
HS51	0.11	16.44	2.99	LS51	0.03	3.31	3.31
HS52	0.01	7.94	1.00	LS52	0.03	3.09	3.09
HS53	0.03	4.40	1.37	LS53	0.02	1.33	1.33
HS54	0.08	10.25	1.14	LS54	0.01	1.00	1.00
HS55	0.02	1.96	1.06	LS55	0.01	1.18	1.18
HS56	0.03	2.22	0.98	LS56	0.01	0.79	0.79
HS57	0.01	1.37	0.69	LS57	0.01	0.89	0.89
HS58	0.01	0.36	0.67	LS58	0.01	0.70	0.70
HS59	0.01	0.81	0.72	LS59	0.01	0.59	0.59
HS60	0.01	1.59	0.61	LS60	0.01	0.58	0.58
HS61	0.01	0.52	0.76	LS61	0.01	0.38	0.38
HS62	0.00	0.39	0.65	LS62	0.01	0.43	0.43
HS63	0.01	0.46	0.62	LS63	0.01	0.39	0.39
HS64	0.01	0.51	0.51	LS64	0.01	0.40	0.40
HS65	0.01	0.60	0.49	LS65	0.00	0.34	0.34
HS66	0.00	0.37	0.41	LS66	0.01	0.38	0.38
HS67	0.01	1.03	0.49	LS67	0.03	0.75	0.75
HS68	0.01	1.29	0.79	LS68	0.01	0.38	0.38
HS69	0.01	0.59	0.93	LS69	0.01	0.37	0.37

RSD% for Cu, Ni and Zn concentrations released from the soil and sediment to the overlying water under low and high salinity treatments

	Cu	Ni	Zn		Cu	Ni	Zn
HS3	0.01	1.73	2.41	HW2	0.15	21.81	28.51
HS3 duplicate	0.01	1.62	2.49	HW2 duplicate	0.15	20.93	28.93
RSD %	6.73	4.47	2.31	RSD %	3.77	2.92	1.03
HS5	0.02	5.48	10.60	HW3	0.03	2.95	7.24
HS5 duplicate	0.02	5.21	9.72	HW3 duplicate	0.03	3.01	7.19
RSD %	8.32	3.54	6.12	RSD %	9.75	1.32	0.49
HS9	0.02	1.51	1.30	HW23	0.03	0.69	0.88
HS9 duplicate	0.02	1.60	1.23	HW23 duplicate	0.03	0.62	0.93
RSD %	8.73	4.23	3.91	RSD %	7.15	7.64	3.99
HS25	0.07	9.50	6.06	HW26	0.21	8.45	2.53
HS25 duplicate	0.06	10.10	5.98	HW26 duplicate	0.19	8.56	2.49
RSD %	9.72	4.33	0.94	RSD %	5.69	0.88	1.13
HS28	0.05	5.81	4.09	HW28	0.17	6.21	1.90
HS28 duplicate	0.05	5.67	4.13	HW28 duplicate	0.18	6.18	1.85
RSD %	5.44	1.78	0.69	RSD %	6.50	0.30	2.08
LS2	0.28	5.18	2.28	LW3	0.10	3.72	3.36
LS2 duplicate	0.25	5.02	2.19	LW3 duplicate	0.11	3.81	3.29
RSD %	7.72	2.11	2.85	RSD %	5.98	1.61	1.49
LS5	0.05	4.36	3.41	LW5	0.18	6.90	5.34
LS5 duplicate	0.05	4.48	3.23	LW5 duplicate	0.17	6.70	5.41
RSD %	2.60	1.83	3.83	RSD %	5.36	2.09	0.92
LS6	0.02	1.93	1.23	LW9	0.08	3.09	2.69
LS6 duplicate	0.02	2.01	1.27	LW9 duplicate	0.09	3.19	2.56
RSD %	2.11	3.10	2.26	RSD %	6.07	2.34	3.50
LS23	0.01	0.41	0.18	LW25	0.21	9.52	9.52
LS23 duplicate	0.00	0.46	0.17	LW25 duplicate	0.25	9.61	9.48
RSD %	1.43	8.99	2.47	RSD %	9.88	0.67	0.30
LS25	0.21	3.34	3.34	LW28	0.04	1.57	2.57
LS25 duplicate	0.20	3.21	3.42	LW28 duplicate	0.05	1.62	2.39
RSD %	4.14	2.81	1.67	RSD %	9.57	2.22	5.13
LS30	0.01	0.69	0.69	LW34	0.02	0.92	0.92
LS30 duplicate	0.01	0.60	0.71	LW34 duplicate	0.02	1.05	1.04
RSD %	6.73	10.16	1.81	RSD %	7.07	9.10	8.43

Appendix 10 Concentrations of simazine, atrazine and diuron (μg L^{-1}) released from the soil and sediment into the overlying water under the low and high salinity treatments

Soil	High salinity treatment				Low salinity treatment		
Sample	Simazine	Atrazine	Diuron	Sample	Simazine	Atrazine	Diuron
HW1	776.10	248.10	45.49	LW1	282.16	119.99	29.69
HW2	419.76	103.61	19.31	LW2	155.91	42.56	9.02
HW3	384.68	100.63	19.87	LW3	130.59	23.39	3.98
HW5	339.22	76.67	14.52	LW5	237.40	35.81	7.83
HW7	321.29	64.45	11.65	LW7	133.10	25.55	4.85
HW9	281.00	29.27	8.00	LW9	106.51	19.64	2.85
HW11	241.47	27.18	6.83	LW11	73.77	4.37	4.47
HW13	115.12	20.70	5.74	LW13	62.25	3.01	4.52
HW15	111.02	17.84	5.00	LW15	36.73	6.79	2.57
HW17	84.60	12.54	2.85	LW17	49.32	7.07	1.06
HW19	71.34	11.67	1.83	LW19	60.53	12.75	2.64
HW21	65.81	10.85	1.37	LW21	61.18	9.23	1.51
HW22	59.45	4.31	0.65	LW22	53.17	6.05	0.41
HW23	419.76	103.61	19.31	LW23	37.80	4.59	0.47
HW24	490.90	189.42	30.96	LW24	602.65	178.67	31.43
HW25	183.64	112.65	19.20	LW25	364.64	124.26	22.44
HW26	146.44	86.29	14.99	LW26	365.03	83.04	13.30
HW28	127.90	92.40	12.08	LW28	234.30	64.45	9.98
HW30	113.74	73.55	10.07	LW30	210.13	50.27	6.94
HW32	133.36	70.93	16.71	LW32	239.67	25.26	6.22
HW34	122.61	63.80	12.78	LW34	200.15	21.44	5.48
HW36	65.49	35.58	6.38	LW36	123.84	22.44	5.44
HW38	59.77	31.52	5.06	LW38	124.83	18.98	5.40
HW40	53.74	27.32	4.37	LW40	58.18	8.38	1.99
HW42	49.08	21.84	2.55	LW42	59.64	9.64	1.57
HW44	39.89	17.21	3.76	LW44	56.52	4.21	0.66
HW45	22.71	17.40	3.31	LW45	25.94	2.74	0.64
HW46	21.36	1.19	2.61	LW46	20.30	1.13	0.75
HW47	532.66	286.54	64.96	LW47	371.68	105.79	15.82
HW48	100.07	51.37	10.01	LU48	276.56	95.68	11.31
HW49	131.14	30.04	3.05	LW49	152.28	70.04	11.39
HW51	135.60	32.00	8.03	LW51	125.72	70.10	9.91
HW53	80.27	17.82	2.80	LW53	101.42	55.84	7.17
HW55	75.69	17.16	2.12	LW55	128.42	83.32	13.56
HW57	82.69	17.25	4.63	LW57	103.20	64.84	11.05
HW59	58.43	11.10	1.85	LW59	52.04	27.26	5.38
HW61	19.57	5.56	1.91	LW61	32.97	13.45	0.18
HW63	51.32	8.29	1.29	LW63	40.12	17.51	1.80
HW65	27.17	2.86	1.52	LW65	49.99	13.99	1.21
HW67	43.83	6.89	1.22	LW67	29.97	11.64	2.25
HW68	46.73	6.56	0.56	LW68	19.75	10.48	0.96
HW69	31.42	3.21	0.23	LW69	19.90	4.59	0.54

Sediment sample	High salinity treatment				Low salinity treatment		
	Simazine	Atrazine	Diuron		Simazine	Atrazine	Diuron
HS1	426.87	106.62	17.76	LS1	229.14	56.33	12.69
HS2	318.81	79.28	12.66	LS2	172.85	16.85	9.40
HS3	152.02	47.52	9.78	LS3	97.70	11.81	1.11
HS5	134.99	37.06	7.09	LS5	199.66	39.56	8.99
HS7	68.87	32.20	5.69	LS7	72.79	9.71	2.31
HS9	55.82	14.26	2.27	LS9	40.79	3.46	1.67
HS11	50.95	8.09	2.26	LS11	129.97	10.80	7.54
HS13	55.05	13.19	2.55	LS13	68.97	9.30	1.04
HS15	93.62	11.20	4.57	LS15	30.33	4.77	1.70
HS17	66.53	6.95	2.22	LS17	29.57	1.47	0.50
HS19	54.47	6.64	2.57	LS19	33.60	2.32	0.18
HS21	72.04	6.87	1.57	LS21	49.27	2.00	1.37
HS22	60.57	4.97	0.93	LS22	50.31	3.90	1.55
HS23	16.98	5.20	0.44	LS23	31.69	2.44	0.83
HS24	303.59	126.12	24.33	LS24	369.31	102.55	17.37
HS25	190.82	107.68	18.96	LS25	223.15	71.84	8.42
HS26	152.23	102.64	15.52	LS26	288.82	36.94	7.06
HS28	160.15	81.93	11.79	LS28	182.20	36.05	7.96
HS30	110.63	67.35	9.42	LS30	174.11	29.98	5.62
HS32	116.67	57.29	7.89	LS32	167.61	18.31	5.59
HS34	102.64	66.43	12.60	LS34	170.61	19.08	5.24
HS36	61.03	30.46	5.10	LS36	87.93	16.48	5.64
HS38	41.64	21.68	3.17	LS38	88.21	12.49	4.74
HS40	42.50	18.27	2.43	LS40	74.30	6.56	2.11
HS42	44.15	15.62	1.33	LS42	47.37	7.89	1.89
HS44	34.85	12.58	3.14	LS44	45.56	2.81	1.85
HS45	15.60	11.92	2.10	LS45	49.89	1.60	0.67
HS46	14.90	9.42	0.95	LS46	19.43	1.09	0.54
HS47	193.54	96.14	11.09	LS47	237.73	109.53	17.79
HS48	28.97	21.53	2.02	LS48	144.99	78.48	13.23
HS49	10.39	13.11	1.66	LS49	118.19	62.14	9.69
HS51	442.95	99.84	17.30	LS51	107.90	66.96	11.65
HS53	124.42	27.74	4.79	LS53	90.09	54.81	7.19
HS55	82.26	14.67	1.21	LS55	115.84	58.20	12.64
HS57	75.25	11.54	1.18	LS57	91.44	41.64	8.85
HS59	41.95	7.58	2.76	LS59	43.99	19.12	3.03
HS61	13.66	3.64	1.77	LS61	36.46	14.01	1.47
HS63	58.33	9.20	1.75	LS63	37.94	15.88	1.96
HS65	30.92	2.47	1.67	LS65	35.00	10.59	0.45
HS67	58.83	6.73	0.71	LS67	31.66	11.53	2.72
HS68	48.17	5.98	1.82	LS68	15.24	3.97	0.11
HS69	36.51	3.36	1.41	LS69	15.73	7.70	4.74

RSD % for simazine, atrazine and diuron concentrations ($\mu g\ L^{-1}$) released from the soil and sediment into the overlying water under the low and high salinity treatments

	Simazine	Atrazine	Diuron		Simazine	Atrazine	Diuron
HS3	152.02	47.52	9.78	HW3	384.68	100.63	19.87
HS3 duplicate	149.91	44.89	9.89	HW3 duplicate	381.39	98.78	18.52
RSD %	0.99	4.02	0.81	RSD %	0.61	1.32	4.97
HS5	134.99	37.06	7.09	HW23	419.76	103.61	19.31
HS5 duplicate	130.23	34.56	6.98	HW23 duplicate	416.89	101.76	21.02
RSD %	2.54	4.93	1.13	RSD %	0.49	1.28	6.01
HS25	190.82	107.68	18.96	HW26	146.44	86.29	14.99
HS25 duplicate	187.87	106.98	18.56	HW26 duplicate	149.26	88.16	13.70
RSD %	1.10	0.46	1.49	RSD %	1.35	1.52	6.36
HS28	160.15	81.93	11.79	HW28	127.90	92.40	12.08
HS28 duplicate	162.01	83.03	11.54	HW28 duplicate	129.01	91.89	13.40
RSD %	0.81	0.94	1.53	RSD %	0.61	0.39	7.31
LS2	172.85	16.85	9.40	LW3	130.59	23.39	3.98
LS2 duplicate	174.23	16.97	9.12	LW3 duplicate	131.20	21.96	3.86
RSD %	0.56	0.51	2.10	RSD %	99.53	106.52	103.14
LS5	199.66	39.56	8.99	LW5	237.40	35.81	7.83
LS5 duplicate	198.76	38.72	8.65	LW5 duplicate	235.54	34.75	7.42
RSD %	0.32	1.51	2.69	RSD %	0.56	2.12	3.82
LS6	31.69	2.44	0.83	LW9	106.51	19.64	2.85
LS6 duplicate	27.99	2.41	0.79	LW9 duplicate	109.10	17.58	2.82
RSD %	8.76	0.90	3.76	RSD %	1.70	7.84	0.64
LS23	174.11	29.98	5.62	LW25	364.64	124.26	22.44
LS23 duplicate	173.24	31.01	5.89	LW25 duplicate	360.59	122.76	20.95
RSD %	0.36	2.39	3.30	RSD %	0.79	0.86	4.86
LS30	223.15	71.84	8.42	LW28	234.30	64.45	9.98
LS30 duplicate	220.78	69.98	7.34	LW28 duplicate	231.98	62.63	8.71
RSD %	0.75	1.85	9.67	RSD %	0.70	2.03	9.64
HW2	419.76	103.61	19.31	LW34	200.15	21.44	5.48
HW2 duplicate	421.21	101.56	18.23	LW34 duplicate	198.60	20.61	5.84
RSD %	0.24	1.42	4.06	RSD %	1.10	5.55	8.26

Appendix 11 DOC concentrations (mg L^{-1}) released into the overlying water from the soil and sediment under the low and high salinity treatments

Soil Sample	High salinity DOM	Low salinity Sample	DOM	Sediment Sample	High salinity DOM	Low salinity Sample	DOM
HW1	562.46	LW1	573.86	HS1	332.16	LS1	215.91
HW2	271.24	LW2	346.76	HS2	142.86	LS2	87.62
HW3	7.12	LW3	116.94	HS3	57.10	LS3	39.72
HW4	2.84	LW4	92.52	HS4	12.72	LS4	51.80
HW5	5.40	LW5	62.32	HS5	21.20	LS5	80.61
HW6	11.24	LW6	35.87	HS6	36.64	LS6	40.31
HW7	12.10	LW7	13.54	HS7	27.00	LS7	35.38
HW8	9.80	LW8	38.71	HS8	25.16	LS8	22.12
HW9	8.34	LW9	57.08	HS9	19.52	LS9	16.70
HW10	9.94	LW10	55.76	HS10	14.02	LS10	22.12
HW11	19.54	LW11	29.66	HS11	24.80	LS11	22.04
HW12	45.98	LW12	38.22	HS12	50.90	LS12	29.76
HW13	39.30	LW13	40.46	HS13	46.28	LS13	31.14
HW14	46.98	LW14	32.18	HS14	50.84	LS14	21.82
HW15	31.16	LW15	33.58	HS15	41.50	LS15	26.01
HW16	30.44	LW16	22.88	HS16	32.68	LS16	18.36
HW17	25.84	LW17	39.66	HS17	35.26	LS17	25.02
HW18	24.98	LW18	30.18	HS18	31.50	LS18	29.06
HW19	26.28	LW19	78.30	HS19	30.12	LS19	30.16
HW20	24.74	LW20	11.38	HS20	29.74	LS20	7.02
HW21	14.78	LW21	14.08	HS21	29.98	LS21	11.44
HW22	11.50	LW22	15.48	HS22	33.94	LS22	14.48
HW23	24.62	LW23	35.54	HS23	49.74	LS23	30.60
HW24	472.68	LW24	677.72	HS24	423.20	LS24	422.24
HW25	292.32	LW25	558.62	HS25	274.14	LS25	323.24
HW26	230.02	LW26	84.84	HS26	217.96	LS26	73.44
HW27	201.10	LW27	77.84	HS27	198.36	LS27	44.80
HW28	172.71	LW28	28.08	HS28	184.10	LS28	34.20
HW29	145.48	LW29	11.08	HS29	155.30	LS29	15.36
HW30	141.88	LW30	20.36	HS30	148.26	LS30	22.84
HW31	59.80	LW31	29.98	HS31	64.96	LS31	21.48
HW32	75.56	LW32	15.00	HS32	70.64	LS32	17.04
HW33	64.30	LW33	9.90	HS33	60.14	LS33	18.48
HW34	21.98	LW34	44.36	HS34	21.32	LS34	56.70
HW35	44.82	LW35	65.14	HS35	43.40	LS35	54.34
HW36	13.98	LW36	65.24	HS36	18.16	LS36	51.98
HW37	25.01	LW37	66.26	HS37	19.96	LS37	53.96
HW38	14.38	LW38	37.64	HS38	10.80	LS38	36.78
HW39	20.24	LW39	42.04	HS39	17.54	LS39	32.30
HW40	4.88	LW40	91.66	HS40	2.76	LS40	42.60
HW41	9.78	LW41	95.86	HS41	14.50	LS41	41.26
HW42	8.58	LW42	62.70	HS42	3.92	LS42	39.86
HW43	10.72	LW43	38.82	HS43	8.68	LS43	53.64
HW44	1.92	LW44	60.62	HS44	0.24	LS44	27.56
HW45	1.14	LW45	41.02	HS45	1.34	LS45	22.20
HW46	0.90	LW46	52.84	HS46	14.02	LS46	25.66
HW47	424.78	LW47	529.02	HS47	136.62	LS47	393.72
HW48	309.44	LW48	543.22	HS48	66.80	LS48	349.96
HW49	10.98	LW49	221.26	HS49	7.50	LS49	237.88
HW50	22.98	LW50	217.42	HS50	24.30	LS50	239.38
HW51	35.30	LW51	243.12	HS51	107.06	LS51	236.84
HW52	39.12	LW52	220.88	HS52	17.84	LS52	219.82
HW53	24.86	LW53	206.46	HS53	46.90	LS53	206.28
HW54	21.20	LW54	76.68	HS54	53.78	LS54	78.72
HW55	33.62	LW55	65.52	HS55	29.58	LS55	87.66
HW56	31.54	LW56	79.10	HS56	40.52	LS56	85.48
HW57	19.30	LW57	29.74	HS57	28.18	LS57	24.14
HW58	22.54	LW58	53.98	HS58	11.24	LS58	59.66
HW59	23.40	LW59	25.98	HS59	22.80	LS59	25.50
HW60	14.30	LW60	32.78	HS60	23.68	LS60	32.28
HW61	17.30	LW61	23.30	HS61	17.30	LS61	17.68
HW62	14.32	LW62	22.64	HS62	9.98	LS62	27.72
HW63	27.02	LW63	8.52	HS63	15.76	LS63	6.40
HW64	13.20	LW64	23.30	HS64	11.54	LS64	22.70
HW65	20.02	LW65	6.24	HS65	24.64	LS65	14.40
HW66	3.52	LW66	16.92	HS66	4.72	LS66	19.40
HW67	11.90	LW67	2.90	HS67	8.58	LS67	2.00
HW68	26.70	LW68	7.46	HS68	12.48	LS68	18.30
HW69	26.04	LW69	11.74	HS69	25.98	LS69	14.12

RSD % for DOC concentrations released into the overlying water from the soil and sediment under the low and high salinity treatments

HS3	57.10	HW3	7.12
HS3 duplicate	56.20	HW3 duplicate	6.89
RSD %	1.12	RSD %	2.32
HS5	21.20	HW23	24.62
HS5 duplicate	20.56	HW23 duplicate	23.40
RSD %	2.17	RSD %	0.33
HS9	19.52	HW26	230.20
HS9 duplicate	20.17	HW26 duplicate	231.98
RSD %	2.32	RSD %	0.54
HS25	274.14	HW28	172.71
HS25 duplicate	273.42	HW28 duplicate	171.02
RSD %	0.19	RSD %	0.70
HS28	184.10	HW47	424.78
HS28 duplicate	182.59	HW47 duplicate	473.26
RSD %	0.58	RSD %	7.63
LS2	87.62	HW50	22.98
LS2 duplicate	86.12	HW50 duplicate	20.32
RSD %	1.22	RSD %	8.69
LS5	80.61	LW3	116.94
LS5 duplicate	82.01	LW3 duplicate	113.93
RSD %	1.22	RSD %	1.84
LS6	40.31	LW5	62.32
LS6 duplicate	39.29	LW5 duplicate	64.38
RSD %	1.81	RSD %	2.30
LS23	30.60	LW9	57.08
LS23 duplicate	28.64	LW9 duplicate	56.13
RSD %	4.68	RSD %	1.19
LS25	323.24	LW25	558.62
LS25 duplicate	322.93	LW25 duplicate	555.82
RSD %	0.07	RSD %	0.36
LS30	22.84	LW28	28.08
LS30 duplicate	24.03	LW28 duplicate	29.41
RSD %	3.59	RSD %	3.27
HW2	271.24	LW34	44.36
HW2 duplicate	269.02	LW34 duplicate	45.21
RSD %	0.58	RSD %	1.34

Appendix 12 pH values in the overlying water under the low and high salinity treatments

Soil	High salinity	Low salinity		Sediment	High salinity	Low salinity	
Sample	pH	Sample	pH	Sample	pH	Sample	pH
HW1	7.5	LW1	7.5	HS1	7.8	LS1	7.8
HW2	7.8	LW2	7.4	HS2	8.1	LS2	7.8
HW3	7.9	LW3	7.5	HS3	7.9	LS3	7.8
HW4	8.0	LW4	7.5	HS4	7.9	LS4	7.8
HW5	8.0	LW5	7.6	HS5	8.0	LS5	7.8
HW6	8.0	LW6	7.5	HS6	8.0	LS6	7.8
HW7	8.0	LW7	7.5	HS7	8.0	LS7	7.7
HW8	8.0	LW8	7.5	HS8	7.9	LS8	7.8
HW9	8.1	LW9	7.5	HS9	8.1	LS9	7.9
HW10	8.0	LW10	7.6	HS10	8.2	LS10	7.9
HW11	8.0	LW11	7.6	HS11	8.2	LS11	7.9
HW12	8.1	LW12	7.5	HS12	8.2	LS12	7.7
HW13	8.1	LW13	7.4	HS13	8.0	LS13	7.6
HW14	8.0	LW14	7.4	HS14	8.1	LS14	7.8
HW15	8.1	LW15	7.3	HS15	8.0	LS15	7.5
HW16	7.9	LW16	7.3	HS16	7.9	LS16	7.5
HW17	8.0	LW17	7.5	HS17	8.1	LS17	7.8
HW18	8.0	LW18	7.3	HS18	8.1	LS18	7.8
HW19	8.1	LW19	7.6	HS19	8.1	LS19	7.7
HW20	8.1	LW20	7.7	HS20	8.1	LS20	7.7
HW21	8.0	LW21	7.5	HS21	8.0	LS21	7.8
HW22	8.0	LW22	7.3	HS22	7.9	LS22	7.5
HW23	8.0	LW23	7.2	HS23	8.1	LS23	7.6
HW24	7.3	LW24	7.2	HS24	7.8	LS24	7.3
HW25	7.9	LW25	7.3	HS25	8.3	LS25	8.0
HW26	8.0	LW26	7.6	HS26	8.0	LS26	7.9
HW27	7.9	LW27	7.6	HS27	7.9	LS27	7.9
HW28	7.9	LW28	7.4	HS28	7.7	LS28	7.4
HW29	8.0	LW29	7.0	HS29	8.2	LS29	7.3
HW30	8.0	LW30	7.4	HS30	7.9	LS30	7.4
HW31	8.0	LW31	7.6	HS31	7.8	LS31	7.9
HW32	8.1	LW32	7.7	HS32	8.1	LS32	8.0
HW33	8.2	LW33	7.6	HS33	8.1	LS33	8.1
HW34	7.8	LW34	7.3	HS34	7.8	LS34	7.5
HW35	7.9	LW35	7.2	HS35	8.2	LS35	7.6
HW36	7.9	LW36	7.2	HS36	8.0	LS36	7.5
HW37	8.2	LW37	7.4	HS37	8.3	LS37	7.3
HW38	8.1	LW38	7.1	HS38	8.1	LS38	7.7
HW39	8.0	LW39	7.2	HS39	7.9	LS39	7.1
HW40	8.2	LW40	7.2	HS40	8.2	LS40	7.6
HW41	8.2	LW41	7.2	HS41	8.1	LS41	7.6
HW42	8.2	LW42	6.9	HS42	8.3	LS42	7.7
HW43	8.3	LW43	6.9	HS43	8.3	LS43	7.2
HW44	7.8	LW44	7.2	HS44	7.8	LS44	7.2
HW45	7.7	LW45	7.2	HS45	7.8	LS45	7.2
HW46	8.0	LW46	7.1	HS46	8.1	LS46	7.7
HW47	7.7	LW47	7.1	HS47	7.9	LS47	7.5
HW48	7.9	LW48	7.2	HS48	8.0	LS48	7.5
HW49	7.9	LW49	7.2	HS49	7.9	LS49	7.5
HW50	8.0	LW50	7.2	HS50	8.0	LS50	7.4

HW51	8.0	LW51	7.3	HS51	8.1	LS51	7.5
HW52	8.0	LW52	7.3	HS52	8.0	LS52	7.4
HW53	8.0	LW53	7.3	HS53	8.0	LS53	7.3
HW54	8.0	LW54	7.3	HS54	8.1	LS54	7.3
HW55	8.1	LW55	7.4	HS55	8.1	LS55	7.5
HW56	8.1	LW56	7.3	HS56	8.1	LS56	7.5
HW57	8.1	LW57	7.4	HS57	8.1	LS57	7.4
HW58	8.1	LW58	7.4	HS58	7.9	LS58	7.4
HW59	7.9	LW59	7.4	HS59	7.9	LS59	7.5
HW60	7.9	LW60	7.3	HS60	7.9	LS60	7.4
HW61	7.9	LW61	7.3	HS61	8.0	LS61	7.4
HW62	8.0	LW62	7.4	HS62	7.9	LS62	7.5
HW63	7.8	LW63	7.3	HS63	7.7	LS63	7.4
HW64	7.8	LW64	7.3	HS64	7.8	LS64	7.4
HW65	8.1	LW65	7.3	HS65	8.1	LS65	7.8
HW66	7.8	LW66	7.4	HS66	8.2	LS66	7.5
HW67	7.8	LW67	7.5	HS67	7.9	LS67	7.4
HW68	7.8	LW68	7.3	HS68	7.8	LS68	7.3
HW69	8.0	LW69	7.1	HS69	8.0	LS69	7.7

Appendix 13 Concentrations of Cu, Ni and Zn (mg L^{-1}) released from the soil and sediment to the overlying water under the first and second drying-rewetting treatment

Soil	First drying-rewetting treatment			Second drying-rewetting			
Sample	Cu	Ni	Zn	Sample	Cu	Ni	Zn
DT1	0.45	32.05	18.10	DW1	0.09	17.96	9.71
DT2	0.25	18.19	16.40	DW2	0.05	8.16	4.81
DT3	0.23	15.10	9.55	DW3	0.13	5.04	3.58
DT4	0.19	14.41	9.14	DW4	0.03	3.22	2.31
DT5	0.20	13.07	8.39	DW5	0.03	2.82	2.04
DT6	0.17	10.92	6.95	DW6	0.03	2.30	1.66
DT7	0.12	6.78	4.70	DW7	0.02	2.06	1.54
DT8	0.11	5.75	4.04	DW8	0.02	1.88	1.41
DT9	0.09	4.93	3.53	DW9	0.07	1.36	1.29
DT10	0.11	5.33	3.97	DW10	0.07	1.68	1.52
DT11	0.78	59.68	35.61	DW11	0.08	5.31	2.41
DT12	0.53	36.11	18.90	DW12	0.08	6.04	2.72
DT13	0.23	13.33	10.40	DW13	0.02	1.93	0.92
DT14	0.23	12.08	9.66	DW14	0.02	1.67	0.87
DT15	0.17	8.64	6.94	DW15	0.02	1.79	0.93
DT16	0.16	7.35	5.89	DW16	0.01	0.93	0.53
DT17	0.15	6.89	5.61	DW17	0.01	0.97	0.54
DT18	0.15	6.54	5.39	DW18	0.01	1.05	0.64
DT19	0.11	4.86	3.93	DW19	0.01	1.16	0.67
DT20	0.11	4.58	3.75	DW20	0.01	1.05	0.64
DT21	0.51	40.30	23.64	DW21	0.02	12.98	5.57
DT22	0.25	22.29	19.19	DW22	0.12	1.62	0.70
DT23	0.14	19.47	6.81	DW23	0.01	0.47	0.21
DT24	0.11	9.21	5.02	DW24	0.03	2.60	1.10
DT25	0.08	6.47	3.10	DW25	0.02	1.18	0.61
DT26	0.10	3.95	4.04	DW26	0.02	1.64	0.88
DT27	0.08	3.98	3.20	DW27	0.02	2.21	1.24
DT28	0.07	3.41	2.72	DW28	0.02	1.46	0.87
DT29	0.08	4.14	3.45	DW29	0.07	5.20	3.08
DT30	0.01	0.50	0.37	DW30	0.06	4.03	2.41

Sediment	First drying-rewetting			Second drying-rewetting treatment			
Sample	Cu	Ni	Zn	Sample	Cu		
DS1	0.04	5.83	2.29	WT1	0.01	2.46	0.95
DS2	0.03	4.50	1.76	WT2	0.01	2.35	0.92
DS3	0.01	1.68	0.84	WT3	0.01	1.65	0.73
DS4	0.01	1.73	0.97	WT4	0.01	1.73	0.79
DS5	0.01	0.64	0.94	WT5	0.01	1.61	0.75
DS6	0.01	0.20	0.10	WT6	0.01	1.74	0.84
DS7	0.01	1.08	0.64	WT7	0.01	1.17	0.77
DS8	0.01	1.05	0.59	WT8	0.01	1.03	0.70
DS9	0.01	1.03	0.63	WT9	0.01	1.00	0.69
DS10	0.01	1.06	0.65	WT10	0.01	0.92	0.70
DS11	0.06	7.21	2.95	WT11	0.02	10.36	1.06
DS12	0.03	5.66	1.58	WT12	0.02	1.79	1.29
DS13	0.01	3.72	1.16	WT13	0.00	2.61	0.60
DS14	0.01	1.74	1.27	WT14	0.01	1.15	0.67
DS15	0.01	1.82	0.91	WT15	0.00	0.73	0.57
DS16	0.01	1.35	0.94	WT16	0.00	0.87	0.55
DS17	0.01	1.09	0.80	WT17	0.00	0.67	0.44
DS18	0.01	1.10	0.97	WT18	0.00	0.63	0.52
DS19	0.01	1.50	0.66	WT19	0.00	0.69	0.42
DS20	0.04	1.04	1.26	WT20	0.00	1.38	0.64
DS21	0.07	6.52	2.57	WT21	0.02	2.99	4.84
DS22	0.04	3.68	1.98	WT22	0.02	3.27	0.50
DS23	0.01	2.07	0.80	WT23	0.01	1.23	0.73
DS24	0.02	2.16	1.02	WT24	0.01	1.15	0.44
DS25	0.01	1.46	0.80	WT25	0.01	0.92	0.35
DS26	0.01	1.43	0.72	WT26	0.01	0.94	0.40
DS27	0.01	1.27	0.68	WT27	0.01	0.72	0.34
DS28	0.01	1.44	0.68	WT28	0.01	0.85	0.35
DS29	0.01	1.01	0.83	WT29	0.01	0.70	0.39
DS30	0.01	2.46	0.56	WT30	0.02	1.02	0.78

RSD% for Cu, Ni and Zn concentrations released from the soil and sediment to the overlying water under the drying-rewetting treatment

	Cu	Ni	Zn
DT2	0.25	18.19	16.40
DT2 duplicate	0.23	17.69	15.92
RSD%	3.55	1.98	2.10
DT12	0.53	36.11	18.90
DT12 duplicate	0.50	34.99	18.21
RSD%	4.41	2.22	2.63
DT25	0.08	6.47	3.10
DT25 duplicate	0.08	5.82	2.91
RSD%	4.11	7.51	4.44
DW7	0.02	2.06	1.54
DW7 duplicate	0.02	2.17	1.69
RSD%	10.10	3.78	6.47
DW15	0.02	1.79	0.93
DW15 duplicate	0.02	1.85	0.89
RSD%	7.49	2.20	2.77
DW25	0.02	1.18	0.61
DW25 duplicate	0.02	1.25	0.52
RSD%	9.57	3.86	10.94
DS3	0.01	1.68	0.84
DS3 duplicate	0.01	1.54	0.92
RSD%	9.20	6.27	6.73
DS14	0.01	1.74	1.27
DS14 duplicate	0.01	1.65	1.32
RSD%	9.63	3.56	2.73
DS28	0.01	1.44	0.68
DS28 duplicate	0.01	1.52	0.74
RSD%	9.74	3.63	6.46
WT5	0.01	1.61	0.75
WT5 duplicate	0.01	1.69	0.69
RSD%	9.43	3.62	5.70
WT12	0.02	1.79	1.29
WT12 duplicate	0.02	1.64	1.18
RSD%	7.84	6.02	6.57
WT21	0.02	2.99	4.84
WT21 duplicate	0.01	2.82	4.79
RSD%	7.68	4.17	0.79

Appendix 14 Concentrations of simazine, atrazine and diuron (µg L^{-1}) released from the soil and sediment to the overlying water under the first and second drying-rewetting treatments

Soil	First drying-rewetting treatment			Second drying-rewetting			
Sample	Simazine	Atrazine	Diuron	Sample	Simazine	Atrazine	Diuron
DT1	740.36	477.50	95.99	DW1	359.12	246.49	38.67
DT3	312.32	221.16	37.20	DW3	166.82	114.11	15.83
DT5	152.12	96.77	15.54	DW5	165.39	110.95	6.06
DT7	86.24	54.07	9.13	DW7	84.03	45.27	4.58
DT9	74.88	39.32	5.81	DW9	75.65	12.68	2.72
DT11	861.78	650.60	92.75	DW11	170.02	105.33	15.84
DT13	574.21	338.43	57.87	DW13	58.79	32.64	6.05
DT15	272.23	177.80	32.15	DW15	53.89	30.451	5.73
DT17	201.96	108.77	22.03	DW17	29.89	14.79	2.66
DT19	158.61	100.56	20.19	DW19	34.95	16.16	2.13
DT21	598.48	314.39	80.93	DW21	264.58	137.24	31.93
DT23	264.45	139.64	32.63	DW23	145.87	75.03	18.46
DT25	33.74	43.65	12.17	DW25	77.83	31.78	7.54
DT27	48.77	26.55	5.85	DW27	69.37	12.72	3.24
DT29	88.73	21.79	4.50	DW29	34.95	9.36	0.41

Sediment	First drying-rewetting			Second drying-rewetting treatment			
Sample	Simazine	Atrazine	Diuron	Sample	Simazine	Atrazine	Diuron
DS1	173.62	132.55	26.37	WT1	183.30	76.12	16.01
DS3	124.90	94.88	13.82	WT3	70.29	51.72	9.72
DS5	83.24	89.59	5.28	WT5	66.52	21.94	10.09
DS7	54.29	24.00	2.27	WT7	36.02	13.84	3.40
DS9	54.45	5.86	1.02	WT9	34.48	37.21	1.52
DS11	108.40	1.03	19.25	WT11	134.95	117.08	19.37
DS13	75.12	7.21	10.42	WT13	88.43	34.36	6.09
DS15	37.99	5.66	6.25	WT15	48.46	28.34	3.82
DS17	23.78	3.72	4.92	WT 17	33.75	15.06	2.10
DS19	22.32	1.74	4.98	WT19	74.46	13.03	3.03
DS21	130.68	1.82	29.44	WT21	154.85	158.58	40.19
DS23	88.86	1.35	15.89	WT23	318.14	62.15	12.86
DS25	62.44	1.09	11.24	WT25	142.40	25.28	4.88
DS27	12.38	1.10	1.41	WT27	62.79	21.61	2.61
DS29	10.42	1.50	1.65	WT29	47.74	11.78	1.57

RSD % for simazine, atrazine and diuron concentrations (µg L^{-1}) released from the soil and sediment into the overlying water under the first and second drying-rewetting treatment.

	Simazine	atrazine	diuron
DT17	201.96	108.77	22.03
DT17 duplicate	199.23	106.87	21.23
RSD%	0.96	1.25	2.61
DT25	33.74	43.65	12.17
DT25 duplicate	32.43	44.79	11.67
RSD%	2.79	1.83	2.98
DW17	29.89	14.79	2.66
DW17 duplicate	28.57	15.03	2.32
RSD%	3.19	1.16	9.73
DW25	77.83	31.78	7.54
DW25 duplicate	76.49	32.54	7.92
RSD%	1.23	1.67	3.50
DS3	124.90	94.88	13.82
DS3 duplicate	123.61	95.28	12.46
RSD%	0.73	0.30	7.30
DS17	23.78	3.72	4.92
DS17 duplicate	22.73	3.82	4.03
RSD%	3.19	1.92	14.01
DS25	62.44	1.09	11.24
DS25 duplicate	61.72	1.20	11.13
RSD%	0.82	6.55	0.68
WT3	70.29	51.72	9.72
WT3 duplicate	71.02	50.56	8.89
RSD%	0.73	1.60	6.33
WT 17	33.75	15.06	2.10
WT17 duplicate	32.67	14.92	2.21
RSD%	2.30	0.67	3.69
WT25	142.40	25.28	4.88
WT25 duplicate	141.72	24.69	5.09
RSD%	0.34	1.68	2.97

Appendix 15 Concentrations of DOC (mg L^{-1}) released from the soil and sediment to the overlying water under the first and second drying-rewetting treatments

Soil	First drying-rewetting	Second drying-rewetting		Sediment	First drying-rewetting	Second drying-rewetting	
Sample	DOM	Sample	DOM	Sample	DOM	Sample	DOM
DT1	720.44	DW1	65.56	DS1	82.02	WT1	18.50
DT2	430.42	DW2	49.12	DS2	51.88	WT2	17.24
DT3	302.70	DW3	32.44	DS3	47.86	WT3	15.04
DT4	256.20	DW4	27.66	DS4	26.32	WT4	14.26
DT5	247.72	DW5	31.24	DS5	30.22	WT5	16.22
DT6	221.18	DW6	22.24	DS6	36.1	WT6	11.28
DT7	39.52	DW7	34.78	DS7	33.16	WT7	14.02
DT8	43.94	DW8	25.42	DS8	32.68	WT8	8.36
DT9	62.06	DW9	28.18	DS9	76.54	WT9	6.82
DT10	27.40	DW10	8.76	DS10	86.98	WT10	7.28
DT11	847.88	DW11	109.65	DS11	159.71	WT11	35.52
DT12	441.28	DW12	98.23	DS12	159.81	WT12	25.44
DT13	195.54	DW13	78.39	DS13	73.73	WT13	23.84
DT14	74.88	DW14	33.18	DS14	28.14	WT14	20.06
DT15	158.24	DW15	8.34	DS15	28.14	WT15	21.24
DT16	116.52	DW16	12.10	DS16	8.22	WT16	12.46
DT17	85.92	DW17	6.88	DS17	4.92	WT17	22.86
DT18	81.74	DW18	6.18	DS18	10.36	WT18	16.80
DT19	43.58	DW19	2.44	DS19	10.34	WT19	18.84
DT20	41.80	DW20	2.44	DS20	0.64	WT20	38.36
DT21	584.90	DW21	37.46	DS21	106.66	WT21	19.72
DT22	336.06	DW22	37.94	DS22	27	WT22	18.84
DT23	245.68	DW23	34.42	DS23	10.78	WT23	13.48
DT24	230.46	DW24	32.56	DS24	24.33	WT24	15.17
DT25	201.36	DW25	34.38	DS25	27.14	WT25	18.80
DT26	86.80	DW26	9.30	DS26	36.94	WT26	20.18
DT27	44.34	DW27	6.96	DS27	56.6	WT27	19.70
DT28	67.22	DW28	22.34	DS28	32.96	WT28	19.52
DT29	76.58	DW29	21.00	DS29	119.74	WT29	21.06
DT30	67.98	DW30	24.68	DS30	87.98	WT30	21.06

RSD % for DOC concentrations (mg L^{-1}) released into the overlying water from the soil and sediment under the drying-rewetting treatment

Sample	DOM
DT3	302.70
DT3 duplicate	301.42
RSD%	0.30
DT10	27.40
DT10 duplicate	25.89
RSD%	4.01
DT27	44.34
DT27 duplicate	45.12
RSD%	1.23
DW9	28.18
DW9 duplicate	28.92
RSD%	1.83
DW20	2.44
DW20 duplicate	2.31
RSD%	3.87
DS8	32.68
DS8 duplicate	30.81
RSD%	4.17
DS17	4.92
DS17 duplicate	4.65
RSD%	3.99
DS26	36.94
DS26 duplicate	35.43
RSD%	2.95
WT4	14.26
WT4 duplicate	15.67
RSD%	6.66
WT10	7.28
WT10 duplicate	6.98
RSD%	2.98
WT23	13.48
WT23 duplicate	12.78
RSD%	3.77

Appendix 16 Cumulative headspace CO_2 (µg CO_2 kg^{-1}), carbon mineralisation rate (µg kg^{-1} day^{-1}) and microbial biomass (µg C g^{-1}) data

Fully wet soil

Sample	CO_2	Carbon mineraliation rate
FW1	9.10	
FW2	14.23	2.56
FW3	14.67	1.86
FW4	15.04	1.49
FW5	16.02	1.38
FW6	20.71	1.45
FW7	26.84	1.97
FW8	20.54	1.14
FW9	25.94	1.53
FW10	21.78	1.06
FW11	20.07	0.73
FW12	19.22	0.63
FW13	24.20	0.89
FW14	23.10	0.78
FW15	16.22	0.37
FW16	9.26	
FW17	14.15	2.45
FW18	14.82	1.85
FW19	15.55	1.57
FW20	17.91	1.73
FW21	19.74	1.31
FW22	22.52	1.47
FW23	19.34	1.01
FW24	21.90	1.15
FW25	19.09	0.82
FW26	19.98	0.71
FW27	22.09	0.80
FW28	26.25	1.00
FW29	27.79	1.03
FW30	20.60	0.60
FW31	5.34	
FW32	11.60	3.13
FW33	12.12	2.26
FW34	12.43	1.77
FW35	13.54	1.64
FW36	15.08	1.22
FW37	20.06	1.64
FW38	17.24	1.19
FW39	20.08	1.34
FW40	18.78	1.12
FW41	23.77	1.23
FW42	23.63	1.14
FW43	26.66	1.25
FW44	27.10	1.21
FW45	17.24	0.63

Fully wet sediment

Sample	CO_2	Carbon mineralisation rate
FT1	9.96	
FT2	12.83	1.44
FT3	15.86	1.97
FT4	18.11	2.04
FT5	20.93	2.19
FT6	27.78	2.23
FT7	27.61	1.96
FT8	26.75	1.68
FT9	27.73	1.62
FT10	28.17	1.52
FT11	29.91	1.33
FT12	28.92	1.18
FT13	31.24	1.25
FT14	32.38	1.25
FT15	28.93	1.00
FT16	13.88	
FT17	15.14	0.63
FT18	17.58	1.23
FT19	20.86	1.75
FT20	23.38	1.90
FT21	30.75	2.11
FT22	28.40	1.61
FT23	27.92	1.40
FT24	29.89	1.46
FT25	29.07	1.27
FT26	30.99	1.14
FT27	29.28	0.96
FT28	32.47	1.09
FT29	33.09	1.07
FT30	27.06	0.69
FT31	8.92	
FT32	12.79	1.94
FT33	14.64	1.91
FT34	15.27	1.59
FT35	18.47	1.91
FT36	25.02	2.01
FT37	26.68	1.97
FT38	26.31	1.74
FT39	25.41	1.50
FT40	27.26	1.53
FT41	29.30	1.36
FT42	29.67	1.30
FT43	30.30	1.26
FT44	32.08	1.29
FT45	32.42	1.24

Dried-rewet soil

Sample	CO_2	Carbon mineraliation rate
DR1	1592.57	
DR2	4674.76	1541.10
DR3	4426.07	944.50
DR4	5150.95	889.60
DR5	6125.10	906.51
DR6	7444.88	975.38
DR7	1767.47	
DR8	4596.54	1501.98
DR9	4345.07	917.50
DR10	5033.55	860.25
DR11	6344.09	950.31
DR12	7280.68	948.02
DR13	1478.77	
DR14	4803.90	1605.67
DR15	4580.10	995.84
DR16	5253.31	915.19
DR17	5865.09	854.50
DR18	7649.79	1009.54

Dried-rewet sediment

Sample	CO_2	Carbon mineraliation rate
DY1	2510.88	
DY2	3779.07	634.10
DY3	4328.19	605.77
DY4	4276.47	441.40
DY5	4618.83	421.59
DY6	4802.60	381.95
DY7	2421.92	
DY8	3475.20	482.16
DY9	4490.26	659.79
DY10	4028.87	379.50
DY11	4299.72	357.77
DY12	4672.41	360.26
DY13	2922.92	
DY14	4033.08	761.10
DY15	4109.35	532.82
DY16	4544.90	508.51
DY17	4697.34	437.29
DY18	4932.92	403.67

RSD % for cumulative headspace CO2 (µg CO_2 kg $^{-1}$)

	CO_2		CO_2
FW7	26.84	FT19	20.86
FW7 duplicate	24.21	FT19 duplicate	19.42
RSD%	7.29	RSD%	5.06
FW14	23.10	FT27	29.28
FW14 duplicate	25.96	FT27 duplicate	28.69
RSD%	8.26	RSD%	1.43
FW23	19.34	FT37	26.68
FW23 duplicate	18.27	FT37 duplicate	25.42
RSD%	4.01	RSD%	3.42
FW35	13.54	FT45	32.42
FW35 duplicate	14.95	FT45 duplicate	30.61
RSD%	7.02	RSD%	4.06
FW44	27.10	DR3	4426.07
FW44 duplicate	26.06	DR3 duplicate	4415.64
RSD%	2.78	RSD%	0.17
FT5	20.93	DY5	4618.83
FT5 duplicate	22.67	DY5 duplicate	4602.61
RSD%	5.64	RSD%	0.25

Microbial biomass (µg C g^{-1} soil/sediment)	
mb1-soil	70.09
mb2-soil	93.04
mb3-soil	87.91
mb4-soil	82.14
mb5-soil	98.84
mb6-soil	97.87
mb7-soil	116.60
mb8-soil	117.86
mb9-soil	102.44
mc1-sediment	104.26
mc2-sediment	79.81
mc3-sediment	95.66
mc4-sediment	85.97
mc5-sediment	77.19
mc6-sediment	67.92
mc7-sediment	68.95
mc8-sediment	81.67
mc9-sediment	63.11

Appendix 17 Linear regression equations for the relationship between DOC, metals and herbicides released from the soil and sediment into the overlying water

Linear regression equations for DOC, metal and herbicide concentrations released from soil

	Linear regression Equation	r^2
Cu	2.852 + (0.872 x DOC)	0.50
Ni	1.044 + (1.107 x DOC)	0.79
Zn	1.482 + (8.20 x DOC)	0.55
Simazine	-0.375 + (1.085 x DOC)	0.76
Atrazine	0.587 + (0.781 x DOC)	0.65
Diuron	1.090 + (0.826 x DOC)	0.68

Linear regression equations for DOC, metal and herbicide concentrations released from the sediment

	Linear regression Equation	r^2
Cu	1.866 + (1.366 x DOC)	0.08
Ni	1.178 + (0.666 x DOC)	0.28
Zn	1.866 + (1.366 x DOC)	0.13
Simazine	-0.162 + (0.811 x DOC)	0.40
Atrazine	0.453 + (0.571 x DOC)	0.31
Diuron	1.011 + (0.453 x DOC)	0.22