Summary

Introduction

Diffuse pollution of nutrients and pesticides from agricultural areas is increasingly recognised as a major problem in water management. Ecotechnological measures such as constructed wetlands and riparian buffer zones clearly have an important role in the reduction of diffuse pollution by removing and modifying pollutants from agricultural runoff. However, the processes that account for the pollution retention capacity are diverse and the performance of buffer zones along climatic gradients and under varying hydrological regimes is largely unknown.

The study described in this thesis was conducted to determine the influence of N-loading rate, vegetation and hydrologic regime on the mechanisms of nitrogen removal in riparian zones along a climatic gradient. We focused our research on nitrogen removal in riparian buffer zones that were down-gradient from intensively fertilised agricultural fields. The research was conducted in the Netherlands and other locations across Europe within the framework of a joint European research project called NICOLAS (NItrogen COntrol by LAndscape Structures in agricultural environments ENV4-CT97-0395). This FP-4 project started in 1998 with a goal of evaluating the natural performance of riparian zones to sustainably buffer waterborne fluxes of diffuse agricultural nitrogen pollution of aquatic environments. Partners in this project were researchers from Rennes (F), Durham (GB), Barcelona (S), Lausanne (CH), Boekarest (R) and Warschau (PL). The main aim of the research described in this thesis was to further improve the understanding of nitrogen transformation processes occurring in natural buffer zones and to evaluate the risk of greenhouse gas emissions during pollutant mitigation. In this summary an
overview is given of the most important results of this research described in
the following major themes;
• dilution or removal,
• plant uptake and denitrification,
• groundwater level and nitrogen transformation,
• nitrous oxide emission, and
• sustainability of buffer zones.

**Dilution or removal**

In the past, the majority of the studies on buffer zones relied on concentration
based input-output analyses to evaluate the water quality functioning. Since
dilution of shallow nitrate-loaded agricultural runoff with groundwater from
a deeper aquifer may cause a significant decrease in nitrate concentrations, this
study focused on the importance of groundwater flow paths in the
groundwater quality dynamics. A forest and a grassland zone along first-order
streams in the Netherlands were selected for this research (Chapter 2).
Hydraulic parameters and water quality were monitored in both riparian zones
on a monthly basis over two years in 50 piezometers. Average nitrate loadings
were high in the forested buffer zone with 87 g NO$_3^-$-N m$^{-2}$ yr$^{-1}$ and
significantly lower in the grassland buffer zone with 15 g NO$_3^-$-N m$^{-2}$ yr$^{-1}$.
Groundwater from a second aquifer played an important role in diluting the
shallow nitrate-loaded agricultural runoff causing a significant decrease in
nitrate concentration and a significant increase in chloride concentration along
its flow path towards the stream. Tracing the groundwater flow paths and
dilution along these pathways revealed that clear spatial differences occurred
in N removal within riparian zones. The observed dilution could cause an
over-estimation of the nitrate removal capacity of up to 60% if this physical
process is not taken into account. Besides the dilution both riparian zones
were capable of reducing nitrate in subsurface runoff by biological N removal,
the grassland riparian zone as a whole removed about 63% of the incoming
nitrate load whereas in the more heavily loaded forested zone clear symptoms
of saturation were visible and only 38% of the incoming nitrate load was
removed.

**Plant uptake and denitrification**

As stated before, the efficiency of nitrate removal from groundwater passing
through riparian zones can vary with climate, landscape setting and nitrate
loading, therefore results often seem somewhat site-specific. The range of sites within the NICOLAS project provided a wide spectrum of climatic, hydromorphic and anthropogenic conditions ideal to evaluate the relative significance of various nitrate removal mechanisms within herbaceous and forested riparian zones (Chapter 6). Plant uptake and denitrification are considered to be the most important processes responsible for N retention and mitigation in riparian buffer zones. However, nutrients taken up by plants remain in the system only temporarily and may be gradually released by mineralization later. Still, plants increase the residence time of nutrients considerably by reducing their mobility. Denitrification is a microbial process involving the stepwise reduction of nitrate through nitrite, nitrogen oxide and nitrous oxide, ending with gaseous nitrogen. The significance of the denitrification process is that it provides a permanent sink for excess nitrate.

In our NICOLAS study the annual N retention in vegetation and litter accounted for 13–99% of the total N removal (Chapter 6). Higher N uptake and higher N retention was found in forested buffers but periodic harvesting of herbaceous biomass contributed considerably to the N retention in sites dominated by herbaceous vegetation. We found no differences in the effectiveness of specific vegetation types (forest or herbaceous) on nitrate removal from shallow groundwater. Denitrification rates measured in soil cores with the acetylene inhibition method varied between 0.11 and 91 mg N m\(^{-2}\) d\(^{-1}\) in the studied European riparian zones. The between-sites comparison showed that denitrification was the dominant process of N removal in most riparian sites, except for the Spanish and Romanian sites where denitrification rates were significantly lower than plant uptake.

**Groundwater level and nitrogen transformation**

Overall, no significant effect of climate has been observed in measurements of N removal efficiency or denitrification rates in a range of European sites. Cosandey et al. (2001) found that the intensity of denitrification in our NICOLAS riparian study sites was strongly related to total soil organic matter content and soil moisture regime. These factors appeared to be more important than climate, type of vegetation or season in predicting denitrification rates. Because water table level is easy to measure and is often indicated on soil maps, we wanted to know whether N process rates could be predicted on the basis of certain water table thresholds. In Chapter 5, we used the NICOLAS data to test whether water table level was a good predictor of nitrogen cycling, particularly regarding sources and sinks of nitrate. Indeed, water table level turned out to be a good predictor of nitrogen processes and N availability in
riparian ecosystems. Three consistent water table thresholds were identified at very different riparian sites in terms of climate and N-loading and vegetation. When water table levels are within -10 cm of the soil surface, ammonification prevails and ammonium accumulates in the topsoil. Average groundwater tables between -10 and -30 cm favor denitrification and therefore reduce the nitrogen availability in soils. At sites with water table levels below -30 cm, nitrate is the main end product as a result of high net nitrification. At these latter sites, denitrification might occur in fine-textured soils, where it is triggered by rainfall events. These water table level thresholds can be used as a proxy to translate the consequences of stream flow regime change to nitrogen cycling in riparian zones and, consequently, to potential changes in nitrogen mitigation.

**Nitrous oxide emission**

Denitrification was identified as the dominant process of N removal in most riparian zones studied, denitrification is however also considered as a major source of the greenhouse gas nitrous oxide (N\(_2\)O). We therefore questioned if riparian buffer zones were useful in solving an environmental problem or rather cause a shift from groundwater pollution with nitrate towards air pollution with nitrous oxide. We assessed the rates of N\(_2\)O emission from riparian buffer zones that receive large loads of nitrate, and evaluated various factors that are purported to control N emissions (Chapter 3). Denitrification, nitrification, and N\(_2\)O emissions were measured seasonally in grassland and forested buffer zones in the Netherlands. Nitrogen process rates were determined using flux chamber measurements and incubation experiments. Nitrous oxide emissions were found to be significantly higher in the forested (20 kg N ha\(^{-1}\) yr\(^{-1}\)) compared with the grassland buffer zone (2-4 kg N ha\(^{-1}\) yr\(^{-1}\)), whereas denitrification rates were not significantly different. Higher rates of N\(_2\)O emissions in the forested buffer zone were associated with higher nitrate concentrations in the groundwater. We conclude that N transformation by nitrate-loaded buffer zones results in a significant increase of greenhouse gas emission.

Tracing the groundwater flow paths and nitrate removal along such groundwater pathways in the Dutch riparian zones revealed high spatial differences within the forested riparian buffer zone. The spatial variability in hydrological flow paths and nitrate removal processes complicates the overall assessment of riparian buffer zone functioning in terms of water quality improvement as well as enhancement of the greenhouse effect by N\(_2\)O.
The objective of the research described in chapter 4 was therefore to find clues for explaining spatial variability in nitrate removal, denitrification and N₂O emission, and to use this insight to help assess the balance between environmental benefits and risks in these habitats. Denitrification and emissions of N₂O were measured in winter and summer along two groundwater flow paths in a forested riparian zone using flux chambers and incubation experiments. In winter, N₂O emissions were significantly higher (12.4 mg N m⁻² d⁻¹) along the flow path with high nitrate removal compared with the flow path with low nitrate removal (2.58 mg N m⁻² d⁻¹). In summer a reverse pattern was observed, with higher N₂O emissions (13.6 mg N m⁻² d⁻¹) from the flow path with low nitrate removal efficiencies in comparison with the flow path with high nitrate removal (4.44 mg N m⁻² d⁻¹). Distinct spatial patterns of denitrification and N₂O emission were observed along the high nitrate removal transect, whereas no clear pattern was found along the low nitrate removal transect, where denitrification activity was very low. On the basis of the studies described in Chapters 2 and 3, ineffective groundwater flow paths in buffer zones (with high nitrate loading rates and low nitrate removal rates) were expected to be detrimental for the environment, because they fail to protect the stream ecosystem and show a relatively high contribution to the emission of the greenhouse gas N₂O. Results described in chapter 4 indicate that denitrification rates were, indeed, quite different between the studied flow paths with more than 2 times higher rates in the flow path with high nitrate removal. On the contrary, total N₂O emissions were quite similar for both flow path, indicating that high nitrate removal transects can also significantly contribute to an increased N₂O emission from riparian zones. Riparian zone management aiming at an increased denitrification activity in buffer zones is worthy from the perspective of water quality improvement, however a certain risk of N₂O emission remains inevitable. Simultaneous minimization of N₂O emissions is only possible if riparian zone management is combined with source-directed measures to drastically reduce the nitrate concentration in agricultural runoff.

**Sustainability of buffer zones**

Few investigators have examined the nitrate removal of riparian zones along headwater streams that receive high groundwater nitrate inputs. In the heavily nitrate-loaded forested riparian zone in the Netherlands, nitrate removal efficiencies were lower than those measured in other European sites with lower N loadings (Sabater et al., 2003). In this respect, questions arise about the sustainability of riparian buffer zones for nutrient retention.
We questioned in our synthesis (Chapter 7) if chronically N-loaded riparian zones were at risk in eventually losing their denitrification potential due to carbon limitation or N saturation. Denitrification is an energy demanding process and the energy required is usually derived from a carbon source (heterotrophic denitrification). In chronically N-loaded riparian zones the C demand of aerobic and anaerobic decomposition might exceed the yearly production of easily degradable C. As litter production is mainly taking place in autumn, a temporal C limitation might occur during summer leading to periodically lower nitrate removal by denitrification. To check this statement the order of magnitude of C consumption by denitrification activity was compared with the annual above-ground C production. This comparison indicated that the C consumption by denitrifiers is very small compared to the C production. Although it is a rather rough comparison we can provisionally conclude from these figures that the annual C production exceeds C decomposition rate and C limitation is not very likely in this system. Additionally, measurements on denitrification enzyme activity (potential denitrification) did not show any signs of C limitation in the forested riparian zone. This leads to the conclusion that there is no clear indication that buffer zones with prolonged N-loading might become C limited due to the high C respiration activity of denitrifiers.

In Chapter 2 we stated that clear symptoms of N saturation were visible in the forested site because i) flow paths with high N loading showed a low N removal efficiency, ii) in situ denitrification rates observed at the highly N-loaded flow paths were not significantly higher than at flow paths with lower nitrate input rates (Chapter 4), iii) rates of N mineralization were extremely high in the Dutch sites compared to other riparian areas (Chapter 5; Aber et al., 1989), and iv) a decrease in absolute removal capacity was observed along the highly N-loaded flow paths, suggesting an inhibitory effect of nitrate on denitrification. Results of denitrification enzyme activity (potential denitrification) measurements in the laboratory (Chapter 7), however, still showed an increase of denitrifier activity in the nitrate-amended soil samples. The significant negative relation found between pH and nitrate concentration in the groundwater may be explained by an inhibitory effect of low pH on denitrification. Detailed studies on denitrification along selected groundwater pathways with high nitrate loading and low nitrate removal efficiencies (Chapter 4) underlined the pH effect on denitrification although low water-filled soil porosity also contributed to the low denitrification activity in the low nitrate removal flow path. Liming of the agricultural fields and riparian zones might therefore increase the nitrate removal efficiency of these riparian zones.
Conclusion

Riparian buffer zones are important additional measures to protect water quality from diffuse pollution in agricultural environments but reduction of fertilizer use in the upland agricultural fields is still essential to protect the aquatic ecosystem from eutrophication. A combination of methods is needed in watersheds with intensively managed agricultural fields, because high N loading of riparian zones may lead to the undesired effect of high N₂O emissions and nitrate concentrations in high loaded riparian zones may not be reduced sufficiently to prevent eutrophication of the surface waters. Apart from the water quality function, riparian ecosystems have other essential functions including: i) stream bank stability and erosion protection, ii) regulation of water temperature and growth of aquatic macrophytes by canopy shading, iii) increasing connectivity in landscapes and iv) increasing biodiversity. Therefore we support the general belief that riparian buffer zones are highly valuable landscape elements, far in excess of their relative surface area, and need to be protected, restored or re-established. Furthermore we recommend performing additional research on greenhouse gas emission from natural and constructed wetlands that are used for water purification. Until now, only the beneficial function of wetlands on water quality improvement has received a lot of attention. To perform a full assessment, however, we have to evaluate the precise consequences of both forms of environmental pollution to determine the environmental risks.