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REPORT

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Effectiveness of Riparian Zones in Contaminant Mitigation

Project acronym: AQUISAFE 1

by

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Title

Effectiveness of Riparian Zones in Contaminant Mitigation

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Abstract

The Aquisafe project aims at mitigation of diffuse pollution from agricultural sources to protect surface water resources. The first project phase (2007-2009) focused on the review of available information and preliminary tests regarding

(i) most relevant contaminants,

(ii) system-analytical tools to assess sources and pathways of diffuse agricultural pollution,

(iii) the potential of mitigation zones, such as wetlands or riparian buffers, to reduce diffuse agricultural pollution of surface waters and

(iv) experimental setups to simulate mitigation zones under controlled conditions.

The present report deals with (iii) and has the purpose to provide a brief overview of the current state of knowledge related to the role of riparian zones as best management practices for water quality improvement at the watershed scale.

Research indicates that landscape hydrogeological characteristics such as topography and surficial geology influence both riparian zone hydrology and biogeochemistry. Topography, depth to a confining layer and soil hydraulic conductivity all affect groundwater input to riparian zones and the water table fluctuation regime throughout the year. Research also indicates that although most biologically mediated reactions in soil are redox dependant, landscape hydrogeology, by affecting riparian hydrology, affects the redox conditions in the soil profile. In turn, microbial processes and changes in element concentrations are predictable as a function of the redox state of the soil.

Variations in biogeochemical conditions directly affect the fate of multiple contaminants in riparian systems. In particular, variations in soil redox potential in riparian zones can affect the evolution of numerous contaminants and solutes within riparian zones like pesticides, phosphorus, NO_3^-, N_2O, NH_4^+, SO_4^{2-}, CH_4, Fe^{2+}/Fe^{3+} or Dissolved Organic Carbon (DOC). Of all the solutes/contaminants mentioned above, nitrate is one of the most important concerning water quality in many areas of the US and Western Europe. Consequently, many studies have investigated nitrate removal in riparian systems. Depending on site conditions, nitrate retention generally varies between 60 and 90 %; however, there are situations where nitrate removal is less or even where a riparian zone becomes a source of N to the stream. Although the riparian literature is clearly dominated by nitrate removal studies, many studies also focus on phosphorus, sediments, pesticides, chloride, bromide and bacteria. Although there are situations where riparian zones have been shown to be sources of P, Atrazine, bromide, E. coli or E. streptococci bacteria, riparian zones generally contribute to the reduction of most contaminants in subsurface flow and overland flow. Nevertheless, although conditions favorable to the reduction or oxidation of a given contaminant at the microbial level are often known, more research needs to be conducted to determine the variables controlling the fate of contaminants other than nitrate in soil at the riparian zone scale.

Finally, although many studies have investigated the hydrological and biogeochemical functioning of riparian zones in the past few decades, much research remains to be conducted in order to quantify and predict the impact of riparian zones on water quality at the watershed scale in a variety of climatic and hydrogeological settings. In particular, better strategies and/or tools to generalize riparian function at the watershed scale need to be developed. Particular areas where research is needed to achieve this goal include: 1) the development of strategies to quantify and model the

cumulative impact of individual riparian zones on water quality at the watershed scale; 2) a better quantification of the importance of spatial and temporal variability in hydrologic and biogeochemical riparian functioning relative to annual nutrient transport; 3) a better understanding of the role of vegetation in terms of its impact on riparian biogeochemical processes and the response of these processes to manipulations of vegetative cover; 4) a better understanding of the impact of human activities and infrastructure on riparian zone function in both urban and rural landscapes; 5) a better understanding of the fate of emerging contaminants in riparian systems.

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Chapter 1

Introduction

The purpose of this document is to provide of brief overview of the current state of knowledge related to the role of riparian zones as best management practices for water quality improvement at the watershed scale. This document is divided in three sections.

CHAPTER 2 will focus on summarizing what is known about the hydrological and biogeochemical functioning of riparian zones. The main variables controlling riparian zone functions will be identified in this section.

CHAPTER 3 will present a summary of the removal efficiency of riparian zones vis-à-vis a wide array of contaminants. This section is based on summaries of many studies published in the literature in the past 20 years.

CHAPTER 4 discusses important aspects of riparian zone management.

CHAPTER 5 will focus on identifying major research needs for riparian zone research as related to water quality for the years to come.

Chapter 2

Riparian Hydrological and Biogeochemical Functioning

2.1 Landscape and climatic influence on riparian zone function

Many studies have shown that landscape hydrogeological characteristics strongly influence riparian zone function (Lowrance et al., 1997, Hill 2000, Gold et al. 2001, Vidon and Hill, 2004a, Vidon and Hill, 2006).

Topography and geology of the landscape surrounding the riparian zone generate points of focused recharge, points of topographic depression and other successions of uplands and lowlands separated by a steeper slope, and ultimately control the development of wet zones and stream riparian zones. Depending on the climate (precipitation) and of the hydrogeological characteristic of the watershed in which the riparian zone is functioning (i.e. regional aquifer, soil thickness), the proportion of groundwater, precipitation and surface water recharging the riparian zone will vary (Vidon and Smith 2007). In temperate climates, precipitation and the amount of solute leached from fields and entering riparian zones vary seasonally. In regions where soil does not freeze during winter months and where no major snow accumulation is observed, like in Western Europe, most nitrate leaching occurs at the same time as the maximum amount of precipitation, from December to March. During the spring and summer, the amount of water and the nitrate load entering the riparian zone generally decreases.

In regions where the soil freezes during the winter and where snow accumulation is observed (Northern United States, Canada, Northern Europe), the low flow period generally occurs in winter and summer and the high flow period occurs in spring, when snow melts, and sometime in the fall if precipitation is significant. During the spring thaw, extensive amounts of water flow through riparian systems and this is the period of the year where runoff and solute loads entering riparian systems are generally the largest. Cold temperature during snowmelt may reduce soil biological activity in surface riparian soils and higher rates of biological activity may only occur in summer when solute fluxes are lower.

Seasonal variations in groundwater input to riparian zones impact their hydrological functioning. For instance, water table dynamics throughout the year will be in part determined by the volume of water moving through the riparian zone. Groundwater input to riparian zones also affects subsurface flow paths and the interaction between groundwater and shallow soil layers where biological activity is often highest.

The size of the upland aquifer recharging the riparian zone also affects groundwater inputs to riparian systems (Lowrance et al. 1997; Hill, 2000). As the depth to the confining layer increases in the upland, and therefore as the size of the upland aquifer increases, greater fluxes with reduced seasonality entering the riparian zone generates a progressive decrease in magnitude of water table variations within the riparian area. Deep confining layers generally allow a better connection between the riparian zone and the upland aquifer. Uplands with deep confining layers also have bigger aquifers that can sustain recharge during summer months. This in turn diminishes seasonal variations in the hydrological functioning of riparian zones. Conversely, riparian zones connected to shallow upland aquifers generally present large water table fluctuations during the year.

The geologic characteristics of the landscape surrounding the riparian zone also alter the chemistry of the water flowing through the riparian zone. For instance, the type of bedrock (limestone, granite, schist, karsts) will control in part the acidity (pH) of subsurface water and its mineral composition, which will influence the nature of biogeochemical reactions occurring within the riparian zone soil.

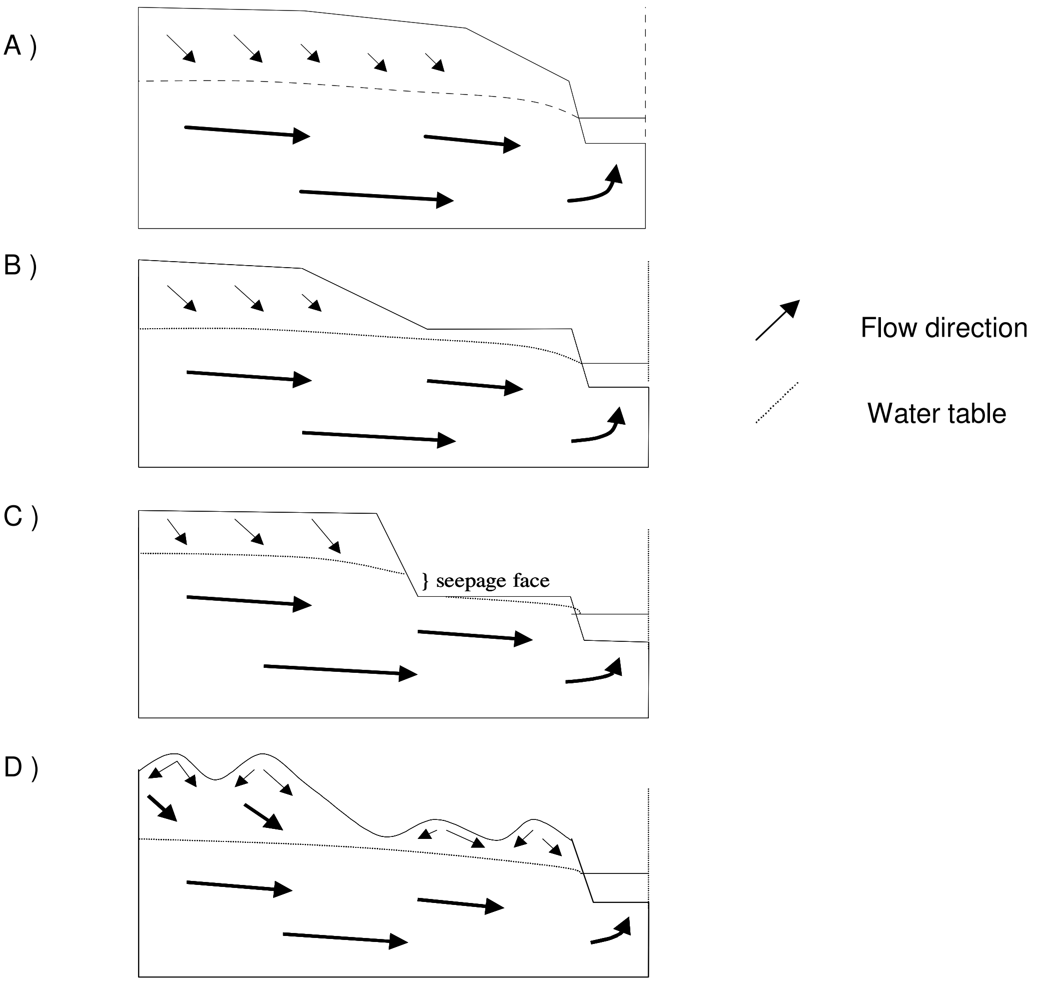
Overall, recent research therefore suggest that climate and landscape hydrogeology impacts riparian zone hydrological functioning and that groundwater flow and groundwater chemistry in the riparian zone are, to some extent, determined by the broader hydrologic setting in which the riparian zone is functioning.

2.2 Variables influencing riparian zone hydrological functioning

Most studies dealing with the hydrological functioning of riparian zones have been conducted in landscapes with impermeable layers close to the surface and relatively shallow flowpaths. However, riparian zones are complex systems, often heterogeneous (large variation in soil hydraulic conductivity, soil structure and micro-topography) and do not systematically have an impermeable layer close to the surface. One critical step to the efficient use of riparian zones as tools to improve water quality is the identification of general patterns of riparian zone functions for a variety of landscape settings.

Topography is a critical variable to take into account when identifying important landscape characteristics susceptible to influence riparian zone hydrological functioning. A simplified representation of the four main types of topography commonly found in riparian zones is shown in Figure 1. Panel A represents riparian zones with convex topography. Convex slopes generally lead water to flow relatively deeply below the ground surface and to bypass the surface horizon of the soil profile where biological activity is often highest. Panels B, C and D represent different types of concave topography that generally leads water to flow closer to the upper soil horizon in the riparian zone, and therefore situations where enhanced interaction between groundwater and shallow soil may occur. Panel B represents the simplest kind of topography where the flow path within the riparian zone is essentially controlled by the average slope of the landscape, the water input to the riparian zone from the upland, the water level in the stream and the nature of the sediment profile. This, along with the soil hydraulic conductivity, will determine the water residence time in the riparian zone soil. In the case of panel C, topography influences more strongly the water flow path through the riparian zone. In particular, the difference in elevation between the upland and the lowland forces the water table to intercept the soil surface and leads to the formation of seeps. Depending on soil saturation conditions, seep water can either re-infiltrate in the riparian zone soil or by-pass the riparian zone entirely as overland flow. Panel D represents riparian zones with a very hilly surface topography that can lead to the formation of local flow patterns, in a direction different than the one of the average topographic gradient of the riparian zone.

Figure 1: Impact of local topography on the general hydraulic functioning of riparian zones

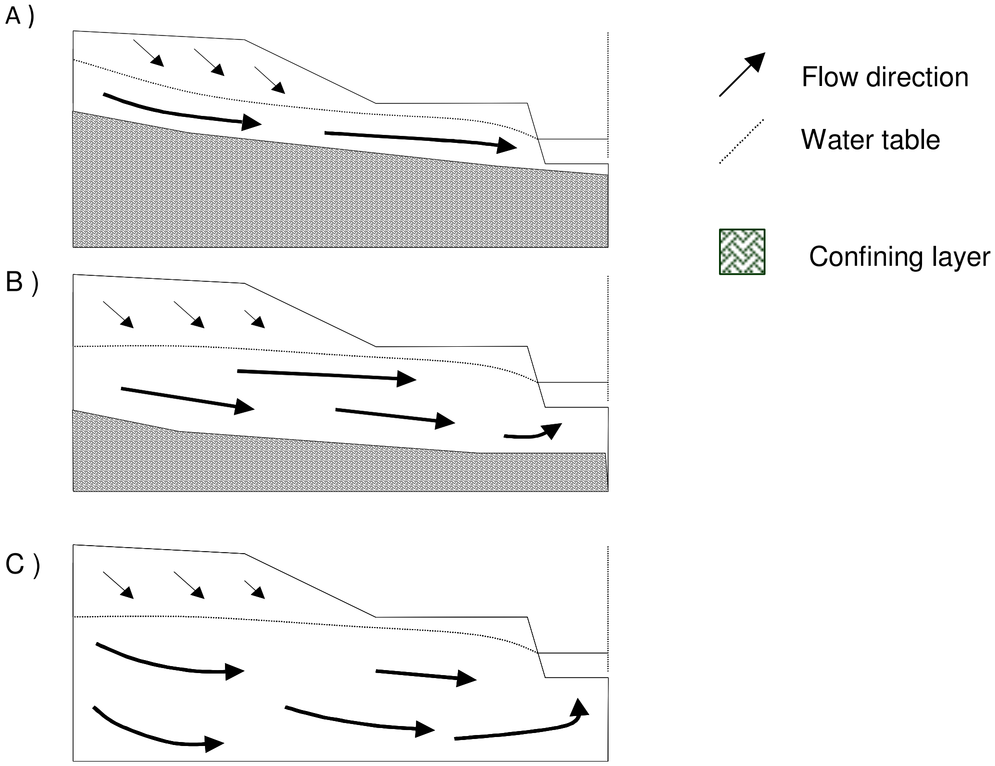


Aside from topography, the depth to a confining layer (clay deposit, till, impermeable bedrock) also strongly influences the hydrological functioning of riparian zones. Figure 2 represents three riparian zone types with various confining layer depths. In particular, they represent a gradient of riparian zones from riparian zones with a confining layer close to the surface to riparian zones without any shallow confining layer.

Panel A represents riparian zones with a confining layer close to the surface (0.5-1 m). This kind of configuration often leads to the development of very shallow flow paths. This type of riparian zones is the one that has been the most extensively studied in the literature dealing with contaminant removal in stream riparian zones (Correll, 2000). Without deep infiltration and with a shallow flow path, the flow is essentially horizontal in the saturated zone of the soil and vertical in the unsaturated zone. The water table level in this type of riparian zone is essentially controlled by the balance between the water input to the riparian zone and the water level in the stream, whereas the average slope and the soil hydraulic conductivity control the water residence time. However, because riparian zones where a shallow confining layer is present are often connected to small upland aquifers (Vidon and Hill, 2004b), groundwater inputs from the upland may be interrupted during summer months and very low during winter. Maximum fluxes associated with a high water table may be limited to spring and late fall, leading to strong seasonal variations in the hydrological functioning of this type of riparian zone.

In the case represented in panel B, the confining layer is deeper (1-3 m) than in case A. Depending on the volume of water recharging the riparian zone and depending on the actual depth to the confining layer, water can flow beneath the most biologically active soil layer. In that case, the contaminant removal efficiency of riparian zones in this category may be relatively limited. Because this type of riparian zone is often connected to a larger upland aquifer, seasonal water table fluctuations are of a lesser magnitude than for riparian zones with a shallow confining layer (0.5-1 m).

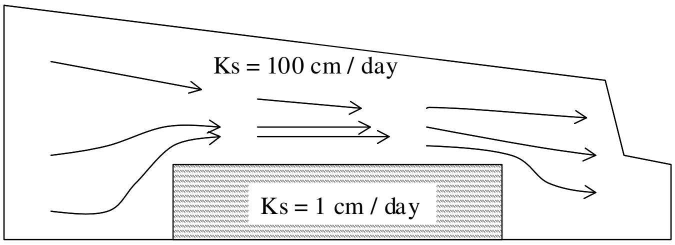
Figure 2: Impact of the geologic setting of a riparian zone on its hydraulic functioning



The riparian zone represented on panel C corresponds to riparian zones connected to a large aquifer and without confining layer close to the surface (confining layer deeper than 3 m). Because a large upland aquifer is generally capable of sustaining flow to the riparian zone throughout the year, limited seasonal variability is observed for these systems (Devito et al. 2000, Hill et al. 2000).

Of course, the various cases presented above are only to be used as general templates to better understand how riparian zone physical characteristics may influence riparian zone hydrological functioning as any combination of topography and geologic setting can be found and lead to complex water flowpaths. Furthermore, the succession of sediment layers with different hydraulic conductivities within the riparian zone soil can also modify the water flowpath in the riparian zone (Figure 3). For instance, a low soil hydraulic conductivity layer (e.g. clay oxbow) can modify the general water flow path in the soil and force water to flow upward or downward. Conversely, gravel lenses can be zones of preferential water flow and can lead water to bypass other parts of the riparian zone where the sediment permeability is lower. Riparian soil hydraulic conductivity also alters soil water velocity, which in turn, can influence the water residence time in the riparian zone. Results reported by Correll (1997) and Cirmo and McDonnell (1997) suggest that soil layers with too high (coarse sand) or too low (loamy-clay) hydraulic conductivities can respectively limit interaction between water and sediments, and reduce the magnitude of groundwater flow through riparian soils.

Figure 3: Interaction between main water flow path and soil layers of different hydraulic conductivities (Ks)



2.3 Variables influencing riparian zone biogeochemical functioning

Research has shown that pH, redox potential, temperature, energy source availability, nutrient concentrations, and to a lesser extent major cation and pollutant concentrations in soils, are the variables that determine the type and the intensity of microbiological reactions taking place in a given environment.

Bacteria in aquifers are chemotrophic organisms, i.e. they obtain energy from the oxidation of organic or inorganic compounds (as opposed to gaining energy from the sun) (Korom, 1992). If the electron donor is organic, the organism is organotrophic, and if the electron donor is inorganic (Mn^{2+}, Fe^{2+}, Sulfides), the organism is lithotrophic. An organotrophic organism virtually always uses cellular carbon as its energy source. Organotrophs are therefore generally also heterotrophic organisms (Korom, 1992). On the other hand, most lithotrophic organisms can obtain carbon from inorganic carbon dioxide. Most lithotrophic organisms are therefore also autotrophic organisms. Therefore, depending on the availability of electron donors, one type of organism will dominate and so will one type of metabolism. Heterotrophic and autotrophic metabolisms do not involve the same chemical compounds and therefore modify concentrations of major ions, nutrients and pollutants in different ways. Also, the availability of electron donors is redox state dependant. For example, under oxidized conditions, cations such as Mn^{2+} or Fe^{2+} seldom exist in solution which offset any autotrophic reaction involving these ions. Therefore, the redox state of the environment, by controlling at least partially the availability of the different types of electron donors in riparian soils, control the type of microbial processes occurring in soils. In turn, those microbial processes influence the concentration of the different chemicals in the soil solution.

In riparian soils, organic carbon is the main electron donor available to microorganisms, therefore most microbial processes are heterotrophic. As briefly mentioned earlier, microbial processes depend of the redox state of the soil. Hill (2000) indicates that "various chemical and biological transformations occur in a predicable sequence within narrow redox ranges" (Hill, 2000, p87). More precisely, Hedin (1998) and Korom (1992) define the sequence of microbial redox reactions that occur in soil during the oxidation of organic matter as the soil redox potential increases or decreases. Under aerobic conditions, dissolved oxygen is used as the electron acceptor for the oxidation of organic carbon: this is aerobic respiration. As the environment becomes more reduced, denitrifying organisms, which are for the most part facultative anaerobes (Korom – 1992), start using nitrate as the electron acceptor when oxygen become less available: this is heterotrophic denitrification. As the redox potential keeps decreasing, the following elements are used as electron acceptors to oxidize organic carbon: Mn^{4+} (MnO_2) is reduced in Mn^{2+} ($MnCO_3$), then Fe^{3+} (FeOOH) is reduced in Fe^{2+} ($FeCO_3$) and then SO_4^{2-} is reduced in HS^-. Under very reduced conditions, CH_2O and CO_2 are reduced to CH_4^+, which is eventually released to the atmosphere. This is methanogenesis. Conversely, when the soil environment becomes less reduced, inverse reactions occur with methane oxidation ($CH_4 > CO_2$), sulfide oxidation ($HS > SO_4^{2-}$), and then nitrification ($NH_4^+ > NO_3^-$). Precise values of the redox range in which each of these reactions occur can be found in Hedin et al. (1998).

Overall, research tends to indicate that microbial processes and changes in element concentrations are predictable as a function of the redox state of the soil (Martin et al., 1999, Hill, 2000, Hedin et al., 1998, Korom, 1992). Nevertheless, at the riparian zone scale, research indicates that the variable controlling riparian zone hydrology also affect redox potential in riparian soils. For instance, the size and seasonality of hydrologic connections with adjacent uplands influence riparian zone water table fluctuations and the extent of surface saturation with subsequent effects on soil redox potential and microbial processes (Roulet 1990; Devito et al. 1996). The depth of permeable sediments overlying a confining layer in riparian zones can influence hydrologic flow paths (Correll 1997; Lowrance et al. 1997). A confining layer at a shallow depth increases the potential for interaction of groundwater with organic-rich surface soils and may favor rapid nitrate removal by denitrification (Hill 1996; Gold et al. 2001). However, when soils are too permeable, the residence time of water may not be long enough for anoxic conditions to develop (Burt et al. 2002). Topography also affects denitrification. At sites with a relatively flat topography, a low hydraulic gradient can increase the water residence time in the riparian zone and enhance the development of anaerobic conditions necessary for denitrification (Vidon and Hill 2004c).

Although at the microbial scale, soil biology is strongly influenced by soil redox conditions, research therefore suggest that many of the variables (i.e. topography, surficial geology) influencing riparian zone hydrology also influence soil redox conditions and ultimately soil microbial reactions taking place in riparian soils.

2.4 Processes controlling contaminant fate in riparian zones

Variations in biogeochemical conditions directly affect the fate of multiple contaminants in riparian systems. In particular, variations in soil redox potential in riparian zones can affect the evolution of numerous contaminants and solutes within riparian zones like pesticides, phosphorus, NO_3^-, N_2O, NH_4^+, SO_4^{2-}, CH_4, Fe^{2+}/Fe^{3+} or Dissolved Organic Carbon (DOC).

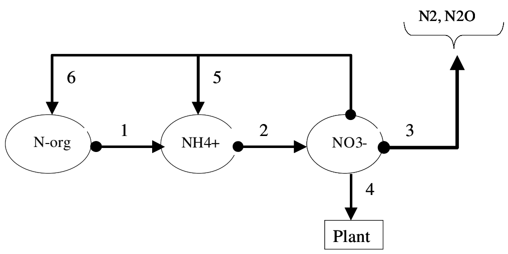
Retention of pesticides within riparian soils is highly variable and depends in part on the pesticide studied. Some pesticides are easily degradable (isoproturon), some need specific bacteria to be degraded (atrazine) and some tend to form bound residues (diflufenicanil) (Harris and Foster, 1996; Benoit et al., 1999). Furthermore, the availability of nutrients and the redox conditions in the soil also affect the retention/degradation of pesticides in riparian zone soils. Although degradation and adsorption rates vary for each pesticide, research indicates that the root zone may be a hot spot for the removal of many pesticides as rhizodeposition of labile organic substrate and the accumulation of organic residue near the root zone may enhance microbial numbers and activity, thereby increasing the potential for mineralization and adsorption of pesticides and pesticide metabolites (Krutz et al., 2006). Benoit et al. (1999) also indicate that the degradation of isoproturon in grassed buffer strip soil was enhanced in the surface layer of the soil profile (0-2 cm depth) containing a high proportion of non-decomposed plant residues.

In soil, phosphorus can be found in dissolved (mainly PO_4^{3-}) or particulate forms. Particulate P includes P associated with soil particles and organic matter eroded from field (Daniel, 1998). Particulate P constitutes the major part of P transported from agricultural fields and consequently the major part of P entering riparian zones. When the soil is well oxidized, important quantities of P can be released following oxidation of organic matter. For instance, Cooke and Prepas (1998) found for a site located in the boreal plain in Canada that most of P export occurred during the summer (driest month).

As previously indicated, other species like NO_3^-, NH_4^+, SO_4^{2-}, Fe^{2+}/Fe^{3+} or Dissolved Organic Carbon (DOC) are also influenced by redox conditions in soil. Aerobic conditions can lead to oxidation of accumulated S and to an important release of SO_4^{2-}. Similarly, under very reduced conditions, methanogenesis can occur. Therefore, although O_2 dominates as an electron acceptor in oxic environments, NO_3^-, N_2O, Mn_4^+, Fe_3^+, SO_4^{2-}, CO_2 and CH_2O can be locally important in anoxic environments (Hedin et al. 1998).

Of all the solutes/contaminants mentioned above, nitrate is one of the most important concerning water quality in many areas of the US and Western Europe. Figure 4 presents a simplified view of the nitrogen cycle in soil.

Figure 4 : Nitrogen cycle in soil



1 : Ammonification

2 : Nitrification

3 : Denitrification

4 : Plant uptake

5 + 6 : Remobilization/Assimilation

Ammonification, nitrification and denitrification are microbial transformations and the rate of these transformations is influenced by the availability of organic carbon (OC) and N in the soil profile (Hedin et al. 1998, Hill et al. 2000). Ammonification is the mineralization of organic N to NH_4^+ as OC is decomposed. This process occurs under aerobic or anaerobic conditions (Hefting et al. 2004) whereas nitrification, which is the oxidation of ammonium into nitrate, is a strictly aerobic process. Denitrification, which is the reduction of nitrate into N gases is a strictly anaerobic process. Because redox conditions in riparian zones are strongly influenced by water table fluctuations, water table fluctuations and water residence time in riparian zones have a strong impact on the N cycle in these systems (Devito et al. 2000, Simpkins et al. 2002, Hefting et al. 2004). Although the distribution of electron donors (OC, CH_4, HS^-, $Fe^{(II)}$, NH_4^+, $Mn^{(II)}$) and acceptors (O_2, NO_3^-, $Mn^{(IV)}$, $Fe^{(III)}$, SO_4^{2-}, CO_2, CH_2O) in riparian soils ultimately control the type of biogeochemical transformation in soils (Korom 1992, Hedin et al. 1998), nitrate (NO_3^-) and dissolved oxygen as an indicator of aerobic vs. anaerobic conditions are the most important electron acceptors for N transformation processes in soils (Vidon and Hill, 2004c). A detailed description of the N cycle in riparian zones can be found in Naiman et al. (2005).

2.5 Role of vegetation at controlling N removal in Riparian Zones

Naiman et al. (2005) provide a detailed review of the traditional view of the role of vegetation on N removal and of the relative importance of vegetation uptake vs. denitrification in riparian zones. Briefly, they indicate that in most riparian zones where an unsaturated aerobic zone develops in the summer owing to water table drawdown, vegetation uptake is an important nitrate uptake mechanism. Conversely, during periods of surface water saturation or in riparian zones where a high water table is found throughout the year, denitrification is often the dominant N removal process. A traditional view is also that denitrification is highest in surficial soil horizons where most biological activity takes place (Pinay et al., 2002, Clement et al., 2002). Traditionally, research therefore suggests that vegetation, by providing labile organic matter, has a significant impact on the fate of nitrogen, and in particular nitrate, in riparian systems. However, many studies have started to challenge this traditional view of the role of vegetation on the fate of nitrate in riparian systems, and suggest that current surface vegetation may actually have little to no impact on the fate of nitrate in riparian systems across a range of geomorphic settings.

In a European study comparing 14 riparian sites across Europe, Sabater et al. (2003) found no correlation between nitrate removal and vegetation. They also found similar N removal rates for herbaceous (4.43%.m^{-1}) and forested sites (4.21%.m^{-1}), suggesting that vegetation had no clear impact on N removal across the range of sites. Hill et al. (2000), Devito et al. (2000), and Vidon and Hill (2004a, c) also showed that nitrate removal in southern Ontario riparian zones was unrelated to vegetation and that differences in patterns of electron donors and acceptors due to differences in hydrogeological setting between sites were the main controls on nitrate removal and denitrification in the riparian zones studied. In particular, Vidon and Hill (2004a, c) showed that patterns of nitrate removal at many southern Ontario riparian sites did not change significantly with seasons. This suggests that nitrate uptake by vegetation was negligible compared to denitrification regardless of the time of year. Similarly, Vidon and Hill (2004a, c) also showed that nitrate removal often occurred abruptly in the subsurface, at locations where high dissolved organic carbon, high nitrate and low dissolved oxygen concentration were found. In all cases, nitrate removal in the subsurface was unrelated to any change in surface vegetation. This suggests that current surface vegetation has little to no impact on nitrate removal in many riparian zones.

Nevertheless, over thousands of years, vegetation does help sustain nitrate removal and denitrification by forming buried organic matter deposits at depth. For instance, Gold et al. (1998) and Jacinthe et al. (1998) found that denitrification occurred in small patches of OC in the C horizon of riparian soils. Hill et al. (2000) reported the occurrence of denitrification at depth at interfaces between sands and peats or buried channel deposits in a southern Ontario riparian zone just meters from areas where no significant denitrification was observed. More recently, Gurwick et al. (2008) showed that buried patches of organic carbon in riparian zones in glaciated landscapes were zones of preferential microbial activity. However, these recent studies did not show any significant correlation between surface vegetation and denitrification at depth.

Overall, research does not suggest that surface vegetation has a significant effect on nitrate removal in riparian zones either by plant uptake or by providing labile organic carbon at depth. Nitrate uptake by vegetation does occur and over thousands of years, vegetation helps sustain denitrification at depth by providing organic matter; however, recent studies generally do not show any significant correlation between N removal across riparian zones or N removal in the subsurface and surface vegetation across a range of geomorphic settings. This suggests that surface vegetation in riparian zones may only play a limited role in the fate of N through riparian zones. Nevertheless, it is important to remember that active surface vegetation is an important component to a healthy riparian system as vegetation helps maintain soil infiltration capacity, provides habitat for wildlife and also contribute to stream bank stabilization and erosion control.

Chapter 3

Contaminant Removal in Riparian Zones

Although many studies specifically focus on the fate of nitrate (NO_3-N) in riparian systems (Hill 1996, Dosskey 2001, Pucket 2004), other water quality constituents that have been examined in riparian transport studies include ammonium (NH_4-N) (Hubbard and Lowrance 1997, Peterjohn and Correll 1984), Soluble Reactive Phosphorus (SRP) (Jordan et al. 1993, Lowrance et al. 1984), sulfate (SO_4^{2-})(Lowrance et al. 1984), Dissolved Organic Nitrogen (DON) (Lowrance et al. 1984, Peterjohn and Correll 1984), Dissolved Organic Carbon (DOC) (Jacinthe et al. 2003, Hook and Yeakley 2005, Nieminen et al. 2005, Inamdar and Mitchell 2006) and some pesticides (Lowrance et al. 1997a). Correll and Weller (1989) also indicate that the pH of groundwater can be altered across riparian zones because below-ground processes often consume or release H+ ions. Jordan et al. (1993) also showed that organic carbon concentration usually increases through riparian zones because of the occurrence of low redox potential. For phosphorus, Uusi-Kamppa (1996) gives example of P removal in runoff between 20 and 93 % in buffer strips in USA, Norway, Sweden and Finland. Other studies also showed that riparian zones could trap sediments in runoff since the water velocity generally decreases when water enters the riparian zone because of its vegetation, which in turn enhances the deposition of suspended particles present in runoff. Efficient retention of pesticides in surface runoff across riparian zones or grassed buffer strips has also been mentioned by numerous authors (Grill et al., 1996; Harris et al., 1996; Patty et al., 1997; Real et al. 1997).

Of all the studies dealing with contaminant retention/removal in riparian zones, most deal with nitrogen, and especially nitrate. In a review of nitrate removal in stream riparian zones, Hill (1996) recorded many studies in which nitrate retention across stream riparian zones was observed with examples from USA (Maryland, Georgia, North Carolina, Pennsylvania, Rhode Island, Illinois), New Zealand, France and Denmark. Depending on sites, nitrate retention varied generally between 60 and 90 %. In terms of quantity of nitrate actually removed from subsurface water, the nitrate removal efficiency of riparian zones is highly variable. Hill (1996) recorded studies where nitrate removal was assessed at 19.4 $kg.N.ha^{-1}yr^{-1}$ in North Carolina (Gilliam, 1994), between 44.1 $kg.N.ha^{-1}yr^{-1}$ and 60.0 $kg.N.ha^{-1}yr^{-1}$ in Maryland (Peterjohn and Correll, 1984, Jordan et al., 1993) or up to 390 $kg.N.ha^{-1}yr^{-1}$ in Denmark (Brusch and Nilsson, 1993).

Nevertheless, recent research indicates that nitrate removal can be extremely variable from site to site depending on the geomorphic setting. For instance, Vidon and Hill (2006) indicate that riparian zones that are large N sinks at the watershed scale are riparian zones where large amounts of water flow through the riparian zone (300-1200 L/d per meter of stream length), where organic matter is available to sustain denitrification, and where high nitrate concentration entering the riparian zone is associated with anaerobic conditions. Riparian zones located in outwash valleys where organic matter has accumulated and where a confining layer (low hydraulic conductivity sediment layer, Ks < 10^{-6} cm/s) forces nitrate-rich groundwater to interact with organic-rich sediment layers (e.g. peat, buried river channel sediments) often fall in this category. Amounts of N removed daily in these riparian zones are typically between 4-10 g N/d per meter stream length (Vidon and Hill, 2004a). This rate can be easily converted into g N/d/m2 based on riparian zone width, if necessary for model applications.

At the other end of the spectrum are riparian zones that have little to no effect on N removal at the watershed scale, or that even act as a nitrogen source to the stream (cold spots). Riparian zones in the former category are typically riparian zones with low groundwater fluxes owing to a low hydraulic gradient and/or a low soil hydraulic conductivity (N removal is then transport limited). For instance, Wigington et al. (2003) report low water (12 L/d meter stream length) and nitrate (0.03 g N/day per meter stream length) fluxes in a riparian zone on nearly level clay terrain in Oregon. Vidon and Hill (2004a) report similar small water and nitrate fluxes in a nearly flat riparian zone in till landscape in Southern Ontario. Riparian zones in this category have little impact on N removal at the watershed scale owing to the small amount of N removed daily. Riparian sites in the latter category (N source) include riparian zones where N rich groundwater bypasses the riparian zone at depth owing to deep riparian sediments with low organic matter content and a high hydraulic conductivity. For instance, Puckett et al. (2002) report results for a riparian zone in Minnesota where sand overlies a confining unit 16 m deep and where groundwater with considerable nitrate concentration originating from an 18-30 m thick upland outwash aquifer is able to move along flowpaths under some areas of the riparian zone to the river with limited nitrate removal. Similarly, on the Delmarva Peninsula in Maryland, nitrate-rich groundwater flowed at depth in a thick sand aquifer beneath a riparian area and discharged upward through the stream bed (Bohlke and Denver, 1995).

Some riparian zones may also be sources or sinks of N in the landscape depending on local conditions at the time of measurement. Riparian zones that typically have close to a 100% nitrate removal efficiency most of the year can have cold moments, i.e. moments where the riparian zone efficiency decreases dramatically, and where the riparian zone becomes a source of N in the landscape. For instance, Wigington et al. (2003) report that nitrate rich water in overland flow bypasses a riparian zone with clay soil in Oregon during storms. Vidon and Hill (2004a) also indicate that nitrate removal drops from >90% to 60% as the water table rises and groundwater fluxes increase from 1.8 L/d to 244 L/d per meter stream length in a riparian zone in southern Ontario. In that riparian zone, a gravel layer near the soil surface allows water to bypass organic rich sediment in the riparian zone during episodic high water table periods. Cirmo and McDonnell (1997) also report that in some forested catchments where soil in the near-stream zone may be draining owing to seasonal water table drawdown, mineralization of organic N in the substrate may be accelerated owing to aerobic oxidation. This may, in turn, result in N input to the stream.

As indicated earlier, although the riparian literature is clearly dominated by nitrate removal studies, many studies also focus on phosphorus, sediments, pesticides, chloride, bromide and bacteria. A review by Dosskey (2001) presents a series of large summary tables documenting contaminant removal efficiency for a variety of contaminants. This study indicates that riparian zones generally contribute to the reduction of most contaminants in subsurface flow and overland flow. Nevertheless, this review also reveals that there are situations where riparian zones can be sources of P, Atrazine, bromide, *E. coli* and *E. streptococci* bacteria. To date, not enough research has been conducted on contaminants other than nitrate to identify general templates of riparian functioning for these contaminants. Conditions favorable to the reduction or oxidation of a given contaminant at the microbial level are often known, but more research needs to be conducted to determine the variables controlling the fate of contaminants other than nitrate in soil at the riparian zone scale.

An alternative to riparian zones is the construction of runoff wetlands between upland cropland and streams/lakes to capture upland runoff (Kovacic et al., 2006). In Illinois, two wetlands (0.16ha {660m3} and 0.4ha {1780 m3}) intercepted surface runoff to Lake Bloomington. Over an 18-month period, Nitrate mass retention was 36% and volume-weighted nitrate concentration was reduced by 31-43% depending on the wetland. P mass retention was 53% and total organic carbon retention was 9%. Still in Illinois, Kovacic et al. (2000) reported that a series of wetlands varying in size from 1200 to 5400 m3 and receiving 4639 kg of N during a 3-year period (96% as nitrate) were able to remove 37% of inputs. When the wetlands were coupled with an additional 15 m buffer strip between the wetland and the river, overall N removal efficiency increased to 46%. P removal was low (2%) during the 3-year period following installation of the wetlands.

As a side note, the discrepancy between the number of publications dealing with nitrate removal in riparian zones versus other contaminants is especially well illustrated in a review by Corell (2000). Out of 700 publications on the functions of riparian buffers, 284 involve nitrate removal. However, only 182 involve phosphorus, 152 involve organic matter, 106 involve suspended sediments, 28 involve pesticides, and 15 deal with heavy metals. Only 14 were found to focus of pH. Even fewer studies dealt with other contaminants such as bacteria or sulfate. Nevertheless, all studies revealed that riparian zones generally had a significant effect on the fate of all contaminants, suggesting that much more research should be conducted on the fate of many contaminants in riparian systems.

Chapter 4
Riparian Zone Management

Vidon et al. (2009, in review) discuss some simple strategies to better manage riparian zones. Efforts could be made to identify and manage riparian areas that are especially sensitive or effective hot spots for contaminant removal over both space and time in order to minimize contaminant inputs to receiving water. For instance, many studies indicate that NO_3^- removal typically occurs quickly within 20 m of the field and riparian zone margin (Hill, 1996; Dosskey, 2001; Vidon and Hill, 2006), suggesting that many riparian zones (>20 m wide) may have some untapped potential for NO_3^- removal. Conversely, some riparian zones do not have the capacity to remove the high NO_3^- loads that occur during storms (Wigington et al., 2003; Vidon and Hill, 2004a). Other riparian zones are N sources following drought periods during which NO_3^- has accumulated near the soil surface owing to water table drawdown and the absence of hydrological flushing (Cirmo and McDonnell, 1997; Mitchell et al., 2006). The recognition of such situations offers an opportunity to better inform management strategies for riparian zones. For instance, surface flow could be directed toward those riparian zones that have untapped potential for contaminant$^-$ removal with level spreaders or grading. Other riparian zones could be widened, especially in some agricultural and exurban areas, to accommodate high hydrologic loadings during storms.

Riparian conditions in already managed or highly disturbed landscapes could also be modified to create hot spots for pollutant removal. Forms of riparian management include: (1) “denitrifying walls” which are strategically-placed trenches that are filled with organic matter such as sawdust to intersect and treat NO_3^--rich groundwater (Schipper et al., 2005); (2) permeable reactive barriers to remove contaminants such as NO_3^- and trace metals from tile drains and subsurface flows (Blowes et al., 1994; Blowes et al., 2000); and (3) vegetation buffers that take up NO_3^- and lower riparian water tables to minimize overland bypass flow (Lowrance, 1998; Yamada et al., 2007). Other riparian zone management techniques also have the potential to impact the development of hot spots for a variety of contaminants by manipulating either redox conditions or assimilation capacity. For instance, biogeochemical processes in riparian zones may be managed by altering the availability of reactive organic matter through brush management, biomass harvesting, and wood chip application (Homyak et al., 2008). Soil grading either adds or removes OM to riparian soils and has the potential to affect the removal of a variety of contaminants in riparian zones. Similarly, the hydrological reconnection of stream channels to riparian soils may promote NO_3^- removal (Kaushal et al., 2008), especially when riparian vegetation and hydrologic regimes are restored so that soils remained (Pinay et al., 1993). The introduction of small organic debris dams across streams may increase bank flooding and riparian soil saturation to create hot spots for nutrient transformations. In contrast, it may be beneficial to remove sediment berms that form at the upland edges of riparian zones, channelize flow, and allow a pulse of nutrients in concentrated surface runoff to bypass the riparian buffer.

Chapter 5

Future Research Needs for Riparian Zone Research

This review of the literature revealed many areas where more research on riparian zone research should be conducted. Recently, Allan et al. (2008) summarized research areas where more research need to be conducted on riparian zones in the years to come.

5.1 Hierarchical Controls on Riparian Zone Function

Various hydrogeomorphic riparian zone classification approaches can be found in the literature (Correll 1997, Lowrance et al. 1997, Hill 2000, Gold et al. 2001, Vidon and Hill 2004b). However, these approaches have generally focused on nitrate only, and do not take into account the position of the riparian zone in the river network. Although hydrogeomorphic approaches are promising for riparian zone classification owing to the improving availability of digital hydrogeomorphic information (topography, soil, surficial geology), two important challenges for the next few decades will be to develop riparian zone classifications that: 1) encompass a broad spectrum of contaminants (phosphorus, metals, pesticides, hormones and pharmaceuticals); and 2) take into account the position of the riparian zone in the river network. Indeed, riparian influence on solute transport at the river basin scale cannot be considered merely as the linear summation of riparian function at the stream reach scale. The interaction of entire river networks with their associated drainage basins must be considered in order to understand how riparian areas influence the downstream delivery of solutes.

5.2 Riparian Function in Urban and Restored Ecosystems

Urban riparian systems are distinguished by their degree of stream incision and channelization, the frequent presence of buried infrastructure, and altered runoff regimes, in particular the degree of stormwater bypass. Many of these characteristics are shared with agricultural systems but the degree of hydrologic alteration through the connection of impervious surfaces to stormwater infrastructure distinguishes them from agricultural systems. A review of the literature reveals few case studies specific to urban riparian systems. The presence of buried infrastructure and stream incision both serve to lower the near stream water table and reduces the potential for denitrification and nutrient uptake by vegetation (Groffman and Crawford 2003). The presence of buried utility structures also alters the groundwater flow field and provides the potential for preferential flow conduits within riparian zones (Sharp et al. 2003). Today, many municipalities are committing considerable resources to restore urban stream reaches that in the end may have limited water quality or ecological benefit (Bernhardt and Palmer 2007). New research efforts aimed at understanding the hydrological and biogeochemical functioning of urban and restored riparian zones is therefore of primary importance to maximize the utilization of urban riparian zones for water quality enhancement.

5.3 Emerging Contaminant Removal in Riparian Zones

Another area of riparian zone science where critical research is needed concerns the fate of emerging contaminants in riparian systems. Contaminants of emerging concern include heavy metals, some pesticides, and a large array of chemical commonly that are increasingly being shown to be endocrine disruptors. These chemicals include some pesticides, pharmaceutical compounds, biphenol A, phthalates and other chemicals known to disrupt the endocrine system. As indicated earlier, riparian zone research typically does not focus on these contaminants (Corell, 2000), yet these chemicals can be potentially important for water quality. It is therefore critical to conduct studies investigating the fate of these chemicals, and their interaction with the degradation of major contaminants such as nitrogen or phosphorus, for a variety of riparian zone types.

5.4 Hot and Cold Spots/Moments of Riparian Zone Function

The majority of annual stream solute export occurs during hot moments of transport (i.e. precipitation, snowmelt). Yet, the majority of riparian field studies have examined riparian water quality function for intra-storm conditions only. These constitute the majority of the annual flow duration but not necessarily flow volume. Experimental and field data indicate that nitrate removal via denitrification can occur extremely rapidly in both riparian zones and streambed sediments (Vidon and Hill, 2004c; Kasahara and Hill, 2006); however, little is known about short term variations in denitrification rates or their importance to annual nitrate removal. Considerable spatial variation also exists in the rates of decomposition, nitrification and denitrification, all of which can produce hot and cold spots of nitrogen availability. Finally, potential water quality goal conflicts might exist where the establishment of conditions that promote denitrification also serve to enhance phosphorus mobility and the production of methyl mercury in some environments. In the future, research efforts should therefore be directed at developing a suitable framework to assess the importance of hot and cold spots/moments in riparian zones, as the current lack of such a framework contributes considerable uncertainty in efforts attempting to quantify and model the overall nutrient removal capacity of streams/riparian zones at all scales.

5.5 Role of Vegetation in Riparian Zone Water Quality Function

The direct and indirect controls of vegetation on riparian water quality function have not been well quantified to date. Vegetation does impact riparian zone water quality function by influencing short term organic matter availability, evapotranspiration (water level), the amount and quality of soil litter, the soil thermal regime and stream bank stability. However, recent research suggests that vegetation may not have a significant direct impact on the degradation of many contaminants in riparian zones. For instance, in a European study comparing nitrate removal in 14 riparian zones across a range of climatic and vegetation conditions, Sabater et al. (2003) observed no correlation between nitrate removal and vegetation type. Overall, direct and indirect vegetation influences on riparian zone function are likely to vary both as a function of the chemical constituent and the climatic and hydrogeological setting. A pressing research need for the future is the examination of the sensitivity of riparian biogeochemical functioning to vegetation disturbance including manipulation and restoration.

5.6 Role of Riparian Zones on Water Quality at the Watershed Scale

In spite of the hundreds of studies focusing on contaminant removal in riparian zones, our understanding of the impact of riparian zones on water quality at the watershed scale is still limited. Concentration of overland and subsurface flow in areas of preferential flow along rivers because of micro-changes in topography or changes in soil characteristics generates points of focused recharge where the ability of the riparian zone to remove nutrients may be overwhelmed. Riparian zone width is also altered by stream meanders and field edges, and as a consequence, nutrient removal in riparian zone is not homogenous along the stream channel. Although research clearly indicates that riparian zones generally have a positive impact on water quality at the watershed scale, there is currently a lack of a solid framework to upscale knowledge obtained at the plot or riparian zone scale to entire watersheds.

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