



Nitrogen dynamics in near-stream zone of forested areas

Literature review

by

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Introduction

In Sweden leaching of total nitrogen from forest soils is generally low, < 1 kg /ha, and the organic fraction dominates (Lfgren, 1991). During the end of the 80-ies forests were considered to be threatened by acid deposition. Together with an increase in N-deposition this could lead to a severe increase in nitrogen leaching due to a decrease in plant uptake by a deteriorated forest (Fleischer and Stibe, 1989). Since then sulfur deposition has diminished, and no damage on the forests due to soil acidification or nitrogen deposition has been observed in Sweden (Binkley and Hgberg, 1997). In the SW parts of the country, however, where the deposition is highest, there are indications on nitrogen saturation and on elevated leaching of inorganic nitrogen (Bringmark and Kvarn s, 1995; Nohrstedt et al., 1996). By contrast with sulfur, nitrate deposition can be expected to be high for a long time (Lvblad et al., 1992) and increasing nitrogen leaching in the future can not be excluded. Nitrogen leaching is however not only a function of deposition. Land use, forestry activities and soil properties, such as C/N ratio and potential nitrification, have been found to be important as well (Lepist et al., 1995; Nohrstedt et al., 1996).

Nitrogen dynamics include biological processes that all show a large spatial and temporal variation. Plant uptake varies with season and depends on weather conditions and soil moisture content and microbial transformations depend on the organic content in the soil, the quality of the organic matter, pH, soil moisture, dissolved oxygen and redox potential which all varies highly within a catchment. Wetlands and wet areas near the stream do particularly diverge from dryer land forms with respect to these variables. The occurrence of wetlands in the catchment have been found to be positively related to leaching of Tot-N (Lundin, 1991) and negatively correlated to nitrate leaching (Lepist et al., 1995). In agricultural landscapes riparian zones have since long been noticed for their ability to retain nutrients and particles from water discharging from upland fields. Many studies are focused on denitrification as this process is the only one that removes nitrogen from the system. Often the capability of retaining nitrogen has been found to depend much on flow patterns through the riparian soil (Hill, 1996). Recently riparian wetlands in forested areas have been noticed as well. The near-stream saturated zone has a high potential to control run-off chemistry, being the end biogeochemical environment of the ground water flow path (Cirimo and McDonnell, 1997). The few studies on riparian wetlands in northern forests found in the literature, show that they may act as both sinks and sources of

nitrogen, but mainly as transformers of inorganic nitrogen into organic nitrogen. The function of a wetland depends much on the flow pattern through the soil (Hill 1997). In Sweden most forests are located on till soils with a ground water table within a few meter, often less, from the ground and with dominating flow paths in shallow ground water. The near-stream zones can be narrow waterlogged strips of mineral soils or larger wetlands and the flow paths vary with soiltype and ground water level.

Along a slope towards a stream the ground water level comes closer to the surface. The higher water supply can support a higher plant production (Lundmark, 1974) which results in a higher litter fall. In coniferous boreal forests where Podzol is the dominating soil type this results in a deeper organic top soil (Troedsson and Nykvist, 1980). Closer to the stream the ground water level may reach the organic soil layer. When a soil with high organic content is waterlogged the dissolved oxygen is soon consumed by respiration of microbes and plant roots. Under anaerobic conditions mineralisation is hampered and an accumulation of peaty organic matter occurs. Anaerobic conditions also hampers tree growth (Lundmark, 1974). The soil types formed under these conditions are classified as Gleysols or Histosols (FAO-Unesco, 1974). The extension of the different soil types depends on the topography and hydraulic properties of the soil and varies along the stream. Hence the near-stream zone may be anything between a dense forest to an open mire strip.

According to the Swedish National Survey of Forest Soils and Vegetation 0.5 % of the soils in productive forests are Gleysol and 7.2 % is Histosol (Anonymous, 1983-87). In the Swedish National Forest Inventory, 3% of plots in productive forest were found within 25 m from a stream or lake. The forest in the near-stream site is older, higher and denser than forests in general and the abundance of broad-leaved trees is higher (Lind, 1998). The figures are only representative for productive forest and nothing is known about the proportion of riparian zones that consists of forest, mire or other land use.

Nitrogen pools and fluxes in the near-stream zone

If the hydraulic conditions admits formation of peat in the near-stream zone, a large pool of organic bound nitrogen is built up. In Swedish coniferous wetlands on till soil, the mean content of total nitrogen in the peat layer was 300 g/m² (Anonymous, 1983-87). The pool of nitrogen in living plants depends on the type of vegetation. For open bogs and fens in general a typical value for plant nitrogen is 10 g/m² (Bowden 1987, p320). In coniferous forests in Sweden biomass pools

between 14 and 86 g/m² are found (Lfgren, 1991). The store of nitrate and ammonium in the soil is usually at least an order of magnitude lower than in plant biomass because of a fast turnover of mineralized nitrogen (Bowden 1987, p319). The transfer between the different pools of nitrogen includes microbial immobilization, plant uptake, mineralisation, nitrification and dissimilatory reduction of nitrate to ammonium (fig. 1).

Generally, the internal cycling of nitrogen is larger than inputs and outputs in most terrestrial (Tamm, 1990) and wetland (Bowden, 1987) ecosystems. In riparian wetlands, however, the ground water flow through the system is large and may contribute with a large flux of nitrogen through the system. If the ground water flow is high this holds true even when the concentration of nitrogen in the ground water is low. In the ground water coming from upland sites, nitrate concentrations is usually higher than ammonium (Stoddard, 1994; Maxe, 1995). In Swedish forests, organic nitrogen concentrations are one to four times higher than concentrations of inorganic nitrogen (Jacks et al., 1994; Staunes et al., 1995).

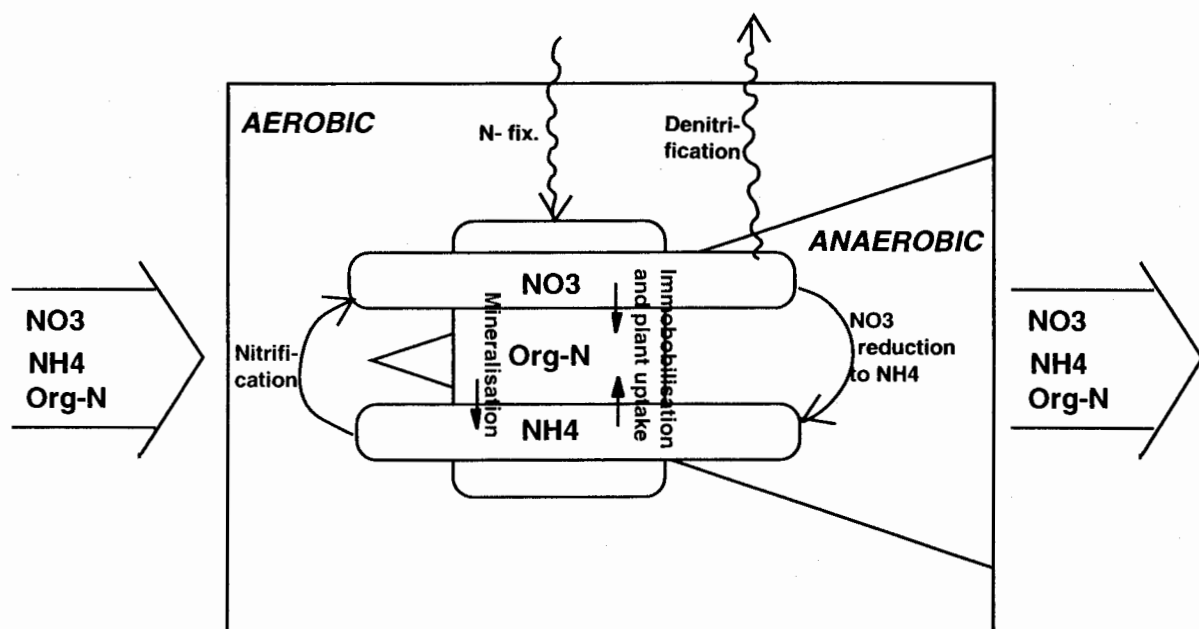


Figure 1. A conceptual model of the nitrogen turnover in a riparian wetland with ground water flowing through the soil. Closer to the stream anaerobic processes becomes more important.

A schematic view of the pools and fluxes of nitrogen in the bank of a forest stream is presented in figure 1. Beside ground water input, deposition and nitrogen fixation may contribute with nitrogen to the system. In the transition zone between wetland and upland the prerequisites for mineralisation and nitrification are good and these areas may be a source for nitrate. If the ground water flows

through soil layers with high organic content, anaerobic conditions can be expected and nitrate may be lost to the atmosphere through denitrification or transformed into ammonium. Finally the riparian zone can be a source for organic nitrogen.

In the following section the different processes involved will be discussed. The importance of the processes in the near-stream zone for the water chemistry in runoff is highly dependent on retention times and flowpaths through the soil, so the next section deals with the hydrology of near-stream zones followed by sections reviewing interactions between hydrology and biochemistry and findings from budget studies on near-stream zones. Finally temporal and spatial variation of runoff in forest streams is discussed in the context of processes in near-stream zones.

Processes of nitrogen transformation

Nitrogen fixation

Besides deposition, fixation of atmospheric nitrogen is the only input of nitrogen to the forest ecosystem. Biological nitrogen fixation is generally considered to be low, $<0,1 \text{ g N/m}^2$, in Scandinavian coniferous forests (Lfgren, 1991). In forest ecosystems, nitrogen fixation can be carried out by free living bacteria in the soil, epiphytic blue-green algae and symbiotic bacteria in root nodules of *Alnus*-species (Haynes, 1986). The difference in fixation rate is high between sites. In a comparison of non-symbiotic nitrogen fixation in 20 forests soils in central Sweden, the highest rates were found in a birch site, $0,14 \text{ g N/m}^2 \text{ yr.}$, and a rich spruce site, $0,1 \text{ g/m}^2 \text{ yr.}$ (Nohrstedt, 1985). The spatial variation within the plots was high. In the same study 85% of the variation could be explained by soil pH with a positive correlation between rate and pH. Nitrogen fixation is also affected by aeration of the soil. (Limmer and Drake, 1996) found that fixation activity increased several times after prolonged anaerobic incubation of soils from deciduous and coniferous forests in Germany. Further, nitrogen fixation was stimulated by shifting from aerobic to anaerobic conditions.

In near-stream zones the prerequisites for nitrogen fixation can be considered as good where discharge of ground water may increase pH to a favorable level. In transition zones between upland and wetland, the fixation may be further favored by altering aerobic and anaerobic conditions caused by a fluctuating water table. In wetlands and mires, fixation by blue-green algae growing on *Sphagnum* may be important (Basilier, 1980). Symbiotic fixation in alder fens may be even higher.

For *Alnus incana* in Scandinavia, nitrogen fixation rates of 0,2-11 g/m² y are reported (Huss-Danell et al., 1991).

Although the nitrogen fixation can be expected to be high in the riparian areas compared to the upland soils, it is questionable if it can be of importance for the nitrogen budget for the whole catchment as these areas only represent a smaller part of the catchment area. It may however be important for nitrogen leaching if this is mainly controlled by processes in the soil close to the stream

Internal cycling of nitrogen

The internal cycling of nitrogen in a forest soil includes mineralisation of organic nitrogen in decaying organic matter, microbial immobilization of mineral nitrogen and plant uptake. Usually only net mineralisation, i. e. the difference between mineralisation and microbial immobilization, is measured. In natural forest ecosystems, where leaching is small, the net mineralisation is balanced by plant uptake. The pool of organic nitrogen in Scandinavian coniferous forest soils varies between 30 and 1000 g/m² where most is in recalcitrant fractions and only a smaller part, 0,5-10 g/m² yr. is mineralized and taken up by plants (Lfgren, 1991). Recent research has shown that in ecosystems where mineral nitrogen is scarce, both *Sphagnum* mosses and vascular plants can shortcut the nitrogen cycle by direct uptake of organic nitrogen without being mineralized (Chapin et al., 1993; Kielland, 1997). The C/N ratio has generally been considered to determine the net flux of nitrogen. Below a critical value of that ratio net mineralisation occurs. This limit has, however, been found to depend on the quality of the organic matter. Berg and Staaf, (1981) found critical values of C/N between 36 and 170 in different forest ecosystems. The ratio depended much on the initial nitrogen content with higher critical ratio for litter with higher decomposition rates. For needle litter from *Pinus sylvestris* in central Sweden the ratio was 67.

Nitrogen turnover processes are favored by a high soil moisture and consequently the turnover rate can be expected to be high in the transition zone between upland and wetland where soil moisture is high. In wetlands however, where the ground water level is found in the organic horizon, both mineralisation and uptake by rooted plants is hampered by oxygen depletion and most of the internal cycling is restricted to the upper aerobic layer (Urban and Eisenreich, 1988).

Besides using organic nitrogen, *Sphagnum* mosses are adapted to nitrogen poor conditions by an efficient use of temporary sources of nitrate. Whereas higher plants have a lag time for taking up nitrate after addition, *Sphagnum* has an

instant uptake (Deising and Rudolph, 1987). This allows an efficient use of episodic supply of nitrate from precipitation or ground water at temporarily elevated ground water table. The annual uptake of nitrogen by *Sphagnum* in a forested Minnesota bog was estimated to 4 g/m² (Urban and Eisenreich, 1988).

The mineralisation rate in peatlands depends to a large extent on the type of substrate. A comparison of soils from a *Scirpus-Carex*-fen and a *Picea-Sphagnum*-bog in Minnesota showed a higher mineralisation rate of nitrogen under anaerobic conditions for *Scirpus-Carex*-peat, whereas the *Picea-Sphagnum*-peat had a higher rate at aerobic conditions (Updegraff et al., 1995).

In riparian wetlands the immobilization of ammonium can be a mechanism for retaining nitrogen from discharging ground water. In a study with field enrichments in two rivulets running over a riparian wetland in central Ontario, Canada, 40-90% of added ammonium was microbially immobilized (Hill and Warwick, 1987). Nitrate may be immobilized as well but as long as ammonium is present, nitrate uptake by microorganisms is inhibited (Recous et al., 1990). Ammonium may also be temporarily retained in organic soils by adsorption. Cation exchange in the upper peat layer has shown to be an efficient retaining mechanism when peat mining water was conducted across a natural Finnish mire (Heikkinen et al., 1995). The peat was saturated within a few months but the retention capacity was probably enhanced by ammonium being removed by nitrification coupled with denitrification. In a riparian zone, cation exchange of ammonium could be a significant mechanism for retention by increasing the hold up time for episodic input of ammonium, giving a longer period for exposure to other retaining mechanisms.

Nitrification

Nitrification is the process where ammonium is transformed into nitrate. As nitrate is more mobile than ammonium, the rate of nitrification is an important factor for nitrogen leakage from the soil. The process is acidifying with a yield of 2 H⁺ for each nitrate formed. Generally, the most important nitrifying organisms in soils are chemoautotrophic which gains energy from the oxidation of ammonium to nitrate (Haynes, 1986). Chemoautotrophic nitrifiers are pH sensitive with an optimum at pH 6-7. In natural ecosystems they are limited by the supply of ammonium. Nitrification may also be performed by heterotrophic organisms that, besides ammonium, can use organic nitrogen compounds to form nitrate. Heterotrophic nitrifiers are less sensitive to low pH than autotrophs and may thus

be of importance in acid forest soils although they are less efficient than autotrophs.

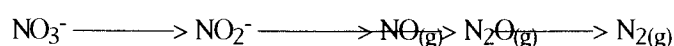
In most forests in Scandinavia nitrification is held for being negligible under undisturbed conditions, but occurs at most clearfelled sites (Jacks et al., 1994). The present knowledge, however, is only based on the conditions in the forest floor and the variation with depth and spatial variation in the landscape is not considered. Persson and Wiren (1995) investigated potential nitrification at different depths in ten forest soils in southern Sweden and Denmark. They found that the potential nitrification was lower in the H-horizon compared to mineral soil although the mineralisation rate of nitrogen was higher in the H-horizon. This was explained by the lower pH in the H-horizons and that the nitrifiers were more sensitive to the low pH in that horizon compared to the organisms in the mineral soil layers.

High concentrations of nitrate are sometimes found at the edge between upland and wetland (Fiebig et al., 1990) which can be an indication on that these areas have high nitrification rates. The process may be favored by a high soil moisture content and an elevated pH caused by discharge of ground water. High concentrations of nitrogen in superficial soils may however not necessarily be an indication of nitrification. Since ammonium is preferred over nitrate by both vegetation and soil microorganisms (Recous et al., 1990), nitrate from precipitation is conserved if the supply of ammonium covers the demand.

Denitrification

Since nitrate depletion is the major scope for most studies on nitrogen dynamics in riparian areas, denitrification will be given a more detailed review.

Denitrification is carried out by a wide range of microorganisms which are basically aerobes that under anaerobic conditions can use nitrate as terminal electron acceptors. The general pathway for denitrification is as follows:



Most denitrifiers possess all the enzyme complexes necessary to reduce nitrate all the way to N_2 which normally is the main end product. However the N_2O reductase seems to be more sensitive to unfavorable environmental conditions than the other enzymes involved, so N_2O may under certain circumstances be the main end product (Haynes, 1986). A comprehensive review of the ecology of denitrifying organisms is presented in (Tiedje, 1988).

Measurements of denitrification

The most used method to measure denitrification rates is the acetylene inhibition method. The sample is amended with acetylene that blocks the last step in the denitrification pathway so that denitrification rate can be measured as N_2O production (Moiser and Klemedtsson, 1994). At low nitrate levels the inhibition may not be complete and the measurement of N_2O emission will be an underestimation of the denitrification (Oremland et al., 1984). An alternative method that can be used in nitrate amended samples is to use ^{15}N marked nitrate in the additions. This method also allows the ratio of N_2O to N_2 to be estimated (Moiser and Klemedtsson, 1994).

Denitrification rate is supposed to have a large variation in the microscale where oxygen depletion occurs first in particles of organic matter. Measurements of *in situ* denitrification should therefore be made on minimally disturbed core samples to avoid compactation and disruption of the soil structure (Moiser and Klemedtsson, 1994). This is particularly important in structured soils not saturated with water. In wet structureless soils, measurements on slurries may be appropriate (Cooper, 1990).

Due to the large temporal and spatial variation of the environmental factors controlling the process, it is difficult to quantify denitrification in wetlands (Smith and Tiedje, 1979; Hill, 1996). When only the spatial variation is considered the measurement of denitrifying enzyme activity, DEA, gives valuable information on the history of the site and can be seen as an integrated measurement of the conditions for denitrification (Tiedje, 1994). Groffman and Tiedje (1989) found a strong correlation between DEA and annual mean denitrification. Further, DEA can be used for comparison of denitrification rates between sites and for modeling of actual denitrification (Parkin and Robinson, 1989; Tiedje, 1994). Estimation of DEA is made by measuring N_2O emission rate during anaerobic incubation of the sample with excess of nitrate and carbon source in the presence of acetylene. Chloramphenicol is added to inhibit synthesis of new enzyme during the incubation (Tiedje, 1994).

If no chloramphenicol is added, the denitrification rate increases after a few hours when new enzymes are synthesized to a new, higher rate that is dependent on both number of soil denitrifiers and environmental factors. The maximum denitrification rate under these conditions is called denitrification potential, D_{pot} . While DEA appears to be better correlated to the average *in situ* denitrification

rate than D_{pot} (Smith and Tiedje, 1979), the latter may however be a laboratory measure of microbial activity and available carbon (J rgensen and Richter, 1992).

Controlling factors

Denitrification is an anaerobic process and the main controlling factor is consequently the oxygen content (Tiedje, 1994). As soil moisture is affecting soil aeration, the drainage level of the soil has shown to be a strong predictor of denitrification rate (Davidson and Swank, 1986; Ambus and Christensen, 1993) and DEA (Groffman and Tiedje, 1989). In unsaturated soil the process is located to anaerobic microsites (Firestone, 1982).

Most denitrifiers are heterotrophs and thus dependent on available carbon for respiration and cellular growth. Available carbon may thus control both the number of denitrifiers through competition under aerobic and the rate of denitrification at anaerobic conditions (Tiedje, 1994). A high carbon content also stimulates the general respiration and thus initiate anaerobic conditions (Haynes, 1986). Organic content and drainage level is usually correlated in soil so the direct effect of available carbon is not easy to evaluate.

Different substrates have different properties as a carbon source for denitrifiers. In a study on cultivated, drained peat soils the D_{pot} was 2 - 5 times lower in sphagnum peat compared to peat formed by reeds, when the upper cultivated layers were excluded (J rgensen and Richter, 1992). In the same study, D_{pot} was correlated to different fractions of organic carbon. Although total organic carbon was the strongest single predictor of D_{pot} , readily hydrolysable glucose and amino-acid C gave the best two factor regression model with an explanation of 82%. The results suggests that available carbon and microbial activity, here represented by amino acid C, are important for the maximum rate of denitrification. The study also found that lignin derived plant parts cannot be degraded under anaerobic conditions (op. cit.). This implies that litter from conifers, having a high lignin content, is a poor substrate for denitrification. In the near-stream zones of boreal forests in Scandinavia, the organic matter mainly consists of *Sphagnum* mosses and conifer litter which are both poor substrates for denitrification. However, in organic soils there is usually enough available carbon to reduce the levels of nitrate occurring under natural conditions (Federer and Klemedtsson, 1988; Cooper, 1990; Davidsson and Leonardson, 1996).

Nitrate is usually scarce in undisturbed forest soils and is only expected to occur in ground water at low concentrations, 0.01-0.1 mg/L (Stoddard, 1994). Higher

concentrations may occur after clear-cut (Wiklander et al., 1991). Theoretically nitrate is limiting for denitrification up to levels of about 3 mg NO₃-N/L (Ambus and Christensen, 1993). In a natural soil, however, where microbial activity is spatially unevenly distributed at the microscale, active sites may be depleted in nitrogen and the diffusion of nitrate can limit the process at much higher levels (Haynes, 1986). Obviously, the presence of nitrate should be a strongly limiting factor for denitrification in natural forests.

The denitrification rate is generally considered to depend on pH with an optimum between pH 6 and 7 and inhibition of the process below pH 6 (Knowles, 1981; Haynes, 1986). However, studies on naturally acid organic substrates occurring in northern boreal forests show contradicting results. N mmik and Thorin (1972) measured a 13 fold increase in DEA when the pH was raised from 4.3 to 6.0 whereas Federer and Klemedtsson (1988) on the contrary found no response on increasing the pH to 5 from original pH of 3.2-3.9. Both studies were made by anaerobic incubation of raw humus but N mmik and Thorin incubated for a longer time and used higher nitrate additions. However, the results shows that denitrification may not necessarily be limited by pH in raw humus from spruce forests. Also for peat there are some contradicting results for the relation between pH and denitrification. (Klemedtsson et al., 1977) concluded that the low pH, 3.5, was the only factor that prevented denitrification in peat but (J rgensen and Richter, 1992) found no correlation between pH and D_{pot} in different peat soils.

In areas with a temperate climate most of the runoff is generated during the dormant season and the relevance for denitrification in controlling nitrate leaching may be limited by temperature which has a high influence on denitrification rate with a Q₁₀ of 2.0 between 10 and 35°C (Knowles, 1981; Haynes, 1986). Still significant denitrification rates have been measured at temperatures just above zero. For example (Christensen and Tiedje, 1990) found, for denitrification in the field, a mean value of 49 mg N /m² day at 4°C whereas at 1°C it was only 0,2 mg N /m² day. (Rhodes et al., 1985) found a denitrification rate of 116 mg N /m² day under a 15 cm snowpack.

In submerged soils, sulfide often is present which has shown to be able to delay the reduction of N₂O and thus increasing the relation of N₂O to N₂ (Tam and Knowles, 1979). On the other hand sulfide was also shown to relief the inhibition by acetylene of N₂O reduction. This implies that the acetylene inhibition method may not be suitable when sulfide is present (Knowles, 1981).

The results from studies on denitrification presented above show that the microbial community performing denitrification seems to adapt to the existing conditions and that the low pH and temperature and the poor quality of the organic matter that can be found in riparian wetlands in Scandinavian forests does not inhibit denitrification, only hamper it. The most limiting factor is rather the low concentrations of nitrate. When elevated nitrate levels occur, as downhill local sites with a high nitrification rate or after a clear-cut, denitrification can be expected to be significant. The rate of nitrate retention is due to the retention time in the biological active soil layers which is controlled by the flow pattern through the riparian zone.

Dissimilatory Nitrate Reduction to Ammonium

An alternative mechanism for nitrate depletion is the reduction to ammonium instead of N_2O and N_2 . The process, that is called dissimilatory reduction of nitrate to ammonia (DNRA), is much less well known than denitrification (Bowden, 1987) and is considered to be a minor process for nitrate reduction (Ambus et al., 1992). The process seems to be favored by a low redox potential and suppressed by high nitrate concentrations and may thus be important in deeper, permanently submerged soil layers with low nitrate concentrations (Hill, 1996). DNRA was measured by (Ambus et al., 1992) by using ^{15}N additions to undisturbed soil cores and slurries of samples from a riparian fen downhill an agricultural field. Only 3%-6% of the reduced nitrate was recovered as ammonium and the highest rate of DNRA was found in the deeper soil layers. Schipper et al. (1994) found an inverse relationship between nitrate and ammonium within a plot in a riparian zone receiving a high nitrate input. Ammonium was mainly found when the ratio of nitrate to organic matter was low. As a low ratio is considered to favor DNRA over denitrification (Tiedje, 1988), the results is an indication of DNRA.

Hydrology of near-stream zones

A general description of the ground water movement along a hillslope down to a stream involves a downward flow component in upslope areas and an upward flow component in near-stream zone (Grip and Rodhe, 1991). In the till soils covering most of the boreal forests there is a marked decrease in hydraulic conductivity with increasing soil depth, resulting in a dominating lateral flow in the upper ground water (Lundin, 1982; Bishop, 1991) and the vertical flow is less important for the total discharge (Bishop, 1994). As the deep ground water has a higher concentration of solutes it may however have a high influence on the water chemistry (Grip and Rodhe, 1991).

A major issue for the hydrologic research during the last decades has been the origin of the stream water during peak flow after rain fall or snow melt (Rodhe, 1987; Bonell, 1993). The use of conservative tracers as different soil water solutes or stable isotopes of O and H has been a powerful tool in this work. Most studies have shown that rain water from the episode only constitutes a minor part of the stream water. The major part consists of water already present in the soil before rain fall (Rodhe, 1987). A large effort has been made to find the mechanisms that make the rain fall to initiate the large outflow of ground water. The mechanism that have been proved to be valid for forested northern till soils is called transmissivity feedback (Bishop, 1991) and was first outlined by (Lundin, 1982).

The ground water level in these soils are mostly close to the ground surface. The zone just above the ground water table has a high water content close to saturation due to capillary forces. Thus only a small amount of infiltrating rain water is enough to raise the water table into highly conductive soil layers which causes an increased discharge into the stream. Subsurface flow in temporary perched water tables may also occur (Chappell et al., 1990). The discharging water consists of pre event soil water mixed with smaller amounts of rainwater and deeper ground water. In wet areas the soil may get saturated and the rain will flow over the soil surface directly to the stream (Bishop, 1991). Overland flow due to infiltration excess does hardly occur in temperate and boreal forest land where rain fall intensity is moderate and infiltration capacity is high (Grip and Rodhe, 1991). The dominance of the subsurface flow in runoff generation focuses on the importance of near-stream zones for the understanding of surface water chemistry as this is the last area of water-soil interaction.

The presented runoff mechanism seems to be valid for forested till slopes in general (Rodhe, 1987; Bonell, 1993). The flow through the near stream zone however is much more diverse (Hill, 1996). The wet conditions in the near stream zone favors the formation of peaty soils and the depth, extent and hydraulic properties of the peat influences discharging water flow paths.

The peat cover can be divided into an upper layer with fluctuating water conditions consisting of live and undecomposed dead vegetation and an underlying permanently water saturated anaerobic layer of more humified peat. The upper layer, called the acrotelm, is usually thinner and has a higher hydraulic conductivity, K , compared to the underlying layer, called the catotelm (Ingram, 1983). In a *Sphagnum* mire in northern Sweden the hydraulic conductivity ranged between 10^{-7} in highly humified layers to $>10^{-3}$ in weakly decomposed layers (recalculated from (Malmström, 1923)). Despite a generally low

permeability in the catotelm the water flow through deeper layers can be high due to macropores (Norrström, 1995) and inhomogeneities in the peat (Chason and Siegel, 1986).

Another important feature of the peat is that the horizontal permeability of the peat is usually higher than the vertical. Malmström (1923) found a five times higher flow in horizontal direction compared to vertical directions with equal potential gradients, in peat from a *Sphagnum* mire. Chason and Siegel (1986) found up to a hundred times higher hydraulic conductivity in horizontal direction compared to vertical, also in *Sphagnum* peat.

Heterogeneity in the peat cover may cause that ground water passes the riparian zone through preferential flow paths. Norrström (1995) found macropores to account for at least 25% of the discharge from a wetland area into a Norwegian lake. Fiebig et al. (1990) found indications of bypass of the riparian zone since the stream water chemistry was more correlated to the ground water from the forest edge 6 m upslope than to ground water in the bank in-between.

Besides the importance of preferential flow paths, the water flow pattern in the riparian zone depends on site characteristics such as depth of the O-horizon, permeability of the mineral soil and morphology. In Svarthölet, a forested, ditched catchment on till soil in northern Sweden, both hydrological measurements (Bishop, 1994) and comparisons with soil solution chemistry from different soil horizons (Bishop et al., 1994) showed that the major flow path in the riparian zone was in a highly conductive mineral soil layer beneath the peat layer. The ground water level was closest to the soil surface within 10-20 m from the stream and the distance between soil surface and maximum ground water table increased towards the stream which was assumed to be a consequence of the ditching.

In areas with deep layers of sand and gravel deposits, the flow pattern may look quite different. An example of this is a riparian wetland within a forested catchment in the Glen Major area near Toronto, where a deep aquifer gives a permanent ground water discharge with a low seasonal variation (Hill and DeVito, 1997). A stream flows over the peat and receives water from three different flow paths, each contributing with about equal parts in the total flow (Roulet, 1990). Shallow ground water discharges in wells at the edge of the wetland and flows in rivulets into the stream. Deep ground water seeps vertically up through the peat and either into the rivulets or direct into the stream. The flow from the deep

ground water system emerged in isolated areas of higher conductivity within the wetland.

In Sweden glacial till is the dominating soil material and the major flow path can be expected to be in the upper mineral soil layer. In more extended mires the upper peat layer may also be an important flow path when ground water level is high.

Impact of flow pattern on nitrogen retention

The spatial variation of redox potential, organic content and pH is high in the riparian zone. As these factors control the nitrogen transforming processes, it is obvious that the flow pattern through the riparian zone is important for nitrate chemistry in runoff. A change in ground water level may change both the soil layers that the ground water will pass as well as the redox conditions in the soil (Hill and DeVito, 1997). Most research on nitrate transformations in riparian zones has been made on nitrate removal in humid agricultural areas (Hill, 1996). The largest retention rates were found where the riparian zones have permeable surface soils and sediments at a depth of 1 to 4 meters underlain by impermeable layers which results in shallow subsurface flow of ground water through biologically active soil layers.

An elucidative example is presented in a study on the organic soils at the base of concave slopes close to a headwater stream draining a pastured catchment in New Zealand (Cooper, 1990). At the base of concave slopes the surface soil was anaerobic and had high levels of available carbon and a high denitrifying enzyme activity. More than 90% of the nitrate was lost from the discharging ground water in these soils. The pockets of organic soil only comprised 12 % of the stream bank. The rest of the stream bank consisted of mineral soil where the nitrate retention ranged between 0 and 62 %. By using the salt dilution technique the increase in stream flow could be followed along the stream. The measurements showed that during low ground water level, as much as 81 % of the discharging water passed through organic soils with a high denitrification rate which resulted in a high total retention of nitrate. At higher ground water levels 63% of the water entered the stream through banks with mineral soil where denitrification was low, which resulted in higher nitrate concentrations in the stream. Although the conditions in this New Zealand example differs from what is found in Scandinavian forests, it is interesting by focusing on the importance of spatial variation of ground water discharge and nitrogen transformations along the stream.

In the Glen Major area mentioned above, different nitrogen transformations were found along the different flow paths in the riparian wetland. The average nitrogen concentrations were 7 g $\text{NO}_3\text{-N}$ /L, 35 g $\text{NH}_4\text{-N}$ /L and 160 g org-N /L in the deep ground water. The shallow ground water was higher in nitrate and somewhat lower in ammonium and org-N with respectively values of 131, 28 and 151 g N /L (Hill, 1991). The concentrations of the nitrogen species decreased in the rivulets on the way to the stream. For nitrate most of the decrease could be explained by dilution of the nitrate rich shallow ground water with deep ground water poor in nitrate. The measured potential for denitrification was low (Warwick and Hill, 1988) and the retention of nitrate was only 4% of the input to the riparian zone. Ammonium, on the other hand, was depleted in the rivulets due to microbial assimilation (Hill and Warwick, 1987), but in the deep ground water seeping through the organic soil ammonium increased. However, as the dominating flow path was through the rivulets, the net retention of ammonium was 68% for the whole studied area. As ammonium only was a minor part of the total nitrogen it only had a small impact on the total retention of nitrogen which was 26% (Hill, 1991). The low retention of nitrate in this ecosystem compared to the other studies can be explained by the fact that most of the nitrate discharges upslope the wetland area and travels over the surface of the organic soil where the microorganisms have plenty of oxygen for respiration and therefore has no need for nitrate as electron acceptor and as long as ammonium is present, microbial assimilation of nitrate is hampered (Recous et al., 1990). The deep ground water that passes through the anaerobic organic layer has a low nitrate concentration and no denitrification takes place.

The relation between soil depth and nitrogen dynamics is illustrated in a comparison of the Glen Major swamp, with a valley wetland with shallow till soils, Plastic swamp (DeVito et al., 1989; Hill and DeVito, 1997). In Plastic Swamp the nitrogen dynamics was related by the high seasonal variation of the hydrologic conditions. During the summer when most ground water flowed through anaerobic peat layers, both nitrate and ammonium was retained to 100%. During snowmelt when overland flow dominated only 28% of nitrate and 75% of ammonium was retained. Organic nitrogen was retained during summer and released during autumn and spring when overland flow dominated.

Seasonal variation in nitrogen retention, with higher nitrate retention during winter, was also found in a downslope wetland in a forested catchment at Tannersjöheden in southwestern Sweden (Jacks et al., 1994). The retention during winter was thought to be due to denitrification and was considered to be favored

by the higher ground water level during this season allowing the water to pass through upper soil layers with fresh organic matter. Denitrification was also favored by a high concentration of nitrate in ground water coming from the upland area.

Variation in flow pattern may not only change the retention rate but also control what mechanism is active for nitrate. Field experiments with additions of nitrate in three riparian soils in Rhode Island, USA, showed on significant retention in poorly drained sites throughout the year (Simmons et al., 1992). During the dormant season when the water table was high and reaching soil horizons with high organic content and denitrifying enzyme activity (DEA), nitrate was removed by denitrification and microbial immobilization (Groffman et al., 1992). During the growth season the water table was deeper in the mineral soil where DEA was undetectable and nitrate retention was caused only by plant uptake.

The presented examples show a large variation in the function of riparian areas. Flow pattern and nitrogen dynamics often varies with season and flow rate and the spatial variation along the stream can be large. In Scandinavian forest soils the upper mineral soil can be considered to be the major flow path through the near-stream zone but in more extended mires the upper peat layer may also be an important flow path when ground water level is high. To estimate the importance of near-stream areas for runoff chemistry, different types of near-stream zones has to be defined and investigations be directed to those areas contributing to most of the stream flow.

Riparian zones as sinks or sources for nitrogen

Investigations of nitrogen budgets for riparian zones have mainly concerned agricultural humid areas. Few of these also include thorough hydrological determinations and in forest land such studies are scarce (Hill, 1996). For Scandinavian boreal forests no budget studies on riparian zones are found in the literature so an assessment of their function with respect to nitrogen dynamics has to rely on findings from other types of ecosystems and indicative results.

The Canadian riparian wetlands discussed above acted mainly as transformers of inorganic nitrogen to organic nitrogen (Hill and DeVito, 1997). In Plastic Swamp 70% of nitrate and 95% of ammonium was retained on an annual basis. For a nearby valley wetland, Harp swamp, with slightly thicker soil layer, 88% of nitrate and 43% of ammonium was retained. In both cases, the retention of inorganic nitrogen was balanced by equal outputs of organic nitrogen. In the

Glen Major swamp there was no nitrate retention, 80% ammonium retention and 29 % retention of organic nitrogen. The total retention of nitrogen was 26% which was just above estimated budget uncertainties.

In the New Zealand case the retention of nitrogen in the riparian zones depended much on the ground water level which determined the proportions of discharge through different types of stream banks. The nitrate retention for the whole riparian zone was calculated to be between 32% and 98% with the highest retention at low water flow (Cooper, 1990). Concentrations of other nitrogen species were not measured but the experimental results supported the hypothesis that these riparian areas act as nitrogen sinks through denitrification.

Although no studies on nitrogen dynamics in riparian zones in Sweden are referred, a study on similar ecosystems was made by Jacks et al. (1994). Tentative nitrogen budgets were made for downslope wetlands in western Sweden. Two of the wetlands were estimated to retain nitrogen and three were nearly in balance. In the site with the highest retention rate, T nnersj heden c. 60%, the upland had been clear-cut 3 years before the study which had been followed by an increased nitrate leaching. The nitrate load with ground water to the wetland in T nnersj heden was 14 kg/ha yr. of upland area, whereas the other sites had nitrate loads around 2 kg/ha yr. of upland area. The high nitrate load at T nnersj heden was assumed to favor denitrification. N deposition in the area was 19-25 kg N /ha.

Indications of nitrate retention in relation to increased nitrate after clear-cut were also found by Ros n and Lundmark-Thelin (1986). In a study on scarification in a coniferous forest in northern Sweden percolating soil water was collected with zero tension lysimeters. The results showed a great loss of nitrogen from the B-horizon to the ground water, 8 - 29 kg N ha⁻¹, on different plots within a catchment, but measurements in the stream draining the catchment showed on a loss of only 4 kg N ha⁻¹. The difference was assumed to depend on denitrification.

Comparing concentrations of nitrogen in ground water along a slope down to a stream can also give indications if the riparian zone alters the nitrogen chemistry of ground water. Decreasing nitrate levels in ground water when comparing moist with mesic downslope sites was found in two catchments in central Sweden (Lundin, 1995b; Maxe, 1995) which can be an indication on nitrate retention. In the Stubbetorp catchment nitrate ranged between 530-2000 g N /L in a discharge area about 60 m from the stream. 30 m closer to the stream the nitrate concentration was only 14 - 450 g N /L . Ammonium was low in both areas. The

mean concentration of nitrate in the stream water was 60 g /L (1986-90) and org-N 280 g /L. Annual wet deposition was 7 kg N ha⁻¹ but during the study the area was affected by fertilization of about 34 kg N ha⁻¹ (Maxe, 1995). In the Risfallet catchment, nitrate decreased from about 140 g N /L to 14 g N /L and ammonium increased from about 28 g /L to about 100 g /L (mean values) along a catena ranging from mesic to moist soil type. The deposition was 5.6 kg N /ha yr. and leaching was 0.9 kg N /ha yr. where 22% was inorganic (Lundin, 1995b). In the Masby catchment, also in central Sweden, there were no clear indications on differences in nitrogen chemistry between ground water from downslope and upslope sites (Lundin, 1995a). This catchment has a deposition of 8.4 kg N /ha which was high for the area due to a high precipitation. Decreasing nitrate concentrations in ground water towards the stream may however not necessarily be due to nitrate retention. It can also be caused by discharge of deep ground water with lower nitrate as was shown in the Glen Major case (Hill and DeVito, 1997). This seems however less likely in these areas since surficial flow paths dominates in Scandinavian till soils (Grip and Rodhe, 1991). Ammonium concentrations were lower and showed slightly higher concentrations in downslope ground water. Organic nitrogen was not reported but DOC in ground water was presented for Risfallet and Masbyn. In both catchments DOC increased downslope.

As leaching of org-N have been found to be related to leaching of organic-C (Kortelainen et al., 1997) it is reasonable that the riparian areas are sources of organic nitrogen in these catchments. Indications of the near stream zone being a source of organic matter in runoff was also found in a small forest stream at Svartberget in northern Sweden (Bishop et al., 1994). A comparison of the different fractions of TOC in stream water and soil water from different soil horizons suggested that the upper mineral soil below the peat in the riparian zone was the main source of organic matter in runoff whereas the superficial soil was less important.

Nitrogen in runoff

The last section deals with how water chemistry varies in Scandinavian forest streams and how it relates to catchment characteristics and what is known about near-stream zones. In most of Scandinavian forests nitrogen leaching is low and the organic fraction dominates the nitrogen in runoff. More than 70% of the total nitrogen consisted of organic nitrogen in 11 of 12 Swedish and Finnish streams, when fertilized and clear-cut catchments were excluded (Lepistö et al., 1995). In

areas with high N-deposition, dominance of nitrate is found in runoff (Wiklander et al., 1991). Lundin (1991) found that leaching of tot-N was several times higher from catchments dominated by wetlands compared to mineral soil areas in the same region. Nitrate leaching from Swedish and Finnish catchments, on the other hand was found to be negatively related to amount of organic soils (Lepistö et al., 1995). This implies that wetlands, including near-stream zones and riparian wetlands, are sinks for nitrate and sources for org-N in runoff from forest land. A positive correlation between flow rate and org-N is often found (Arheimer et al., 1996) which can be due to that a larger proportion of the ground water flows through organic soil layers when the ground water level is high.

The concern of nitrogen leaching from forest relates to problems with eutrophication in lakes and coastal areas. The question whether the org-N contributes to the eutrophication cannot be answered as little is known about the bioavailability of the organic matter. Organic matter in runoff from forests generally consists of humic substances (Ahl, 1994) which are considered to be recalcitrant. However, experimental additions of humic substances from rivers have shown that humic substances can stimulate phytoplankton growth and indicates that humic bound nitrogen can be utilized by bacteria (Carlsson et al., 1993). An interesting approach for comparing bioavailability of org-N from different sources are bioassays which measures the potential availability of org-N for microorganisms (Bushaw et al., 1996).

For nitrate the eutrophying effect is more evident. Besides clear-cutted, fertilized or rocky catchments, high nitrate levels are only found in SW Sweden where nitrate deposition is close the threshold for nitrogen saturation (Dise and Wright, 1995). In the more usual org-N dominated streams, nitrate is usually higher than ammonium but the opposite is also found (Lepistö et al., 1995). Increased nitrate concentrations are often found at the beginning of peak flow when the ground water table is raising (Roberts et al., 1984; Creed et al., 1996). Arheimer et al. (1996) found significant higher nitrate concentrations during increasing flow in 40% of the 20 catchments in Finland and Sweden and the correlation was, with one exception, only valid for spring. The correlation between increasing flow rate and concentration may however be underestimated as a fixed 5 day period for calculating change in flow was used and the length of the relevant period may vary with season (Creed et al., 1996) and catchment area. The concentration peaks are caused either by that nitrogen in precipitation passes through the soil during the dormant season when there is no plant uptake (Stoddard, 1994), or by flushing of mineralized nitrogen at the beginning of a flow peak when the ground water

level is elevating (Roberts et al., 1984; Creed et al., 1996). The spring peaks of nitrate in the Swedish and Finnish streams were most pronounced in the southern streams where the mineralisation rate is higher and the snowpack is thinner or lacking. Hence it seems reasonable that the flushing mechanism is the most relevant for these streams. It is possible that transition zones between wetland and upland, which are temporarily saturated during high ground water levels, are the main sources for nitrate in runoff.

Conclusions

The scope of this review was to find out if processes in the near-stream zones are important for the nitrogen chemistry in Scandinavian forest soils. The question can not easily be answered as no direct studies have been made on the subject and my assessment has to rely on indicative results and findings from similar ecosystems. From this review the following can be concluded:

- N fixation can be expected to be high in the riparian areas compared to the upland forest, but it is questionable if it can be of importance for the nitrogen budget for the whole catchment as these areas only represent a smaller part of the catchment area. It may however be important for nitrogen leaching if this is mainly controlled by processes in the soil close to the stream
- Ammonium can be retained by plant uptake, microbial immobilization and cation exchange in wetlands.
- Nitrification may be important in the transition zone between upland and wetland.
- Denitrification is usually limited by the low nitrate concentration but downhill clear-cuts and locations with a high nitrification rate it can be expected to be important although it is hampered by low pH, and temperature and the poor quality of the organic matter found in riparian wetlands in Scandinavian forests.
- Reduction to ammonium (DNRA) is usually a minor pathway for nitrate but may be of importance in submerged organic soils where the redox potential and the ratio nitrate to organic matter is low.
- The upper mineral soil can be considered to be the major flow path through the near-stream zone. In more extended mires the upper peat layer may also be an important flow path when the water table is high.

- Flow pattern and nitrogen dynamics often vary with season and ground water level. The spatial variation along the stream can be large. Nitrogen dynamics depend on biological activity and redox potential in the major flow path.
- Wetlands and near-stream zones can act both as sources and sinks for different nitrogen species and their function varies with ground water level and season.
- Nitrogen is mostly in organic form in runoff from Scandinavian forests but in clear-cut or fertilized areas and in high deposition regions, nitrate may dominate.
- In catchments with a high proportion of wetlands, nitrate leaching is lower and tot-N leaching is higher.

In Sweden, it is probable that near-stream zones to some extent act as a sink for inorganic nitrogen and a source of organic nitrogen. In most of the Swedish forest soils the concentrations of inorganic nitrogen is low and leaching of organic nitrogen can be expected to be more important than retention of inorganic nitrogen. In areas with elevated nitrate levels, as after a clear-cut or with high deposition, denitrification is probably important. During increasing flow after drought, the upper soil in the near-stream zone is flushed and may temporarily act as sources of inorganic nitrogen. A coupling of nitrate leaching from transition zones and nitrate reduction in downhill wetlands is possible. As nitrogen dynamics in riparian areas has shown to differ so much between sites, further research has to be based on a more detailed knowledge of which types of riparian zones that are quantitatively important for the runoff from the Swedish forests. Are they mineral soils with a peat cover close to the stream or does most of the runoff enter the stream through more extended wetlands? In order to study the impact of near-stream zones for the runoff chemistry, the catchment should be divided into subcatchments representing different types of near-stream zones and each type studied separately. Further, the measurements should be concentrated to stream bank sections, representing most of the runoff. A promising approach that takes the spatial distribution into account is the use of a topography based hydrological model, such as TOPMODEL, combined with a rather simple model for nitrogen leaching, such as done by (Creed et al., 1996).

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