The effects of fluctuating climatic conditions and weather events on nutrient dynamics in a narrow mosaic riparian peatland

Ain Kull[1], Anne Kull[1,2], Jaak Jaagus[1], Valdo Kuusemets[2] and Ülo Mander[1]

[1] *University of Tartu, Institute of Ecology and Earth Sciences, Department of Geography, 46 Vanemuise St., Tartu 51014, Estonia (e-mail: ain.kull@ut.ee)*

[2] *Estonian University of Life Science, Department of Agriculture and Environmental Protection, 5 Kreutzwaldi St., Tartu 51014, Estonia*

N_{tot}, NO_3-N, NO_2-N, NH_4-N, P_{tot}, PO_4-P, SO_4, Fe, Ca, Al, K, Mg and dissolved O_2 concentrations, as well as water temperature, pH, Oxidation-Reduction Potential (ORP) and electric conductivity were measured in soil water and ground water sampled from different plant communities located along topo-edaphic gradients from moraine upland to stream valley in two small agricultural catchments in southeastern Estonia. The production rate and the N and P content in plant biomass were also analyzed. The mosaic soil and vegetation pattern had a significant influence on soil water quality. In the arable land, the mean annual concentration of total inorganic nitrogen (NH_4-N + NO_2-N + NO_3-N) in piezometer water was 3–40 mg N l^{-1}, but in the riparian grey alder forest (*Alnus incana*) total inorganic nitrogen never exceeded 1 mg N l^{-1}. The most significant reduction was in the average concentration of NO_3-N content, which was reduced from 25 mg l^{-1} under the arable land to 0.5 mg l^{-1} in both the alder forest and the sedge-dominated floodplain. The average P_{tot} concentration also decreased under the alder stands, being 0.2–1.5 mg P l^{-1} in the arable land and less than 0.2 mg P l^{-1} in the alder forest. Wetland herb communities (*Carex elata* association, *Filipendula ulmaria*, *Cirsium oleraceum* and *Aegopodium podagraria* dominated communities) also had a significant influence on soil water quality, increasing the internal cycling of N and P within the peatland. The plant biomass (the sum of above- and below-ground biomass) of riparian and wetland communities accumulates up to 54.3 g N m^{-2} and up to 5.3 g P m^{-2} during the growth season. The following factors have the highest priority in weather-induced changes in the nutrient fluxes in riparian peatlands: (a) the duration of frozen surface, (b) snowpack peak water, (c) the precipitation pattern over the warm period, (d) the duration and continuity of certain weather, (e) the occurrence of night frost events and soil freeze-thaw cycles. When night frost events start, the importance of autumn rainfalls is enhanced, as the high water-table intensifies the denitrification process but also increases Ca, Mg, K, N and P losses released during the frost–thaw cycle.

Introduction

The effects of riparian peatlands on nutrient dynamics and river quality have been examined in several studies (Seitzinger 1994, Mander *et al.* 1995, Cirmo and McDonnell 1997, Liljaniemi *et al.* 2003, Jacks and Norrström 2004, McHale *et al.* 2004, Bonnett *et al.* 2006). Some of these studies concentrate on water quality dynamics in vegetated ditches within the complex riparian peatland zone (Scholz and Trepel 2004, Trepel and Kluge 2004, Kieckbusch *et al.* 2006). Only few investigations consider the possible seasonal effects and climate change influence on the intensity of nutrient and carbon cycling in riparian peatlands (McHale *et al.* 2004, Bonnett *et al.* 2006). On the other hand, it is well-known that short-term weather events significantly alter the dynamics of various nutrients content in subsurface water.

It is well documented that increasing frequency of freezing and thawing cycles, one indicator of a change towards milder winters, causes a significant increase in NO_3-N concentration in soil water (Deluca *et al.* 1992, Scherer *et al.* 1992, Müller *et al.* 2002), followed by an increase in denitrification activity (Johnsson *et al.* 1991, Steinheimer *et al.* 1998) and an increase in nitrous oxide (N_2O) flux (Müller *et al.* 2002). Kaiser *et al.* (1998) reported that up to 47% of the annual N_2O emission was observed during freeze–thaw events in winter. Likewise, ammonification activity (Freppaz *et al.* 2006) and N accumulation in soils due to the death and lysis of soil microorganisms (Ryan *et al.* 2000) increased during the freezing and thawing events. According to several investigations (Tobias *et al.* 2001a, Müller *et al.* 2003), accumulation of N and increased NH_4-N concentrations might be caused by the dissimilative nitrate reduction to ammonium (DNRA). The frequent change of redox potential typical of freeze-thaw cycles is also beneficial for DNRA (Pett-Ridge *et al.* 2006). Some investigations demonstrate that the rapid increase in soil water temperature after a long-term freezing significantly decreases bacterial activity and biomass in soils (Lipson *et al.* 1999). In addition, elevated soluble carbon (Harris and Safford 1996) and phosphorus (Bechmann *et al.* 2005) concentrations may result from frequent freeze–thaw events.

Among other weather events, severe rainfalls and drought periods can significantly influence the nutrient dynamics of riparian peatlands. Water erosion transports significant masses of soil and particulate materials to such peatlands (Mander *et al.* 1995, Phillips *et al.* 2001). Drought periods and related water table lowering in peatlands may cause significant mineralization of nitrogen, an increase in the emission of CO_2 and N_2O (Freeman *et al.* 1993, Martikainen *et al.* 1993), and the flushing of dissolved organic carbon (DOC) from the peatland during the subsequent rewetting of the peatland (Hughes *et al.* 1998). On the other hand, drought also causes sulphate reduction and the suppression of methane emissions (Dowrick *et al.* 2006). Generally, it has been found that the smaller and more uniform the catchment is, the higher the influence of weather on nutrient losses (Hill 1978, Høyås *et al.* 1997).

The frequency and regularity of water sampling is one of the critical issues in characterizing the impact of weather events on water quality. Discrete random sampling is not very effective in describing nutrient losses in small catchments. The random discrete sampling strategy normally used for monitoring purposes underestimates P loss in certain cases by more than 50%, because most of the P loss occurs during storm events (Grant *et al.* 1996). For predictive models it is very important to follow certain critical periods when biological and chemical processes are switched from one type to another.

Results of previous studies on long-term (1987–2003) changes in stream water quality and nutrient runoff show a clear response to changes in weather pattern and land-use intensity in southeastern Estonian catchments (Mander *et al.* 1998, Mander *et al.* 2000, Järvet *et al.* 2002). In this period land-use intensity has drastically dropped for socio-economic reasons: the proportion of arable land decreased from 58.5% to 19.6%, and fallow land increased from 1.2% to 26.5%, a slight increase also occurred in the area of grasslands and forest (*see* Mander *et al.* 2000). As a consequence of the change in weather conditions and land use, decrease of mean annual water discharge from 0.05 to 0.02 $m^3 s^{-1}$ was observed in the Sipe River catchment (Kull and Oja 2001). The most significant

Fig. 1. Location of the Porijõgi catchment, its Tatra River subcatchment and Sipe River subcatchment. Black dots on the overview map of the Porijõgi mark the location of the transects established in 1991, the detailed study area coincides with the transect located in the upper course of the Sipe River.
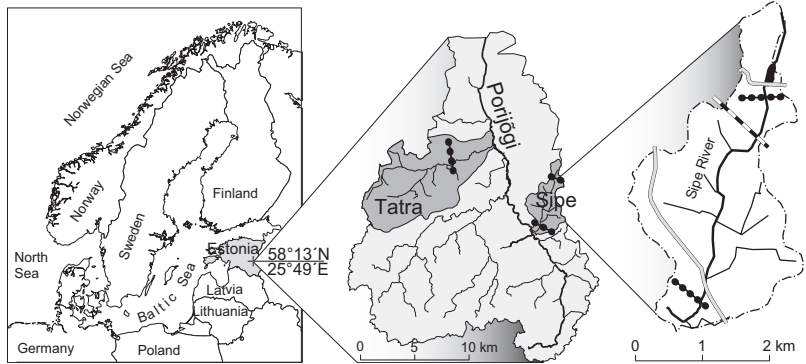
changes were observed in spring, when peak flows became rare. A strong fall in nutrient losses was also observed: the loss of N_{tot} dropped from 3.8 kg ha^{-1} yr^{-1} in 1987 to 0.2 kg ha^{-1} yr^{-1}, and P_{tot} from 0.32 to 0.01 kg ha^{-1} yr^{-1}. In addition to the drastically reduced amount of nutrient loss, which was mainly caused by less intensive land-use, the monthly pattern of nutrient runoff in stream water became significantly different (Mander and Kull 1997, Mander *et al*. 1998, Mander *et al*. 2000). Based on this background information about changes in stream-water quality the present paper concentrates on weather-induced changes in ground- and subsurface water chemistry in riparian peatlands with various vegetation types covering partly the same period and region (Sipe and Tatra tributaries of the Porijõgi). While including years with highly variable weather typical for boreonemoral region, the second half of our 12-year study period (1992–2003) was characterized by milder winters and different annual precipitation distribution as compared with the average for the climatologically long period. This has made it possible to analyse nutrient fluxes in mosaic riparian peatlands also by means of climatic seasons in context of climatic changes.

This paper examines in-depth the effects of different weather types and meteorological characteristics that influence nutrient fluxes in the catchments of small rivers, and especially in their riparian peatland areas. Against the background of monitoring the nutrient loss in the catchments of the Sipe and Tatra Rivers, seasonal variation and processes leading to nutrient release were studied in detail along the topo-edaphic gradient in the riparian peatland zones. The main

objective of this study was to find answers to the following questions: (1) what is the influence of mosaic soil, hydraulic and plant cover conditions on subsurface and groundwater quality in riparian zone? (2) what are the main effects of long-term climate fluctuations and short-term weather events on nutrient cycling within the riparian peatland zone? and (3) what is the effect of vegetation and climatic these changes on the long-term buffering capacity of the riparian peatland ecotones?

Materials and methods

Study area

The Porijõgi catchment (258 km^2) is situated in southern Estonia, 10 km southeast of Tartu (Fig. 1). This is a typical small river drainage area within the southeast Estonian moraine plain, which has undulating orography and numerous dissecting primeval valleys. The dominant soils are planosols, podzols and podzoluvisols, which are mainly in agricultural use, while gleysols and histosols predominate in the valleys. We studied the nutrient dynamics in groundwater flow from the moraine plateau to the stream valley and its transformation in mosaic riparian peatland zone at Tatra and Sipe river subcatchments of the Porijõgi.

The Tatra River subcatchment (38 km^2) occupies a deep branch of the Porijõgi primeval valley. It lies at 33–140 m a.s.l., and the relative height of landforms is mostly between 15 and 30 m. About 45% of the area was used as arable land during the study period, while 28% was

covered by forest, and equally 6% was occupied by wetlands, natural grasslands and cultivated grasslands.

One transect consisting of 5 piezometers was established in the middle course of the Tatra River in autumn 1991 along a topo-edaphic gradient (Fig. 1, *see* also Mander *et al.* 1995). Each piezometer (PVC pipes, diameter 100 mm, length 1–5.5 m, the lower part of which is perforated and covered with glass-fiber material) on the landscape profile was installed on the boundary between different plant communities. Toposequentially (from the upper towards the lower part of the gradient), the following communities were found: (1) *Elytrigia repens* and *Dactylis glomerata* dominated grassland, (2) *Phleum pratense* and *Alopecurus pratensis* dominated cultivated grassland, (3) a sedge fen of large sedges dominated by *Carex elata*, (4) a *C. elata* dominated sedge fen with *Betula pubescens* trees, (5) a sedge fen dominated by various small sedges (*C. davalliana*, *C. paniculata*, *Eleocharis palustris*, *Scoenus ferrugineus*) and rich in rare orchid species (*Epipactis palustris*, *Gymnadenia conopsea*, *Herminium monorchis*, *Listera ovata*, *Ophrys insectifera*, *Orchis baltica*, *O. incarnata*, *O. russowii*), and finally (6) a grey alder (*Alnus incana*) stand on the river bank.

The Sipe River subcatchment (8.9 km²) lies at 60–100 m a.s.l. The Sipe River is flowing in a small primeval valley where relative height of landforms mostly remains between 5–20 m. The orography of the area clearly defines the watershed boundary and main flow paths through different vegetation and land-use units. Arable land was dominant land use type (46%) during the study period, followed by forest (41%), natural grassland (9%) and cultivated grasslands (3%). Wetlands were present along the Sipe River valley and occupied 1% of the subcatchment area.

One transect consisting of 5 piezometers was established on the upper course and one transect consisting of 4 piezometers was established on the lower course of the Sipe River in autumn 1991 (Fig. 1). In 1997, four additional transects, each consisting of 4 piezometers, were established along the upper course of the Sipe River, in addition to the transect established in 1991. All transects were perpendicular to the stream,

constituting an almost regular grid. The piezometers on the transects were located at a distance of 100–200 m from each other along the river, and at 15–90 m across the river. However, the exact location of sampling wells was determined on the basis of features such as vegetation pattern, soil properties and hydrological conditions. The piezometers were located on both sides of the river, according to the dominant vegetation and land-use type (e.g. grassland, wetland with *Carex* spp. domination, *Salix* bush, etc.). Three weirs were established in the river, and water samples were also taken there. The weirs correspond to the following sites: (i) the inflow to the study area, (ii) the middle part of the riparian peatland, and (iii) the outflow from the area of detailed study on the upper course of Sipe River. The stream discharge of the upper course area of Sipe River studied in detail consists of base flow originating from groundwater and outflow from the lake adjacent to the upper course study area. During droughts no water discharge from the lake may occur. The relative height difference of the valley in the area of detailed study is 11 m. Slopes usually achieve 3–8°, in some sections more than 15°. The bottom of the valley is occupied by a floodplain meadow. The clay substrate underlying the wetland results in a shallow perched water-table, poorly drained and highly organic soils, and reduced inputs of regional groundwater. The depth of organic sediments in the riparian peatland area is up to 6 m in most of the area, fluctuating between 2 and 4 m. The deepest layers also include gyttja. The dominant vegetation patterns in the riparian peatland consist of *Carex* spp., *Filipendula ulmaria*, gramineous plants, *Geranium* spp., *Anthriscus sylvestris*, *Urtica dioica* and *Salix* spp.

Field study

In 1992–1994 water samples were collected and the groundwater height was measured once a month with piezometers located in the middle course of the Tatra River and in the lower and upper courses of the Sipe River. The stagnant water was pumped from the piezometer before water samples were taken. Water samples were analysed in the laboratory for NH_4-N, NO_3-N,

NO_2-N, PO_4-P, P_{tot} and SO_4 contents (APHA 1981).

Since the establishment of additional transects of piezometers in the upper course of the Sipe River in 1997, water sampling intensity increased. To follow certain critical periods when biological and chemical processes are switched from one type to another or hydrological and meteorological characteristics change rapidly, the process-oriented sampling method was used instead of the traditional random sampling. Detailed observations took place in connection with changes in weather conditions, on average once per 1–2 weeks. These were more frequent in spring and autumn, when weather variability is higher than in summer or winter. During detailed observations, water samples were taken for laboratory chemical analyses (N_{tot}, NO_3, NO_2, NH_4, P_{tot}, PO_4, SO_4, Fe, Ca, Al, K, Mg), and the following water parameters were measured: groundwater level, temperature, dissolved O_2, pH, Oxidation-Reduction Potential (ORP), electric conductivity and salinity. In-depth observations at 3-hour intervals were carried out in the case of specific weather events to determine short-term changes in physicochemical parameters (groundwater level, temperature, dissolved O_2, pH, ORP, electric conductivity and salinity) in surface- and groundwater and their response to meteorological phenomena in their different phases. Acrotelm and catotelm layer depth was determined on the basis of peat coring results. Water quality indicators were determined using Mettler-Toledo (pH, t°), Evikon (O_2, pH, t°) and WTW (t°, O_2, pH, ORP, electric conductivity and salinity) portable equipment.

Above-ground and below-ground biomass of the herbaceous layer was determined in 1992 in the middle course of Tatra, and in 1997, 2001 and 2003 in the upper course of Sipe. Five replicates of 1×1 m squares were established at each location. Below-ground root biomass was estimated from sequential coring. Three cores were taken from each harvested quadrate from April to September, once every 2 months. In-growth cores (mesh bags $\varnothing$ 40 mm, mesh size 6 mm) used for assessing the herbaceous layer root production were filled with original root-free soil according to soil genetical horizons. Samples were collected during the growing season once after first year and three times in the second and third years. Herb roots were separated from soil by washing. The fresh, oven-dry, and ash-free mass of both the above-ground and below-ground parts of the herbs were estimated (Persson 1983). A total of 5 herbaceous plant associations were sampled at the Tatra, and 11 at the Sipe subcatchment, each sampling site with 5 replicas. All plant material samples for chemical analysis were air-dried (40 °C), ground, and analysed for N using the Kjeldahl procedure and P, Ca, K and Mg contents (APHA 1981). Soil samples were collected from two depths (0–10 cm which is most influenced by roots of herbaceous plants and 30–40 cm below main root zone at border of acrotelm and catotelm) at each piezometer and vegetation community to analyse for N (Kjeldahl), C, P, Ca, K and Mg contents. Phosphorus in the soil was extracted with ammonium lactate and measured using flow injection analysis (Tecator ASTN 9/84), cations were determined from the same solution with the flame photometric method (Ruzicka and Hansen 1981). C content was determined from ash content (at 550 °C) and loss of ignition (at 360 °C).

Meteorological observations

Long-term meteorological analyses were based on data measured at the Tartu Meteorological Station of the Estonian Meteorological and Hydrological Institute. The meteorological station was located in the northern part of the Porijõgi catchment, 5 km north of the transect on the middle course of the Tatra River, and 10 km NW from Sipe River subcatchment transects.

Since 1998, additional meteorological observations were carried out in the upper course of the Sipe River. A GroWeather automatic weather station was installed at the study area in the upper course of Stipe in the middle of the riparian peatland. The following meteorological parameters were registered at 1-hour intervals: minimum, maximum and average air temperatures (°C), soil temperature (°C at 10 cm depth), intensity of solar radiation (W m^{-2}), solar energy (Ly), air pressure (mb), wind speed (m s^{-1}), maximum wind speed (m s^{-1}), wind direction (°), wind chill (°C), precipitation (mm), precipitation intensity

(mm hour^{-1}), relative humidity (%) and dew point (°C). The evapotranspiration rate was estimated according to the Penman-Monteith model (Allen *et al.* 1989).

Climatic seasons

Our 12-year study period (1992–2003) was typical for the climate in the boreo-nemoral zone with a normal range of mean annual temperature and precipitation variation (from 4.6 °C to 7.0 °C and from 414 mm to 696 mm), while it showed a slight increase in temperature, mainly associated with winter and more continental type of precipitation distribution over the course of the study period compared to the average for the climatologically long period (Fig. 2).

Wide range of weather types associated with the process-oriented sampling method of ground water allowed us to analyse nutrient fluxes in mosaic riparian peatland within climatic seasons in context of climatic changes. Each weather event was assumed to have distinctive influence on nutrient flows by altering content of various nutrients in subsurface water, thus being reflected in series of water samples. All observation results were grouped according to weather type and thereupon by climatic seasons. Average value and standard deviation of each nutrient was calculated both for specific weather event and climatic season. Climatic seasons, different

periods of the year distinguished according to strict criteria (Jaagus and Ahas 2000) have their specific sets of weather types and determined directions of weather changes. Climatic seasons begin at different times and have a different duration every year, depending on weather conditions.

Meteorological data from the Tartu station were used to calculate climatic seasons on an annual basis for the period 1891–2003, and to define any climate-induced changes in climatic seasons (Table 1).

According to the linear trend for 1891–2003, climatic seasons changed significantly ($p < 0.05$). Summer (11 days), autumn (5 days), early winter (18 days), and late winter (7 days) have become longer. The decrease in spring (3 days) and late autumn (9 days) lengths are not significant, but the decrease in winter length (29 days) is significant at $p < 0.01$ (Table 1). This tendency is expected to continue with climate change, and will lead to higher instability of weather in the boreo-nemoral zone due to intensive cyclonic activity in the North Atlantic. A significant trend towards milder winters was correlated with an increase in the frequency of freezing and thawing cycles in winter. On the other hand, increasing air temperature was closely related to more frequent and longer drought periods in summer.

To predict the relationship between weather types and pattern of nutrient loss under climate change we used the method of historically analo-

Table 1. Change in climatic seasons during the period 1891–2003 in Tartu. A statistically significant ($p < 0.05$) change in season is shown in boldface. Duration of the seasons and standard deviations are in units of "Days".

Climatic season or period	Average		Standard deviation		Change	
	Start date	Duration	Start date	Duration	Start date	Duration
Early spring	2 Apr.	19	14.6	13.9	–6	1
Spring	21 Apr.	41	10.1	16.6	–5	–4
Spring in total		60		18.3		–3
Summer	1 Jun.	94	13.9	17	–8	**11**
Autumn	3 Sep.	47	8.6	13.5	3	5
Late autumn	20 Oct.	22	11.6	15.5	**8**	–9
Autumn in total		69		15.6		–4
Early winter	11 Nov.	30	13.9	25.1	–1	**18**
Winter	11 Dec.	81	25.2	32.9	**17**	**–29**
Late winter	3 Mar.	31	22.5	19.2	–13	7
Winter in total		141		20.5		–5
Growing season		182		16.7		**13**
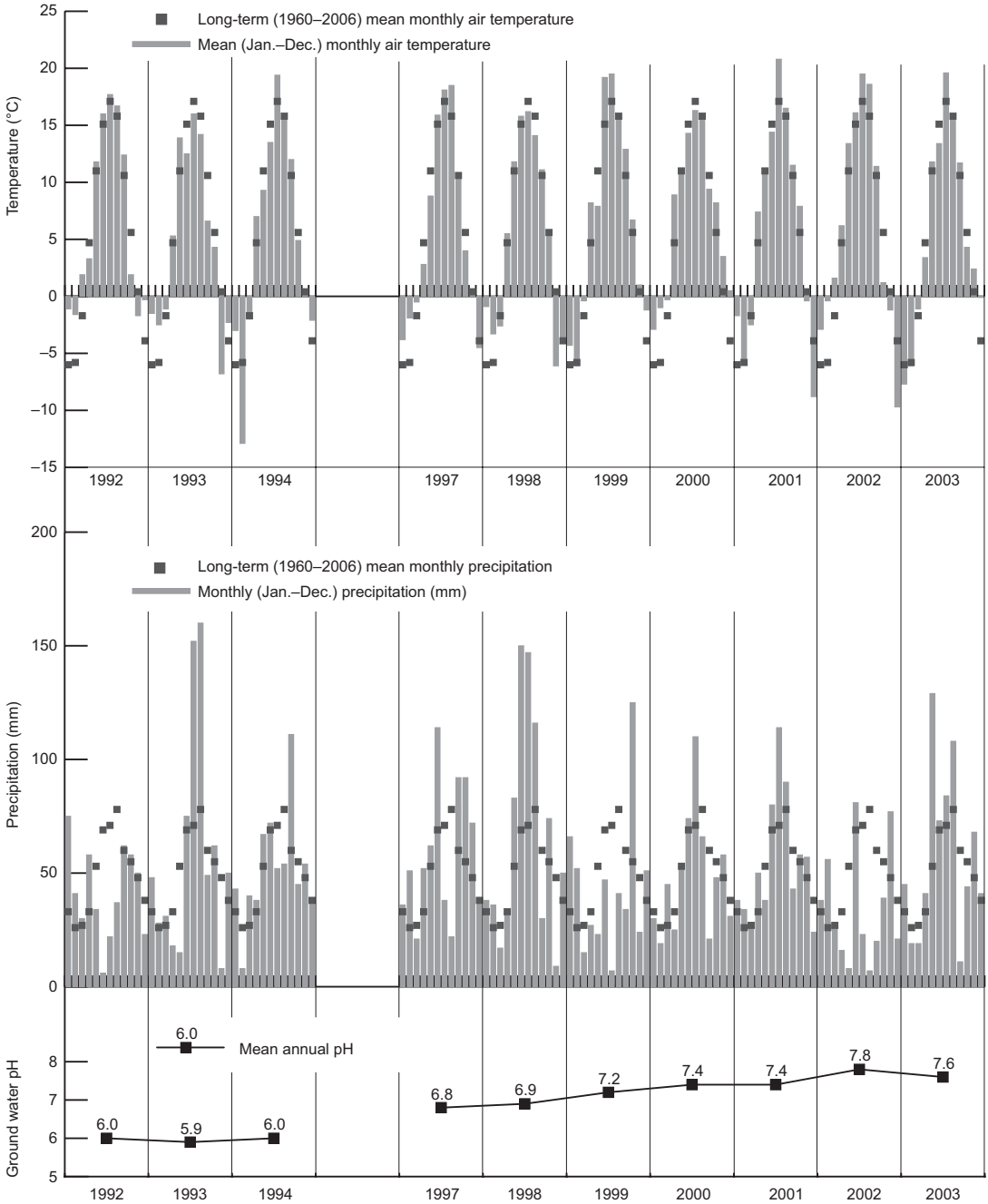
Fig. 2. Mean monthly air temperature (°C) and precipitation (mm) of the study period compared to the long-term average. The lower graph shows the dynamics of the mean annual value of ground water pH in the riparian zone in the study area on the upper course of the Sipe River.

gous years, which is widely used in long-term weather prediction. We assumed that despite of climate change character of all main weather types and climatic seasons will remain the same as nowadays but will have different duration and frequency of occurrence. Therefore linear trends of climatic seasons were extrapolated until 2050 and expected seasonal patterns of nutrients losses

were predicted on the bases of analogous years from observed database.

Statistical analysis of data

The normality of distributions of measured nutrients parameters was tested using Lilliefors' and Shapiro-Wilk's tests (STATISTICA 7.0 software). For normally distributed variables Pearson's correlation was used to correlate groundwater chemistry parameters and to analyse their relationship with weather parameters. The level of significance of $\alpha = 0.05$ was accepted in all cases. Regression analysis was used to analyse a relationship between rainfall amount and water-table level, and to determine water runoff on the basis of measured stream water level.

Results and discussion

The general influence of riparian peatlands on shallow groundwater quality

The most variable water quality parameter in riparian peatland was NH_4-N. The average values of NH_4-N in all piezometers were between 0.005 and 3.7 mg l^{-1} during the first part of the study period (1992–1994). The lowest values (0.005–0.1 mg l^{-1}) were found in sandy soils under arable land. This appears to be the result of relatively good aeration in light soils, which guarantees good conditions for nitrification (*see* Peterjohn and Correll 1984). The highest average ammonium concentrations for the whole period (2–3.7 mg NH_4-N l^{-1}) were under perennial cultivated grasslands that have not been ploughed for at least 7 years. It was also observed that significantly higher NH_4-N concentrations in piezometer water were associated with spring fen communities, owing to mineralization under anaerobic conditions in the peat. The NH_4-N concentration in groundwater from the grey alder forest was lower, averaging less than 0.2 mg l^{-1}.

Nitrite nitrogen values in transects varied very little and were always less than 0.05 mg l^{-1}. This was the same in the case of stream water quality.

The transformation of nitrate nitrogen in riparian ecosystems is complex, NO_3-N concentration normally has a relatively small temporal variation but a high spatial variation. Very high values of NO_3-N (15–25 mg l^{-1} in the lower course of the Sipe River transect) were found in piezometer water under the intensively fertilized arable lands. Under perennial grasslands on mineral soils, the average NO_3-N concentration did not exceed 2.0 mg l^{-1}, and in alder forests the NO_3-N content was always less than 0.5 mg l^{-1}. A significant increase in the average NO_3-N concentration in shallow groundwater was also found in the transition zone between sedge and spring fen communities in the valley bottom of the Tatra River, where the NO_3-N content increased by as much as 6 mg l^{-1}. This was due to seeping groundwater layers that transport nitrate to the valley bottom.

All values of PO_4-P concentration in piezometers were about 30%–40% smaller than P_{tot} values. The correlation between these two parameters was highly significant ($R^2 = 0.85$). Nevertheless, PO_4-P and P_{tot} concentrations varied largely over both time and space. The lowest variations of P_{tot} over time occurred in the transect of the lower course of the Sipe River (less than 20% of mean values over the study period). In the highest piezometer of this transect, the average P_{tot} content reached 1.3 ± 0.31 mg l^{-1}. This was probably the result of local anaerobic conditions in the soil, causing a leachate of orthophosphorus. A significant leaching of phosphorus appeared in the sandy colluvial soil under the cultivated grassland. This was most intensive in summer, when the average P_{tot} content in piezometer water reached 0.6 mg l^{-1}. The average P_{tot} concentration in the piezometer water under the cultivated grassland was 0.25 ± 0.17 mg P l^{-1} for the study period. However, under the wet meadow (*Filipendula ulmaria–Cirsium oleraceum–Aegopodium podagraria* community), the mean P_{tot} concentration and its standard deviation were significantly smaller: 0.10 ± 0.08 mg l^{-1}. A significant decrease in P_{tot} concentration within the spring fen in the transect middle course of the Tatra transect was probably a combined result of deeper groundwater seeping and the mineralization of organic P to orthophosphorus, which was then leached under anaerobic conditions into the fen.

During the second part of the study period (1997–2003), which was warmer, with reduced snow pack and less precipitation, there was no significant change in NO_2-N (0.005–0.14 mg l^{-1}) and NO_3-N (0.1–1 mg l^{-1}), which remained low. NH_4-N was still most variable and dominant among total inorganic nitrogen, with average concentrations between 1–5 mg l^{-1}. However, every year at the end of summer or in autumn (August–October), extremely high NH_4-N concentrations (16–58 mg l^{-1}) were observed at the piezometer located on the border between cultivated grassland and peatland. A similar peak in NH_4-N but on a smaller scale (8–14 mg l^{-1}) was also observed at the neighbouring piezometers (35 m downgradient) located within the riparian peatland (*Filipendula ulmaria* and *Geranium–Anthriscus sylvestris* community). Depending on the year and piezometer, the duration of the high NH_4-N peak lasted from 14–36 days. Extreme NH_4-N peaks always coincided with high PO_4 (2–6 mg l^{-1} instead of average 0.2–0.5 mg l^{-1}), K (10–22 mg l^{-1} instead of average 0.6–3 mg l^{-1}) and pH value (7.5–8.0). The above-average SO_4 concentration (17–30 mg l^{-1}) was usual, but the highest SO_4 concentrations (41–102 mg l^{-1}) did not coincide with maximum NH_4-N concentrations, but instead preceded this event during dry summers. There was also a slight increase in NO_2-N concentration, but no significant change in NO_3-N. It is assumed that this phenomenon of the sudden extreme increase in NH_4-N is related to dissimilatory nitrate reduction to ammonium (DNRA) process. DNRA is a heterotrophic reaction, which can compete with denitrification and assimilatory uptake in controlling the fate of nitrate in a riparian peatland ecosystem and is dependent on pH level (Stevens *et al.* 1998, Brunet and Garcia-Gil 1996). DNRA is potentially an important process because it maintains nitrogen in the system as ammonium, a biologically available form, is a component of oxygen consumption and may potentially play a role in controlling excess N in the environment (Kull *et al.* 2005, Tiedje *et al.* 1988). Tobias *et al.* (2001b) showed that despite high rates of DNRA, the NH_4-N produced was not a long-term repository for groundwater-derived N but was instead rapidly immobilized into marsh particulate organic nitrogen and retained on longer timescales. Several investigations demonstrated that DNRA is a common N transformation process in streams of agricultural landscapes (Kelso *et al.* 1999), in the hyporheic zone of pastoral streams (Storey *et al.* 2004), and in riparian meadows (Revsbech *et al.* 2005) competing with denitrification and sometimes being much more intensive than it (Burger and Jackson 2004). DNRA has even been reported as an important process in mineral soils (Fazzolari *et al.* 1998, Bengtsson and Bergwall 2000, Silver *et al.* 2005, Groffman *et al.* 2006). Our assumption concerning the prevalence of DNRA in the peatland ecotone of the Sipe River supports two measurement series of closed-chamber-based greenhouse gas measurements we carried out in November and December 2006 (*see* methods in Teiter and Mander 2005): the nitrous oxide flux varied from –0.4 to 1.8 μg N_2O-N m^{-2} hour^{-1}, being a magnitude lower than in riparian alder forests, and 2–3 magnitudes lower than that in constructed wetlands for wastewater treatment (Teiter and Mander 2005). Also, a rapid increase in NH_4-N in some piezometers is typical of DNRA and has also been reported by other authors (Burger and Jackson 2004).

In the Sipe catchment, no significant changes in average annual nitrogen and phosphorus concentration in runoff have been measured since 1989. On the other hand, outwash of both nitrogen and phosphorus was observed from some riparian buffers on mineral soils of the Porijõgi, mainly due to the lowering of the initial loading of lateral fluxes from the upland (Kuusemets *et al.* 2001). This outcome suggests that the peatland zones along the Sipe and Tatra rivers can function effectively regardless of initial loadings.

Herbaceous biomass and plant uptake of nitrogen and phosphorus

In 1992 the above-ground biomass of herbaceous plants varied from 469 to 2081 g DW m^{-2} being lowest in the cultivated grassland and highest in the large-sedge community (both in Tatra transect; Table 2).

In the Sipe test area, the above ground biomass was lowest (538 g DW m^{-2}) in the *Geranium* and *Poa* spp. dominated communities and

Table 2. Herbaceous layer biomass (g DW m^{-2}) and plant uptake of nitrogen and phosphorus (g m^{-2}) in various plant communities.

Transect	Vegetation community	Biomass			Nitrogen in biomass			Phosphorus in biomass		
		Above-ground	Below-ground	Total	Above-ground	Below-ground	Total	Above-ground	Below-ground	Total
Tatra	Grassland	904	778	1682	9.7	8.4	18.1	1.14	0.88	2.02
	Cultivated grassland	469	355	824	8.9	3.8	12.7	1.60	0.42	2.02
	Sedge fen	2081	2443	4524	33.3	21	54.3	3.20	2.10	5.30
	Sedge fen	601	1690	2291	8.9	13.2	22.1	0.64	0.65	1.29
	Sedge fen	1369	805	2174	24.4	10.9	35.3	2.44	0.67	4.06
Sipe upper	Sedge	824	302	1126	14.5	4.4	18.9	3.08	0.97	4.05
	Filipendula ulmaria	1021	62	1083	15.4	0.9	16.3	2.06	0.10	2.16
	Geranium spp. and *Poaceae*	538	32	570	8.5	0.7	9.2	1.44	0.08	1.52
	Poaceae and *Vicia cracca*	801	77	878	13.6	1.4	15	1.98	0.14	2.12
	Cirsium oleraceum	661	31	692	15.3	0.6	15.9	2.08	0.07	2.15
	C. oleraceum and *Urtica dioica*	742	87	829	20.1	2.0	22.1	4.16	0.30	4.46
	C. oleraceum and *Geranium* spp.	621	51	672	10.9	1.1	12.0	1.25	0.10	1.35
	Elytrigia repens	808	89	897	19.5	2.0	21.5	1.34	0.14	1.48
	Aegopodium podagraria	957	51	1008	9.5	0.4	9.9	1.59	0.08	1.67

highest (1021 g DW m^{-2}) in the *Filipendula ulmaria* community.

The highest below-ground biomass was also found in the Tatra transect (up to 2443 g DW m^{-2}) where in large-sedge fens the below-ground biomass was significantly higher than the above-ground biomass. The nitrogen uptake by the above-ground and below-ground herbaceous biomass varied from 8.5 to 33.3, and from 0.44 to 13.15 g N m^{-2}, respectively. The corresponding range for phosphorus concentration was 0.64–4.16 and 0.07–2.1 g P m^{-2}; Table 2).

Many studies show that both biomass and nutrient uptake in peatland herbaceous vegetation can significantly vary over a long period depending on phenological aspects, and temporal-spatial variation of biophysical factors (Mander *et al.* 1995, Perez Corona and Verhoeven 1996, Aerts *et al.* 1995, Gusewell and Bollens 2003). In our study, the plant biomass and the N and P uptake data from the Tatra transect are from one year (1992) while the data from the Sipe transect are from three years (1997, 2001 and 2003), therefore, they serve as background information for the interpretation of nutrient dynamics in peatland soil and water.

Water-table dynamics in riparian peatland

In a small watershed with a low relief, water-table level was strongly influenced by seasonal fluctuations in the level of regional groundwater, ephemeral runoff initiated by spring snow melting and episodic precipitation. After a rainy period in autumn (from September to November), when the average monthly precipitation was 62 mm against the norm of 48 mm, the recharge of the peat layer occured in the river valley after a long discharge period from April to July, and the water-table level was close to the ground level. The water-table level gained in late autumn was lasting under a frozen surface through winter, with a minor falling tendency. However, any sustained thaw periods which led to intensive snow melt that also affected the frozen surface were sharply increasing the water level by up to 15 cm. Shorter thaw cycles were observed not to affect the water-table level, but

snow melt water formed an intensive overland flow over the frozen surface. After snow melt during spring, the water-table level was determined mainly by drainage through macropore flow. Precipitation and evapotranspiration were less important in this period, but as the water-table fell, their role was gradually increasing. In summer, when the water table dropped 40–50 cm below the ground level, only major episodic precipitation events (> 10 mm) were reflected in the groundwater level. All minor rainfall events were increasing soil humidity at the acrotelm, and water stored in the surface layer was lost by evapotranspiration. With intensive loss of water by evapotranspiration during summer, the volume of peat sediments in the riparian peatland decreased because of contraction, which led to lowering of the ground level. In areas where the peat deposit was nearly 6 m thick, a difference as large as 32 cm was found between the position of the surface level of the peatland in spring, when the peat layer was saturated with water and had the highest volume, and summer, when the volume was at its smallest.

Special attention has to be paid to the seasonal variation of the water-table level, as it is the most important factor determining general hydraulic flow parameters, and through that, nutrient losses to the river. During a high water-table level, the water exchange rate in the riparian peatland is high. The main water flow is taking place in the subsurface layer; however, in low-lying areas by the riverside, the surface flow often dominates. Intensive rainstorms (precipitation > 15 mm with intensity of > 25 mm hour^{-1}) resulted in an intensive overland flow when the water-table level was high (< 15 cm below ground level), and due to the confined aquifer in low-lying areas, slightly pressured subsurface water appeared (up to 5 cm above ground water column level).

The falling water-table level in summer resulted in a dual character of the water flow. The main water flow took place at a depth of > 50 cm below the ground level and episodic precipitation brought forth a subsurface flow in the acrotelm. Seepage of water in the surface layer induced by individual precipitation events did not lead to water exchange between surface water and groundwater because of a dense peat layer with low permeability between acrotelm and catotelm. The dense peat layer usually occured at a depth of 30–60 cm, marking the greatest depth that was still affected by drought events in summer. The permeability of the dense peat layer increased in the case of wet periods lasting for 2–4 weeks (total precipitation > 50 mm) resulting in an almost homogeneous aquifer. The same processes also took place in autumn, when the acrotelm got saturated and the groundwater level increased stepwise due to precipitation. In such periods when the peat layer permeability is high, the key factors are the amount of precipitation and the intensity of rainfall, rather than the duration and continuity of the rainy period.

After the saturation of the deeper peat layer, the response of the water table to precipitation events is rapid. The water table can rise greatly with a small amount of infiltration. Two processes, air entrapment beneath an inverted water-table and infiltration into the capillary fringe, can cause the water-table to rise more than ten times the amount of infiltration (Gerla 1992). Linear regression between the amount of precipitation x (mm) and water-table rise y (mm) accurately reflects the precipitation-induced change in the water table three and six hours after the event:

$$y_{3h} = 2.63x + 12.3, (R^2 = 0.434) \qquad (1)$$
$$y_{6h} = 4.16x + 17.5, (R^2 = 0.674) \qquad (2)$$

No significant correlation was found in less than three hours after a precipitation event, and correlation begins to decrease after more than nine hours have passed from the rainfall. On average, the precipitation-induced water-table level rise in sites with an average water-table deeper than 50 cm below the ground level reached the maximum within six hours after the precipitation event and started to drop due to subsurface flow via both macropores and micropores (Fig. 3). After three and six hours, the correlation between the precipitation event (mm) and the subsequent water-table rise was significant ($R^2 = 0.434$, $p < 0.05$ and $R^2 = 0.674$, $p < 0.05$, respectively), whereas after nine hours no significant correlation could be found ($R^2 = 0.081$; $p > 0.05$).

In saturated areas (aerated zone < 50 cm) the water-table level was on average highest
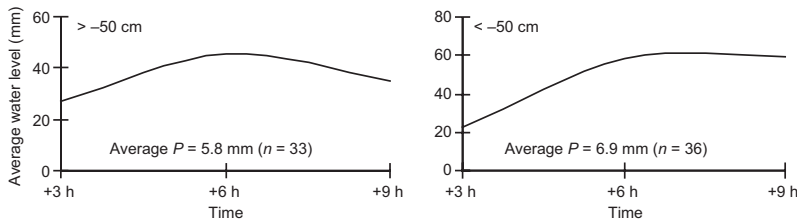
Fig. 3. Water level response (mm) to rainfall (*P*) 3, 6 and 9 hours after precipitation events in areas with a high (< –50 cm) and low (> –50 cm) water-table levels.
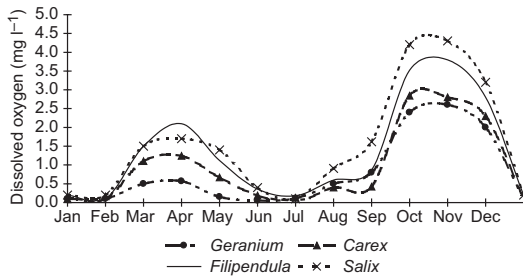
Fig. 4. General annual pattern (1997–1999) of dissolved oxygen concentration in subsurface water according to vegetation type in the riparian zone in the study area in the upper course of the Sipe River.

six to nine hours after the precipitation event, and remained at a high level until the stream discharge and evapotranspiration exceeded the additional acrotelm water flow from the adjacent saturated contributing areas. Thus in regions with a high water-table, the correlation between the precipitation event (mm) and subsequent water-table rise was non-significant after three hours ($R^2 = 0.199$, $p > 0.05$), but showed highly significant values after six and nine hours ($R^2 = 0.811$, $p < 0.01$ and $R^2 = 0.792$, $p < 0.01$, respectively).

The annual course of hydrological parameters and the ephemeral runoff producing events determine to a great extent the biogeochemical processes that contribute to the nutrient release and directly affect nutrient runoff. Any changes in the seasonal weather pattern will result in changes in the local groundwater level, and its effect will appear during later periods via different flow patterns, mineralization rate and stream water chemistry.

Dynamics of dissolved oxygen in riparian peatland

Dissolved oxygen content in the riparian peat-

land is one of the key factors regulating nutrient losses and transformation. Spatial and temporal fluctuations in dissolved oxygen content rather than stable O_2 level, and surface water–groundwater interface play the most important role (Dahm *et al*. 1998, Frazer and Williams 1998).

Dissolved oxygen clearly formed an annual pattern with high oxygen concentration in spring and autumn (Fig. 4).

Low concentration was characteristic of winter and summer. The interannual variation in dissolved oxygen concentration was smallest in spring, when the increase in O_2 concentration is caused by snow melt water. In this period the soil matrix water saturation was exceeded in riparian peatlands. However, weather conditions in winter, such as snowpack, air temperature, the number and duration of thaw cycles had an influence on the O_2 concentration in groundwater, as these parameters reflected the water availability for infiltration in spring after surface thaw. As the temperature rise sets in and the water level started to drop in spring by drainage and evapotranspiration, the dissolved oxygen concentration decreased. The higher the mean air temperature, the faster was the depletion of O_2. An increase in mean air temperature in two weeks within a range of 13 °C, from 9 °C of mean daily temperature to 22 °C, led to a reduction of oxygen in the range of 2.5–3 mg l⁻¹ according to different vegetation patterns. During the whole summer, the concentration of dissolved O_2 remained at a very low level (0–0.8 mg l⁻¹), and oxygen enrichment depended only on individual rainstorms. Since autumn, when frequent rainfalls started, the dissolved oxygen concentration increased gradually after each precipitation event. The highest oxygen concentration (4–8 mg l⁻¹) in groundwater was reached in late autumn, before the surface froze. However, the interannual variation of O_2 in autumn was much higher than that

in spring, because of the more variable hydrological conditions in autumn, depending on the preceding water-table level in summer. The lower the water-table level in summer, and the greater the amount of precipitation in autumn, the higher the dissolved concentration of oxygen (up to 8.7 mg l^{-1}). After a summer with a high water-table level, the groundwater oxygen concentration will remained low (0.5–3 mg l^{-1}), because of the limited vertical water exchange between precipitation and groundwater at high table level. The earlier the surface freezes, the shorter the period when groundwater was enriched with oxygen. Since the surface is frozen, the water exchange becomes limited, and due to low temperature during winter, the dissolved O$_2$ will be used slowly in biogeochemical processes stabilizing at a level of 0.01–0.2 mg l^{-1}. Episodic rises in O$_2$ may take place in winter if a long-lasting thaw (> 1 week) accompanied by intensive snow melt occurs. It generally results in an increase in O$_2$ concentration 4–6 mg l^{-1} in surface water, while the concentration in groundwater changes less, remaining below 0.8 mg l^{-1}.

During the vegetation period and in late autumn, which is a period of intensive decomposition of organic debris, the surface and groundwater oxygen concentrations are influenced by vegetation. Despite a high water-table level in areas dominated by a *Carex* community, the concentration of dissolved O$_2$ was rather low, and exhibited no significant change in periods of quick oxygen depletion in neighbouring areas, as *Carex* species are able to aerate the root zone (Busch and Müller 1998) keeping O$_2$ concentration at a level of least 0.2 mg l^{-1}. A similar effect can be expected also in the case of a *Filipendula* community where dissolved oxygen concentration in the vegetation period does not drop below 0.2 mg l^{-1}. However, in these areas high O$_2$ concentrations in spring and autumn were induced by a higher infiltration rate, which is partly enhanced by higher soil porosity due to the decomposing old root system.

Short-term fluctuations in oxygen content are very common for surface water in summer, and to a smaller extent also for groundwater. The daily variation of O$_2$ in groundwater may reach 1.3 mg l^{-1} after intensive rainfalls, while minor episodic precipitation events (< 5 mm)

only affect the biologically active top layer (< 30 cm). The duration of oxygen fluxes depends mostly on the preceding precipitation event, air and soil temperature, lasting usually 3–12 hours in the acrotelm and from six hours to several days in groundwater.

Influence of ORP on nutrient fluxes

Despite the high variability of ORP, a clear annual trend — generally similar to that of O$_2$ concentration in groundwater — could be found, but the rise in the ORP value was not as strong in spring. Extremely high differences (> 60 mV) existed also between the years. The lowest ORP values occurred in winter under frozen surface conditions (–5 to –150 mV) and in summer (+180 to –290 mV). In spring ORP values usually remained between +40 and –120 mV, and had the highest mean value (–14 mV) in autumn, which was also the only season when ORP had a relatively low variation and stabilized in the range of +30 to –40. However, it should be emphasized that the spatial and temporal variability of ORP can be extremely high: variation of up to 137 mV within an interval of three hours in the same place, and at the same time a variation of 151 mV within a 10 m distance have been observed.

Vegetation patterns coincided closely with areas of similar ORP values and temporal behaviour. The highest mean annual ORP value in groundwater was characteristic of *Filipendula* communities (–1 mV) and *Salix* forests (–11 mV), while it was slightly lower in vegetation patches with equal dominance of *Urtica*/*Filipendula* (–28 mV) and *Urtica* communities (–41 mV). *Carex* communities (–70 mV) and gramineous plants (–111 mV) occurred within regions of low mean annual ORP.

ORP response to weather conditions in areas with different hydrological and vegetation conditions showed clearly different behaviour (Fig. 5). In dry areas with *Geranium* dominance (average water-table depth > 60 cm), the mean ORP value in the period 25 May 1999–18 Feb. 2000 was –101 mV (SD = 86 mV), seasonal variation was very high and changes were rapid. In spring, infiltrated stagnant snowmelt water
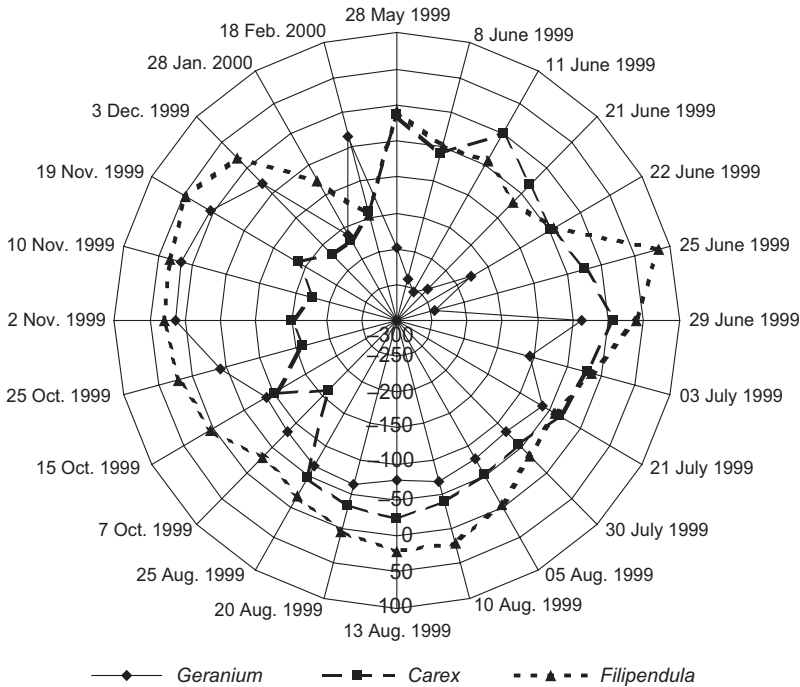
Fig. 5. ORP response to seasonal changes and episodic weather events in plots with different vegetation communities. 28 May 1999: cessation of snowmelt influence; 21–25 June 1999: rainy period (*P* = 29 mm); 20 Aug. 1999: start of long-lasting rainy period in autumn; since 3 Dec. 1999: prolonged cold period (< 0°) with snowcover; 18 Feb. 2000: intensive snowmelt event.

resulted in a low ORP value, which started to increase after rainfalls (21–25 June 1999) as subsurface flow intensified. Intensive infiltration and water exchange due to subsurface runoff were also the main factors increasing the ORP value during a long-lasting rainy period. Contrary to *Geranium* patches in dry areas, the ORP gradually decreased during rainy autumns in low-lying areas with *Carex* dominance, because of the saturated soil. However, in summer when evapotranspiration was higher than precipitation, the ORP value was slightly higher after episodic precipitation events. The lowest changes in ORP were observed in *Filipendula* communities, which naturally have good subsurface drainage. ORP response to the formation of snow- and ice cover was similar for all sites. Snow cover caused a reduction in ORP (–150 to –200 mV), until an intensive snowmelt event resulted in infiltration and water exchange between the stagnant water layer and the surface water.

ORP is a highly variable parameter that depends on the physicochemical properties of groundwater but at the same time causes the alteration of chemical processes taking place in groundwater. It has a strong influence on the nitrogen cycle in the riparian peatland, but through complex chemical processes also on other chemical elements in soilwater.

Highly fluctuating ORP conditions favour intensive denitrification processes. In anaerobic groundwater conditions, decomposition processes result in high ammonium concentrations (3.5–6.6 mg l^{-1}) compared with nitrate (0.005–1.5 mg l^{-1}). Under aerobic conditions, usually after episodic precipitation events or long-lasting dry periods, nitrifying bacteria oxidize ammonium to nitrate. If nitrate is transported to regions with a low concentration of dissolved oxygen, it can be denitrified or, in the sufficient presence of dissolved organic carbon, reduced back to ammonium.

In periods of very low ORP, higher Al and Fe runoff was observed. ORP values about two times lower than the mean annual characteristic for a particular vegetation pattern led to an increase in Al losses 2–4 times higher (up to 0.89 mg l^{-1}) than the mean annual Al runoff. Under the same conditions, Fe concentrations were about twice as high (3.38 mg l^{-1}) as the annual mean. The behaviour of sulphur in a riparian peatland under different ORP conditions is still unclear. Most sulphur release is explained by decomposition and mineralization processes, but

very low ORP in summer indicated the possibility that sulphates could be reduced, which is suggested also by Janssen *et al.* (1998).

## Nutrient fluxes under certain weather events

The long-term monitoring of nutrient runoff in the boreal zone shows a clear annual course with peak flow in the early spring, high nutrient losses in autumn, and the lowest nutrient runoff in summer (Proctor 1994, Mander and Kull 1997, Ulen 1995). Low temperature, thick snowpack (> 20 cm), frozen surface and low water discharge are the main factors that keep nutrient losses at a low level during winter. However, the instability of weather due to intensive cyclonic activity in northern Europe may cause thaw periods of 1–2 weeks which greatly alter surface- and stream-water chemistry (Stottlemyer and Toczydlowski 1996). Milder winters also result in higher runoff in winter, lesser peak flow in spring and a higher share of overland flow above partly melted surfaces, leading to higher N and particulated P losses (Mander and Kull 1997).

In spring, snowmelt water partly enters the unfrozen soil and partly forms overland flow at the frozen surface. The share of infiltration and overland flow can be characterized by the sum of minus degree-days in winter. The faster the rise of air temperature and snow melt, the higher is nutrient loss by overland flow. Nutrient concentration and runoff by infiltrated snowmelt water are high due to intensive leaching from thawed soil and decomposed debris. The high effect of winter frost processes on nutrient release, especially on N_{tot} and Ca in the ecotonal zone, was also clearly demonstrated in Swedish watersheds (Renman 1993). In the riparian peatland in spring, when the groundwater level was close to the surface and both soil matrix and macropore transmissivity were exceeded, overland flow occurred. This led to high nutrient losses but rather low variation in stream water chemistry, where the concentrations remained 4–5 mg l^{-1} for TIN, 0.03–0.06 mg l^{-1} for P_{tot} and 2–10 mg l^{-1} for SO_4.

In summer the water-table level determined mainly the nutrient concentration and runoff in a riparian peatland. In dry summers, when precipitation was less than 150 mm in May–September and the water-table level was more than 50 cm below ground level, the spatial variation in nutrient concentration was high. As compared with the interannual mean value, the concentrations of TIN, NO_2, K and P_{tot} were lower in dry summers, while those of Mg, Ca, NH_4, Fe and Al had a tendency to increase. In wet summers, when precipitation exceeded 500 mm from May to September and the water-table level was only 0–35 cm below the ground level, the nutrient concentration was spatially relatively uniform (1–2 mg l^{-1} NH_4-N, 2–4 mg l^{-1} TIN, 0.04–0.3 mg l^{-1} PO_4-P), but nutrient losses were high due to intensive subsurface flow and high water discharge. However, nitrogen removal was expected to be intensive due to the denitrification process in wetlands and river valleys. As compared with the interannual mean value (Fig. 6A) the concentrations of N_{tot}, NO_2, K and P_{tot} were lower in dry summers (Fig. 6B), while those of Mg, Ca, NH_4, Fe and Al had a tendency to increase. Decreased water discharge kept nutrient losses at a low level. A dry summer followed by intensive rainfalls resulted in a steep increase in nutrient losses and concentration of SO_4 (from 8 to 50 mg l^{-1}), P_{tot} (from 0.03 to 0.6 mg l^{-1}), NH_4 (from 1.8 to 2.9 mg l^{-1}) and NO_2 (from 0.005 to 0.1 mg l^{-1}) (Fig. 6C). A tendency towards increasing concentration was also shown by NO_3, N_{tot}, PO_4 and Ca. Mg and Al showed no clear trend, and the concentration of Fe was slightly decreasing, but clearly falling concentrations after rainfalls were characteristic of K (from 15 to 5 mg l^{-1}). Changes in Mg and K concentrations were mainly due to dilution. Changes in different nitrogen forms during rainy periods (Fig. 6D) indicated highly intensified denitrification, which benefited from (especially after a long drought period) infiltrating precipitation and changes in O_2, ORP and humidity (Burns *et al.* 1996, Flessa *et al.* 1998).

Denitrification fluxes remained high even in late autumn. A very important factor affecting nutrient fluxes is the soil freeze–thaw cycle (Chen *et al.* 1995). Short-term freeze–thaw cycles in autumn promote NO_2 and N_2O fluxes (Fig. 6E), especially the former. The freeze–thaw cycle increased denitrification and nutrient release in the whole riparian peatland, but the magnitude
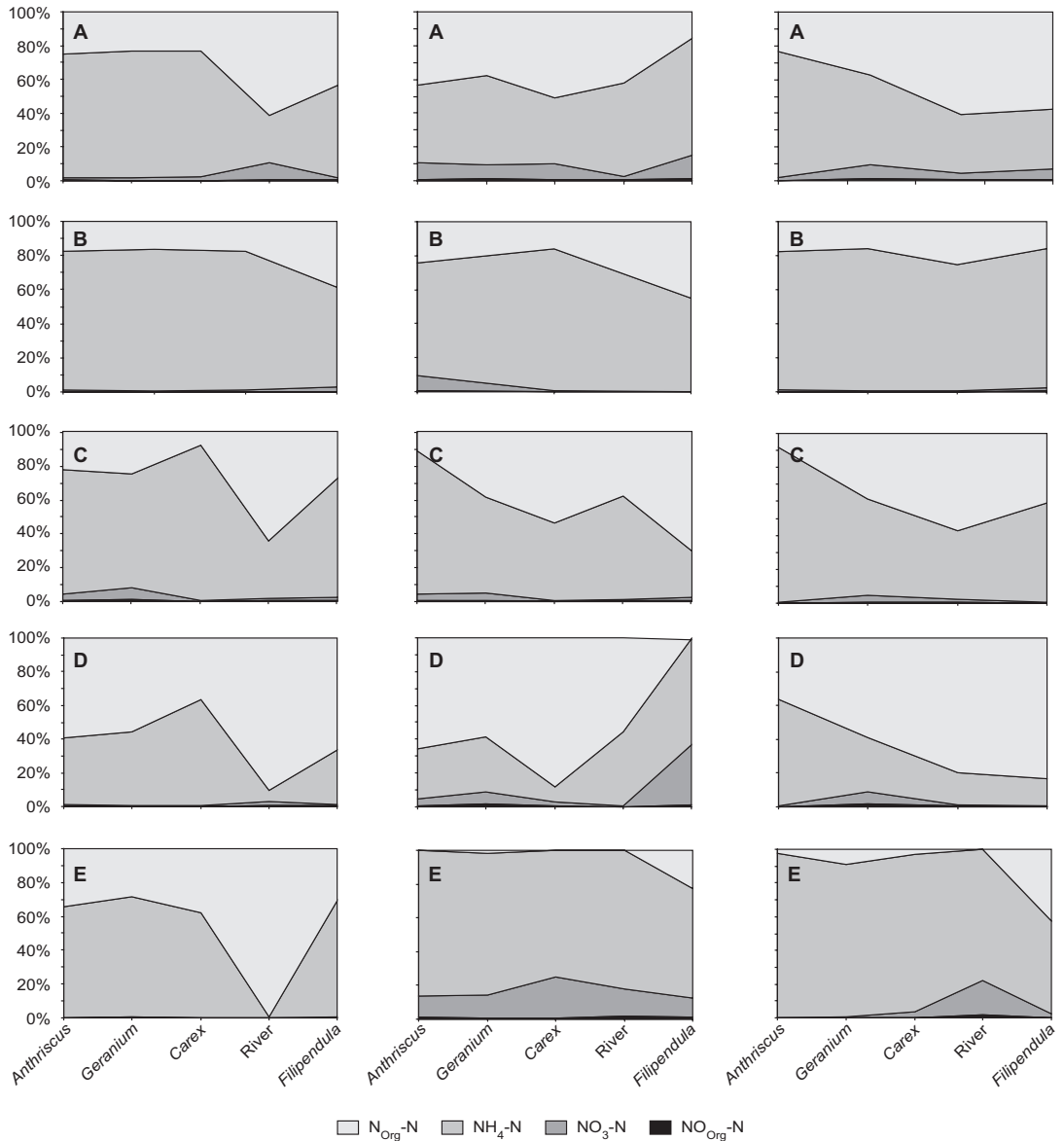
Fig. 6. Response of the nitrogen species in subsurface water to certain weather events according to vegetation type in riparian peatland. — **A**: Average, — **B**: Drought 27 July–30 Aug. 2002, — **C**: Hot, rainy period 20 June–16 July 2001, — **D**: Rainy period 31 May 2000–22 May 2001, — **E**: Before intensive night frost event 2 Oct. 1998 (left-hand-side panel), Intensive night frost event 5 Oct. 1998 (middle panel), After intensive night frost event 15 Oct. 1998 (right-hand-side panel).

of release varied from one vegetation community to another. The highest response was given by the *Carex* community (increase in NO_3 from 0.005 to 1.49 mg l^{-1} and P_{tot} from 0.028 to 0.059 mg l^{-1}), where due to the high water-table level the ice formation probably disintegrated aggregates more effectively. A short high NO_3 flux

was also characteristic of the *Salix* forest (NO_3 from 0.005 to 1.09 mg l^{-1}), while the response in the *Filipendula* community was similar in extent but with a longer time lag. The strongest pulse was triggered by the first strong night-frost episode or frost period, the following freeze–thaw cycles induced gradually weaker fluxes, until the

surface froze in winter and the next strong pulse took place in spring. P_{tot} was observed to be less influenced by frost, but it appeares that P_{tot} release is more complex and it also depends on other parameters (water level, ORP, O_2).

The release of cations showed a different behaviour during the freeze–thaw cycle than did nitrogen or phosphorus (Table 3). In peatland areas, accumulation in biomass is important for Ca, storage on ion exchange sites in peat is most important for Mg, and green plant tissues are the dominant location for K storage. Therefore different communities in floodplains respond differently to cation release during a night-frost event. Mg is not a limiting factor in the *Carex* community, and therefore a frost event did not cause any significant response, while in *Filipendula* (from 2.92 to 3.72 mg l⁻¹) and *Salix* communities (from 2.98 to 4.41 mg l⁻¹), an increased flux of Mg set in after a frost event. Despite the high biomass in a *Filipendula* community, the potassium concentration did not increase after a frost event, as most nutrients had already been allocated in September. Communities with a longer vegetation period, such as *Carex* and *Salix* (K from 1.82 to 3.10 mg l⁻¹), were more strongly influenced by night frost.

Following trends in climatic seasons, the main impact of climate change on riparian peatlands will be expressed both in the annual polarisation of nutrient flows and the increased share of irregular short-term fluxes as compared with the present situation in the boreo-nemoral region. The main nutrient losses will occur in October–April; they are replenished in summer when losses due to water shortage are minimal. Higher cyclonic intensity in winter will cause frequent thaw periods with a duration of 1–2 weeks, which highly alter surface- and stream-water chemistry, leading to higher N and particulate-P losses. Most of the winter will be replaced by the weather types of early and late winter. In spring, when the groundwater level is close to the surface and both soil matrix and macropore transmissivity are exceeded, overland flow will occur. This will lead to high nutrient losses but a rather low variation in stream water chemistry, where the concentrations will remain 3–9 mg l⁻¹ for N_{tot}, 0.06–0.6 mg l⁻¹ for P_{tot} and 12–28 mg l⁻¹ for SO_4. In a wet summer nutri-

Table 3. Magnesium, potassium, nitrogen and phosphorus release during night frost episode in different plant communities.

Date	Min. temp. (°C)	Mg (mg l⁻¹)			K (mg l⁻¹)			NO₃-N (mg l⁻¹)			Total P (mg l⁻¹)		
		Carex spp.	Filipendula ulmaria	Carex spp.	Carex spp.	Filipendula ulmaria	Salix spp.	Filipendula ulmaria	Salix spp.	Salix spp.	Carex spp.	Filipendula ulmaria	Salix spp.
2 Oct. 1998	–0.6	23.40	2.92	2.98	12.05	1.183	1.822	0.005	0.005	0.005	0.028	0.058	0.365
5 Oct. 1998	–8.4	23.80	3.72	4.27	14.28	1.822	3.100	1.49	0.96	1.09	0.059	0.081	0.494
15 Oct. 1998	+6.2	23.00	3.72	4.41	16.20	1.225	2.141	0.22	1.09	0.03	0.038	0.072	0.455

ent concentrations will be spatially relatively uniform (3–6 mg l^{-1} N$_{tot}$, 0.04–0.3 mg l^{-1} P$_{tot}$), but nutrient losses will be high due to intensive subsurface flow and high water discharge. However, nitrogen removal is expected to be intensive due to increased plant uptake and the denitrification process in wetlands and river valleys. As compared with the interannual mean value, the concentrations of N$_{tot}$, NO$_2$, K and P$_{tot}$ will be lower in a dry summer, while those of Mg, Ca, NH$_4$, Fe and Al will have a tendency to increase. Decreased water discharge will keep nutrient losses at a low level. A dry summer followed by intensive rainfalls will result in a steep increase in nutrient losses and the concentration of SO$_4$ (from 8 to 50 mg l^{-1}), P$_{tot}$ (from 0.03 to 0.6 mg l^{-1}) and NO$_2$ (from 0.005 to 0.1 mg l^{-1}). A tendency towards increasing concentrations will also be shown by NO$_3$, N$_{tot}$, PO$_4$ and Ca. Mg and Al will show no clear trend, the concentration of Fe will be slightly decreasing, but clearly falling concentrations after rainfalls will be characteristic for K (from 15 to 5 mg l^{-1}). Changes in Mg and K concentration are mainly due to dilution. Changes in different nitrogen forms indicate highly intensified denitrification, which will benefit (especially after long drought) infiltrating precipitation and changing O$_2$, ORP and humidity. More frequent O$_2$ ingress during climatic extremes could release the enzymic latch mechanism, allowing greater decomposition and mineralization (Freeman *et al.* 2001). Denitrification fluxes will also remain high in late autumn and in early winter. On the other, diversion of water inflows would cause a significant increase in nitrate release and a remarkable decline in nitrous oxide emission. Morover, the experiments carried out by Freeman *et al.* (1997) demonstrate that the wetlands' responses can be instantaneously reversible upon re-initiation of the nitrate inflow, indicating a close hydrological coupling between nitrate removal and nitrous oxide emission processes.

Conclusions

Changing climatic conditions (a significantly shorter winter period and longer summer and growing season), as well as decreasing fertiliza-

tion intensity in the catchment area during the study period (1992–2003) caused the following effects:

- falling water table and significantly lower water discharge due to lower snow depth and missing snowmelt peak flows;
- increasing trend of pH due to decreasing lateral nitrogen flow from adjacent fields.

The following weather events caused a series of changes in nutrient dynamics:

- frequent freezing and thawing cycles in late autumn, winter, and early spring caused an elevated NH$_4$-N level (due to enhanced DNRA), as well as higher P$_{tot}$, PO$_4$-P, Ca, Mg and K concentrations in piezometers (due to the disaggregation of soil aggregates and plant tissues, death and the lysis of microbes);
- drought and torrential rainstorm caused an intensive flux of sulfates, higher NH$_4$-N concentrations during drought, and an intensive flush of organic N and PO$_4$-P during the subsequent rainstorm;
- long lasting (1.5–2 weeks) autumn rainfalls increase the O$_2$ level in soil water and enable vertical exchange between soil horizons;
- highest dissolved oxygen concentrations follow the snowmelt in spring and after the rainy period, low oxygen concentrations are typical of summer and winter by frozen surface.

The mosaic pattern of peatland abiotic and biotic factors causes significant spatial differences in water quality characteristics, which are greater than the temporal variations (the extremely high variability of ORP and conductivity value). In other words, the high patchiness of riparian peatland supports different biogeochemical processes and guarantees buffering efficiency. It results in stable buffering capacity over the long term (since 1989 no significant changes in N$_{tot}$ and P$_{tot}$ in runoff from the catchment have been observed).

In contrast to watershed nutrient runoff investigations with sampling frequency of 1–4 times giving satisfactory results, a comprehen-

sive monitoring of riparian buffers requires a high frequency of sampling and measurements according to weather events, otherwise many important short-term fluctuations cannot be registered.

References

Aerts R., Van Logtestijn R., Van Staalduinen M. & Toet S. 1995. Nitrogen supply effects on productivity and potential leaf-litter decay of *Carex* species from peatlands differing in nutrient limitation. *Oecologia* 104: 447–453.

Allen R.G., Jensen M.E., Wright J.L. & Burman R.D. 1989. Operational estimates of reference evapotranspiration. *Agronomy J.* 81: 650–662.

APHA 1981. *Standard methods for examination of water and waste water*, 15th ed. American Public Health Organization, Washington.

Bechmann M.E., Kleinmann P.J.A., Sharpley A.N. & Saporito L.S. 2005. Freeze-thaw effects on phosphorus loss in runoff from manured and catch-cropped soils. *J. Environ. Qual.* 34: 2301–2309.

Bengtsson G. & Bergwall C. 2000. Fate of 15N labeled nitrate and ammonium in a fertilized forest soil. *Soil Biol. Biochem.* 32: 545–557.

Bonnett S.A.F., Ostle N. & Freeman C. 2006. Seasonal variations in decomposition processes in a valley-bottom riparian peatland. *Sci. Total Environ.* 370: 561–573.

Brunet R.C. & Garcia-Gil L.J. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. *FEMS Microbiol. Ecol.* 21: 131–138.

Burger M. & Jackson L.E. 2004. Plant and microbial nitrogen use and turnover: rapid conversion of nitrate to ammonium in soils with roots. *Plant Soil* 266: 289–301.

Burns L.C., Stevens R.J. & Laughlin R.J. 1996. Production of nitrite in soil by simultaneous nitrification and denitrification. *Soil Biol. Biochem.* 28: 609–616.

Busch J. & Müller P.E. 1998. The gas exchange of *Carex* species and its dependence on soil water and soil oxygen availability. In: Farina A., Kennedy J. & Bossu V. (eds.), *Proceedings of the 7th International Congress of Ecology*, Effa, Florence, p. 66.

Chen Y., Tessier S., Mackenzie A.F. & Laverdiere M.R. 1995. Nitrous-oxide emission from an agricultural soil subjected to different freeze-thaw cycles. *Agr. Ecosyst. Environ.* 55: 123–128.

Cirmo C.P. & McDonnell J.J. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate forested catchments: a reviw. *J. Hydrol.* 199: 88–120.

Dahm C.N., Grimm N.B., Marmonier P., Valett H.M. & Vervier P. 1998. Nutrient dynamics at the interface between surface waters and groundwaters. *Freshwater Biol.* 40: 427–451.

Deluca T.H., Keeney D.R. & McCarty G.W. 1992. Effect of freeze-thaw events on mineralization of soil nitrogen. *Biol. Fert. Soils* 14: 116–120.

Dowrick D.J., Freeman C., Lock M.A. & Reynolds B. 2006. Sulphate reduction and the suppression of peatland methane emissions following summer drought. *Geoderma* 132: 384–390.

Fazzolari E., Nicolardot B. & Germon J.C. 1998. Simultaneous effects of increasing levels of glucose and oxygen partial pressures on denitrification and dissimilatory nitrate reduction to ammonium in repacked soil cores. *Eur. J. Soil Biol.* 34: 47–52.

Flessa H., Wild U., Klemisch M. & Pfadenhauer J. 1998. Nitrous oxide and methane fluxes from organic soils under agriculture. *Eur. J. Soil Sci.* 49: 327–335.

Frazer B.G. & Williams D.D. 1998. Seasonal boundary dynamics of a groundwater/surface-water ecotone. *Ecology* 79: 2019–2031.

Freeman C., Lock M.A., Hughes S. & Reynolds B. 1997. Nitrous oxide emissions and the use of wetlands for water quality amelioration. *Environ. Sci. Technol.* 31: 2438–2440.

Freeman C., Lock M.A. & Reynolds B. 1993. Fluxes of CO_2, CH_4 and N_2O from a Welsh peatland following simulation of water table draw-down — potential feedback to climatic change. *Biogeochemistry* 19: 51–60.

Freeman C., Ostle J. & Kang H. 2001. An enzymic latch on a global carbon store. *Nature* 409: 149.

Freppaz M., Williams B.L., Edwards A.C., Scalenghe R. & Zanini E. 2007. Simulating soil freeze/thaw cycles typical of winter alpine conditions: Implications for N and P availability. *Appl. Soil Ecol.* 35: 247–255.

Gerla P.J. 1992. The relationship of water-table changes to the capillary-fringe, evapotranspiration, and precipitation in intermittent wetlands. *Wetlands* 12: 91–98.

Grant R., Laubel A., Kronvang B., Andersen H.E., Svendsen L.M. & Fuglsang A. 1996. Loss of dissolved and particulate phosphorus from arable catchments by subsurface drainage. *Water Res.* 30: 2633–2642.

Groffman P.M., Altabet M.A., Böhlke J.K., Butterbach-Bahl K., David M.B., Firestone M.K., Giblin A.E., Kana T.M., Nielsen L.P. & Voytek M.A. 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecol. Appl.* 16: 2091–212.

Gusewell S. & Bollens U. 2003. Composition of plant species mixtures grown at various N:P ratios and levels of nutrient supply. *Basic Appl. Ecol.* 4: 453–466.

Harris M.M. & Safford L.O. 1996. Effects of season and four tree species on soluble carbon content in fresh and decomposing litter of temperate forests. *Soil Sci.* 161: 130–135.

Hill A.R. 1978. Factors affecting the export of nitrate-nitrogen from drainage basins in southern Ontario. *Water Res.* 12: 1045–1057.

Høyås T.R., Vagstad N., Bechmann M. & Eggestad, H.O. 1997. Nitrogen budget in the River Auli catchment: a

catchment dominated by agriculture, in southeastern Norway. *Ambio* 26: 289–295.

Hughes S., Reynolds B., Brittain S.A., Hudson J.A. & Freeman C. 1998. Temporal trends in bromide release following rewetting of a naturally drained gully mire. *Soil Use Manage*. 14: 248–250.

Jaagus J. & Ahas R. 2000. Space-time variations of climatic seasons and their correlation with the phenological development of nature in Estonia. *Climate Res*. 15: 207–219.

Jacks G. & Norrström A.-C. 2004. Hydrochemistry and hydrology of forest riparian wetlands. *Forest Ecol. Manage*. 196: 187–197.

Janssen A.J.H., Meijer S., Bontsema J. & Lettinga G. 1998. Application of the redox potential for controlling a sulfide oxidizing bioreactor. *Biotechnol. Bioeng*. 60: 147–155.

Johnsson H., Klemedtsson L., Nilsson A. & Svensson B.H. 1991. Simulation of field scale denitrification from soils under grass ley and barley. *Plant Soil* 138: 287–302.

Järvet A., Mander Ü., Kull A. & Kuusemets V. 2002. Nutrient runoff change in a rural catchment in South Estonia. *Arch. Hydrobiol. Suppl* 141: 305–319.

Kaiser E.-A., Kohrs K., Kücke M., Schnug E., Munch J.C. & Heinemeyer O. 1998. Nitrous oxide release from arable soil: importance of perennial forage crops. *Biol. Fert. Soils* 28: 36–43.

Kelso B.H.L., Smith R.V. & Laughlin R.J. 1999. Effects of carbon substrates on nitrite accumulation in freshwater sediments. *Appl. Environ. Microb*. 65: 61–66.

Kiekbusch J., Schrautzer J. & Trepel M. 2006. Spatial heterogeneity of water pathways in degenerated riverine peatlands. *Basic Appl. Ecol*. 7: 388–397.

Kull A. & Oja T. 2001. Influence of climate change on nutrient flows in boreonemoral floodplain ecosystem. In: Villacampa Y., Brebbia C.A. & Uso J.L. (eds.), *Ecosystems and sustainable development*, Wessex Institute of Techonology Press, Southampton, Boston, pp. 585–594.

Kull A., Kull A., Uuemaa E., Kuusemets V. & Mander Ü. 2005. Modelling of excess nitrogen in small rural catchments. *Agriculture, Ecosystems and Environment* 108: 45–56.

Kuusemets V., Mander Ü., Lõhmus K. & Ivask M. 2001. Nitrogen and phosphorus variation in shallow groundwater and assimilation in plants in complex riparian buffer zones. *Water Sci. Technol*. 44: 615–622.

Liljaniemi P., Vuori K.-M., Tossavainen T., Kotanen J., Haapanen M., Lepistö A. & Kenttämies K. 2003. Effectiveness of constructed overland flow areas in decreasing diffuse pollution from forest drainages. *Environ. Manage*. 32: 602–613.

Lipson D.A., Schmidt S.K. & Monson R.K. 2000. Carbon availability and temperature control the post-snowmelt decline in alpine soil microbial biomass. *Soil Biol. Biochem*. 32: 441–448.

Mander Ü. & Kull A. 1997. Variation of runoff and nutrient fluxes in an agricultural watershed: influence of land use changes and climatic fluctuations. In: Usó J.L., Brebbia C.A. & Power H. (eds.), *Ecosystems and sustainable development. Advances in ecological sciences*, vol. 1, Computational Mechanics Publications, Southampton, Boston, pp. 183–192.

Mander Ü., Kuusemets V. & Ivask M. 1995. Nutrientdynamics of riparian ecotones — a case study from the Porijõgi River catchment, Estonia. — *Landscape and Urban Planning* 31(1–3): 333–348.

Mander Ü., Kull A., Kuusemets V. & Tamm T. 2000. Nutrient runoff dynamics in a rural catchment: influence of land-use change, climatic fluctuations and ecotechnological measures. *Ecol. Eng*. 14: 405–417.

Mander Ü., Kull A., Tamm V., Kuusemets V. & Karjus R. 1998. Impact of climatic fluctuations and land use change on runoff and nutrient losses in rural landscapes. *Landscape Urban Plann*. 41: 229–238.

Martikainen P.J., Nykänen H., Crill P. & Silvola J. 1993. Effect of a lowered water table on nitrous oxide fluxes from northern peatlands. *Nature* 366: 51–53.

McHale M.R., Cirmo C.P., Mitchell M.J. & McDonnell J.J. 2004. Wetland nitrogen dynamics in an Adirondack forested watershed. *Hydrol. Process*.18: 1853–1870.

Müller C., Martin M., Stevens R.J., Laughlin R.J., Kammann C., Ottow J.C.G. & Jäger H.-J. 2002. Processes leading to N₂O emissions in grassland soil during freezing and thawing. *Soil Biol. Biochem*. 34: 1325–1331.

Müller C., Stevens R.J. & Laughlin R.J. 2004. A ¹⁵N model to analyse N transformations in old grassland soil. *Soil Biol. Biochem*. 36: 619–632.

Perez Corona M.E. & Verhoeven J.T.A. 1996. Effects of soil P status on growth and P and N uptake of Carex species from fens differing in P-availability. *Acta Bot. Neerl*. 45: 381–392.

Persson H. 1983. The distribution and productivity of fine roots in boreal forests. *Plant Soil* 71: 87–101.

Peterjohn W.T. & Correll D.L. 1984. Nutrient dynamics in an agricultural catchment: observations on the role of riparian forest. *Ecology* 65: 1466–1475.

Pett-Ridge J., Silver W.L. & Firestone M.K. 2006. Redox fluctuations frame microbial community impacts on N-cycling rates in a humid tropical forest. *Biogeochemistry* 81: 95–110.

Phillips D.H., Foss J.E., Stiles C.A., Trettin C.C. & Luxmoore R.J. 2001. Soil-landscape relationships at a lower reaches of a watershed at Bear Creek near Oak Ridge, Tennessee. *Catena* 44: 205–222.

Proctor M.C.F. 1994. Seasonal and shorter-term changes in surface-water chemistry on four English ombrogenous bogs. *J. Ecol*. 82: 597–610.

Renman G. 1993. Frost formation in the ecotonal zone and its role for release of nutrients. *Hydrobiologia* 251: 65–72.

Revsbech N.P., Jacobsen J.P. & Nielsen L.P. 2005. Nitrogen transformations in microenvironments of river beds and riparian zones. *Ecol. Eng*. 24: 447–455.

Ruzicka J. & Hansen E.H. 1981. *Flow injection analysis*. John Wiley and Sons, Inc., New York, USA.

Ryan M.C., Kachanoski R.G. & Gillham R.W. 2000. Overwinter soil nitrogen dynamics in seasonally frozen soils. *Can. J. Soil Sci*. 80: 541–550.

Scherer H.W., Werner W. & Rossbach J. 1992. Effects of pretreatment of soil samples on N mineralization in incubation experiments. *Biol. Fert. Soils* 14: 135–139.

Scholz M. & Trepel M. 2004. Water quality characteristics of vegetated groundwater-fed ditches in a riparian wetland. *Sci. Total Environ.* 332: 109–122.

Seitzinger S.P. 1994. Linkages between organic matter mineralization and denitrification in 8 riparian wetlands. *Biogeochemistry* 25: 19–39.

Silver W.L., Thompson A.W., Reich A., Ewel J.J. & Firestone M.K. 2005. Nitrogen cycling in tropical plantation forests: Potential controls in nitrogen retention. *Ecol. Appl.* 15: 1604–1614.

Steinheimer T.R. & Scoggin K.D. 1998. Agricultural chemical movement through a field-size watershed in Iowa: Surface hydrology and nitrate losses in discharge. *Environ. Sci Technol.* 32: 1048–1052.

Stevens R.J., Laughlin R.J. & Malone J.P. 1998. Soil pH affects the processes reducing nitrate to nitrous oxide and di-nitrogen. *Soil Biol. Biochem.* 30: 1119–1126.

Stottlemyer R. & Toczydlowski D. 1996. Precipitation, snowpack, stream-water ion chemistry, and flux in a northen Michigan watershed, 1982–1991. *Can. J. Fish. Aquat. Sci.* 53: 2659–2672.

Stottlemyer R. & Toczydlowski D. 1999. Seasonal relationships between precipitation, forest floor, and streamwater nitrogen, Isle Royale, Michigan. *Soil Sci. Soc. Am. J.* 63: 389–398.

Storey R.G., Williams D.D. & Fulthorpe R.R. 2004. Nitrogen processing in the hyporheic zone of a pastoral stream. *Biogeochemistry* 69: 285–313.

Teiter S. & Mander Ü. 2005. Emission of N_2O, N_2, CH_4 and CO_2 from constructed wetlands for wastewater treatment and from riparian buffer zones. *Ecol. Eng.* 25: 528–541.

Tiedje J.M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. In: Zehnder A.J.B. (ed.), *Biology of anaerobic microorganisms*, John Wiley and Sons, New York, USA, pp. 179–244.

Tobias C.R., Anderson I.C., Canuel E.A. & Macko S.A. 2001a. Nitrogen cycling through a fringing marsh-aquifer ecotone. *Mar. Ecol. Prog. Ser.* 210: 25–39.

Trepel M. & Kluge W. 2004. WETTRANS: a flow-path-oriented decision-support system for the assessment of water and nitrogen exchange in riparian wetlands. *Hydrol. Process.* 18: 357–371.

Ulen B. 1995. Episodic precipitation and discharge events and their influence on losses of phosphorus and nitrogen from tiledrained arable fields. *Swed. J. Agr. Res.* 25: 25–31.

Urban N.R., Verry E.S. & Eisenreich S.J. 1995. Retention and mobility of cations in a small peatland — trends and mechanisms. *Water Air Soil Poll.* 79: 201–224.

Vagstad N., Eggestad H.O. & Høyås T.R. 1997. Mineral nitrogen in agricultural soils and nitrogen losses: relation to soil properties, weather conditions, and farm practices. *Ambio* 26: 266–272.