Control of runoff chemistry by processes in the near-stream zone

Licentiate Thesis

by

Jens Fölster

Department of Environmental Assessment
Swedish University of Agricultural Sciences
Box 7050 SE-750 07 UPPSALA

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Jens Fölster

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Abstract

The near-stream zone has been identified as an important control of runoff chemistry. In northern forested areas, near-stream zones have been found to be both natural sources and sinks for acidity. The near-stream zone can be a buffer against acidity by cation exchange and sulphate reduction. Oxidation of sulphide and leaching of organic acids are natural sources of acidity from the near-stream zone. A relatively high pH and base saturation in the near-stream zone favours nitrogen cycling processes. Hence, the near-stream zone has a potential to control nitrogen leaching from the catchment. Nitrogen can be retained by denitrification, microbial immobilisation and plant uptake. On the other hand, mineralisation, nitrification and leaching of organic matter can make the near-stream zone into a source for nitrogen to the stream water. The geomorphology and the hydrological flow paths are likely to be crucial for the function of the near-stream zone.

This thesis reports the results from an investigation on a small forested catchment in central south Sweden, designed to clarify the effect of processes in the near-stream zone on acidity and nitrogen chemistry in runoff. Both hydrological and water chemistry data suggested that runoff was dominated by superficial ground water, which agrees with what is commonly found in Swedish till soils. The Kindla catchment is heavily affected by acidification with a pH in the stream water between 4.4 and 4.6. Despite the severe acidification, there were no indications of forest decline at the Kindla catchment that retains nitrogen in deposition efficiently. The leaching of inorganic nitrogen was only 3% of bulk deposition. There were no indications that the near-stream zone acted as a buffer against acidity or nitrogen leaching from upland soils. The main function of the near-stream zone at Kindla with respect to runoff chemistry was rather to serve as a source for organic acids and organic nitrogen and, to a small extent, nitrate and ammonium. The contribution of organic anions to acidity was however overshadowed by a high sulphate concentration, except during a spring flood episode when organic matter was flushed out. Indications of sulphate reduction in the ground water were found but this probably had no influence on stream water chemistry. Ammonium was almost only found during the spring flood episode, when 72% of the annual transport of ammonium in the stream took place. Nitrate was found more frequently, but mainly at concentrations below 100 $\mu g\ L^{-1}$. This nitrate probably originated in the near-stream zone.

The results contrasted to what was found by other authors with respect to the influence of the near-stream zone on stream water chemistry. This would imply that since the function of the near-stream zone appears to vary greatly between catchments, there is a need for further catchment studies that also account for within catchment variation in order to achieve a more general picture of the impact of near-stream zones on runoff chemistry.

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Abstract

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Author's address: Jens Fölster, Department of Environmental Assessment, SLU, Box 1050, S-750 07 Uppsala, Sweden

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List of papers

The presented thesis is based on the following papers, which will be referred to by their Roman numbers.

I Fölster, J. Significance of processes in the near-stream zone on stream water acidity in a small acidified forested catchment. Manuscript.

II Fölster, J. The near-stream zone is a source of nitrogen in a Swedish forested catchment. Submitted to *Journal of Environmental Quality*

Background

Effects of deposition of anthropogenic acidifying and eutrophying pollutants has been a concern in Scandinavia since the early 1970's. In large parts of this region, sulphur deposition has caused acidification of surface waters. This has had disastrous effects on the biota in many lakes and streams. Nitrogen deposition has contributed to eutrophication in coastal waters (Olsson and Löfgren, 1990) and may have affected oligotrophic lakes as well (Smith, 1982; Wilander, 1995). During the last two decades sulphur emissions have decreased, but the recovery of surface waters appears to be slow (Wilander, 1997). For nitrogen the deposition has been constant during the last two decades but in most parts of Scandinavia at a level below the limit of 10 kg ha^{-1} yr^{-1} when high nitrate leaching from forest soil can occur (Dise and Wright, 1995). Still the nitrogen deposition is up to several times above the natural background level and the long-term effect of this is not known. Negotiations for further reductions of emissions are going on, but better models for calculation of critical loads, a limit for harmful effects on the environment, are desirable (Rapp, 1998). Hence, a better knowledge of the long-term effect of deposition of pollutants is needed. Leaching from forest soils is of special interest since forests cover most of the area of Scandinavia and even small changes in leaching from these soils would have large effects on downstream surface waters.

The soils adjacent to the stream in what is often termed the "near-stream zone" have been identified as an important control of runoff chemistry (Bishop *et al.*, 1990; Simmons *et al.*, 1992; Hill, 1996; Cirmo and McDonnell, 1997). Climatically controlled variation between seasons and years in runoff chemistry has also been related to processes in the near-stream zone (DeVito and Dillon, 1993; LaZerte, 1993)

Although there is an agreement on the importance of the near-stream zone, the influence on runoff chemistry has been found to be highly variable between catchments. In northern forested areas, near-stream zones have been found to be both natural sources and sinks for acidity and nitrogen (Bishop, 1991; LaZerte, 1993; Norrström, 1995; Hill and DeVito, 1997; Lundin, 1998). The variable findings are, however, not surprising since these areas are hydrologically and biogeochemically complex. In the near-stream zone, water flowing along different pathways mixes and continues through soil layers with a high organic content where microbial activity and redox conditions vary significantly both in time and space. The geomorphology and the hydrological flow paths are likely to be crucial for the function of the near-stream zone, as well as the upslope conditions, deposition history and stage of acidification/recovery. Given the importance and complexity of the near-stream zone, there is a great need for further studies so that a more comprehensive understanding of its function can be achieved. This will improve the ability to predict the ecosystem status and future development at a more detailed scale than is now possible.

This thesis reports the results from an investigation on a small forested catchment in central south Sweden designed to clarify the effect of processes in the near-stream zone on acidity and nitrogen chemistry in runoff. The study area was located within a catchment that is part of a European program for integrated monitoring (IM) related to the UN/ECE Convention for Long Term Transboundary Air Pollution. The aim of the program is to differentiate between natural ecological variation and anthropogenic perturbations caused by air pollution as well as to predict long-term changes of the ecosystem through the application of dynamic modelling (Pylvänäinen, 1993). The results from the present study should be used for interpretation of data from the IM program. At the same time the IM-program supported the study with background data at a suitable temporal and spatial scale.

Hydrology of near-stream zones

The ground water flow pattern in the near-stream zone varies greatly, depending on the geomorphology of the catchment (Hill and DeVito, 1997). In deep aquifers with highly permeable soils, deep flow paths are important and close to the stream a discharge area with upward flow can be found. In the till soils covering most of the Scandinavian forests however, there is a marked decrease in hydraulic conductivity with increasing soil depth. This results in predominantly lateral flow in superficial ground water (Lundin, 1982; Bishop *et al.*, 1990) while the vertically upward flow is less important for the total discharge (Bishop, 1994).

The wet conditions in the near-stream zone favour the growth of *sphagnum* and formation of peaty soils. The depth, extent and hydraulic properties of the peat direct the flow pattern of the ground water through the last soil section before it discharges into the stream. The peat cover can be divided into a superficial layer consisting of living and undecomposed dead vegetation and an underlying anaerobic layer of more humified peat. The superficial layer is usually thinner and has a higher hydraulic conductivity compared to the underlying layer. Ground water may flow either in the mineral soil under the peat layer or through the superficial peat layer. The latter flow path can be expected to become more important when the ground water level is raised. Flow through the impermeable humified peat layer can only occur if there exist macropores (Norrström, 1995). An intermediate layer between the peat and the mineral soil with a high hydraulic conductivity and organic content has also shown to be an important flow path (Bishop *et al.*, 1995). Many forest streams in Sweden have been ditched, which has lowered the flow paths through the near-stream zone (Bishop *et al.*, 1995) (Fig. 1).

Since different biogeochemical processes are located in different soil layers, the flow pattern in the near-stream zone is crucial to its influence on discharge chemistry. There are however, few studies that integrate hydraulic measurements with biogeochemical studies. Such studies are difficult to perform because of the large spatial variability. Instead a comparison of the chemistry in ground water and stream water has been suggested for finding the important flow paths (Fiebig *et al.*, 1990; Norrström, 1995)

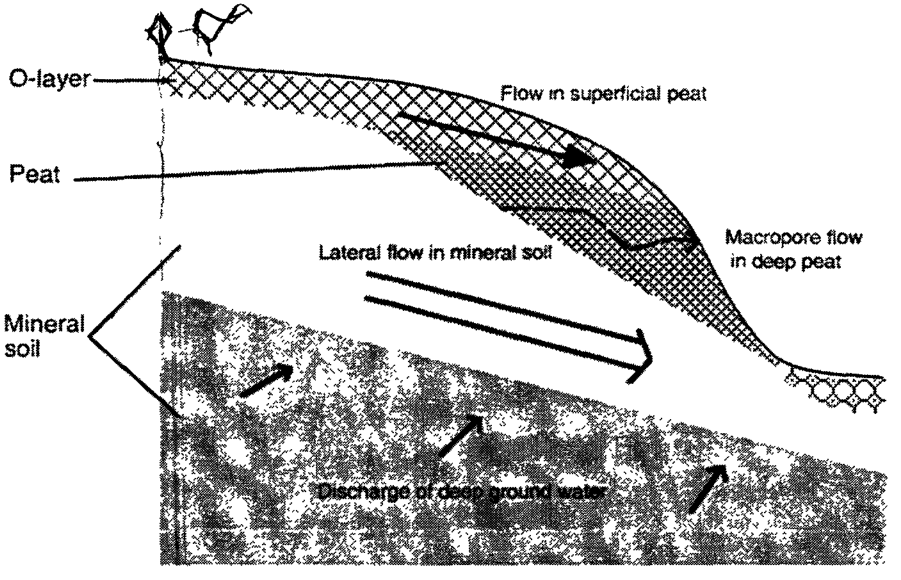

Figure 1. Possible hydraulic flow paths in the near-stream zone in Scandinavian till soils with lateral flow in the superficial mineral soil as the dominating path.

Influence on acidity by the near-stream zone

The near-stream zone has been argued to act both as a natural buffer against acidification by cation exchange (Norrström, 1995) and as a natural source of organic acidity (Bishop *et al.*, 1990). The riparian peat cover offers a large pool of cation exchange sites and the base saturation has been found to be higher in downslope wetlands compared to upland soils (Norrström, 1995; Giesler *et al.*, 1998). At a former stage of acidification, hydrogen and aluminium ions in ground water from upland areas may be exchanged with base cations in the near-stream zone, then acting as a buffer against acidification (LaZerte, 1993). As the acidification of the soil continues, the base cation supply in the near-stream zone is exhausted and the acidification of the runoff increases.

The export of organic matter from the near-stream zone has been found in many studies (e.g. Bishop *et al.*, 1990; LaZerte, 1993). Further, the export of organic matter often increases during high flow events as a rise in ground water level alters the flow path into more organic rich soil layers. In low acid deposition areas as in Northern Sweden, the organic acids are the main source for acidity during flow peaks (Laudon and Bishop, 1999). The importance of flow paths for the export of acidity has been shown in a study of two adjacent ditched streams. A high leaching of organic matter from the near-stream zone was found in the stream with the deepest peat layer where the ground water level extended up into the peat and an organic rich intermediate layer. In the other stream, the peat cover was thinner and ditching had lowered the water table below the organic rich soil layer (Bishop, 1994).

Redox reactions of sulphur compounds can also have an impact on the acidity of the discharging ground water. In the water saturated organic soil near the stream, anaerobic conditions easily occur which can result in microbial reduction of sulphate into sulphide (DeVito, 1995). The process is a hydrogen consuming processes and hence microbial sulphate reduction may be a sink for acidity. In an area with riparian peat where the hydraulic conductivity was highly variable, the sulphate concentration was lowest where the permeability of the soil was lowest (Norrström, 1995). The results indicated that sulphate reduction only has an impact on the sulphate concentration in stagnant areas with a low contribution to runoff. This reduces the potential for the process to be important on a catchment basis. Furthermore, during dry years when the water table is low, sulphide is oxidised as the soil is aerated. This has an acidifying effect on the soil (LaZerte, 1993).

Nitrogen dynamics in the near-stream zone

Internationally, near-stream zones are recognised as important nitrogen retention sites (Haycock *et al.*, 1993). Several processes may be involved (Fig. 2), but denitrification is the process that has been most noticed since it removes available nitrogen from the system whereas other processes such as plant uptake and microbial immobilisation only transform mobile forms into less mobile forms. Denitrification is the microbial reduction of nitrate into gaseous compounds such as dinitrogen oxide and elementary nitrogen. The process occurs under oxygen free conditions and is thus favoured by both the water-saturated conditions (Davidson and Swank, 1986; Ambus and Christensen, 1993) and the high content of organic matter in the near-stream zone (Federer and Klemedtsson, 1988). In most forests in Sweden, however denitrification does not usually take place because of the negligible concentrations of nitrate in the soil (Hallgren *et al.*, 1996). During events with temporarily elevated nitrate concentrations however, denitrification may be important. Further, after clearcuts, when high nitrate concentrations are found (Vitousek *et al.*, 1979) denitrification in downslope wetlands and near-stream zones can also be important (Rosén and Lundmark-Thelin, 1986; Jacks *et al.*, 1994).

Other retaining mechanisms for nitrogen are plant uptake and microbial immobilisation where ammonium and nitrate is taken up and incorporated into the pool of soil organic matter. In the forests in most parts of Sweden, uptake and immobilisation in the canopy and the upper soil layer is enough to retain all the nitrogen in atmospheric deposition. Thus inorganic nitrogen is rarely found in soil leakage at 0.5 m depth (Hallgren *et al.*, 1996). The organically bound nitrogen can then be decomposed into forms available for plant uptake. This internal circulation of nitrogen is in the range of 0.5 – 10 g m^{-2} yr^{-1} in Scandinavian forests (Löfgren, 1991). This can be compared to the total pool of soil organic matter, which is between 30 and 1000 g m^{-2} (*op. cit.*). The atmospheric deposition, on the other hand, is in the range of 0.2 – 1.0 g m^{-2} yr^{-1} (*op. cit.*). Ammonium may further be transformed into nitrate through nitrification. Nitrification is generally considered to be of less importance in undisturbed coniferous systems, but recent studies including measurements of gross nitrification using ^{15}N dilution has shown both high (Stark and Hart, 1997) and low (Tietema, 1998) nitrification rates. A high pH and base saturation generally favour nitrogen cycling processes. Since downslope areas with the ground water level close to the ground surface, such as near-stream zones, have a relatively high pH and base saturation, the nitrogen turnover is expected to be high (Giesler *et al.*, 1998). These areas have the potential to be either sources or sinks for inorganic nitrogen in runoff. Budget studies have shown that both cases are found depending of hydrological flow paths and concentrations of nitrogen in the ground water coming from upland areas (Hill and DeVito, 1997; Lundin, 1998).

A general feature of near-stream zones is that they are more or less a source for organic nitrogen (Hill and DeVito, 1997; Lundin, 1998). The organic matter however, mostly consists of humic substances that are not easy available for algal growth and hence have a low eutrophying effect.

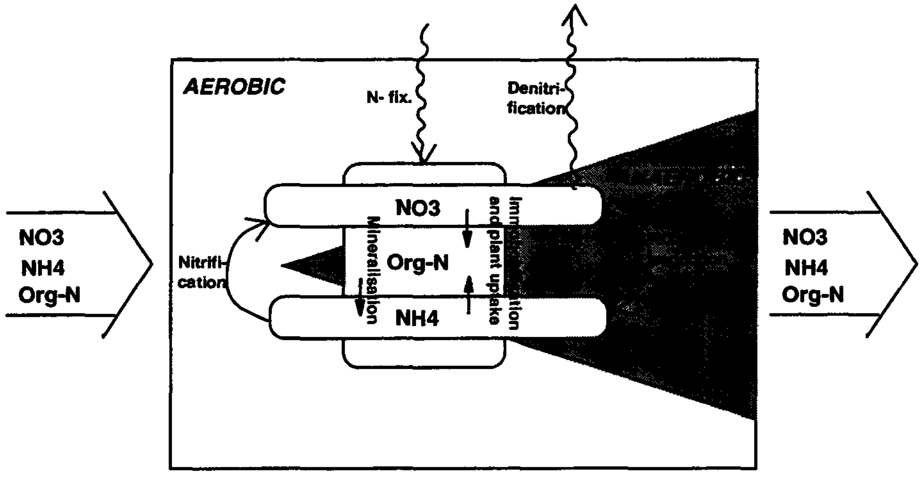

Figure 2. A conceptual model of the nitrogen turnover in a riparian wetland with ground water flowing through the soil. Closer to the stream anaerobic processes become more important.

Objectives

The objective of the investigation was to describe spatial and temporal variation of ground water and soil water chemistry in the near-stream zone as well as the relation of these to stream water chemistry in a small forested catchment. Furthermore, the spatial variation of hydraulic conductivity and spatial and temporal variation of ground water level and hydraulic potential was studied. The outcome was determination of the function of the near-stream zone with respect to nitrogen and acidity.

Study area

The main study area was located along a stream, bordered with riparian peat, running from a small poor fen (0.2 ha). The area is located within

Study area

The main study area was located along a stream, bordered with riparian peat, running from a small poor fen (0.2 ha). The area is located within the Kindla catchment that has been an object for Integrated Monitoring since 1997. The catchment is 19 ha and located in central south Sweden (59°45'N, 14°55'E) at an altitude of 320-410 m above mean sea level. This is above the highest coastline after the last glaciation. The soil material is a sandy silty till with low boulder frequency. Podzols are the dominant soil type, but close to the stream there are dystric gleysols and histosols. No forestry activities have been carried out during the last 100 years.

Methods

Ground water and soil water were sampled by using piezometers and ceramic cups respectively. A number of 24 locations were sampled three times during 1997. The piezometers were used for measuring ground water levels, hydraulic potential and hydrologic conductivity. Stream water was sampled biweekly at two gauges located upstream and downstream from the study area. A more intensive sampling was performed during a spring flow episode. Stream flow was recorded continuously at the gauges. Bulk deposition and throughfall were sampled monthly. All chemical analyses were made with standard methods. More details and maps of the study area are presented in papers I and II.

Results and discussion

Superficial flow paths dominated in the near-stream zone (Paper I and II).

Both hydrological and water chemistry data suggested that runoff was dominated by superficial ground water, which agrees with what is commonly found in Swedish till soils. An upward flow component, measured as an increase in hydraulic potential with depth, was only measured occasionally in a few points, and there was no area of permanent upward flow. Furthermore, the concentrations of base cations and silica found in ground water in upper soil layers in the near-stream zone were close to what was found in the stream. The concentrations in ground water at 1 m depth however, were much higher. Thus the contribution from this flow path must have been negligible, presuming that there was no decrease in concentrations as the ground water moved towards the stream.

In the near-stream locations the ground water table was close to the ground surface even at base flow. Here the highly conductive superficial peat may have been a significant flow path, especially during flow peaks. A comparison of the C/N ratio in the dissolved organic matter in the stream water and ground water at different levels, indicated that the intermediate layer below the peat cover was the most important flow path. These results could however, also have been caused by a higher leaching rate of organic matter in the intermediate zone.

The near-stream zone has a small influence on stream water acidity at the Kindla catchment (paper I).

The Kindla catchment is heavily affected by acidification with a pH in the stream water between 4.4 and 4.6 and an acid neutralising capacity (ANC) of -84 – -21 µeq L^{-1}. The normal variation in stream water pH with dips during flow peaks was not seen since the ground water discharging during base flow was already acidified. Sulphate was the dominant anion, which means that sulphuric acid is probably the dominant source of acidity. However the sulphur transport out of the catchment, 70 meq m^{-2} yr^{-1}, was more than twice as high as the input with throughfall, 30 meq m^{-2} yr^{-1}. Since the sulphate concentration decreased slightly in the ground water along the transects towards the stream, the source for sulphate can not have been the near-stream zone but rather desorption from iron and aluminium oxides in the B-horizon of podzols in upslope areas (Karltun, 1995).

The tendencies of decrease in sulphate as the ground water moved down the slope, and a correlation of low sulphate concentrations with anoxic conditions, implied microbial reduction of sulphate to sulphide in the near-stream zone. Since this process consumes acidity, the process reduces the sulphur related acidification of the ground water. Locations with decreased sulphate concentrations were however, mostly found in transects with small upland areas and hence contributing little to stream discharge. Further, the sulphate concentration was correlated to calculated ground water flow velocity, although not significantly. This indicates that sulphate reduction was more significant in locations with a lower contribution to stream flow. The comparison of sulphate concentrations in ground water with stream water also suggested that the influence of sulphate reduction was negligible for stream water chemistry. Hence, the results agree with what was found by Norrström (1995).

A small peak in calcium concentration at the beginning of a spring flow episode indicated a small buffering of acidity by cation exchange in the near-stream zone. However it only influenced stream water acidity by c. 0.02 meq L^{-1}. When the discharge had reached its maximum, the calcium peak was gone. Besides the episode, there were no indications of buffering by cation exchange in the near-stream zone, as was suggested by Norrström (1995). The results from Kindla are rather closer to the findings by Bishop *et al.* (1990) that the near-stream zone is a source for acidity by leaching of dissolved organic carbon. In Kindla however, the organic acidity was overshadowed by sulphate during base flow. During the episode, though, the impact of organic anions became important. The sulphate concentration during the episode decreased due to dilution of ground water with precipitation lower in sulphate, while the concentration of organic anions increased due to flushing of organic matter. At the flow peak, the concentration of dissociated organic acid anions was equal to that of sulphate anions. This is an indication that there was a natural component of episodic acidification on this site prior to anthropogenic acidification.

The near-stream zone is a source of nitrogen for the stream (paper II)

Despite the severe acidification, there were no indications of forest decline at the Kindla catchment that retains nitrogen in deposition efficiently both in the forest canopy and the soil. This is in agreement with other findings that the earlier fears (Fleischer and Stibe, 1989) that acidification would lead to forest decline followed by high nitrate leaching have not been fulfilled (Binkley and Högberg, 1997). No inorganic nitrogen was found in the ground water at upslope locations and the concentration of DON was low, c. 100 µg N L^{-1}.

According to the findings in ground water and soil water, the near-stream zone was the main source for runoff nitrate in this catchment (see below). The nitrogen leaching however was small. The export from the catchment was only 0.04 kg NO_3-N (ha yr)$^{-1}$ and 0.1 kg NH_4-N (ha yr)$^{-1}$ which can be compared to 2.9 kg NO_3-N (ha yr)$^{-1}$ and 2.6 kg NH_4-N (ha yr)$^{-1}$ in bulk deposition. For ammonium and organic nitrogen, a large part of the annual transport in the stream took place during the few days of the spring flow episode and was missed by the biweekly sampling program of the integrated monitoring. If the transport was estimated solely by the biweekly samples, the transport of ammonium and organic nitrogen was underestimated by 72% and 30 % respectively, compared to when episode samples were included.

The concentrations of inorganic nitrogen in ground water and soil water was generally low. In near-stream locations, nitrate only occurred occasionally and locally, usually when the ground water level was lowered. Furthermore, nitrate was predominantly found in locations with relatively high pH and high concentrations of dissolved oxygen. Since nitrification is an oxygen demanding process and is favoured by high pH, the findings indicated that the nitrate found in the soil originated from nitrification coupled to mineralization of organic matter in the soil. The spring flow excluded, nitrate only occurred temporarily in the stream and mainly at concentrations below 100µg L^{-1}. Since nitrate was correlated to increasing concentrations of silica in the stream, it was concluded that nitrate in the stream had a microbial origin, and was not caused by precipitation passing directly to the stream. A high contribution of precipitation would give a decrease in silica concentration, which was found during the spring flow episode when no nitrate was found in the stream water.

The ammonium concentrations showed a totally different distribution pattern, both in time and space. In the ground water, ammonium was found at stable concentrations in the near stream zone in locations with low oxygen concentrations. Since no ammonium was found in the stream, with the exception of the spring flood, it is possible that the ammonium rich locations were primarily soils with low hydraulic conductivity that made a small contribution to runoff. During the spring flood, an ammonium concentration up to 90 µg L^{-1} was found. The ammonium peak was probably caused by both flushing in the beginning of the episode and direct contribution from the atmospheric deposition at peak flow.

The nitrate concentration was negligible during the whole spring flow episode, which indicates that the nitrate in the precipitation must have been retained, either by microbial immobilisation or by denitrification. The magnitude of this retention was in the order of 2 g N ha-$^{-1}$ h^{-1}. The retention rate is unexpectedly high since the temperature was close to 0°C. If ammonium from the precipitation passed to a large extent unaltered through the catchment during the episode, it is unlikely that nitrate was immobilised since ammonium is preferred to nitrate by microbes. Denitrification however has been found to be favoured by freezing and thawing that releases available carbon. Indications of release of fresh microbial carbon during the episode were found in a decrease of the C/N ratio of the dissolved organic matter in the stream water.

The near-stream zone was the main source for organic nitrogen as well. The concentration of organic nitrogen increased progressively as the ground water moved down the slope. The C/N ratio in the ground water in the near-stream zone was higher in the organic soil compared to the underlying soil layers. In the stream, the C/N ratio was close to the ratio in the transition zone between organic and mineral soil in the near stream soil profile. Hence, this soil layer was probably the main source of organic matter during base flow. The dissolved organic matter in forest streams mainly consists of recalcitrant humic substances that have low value as a nitrogen source in downstream lake production (Wetzel, 1983). A flush of fresh microbial organic nitrogen during spring flow may however be of ecological relevance.

Concluding remarks

There were no indications that the near-stream zone acted as a buffer against acidity or nitrogen leaching from upland soils. The main function of the near-stream zone at Kindla with respect to runoff chemistry was rather to serve as a source for organic acids and organic nitrogen and, to a small extent, nitrate and ammonium. In the present acidified state of the soil and stream, the near-stream zone only had little influence on acidity of water passing from the upslope region into the stream. In the near future, however, when the acidity related to adsorbed sulphate is washed out from the soil, it is likely that the influence of organic anions from the near-stream zone will be of more importance. It is likely that the base saturation of the soil has decreased during the last decades of acidification. At the onset of acidification, the near-stream zone may have had a buffering effect, but as the acidification continued, the supply of exchangeable base cations may have been exhausted (LaZerte, 1993; Norrström, 1995).

The results in this study contrasted with what was found by both Bishop *et al.*, (1990) and Norrström, (1995) with respect to the influence of the near-stream zone on stream water acidity. Since the function of the near-stream zone appears to be totally different between catchments, there is a need for further catchment studies that also account for within catchment variation in order to achieve a more general picture of the impact of near-stream zones on stream chemistry. The function of these zones is also likely to change over time. It is therefore important that they are included in long term monitoring programs so that any changes in the catchment budget could be interpreted in a more informed way.

The findings of the small-scale spatial and temporal variation have some important implications for long term monitoring of near-stream zones. The large spatial variation of ground water and soil water makes it expensive to make reliable estimations of the different elements in these compartments. A study of the covariation in time between different locations within the catchment would show if an economically reasonable number of sampling points is enough to describe the temporal variation in concentrations in ground water and soil water. For modelling and the study of trends this would be enough since only the dynamics of the concentrations are needed.

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