A review of processes important in the floodplain setting

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Summary

This report reviews the physical and geochemical processes reported in the literature and likely to be operating in the floodplain setting. The review supports a study of the Port Meadow, located within the floodplain of the River Thames to the northwest of the city of Oxford, an area affected by urban pollution. It focuses on floodplains but includes both material for the hyporheic zone and also generally for riparian zones. It describes the processes, generically covers case studies where these processes have been studied and then assesses the impact on nutrient and other pollutant attenuation.

Floodplains are periodically-flooded areas along rivers and lakes and we can envisage the floodplain setting as a heterogeneous and constantly changing environment where nutrients and other contaminants are attenuated or removed from groundwater discharging to surface water. These changes may be controlled predominantly by water levels. The surface water/groundwater interface is a crucial control point for lateral nutrient fluxes between uplands and aquatic ecosystems and for longitudinal processes along rivers and wetlands.

The concept of redox zones constitutes an important framework for understanding the behaviour of nutrients and contaminants in groundwater. The addition of low molecular weight carbon from the river to shallow groundwater during seasonal inundation of flood plains provides the potential to further stimulate the redox environment.

To understand water movement and hence nutrient movement in floodplains we need to understand residence times, the character of multiple flow paths, and if and when hydraulic gradient reversal occurs. Nutrient migration is therefore controlled by water levels, the distribution of subsurface permeability, plant uptake and redox zone patterns.

In contrast, point sources, such as landfills, unlined animal waste stores and leaking sewers, appear to lead to a relatively stable system with a carbon and nutrient-rich source term which generates an established redox sequence in a limited volume of groundwater down gradient. The shape and size of such plumes may be affected by drought or heavy rainfall. On-site sanitation systems demonstrate the same sequence of redox zones but the highly reducing conditions are found within the tank and such schemes may rely on oxidation of reduced species in the effluent during transport through the unsaturated zone.

Nitrate, the predominant oxidised form of nitrogen, is readily transported in water and is stable under a range of concentrations. However, anaerobic carbon-rich sediments, such as those in floodplains, have the potential to support large populations of denitrifying bacteria. Denitrification is rapid compared to groundwater flow particularly under low flow conditions and nitrate is lost from the groundwater system under these conditions. In contrast, phosphorus removal by soil or sediment retention and biota uptake results in accumulation within the system. Sediments can be both a source and a sink of dissolved phosphorus in surface water and shallow groundwater. Opposite conditions are favourable for nitrogen and phosphorus management with anaerobic conditions favouring denitrification but enhanced desorption and release of phosphorus.

The important processes affecting other contaminants, such as those present in landfill leachate, dissolved organic matter, xenobiotic organic compounds, inorganic macrocomponents, and heavy metals are dilution, sorption, ion exchange, precipitation, redox reactions and degradation. For many contaminants these processes provide significant natural remediation, limiting the effects of the leachate on groundwater.

In peri-urban environments, such as the Oxford Port Meadow, there will be many different sources of nutrients and contaminants and the distribution of zones of low redox may be both

spatially and temporally variable. Other indicators will need to be applied, such as co-contaminants, to help to understand fate and transport of nutrients and contaminants.

1 Introduction

1.1 IMPORTANCE OF UNDERSTANDING FLOODPLAIN PROCESSES

Floodplains are areas of low-lying ground adjacent to rivers, formed mainly of unconsolidated river sediment, and subject to frequent flooding. Lowland floodplains are a landscape-hotspot of biogeochemical activity. They are an area where hydrological flowpaths converge with substrates, groundwater flowpaths and the hyporheic zone, which contain complementary or missing reactants. This creates disproportionally high reaction rates relative to the surrounding matrix (McClain et al., 2003). Such floodplains may be, therefore, a key conduit for, or barrier to, aqueous fluxes between land, rivers and groundwater.

Historically floodplains were attractive for human settlement; the availability of fertile land, freshwater supply and transportation led to the beginnings of modern urban areas (Ellis et al., 2007; Montz, 2000). After decades and even centuries of development, anthropogenic influence has introduced new contaminants to these floodplains, particularly at the margins of such urban development: the peri-urban interface. This is an interaction zone, where urban and rural activities are juxtaposed, and landscape features are subject to rapid modifications, inducing by human activities (Douglas, 2006). Peri–urban zones tend to be more environmentally unstable than either urban or rural settings (McGranahan et al., 2004) and they generally support large industrial development with an ongoing legacy of local pollutant release.

Peri-urban areas are frequently characterised by valuable natural environments and resource bases, and provide essential life-support functions for catchment ecosystems. In the peri-urban environment there is a broader spectrum of potential water contaminants mixed with autochthonous groundwater. The biogeochemical processing afforded by lowland floodplains is potentially crucial in reducing pollutant loads to receiving watercourses. Major UK river systems (e.g. the Mersey, Trent, Severn, and Thames) have associated wide floodplains that support urban and industrial developments. These areas are already pressured and expanding.

The natural attenuation capacity of riparian floodplains can play an important role in reducing potential contaminant fluxes from aquifer to river and hence has relevance to the meeting of the river water quality standards required by the EU Water Framework Directive and its daughter Groundwater Directive. The setting of measures relating to other policy, such as flood risk management (Flood and Water Management Act) and ecosystem protection (Habitats Directive), may have implications for the attenuation capacity of floodplains. Further, this understanding will help predict how changes in the hydrological regime associated with long term changes in the climate will affect the flux of pollutants into rivers.

Our poor currently poor understanding of the mechanisms underlying the biogeochemical functioning of lowland floodplains not only leaves unanswered a series of fundamental scientific questions, but also severely limits our ability to provide effective decision-support which is essential to implement effective environmental management strategies for the future (Wheater and Peach, 2004).

1.2 BACKGROUND AND AIMS OF THE REVIEW

This review forms part of a groundwater-surface water interaction study of Port Meadow, a section of the River Thames floodplain adjoining the northwest of the city of Oxford, which is being undertaken by the British Geological Survey. The aim of the study is to improve the understanding of the hydrochemical processes within floodplain sediments and the implications for the attenuation of groundwater pollutants.

This report reviews the physical and geochemical processes reported in the literature and likely to be operating in the floodplain setting. It focuses on floodplains but includes both material for the hyporheic zone and also generally for riparian zones. It also covers groundwater impacted by landfill leachate in a comparable way as this is relevant to the Oxford Port Meadow setting.

It first describes the processes in a generic way, covers case studies where these processes have been studied and then assesses the impact on nutrient and other pollutant attenuation.

2 Processes

2.1 FLOW PATHS

Riparian zones can be broadly defined as semi-terrestrial areas lying at the interface of the terrestrial and the aquatic environments (Vidon et al., 2010). They are often influenced by overbank flooding events and connect the terrestrial and aquatic environments through surface and hydrologic flow paths (Figure 2.1). They can act as both a conduit and a barrier to fluxes and provide a highly biochemically active zone.
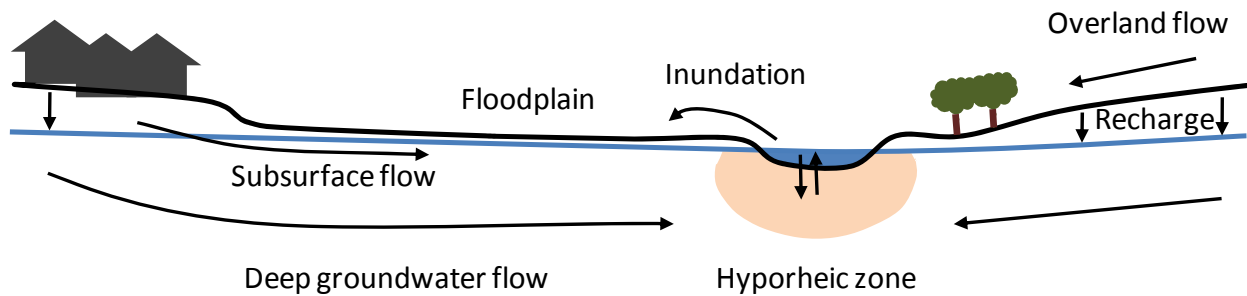
Figure 2.1 Flow paths in the riparian zone

2.1.1 Floodplains

Floodplains act as the collection point for groundwater, overland flow and river water (Burt et al., 2002a). Burt (2006) describe the water balance of the riparian zone as comprising the units shown in Table 2.1. As a result the water table is usually close to the surface and the soil and any unsaturated zone will be close to saturation. A number of studies have shown that flow paths are affected by inundation pattern, hydraulic connectivity in the system and the degree of floodplain saturation.

Lewin and Hughes (1980) assessed the relationship of inundating waters to patterns of floodplain relief in terms of an inundation model involving types of input, output and transfer processes. This model was applied to floods observed in the rivers Dyfi and Teifi in mid-Wales from 1973-1977. These show complex patterns of actual inundation sequences, involving hysteretic effects in the relationship between river stage and flood extent, and varying effects arising from human floodplain modifications, different rates of stage fluctuation, and the local incidence of floodplain forms.

Table 2.1   Riparian zone water balance

Inputs	Outputs
Overland flow from upslope	Overland flow to the river from the riparian zone
Subsurface flow from upslope	Subsurface discharge to the river
Direct precipitation	Evaporation
Groundwater discharge from local aquifers	Percolation to underlying aquifer
Seepage from river through bank	
Overbank flooding inundating floodplain surface	

Burt et al. (2002a) studied a complex series of hydrological interactions during flood events in the floodplain of the River Severn. During inundation conditions a reverse groundwater ridge can develop in the floodplain subsurface resulting in groundwater movement towards the base of slopes adjoining the floodplain. This could switch off overland flow inputs to the riparian zone. Such inputs to the floodplain are also switched off' if the flood stage is high. In smaller floods, water continues to move from slope to floodplain, although coupling between slope and channel is only re-established later in the recession. These mechanisms can allow overland flow to enter the river directly without passing though the unsaturated zone.

In a study of a thick sand and gravel aquifer in the floodplain of the Lower Wisconsin River Pfeiffer et al. (2006) showed that the topographic features of the system are all important in controlling the flow system. Local recharge events and changes in river stage leading to floodplain inundation are both essential for creating temporal variability and opportunities for mixing of water sources.

Junk et al. (1989) and Tockner et al. (2000) suggest that the flood pulse concept describes the major influence on the degree of connectivity and the exchange of material across the river-floodplain gradient, and its relationship to ecosystems. In a catchment in western Australia, Ocampo et al. (2006) showed that the water in the riparian zone may not be hydraulically connected to upland parts of the system except where a shallow groundwater system is established in the winter. Brunke et al. (2003) showed how the extent and nature of connectivity between ground and surface water in floodplains is important for sustaining ecological diversity in two catchments in Switzerland.

Mertes (1997) showed how the saturation status of the floodplain at the time of inundation can control the transfer of water and sediment between the river and the surrounding water, although they do not illustrate subsurface water in their discussion. Macdonald et al. (submitted) discuss the complexity of the interaction between rivers and groundwater during flood events in floodplain environments, with the distribution of regional rainfall having a significant influence on the relative contribution of direct rainfall recharge and high river levels.

2.1.2   The hyporheic zone

The hyporheic zone is the active zone between the surface stream and groundwater. In a review of the functional significance of the hyporheic zone, Boulton et al. (1998) showed that exchanges of water, nutrients, and organic matter (OM) occur in response to variations in discharge and bed topography and porosity. Upwelling subsurface water supplies stream organisms with nutrients while downwelling stream water provides dissolved oxygen and OM to microbes and invertebrates in the hyporheic zone. In an analogous way Mertes (1997) defines the area of the flood plain where periods of inundation occur as the perirheic zone, although this does not seem to be widely used.

Dynamic gradients exist at all scales in the hyporheic zone and vary temporally (Boulton et al., 1998):

- at the microscale, gradients in redox potential control chemical and microbially mediated nutrient transformations occurring on particle surfaces
- at the stream-reach scale, hydrological exchange and water residence time are reflected in gradients in hyporheic faunal composition, uptake of dissolved organic carbon, and nitrification
- at the catchment scale the hyporheic corridor concept describes gradients, extending to alluvial aquifers kilometres from the main channel.

Across all scales, the functional significance of the hyporheic zone relates to its activity and connection with the surface stream. Findlay (1995) proposed an organizational scheme for grouping stream systems into clusters of minimal, moderate, and maximal contribution of hyporheic metabolism to the overall ecosystem.

2.2 GEOCHEMICAL PROCESSES

2.2.1 Redox

Organic carbon (OC) is very important for the evolution of different redox regimes in aqueous environments, and the amount and reactivity of the organic carbon in the aquifers is therefore an important parameter when evaluating the state and trends of groundwater quality. However, the amount of total/dissolved OC (TOC/DOC) itself does not provide information on how reactive or reducing the environment is. Generally, the biologically viable TOC/DOC in UK groundwaters is likely to originate from the soil, as any OM present in the rock matrix is mostly unavailable to microorganisms. The majority of DOC that travels from the soil zone to deep within the aquifer will be old and highly recalcitrant, and therefore not prone to further microbial breakdown over the timescales of more active groundwater circulation (Darling and Gooddy, 2006). However, in a floodplain environment and the hyporheic zone there is the potential for the introduction of fresh OM from river water inundation and groundwater surface water exchange (Lapworth et al., published online; Lapworth et al., 2009). This could provide a seasonal impetus for microbial action and the formation of transitory redox zones.

Lovley and Chapelle (1995) showed that subsurface redox processes proceed sequentially from the highest energy yield downwards and there are both chemical equilibria and kinetic/microbial reasons why such sequences are followed. Table 2.2 shows the sequence commonly encountered in subsurface environments.

Aerobic conditions are defined by free oxygen (generally in excess of 1 mg L^{-1}) and low concentrations of all reduced species. Nitrate (NO_3) reduction can occur even where free oxygen is determined (Pedersen et al., 1991). The processes for aerobic respiration and denitrification are relatively similar. Most known denitrifying microorganisms are able to use oxygen preferentially when available and in some cases the two are used together. These processes can be carried out by a single organism. It is also possible for dissimulatory NO_3 reduction directly to ammonia (NH_4) to occur (Tiedje, 1988) quoted in Lovley and Chapelle (1995).

Table 2.2   Redox processes in order of decreasing energy yield and criteria for assigning redox status (after Lyngkilde and Christensen (1992b) and Bjerg et al (1995))

Respiration	Energy yielding process	Description	Concentration (mg L^{-1})									
			O_2	NO_3	NO_2	N_2O	NH_4	Mn	Fe	SO_4	S	CH_4
Aerobic	Reduction of O_2		>1.0	-	<0.1	-	<1.0	<0.2	<1.5	-	<0.1	<1.0
Anaerobic	Nitrate reduction	Denitrification to N_2 and dissimulatory reduction to NH_4	<1.0	-	>0.1	>1	-	<0.2	<10	-	<0.1	-
	Manganese reduction	Mn^{4+} reduction to Mn^{2+}	<1.0	<0.2	<0.1	<1	-	<5	<10	-	-	-
	Iron reduction	Fe^{3+} reduction to Fe^{2+}	<1.0	<0.2	<0.1	<1	-	<5	<150	-	-	-
	Sulphate reduction	SO_4 reduction to S^{2-} or H_2S	<0.2	<0.2	<0.1	<1	-	<5	<150	-	>0.1	-
	Methanogenesis	Methane production	<1.0	<0.2	<0.1	<1	-	<5	<150	-	-	>25

In the NO_3-reducing zone, the concentration of oxygen must be low but no criteria are associated with the NO_3 concentrations. These could be high if the availability of OC the limiting factor or low if NO_3 is the limiting factor (Lyngkilde and Christensen, 1992b). The manganese (Mn) and iron (Fe) reduction zones are defined by the presence of substantial concentrations of dissolved Mn and/or Fe (Lyngkilde and Christensen, 1992b). The anaerobic respiration in these and more-reducing zones depends on processes which are different since individual types of organism are limited in the types of OM that can be used and two or three step processes required are required to break down larger organic molecules (Lovley and Chapelle, 1995). For example sugars and amino acids are first fermented to acetate and short chain fatty acids.

The SO_4-reducing zone should contain some sulphide but the presence of reduced Fe and Mn may cause precipitation of metal sulphides and may lead to very low concentrations of sulphide (Lyngkilde and Christensen, 1992b). At the same time, SO_4 may be high if the reduction process is limited by availability of OM. Chapelle et al. (2009) recommend using a combination of dissolved Fe and sulphide (defined as total reduced sulphur species) to distinguish the Fe-reducing from the SO_4-reducing zones.

The methanogenic zone may be difficult to distinguish but should have significant concentrations of methane and SO_4 concentrations that are not too high. Methane produced in this zone may spread to other zones by water flow and may only be slowly oxidised by SO_4 or NO_3 (Lyngkilde and Christensen, 1992b). It is also the case that Fe can be transported through the groundwater system as colloids and nanoparticles and may not be related to a local source or redox conditions.

These processes produce a typical sequence along the flow paths in many aquifers where there is no oxygen input along the flow path, such as confined aquifers, or where oxygen is consumed by inputs of degradable OC. Chemical equilibria would allow any of the reactions to take place as long as they are energetically favourable, but the competition between different types of microorganism leads to the segregation of the different zones (Lovley and Chapelle, 1995).

The sequence of processes may also be limited by the availability of electron acceptors in the aquifer matrix of by limitations on solubility of certain phases (e.g. rhodocrosite solubility control on Mn and Fe-hydroxide depletion as described by Amirbahman et al.(1998))

Diverse microbial communities have been identified in leachate plumes and control these redox processes (Christensen et al., 2001). DOC in the leachate, although it appears to be only slowly degradable when the volatile organic acids are gone, apparently acts as substrate for the microbial redox processes (Baker and Curry, 2004).

2.2.2 Other geochemical processes

As well redox, concentrations of dissolved species are governed by dilution, abiotic dissolution of sediment minerals, ion exchange, precipitation/redissolution, complexation with DOC and colloidal or particulate transport. It is important to note that the typical phenoxy, hydroxy and carboxylic multi-functionality of the dissolved OM has an important role to play in ion-exchange, metal chelation and transport processes (Koopal et al., 2001). Understanding the factors controlling DOM reactivity is especially important because land-use and water-management practices can result in significant changes in the nature and reactivity of the DOM from those present under more pristine conditions (Aiken et al., 2011).

3 Settings

3.1 Riparian zone

On the landscape scale the floodplain is regarded as a reactive interface between the upland and the river (Lewandowski and Nützmann, 2010). On the floodplain scale the hyporheic zone is the reactive interface between the aquifer and surface water. In both interfaces the flow paths and flow velocities are of importance for biogeochemical processes. The same processes that occur in the floodplain also occur in the hyporheic zone although higher concentrations in the river bed sediments indicate more intense processes.

3.1.1 Denitrification zones

Anaerobic carbon-rich sediments, characteristic of floodplains have the potential to support large populations of denitrifying bacteria. Chung et al. (2004) were able to demonstrate the development of a denitrifying zone in lysimeters packed with floodplain sediments on irrigation with river water due to oxygen depletion in the surface layer by OM degradation. The denitrification potential generally increases with OM content towards the soil surface (Burt et al., 1999) with consequent potential for denitrification increasing as the water table rises. Kellogg et al. (2005) found that the denitrification potential of a riparian wetland varied with depth and distance from the stream and was also correlated with sediment OC content. Other authors have also shown a relationship with soil texture, discrete flow zones, channel shapes and fluctuating water levels. For example Dahm et al. (1998) found that hydrological and biogeochemical dynamics of the interface were linked to the sediment characteristics of the floodplain and stream bed and also to the degree of channel constraint, the availability of specific chemical forms of electron donors and electron acceptors and temporal changes in discharge.

Pinay et al. (2000) investigated the relationships between denitrification process and structures of the floodplain visible at a larger scale along a 30 km long stretch of the Garonne River France. On an annual basis, they found that average denitrification rates did not show any significant trend with flood frequency or duration. However they proposed that if flood events do not last long enough to maintain waterlogging conditions conducive to sustain denitrification activity for long periods, they indirectly affect the spatial distribution of denitrification activity through the sorting of sediment deposits. These authors did find a significant relationship between denitrification rates in the floodplain soils and their texture; highest rates were measured in fine textured soils with high silt + clay content. Below a threshold of 65% of silt and clay content, the floodplain soils did not present any significant denitrification rates. Above that threshold denitrification increased linearly.

Pfeiffer et al. (2006) found evidence of NO_3 attenuation at depth which depended on topographic features and temporal variability. This flow system provided sources of DOC to deeper groundwater flowpaths leading to the consumption of dissolved oxygen and generating redox conditions suitable for denitrification and subsequently Fe reduction. McCarty et al. (2007) also showed that the denitrification potential of a riparian wetland was both stratified and was limited by the presence of discrete seepages or upwelling zones rather than a uniform distribution.

Burt et al. (2002b) show how fluctuating water levels can control the degree of denitrification. Since denitrification potential generally increases towards the soil surface, water table elevation can control the degree to which NO_3 reduction is optimised. Where the riparian zone was flat, the water level in the adjoining river or lake proved significant in controlling water table levels within the riparian zone.

Alewell et al. (2008) indicate that redox processes are not completely controlled by the sequential reduction chain (that is electron acceptor availability) but that electron donor

availability may be an important regulator. They hypothesised was that only sites which are limited in their electron donor availability low concentrations of DOC follow the concept of the sequential reduction chain.

3.1.2 Hot spots and hot moments

McClain et al. (2003) showed that rates and reactions of biogeochemical processes vary in space and time and these variations are often enhanced at terrestrial-aquatic interfaces. They defined biogeochemical "hot spots" as patches that show disproportionately high reaction rates relative to the surrounding matrix, whereas "hot moments" were short periods of time that exhibit disproportionately high reaction rates relative to longer intervening time periods. Hot spots occur where hydrological flowpaths converge with substrates or other flowpaths containing complementary or missing reactants. Hot moments occur when episodic hydrological flowpaths reactivate and/or mobilize accumulated reactants.

McClain et al. (2003) review how detecting these hot spots is scale-related using denitrification as an example. At the scale of a soil profile (1-10 m) hot spots occur around patches of labile OM, at the centre of large aggregates. Reactants are transmitted by percolating water. In the unsaturated zone flow paths will be intermittent and denitrification hot spots will be active during hot moments. At the 10-100 m scale the distribution is controlled by soil texture and drainage that affect the duration and timing of soil saturation and the accumulation of OM. At the 100-1000 m scale the interface between the upland and the riparian zone is typically a hot spot. Denitrification is triggered by allochthanous NO_3 input from uplands along groundwater pathways. In most cases the hot spots are a few m wide at the upland margin, although they can occur at the river bed–wetland interface or elsewhere depending on flowpaths and seasonal variations. At the same scale hot spots have also been identified within rivers in association with the hyporheic zone. Instream denitrification is most prevalent at downwelling sites, typically where surface water infiltrates into the hyporheic zone where anoxic organic carbon-rich subsurface zones receive NO_3 from surface water.

Harms and Grimm (2008) suggested that a hot moment of N retention and removal was indicated in a semiarid riparian zone by elevated rates of microbial processes during the summer monsoon season. At the same time, elevated C was observed in soil microbial biomass for both surface soils and soils in the seasonally saturated zone. Analyses of C-use profiles for soil microbes, coupled with trends in stream and shallow-groundwater chemistry, further suggest that this hot moment of N removal was fuelled by newly available, labile organic material. In a spatial context, patchiness in soil resources, microbial biomass, and potential denitrification were best explained by variation in micro-topography; low-elevation landscape positions were hot spots of resource availability and microbial activity. Vertical heterogeneity also corresponded with variation in the factors influencing N transformation rates. OM was more frequently a significant factor explaining N transformation rates in saturated soils whereas soil water content was more often important in surface soils.

Vidon et al. (2010) suggest that hot spots and/or moments are generally governed by subtle changes in electron acceptor and donor availability, redox conditions and hydrological conditions and set out the processes favourable for the development of hot spots and hot moments due to both biogeochemical and transport processes (Table 2.2 and Table 3.1). Groffman et al. (2009) concluded that hot spots have been easier to measure than hot moments but that hot moments will be more amenable to modelling. They stress the importance of a good coupling between model and data, and the incorporation of hot spots and moment in project data collection design.

Table 3.1   Phenomena and processes favourable to the development of biochemical process-driven hot spots and hot moments

Constituent	Phenomenon	Favourable conditions	
		Hot Spot	**Hot Moment**
NO_3	Denitrification	Continuous anaerobic conditions, high OM, high NO_3 concentration, medium to large continuous water fluxes	Ephemeral soil saturation, high OM, high NO_3 concentration, ephemeral medium to large water fluxes (e.g., inundated floodplain)
P	Desorption	High soil P content, reducing conditions (Eh < 250 mV), medium to large continuous water fluxes	High soil P content and ephemeral reducing conditions, medium to temporary high water table, and large water fluxes
OM	Mineralisation	Large soluble or decomposable OM pool, continuous moist conditions, aerobic conditions	Ephemeral large OM input (e.g., leaf fall) and ephemeral moist and aerobic conditions (freeze ⁄ thaw cycle, wetting ⁄ drying cycle)
Pesticides	Degradation	Large OM pool, continuous moist conditions, aerobic conditions	High OM, ephemeral pesticide input and ephemeral moist and aerobic conditions

Table 3.2   Processes favourable to the development of transport process-driven hot spots and hot moments

Constituent	Favourable conditions	
	Hot Spot	**Hot Moment**
NO_3	High NO_3 concentration and flux, and high soil hydraulic conductivity relative to rest of riparian areas in watershed	Ephemeral high NO_3 concentration and high NO_3 flux (overland flow or subsurface) owing to extreme event (storm, snowmelt)
P	Upland P source and continuous overland flow (seeps) or preferential subsurface flow (e.g., toe slope seeps)	Ephemeral P transport through riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow
OM	High flux of water and reactive solutes through a large OM pool or high flux of POM⁄DOM from an area and high soil hydraulic conductivity relative to rest of riparian areas in watershed	Ephemeral POM⁄DOM transport through riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow
Pesticides	Continuous pesticide source and high soil hydraulic conductivity relative to rest of riparian areas in watershed	Ephemeral pesticide input to riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow

3.2 LANDFILL AND WASTE LEACHATE PLUMES

In a key paper Lyngkilde and Christensen (1992b) describe the sequence of redox zones associated with the municipal waste landfill at Vejen, Denmark. This showed a methanogenic zone within 50 m of the landfill surrounded by a discontinuous SO_4-reducing zone, which was split into two layers (Figure 3.1). The Fe-reducing zone was the most extensive extending up to 350 m downgradient. A continuous Mn-reducing zone was not observed and this was ascribed to a low initial content of oxidised Mn in the sediments. A significant NO_3 reduction zone enveloped the Fe-reducing zone. A similar study by Bjerg et al. (1995) and (Ludvigsen et al. (1998) at the Grindsted landfill was able to distinguish the zones more clearly and also found mixed zones between these defined zones (Figure 3.2).

Ludvigsen et al. (1998) found that in many cases, several redox processes took place simultaneously, but in all samples one process dominated accounting for more than 70% of the equivalent carbon conversion. Bioassays showed that the redox zones in the plume identified from the groundwater composition (e.g. as methanogenic and SO_4-reducing) locally hosted also other redox processes (e.g. Fe reduction). This may have implications for the potential of the redox zone to degrade trace amounts of organic chemicals and suggests that unamended bioassays may be an important supplement to other approaches in characterizing the redox processes in an anaerobic plume.

After this early work there have been a number of studies delineating landfill leachate plumes in groundwater. Basberg et al. (1998) studied the distribution of redox sensitive species downgradient of a leachate plume at Trandum landfill, Norway. Groundwater exhibited an excess of alkalinity relative to calcium which was assumed to be derived from degradation of OM. Groundwater immediately below and downstream of the landfill contained elevated concentrations of Fe and Mn, largely mobilized under reducing conditions from the aquifer matrix and reflected in depleted HNO_3-extractable Fe and Mn in sediment samples from the same area. Groundwater samples allowed the tentative identification of redox zones based on oxidized and reduced forms of Fe, Mn, N and S. A methanogenic zone was not observed.
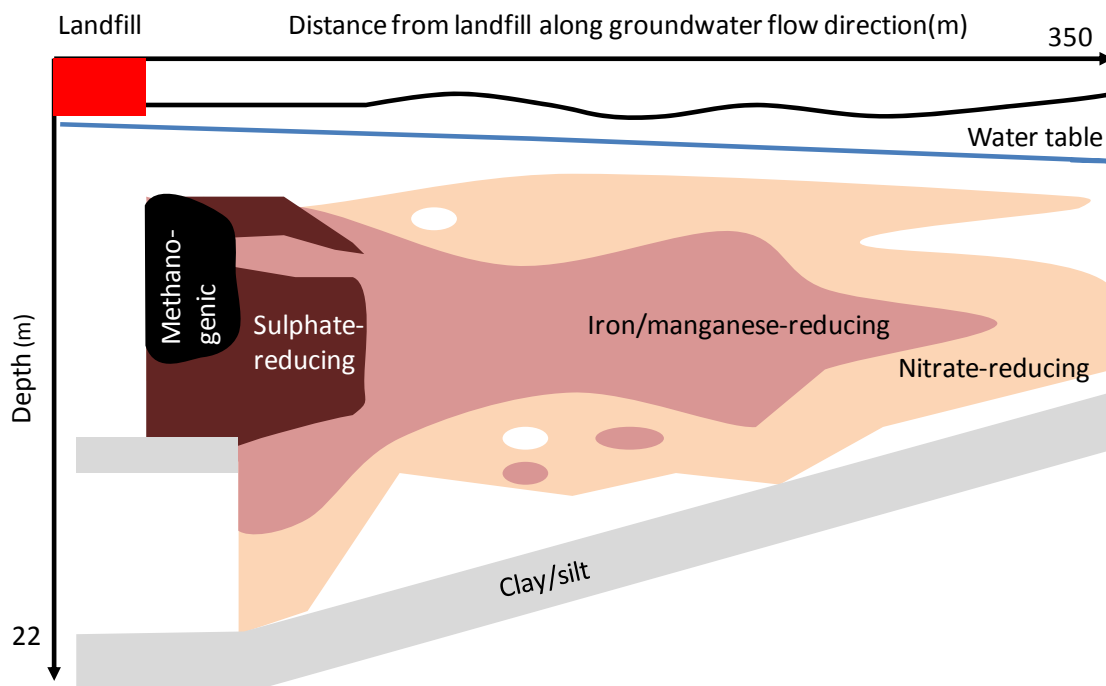

Figure 3.1 Schematic distribution of redox zones downgradient of Vejen landfill (after (Lyngkilde and Christensen, 1992b)
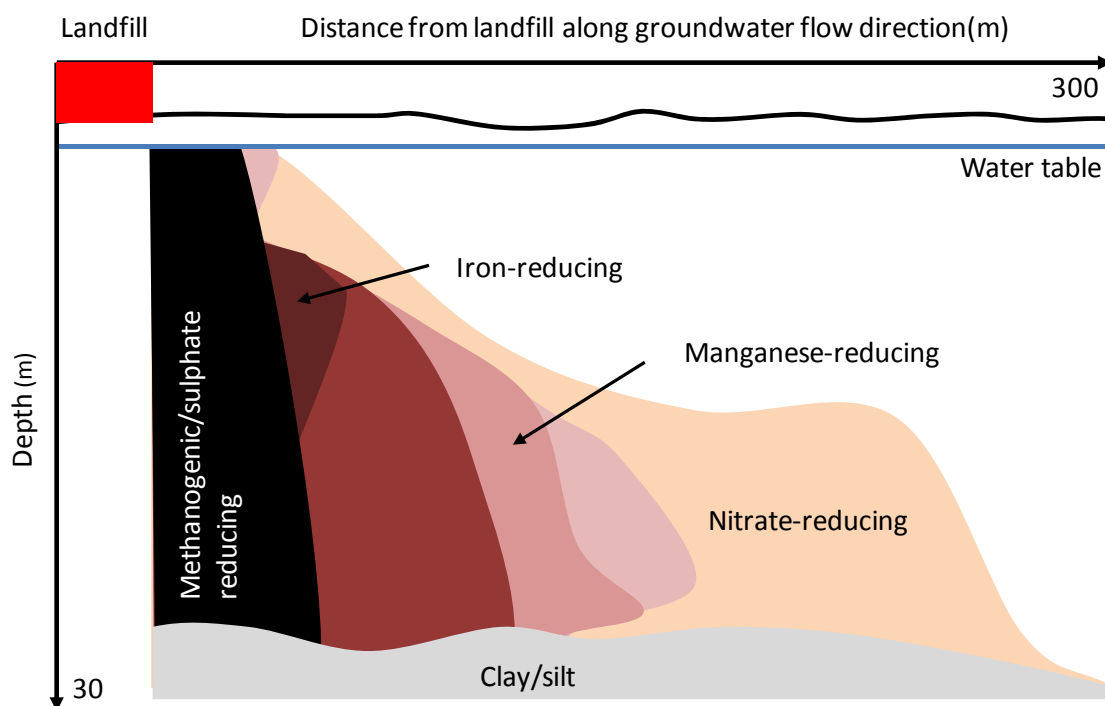
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Figure 3.2 Schematic distribution of redox zones downgradient of Grindsted landfill (after Bjerg et al (1995))

Amirbahman et al. (1998) measured redox-sensitive species under the Winterthur landfill, Switzerland and demonstrated the presence of aerobic respiration, denitrification/NO_3- reduction, and Fe and Mn reduction processes under the landfill. The lack of significant SO_4 reduction and methanogenesis was ascribed to a limit on the available and released OM. Modelling indicated that dilution has the most significant influence on the concentrations of the dissolved organic and inorganic carbon. Downgradient along the leachate plume, where no Fe reducing processes are currently observed, decreased concentrations of solid Fe phases and the presence of Fe sulphide phases suggest that, in the past, Fe and SO_4-reducing processes have taken place, presumably due to the historical presence of higher concentrations of available OM.

At an unlined municipal landfill on the Canadian River alluvial plain, Oklahoma, Scholl et al. (2006) found that seasonal recharge and water table fluctuations appeared to drive a cycle of sulphide oxidation and SO_4 reduction and possible also ammonium oxidation and denitrification. This was interpreted as the seasonal ingress of NO_3 and SO_4 in recharge into a system where degradation of OM was otherwise limited by the availability of electron acceptors.

The occurrence of redox processes was investigated at the top fringe of a landfill leachate plume at Banisveld, the Netherlands (van Breukelen and Griffioen, 2004). Bromide appeared to be as good as chloride as a conservative tracer to calculate dilution of landfill leachate, and its ratio to chloride was high compared to other possible sources of salt in groundwater. The plume fringe rose steadily from a depth of around 5 m towards the surface in the period 1998-2003. The plume uplift may have been be caused by enhanced exfiltration to a brook downstream from the landfill, due to increased precipitation over this period and an artificial lowering of the water level of the brook. This rise induced cation exchange including proton buffering, and triggered degassing of methane. A 1-D vertical reactive transport model using PHREEQC-2 showed that solid OC and not clay minerals controlled retardation of cations. Cation exchange resulted in spatial separation of the Fe, Mn and NH_4 fronts from the fringe, and thereby prevented possible oxidation of these secondary redox species. Re-dissolution of methane escaping from the plume

and its subsequent oxidation explained the absence of previously present NO_3 and the anaerobic conditions in pristine groundwater above the plume.

In their comprehensive review of landfill biogeochemistry, Christensen et al. (2001) show that most leachate contamination plumes are relatively narrow and do not exceed the width of the landfill. As an example, Mikac et al. (1998) described the extent of contamination from the main landfill serving the city of Zagreb where waste was disposed onto highly permeable alluvial sediments. A relatively narrow non-continuous Fe-reducing zone was found along the edge of the landfill in the prevailing directions of the groundwater flow. Even after a distance of 1200 m the redox conditions in the aquifer still remained anaerobic (NO_3-reducing), while a permanently aerobic zone was present only upstream from the landfill. The horizontal distribution of the contaminants was highly dependent on the hydrological regime, but the preferential direction of spreading was in the direction of groundwater flow. Moreover, it was shown that this aquifer section is polluted not only in the surface layer but across its whole vertical profile as deep as 60 m.

Klinck et al. (1999) describe the changes in water quality in the plume associated with closure of an unlined landfill in Thailand, with a steep decline in NO_3 measured in a downgradient well over a 9-year period. Klinck et al. (1999) also observed seasonal fluctuations in the conformation of the plume. There was a change in flow direction during the rainy season. Evidence was seen for a pulse of contaminants, as shown by TDS, migrating across the study area away from the landfill as the rainy season progressed. There were also changes in the redox conditions. In the dry season conditions were anaerobic and NO_3 was only present at a few sites. Mn and Fe were widely detected in the aquifer and there was evidence of depression of SO_4 concentrations close to the landfill. In the wet season the picture was more complex with NO_3 and nitrite widely present, but with Fe and Mn persisting.

3.3 ANIMAL WASTE STORAGE AND DISPOSAL, AND SEPTIC SYSTEMS

Animal wastes and septic effluent have a high carbon and nitrogen (N) content and can impact on groundwater quality. These lagoons may form distinct redox zones beneath them in a similar manner to landfills. Infiltration from dairy cattle waste storage ponds was identified by Arnold and Meister (1999) as a significant source of groundwater NO_3, NH_4 and Cl, particularly from those with puddled clay liners. Mean groundwater N concentrations from sites close to wastewater lagoons doubled over the study period from 1992-1999.

A number of studies in the UK carried out by Gooddy et al. (2002) measured the DOC and N concentrations beneath unlined waste lagoons used for storing cattle manure. Concentrations up to 200 mg C L^{-1} and 500 mg N L^{-1} can be observed, nearly 100 times greater than a typical groundwater value observed in reference aquifers throughout Europe (Gooddy and Hinsby, 2008). Cronk (1996) describes the construction of artificial wetlands to treat dairy and pig wastewater by denitrification.

A number of studies have also been carried out on septic systems which also display redox zonation and provide a good analogue for a nutrient rich floodplain. Wilhelm et al. (1994a) set out the sequence of redox transformations in septic systems. The first redox zone is in the septic tank where the high concentrations of OC and microorganisms produce CO_2, H_2, methane and sulphide, equivalent to the methanogenic zone in landfills. Most N is released from organic molecules as NH_4. The effluent then flows into the aerobic unsaturated zone where almost complete oxidation of the reduced wastewater components occurs in a properly functioning system; adequate oxygen diffuses in, OC is oxidised to CO_2 and NH_4 is oxidised to NO_3. There is little further oxidation in the saturated zone due to the slow diffusion of oxygen.

Robertson et al. (1991) studied the development of the plume downgradient of a septic system. After 1.5 years the NO$_3$-rich plume reached the organic-rich sediments of a river bed about 20 m distant and complete denitrification was observed within the last 2m.

3.4   MAIN POINTS FOR SETTINGS

Overall we can envisage the floodplain setting as a heterogeneous and constantly changing environment. Changes may be controlled predominantly by water levels. They are envisaged as zones where nutrients and other contaminants are attenuated or removed from groundwater discharging to surface water. The potential for the addition of low molecular weight carbon from the river during inundation provides the potential to further stimulate the redox environment in a transitory manner.

In contrast point sources, such as landfills, unlined animal waste stores and leaking sewers, appear to lead to a relatively stable system with a source term which generates an established redox sequence in a limited volume of groundwater down gradient. The shape and size of the plume may be affected by drought or heavy rainfall.

On-site sanitation systems demonstrate the same sequence of redox zones but the highly reducing conditions are found within the tank and such schemes may rely on oxidation of reduced species in the effluent during transport through the unsaturated zone.

4 Nutrient transport

4.1 NUTRIENTS

Mineralised forms of N, such as NO_3, are readily transported in water and are stable under a range of concentrations. However, anaerobic carbon-rich sediments have the potential to support large populations of denitrifying bacteria and NO_3 can be converted to N_2O or N_2 gas and lost from the system. Denitrification is fast compared to groundwater flow particularly under low flow conditions (Lewandowski et al., 2009). There may also be dissimulatory reduction to NH_4 (Scott et al., 2008). During periods of high water levels even narrow buffer zones along rivers are effective in NO_3 removal. N fixation in sediments can be high where NO_3 in the overlying water is low and such NO_3 can sustain a population of NO_3 reducers (Scott et al., 2008).

Unlike NO_3, phosphorus (P) removal by soil or sediment retention and biota uptake results in accumulation within the system. Sediments can be both a source and a sink of dissolved P in surface water and shallow groundwater (Surridge et al., 2007). Lewandowski and Nützmann (2010) state that opposite conditions are favourable for N and P management; anaerobic conditions favouring denitrification but enhanced desorption and release of P.

Major solubility controls of P are related to coprecipitation and adsorption as well as to uptake by biota. The precipitation of P-containing minerals, onto mineral surfaces, and the sorption of phosphate ions by ferric and Mn oxyhydroxides can limit the concentrations in solution in most waters (Hem, 1989). Adsorption onto mineral surfaces is favoured by low pH whereas apatite solubility limits concentrations under alkaline conditions (Jahnke, 1992). P can mobilised by the reductive dissolution of ferric oxyhydroxides and other P-containing redox-sensitive compounds (Lewandowski and Nützmann, 2010).

A recent review by Ranalli and Macalady (2010) showed that undisturbed headwater catchments have been shown to be very retentive of N, but the importance of biogeochemical and hydrological riparian zone processes in retaining N in these catchments has not been demonstrated as it has for agricultural catchments. There is, however, a considerable body of literature relating to nutrient migration in other riparian and flood plain settings. Important factors are spatial variations in permeability and soil type, seasonal hydrological variations, particularly water levels, and electron donor/receptor availability. The following section summarises case studies from the literature under these headings.

4.2 FACTORS INFLUENCING NUTRIENT TRANSPORT

To understand water movement we need to understand residence times, multiple flow paths and hydraulic gradient reversal. These will be affected by subsurface permeability and hydraulic conditions, including inundation frequency. Nutrients will also be controlled by uptake by vegetation and by redox conditions.

4.2.1 Permeability, soil type and buried channels

In their review Dahm et al. (1998) show that the surface water/groundwater interface is a crucial control point for lateral nutrient fluxes between uplands and aquatic ecosystems and for longitudinal processes along rivers and wetlands. The magnitude of SW/GW interactions in these systems is predicted to be a major determinant of solute retention. Channel morphology, stream bed composition and discharge are predicted to be important controls on SW/GW interactions.

Inherent site attributes can generate substantial variation in the ground water NO_3 removal capacity of riparian zones. Site attributes, such as hydric soil status (soil moisture) and geomorphology, affect the interaction of NO_3-enriched ground water with portions of the soil

ecosystem possessing elevated biogeochemical transformation rates (i.e., biologically active zones) (Gold et al., 2001). At riparian sites in the north east USA, high ground water nitrate-N removal rates were restricted to hydric soils (Gold et al., 2001). Geomorphology provided insights into ground water flowpaths with sites located on outwash and organic/alluvial deposits having high potential for NO_3-enriched ground water to interact with biologically active zones. In till deposits, ground water NO_3 removal capacity may be limited by the high occurrence of surface seeps that markedly reduce the time available for biological transformations to occur within the riparian zone.

Devito et al. (2000) investigated the floodplain of the Boyne River which is connected to a large upland sand aquifer in an agricultural region near Alliston, Ontario, Canada. Ground water discharging to the forested floodplain from the sand aquifer exhibited large spatial variability in nitrate-N concentrations (10-50 mg L^{-1}). The transport and depletion of NO_3 was strongly influenced by floodplain geometry and lithology. Little ground water flow occurred through the low-conductivity matrix of peat in the floodplain. Plumes of NO_3-rich ground water passed beneath the riparian wetland peat and flowed laterally in a 2- to 4-m-thick zone of permeable sands across the floodplain to the river. Analyses of the distribution of the nitrate-N concentrations, isotopes, and DOC within the floodplain indicate that denitrification occurred within the sand aquifer near the river where NO_3-rich ground water interacted with buried channel sediments and surface water recharged from peat to the deeper sands.

Tobias et al. (2001) used isotope techniques to trace the evolution and transformations within a groundwater NO_3 plume in a mesohaline salt marsh. They characterised both dissimulatory NO_3 reduction to ammonium and denitrification within the groundwater system and found that ammonium was not the major N sink within this system but rather the immobilisation of particulate organic N, which can be retained over long timescales within the groundwater system. The undersaturation of dissolved argon indicated that a relatively small component of N was released as N_2O and N_2 to the atmosphere over relatively short time scales.

At the Boyne site, for P, low soluble reactive P (SRP) concentrations (<25 µg L^{-1}) occurred in a plume of groundwater within the sands with DO concentrations >3 mg L^{-1} and Fe^{2+} concentrations <0.2 mg L^{-1} which extended for a horizontal distance of 100-140 m across the riparian zone (Carlyle and Hill, 2001). High SRP concentrations (50-950 µg L^{-1}) were associated with low DO and high Fe^{2+} concentrations which exceeded 1 mg L^{-1} in buried channel sediments near the river bank. Sediment P fractionation indicated that the buried channel sediments contained a much higher pool of total P than the sands. Groundwater SRP concentrations at the river bank were 25-80 µg L^{-1} compared to <10 µg L^{-1} in river water indicating that the floodplain was a source of SRP to the river. Areas of elevated SRP and Fe^{2+} within the floodplain expanded in August when DO concentrations in groundwater were lower than in late spring or autumn. These data suggest that the microbial reduction of Fe^{3+} to soluble Fe^{2+} in anaerobic conditions influences groundwater SRP concentrations in the riparian zone.

Lapworth et al. (published online) used tangential flow fractionation (TFF) to investigate P-colloid associations in the hyporheic zone of a groundwater-dominated chalk stream. P speciation is similar for the river and the deeper Chalk aquifer beneath the hyporheic zone, with 'dissolved' P (<10 kDa) accounting for 90% of the P in the River and >90% in the deep groundwaters. Within the hyporheic zone the proportion of 'colloidal' (<0.45 µm>10 kDa) and 'particulate' (>0.45 um) P is high, accounting for 30% of total P. These results suggest that zones of interaction within the sand and gravel deposits directly beneath and adjacent to the river system generate colloidal and particulate forms of fulvic-like organic material and regulate bioavailable forms of P, perhaps through co-precipitation with $CaCO_3$. OM decomposition and nitrification in the hyporheic zone could be the source of both fulvic-like dissolved OM and nitrate-N. While the aquifer provides some degree of protection to the sensitive surface water ecosystems through physicochemical processes of P removal, where flow is maintained by

groundwater, ecologically significant P concentrations (20-30 µg L^{-1}) are still present in the Chalk groundwater and may be an important source of bioavailable P during baseflow conditions.

4.2.2 Hydrological variations and water levels

Burt (2006) reviews the implications of denitrification in riparian buffer zones for the management of diffuse pollution. There is a need to maintain water levels in both the mid-river sections where denitrification may be favoured. This function can be lost due to lowering of water levels e.g. by land drainage.

Spatio-temporal variations in N and P concentrations in groundwater were analysed and related to the variations in hydrological conditions, vegetation type and substrate in an alluvial ecosystem in the Illwald forest in the Rhine Plain (eastern France) to assess the removal of nutrients from groundwater in a regularly flooded area (Takatert et al., 1999). Lower concentrations of NO_3 and phosphate in groundwater were observed under forest than under meadow, which could be explained by more efficient plant uptake by woody species than herbaceous plants. Thus NO_3-N inputs by river floods were reduced by 73% in the shallow groundwater of the forested ecosystem, and only by 37% in the meadow. The lowest NO_3-N and the highest NH_4-N concentrations were measured in the deep layer (under the gley horizon at 2.5 m depth), which suggests that the reducing potential of the anoxic horizon in the gley soils contributes to the reduction of NO_3. Phosphate concentrations in both shallow and deep groundwater were less than 62 to 76% of those found in surface water ascribed to the retention capacity of the clay colloids of these soils. The temporal variations in nutrient concentrations in groundwater were directly related to seasonal variations in groundwater level resulting from presumed redox changes.

Puckett et al. (2002) used a combination of chemical and dissolved gas analyses, chlorofluorocarbon age dating and hydrological measurements to determine the degree to which biogeochemical processes in a riparian wetland were responsible for removing NO_3 from ground waters discharging to the Otter Tail River, Minnesota. Nitrate concentrations in the river increased in the lower half of the study reach as the result of ground-water discharge to the river. Ground-water head measurements along a study transect through the riparian wetland revealed a zone of ground-water discharge extending beneath the river. Water chemistry under the riparian wetland was controlled largely by up-gradient ground waters that followed flow paths up to 16 m deep and discharged under the wetland, creating a pattern of progressively older, more chemically reduced, low NO_3 water the further one progressed from the edge of the wetland towards the river. These progressively older ground waters entered the aquifer in earlier years when less fertilizer was being used. Nitrate concentrations originally present in the ground water had also decreased in the up-gradient aquifer as a result of denitrification and progressively stronger reducing conditions there. The resulting pattern of decreasing NO_3 concentrations across the riparian zone was not therefore evidence of denitrification losses.

Noe and Hupp (2007) quantified the net uptake, release or transformation of N, P and suspended sediment species during brief periods (1–2 days) of overbank flooding through a 250-m floodplain flowpath on a stream in Maryland U.S.A. Concentrations of NO_3 increased significantly in surface water flowing over the floodplain in three of the four floods, suggesting the floodplain was a source of NO_3. The upper portion of the floodplain flowpath consistently exported ammonium, most probably due to the hyporheic flushing of floodplain soil NH_4, which was then likely nitrified to NO_3 in floodwaters. The floodplain was a sink for particulate organic P during two floods and particulate organic N and inorganic suspended sediment during one flood. Large releases of all dissolved inorganic N and P species occurred following a snowmelt and subsequent cold winter flood. Although there was little consistency in most patterns of nutrient processing among the different floods, this floodplain, characterized by brief inundation,

low residence time and low nutrient loading, behaved oppositely from the conceptual model for most floodplains in that it generally exported inorganic nutrients and imported organic nutrients.

The biogeochemistry at the interface between sediments in a seasonally-ponded wetland and an alluvial aquifer contaminated with landfill leachate was investigated to evaluate factors that can effect natural attenuation of landfill leachate contaminants in areas of groundwater/surface-water interaction (Lorah et al., 2009). The biogeochemistry at the wetland-alluvial aquifer interface differed greatly between dry and wet conditions. During dry conditions vertically upward discharge was focused at the centre of the wetland from the fringe of a landfill-derived ammonium plume in the underlying aquifer, resulting in transport of relatively low concentrations of ammonium to the wetland sediments with dilution and dispersion as the primary attenuation mechanism. In contrast, during wet conditions leachate-contaminated groundwater discharged upwards near the upgradient wetland bank, where ammonium concentrations in the aquifer where high. Relatively high concentrations of ammonium and other leachate constituents also were transported laterally through the wetland porewater to the downgradient bank in wet conditions. Concentrations of the leachate-associated constituents chloride, ammonium, non-volatile DOC, alkalinity, and Fe^{2+} more than doubled in the porewater on the upgradient bank during wet conditions. Chloride, non-volatile DOC and bicarbonate acted conservatively during lateral transport in the aquifer and wetland porewater, whereas ammonium and potassium were strongly attenuated. Sorption, probably by cation exchange, was the primary attenuation mechanism for ammonium during lateral transport. Enhanced attenuation of the leachate contaminants in the wetland sediment porewater compared to the aquifer was not observed. The lack of enhanced attenuation can be attributed to the fact that the anoxic plume, comprised largely of recalcitrant DOC and reduced inorganic constituents, interacted with anoxic wetland sediments and porewaters, rather than encountering a change in redox conditions that could cause transformation reactions.

Lapworth et al. (2008) investigated the importance of upland groundwater systems in providing a medium for N transformations and processes along flow paths was investigated within the Afon Gwy moorland catchment, Plynlimon, mid-Wales. A conceptual model of N processes is proposed based on a detailed study along a transect of nested boreholes and soil suction samplers within the interfluve zone. Shallow groundwater N speciation reflects the soilwater N speciation implying a rapid transport mechanism and good connectivity between the soil and groundwater systems. Median NO_3 concentrations were an order of magnitude lower within the soil zone (< 5–31 µg L^{-1}) than in the shallow groundwaters (86–746 µg L^{-1}). Given the rapid hydrostatic response of the groundwater level within the soil zone, the shallow groundwater system is both a source and sink for dissolved N. Results from dissolved N_2O, N_2/Ar ratios and dissolved N chemistry suggests that microbial N transformations (denitrification and nitrification) play an important role in controlling the spatial variation in soil and groundwater N speciation. Reducing conditions within the groundwater and saturated soils of the wet-flush zones on the lower hillslopes, a result of relatively impermeable drift deposits, are also important in controlling N speciation and transformation processes. Dissolved organic N (DON) was found to be the most abundant form of dissolved N in most soils and groundwaters, accounting for between 47 and 72% of total dissolved N in shallow groundwater samples and up to 80% in deeper groundwaters. Groundwater DON may also be an important source of bio-available N in surface waters and marine systems fed by upland catchments.

4.2.3   Plant uptake

Andersen (2004) characterized a relatively undisturbed, seasonally inundated Danish floodplain wetland. The main inputs of water were precipitation and percolation during ponding and unsaturated conditions with low lateral saturated subsurface flow. The low hydraulic conductivity of a silt–clay deposit on top of the floodplain maintained ponded water during winter, and parts of autumn and spring. The capillary fringe extended to the soil surface, and

capillary rise from groundwater during summer maintained near-saturated conditions in the root zone, and allowed a permanently very high evapotranspiration rate. The floodplain sediments were in a very reduced state as indicated by low SO_4 concentrations and all NO_3 transported into the wetland was denitrified. However, owing to modest water exchange with surrounding groundwater and surface water, the overall mass of NO_3 removed was low; 71 kg NO_3-N ha^{-1} during 1999. Reduction of NO_3 diffusing into the sediments during water ponding accounts for 75% of NO_3 removal. Biomass production and consequent N uptake in above-ground vegetation was high − 103 kg N ha^{-1} year^{-1}. Subsurface ammonium concentrations are high, and convective upward transport into the root zone driven by evapotranspiration amounted to 12·8 kg N ha^{-1}year^{-1}. The floodplain wetland sediments had high N content, and conditions are very favourable for mineralization. Mineralization thus constitutes 72% of above-ground plant uptake.

Kiedrzynska et al.(2008) present an ecohydrological approach to the reduction in the P load transported by the Pilica River into a lowland reservoir in the central region of Poland. The research was carried out on a section of the river floodplain where vegetation was the important component accumulating P. In summer, the biological potential for P retention in the floodplain was estimated to be as high as 255 kg P over the 25 ha site and this potential could be increased by planting fast-growing patches of willow. In the long run, an appropriate management strategy (cutting and removing the biomass from the floodplain) should favour a decrease in nutrient transport downstream.

4.2.4 Electron acceptor/donor patterns

Vidon and Hill (2005) examined the linkages between hydrologic flow paths, patterns of electron donors and acceptors and the importance of denitrification as a NO_3 removal mechanism in eight riparian zones on glacial till and outwash landscapes in southern Ontario, Canada. NO_3-N concentrations in shallow groundwater from adjacent cropland declined from levels that were often 10–30 mg L^{-1} near the field-riparian edge to 1 mg L^{-1} in the riparian zones throughout the year. Chloride data suggest that dilution cannot account for most of this NO_3 decline. Despite contrasting hydrogeological settings, these riparian zones displayed a well-organized pattern of electron donors and acceptors that resulted from the transport of oxic NO_3-rich groundwater to portions of the riparian zones where low DO concentrations and an increase in DOC concentrations were encountered. The natural abundances of $\delta^{15}N$ and in situ acetylene injection to piezometers indicate that denitrification is the primary mechanism of NO_3 removal in all of the riparian zones. The results indicated that effective NO_3 removal by denitrification occurred in riparian zones with non-hydric soils as well as in hydric riparian zones and that a shallow water table is not always necessary for efficient NO_3 removal by denitrification. The location of hot spots of denitrification within riparian areas could be explained by the influence of key landscape variables such as slope, sediment texture and depth of confining layers on hydrologic pathways that link supplies of electron donors and acceptors.

Puckett and Cowdery (2002) used a combination of ground-water modelling, chemical and dissolved gas analyses, and chlorofluorocarbon age dating of water to determine the relation between changes in agricultural practices, and NO_3 concentrations in ground water of a glacial outwash aquifer in west-central Minnesota. The results revealed a redox zonation throughout the saturated zone with oxygen reduction near the water table, NO_3 reduction immediately below it, and then a large zone of Fe^{3+} reduction, with a small area of SO_4 reduction and methanogenesis near the end of the transect. Modelling supported the hypothesis that OC was the electron donor for the redox reactions. Denitrification rates were small and were limited by the small amounts of OC, 0.01 to 1.45%. In spite of the OC limitation, denitrification was virtually complete because residence time was sufficient to allow even slow processes to reach completion. Ground-water sample ages showed that maximum residence times were of the order of 50-70 years. Reconstructed NO_3 concentrations, estimated from measured NO_3 and dissolved N gas

showed that NO_3 concentrations have been increasing in the aquifer since the 1940s due to an increase in agricultural use of fertilizer.

Surridge et al. (2007) studied the influence of flooding with deionised water and simulated river water on P release to solution using laboratory mesocosms, comprising sediment columns taken from a riparian wetland. Results showed that rather than retaining nutrients, sediments in the riparian zone may be a significant source of P. The reductive dissolution of P-bearing Fe oxides was the likely mechanism responsible for P release. Dissolved P to Fe molar ratios in anaerobic samples were approximately 0.45 when columns were flooded with water that simulated the chemistry of the adjacent river. This suggests there was insufficient Fe in the anaerobic samples to precipitate all P if the solutions were oxygenated or transported to an aerobic environment. If the anaerobic wetland solutions were delivered to oxygenated rivers and streams adjacent to the riparian zone, the equilibrium concentration of P in these systems could rise. The timing of P release was inversely related to the NO_3 concentration in floodwater.

In the Lake Waco Wetland (LWW), near Waco, Texas, USA, NO_3 concentrations are reduced by more than 90% in the first 500 m downstream of the inflow, creating a distinct gradient in NO_3^- concentration along the flow path of water (Scott et al., 2008). The relative importance of sediment denitrification, dissimulatory NO_3 reduction and N fixation was assessed along the NO_3 concentration gradient in the wetland. Potential denitrification was observed in all months, potential dissimulatory reduction was observed only in summer months and N fixation was variable. Both sediments and the wetland were NO_3 sinks and accounted for 50% of wetland NO_3 removal. Sediments were an ammonium source, but the wetland was often a net sink. The importance of dissimulatory NO_3 reduction in freshwater sediments appears to be minor relative to denitrification. Furthermore, sediment N fixation can be extremely high when NO_3 in overlying water is consistently low. The data suggest that newly fixed N can support sustained N transformation processes when surface water inorganic N supply rates are low.

For the Spree River in Germany, Lewandowski and Nützmann (2010) found that the biogeochemical composition of subsurface water was characterized by little temporal variability while spatial heterogeneity is high on the hectometre scale of the study site as well as on the centimetre scale of the bed sediments. Nitrate was eliminated very efficiently by denitrification in the anoxic aquifer of the floodplain while ammonium and phosphate concentrations increased under anoxic conditions. Phosphate and ammonium were thought to originate from the mineralization of OM and phosphate was additionally released by reductive dissolution of Fe-bound P and weathering of bedrock. Sorption-desorption processes equalized temporal fluctuations of phosphate concentrations. The redox patchiness of floodplain aquifers favours NO_3 and phosphate removal, i.e. a temporal and spatial sequence of anoxic and oxic conditions eliminates N and causes phosphate storage. On the groundwater's path from the upland to the river further phosphate is released in the bed sediments. It originates from previously settled particulate compounds containing P.

4.2.5   Flood frequency

Puchalski (2003) show how flood events lead to what they describe as 'mosaics' of sequestrational distribution of OM fractions. This produces gradients of nutrient-transforming zones on the main direction of surface or groundwater flow. This allows for more-efficient NO_3 removal in flood-prone floodplains.

4.2.6   On-site sanitation

Wilhelm et al.(1994b) describe the processes occurring along the flow path of effluent from a small septic tank. In the unsaturated zone, the availability of oxygen leads to the aerobic oxidation of the reduced C, N and S of the effluent. The oxidation of organic N and NH_4 creates high NO_3 concentrations but some N is removed from the effluent. Some P is also removed from

the effluent. In the saturated zone P rapidly decreases to near-background, ascribed to sorption onto $CaCO_3$ and precipitation with Ca, whereas organic N and NH_4 are oxidised to NO_3

Fourie and van Ryneveld (1995) review a number of earlier studies which demonstrated that retention in the unsaturated zone was unlikely to remove high concentrations of NO_3. Reide Corbett et al., 2002) (2002) showed that N from on-site sewage treatment and disposal systems was attenuated to a greater extent than P relative to a conservative tracer.

5 Non-nutrient attenuation processes

Christensen et al. (2001) have comprehensively reviewed the literature on the attenuation processes governing contaminants in leachate-affected aquifers. The concept of redox zones in the plume constitutes an important framework for understanding the behaviour of the contaminants in the plume as the leachate migrates away from the landfill. The important processes were identified in no particular order as dilution, sorption, ion exchange, precipitation, redox reactions and degradation. The review focussed on dissolved OM, xenobiotic organic compounds, inorganic macrocomponents as anions and cations, and heavy metals. The attenuation processes in leachate plumes may for many contaminants provide significant natural remediation, limiting the effects of the leachate on the groundwater to an area usually not exceeding 1000 m from the landfill.

Wilhelm et al. (1994b) describe similar processes occurring along the flow path of effluent from a small septic tank. In the unsaturated zone, the availability of oxygen leads to the aerobic oxidation of the reduced C, N and S of the effluent. The carbonate system provided buffering of these acid-producing reactions resulting in only minor pH decreases. In the saturated zone the main reactions are interactions with the solid matrix as described below for landfills.

Abrams and Loague (2000a, b) describe a one-dimensional, coupled geochemical/solute transport simulation to represent the evolution of redox zones dynamically in time and space. The model successfully simulated the development of redox zones at the field scale, including trends in pH and alkalinity. Thermodynamic constraints were used to prevent lower-energy redox reactions from occurring under unfeasible geochemical conditions without imposing equilibrium among all redox species.

5.1 ANIONS

Anions in leachate plumes are mainly important for their capability of forming complexes and taking part in dissolution precipitation processes. The formation of complexes may increase the mobility of cations and heavy metals. In addition many reactions are influenced by pH, which is to a large extent governed by HCO_3.

5.2 CATIONS

The behaviour of cations in leachate plumes is strongly influenced by exchange with the sediment (Christensen et al., 2001). Potassium has a high affinity for ion exchange and will typically be the most retarded of the cations. Absorption in the lattices of clay minerals may constitute an additional attenuation mechanism (Bolt et al., 1976). Sodium is likely to be only slightly retarded relative to chloride (Kimmel and Braids, 1980). Calcium has a high affinity for exchange sites but will often move with the leachate front as it is often the base dominating ion. Calcium may be involved in complex formation with bicarbonate or OC and in dissolution/precipitation reactions involving calcite or siderite (Bjerg et al., 1995). Magnesium resembles calcium in its behaviour.

Ammonium is a major reducing agent in many landfill leachates, a critical long-term pollutant and also is an important nutrient. Ammonium exhibits a high affinity for ion exchange and may be incorporated into clay mineral lattices. It appears to be subject to anaerobic oxidation, but the mechanisms are poorly understood (Cutrofello and Durant, 2007; Kimmel and Braids, 1980; Ludvigsen et al., 1998).

Fe and Mn are subject to redox processes. Reduction of solid Fe and Mn oxides may lead to a substantial input of reduced Fe and Mn in groundwater. Concentrations are governed by dilution,

redox, abiotic dissolution of sediment minerals, ion exchange, precipitation (as sulphides) and possibly complexation with DOC. These processes tend to lower Fe and Mn along flow lines, but reduction of sediment-associated Fe and Mn may increase their concentrations further out in the plume.

5.3 TRACE METALS

Trace metal dynamics are determined by processes of retention and release, which are influenced by a number of soil properties including pH value, redox potential, OM, type and amount of clay minerals, Fe-, Mn- and Al-oxides (Schulz-Zunkel and Krueger, 2009). In floodplains processes occur at the oxic-anoxic interface and in the anoxic layers which mainly result in the inclusion of metals in precipitates or the dissolution of metal-containing precipitates. The kinetics of these processes are of great importance for these soils as the location of the oxic-anoxic interface is subject to change due to fluctuating water table levels (Du Laing et al., 2009). In their review of trace metal behaviour in floodplain sediments Du Laing et al. (2009) state that the spatial occurrence of processes affecting metal mobility and availability is largely determined by the topography.

Today floodplains act as important sinks for contaminants but under changing hydraulic and geochemical conditions they may also act as sources for pollutants (Schulz-Zunkel and Krueger, 2009). In floodplains extremes in flooding or dry periods can lead to altered redox potentials and that in turn influence the pH, the mineralization of OM as well as the charge of the pedogenic oxides (Schulz-Zunkel and Krueger, 2009). Such reactions may affect the bioavailability of trace metals in soils, an important factor for estimating trace metal remobilization in floodplain soils.

Heavy metals do not seem to constitute a significant pollution problem at landfills, partly because the heavy metal concentrations in the leachate often are low, and partly because of strong attenuation by sorption and precipitation (Christensen et al., 2001). Although complexation of heavy metals with dissolved OM is significant, the heavy metals are in most cases still strongly attenuated in leachate-polluted aquifers.

Important processes and factors affecting metal mobility in soils are:

- sorption to negatively-charged surfaces of OM, clay particles and Fe and Al oxides
- enhanced mobility as organic complexes and reduced availability by high molecular weight complexes
- accumulation by microorganisms
- sulphur cycling if metal sulphides are formed
- increase of mobility by drop in pH causing reduction of negative charges on surfaces
- buffering of system by carbonate
- direct precipitation of metals by carbonates
- uptake by vegetation

Many authors report highly significant correlations between cation exchange capacity, clay or OM contents and metal contents in floodplain soils (Du Laing et al., 2009). Fe and Mn (hydr)oxides were found to be the main carriers for Cd, Zn and Ni under oxic conditions, whereas the organic fraction was most important for Cu. Plants can affect the metal mobility in floodplain soils by oxidising their rhizosphere, taking up metals, excreting exudates and stimulating the activity of microbial symbionts in the rhizosphere (Du Laing et al., 2009).

In the Aire valley, Dawson and Macklin (1998) showed that Pb and Zn were primarily associated with Fe/Mn oxides whereas Cu was associated with the organic fraction and Cd with exchangeable and surface oxides and carbonate metal ions. They also observed significant variations in speciation laterally across the flood plain and vertically through the soil profile.
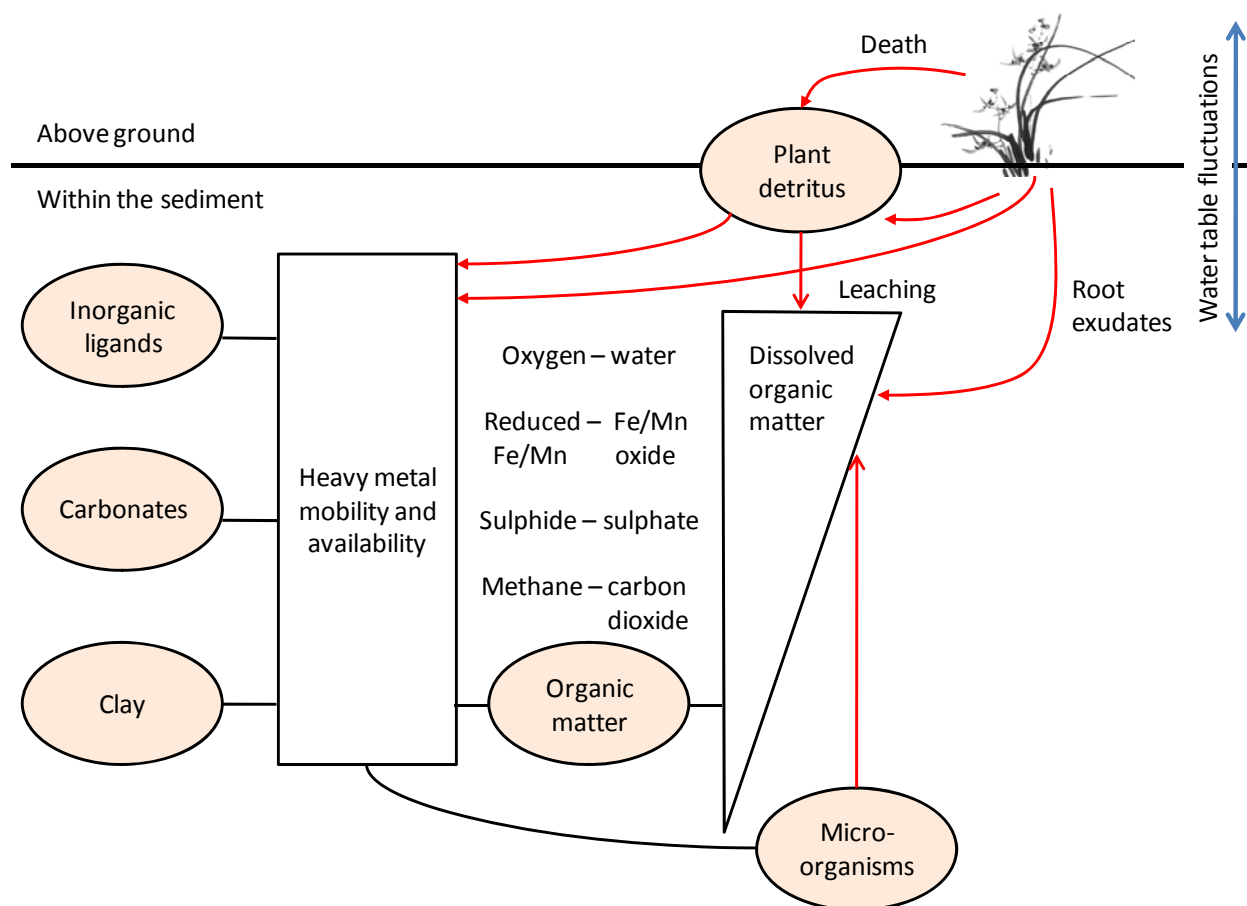
Figure 5.1 Overview of possible interactions and factor affecting metal mobility in wetland soils (after (Du Laing et al., 2009)

In the northern Oderbruch floodplain, Germany, Merz et al. (2009) found a high variability of Fe, Mn, Zn, Cu and As depending on the predominant hydraulic connectivity. They discuss the implication for the release of trace metals to surface water due to flow and water level changes, and conclude that water levels should be maintained to prevent oxidation of the sediments.

In the landfill context Baun and Christensen (2004) reviewed the speciation of heavy metals in landfill leachate, with respect to physical fractionation (particulate, colloidal, dissolved), chemical fractionation (organic complexes, inorganic complexes, free metal ions and free metal ions. Colloids as well as organic and inorganic complexes are important for all heavy metals in landfill leachate. The free metal ion constitutes less than 30%, typically less than 10%, of the total metal concentration.

Jensen et al.(1999) studied anaerobic leachate polluted groundwater collected downgradient of a Danish landfill and spiked with heavy metals. The distribution of the heavy metals between the different size-fractions showed that a substantial, but highly varying proportion of the heavy metals was associated with the colloidal fractions. These colloidal bound metals were associated primarily with the organic fraction, except for Zn, which was associated mainly with the inorganic fractions. Dissolved Cd, Cu and Pb were mainly associated with DOC, while Ni was also present as carbonate complexes and Zn as carbonate complexes and free divalent Zn. Very little metal was found in colloids larger than 0.40 μm.

Ettler et al. (2006) investigated metal contamination (Zn, Pb, Cu, Ni, Cd) in the vicinity of an old unmonitored municipal landfill in Prague, Czech Republic, where the leachate is directly drained into a surface stream. The metals (Zn, Pb, Cu, and Ni) were mainly considered to be present as carbonate complexes in leachate-polluted surface waters. These waters were oversaturated with respect to Fe oxyhydroxides, calcite ($CaCO_3$) and other carbonate phases. Three metal

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attenuation mechanisms were identified in leachate-polluted surface waters: (i) spontaneous precipitation of metal-bearing calcite exhibiting significant concentrations of trace elements (Fe, Mn, Mg, Sr, Ba, Pb, Zn, Ni); (ii) binding to Fe oxyhydroxides (Pb, Zn, Cu, Ni); and (iii) preferential bonding to sediment OM (Cu). These processes act as the key scavenging mechanisms and significantly decrease the metal concentrations in leachate-polluted water. Under the near-neutral conditions governing the sediment/water interface in the landfill environment, metals are strongly bound in the stream sediment and remain relatively immobile.

Colloids (defined as particles between 1 nm and 1 μm and nanoparticles (defined as less than 0.1 μm), (Lead and Wilkinson, 2006), are ubiquitous in aquatic systems and reflect the mineral composition of the aquifer with calcareous colloids and/or silicates dominating the composition (Baumann et al., 2006). The formation of Fe and mixed organic/Fe nanoparticles in redox environments plays an important role in controlling dissolved groundwater chemistry. Owing to their large surface areas and small size, Fe-nanoparticles can have a large influence on the transport of contaminants in groundwater systems. Colloids inside disposal sites reflected the waste composition and degradation, and heavy metal ions will be associated with colloids and particles as well as the free phase. The association of Fe and Mn to colloids is dominated by the redox conditions inside the disposal sites; where there was a reducing environment, Fe and Mn were dissolved. Downgradient of sites, an increase of Fe-precipitates and salt colloids, together with organic colloids is anticipated, particularly where there is an oxidizing environment. Baumann et al. (2006) determined an association of Cd, Co, Cu, Ni, Pb and Zn to colloids coinciding roughly with the colloid size distribution. The change of hydrochemical conditions at the interface, from a reducing, high ionic strength environment inside the disposal sites to an oxidizing, low ionic strength environment in groundwater together with physical filtration effects for the larger particles, may form a chemical barrier for colloids. Colloids can form a persistent coating around the aquifer matrix that reduces the hydraulic conductivity and enhances the sorption capacity of the aquifer close to the waste disposal sites.

5.4 XENOBIOTIC ORGANICS

Most xenobiotic organic compounds fall into the categories:

- aromatic hydrocarbons
- halogenated hydrocarbons
- phenols
- pesticides

Anilines and sulphonated compounds are also found. Attenuation is due to sorption and degradation as well as dilution and in some cases volatilisation (Christensen et al., 2001).

Sorption is well described in the literature for non-polar compounds; polar compounds have been less researched. Sorption in leachate affected aquifers for non-polar compounds has been addressed in a few cases e.g. Larsen et al. (1992). Most aquifers are poor in OM and sorption is relatively limited, however it will be more significant for the floodplain setting where there is more natural OM. The presence of leachate does not appear to affect sorption.

Several xenobiotic organic compounds (XOC) have been found to be degradable in leachate-contaminated groundwater, but degradation rates under anaerobic redox conditions have only been determined in a few cases (Christensen et al., 2001). Many XOC appear to be degraded in the intermediate redox zones

Samples from the landfill leachate pollution plume below the Vejen Landfill in Denmark revealed a significant disappearance of specific organic compounds within the first 100 m of the plume. Since sorption and dilution could not account for the decreasing concentrations, degradation was considered to be the governing process. Non-volatile OC (NVOC) suffered a corresponding fate, probably acting as a substrate for the microbial processes. The first 20 m of

the plume are methanogenic/sulphate-reducing judged on the chemistry of the groundwater, followed by a significant iron-reducing zone exhibiting a substantial capacity to degrade the OC. The presence of intermediary products (here an oxidized camphor compound) supports the concept of degradation within the Fe-reducing zone. This investigation draws the attention to the significant natural attenuation of organic contaminants and to the so far neglected Fe-reducing zone in controlling the fate of organic contaminants in leachate plumes (Lyngkilde and Christensen, 1992a).

The fate of other organic compounds (aromatic and chlorinated aliphatic hydrocarbons phenols) was studied in microcosms and shown to be variable and redox-dependent (1995a; Nielsen et al., 1995b). Nitrobenzene was transformed at all distances from the landfill in methanogenic, and Fe and NO_3-reducing conditions. Benzene, o-xylene, p-dichlorobenzene, o-dichlorobenzene, naphthalene and biphenyl appeared to be recalcitrant in the study time scale. In the methanogenic part of the aquifer 2 m from the landfill, 1,1,1-trichloroethane, tetrachloromethane and tetrachloroethene were transformed in in-situ experiments while trichloroethene was not. Tetrachloromethane was furthermore transformed at distances of up to 250 m from the landfill in Fe reducing conditions but not in NO_3-reducing conditions at 350 m from the landfill. Abiotic processes apparently contributed to the transformation of tetrachloromethane. (Baun et al., 2003) report on a revisit to the same plume 10 years later. The plume showed fairly stationary features over the 10-year period except that the XOC level as well as the level of chloride and NVOC in the plume had decreased somewhat. Most of the compounds studied were subject to degradation in addition to dilution. Exceptions were benzene, the herbicide mecoprop and NVOC.

Lønborg et al. (2006) calculated first-order degradation rates of six organic compounds (benzene, toluene, ethylbenzene, o-xylene, m/p-xylene, and naphthalene) in the methanogenic/SO_4- and Fe-reducing zones at the Vejen site. The numerical simulations show that all compounds are anaerobically biodegraded, but at very different rates. High rates of biodegradation of most of the compounds (except benzene) were found in the Fe-reducing zone. These rates generally agree with previously published rates. Only o-xylene and toluene were significantly biodegraded in the methanogenic/SO_4-reducing environment. All rates in this redox zone are generally much lower than previously published rates.

Mass loss of chlorofluorocarbons (CFCs) in anaerobic environments has been widely documented as part of their application as age dating tracers (Oster et al., 1996), probably by SO_4-reducing bacteria (Horneman et al., 2008). The apparent rate of CFC-11 degradation in temperate climates is much greater that CFC-12 with Cook and Solomon (1995) finding no CFC-12 degradation.

Recent work found loss of all three CFCs studied in a denitrifying horizon (Sebol et al., 2007). Field data were consistent with first-order degradation rates of 0.3 yr^{-1} for CFC-12, 0.7 yr^{-1} for CFC-11, and 1.6 yr^{-1} for CFC-113. CFC attenuation at this site coincides with a zone where reduced S (pyrite) is actively oxidized by NO_3 and dissolved oxygen. The mass loss was ascribed to depletion of CFC by gas stripping during N bubble forming during denitrification. Visser et al. (2009) also showed that CFCs appear to be subject to significant degradation in anoxic groundwater.

6 Conclusions

Floodplains are periodically-flooded areas along rivers and lakes and are heterogeneous and constantly changing environments where nutrients and other contaminants are attenuated or removed from groundwater as it discharges to surface water. The surface water/groundwater interface is a crucial control point for lateral fluxes between uplands and aquatic ecosystems and for longitudinal processes along rivers and wetlands. These environmental changes are probably controlled predominantly by water levels. To understand water movement and hence nutrient movement in floodplains we need to understand residence times, the character of multiple flow paths and if and when hydraulic gradient reversal occurs.

Characterising redox zones constitutes an important framework for understanding the behaviour of nutrients and contaminants in groundwater. Redox processes proceed sequentially from the highest energy yield downwards progressively reducing nitrate, manganese, iron, sulphate and carbon dioxide depending on the amount and reactivity of organic carbon present. The majority of dissolved organic carbon that travels from the soil zone to deep within the aquifer will be old and highly recalcitrant to degradation. However, in a floodplain environment and the hyporheic zone there is the potential for the introduction of fresh organic matter from river water inundation and groundwater surface water exchange. This can provide a seasonal impetus for microbial action and the formation of transitory redox zones.

In contrast point sources, such as landfills, unlined animal waste stores and leaking sewers, whilst controlled by the same flow and redox processes, appear to lead to a relatively stable system with a carbon and nutrient-rich source term which generates an established redox sequence in a limited volume of groundwater down gradient. The shape and size of such plumes may however be affected by drought or heavy rainfall. On-site sanitation systems demonstrate the same sequence of redox zones but the highly reducing conditions are found within the tank and such schemes may rely on oxidation of reduced species in the effluent during transport through the unsaturated zone.

Nutrient migration in floodplains is therefore controlled by redox distribution as well as water levels, the distribution of subsurface permeability and plant uptake. Nitrate, the predominant oxidised form of nitrogen, is readily transported in water and is stable under a range of concentrations. However, anaerobic carbon-rich sediments, such as those in floodplains, have the potential to support large populations of denitrifying bacteria. Denitrification is rapid compared to groundwater flow particularly under low flow conditions and N is lost from the groundwater system under these conditions. In contrast, phosphorus removal by soil or sediment retention and biota uptake results in accumulation within the system. Sediments can be both a source and a sink of dissolved phosphorus in surface water and shallow groundwater. Opposing conditions are favourable for nitrogen and phosphorus management, with anaerobic conditions favouring denitrification but enhanced desorption and release of phosphorus.

The important processes affecting other contaminants, such as those present in landfill leachate, dissolved organic matter, xenobiotic organic compounds, inorganic macrocomponents, and heavy metals are dilution, sorption, ion exchange, precipitation, redox reactions and degradation. For many contaminants these processes provide significant natural remediation, limiting the effects of the leachate on the groundwater to an area usually not exceeding 1000 m from the landfill.

In peri-urban environments, such as the Oxford Port Meadow, there will be many different sources of nutrients and contaminants and the distribution of zones of low redox may be both spatially and temporally variable. Other indicators will need to be applied, such as co-contaminants, to help to understand fate and transport of nutrients and contaminants.

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

ABRAMS, R H, and LOAGUE, K. 2000a. A compartmentalized solute transport model for redox zones in contaminated aquifers 2. Field-scale simulations. *Water Resources Research*, Vol. 36, 2015-2029.

ABRAMS, R H, and LOAGUE, K. 2000b. A compartmentalized solute transport model for redox zones in contaminated aquifers: 1. Theory and development. *Water Resources Research*, Vol. 36, 2001-2013.

AIKEN, G R, GILMOUR, C C, KRABBENHOFT, D P, and OREM, W. 2011. Dissolved organic matter in the Florida Everglades: Implications for ecosystem restoration. *Critical Reviews in Environmental Science and Technology*, Vol. 41, 217-248.

ALEWELL, C, PAUL, S, LISCHEID, G, and STORCK, F R. 2008. Co-regulation of redox processes in freshwater wetlands as a function of organic matter availability? *Science of the Total Environment*, Vol. 404, 335-342.

AMIRBAHMAN, A, SCHONENBERGER, R, JOHNSON, C A, and SIGG, L. 1998. Aqueous- and solid-phase biogeochemistry of a calcareous aquifer system downgradient from a municipal solid waste landfill (Winterthur, Switzerland). *Environmental Science & Technology*, Vol. 32, 1933-1940.

ANDERSEN, H E. 2004. Hydrology and nitrogen balance of a seasonally inundated Danish floodplain wetland. *Hydrological Processes*, Vol. 18, 415-434.

ARNOLD, S D, and MEISTER, E A. 1999. Dairy feedlot contributions to groundwater contamination - A preliminary study in New Mexico. *Journal of Environmental Health*, Vol. 62, 16-19.

BAKER, A, and CURRY, M. 2004. Fluorescence of leachates from three contrasting landfills. *Water Research*, Vol. 38, 2605-2613.

BASBERG, L, BANKS, D, and SAETHER, O M. 1998. Redox processes in groundwater impacted by landfill leachate. *Aquatic Geochemistry*, Vol. 4, 253-272.

BAUMANN, T, FRUHSTORFER, P, KLEIN, T, and NIESSNER, R. 2006. Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Research*, Vol. 40, 2776-2786.

BAUN, A, REITZEL, L A, LEDIN, A, CHRISTENSEN, T H, and BJERG, P L. 2003. Natural attenuation of xenobiotic organic compounds in a landfill leachate plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 65, 269-291.

BAUN, D L, and CHRISTENSEN, T H. 2004. Speciation of heavy metals in landfill leachate: A review. *Waste Management & Research*, Vol. 22, 3-23.

BJERG, P J, RUEGGE, K, PEDERSEN, J K, and CHRISTENSEN, T H. 1995. Distribution of redox-sensitive groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environmental Science & Technology*, Vol. 29, 1387-1394.

BOLT, G H, BRUGGENWERT, M G M, and KAMPHORST, A. 1976. Adsorption of cations by soil. 54-90 in *Developments in Soil Science*. BRUGGENWERT, M G M, and BOLT, G H (editors). Volume 5. (Elsevier.) ISBN 0166-2481

BOULTON, A J, FINDLAY, S, MARMONIER, P, STANLEY, E H, and VALETT, H M. 1998. The functional significance of the hyporheic zone in streams and rivers *Annual Review of Ecology and Systematics*, Vol. 29, 59-81.

BRUNKE, M, HOEHN, E, and GONSER, T. 2003. Patchiness of river-groundwater interactions within two floodplain landscapes and diversity of aquatic invertebrate communities. *Ecosystems*, Vol. 6, 707-722.

BURT, T P. 2006. Linking hydrology and biogeochemistry in complex landscapes: implications for diffuse nitrate pollution. *BHS 9th National Hydrology Symposium*, Durham, 15-20.

BURT, T P, BATES, P D, STEWART, M D, CLAXTON, A J, ANDERSON, M G, and PRICE, D A. 2002a. Water table fluctuations within the floodplain of the River Severn, England. *Journal of Hydrology*, Vol. 262, 1-20.

BURT, T P, MATCHETT, L S, GOULDING, K W T, WEBSTER, C P, and HAYCOCK, N E. 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes*, Vol. 13, 1451-1463.

BURT, T P, PINAY, G, MATHESON, F E, HAYCOCK, N E, BUTTURINI, A, CLEMENT, J C, DANIELESCU, S, DOWRICK, D J, HEFTING, M M, HILLBRICHT-ILKOWSKA, A, and MAITRE, V. 2002b. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology*, Vol. 265, 129-148.

CARLYLE, G C, and HILL, A R. 2001. Groundwater phosphate dynamics in a river riparian zone: effects of hydrologic flowpaths, lithology and redox chemistry. *Journal of Hydrology*, Vol. 247, 151-168.

CHAPELLE, F H, BRADLEY, P M, THOMAS, M A, and MCMAHON, P B. 2009. Distinguishing iron-reducing from sulfate-reducing conditions. *Ground Water*, Vol. 47, 300-305.

CHRISTENSEN, T H, KJELDSEN, P, BJERG, P L, JENSEN, D L, CHRISTENSEN, J B, BAUN, A, ALBRECHTSEN, H-J, and HERON, G. 2001. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry*, Vol. 16, 659-718.

CHUNG, J B, KIM, S H, JEONG, B R, and LEE, Y D. 2004. Removal of organic matter and nitrogen from river water in a model floodplain. *Journal of Environmental Quality*, Vol. 33, 1017-1023.

COOK, P G, and SOLOMON, D K. 1995. Transport of atmospheric trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and krypton 85. *Water Resources Research*, Vol. 31, 263-270.

CRONK, J K. 1996. Constructed wetlands to treat wastewater from dairy and swine operations: a review. *Agriculture, Ecosystems & Environment*, Vol. 58, 97-114.

CUTROFELLO, M, and DURANT, J L. 2007. Fate of high loads of ammonia in a pond and wetland downstream from a hazardous waste disposal site. *Chemosphere*, Vol. 68, 1365-1376.

DAHM, C N, GRIMM, N B, MARMONIER, P, VALETT, H M, and VERVIER, P. 1998. Nutrient dynamics at the interface between surface waters and groundwaters. *Freshwater Biology*, Vol. 40, 427-451.

DARLING, W G, and GOODDY, D C. 2006. The hydrogeochemistry of methane: Evidence from English groundwaters. *Chemical Geology*, Vol. 229, 293-312.

DAWSON, E J, and MACKLIN, M G. 1998. Speciation of heavy metals in floodplain and flood sediments: a reconnaissance survey of the Aire Valley, West Yorkshire, Great Britain. *Environmental Geochemistry and Health*, Vol. 20, 67-76.

DEVITO, K J, FITZGERALD, D, HILL, A R, and ARAVENA, R. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality*, Vol. 29, 1075-1084.

DOUGLAS, I. 2006. Peri-urban ecosystems and societies, transitional zones and contrasting values. 18-29 in *Peri-Urban Interface: Approaches to Sustainable Natural and Human Resource Use*. MCGREGOR, D, SIMON, D, and THOMPSON, D (editors). (London, UK: Earthscan Publications Ltd.)

DU LAING, G, RINKLEBE, J, VANDECASTEELE, B, MEERS, E, and TACK, F M G. 2009. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. *Science of the Total Environment*, Vol. 407, 3972-3985.

ELLIS, P A, MACKAY, R, and RIVETT, M O. 2007. Quantifying urban river-aquifer fluid exchange processes: A multi-scale problem. *Journal of Contaminant Hydrology*, Vol. 91, 58-80.

ETTLER, V, MATURA, M, MIHALJEVIČ, M, and BEZDIČKA, P. 2006. Metal speciation and attenuation in stream waters and sediments contaminated by landfill leachate. *Environmental Geology*, Vol. 49, 610-619.

FINDLAY, S. 1995. Importance of surface-subsurface exchange in stream ecosystems: The hyporheic zone. *Limnology and Oceanography*, Vol. 40, 159-164.

FOURIE, A B, and VAN RYNEVELD, M B. 1995. The fate in the subsurface of contaminants associated with on-site sanitation: A review *Water SA*, Vol. 21, 101-111.

GOLD, A J, GROFFMAN, P M, ADDY, K, KELLOGG, D Q, STOLT, M, and ROSENBLATT, A E. 2001. Landscape attributes as controls on groundwater nitrate removal capacity of riparian zones. *JAWRA Journal of the American Water Resources Association*, Vol. 37, 1457-1464.

GOODDY, D C, CLAY, J W, and BOTTRELL, S H. 2002. Redox-driven changes in porewater chemistry in the unsaturated zone of the chalk aquifer beneath unlined cattle slurry lagoons. *Applied Geochemistry*, Vol. 17, 903-921.

GOODDY, D C, and HINSBY, K. 2008. Organic quality of groundwaters. 59-70 in *Natural groundwater quality*. EDMUNDS, W M, and SHAND, P (editors). (Oxford: Blackwell.)

GROFFMAN, P, BUTTERBACH-BAHL, K, FULWEILER, R, GOLD, A, MORSE, J, STANDER, E, TAGUE, C, TONITTO, C, and VIDON, P. 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry*, Vol. 93, 49-77.

HARMS, T K, and GRIMM, N B. 2008. Hot spots and hot moments of carbon and nitrogen dynamics in a semiarid riparian zone. *Journal of Geophysical Research*, Vol. 113, G01020.

HEM, J D. 1989. Study and interpretation of the chemical characteristics of natural water. *U S Geological Survey Water-Supply Paper* 2254.

HORNEMAN, A, STUTE, M, SCHLOSSER, P, SMETHIE JR, W, SANTELLA, N, HO, D T, MAILLOUX, B, GORMAN, E, ZHENG, Y, and VAN GEEN, A. 2008. Degradation rates of CFC-11, CFC-12 and CFC-113 in anoxic shallow aquifers of Araihazar, Bangladesh. *Journal of Contaminant Hydrology*, Vol. 97, 27-41.

JAHNKE, R A. 1992. The phosphorus cycle. 301-315 in *Glocal Biochemical Cycles*. BUTCHER, S S, CHARLSON, R J, ORIANS, G H, and WOLFE, G V (editors). (London: Academic Press.)

JENSEN, D L, LEDIN, A, and CHRISTENSEN, T H. 1999. Speciation of heavy metals in landfill-leachate polluted groundwater. *Water Research*, Vol. 33, 2642-2650.

JUNK, W J, BAYLEY, P B, and SPARKS, R E. 1989. The flood-pulse concept in river-floodplain systems. *Proceedings of the International Large River Symposium* Canadian Special Publication of Fisheries and Aquatic Sciences, Vol. 106, 110-127.

KELLOGG, D Q, GOLD, A J, GROFFMAN, P M, ADDY, K, STOLT, M H, and BLAZEJEWSKI, G. 2005. In situ ground water denitrification in stratified, permeable soils underlying riparian wetlands. *Journal of Environmental Quality*, Vol. 34, 524-533.

KIEDRZYNSKA, E, WAGNER, I, and ZALEWSKI, M. 2008. Quantification of phosphorus retention efficiency by floodplain vegetation and a management strategy for a eutrophic reservoir restoration. *Ecological Engineering*, Vol. 33, 15-25.

KIMMEL, G E, and BRAIDS, O C. 1980. Leachate plumes in ground water from Babylon and Islip landfills, Long Island, New York. *US Geological Survey Geological Survey Professional Paper*, 1085.

KLINCK, B L, STUART, M E, RAMNARONG, V, BUAPENG, S, and SINPOOL-ANANT, S. 1999. Human risk in relation to landfill leachate quality: case studies from Thailand. *British Geological Survey Technical Report*, WC/99/15.

KOOPAL, L K, VAN RIEMSDIJK, W H, and KINNIBURGH, D G. 2001. Humic matter and contaminants. General aspects and modelling metal ion binding. *Pure and Applied Chemistry*, Vol. 73, 2005-2016.

LAPWORTH, D, GOODDY, D, and JARVIE, H. published online. Understanding phosphorus mobility and bioavailability in the hyporheic zone of a chalk stream. *Water, Air & Soil Pollution*.

LAPWORTH, D J, GOODDY, D C, ALLEN, D, and OLD, G H. 2009. Understanding groundwater, surface water and hyporheic zone biogeochemical processes in a Chalk catchment using fluorescence properties of dissolved and colloidal organic matter. *Journal of Geophysical Research*, Vol. 114, 10.

LAPWORTH, D J, SHAND, P, ABESSER, C, DARLING, W G, HARIA, A H, EVANS, C D, and REYNOLDS, B. 2008. Groundwater nitrogen composition and transformation within a moorland catchment, mid-Wales. *Science of the Total Environment*, Vol. 390, 241-254.

LARSEN, T, CHRISTENSEN, T H, PFEFFER, F M, and ENFIELD, C G. 1992. Landfill leachate effects on sorption of organic micropollutants onto aquifer materials. *Journal of Contaminant Hydrology*, Vol. 9, 307-324.

LEAD, J R, and WILKINSON, K J. 2006. Aquatic colloids and nanoparticles: Current knowledge and future trends. *Environmental Chemistry*, Vol. 3, 159-171.

LEWANDOWSKI, J, LISCHEID, G, and NÜTZMANN, G. 2009. Drivers of water level fluctuations and hydrological exchange between groundwater and surface water at the lowland River Spree (Germany): field study and statistical analyses. *Hydrological Processes*, Vol. 23, 2117-2128.

LEWANDOWSKI, J, and NÜTZMANN, G. 2010. Nutrient retention and release in a floodplain's aquifer and in the hyporheic zone of a lowland river. *Ecological Engineering*, Vol. 36, 1156-1166.

LEWIN, J, and HUGHES, D. 1980. Welsh floodplain studies: II. Application of a qualitative inundation model. *Journal of Hydrology*, Vol. 46, 35-49.

LØNBORG, M J, ENGESGAARD, P, BJERG, P L, and ROSBJERG, D. 2006. A steady state redox zone approach for modeling the transport and degradation of xenobiotic organic compounds from a landfill site. *Journal of Contaminant Hydrology*, Vol. 87, 191-210.

LORAH, M M, COZZARELLI, I M, and BOHLKE, J K. 2009. Biogeochemistry at a wetland sediment-alluvial aquifer interface in a landfill leachate plume. *Journal of Contaminant Hydrology*, Vol. 105, 99-117.

LOVLEY, D R, and CHAPELLE, F H. 1995. Deep subsurface microbial processes. *Reviews of Geophysics*, Vol. 33, 365-381.

LUDVIGSEN, L, ALBRECHTSEN, H J, HERON, G, BJERG, P L, and CHRISTENSEN, T H. 1998. Anaerobic microbial redox processes in a landfill leachate contaminated aquifer (Grindsted, Denmark). *Journal of Contaminant Hydrology*, Vol. 33, 273-291.

LYNGKILDE, J, and CHRISTENSEN, T H. 1992a. Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 10, 291-307.

LYNGKILDE, J, and CHRISTENSEN, T H. 1992b. Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 10, 273-289.

MCCARTY, G, MOOKHERJI, S, and ANGIER, J. 2007. Characterization of denitrification activity in zones of groundwater exfiltration within a riparian wetland ecosystem. *Biology and Fertility of Soils*, Vol. 43, 691-698.

MCCLAIN, M E, BOYER, E W, DENT, C L, GERGEL, S E, GRIMM, N B, GROFFMAN, P M, HART, S C, HARVEY, J W, JOHNSTON, C A, MAYORGA, E, MCDOWELL, W H, and PINAY, G. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, Vol. 6, 301-312.

MCGRANAHAN, G, SATTERTHWAITE, D, and TACOLI, C. 2004. Rural-urban change, boundary problems and environmental burdens. *International Institute for Environment and Development Human Settlements Working Paper Series Rural-Urban Interactions and Livelihood Strategies*, No. 10.

MERTES, L A K. 1997. Documentation and significance of the perirheic zone on inundated floodplains. *Water Resources Research*, Vol. 33, 1749-1762.

MERZ, C, WINKLER, A, and PEKDEGER, A. 2009. Trace elements in streambed sediments of floodplains: consequences for water management measures. *Environmental Earth Sciences*, Vol. 59, 25-38.

MIKAC, N, COSOVIC, B, AHEL, M, ANDREIS, S, and TONCIC, Z. 1998. Assessment of groundwater contamination in the vicinity of a municipal solid waste landfill (Zagreb, Croatia). *Water Science and Technology*, Vol. 37, 37-44.

MONTZ, B E. 2000. The generation of flood hazards and disasters by urban development of floodplains. 116-127 in *Floods*. PARKER , D (editor). (London, UK: Taylor & Francis.)

NIELSEN, P H, ALBRECHTSEN, H-J, HERON, G, and CHRISTENSEN, T H. 1995a. In situ and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume, 1. Experimental conditions and fate of phenolic compounds *Journal of Contaminant Hydrology*, Vol. 20, 27-50.

NIELSEN, P H, BJARNADÓTTIR, H, WINTER, P L, and CHRISTENSEN, T H. 1995b. In situ and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume, 2. Fate of aromatic and chlorinated aliphatic compounds. *Journal of Contaminant Hydrology*, Vol. 20, 51-66.

NOE, G B, and HUPP, C R. 2007. Seasonal variation in nutrient retention during inundation of a short-hydroperiod floodplain. *River Research and Applications*, Vol. 23, 1088-1101.

OCAMPO, C J, SIVAPALAN, M, and OLDHAM, C. 2006. Hydrological connectivity of upland-riparian zones in agricultural catchments: Implications for runoff generation and nitrate transport. *Journal of Hydrology*, Vol. 331, 643-658.

OSTER, H, SONNTAG, C, and MÜNNICH, K O. 1996. Groundwater age dating with chlorofluorocarbons. *Water Resources Research*, Vol. 32, 2989-3001.

PEDERSEN, J K, BJERG, P L, and CHRISTENSEN, T H. 1991. Correlation of nitrate profiles with groundwater and sediment characteristics in a shallow sandy aquifer. *Journal of Hydrology*, Vol. 124, 263-277.

PFEIFFER, S M, BAHR, J M, and BEILFUSS, R D. 2006. Identification of groundwater flowpaths and denitrification zones in a dynamic floodpain aquifer. *Journal of Hydrology*, Vol. 325, 262-272.

PINAY, G, BLACK, V J, PLANTY-TABACCHI, A M, GUMIERO, B, and DÉCAMPS, H. 2000. Geomorphic control of denitrification in large river floodplain soils. *Biogeochemistry*, Vol. 50, 163-182.

PUCHALSKI, W. 2003. The importance of accumulated organic matter in nutrient transport and storage in floodplains. *International Conference "EcoFlood: Towards natural flood reduction strategies"*, Warsaw, EU Framework 5.

PUCKETT, L J, and COWDERY, T K. 2002. Transport and fate of nitrate in a glacial outwash aquifer in relation to ground-water age, land use practices and redox processes. *Journal of Environmental Quality*, Vol. 31.

PUCKETT, L J, COWDERY, T K, MCMAHON, P B, TORNES, L H, and STONER, J D. 2002. Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system. *Water Resources Research*, Vol. 38.

RANALLI, A J, and MACALADY, D L. 2010. The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds – A review of the scientific literature. *Journal of Hydrology*, Vol. 389, 406-415.

REIDE CORBETT, D, DILLON, K, BURNETT, W, and SCHAEFER, G. 2002. The spatial variability of nitrogen and phosphorus concentration in a sand aquifer influenced by onsite sewage treatment and disposal systems: a case study on St. George Island, Florida. *Environmental Pollution*, Vol. 117, 337-345.

ROBERTSON, W D, CHERRY, J A, and SUDICKY, E A. 1991. Ground-water contamination from two small septic systems on sand aquifers. *Ground Water*, Vol. 29, 82-92.

SCHOLL, M A, COZZARELLI, I M, and CHRISTENSON, S C. 2006. Recharge processes drive sulfate reduction in an alluvial aquifer contaminated with landfill leachate. *Journal of Contaminant Hydrology*, Vol. 86, 239-261.

SCHULZ-ZUNKEL, C, and KRUEGER, F. 2009. Trace metal dynamics in floodplain soils of the River Elbe: a review. *Journal of Environmental Quality*, Vol. 38, 1349-1362.

SCOTT, J, MCCARTHY, M, GARDNER, W, and DOYLE, R. 2008. Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. *Biogeochemistry*, Vol. 87, 99-111.

SEBOL, L A, ROBERTSON, W D, BUSENBERG, E, PLUMMER, L N, RYAN, M C, and SCHIFF, S L. 2007. Evidence of CFC degradation in groundwater under pyrite-oxidizing conditions. *Journal of Hydrology*, Vol. 347, 1-12.

SURRIDGE, B W J, HEATHWAITE, A L, and BAIRD, A J. 2007. The release of phosphorus to porewater and surface water from river riparian sediments. *Journal of Environmental Quality*, Vol. 36, 1534-1544.

TAKATERT, N, SANCHEZ-PEREZ, J M, and TREMOLIERES, M. 1999. Spatial and temporal variations of nutrient concentration in the groundwater of a floodplain: effect of hydrology, vegetation and substrate. *Hydrological Processes*, Vol. 13, 1511-1526.

TIEDJE, J M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. 179-244 in *Biology of Anaerobic Microorganisms*. ZEHNDER, A J B (editor). (New York: John Wiley.)

TOBIAS, C R, MACKO, S A, ANDERSON, I C, CANUEL, E A, and HARVEY, J W. 2001. Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: A combined tracer and in situ isotope enrichment study. *Limnology and Oceanography*, Vol. 46, 1977-1989.

TOCKNER, K, MALARD, F, and WARD, J V. 2000. An extension of the flood pulse concept. *Hydrological Processes*, Vol. 14, 2861-2883.

VAN BREUKELEN, B M, and GRIFFIOEN, J. 2004. Biogeochemical processes at the fringe of a landfill leachate pollution plume: potential for dissolved organic carbon, Fe(II), Mn(II), NH$_4$, and CH$_4$ oxidation. *Journal of Contaminant Hydrology*, Vol. 73, 181-205.

VIDON, P, ALLAN, C, BURNS, D, DUVAL, T P, GURWICK, N, INAMDAR, S, LOWRANCE, R, OKAY, J, SCOTT, D, and SEBESTYEN, S. 2010. Hot spots and hot moments in riparian zones: Potential for improved

water quality management1. *JAWRA Journal of the American Water Resources Association*, Vol. 46, 278-298.

VIDON, P, and HILL, A. 2005. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. *Biogeochemistry*, Vol. 71, 259-283.

VISSER, A, SCHAAP, J D, BROERS, H P, and BIERKENS, M F P. 2009. Degassing of ^{3}H/^{3}He, CFCs and SF$_6$ by denitrification: Measurements and two-phase transport simulations. *Journal of Contaminant Hydrology*, Vol. 103, 206-218.

WHEATER, H S, and PEACH, D. 2004. Developing interdisciplinary science for integrated catchment management: The UK LOwland Catchment Research (LOCAR) Programme. *International Journal of Water Resources Development*, Vol. 20, 369-385.

WILHELM, S R, SCHIFF, S L, and CHERRY, J A. 1994a. Biogeochemical evolution of domestic waste water in septic systems: 1. Conceptual model. *Ground Water*, Vol. 32, 905-916.

WILHELM, S R, SCHIFF, S L, and ROBERTSON, W D. 1994b. Chemical fate and transport in a domestic septic system: Unsaturated and saturated zone geochemistry. *Environmental Toxicology and Chemistry*, Vol. 13, 193-203.