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**Dynamics of vegetation, nitrogen and carbon
as indicators of the operation of peatland buffers**

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Academic dissertation

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ABSTRACT

Forestry in peatlands may result in an increased release of inorganic nitrogen (N), phosphate phosphorus ($\text{PO}_4\text{-P}$), dissolved organic matter (DOM) and solids. Peatland buffers with sedimentation ponds have been constructed in order to prevent leaching of solids and nutrients to the watercourses. Results of peatland buffer functionality have been contradictory probably because the potential nutrient retention capacity of the peat, the biomass of nutrient binding microorganisms and vegetation, and the amount of N liberated in a gaseous form to the atmosphere varies between buffers. Therefore, a detailed knowledge of N cycling in peatland buffers is crucial. In addition, the possible impact of the quality of DOM on nitrous oxide (N_2O) dynamics is unknown.

Three buffers were constructed in eastern Finland: a spruce swamp and a brook margin meadow (constructed prior to our study in 1997) and a spruce-pine mire with lake margin fen during the research period in 2005. Fluxes of N_2O were measured in buffers and a clear-cut area in the catchment of the spruce-pine mire with lake margin fen and the rate of N_2O accumulation was determined for peat profiles cored in the spruce swamp. In addition, the production capacity of $\text{N}_2\text{O-N}$ under different fertilization levels was measured from peat samples cored from the spruce swamp in the laboratory. Nutrient concentrations were measured and DOM characterized by means of DOC from the surface waters entering the buffer and from the vadose water. The quality of DOC was characterized in terms of molecular size fractions and aromaticity indexes. The dynamics of DOM characteristics were related to those of N_2O by evaluating the significance of DOC quality on the N_2O flux. Vegetation cover was monitored temporally and spatially over a three year period in order to evaluate possible vegetation change following buffer construction.

In the buffers and the sedimentation pond, N_2O emissions were low, although fluxes from the sedimentation pond were higher than those from N loaded humic lakes. The rate of N_2O accumulation and N_2O emissions after fertilization were high in the peat samples cored from the spruce swamp indicating a high capacity to produce N_2O if free nitrate (NO_3^-) enters the buffer. However, the observed concentrations of N inflow to the buffers were low; supporting low N_2O emissions even near the water inflow. The presence of low molecular weight DOC seems to be a significant controller for N_2O efflux between the soil and the atmosphere after forestry operations.

Concentrations of $\text{PO}_4\text{-P}$ were occasionally higher in the water outflow than those in the inflow in the buffers indicating a possible nutrient leak. Thus, the changes in vegetation cover reflected an area of effective water flow paths within the buffer rather than eutrophication. Changes in above-ground biomass or its N content did not indicate an increased nutrient binding capacity in the buffer vegetation. Small buffers on organic soils may often have more importance in preventing the flow of solids rather than nutrients. The significance of buffers as a source of the greenhouse gas N_2O was negligible, both because of the low flux rates, and the small area used for water protection.

Keywords: denitrification, DOM, N_2O , $\text{PO}_4\text{-P}$, peatland buffers, peatland forestry

Saari, P. 2014. Kasvillisuuden, typen ja hiilen dynamiikka suometsätalouden pintavalutus-kenttien toiminnan kuvaajina. *Dissertationes Forestales* 173. 49 s.

TIIVISTELMÄ

Suometsätalouden toimenpiteissä vapautuu metsänkäsittelyalueilta epäorgaanista typpeä (N), fosfaattifosforia ($\text{PO}_4\text{-P}$), liukoista orgaanista ainesta (DOM) ja kiintoainetta. Niiden vesistöihin huuhtoutumisen vähentämiseksi metsänkäsittelyalueen ja vesistön tai pienveden väliin jätetään pintavalutuskenttä, jolle metsätalouden valumavedet ohjataan laskeutusaltaan kautta. Pintavalutuskenttien toimivuus riippuu turpeen ravinteiden pidätyskyvystä, ravinteiden sitoutumisesta mikrobi- ja kasvibiomassaan sekä typen vapautumisesta kaasumaisessa muodossa ilmakehään. Typen kierron tunteminen pintavalutuskentillä olisikin tärkeää. Myös DOM:n laadun merkitys dityppioksiidi- eli N_2O -dynamiikkaan on vielä epäselvä.

Itä-Suomessa tutkittiin kahta aiemmin ja yhtä tutkimuksen aikana perustettua pintavalutuskenttää: korpi- ja luhtaniittykenttä oli perustettu 1997 sekä järvenlaidenevakenttä 2005. Kentiltä ja järvenlaidenevan yläpuoliselta hakkuualueelta mitattiin N_2O -vaihtoa sekä määritettiin turveprofiilin N_2O -kertymänopeutta korpikentältä kairatuista näytteistä. Laboratoriokokeella tutkittiin eri lannoitetasojen vaikutuksia N_2O :n vapautumiseen korpikentältä kairatuista turvenäytteistä. Lisäksi kentille saapuvasta ja lähtevästä vedestä sekä vajovedestä määritettiin ravinnepitoisuuksia sekä DOM:n määrää ja laatua DOC:n kautta yläpuolisella valuma-alueella sekä tutkittiin DOM:n vaikutusta N_2O -dynamiikkaan ja arvioitiin DOC:n laadun merkitystä N_2O -vuolle. Myös kasvillisuusmuutosta seurattiin kolmen vuoden aikana tarkkaillen pintavalutuskentän perustamisen vaikutusta kasvilajistoon ja lajien peittävyksiin.

Pintavalutuskenttien ja järvenlaidenevan laskeutusaltaan N_2O :n tuotto oli vähäistä, vaikka laskeutusaltaan N_2O -päästö ylittikin typpikuormittuneiden humuspitoisten järvien päästöt. N_2O :n kertymänopeus ja lannoitekokeen N_2O :n päästö olivat korkeita, minkä perusteella pintavalutuskentiltä vapautuisi N_2O :a, mikäli sinne saapuu nitraattia (NO_3^-). Kentille tulevasta vedestä mitatut epäorgaanisen typen pitoisuudet olivat alhaisia, mitä tukee myös vähäinen N_2O :n tuotto jopa lähellä laskeutusallasta. Pienen molekyylipainon DOM:n saatavuus vajovedessä näyttäisi olevan merkittävä maaperän ja ilmakehän välisen N_2O -vuon säätelijä metsätaloustoimenpiteiden jälkeen. $\text{PO}_4\text{-P}$:n pitoisuus kentältä lähtevässä vedessä ylitti ajoittain tulevan veden pitoisuuden, mikä kertoo mahdollisesta ravinteiden huuhtoutumisesta pintavalutuskentältä. Kenttien kasvillisuusmuutokseen ei luhtalajien lisääntymisen ja metsälajiston taantumisen perusteella viitannut ravinteisuuden lisääntymiseen, vaikka osoittaakin alueen, jolle pintavalutus kohdistuu. Myöskään kasvillisuuden maanpäällinen biomassa tai sen typpipitoisuus ei kerro lisääntyneestä ravinteiden pidätyksestä pintavalutuskentillä. Pinta-alaltaan pienillä pintavalutuskentillä on todennäköisesti enemmän merkitystä kiintoaineen kuin ravinteiden pidättäjinä. Kasvihuonekaasujen vapauttajina pintavalutuskenttien merkitys N_2O :n osalta todettiin vähäiseksi ja jo pintavalutukseen käytetyn pienen pinta-alan vuoksi kaasupäästöjen merkitys on marginaalinen.

Asiasanat: denitrifikaatio, DOM, N_2O , $\text{PO}_4\text{-P}$, pintavalutuskenttä, suometsätalous

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Kokkola 6.1.2014

Päivi Saari

LIST OF ORIGINAL ARTICLES

This thesis is based on the following papers, which are referred to in the summary by their Roman numerals:

- I Saari P., Saarnio S., Kukkonen J.V.K., Akkanen J., Heinonen J., Saari V., Alm J. (2009). DOC and N₂O dynamics in upland and peatland forest soils after clear-cutting and soil preparation. *Biogeochemistry* 94: 217–231.
DOI 10.1007/s10533-009-9320-1

- II Saari P., Saarnio S., Saari V., Heinonen J., Alm J. (2010). Initial effects of forestry operations on N₂O and vegetation dynamics in a boreal peatland buffer. *Plant and Soil* 330: 149–162.
DOI 10.1007/s11104-009-0188-6

- III Saari P., Saarnio S., Saari V., Heinonen J., Alm J. (2013). Emissions of N₂O from peatland buffer receiving water flows from catchment with peatland forestry. *Boreal Environment Research* 18: 164–180.
<http://www.borenv.net/BER/pdfs/ber18/ber18-164.pdf>

- IV Saari P., Saari V., Luotonen H., Alm J. (2010). Vegetation change in peatland buffer as an indicator of active areas of run-on from forestry. *Annales Botanici Fennici* 47: 425–438.
<http://www.sekj.org/PDF/anb47-free/anb47-425.pdf>

Author's contribution

The idea to study nitrous oxide and methane emissions, dissolved organic matter characteristics and vegetation change in peatland buffers was that of my supervisors Jukka Alm, Jussi V.K. Kukkonen and Sanna Saarnio. I participated in the planning, field measurements and fertilization experiment, and I decided the themes of the articles. I was also responsible for the collection of the data, which were collected with the assistance of Veli Saari, many trainees and laboratory staff in the Finnish Forest Research Institute in Joensuu Research Unit and research assistants in Nurmes office. I analyzed the data with Jaakko Heinonen and Jukka Alm. I was responsible for the interpretation of the results and the writing of the manuscripts, which the co-authors have commented upon. I am the corresponding author for all the publications.

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1 INTRODUCTION

1.1 Regulation of peatland forestry in Finland

There are about 4.8 million hectares of peatlands drained for forestry in Finland (Finnish Statistical Yearbook... 2011, p. 55). Finnish society has favored the use of peatland forests. In 1928, in the Forest Improvement Act (140/1928), forest drainage of peatlands was encouraged by the subsidization of ditching practices. During the 1960s, government funds were especially earmarked for forest drainage via the forestry financing programs (MERA I–III). Forest drainage operations peaked in the 1960s, when in 1969 alone a total of 295 000 hectares were drained (Paaivilainen and Päivänen 1995). Ditching has caused a leaching of solids and nutrients to the watercourses and has demonstrated the need for water protection.

After the initial drainage, supplementary drainage and cleaning of the ditches have been considered necessary to maintain the drainage effect. After 1987, ditch cleaning could receive government funding and in the Financing of Sustainable Forestry Act (12.12.1996/1094) funding of ditch cleaning was ensured. In the 2000s, this Act was renewed (11.5.2007/544) to also include funding of ditch networks, digging of supplementary ditches, water protection measures and the building of drainage area edge roads. Under this Act, a water protection plan is pre-supposed.

The aims of (1) decreasing the load of solids and nutrients that enter water courses due to the forestry enterprises and (2) limiting the negative impacts of that load, have been included in the following decisions-of-principle: the Guidelines for water protection by 2015 (Decision of principle by the government 23.11.2006) and the National Forest Program 2015 (Decision of principle by the government 27.3.2008). Government decisions of principles are closest to political statements, intended to guide authorities in administrative preparations. The final objective is to achieve a good ecological level in aquatic ecosystems by 2015, in accordance with the Water Framework Directive of the European Union (2000/60/EY). The adverse effects of peatland forestry on the watercourses have been regulated through legislation (predominantly in the Water Act 587/2011, the aim of the Act on Regulation of Water and Sea Treatment 30.12.2004/1299 and change 272/2011, the Environment Protection Act 4.2.2000/86, and the Forest Act 12.12.1996/1093 and change 1085/2013).

According to the 11th National Forest Inventory (VMI 11) the growing stock on peatland forests amounts to 519 million m³ (Finnish Statistical Yearbook... 2011, p. 69), which corresponds to about 25% of the total growing stock in Finland. Of the total annual increment of 85.2 million m³ y⁻¹ on all forest land in Finland, the annual increment of peatland forests is 24% (Tomppo 2005, p. 33, 9th National Forest Inventory, VMI 9). Costs of peatland forestry are higher than those in upland forestry, so public funding is an effective way to increase or decrease peatland forestry operations and to affect the amount and quality of water protection operations.

Besides legislation, forest drainage is nowadays restricted by forest certification. About 95% (20.7 million hectares) of the commercial forests in Finland are included in and use the badge of the Finnish Forest Certification System (FFCS), which is part of the Programme for the Endorsement of Forest Certification Schemes (PEFC). A few years ago, less than 1% were included in the Forest Stewardship Council (FSC) certificate program (the Finnish Forest foundation 2005) by 2013, however, the areas involved amounted to 460 000 ha (Forest Stewardship Council 2014), which equates to over 2% of the Finnish forest area (22.1 million ha, Finnish Forest Research Institute 2014). The criteria of the forest certification prohibit drainage of pristine peatlands (PEFC FI 1002:2009 criterion 2.11, PEFC FI 1003:2009 criterion 2.9, FSC criterion 6.4.1.2).

1.2 Increased loading of solids and nutrients, and other environmental impacts of peatland forestry

About 2.7 million hectares of peatland forests are ready for harvesting or improvement of sapling or young stands, and on 1.7 million hectares the need for ditch cleaning is imminent (Tomppo 2005, p. 35). The increase in ditch cleaning may also enhance the negative environmental impacts of forestry especially to water courses. The drainage of peatlands has also negative climate impacts because under the aerobic conditions that follow drainage carbon (C) is released from the peat to the atmosphere as carbon dioxide (CO₂) particularly in nutrient rich sites, where ditch cleaning is economically profitable (see Ojanen et al. 2010). At the same time, the production of methane (CH₄) and often also nitrous oxide (N₂O) decreases, but this does not compensate for C release. In addition, biodiversity of the peatlands is decreased as a consequence of large scale drainage.

Drainage also affects the hydrology of the surrounding areas; intensifying and causing extreme runoffs in the downstream of the catchment, which increases erosion with an enhanced load of solids (see e.g. Finér et al. 2010). Finér et al. (2010) estimated the annual background leaching from unmanaged forested catchments in Finland to be on average 5.1 kg solids ha⁻¹ (range from 0.92 to 47.5 kg ha⁻¹ y⁻¹). Peatland ditch maintenance increases the solid load by about 420 kg ha⁻¹ during the first year after ditch cleaning if sedimentation ponds are used as water protection methods. In the tenth year, the increased load is only about 7 kg ha⁻¹. From old ditch networks the solid load is about 11 kg ha⁻¹ y⁻¹ (Joensuu et al. 2002). However, Marttila and Kløve (2012) noticed, that the total load estimation of sediment from peatland drainage must be based on continuous turbidity measurements because the calculated load from continuous turbidity measurements and from individual water samples differ greatly.

Forest management practices increase nutrient loading in the watercourses (e.g. Joensuu et al. 2002; Nieminen 2003 and 2004; Finér et al. 2010; O'Driscoll 2011). Background leaching from unmanaged forested catchments in Finland is on average 1.3–1.4 kg N_{TOT} ha⁻¹ y⁻¹ and 0.05–0.054 kg P_{TOT} ha⁻¹ y⁻¹ (Kortelainen et al. 2006; Mattsson et al. 2003). From old ditch networks the nutrient load is about 2.0 kg N_{TOT} ha⁻¹ y⁻¹ and 0.15 kg P_{TOT} ha⁻¹ y⁻¹ (Joensuu et al. 2002). Properly chosen, dimensioned and effectively carried out water protection methods may decrease the load in watercourses significantly.

The solid and nutrient loads from forestry in general (Table 1) mainly emanate from large-scale forest regeneration, ditch cleaning and fertilization enterprises (Finér et al. 2008). For instance, in 2010, a total of 729 000 hectares of forest were felled, 98 000 hectares underwent soil preparation, 59 000 hectares received ditch cleaning and supplementary ditching and 45 000 hectares were fertilized (Finnish Statistical Yearbook... 2011, p. 131).

Despite the large areas of forest and the magnitude of annual forest operations, the proportion of the nutrient load from forestry is not remarkable in Finland: of the total anthropogenic load that burden aquatic ecosystems forestry accounts for about 8% and less than 6% of the loads of P (phosphorus) and N (nitrogen), respectively (Finnish Environment Institute 2009). Despite the relatively low loads, the high spatial extent of forestry makes leaching widespread, particularly as it is directed at small headwaters, where other anthropogenic loading is often low. In this thesis, attention is paid only to the nutrients P and N.

Although the nutrient load, and not the solid load, is interpreted as contamination under the Water Act (587/2011), the most adverse effect on water courses is probably the strong increase of the solid load caused by ditch cleaning (e.g. Heikurainen et al. 1978; Ahtiainen 1992; Ahti et al. 1995 and 2005; Joensuu et al. 2002; Nieminen et al. 2005a). The volume of

Table 1. Effects of forestry operations for N, P, and DOC leaching. The symbol “+” means increased leaching, symbol “-“ decreased leaching and “+/-“ no change.

Forestry operation	Nitrogen	Phosphorus	DOC	Remarks	Reference
Harvesting and soil preparation	+ (NH ₄ ⁺ , NO ₃ ⁻ and organic	+ (PO ₄ ³⁻), short duration and slightly, bound to Al and Fe oxides	+, short duration	On upland mineral soils, from below B-horizon over the five years	Piirainen et al. 2004 and 2007
	+ (N _{tot} , NO ₃ ⁻ , NH ₄ ⁺)	+ (PO ₄ ³⁻)		Peatland forests	Ahtiainen 1992
	+ (DON, NH ₄ ⁺ , NO ₃ ⁻)	+/-	+	During a 3-year period	Nieminen 2004
		+/-	+/-	Ground water, peat and mineral soils	Mannerkoski et al. 2005
Peatland drainage and ditch cleaning	+ (NO ₃ ⁻), - (N _{tot} , NH ₄ ⁺)	+ (P _{tot}), - (PO ₄ ³⁻)	-	Drainage	Lundin and Bergquist 1990
	+ (NH ₄ ⁺ , NO ₃ ⁻), - (organically bound)		- or +	Ditch cleaning	Ahti et al. 1995 and 2005
		+ or -	-	Ditch cleaning	Joensuu et al. 2001a,b and 2002
		+ (from restoration area)		Peatland restoration	Vasander et al. 2003
Fertilization			+	Drainage	Sallantausta 1995
			-	Ditch cleaning	Heikurainen et al. 1978
		+			Liljanemi et al. 2003
	+/-	+/-		NP-fertilization, upland mineral soils	Saura et al. 1995
	+		PK-fertilization, peatlands	Saura et al. 1995	
	+/-		Iron-PK-fertilizer	Nieminen 2005	
	+/-		Urea*, during the soil frost-free period	Nieminen and Ahti 1993 and 2000	

* Normally peatland forests are not fertilized with fertilizers containing N (Päivänen 2007).

the solid load may increase by over 200-fold from the pre-treatment level (Ahtiainen 1992); e.g. after ditch cleaning the increase in the solid load is on average $420 \text{ kg ha}^{-1} \text{ y}^{-1}$ in the first year after operations (Finér et al. 2010). Solids are also released from soil preparation and energy wood and stump harvesting.

Solids have multiple effects on the watercourses. Solids may cover the spawning grounds or the habitats of fishes and other organisms. In addition, the profile of the watercourses may change (e.g. deep parts can be filled with sediments) or matter may serve as new habitats for new colonizing vegetation. The decomposition of the organic fraction may cause an oxygen deficiency, which may result in the death of organisms e.g. fishes. Solids may also bind and carry nutrients. Nutrient loading causes eutrophication, which may result in a change in the species composition in the ecosystem, eventual mass occurrences of some species, which in turn have implications for the recreational use of at least some parts of the watercourses.

In addition to solid and nutrient loading, the release of dissolved organic matter (DOM) after the forestry operations (e.g. Nieminen 2004; Piirainen et al. 2007; Morris 2009) may play an important role as a nutrient source for microbes in the recipient watercourses (e.g. Killham 1994). Besides dissolved nutrients, DOM also contains dissolved organic carbon (DOC), which is a source of C and energy for micro-organisms (e.g. Killham 1994; Qualls and Richardson 2003; Jansson et al. 2006). DOM with dissolved nutrients and C may promote an eutrophication process. In the near future, there will be a need for more water protection measures within the scope of peatland forestry.

1.3 Water protection methods in peatland forestry and their effectiveness in solid and nutrient retention

The water protection measures in peatland forestry typically include various methods of slowing down the current exiting the site: sedimentation ponds, silting pits, bottom dams, ditch breaks in and breaks in ditch cleaning lines as well as peatland buffers and other types of infiltration areas (Metsätalouden kehittämiskeskus Tapio 2007, p. 19; Päivänen 2007, p. 288). Infiltration areas may include different types of peatland buffers, buffer strips or wetlands (contains wet areas with deep and shallow water levels; also often open water areas) differing, for example, in size, mire classification type and distance to watercourse. The moderation of the water flow from the ditch cleaning area to the water courses with different types of dams or other above-mentioned methods may not only decrease the load of solids, but may also reduce runoff peaks in the downstream ditches. Intensive planning of ditch cleaning is recommended as one method to achieve a good ecological level in the aquatic ecosystems by 2015 (the Water Framework Directive of the European Union 2000/60/EY).

The most common water protection method in forestry is probably buffer strips. This is because felling is the most common forestry practice method (Finnish Statistical Yearbook... 2011, p. 131) and certification requires the installation of buffer strips. In peatland forestry, and especially in ditch cleaning (59 000 ha in 2010, Finnish Statistical Yearbook... 2011, p. 131), the primary methods used are silting pits, ditch breaks and breaks in ditch cleaning lines and sedimentation ponds. In addition, different types of peatland buffers or wetlands may be used to intensify the water protection measures. However, not all possible methods are commonly applied, or are applied only at a small scale level. Structures for peak runoff control (PRC) techniques are probably more commonly used for water protection than buffer areas or wetlands e.g. in Central Finland. The PRC method is described by Marttila (2010).

Knowledge of the effectiveness of buffer strips, silting pits, ditch breaks and breaks

ditch cleaning lines is minimal. Instead, the effectiveness of sedimentation ponds, PRC and peatland buffers have been studied. Coarse mineral subsoil or peat particles effectively stay in the sedimentation ponds but finer suspended solids may reach the buffer zone (for related work see e.g. Joensuu et al. 1999; Nieminen et al. 2005a; Silver et al. 2009). Factors affecting sediment accumulation in the sedimentation ponds are residence time, already accumulated sediment volume, the amount of water, flow rate, surface load, and characteristics of the subsoil in the drainage basin (Joensuu 1997; Joensuu et al. 1999). Decrease in the residence time or an increase in any of the other mentioned factors above reduces sediment accumulation in the ponds. Correctly sized sedimentation ponds may even retain over 90% of the solid material entering the pond (Joensuu et al. 1999). In practice, only half of the sedimentation ponds measured 1–3 years after forestry operations reduced the concentration of suspended solids and their average reduction was only 30%. Sedimentation ponds are often so small and flow rates so high, that only the largest particles can accumulate (Joensuu 1997). In PRC structures, the average reduction in loads of suspended solids, total P and total N was 86%, 67% and 65%, respectively in seven peatland forestry drainage sites in Central Finland (Marttila 2010, p. 68). The P and N retention occurred mainly through retention of particle-bound nutrients. Similarly to PRC, most other water protection methods moderate the discharge by providing longer retention times for the eroded sediment; i.e. Johannesson et al. (2011) reported that the dominant retention process was sedimentation in constructed wetlands. Thus, efficiency of water protection methods depends on the soil type of the catchment and its characteristics and may change on a case-by-case basis.

In some cases, water protection has been improved by peatland buffers constructed specifically to enhance solid and nutrient binding. The good practice guidance by Metsätalouden kehittämiskeskus Tapio (2007, p. 71) and Joensuu et al. (2012, p. 65) recommends that a peatland buffer should consist of at least 1% of the whole catchment area (maximum 50 hectares). The waters entering the buffer should be distributed evenly over the area without shortcut streams. Furthermore, flooding downstream must not reach the buffer in order to prevent bound solids and nutrients leaching to the watercourses. Peatland buffers constructed as recommended may reduce the loads of solids by over 70% (Nieminen et al. 2005a) and nutrients (N and P) by over 90% (Silvan et al. 2002, 2003 and 2004; Väänänen et al. 2008; Hynninen et al. 2010). After all, buffers are specific in their retention characteristics. They may even release more nutrients than they bind (see e.g. Sallantausta et al. 1998; Hynninen et al. 2011). The biogeochemical processes behind the observed net retention or release are incompletely known.

1.4 The fate of retained nutrients and carbon

1.4.1 Nitrogen

In nutrient addition experiments that simulated the leaching process, about 70% of added N was shown to be retained in the vegetation (Silvan et al. 2004), about 15% in the microbial biomass (Silvan et al. 2003) and about 15% was released as a gaseous form to the atmosphere (Silvan et al. 2002). Although those studies indicated that all the N was retained in the buffer or released to the atmosphere from the buffer, Hynninen et al. (2011) reported that buffers may release ammonium ($\text{NH}_4\text{-N}$) into through-flowing waters if the concentrations in the buffer inflowing waters are near the background levels of the upper forested catchment areas before forestry operations.

For N immobilization, the role of microbes may be more important than that of plants (Vitousek and Matson 1984), although the transformation mechanisms can vary. Heikkinen et al. (1994) and Vought et al. (1994) suggested that denitrification may be the most significant way to decrease inorganic N in through-flowing waters by converting it to a gaseous form within buffers constructed for peat mining and agriculture. N_2O may be a by-product of nitrification under oxic conditions (Fig. 1a). N may also be released under anoxic conditions through denitrification e.g. as N_2O or dinitrogen (N_2 , Fig. 1b, e.g. Heikkinen et al. 1994; Silvan et al. 2002; Liikanen et al. 2006).

In their nutrient addition experiment, Silvan et al. (2002) found that N_2O emissions greatly increased in the peatland buffer making it a N_2O hot spot. Hot spots can be considered as areas with emissions distinctively higher than those in the surroundings. Silvan et al. (2002) reported emissions from 5 to 20 kg N $ha^{-1} y^{-1}$ (corresponding to average daily fluxes from 1.4 to 5.6 mg $N_2O-N m^{-2} d^{-1}$) from low and high NO_3^- additions, respectively. In contrast, Liikanen et al. (2006) reported low N_2O emissions (0.22–0.29 mg $N_2O-N m^{-2} d^{-1}$) from a buffer constructed 5 to 15 years earlier to purify peat mining runoff waters: however, N loading increased N_2O emissions compared to the pristine level (-0.02–0.13 mg $N_2O-N m^{-2} d^{-1}$, Regina et al. 1996).

If the catchment is not a source of N_2O , extra nutrients in the buffer might potentially make it a hot spot and the catchment an overall source of N_2O . Gas exchange would seem to depend on the area of active forest management, its hydrology and the impact of operations on hydrological conditions. Drainage of peatlands and peatland forests change soil conditions (Von Arnold et al. 2005; Macrae et al. 2013) and drained N-rich (low C:N ratio) peatland

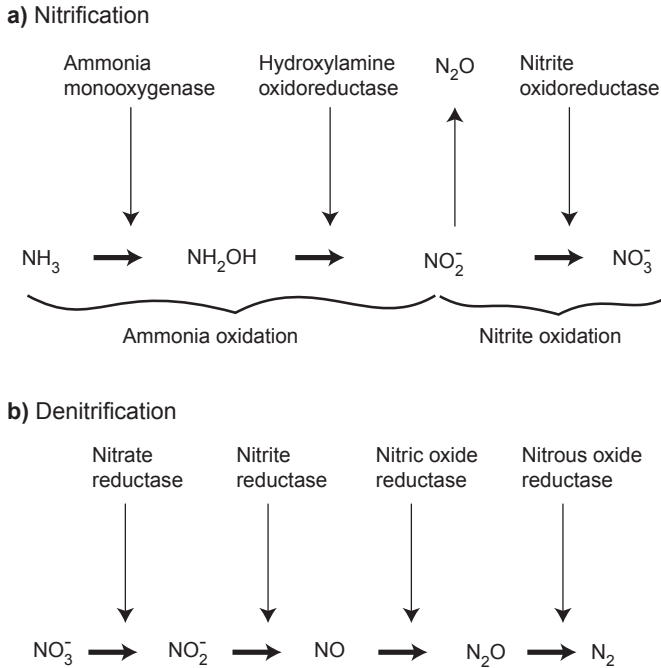


Figure 1. a) Nitrous oxide is a by-product of nitrification. **b)** N_2O release as a by-product of denitrification, which produces N_2 as an end product. Figures are modified from Wrage et al. (2001).

forests may be a significant source of N_2O (Nykänen et al. 1997; Regina et al. 1998). Von Arnold et al. (2005) reported flux rates of 20 to 30 $mg\ m^{-2}\ y^{-1}$ (corresponding to daily averages from 0.04 to 0.05 $mg\ N_2O-N\ m^{-2}\ d^{-1}$) in undrained organic soil sites compared to 30 to 90 $mg\ m^{-2}\ y^{-1}$ (0.05 to 0.16 $mg\ N_2O-N\ m^{-2}\ d^{-1}$) in drained sites. Schiller and Hastie (1996) did not find any increase in N_2O fluxes caused by drainage. Klemetsson et al. (2005) found a strong negative relationship between N_2O emissions and soil C:N ratios. The emissions from drained forested soils increased with time if the soils were kept well drained and the C:N ratio declined. N_2O emissions may also increase as a result of prolonged soil frost, which increase the soil NO_3^- concentration in winter and early summer at least in the spruce forest (Maljanen et al. 2010). Also, clear-cutting may increase N_2O emissions in peatland forests in the short term as a consequence of a raised water table level and increased peat temperature (Huttunen et al. 2003). Similarly, Nieminen (1998) found a small increase in N_2O (on average less than 1.0 $kg\ N_2O-N\ ha^{-1}$ during the frost-free period or about 200 days per year, corresponding to daily average of 0.5 $mg\ N_2O-N\ m^{-2}\ d^{-1}$) during the frost free period after clear-cutting. N_2O emissions depend on several variables, which make it difficult to estimate the importance of N_2O efflux from buffers or catchments in regard to climate change. Thus more research in relation to the impacts of forestry operations on the N_2O dynamics in the buffer and the surrounding catchment are still needed.

1.4.2 Phosphorus

The retention of phosphate (PO_4-P) in the wet soil of buffers depends on several factors. P can be adsorbed to the surface of particles as a result of surface charges (Vought et al. 1994; Guppy et al. 2005). On the other hand, humic compounds may compete for the same sorption sites with P in the peatlands (Guppy et al. 2005; Nieminen et al. 2008). Chemical sorption is probably the most important process in PO_4-P retention in peatlands (Heikkinen et al. 1995; Liikanen et al. 2004; Väänänen et al. 2006). PO_4-P can be mainly bound in the soil to iron (Fe) and aluminium (Al) at low pH levels and to calcium (Ca) complexes at high pH levels (e.g. Vought et al. 1994; Heikkinen et al. 1995; Nieminen et al. 2008). In contrast to the weathered and eluviated horizon in mineral forest soils, the concentrations of Fe and Al are low in peat. Consequently, the P retention capacity of surface peat layers is often less than 5 $kg\ ha^{-1}$ (Richardson 1985; Nieminen et al. 2008) especially in bogs (Nieminen et al. 2008). However, because of the great variation in Fe and Al content in peat between different mires, the maximum P retention in the surface peat varies from zero to 673 $kg\ P\ ha^{-1}$ in the 0–30 cm layer in drained mires (Nieminen and Jarva 1996; Nieminen et al. 2008). Long-term P storage probably depends solely on PO_4-P adsorption by the peat (Richardson 1985; Huttunen et al. 1996). Heikkinen et al. (1995) estimated that the theoretical effective P sorption time for a buffer zone purifying peat mining waters can be from 20 to 25 years.

In addition to P retention in the peat, PO_4-P may be immobilized in the microbial biomass or taken up by vegetation (e.g. Richardson 1985; Heikkinen et al. 1995; Baum et al. 2003; Väänänen et al. 2006). In fertilization experiments, peatland buffers bound 16–100% of the increased P load (Väänänen et al. 2006 and 2008). During snowmelt peak flow in spring, only 16% of added P (60 $kg\ PO_4-P\ ha^{-1}$) was bound: of which 92% was bound in the soil, 3% in the vascular plants and 5% in the mosses (Väänänen et al. 2006). In other fertilization experiments, about 25% (30 $kg\ P\ ha^{-1}$) of the added P was immobilized in the microbial biomass and 25% in the vegetation (Silvan et al. 2003 and 2004). The retention capacity of vegetation and microbial biomass may be high in the buffer but may reach a saturation point within a few years (Richardson 1985; Heikkinen et al. 1995). The retained P may be released

from the senescent vegetation and probably from dying microbes, although the composition of plant species, for example, may affect how much nutrients are trapped in or released from the buffer. For microbes in peat soils where C is readily available, P may be the limiting factor (Qualls and Richardson 2000; Baum et al. 2003). Addition of P may thus cause a temporary increase in microbial biomass: The highest microbial P contents are found near the peat surface and decrease with peat depth (Baum et al. 2003; Silvan et al. 2003). Thus, surface peat has a major role in chemical and microbial P binding.

Despite the potential of buffers to decrease P entering water courses, buffers can also release nutrients: In anaerobic conditions, the iron complex may change from Fe^{3+} to Fe^{2+} and earlier bound P is released back into the soil solution (Vought et al. 1994; Jensen et al. 1999; Nieminen et al. 2008). Accordingly, peatland buffers have been reported to release PO_4^{3-} in particular after buffer construction (e.g. Sallantausta et al. 1998; Liljaniemi et al. 2003; Väänänen et al. 2008). For example, in the constructed peatland buffers that receive drainage waters from forests, the concentration change of $\text{PO}_4\text{-P}$ ranged from 60% retention to 250% release (Liljaniemi et al. 2003). Also over the long term, buffers may release P (Nieminen et al. 2005b). Peat decomposition may transform organic P to inorganic P and enhance the $\text{PO}_4\text{-P}$ input to the soil solution (Baum et al. 2003). An explanation for the low P sorption capacity of peat may also be the saturation of peat P sorption sites (Liljaniemi et al. 2003; Väänänen et al. 2007).

Before buffer construction, the capacity of a buffer to bind or release P should be assessed. Drained peatlands may be at greater risk in terms of a release of P to the soil solution after buffer construction than pristine sites (see. e.g. Ihme 1991; Heikkinen and Ihme 1995; Sallantausta et al. 1998). Better knowledge from biogeochemical processes in the buffer could help to avoid the use of risk sites to the buffers.

1.4.3 Dissolved organic matter

Retention of dissolved organic matter (DOM, measured as dissolved organic carbon = DOC) in the soil depends on the content of soil organic C, Al and Fe hydroxides, pH and the amount of clay minerals (e.g. Moore et al. 1992; Kaiser et al. 1996; Kaiser and Zech 1998; Shen 1999; Kaiser and Zech 2000). The retention of DOM is increased by the abundance of Fe- and Al-oxides, whereas soil organic C leads to a decrease in the retention of DOM (Kaiser et al. 1996; Kaiser and Zech 1998). As a result, peatland buffers should, theoretically, be a source of DOM rather than a sink.

If some DOM is bound in peatland buffers, the DOM sorption should be most effective at a pH level of between 4–5 (Jardine and McCarthy 1989; Shen 1999). According to Shen (1999), many of the functional groups in DOM are acidic and are deprotonated at pH levels typical for most natural waters (pH 6–8). As pH decreases, the charge of the molecules becomes less negative and the mineral surface of a soil can adsorb more DOM molecules. In addition, the quality and molecular size of DOM may affect the availability of DOM for microorganisms.

Nieminen et al. (2005b) showed that buffers receiving water from forest drainage mainly release DOC to outflow water. In their study, only one large buffer, which was about 5% of the catchment area, decreased DOC concentrations in the through-flow water. A buffer wetland purifying peat mining waters decreased organic C only marginally ($12 \text{ mg m}^{-2} \text{ d}^{-1}$), although concentrations were high in the water inflow ($360 \text{ mg m}^{-2} \text{ d}^{-1}$, Liikanen et al. 2006). More research is needed in regard to the potential of peatland buffers to decrease DOM concentrations.

1.5 Objectives of the study

Although peatland buffers have been constructed for peatland forests in Finland during the last few decades, their efficiency in the retention of nutrients is still unclear. In addition, high N₂O emissions to the atmosphere have been recorded from nutrient application experiments on such buffers (Silvan et al. 2002) indicating a risk that well-working buffers may be hot spots of N₂O emissions and thus potentially enhance climate change. This study was constructed to further investigate the nutrient, greenhouse gas and vegetation dynamics in peatland buffers after different forestry operations, such as harvesting and ditch cleaning in order to find out 1) whether buffers are generally a significant source of greenhouse gases, especially N₂O, 2) which factors regulate the N₂O dynamics in the catchment and the buffers and 3) whether vegetation monitoring could be used as an indicator of the effectiveness of nutrient retention in the buffer. Two long-term monitored peatland buffers (III, IV) and one new peatland buffer (II), together with a clear-felled area in the catchment (I) were chosen for the investigation. In the long-term monitored sites, the North Karelia Regional Environment Centre had monitored nutrient flows (N_{TOT}, NH₄⁺, NO₂⁻+NO₃⁻, P_{TOT} ja PO₄³⁻-P) since 1997 and this background data was utilized in this study (III, IV).

Specific questions and how they were assessed (Fig. 2):

- Do the forestry enterprises undertaken in the catchment area cause elevated N₂O emissions from peatland buffers? How much N is emitted to the atmosphere in the form of the greenhouse gas N₂O?
 - * We measured N₂O fluxes from the treated forestry areas (clear-felling + ditch cleaning, I), the sedimentation pond receiving the runoff water (II) and the buffer wetlands (II, III). We also measured methane (CH₄) fluxes from the clear-felled area.
- Are peatland buffers potential N₂O sources under suitable conditions, i.e. with sufficient N supply, high soil temperature and hypoxic conditions?
 - * We studied the maximum N₂O production capacity in laboratory conditions and calculated how much added N fertilizer contributed to total N₂O (III).
- Does the quality of the DOM in vadose or ground water affect N₂O dynamics in the catchment?
 - * We determined the DOC concentration and characterized the molecule sizes and aromaticity of the DOC from water samples in order to estimate the role of the DOM in the C cycle (I). The quality of DOC was compared to N₂O dynamics in order to find possible links between the N and C cycles (I).
- Do changes in the field layer and moss vegetation indicate alterations in the performance of the peatland buffer (II, IV) or do these and the possible dying of the tree stand affect the efficiency of the buffer wetland to retain nutrients?
 - * We monitored changes in the vegetation on two buffers (II, IV) and biomass with N content in one on them (IV). In addition we estimated the potential N and P liberation from trees killed by an increased water table level after buffer construction (IV).

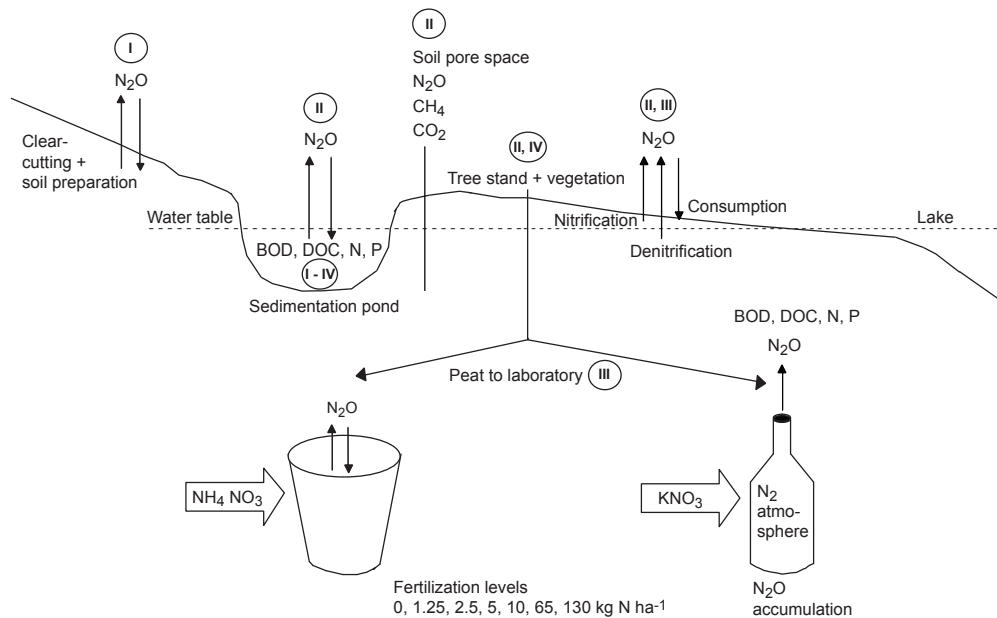


Figure 2. Summary of the measurements/studied phenomena and relevant papers where more detailed descriptions and results are given.

2 METHODS

2.1 Study sites

2.1.1 General description

One new and two old peatland buffer sites were studied in Nurmes, eastern Finland (Fig. 3a). A drained spruce-pine mire associated with a lake margin fen ($63^{\circ} 39'26\text{N}$, $29^{\circ} 29'34\text{E}$, 204 m a.s.l., Fig. 3b–c, I and II) was established in the catchment of lake Kaatiolampi in 2005. Measurements were started in 2004 before the construction of the buffer and the onset of forest management operations in the catchment area (I). Two older peatland buffers, a spruce swamp ($63^{\circ} 38'\text{N}$, $29^{\circ} 25'\text{E}$, 192 m a.s.l., Fig. 4, III and IV) and a brook margin meadow ($63^{\circ} 37'\text{N}$, $29^{\circ} 30'\text{E}$, 186 m a.s.l., Fig. 5, IV) were established in 1997 in the catchment of lake Kuohattijärvi. The buffer sites will be described in more detail in the following chapters.

The catchments of the buffers draining into the lakes were delineated based on the topographic maps of the areas (Fig. 3b, 4a and 5a). There were 20–22 fixed sampling points, equipped with vadose water wells used for water table measurements and water sampling when the soil was unfrozen. The catchment area of the drained spruce-pine mire associated with a lake margin fen was equipped with piezometers used for ground water sampling. In this thesis, water in the soil is considered to be either vadose when it infiltrates through the ca. 1 m deep topsoil, especially within the peat layer, or ground water when running over the bedrock (I).

In Nurmes, the annual mean temperature was $+3.0^{\circ}\text{C}$ and the average annual precipitation

sum was 533 mm during the study period (Finnish Meteorological Institute 2003–2006). Over 30% of precipitation falls as snow in the region. The most significant hydrological event is the spring flood during the snow melt. The snow free period lasted about 240 d and the winter period about 120 d.

2.1.2 The drained spruce-pine mire associated with a lake margin fen

Catchment area

The catchment of the drained spruce-pine mire associated with a lake margin fen was clear-cut in 2005, corresponding to 18% of its total area (28 ha, Fig. 3b). Of the approximate 5 ha that was harvested, about 3 ha was on mineral soil and the rest was on peat. Before clear-cutting, the catchment was covered with pine, spruce and birch stands with an average tree height of 18 m and a mean volume of 150, 100 and 40 m³ ha⁻¹, respectively (Seppo M. Heikkinen, personal communication, Finnish Forest and Park Service).

Before clear-cutting, the forest ground layer was dominated by shrubs, such as *Vaccinium myrtillus* and *V. vitis-idaea*, and the bottom layer by mosses (e.g. *Pleurozium schreberi*, *Aulacomnium palustre*). After the clear-cut, the forest shrubs and mosses died, and during the summers of 2006 and 2007 the area was dominated by *Epilobium angustifolium* and *Deschampsia flexuosa*, and in some spots by mosses *Polytrichum commune*, *P. juniperinum*, *P. strictum*, and *Pleurozium schreberi*.

In the clear-cut area, the zero-tension soil lysimeters and the piezometers, used for capturing the vadose water and ground water, respectively, were drilled in 2005. A more detailed description of the lysimeters and piezometers is given in paper I. In the podzolized mineral soil, the average pH of the vadose water was 6.2, and in the peat 5.1. After clear cutting, a sedimentation pond of ca. 20 m² was constructed, the soil was prepared and the ditches cleaned. After the sedimentation pond, the runoff was channeled to spread over an area of 0.1 ha reserved as a buffer between the pond and the lake. The size of the buffer was about 0.4% of the catchment area and 2% of the clear-cut area.

Buffer area

The drained spruce-pine mire associated with a lake margin fen was divided into four sub-sites based on the location in relation to the lake and incoming water flows from the catchment. The sub-sites were named; the spruce-pine mire buffer (SB), the spruce-pine mire reference (SR), the lake margin fen buffer (LB) and the lake margin fen reference (LR, Fig. 3c). The water from the catchment flowed mainly towards the SB, where the vegetation was the most affected. There the vegetation consisted of vascular plants such as *Eriophorum vaginatum*, *Andromeda polifolia*, *Vaccinium oxycoccos* and *Carex pauciflora* and the moss layer consisted of *Sphagnum angustifolium*, *S. magellanicum*, *S. girgensohnii*, *S. riparium*, *Pleurozium schreberi* and *Aulacomnium palustre*. Forest mosses dominated the ground layer before buffer construction on the spruce-pine mire, but the coverage of *Sphagna* on the ground layer and *Betula pubescens* on the shrub and ground layers in the buffer increased after buffer construction. Vegetation is described in more detail in paper II.

Peat depth was on average 2.90 m in the buffer and mean pH in the vadose water was on average 4.8 in the SB, 4.9 in the SR, 4.6 in the LB and 4.6 in the LR during the frost free periods in 2005–2007. The lake flooded both the buffer and the reference areas, mainly during the spring and autumn, leading to higher water levels and possibly interfering with the biogeochemistry of the buffer.

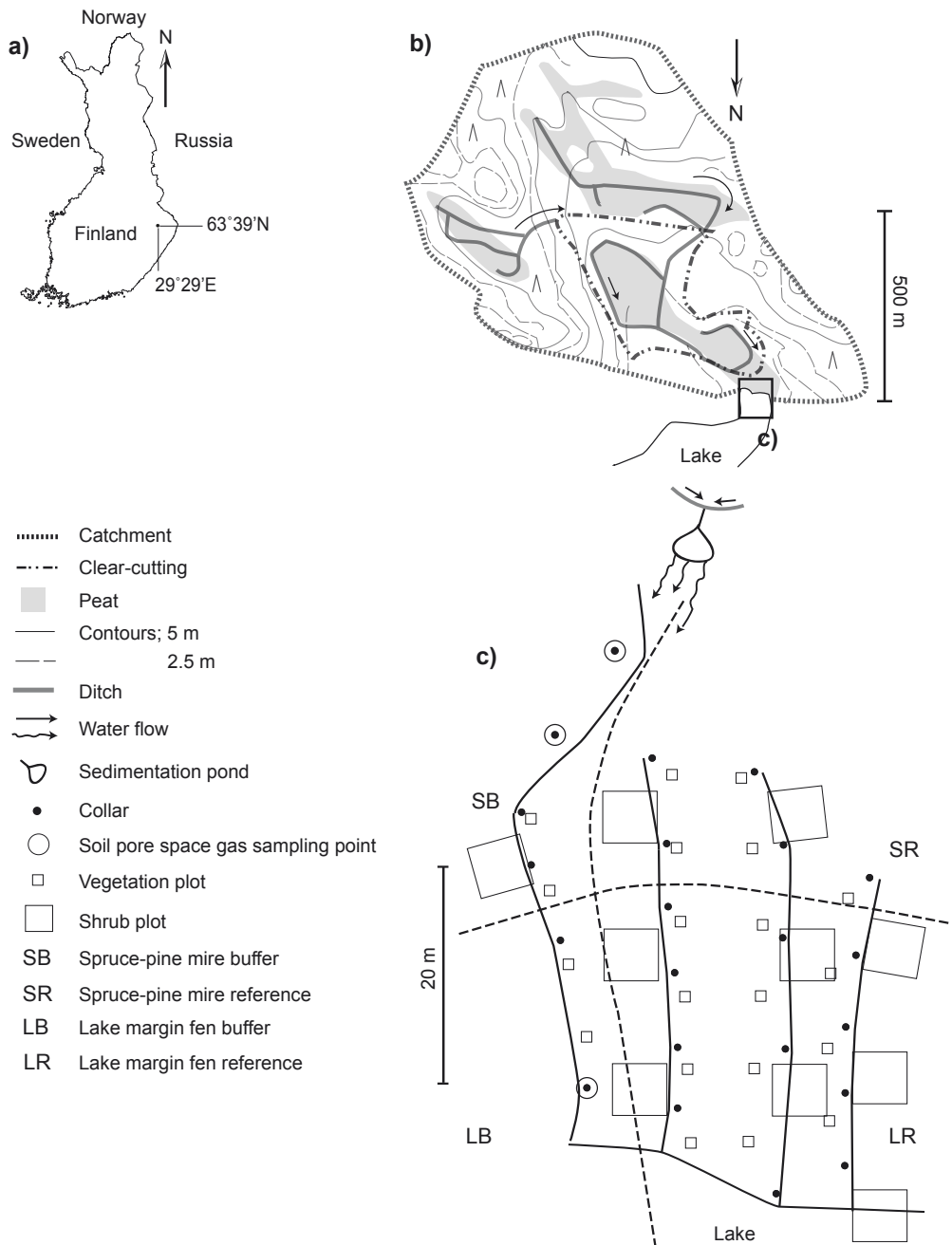


Figure 3. a) The location of the spruce-pine mire associated with the lake margin fen study area in Nurmes, eastern Finland, b) the structure of the whole catchment and c) the study area with gas measurement, field and bottom layer vegetation plots and shrub plots. Continuous black lines indicate the boardwalks and dashed black lines separate the sub-sites spruce-pine mire buffer (SB), spruce-pine mire reference (SR), lake margin fen buffer (LB) and lake margin fen reference (LR). Peat depth was on average 2.90 m in the buffer.

2.1.3 The spruce swamp

The area of forest catchment of the spruce swamp buffer was 72 ha. It included 13 ha of ditch cleaning in 1998, 15 ha of PK-fertilization in 1998, 22 ha of thinning in 1998, and 5 ha of harvesting in 2006. The buffer represented 0.5% of the catchment area. The spruce swamp was divided into the fern spruce mire with flood indicators and the *Myrtillus* spruce mire with the original vegetation of forest herbs and mosses. Four transects were established at

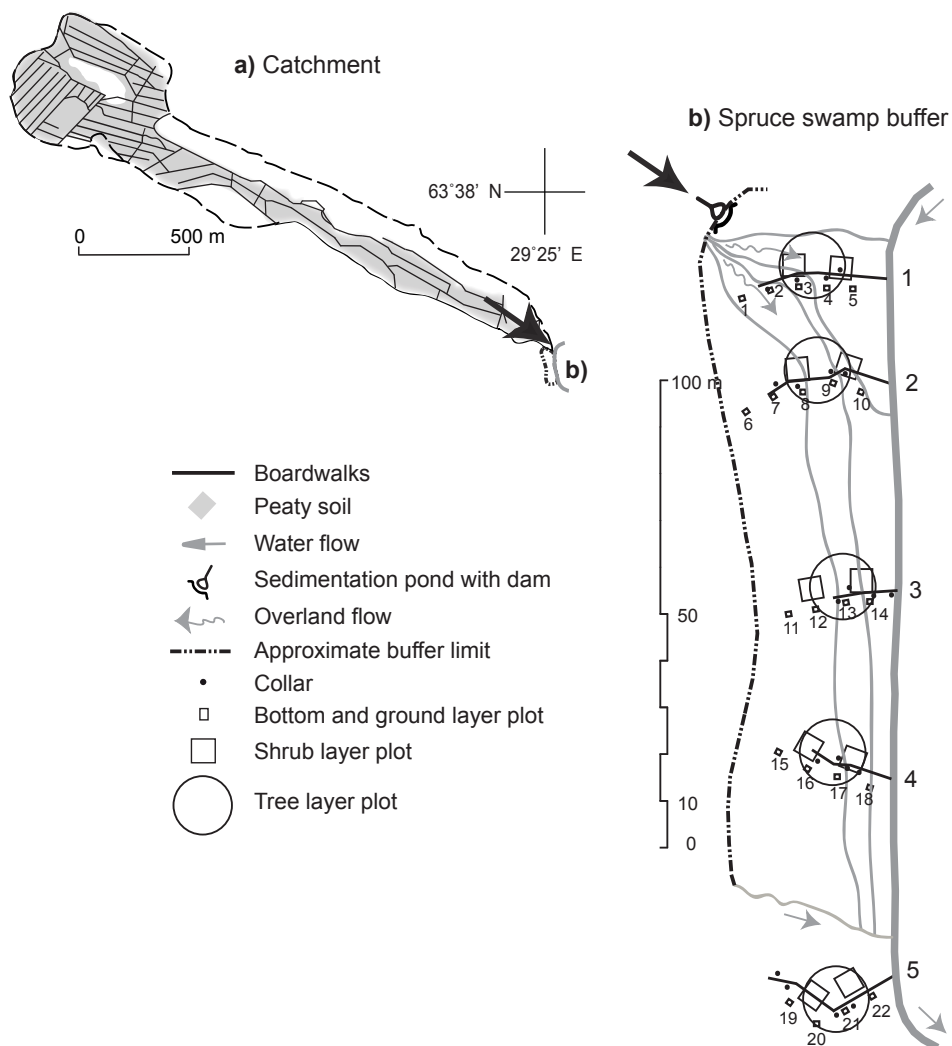


Figure 4. a) The structure of the catchment of the spruce swamp study area (buffer consists of transects 1–4 and outside the buffer in transect 5) and **b)** the study area with gas measurement, vegetation and shrub plots. Continuous black lines indicate the boardwalks, the thick grey line describes the brook and thin grey lines describe overland flows. During dry spells the water flow between boardwalks 4 and 5 dried out completely. The peat layer was on average 0.6 m in the buffer and 0.3 m outside the buffer in transect 5.

increasing distances from the water inflow and one transect outside the buffer as a reference (transect 5, Fig. 4).

The tree stand was a Norway spruce stand (*Picea abies*). The ground vegetation on the buffer was characterized by grasses and herbs, such as *Calamagrostis purpurea*, *Carex canescens* and *Trientalis europaea* and mosses e.g. *Sphagnum riparium* and *S. girgensohnii*. On transect 5 outside the buffer, there were grasses and herbs, such as *Dryopteris expansa*, *Equisetum sylvaticum*, *Gymnocarpium dryopteris*, *Vaccinium myrtillus* and mosses, such as *Pleurozium schreberi*, *Brachythecium* sp. and *S. girgensohnii*.

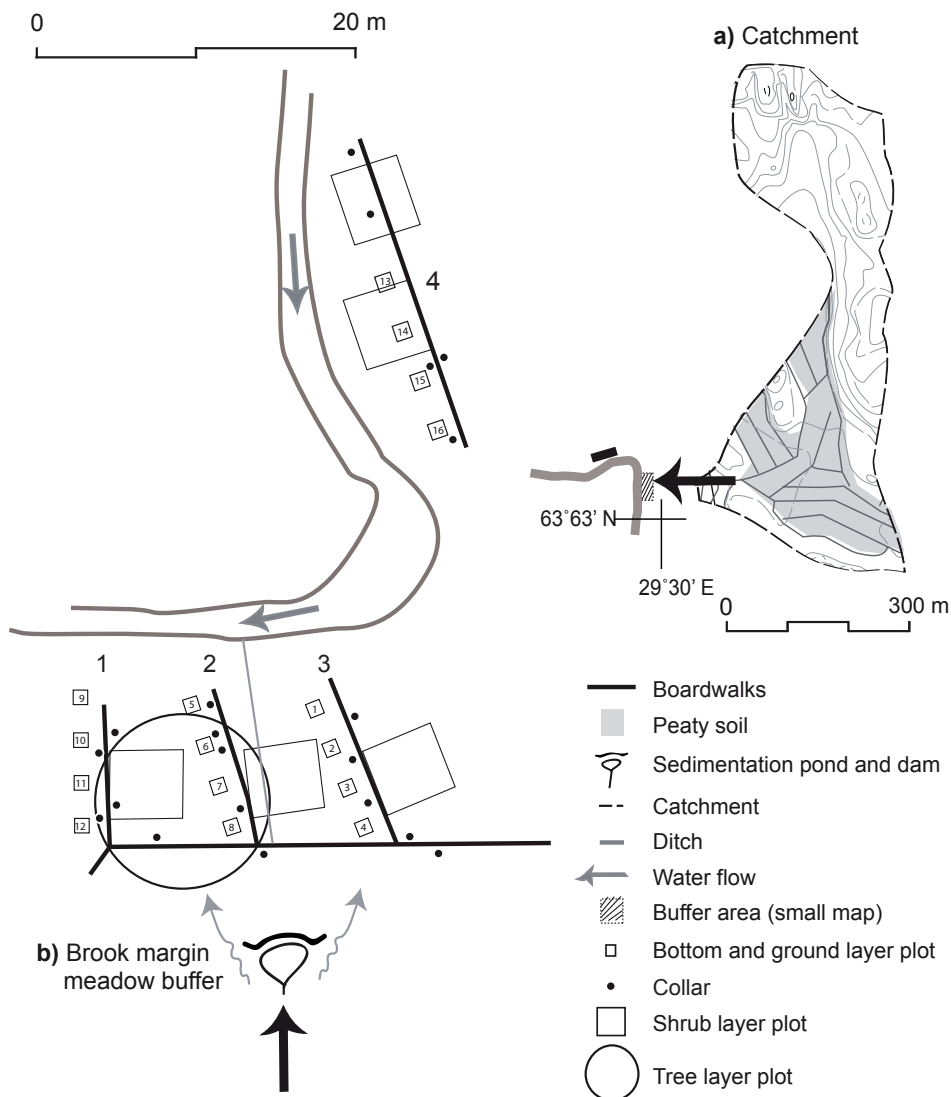


Figure 5. a) The structure of the catchment of the brook margin meadow study area and b) the study area with gas measurement, vegetation and shrub plots. Continuous black lines indicate the boardwalks. Peat depth was 1.9 m in the buffer and 1.5 m outside the buffer.

In transect 5 the peat layer was thin, on average 0.6 m in the buffer and 0.3 m outside the buffer. In the buffer, the peat was less decomposed and more acidic *Sphagnum* peat dominated than outside the buffer, where the peat was more decomposed with woody remains. Mean pH in the vadose water was on average 5.2 in the buffer and 5.8 in transect 5 during the frost free periods in 2005–2006.

2.1.4 The brook margin meadow

The brook margin meadow represented 0.16% of the 29 ha catchment with 7 ha of thinning and 8 ha of PK-fertilization in 1999. Four transects were established in the study area. Transects 1–3 were located below the sedimentation pond, while transect 4 was located outside the buffer at a paludified upstream bank of the brook and acted as the reference for the buffer area, which receives waters from the catchment during forestry operations. Both the buffer and transect 4 were annually left under the spring flood, which is contrary to the buffer construction recommendations.

On the brook margin meadow, the buffer vegetation type represented a temporarily flooded herb-grass spruce mire and transect 4 was a swamp fen (Fig. 5). The natural flooding effect was indicated by vegetation (*Calla palustris*, *Lysimachia thyrsiflora* and *Sphagnum riparium*) on the herb-grass spruce mire type, especially close to the brook (IV). *Calamagrostis purpurea* and *Carex canescens* were the most abundant species just below the sedimentation pond. The moss layer consisted *Calliergon stramineum* and *S. girgensohnii* for example. Transect 4 outside the buffer had retained *Menyanthes trifoliata*, *Calla palustris*, *Carex lasiocarpa* and *Sphagnum fallax*. The coverage of the shrub layer varied between 7–50% within the whole buffer and between 1–30% particularly on transect 4 (Fig. 5). The tree stand was dominated by *Betula pubescens* and *Salix phylicifolia*. In addition, *Alnus incana* was found on the buffer and *Pinus sylvestris* and *Salix aurita* on transect 4.

Peat depth was 1.9 m in the buffer and 1.5 m outside the buffer. Mean pH in the vadose water was on average 6.1 in the buffer and outside the buffer during the frost free periods in 2005–2006.

2.2 N₂O and CH₄ measurements

2.2.1 Chamber measurements

The exchange of N₂O between soil and atmosphere was measured using the static chamber technique during the snow free periods or during times when there was a thin snow layer (I, II, III). Chambers (21 dm³) were made from tin plate and the diameter (Ø) and height of chambers were 30 cm. Rubber gaskets were glued on the edges of the chambers. At the beginning of the measurement, the chamber was placed upon a collar and interlocked to produce an air-tight seal using adjustable clips. During the period of a shallow snow layer in autumn and spring, the chambers were placed directly on the soil surface near the collar and sealed by padding with snow.

30 ml air samples were taken using 50 ml polypropylene syringes equipped with 3-way stop-cocks. Over a 20–40 minute period, a sample was taken every 5 or 10 minutes: the first sample was taken 5 or 10 minutes after the start of the incubation depending on the total incubation time. The temperature of chamber air was measured at each sampling time using a multi-thermometer or digital-thermometer (Suomen lämpömittari Oy), and the average of

all four temperature measurements was used in the flux calculation. The temperature of the soil profile (soil surface, -2, -5, -10, -15, -20, -25, -30, -40 and -50 cm) was measured using a Fluke 52 K/J thermometer.

The gas concentrations were determined using a gas chromatograph (Shimadzu GC-14-A, Kyoto, Japan) equipped with the flame ionization detector (FID) and the electron capture detector (ECD). The detection limit of the detector was 0.03 ppm for CH₄ (FID) and 20 ppb for N₂O (ECD). The gas fluxes were calculated from the linear change in gas concentration in the combined airspace of chamber and the collar. The airspace within the collars were measured every summer, and added to the total headspace of the chamber.

2.2.2 Gradient measurements

The exchange of N₂O and CH₄ between soil and atmosphere was measured using gradient measurements in winter (I, II, III). The gas fluxes were determined by sampling (30 ml) the gas concentrations from close to the soil surface below the snowpack and from the air above the snow (Sommerfeld et al. 1993; Alm et al. 1999). The samples were taken into 3-way stopcock syringes using a 4 mm diameter metal pipe. Gas samples were also taken from different depths of the snow pack to examine the gas concentration gradient in the snow profile. The concentration of CH₄ and N₂O in the sampled air was analysed using the gas chromatograph described above.

The snow depth was measured from volumetric profiles taken through the snowpack using a 54 mm inside diameter plastic tube. The snow samples were weighed and the average porosity of the profiles calculated with reference to the density of solid ice (0.9168 g cm⁻³). The gas fluxes were calculated using Fick's first law of diffusion through a porous medium $J_g = D_g(dC_g/dz)f$, where J_g is the diffusive gas (g) flux, D_g is the diffusion coefficient for the gas in air, dC_g/dz is the measured vertical concentration gradient through the snow pack (z cm), and f is the snow porosity. The values used for D_g were 0.139 cm² s⁻¹ for N₂O and 0.22 for CH₄ (Sommerfeld et al. 1993, I).

2.2.3 Sampling of soil pore space N₂O, CH₄ and CO₂

Concentrations of N₂O, CH₄ and CO₂ in the soil pore space were monitored in the drained spruce-pine mire associated with a lake margin fen. This was done using silicone tubes that were installed at different depths in the soil profile in the sub-sites of the spruce-pine mire buffer and the lake margin fen buffer. Five 1 m long silicone tubes with 3-way stop-cocks on the top of the PVC-plastic tube were installed near three collars used for measuring gas exchange between the soil and the atmosphere (Fig. 3c) below and above the average water table levels. Air samples were taken with syringes and the concentrations of CH₄ and N₂O in the sample air was analysed as described above. CO₂ was analysed with a thermal conductivity detector (TCD). The detection limit of the TCD was 6 ppm. A more detailed description of the depths of silicone tubes, sampling and analysis is provided in paper II.

2.2.4 Fertilization experiment in the laboratory

In the spruce swamp, peat samples (Ø and height 15 cm) were cored from the uppermost part of the soil profile in transect 3 in October 2007. Samples were put into plastic pails in the laboratory and maintained under controlled conditions (temperature 19.8 ± 0.5°C, water table level -2 cm). The green parts of the vascular vegetation and moss were cut off. The samples

were fertilized using NH_4NO_3 at rates of 1.25, 2.5, 5.0, 10.0, 65.0 kg N ha^{-1} ($n = 5$ for each fertilization level) and 130.0 kg N ha^{-1} ($n = 6$). The highest N fertilization level corresponds to N fertilization recommendations (about 100 kg N ha^{-1}) by Päivänen (2007, p. 256). Ten samples received no fertilization and were left as controls. Air samples (30 ml) were taken, analyzed, and the fluxes calculated as described above with the field measurements (Note that a smaller chamber (4.2 dm^3) was used in the laboratory). The chamber was put on the plastic pail and sealed with a rubber gasket. The temperature of the headspace was measured using a Fluke 52 K/J thermometer. Peat samples were watered as needed using de-ionized water. Before fertilization, at least one sampling of N_2O flux rates was performed. A more detailed description is provided in paper III.

2.2.5 Production of N_2O

In the spruce swamp, volumetric peat profile samples were cored along transects 1, 3, 4 and 5 in October 2005 and May 2006 using a 6 x 6 cm^2 box corer. The peat samples were cut in 5 cm slices, incubated in glass bottles under controlled conditions (water saturated, temperature 21.7 ± 1.0 °C, with N_2 atmosphere and KNO_3 -fertilization) in the laboratory. The first 30 ml samples from the bottles were taken immediately after the headspace was flushed with 99.95% quality N_2 . The following samples were taken 2–4 times a day, depending on the observed rate of N_2O production so that more daily samples were taken from bottles with a high increase in N_2O . 30 ml of N_2 was injected into the headspace of the bottle after an air sample was drawn in order to maintain the pressure in the bottle. The sampling was stopped when three consecutive analyses showed a decreasing trend in the headspace N_2O concentration, indicating the cessation of N_2O production in the soil sample. N_2O concentrations were measured by a gas chromatograph (ECD) similar to detailed above with the field N_2O measurements. The wet weight of the peat sample was measured before the incubation and dry weight was weighed after 2 days drying at 105°C. A more detailed description of method is provided in paper III.

2.3 Vegetation characteristics

The development of the ground vegetation was monitored at each study site by repeating a projection cover analysis three times in July 2005, 2006 and 2007 (II, IV). The cover analysis was done separately for vascular plants and mosses (field and bottom layers) (Fig. 3c, 4b, 5b). Percentage values used were + (species present), 0.5, 1, 2, 3, 5, 7, 10 and at five percentage intervals after that up to 100%. The proportion of litter and dead plants were also estimated. Coverage was estimated on 20, 22 and 16 plots of 1 m^2 along transects on the drained spruce-pine mire associated with a lake margin fen, on the spruce swamp and on the brook margin meadow, respectively (Fig. 3c, 4b, 5b). The site types on the buffer and outside the buffer were classified according to the Finnish classification of ecological mire site types (Eurola et al. 1995). On the clear-cut area above the spruce-pine mire buffer, the vegetation coverage was estimated in 2006 and 2007 on seven 7 dm^2 collars in the mineral soil area and on five collars in the peat area, respectively.

In the spruce swamp, above-ground parts of vascular plants and moss capitula were collected from one 0.25–1 m^2 vegetation plot per transect and outside the buffer (plots 4, 9, 14, 18 and 21, see the map in paper IV). Peat samples were collected at a depth of 10 cm below the moss capitula. Vegetation, moss and peat samples were dried at 40°C,

homogenized, and measured for moisture using standard ISO 11465 and total N content using standard VYH -76.

The coverage of the shrub/bush layer was estimated as a percentage of projection cover (from 1, 2, 3, 5, 7, 10 and at five percentage intervals after that) similar to ground vegetation in July 2005, 2006 and 2007 on ten 25 m² plots on the drained spruce-pine mire associated with a lake margin fen and in the spruce swamp and five plots on the brook margin meadow.

The tree stand density and canopy coverage were estimated, tree heights and trunk diameter at 1.3 m was measured in 2007 using two and five replicate 0.01 ha circular plots on the drained spruce-pine mire associated with a lake margin fen and on the spruce swamp, respectively and one plot on the brook margin meadow first in October 2005 and repeated in May 2007. In addition heights and diameters of dead trees and stumps were measured in tree layer plots. The data was used for counting the biomass and P and N contents of the growing stock, dead trees and stumps in the spruce swamp study site. The aim was to estimate the effects of buffer construction on the tree stand at different distances from the water inflow (sedimentation pond) towards transect 5 and thus the live or dead status for all trees and old stumps was also recorded along transects 1–5.

2.4 N measurements

In the drained spruce-pine mire associated with a lake margin fen, water samples for the determination of total nitrogen (N_{TOT}), nitrate (NO_3^-) and NH_4^+ were taken from the sedimentation pond and from four vadose water wells 1–3 times per month from May to September 2007 (I, II). Concentrations of N_{TOT} , NO_3^- and NH_4^+ were analyzed from filtered (Schleicher and Schuell GF 52, glass fibre, 1–1.2 μm , \varnothing 47 mm and Schleicher and Schuell membrane filter ME 25, 0.45 μm , \varnothing 47 mm) and deep-frozen water samples. N_{TOT} and NH_4^+ were measured with a spectrophotometer (FIA-Star 5000 Analyzer FOSS TECATOR) applying standard methods ISO 13395 and ISO 1173, respectively. Nitrite (NO_2^-) was measured with an ion chromatography (DIONEX 500) using standard method SFS-EN ISO 10304.

In the spruce swamp, water samples for the analysis of N_{TOT} , NH_4^+ , and $NO_2^-+NO_3^-$ were taken 2–10 times per year from the sedimentation pond and the water outflow beyond transect 4 during the years 2000–2005 (III, IV). In the brook margin meadow, water samples were taken 3–10 times per year from the sedimentation pond and the water outflow running to the brook during the years 1998–2005 (IV). N_{TOT} , $NO_2^-+NO_3^-$ and NH_4^+ were measured using the standard methods of SFS-EN ISO 11905-1, SFS-EN ISO 13395 and SFS 3032, respectively.

2.5 P and metal analysis

In the spruce swamp, concentrations of Al, Fe, P_{TOT} and PO_4^{3-} were measured during the years 2000–2005 from samples taken from the water inflow and outflow. In addition, one Al and Fe sampling round was performed in the drained spruce-pine mire associated with a lake margin fen and in the spruce swamp in August 2007, when vadose water samples were taken in order to compare the proportions of active Fe (Fe^{2+} and Fe^{3+}) with Al^{3+} and Fe_{TOT} in the vadose water. Metal contents and their form may indicate the P binding capacity of the area. P_{TOT} and PO_4^{3-} -P were sampled from April 2006 to September 2007 in the drained spruce-

pine mire associated with a lake margin fen. The AAS graphite oven method (SFS 5503 and SFS 5074) was used for Al and concentrations of Fe, P_{TOT} and PO_4^{3-} were measured using spectrophotometrical methods SFS 3028 (Fe) and SFS-EN ISO 6878 (P_{TOT} and PO_4^{3-}).

2.6 Quantification and characterization of DOC, BOD and pH

Dissolved organic carbon (DOC) is defined as the fraction of organic C that passes through a 0.45 μm filter (e.g. Thurman 1985, p. 2; McDonald et al. 2004). DOC concentrations were measured on the catchment of the drained spruce-pine mire associated with a lake margin fen from vadose water lysimeters, from the ditch within the forest management area, the margin ditch that leads to the sedimentation pond and from the waters leaving the sedimentation pond to the buffer. It was hypothesized that dynamics of DOC after clear-cutting and soil preparation may be reflected in the soil-atmosphere N_2O exchange and vegetation dynamics.

The absolute content of DOC (mg l^{-1}) was measured by TOC 5000A (Total Organic Carbon Analyzer, Shimadzu) from filtered water samples. Water samples were taken at least once a month. The quality of DOC was characterized by measuring the specific UV and visible absorbency and by counting specific UV absorbency ($sUVa_{\lambda,254\text{nm}}$), specific visible absorbency ($sVISA_{\lambda,400\text{nm}}$) and specific absorption ratios (SAR_{UV} and SAR_{VIS}). The $sUVa$ and $sVISA$ values reflect the degree of aromaticity (Traina et al. 1990; Akkanen et al. 2004).

Descriptions of the quantification and characterization of DOC and measurement of biological oxygen demand (BOD) are provided in paper I. pH was measured from the filtered water samples using a PHM 92 Radiometer (Copenhagen).

A more detailed description of DOC quantification and characterization is provided in paper I.

2.7 Statistical tests

Pearson correlations were computed to find associations e.g. between pH or soil temperature, DOC, CH_4 and N_2O . For the non-linear relationships with water table, Spearman correlation was chosen in the spruce swamp study area. A linear mixed model was used for testing the differences in gas fluxes, water table and other environmental variables (e.g. pH, DOC and its characteristics) between the different parts or treatments in each study site. For example, gas fluxes, depth of the water table or pH were tested using covariates. Collars constituted the random effect. If the observations were correlated in space and time, the spatial correlation was taken into account in the model by defining fixed spatial terms such as transect or sub-site. The temporal correlation was taken into account by setting year and season as fixed effects. Correlations of residuals were modeled using a first order autoregressive covariance structure of the consecutive measurements of a random season within the year and collar subjects. The normality of the marginal distribution of the residuals and the homogeneity of the variance of the residuals were checked graphically, and selection of the covariance structure was based on Akaike's information criteria. More detailed descriptions of the linear mixed models used are provided in papers I, II and III.

A variance analysis was used for testing the differences in N_2O emissions between the different fertilization levels and the controls of the peat samples from the spruce swamp buffer (III). In addition, N_2O accumulation and bulk and particle density were estimated for the peat sample of the spruce swamp buffer and transect 5 outside the buffer. N_2O production

kinetics was described with a sigmoid formula and the differences between the maximal N_2O concentration and the rate of N_2O formation were tested using ANOVA (III): Differences in the amount and the rate of N_2O production were tested between profiles and seasons (autumn 2005 and spring 2006).

Changes in vegetation coverage (%) on the vegetation plots within the different sub-sites of the study sites were illustrated as a re-location of scores computed using Detrended Correspondence Analysis (DCA) using PcOrd5. The analysis was run using standard options, with down-weighting of rare species. The matrix consisted of vegetation monitoring plots (Fig. 3); 59 species on the drained spruce-pine mire associated with a lake margin fen, vegetation plots (Fig. 4), 47 species on the spruce swamp and vegetation plots (Fig. 5) and 46 species on the brook margin meadow. Vegetation monitoring data was collected three times in each study site during the three years of the study, so analyzed data included observations from vegetation plots from these years. DCA analysis was made for each study site separately because vegetation differed so widely between study sites as a result of different mire types and ages. Our aim was monitor vegetation dynamics inside the buffers; how the construction of the buffer changed vegetation composition from the original plant composition in different areas. A more detailed description of vegetation analyses are provided in papers II and IV.

The effects of buffer construction on N and P release in the spruce swamp were estimated from the dead tree stand by comparing N and P amounts bound by dead and live tree biomass (IV) using functions and parameters published for the different species by Repola et al. (2007) and Finér (1989).

3 RESULTS AND DISCUSSION

3.1 Vegetation change on buffers indicates the active area of run-off from forestry

3.1.1 Vegetation change

Vegetation on the buffers may change after buffer construction due to the rising water table level, increased nutrient load from the forest management areas and an increase in light after the dying of trees. High water table level may increase the occurrence of the flood tolerant plant and moss species. Forest fertilization reduces dwarf shrubs and forest mosses and enhances grasses and nitrophilous herbs (Strengbom and Nordin 2008). The increase of light after tree stand dying may decrease forest species and increase light favoring species, such as some grasses and herbs.

It would seem that although our three buffers were different before the buffer construction, their vegetation has developed in a similar direction after buffer construction and the subsequent water flows from forestry areas. We found a decline or expansion of some species occupying the buffers before buffer construction rather than a disappearance or appearance of species (II, IV). In the spruce swamp, the species that indicate flooding (see Eurola et al. 1995), e.g. *Calamagrostis purpurea*, *Sphagnum riparium*, *S. girgensohnii*, increased while the forest mosses and shrubs (e.g. *Vaccinium myrtillus*, *Pleurozium schreberi* and *Hylocomium splendens*) decreased in coverage (Fig. 6). Similarly, in the spruce-pine mire buffer, the coverage of *Betula pubescens* on the shrub and ground layers and *Sphagna* on the bottom layer increased and forest species (*V. myrtillus*, *V. vitis-idaea* and *P. schreberi*) decreased near the water inflow. In the brook margin meadow, differences in vegetation were

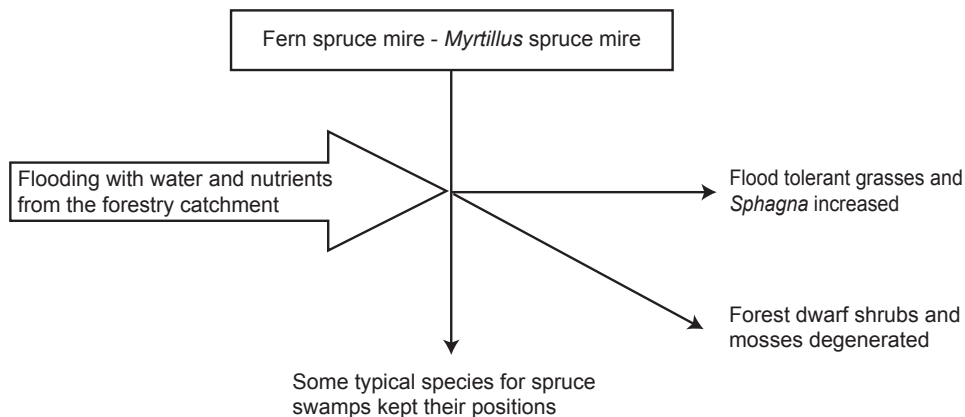


Figure 6. Example from the vegetation change caused by the buffer construction on the spruce swamp.

not so clear because the buffer was constructed too close to the flooded area of the brook in contravention of buffer construction recommendations (see Joensuu et al. 2004). However, the cover of *Calamagrostis purpurea* and *Carex canescens* seemed to be increased after buffer construction, because they were the most abundant species just below the sedimentation pond. Some species, such as *Viola palustris* or *Trientalis europaea*, had adapted well to the habitat under the influence of runoff waters from the forestry area, although they probably were an original species on the spruce swamp and on the brook margin meadow.

The increased cover of species, such as *C. purpurea*, *B. pubescens*, *S. riparium* and *S. squarrosus* is probably more indicative of a raised water table level than an increased availability of nutrients in our peatland buffers given what is empirically known of how some species can act as indicators of flooding and nutrient status in mire biotope classifications (Euroala et al. 1995). The potential nutrient load from the forest management areas was apparently so low that it did not enhance species, which would indicate a higher nutrient status in the buffer. Even after PK and N addition, Sheppard et al. (2013) observed only an expansion of *Epilobium angustifolium*, *Epilobium palustre*, *Juncus effusus*, *Digitalis purpurea* and *Dryopteris dilatata* and a decrease of *Calluna* and *S. capillifolium*. However, the changes in vegetation cover in our study sites outlined the area of effective water flow paths within the planned buffer area. Thus, vegetation change can be used as a tool to indicate water level and dispersion on the buffer site.

3.1.2 Does buffer construction affect vegetation N content?

In the spruce swamp, we measured the plant above-ground biomass. It varied from 129 to 177 g dry mass m⁻² between vegetation plots. In our limited data, the total above-ground biomass, excluding the trees, was quite similar both within different parts of the buffer and outside the buffer although water runoff seemed to increase the moss biomass (IV). The combined vascular plant biomass was highest on the fern spruce mire type outside the buffer. In the buffer, the biomass was higher on the wet end than on the dry end. The change in vegetation may be still ongoing because the largest exchange of forest species to aquatic tolerant ones has taken place predominantly at the uppermost end of the buffer (IV).

Total N content of above-ground plant biomass was analyzed because the decrease of the forest species and increase of flood tolerant species may have affected both the vegetation biomass and N content. The total N content of the above-ground parts of vegetation and surface peat layer were similar in the buffer and in transect 5 outside the buffer in the spruce swamp (IV). N content of the vascular plant biomass varied from 22.5 to 26.3 g N kg⁻¹ dry mass on the buffer and 22.4 g N kg⁻¹ dry mass outside the buffer. Peat N concentrations were less than half in the buffer *Sphagnum*-peat than was found outside of the buffer in transect 5. The peat inside the buffer consisted of moderately decomposed *Sphagnum* remains, while outside the buffer, the peat was more decomposed peat and comprised mainly of other plant materials. Correspondingly, the N content of mosses varied from 17.0 to 19.0 g N kg⁻¹ on the buffer and 16.3 g N kg⁻¹ outside the buffer. Changes in biomass or the N content of peat and plant biomass did not indicate a clear increase in the nutrient binding capacity in the buffer vegetation. Instead, in a buffer receiving peat mining runoff waters, the increase in vegetation biomass and N concentration resulted in a 40% enhancement in N retention (Huttunen et al. 1996). In addition, Silvan et al. (2004) reported enhanced N retention in increased vegetation in a buffer of peatland forestry after a fertilization experiment.

The decrease of perennial shrubs may decrease the nutrient binding in vegetation over the long term because the perennial shrubs store nutrients for several years unlike the annual grasses and herbs. For example, Macrae et al. (2013) found that the spatial patterns in nutrient availability may be regulated by differences in vegetation, mainly *Sphagnum* moss cover. It is likely that only peat forming *Sphagna* have the potential to trap nutrients from the active nutrient cycle on the spruce swamp buffer. Large quantities of nutrients may not be bound over the long term in the below-ground biomass of the spruce swamp buffer because there were no species with a large below-ground biomass, such as *Carex* species or *Eriophorum vaginatum*. On the contrary, Huttunen et al. (1996) reported that in a buffer receiving peat mining waters, the most important increase in plant biomass is the below-ground biomass. On the other hand, a high proportional increase in the above-ground biomass has been reported for the buffer of peatland forests after a nutrient addition experiment (Silvan et al. 2004) and for a peatland buffer receiving peat mining effluents (Liikanen et al. 2006). Plant biomass is principally a temporary storage for nutrients because immobilized nutrients are later released during senescence. In contrast, peat can store nutrients over the long term.

3.2 Are peatland forestry buffers hot spots of N₂O emissions?

The fluxes of N₂O-N from the sedimentation pond varied from -0.10 to 1.26 mg m⁻² d⁻¹ (II). Fluxes of that magnitude were not especially high, but higher than those from humic lakes with a high N load (-0.06–0.24 mg N₂O-N m⁻² d⁻¹, Huttunen et al. 2003). Emissions of N₂O in our buffers (Table 2) were at the low end of the range observed for organic forest land in Fennoscandia, in line with their relatively low soil N concentrations. The spruce swamp was the most nutrient rich site and N₂O emissions were highest there and average emissions in our all study sites were higher than Pearson et al. (2012) reported for nutrient-poor, clear-cut peatland forests (0.05–0.08 g N₂O m⁻² y⁻¹, simply converted to 0.09–0.14 mg N₂O-N m⁻² d⁻¹). Alm et al. (2007) reported 0.52–1.41 mg N₂O-N m⁻² d⁻¹ in Finnish spruce mires and Ernfors et al. (2007), using the C:N ratio of Swedish drained organic forest soils, calculated an average efflux of 0.31 g N₂O m⁻² y⁻¹ (range 0.01–4.41 g N₂O m⁻² y⁻¹), corresponding to a daily average of 0.55 mg N₂O-N m⁻² d⁻¹ and ranged from 0.02 to 7.80 mg N₂O-N m⁻² d⁻¹, respectively. The formation of N₂O emissions requires N₂O production via nitrification or

denitrification and an inorganic N supply for these processes. Inorganic N is produced during the decomposition of organic matter but it can also be available for these processes from leaching or fertilization. Overall, none of the studied buffers was a hot spot of N_2O in spite of rare “hot moments”, especially in spring time.

The reason for low N_2O emissions may be due to a low inorganic N load to the buffers. In our study sites, the majority of leached N was in an organic form (II, IV) similar to those reported earlier, for example, by Liljaniemi et al. (2003) and Nieminen (2004) and thereby not directly available for nitrifying and denitrifying micro-organisms. The amount of inorganic N in the incoming water was probably too small for the higher rate of nitrification and denitrification (II, III). In the spruce swamp buffer, concentrations of NH_4^+ and $NO_2^- + NO_3^-$ in the incoming water were on average 14 and 19 $\mu g\ l^{-1}$, respectively. In the spruce-pine mire buffer the concentrations were somewhat higher, on average 49 and 75 $\mu g\ l^{-1}$. In the fertilization experiment, N_2O emissions from the pails with a fertilization level of 2.5 kg $NH_4NO_3-N\ ha^{-1}$ or higher differed significantly from the control (III). The load of 2.5 kg N ha^{-1} is, however, higher than the inorganic N load (0.95–2.08 kg ha^{-1}) leached after peatland forestry operations during three growing seasons (Nieminen 2004). If higher inorganic N pulses exist during the spring flooding, they are short-lived and support higher N_2O release only during short hot moments. This should be verified by water sampling, since a possible explanation for the hot moments in the spring may also be that N_2O stored under an ice cover is released during melting and spring thaw. During all the study years, we found only one such hot moment in one spring at one site (spring 2007 in the spruce-pine mire associated with lake margin fen, II).

Higher N_2O fluxes observed in fertilization experiments and in agricultural land may be the result of the high nutrient supply. For example, Silvan et al. (2002) reported that the nutrient supply to the buffer from which high N_2O emissions were observed after nutrient addition (45 kg N y^{-1}) was approximately 100-fold higher than the natural level. Finér et al. (2010) estimated that ditch cleaning does not increase N leaching, however felling and soil preparation increase the N load from peatland sites even during the first three years after

Table 2. Average, minimum and maximum N_2O fluxes in buffers and outside of the buffers during the snow free periods (II, III).

Buffer	Average N_2O emission, $mg\ N_2O-N\ m^{-2}\ d^{-1}$	Minimum N_2O flux, $mg\ N_2O-N\ m^{-2}\ d^{-1}$	Maximum N_2O emission, $mg\ N_2O-N\ m^{-2}\ d^{-1}$
Spruce swamp	0.52	-1.71	10.48
Brook margin meadow	0.21	-5.48	5.91
Spruce-pine mire	0.27	-4.93	7.59
Outside of the buffer or before buffer construction			
Spruce swamp*	0.50	-2.65	5.29
Brook margin meadow*	0.41	-4.72	13.09
Spruce-pine mire**	0.18		

*Outside of the buffer

**Before buffer construction

operations; $4.3 \text{ kg ha}^{-1} \text{ y}^{-1}$ and from a mineral soil less than $1 \text{ kg ha}^{-1} \text{ y}^{-1}$. If forestry N_2O emissions were compared to those from organic agricultural lands, the nutrient loading is higher. Even afforestation does not decrease N_2O emissions from organic agricultural soils (emissions $12.8 \pm 9.4 \text{ kg N}_2\text{O-N ha}^{-1}$, Maljanen et al. 2012). In forest management fertilization somewhat corresponds to agricultural practices, although agriculture is much more intensive. N fertilization in mineral soils increases the N load by 12 kg ha^{-1} during the first year after fertilization and by 3 kg ha^{-1} in the second year (Finér et al. 2010). Otherwise the typical N load from forestry operations is so low that the risk of high N_2O release from buffers, similar to that detected in the nutrient addition experiment, is unlikely, provided that the fertilization areas are not vast.

According to the forestry guidelines, if N fertilization is needed in the peatland forest, the N addition should be approximately 100 kg ha^{-1} . However, a tree stand ($48\text{--}148 \text{ tonnes ha}^{-1}$) takes up only $26\text{--}42 \text{ kg N ha}^{-1}$ annually from the soil on peatland forests (Finér 1989). Thus, only part of the added N will be fixed in the tree stand and the remainder may be trapped chemically and physically by the soil, be bound by micro-organisms and by ground vegetation, leached to the watercourses or released to the atmosphere in a gaseous form. According to our production and fertilization experiments in the laboratory (III), N_2O formation may be high in peat under suitable conditions (e.g. sufficient inorganic N supply, soil temperature, hypoxic conditions) and over 50% of inorganic N addition may be released as N_2O . Thus, N fertilization may make peatland forests potential N_2O hot spots. N fertilization may be used, for example, to ensure similar growth rates of stands in different peatland forest figures to improve the profitability of silvicultural measures. However, at present N fertilization is minimal and at a small scale in Finnish peatland forests indicating a minimal risk of high N_2O emissions.

3.3 Does the quality of the DOM affect N_2O dynamics in the catchment?

N_2O dynamics were associated with the C cycle: Both CH_4 and CO_2 concentrations showed a negative correlation with the concentration of N_2O in the soil solution (II). High concentrations of CH_4 and CO_2 were observed in the soil solution with low N_2O concentrations, mainly below the water table level, while in turn low CH_4 and CO_2 concentrations occurred with high N_2O concentrations above the groundwater table. C cycles in peat soils in a gaseous form, but also in a dissolved form in DOM. DOM provides a potential C source and nutrient supply for microbial growth (Meyer et al. 1987; Tranvik 1992; McDowell et al. 2006) and in peatlands, microbial growth may primarily be limited by the availability of P and secondarily by that of labile C (Sundareshwar et al. 2003). DOM and its quality are associated with the N cycle in organic layers of mineral soils (Laurén et al. 2012) and they may be associated with N_2O dynamics in peatland forestry as well (I). Also Billett et al. (2012) reported that the various forms of C released to the aquatic system from forested peatlands indicates a strong connectivity between C cycling in the soil–plant–water system.

We measured net uptake of N_2O in the first year after the clear-cutting, which turned to a net release in the second year. N_2O liberation after clear-cutting and site preparation seemed to be controlled by the presence of low molecular weight DOC fractions (I). The low molecular weight fractions of DOC were almost absent in the year following the clear-cutting but increased after two years. N_2O and DOC dynamics could be accounted for by the growth of decomposers in the logging residues (c.f. Palviainen et al. 2004; Mäkiranta et al. 2012) and in the detritus from the degenerating ground vegetation, resulting in the immobilization of N by the biomass of the decomposers. The more refractory, high molecular weight fraction

of DOC decreased two years after the clear-cutting when both the fraction of low molecular weight DOC and N_2O emissions increased. It is probable that decomposition of the microbial biomass served as a source of N for a new population of decomposers. A lag in available C may have limited the growth of microbes and could be a reason for the decrease of microbial biomass, particularly if the most degradable DOC was used by microorganisms during the first year after the clear-cutting. High availability of low molecular weight DOC also correlated positively with N_2O emissions from the sedimentation pond, so the availability of C for the nitrifying and denitrifying microorganisms may limit those processes (I). Thus, the quality of DOC and in particular the dynamics of labile C compounds seem important to N_2O production and consumption. However, the role of DOC quality in relation to N_2O dynamics requires further investigation.

3.4 A risk of P release from the peatland buffer

The concentrations of total P and PO_4^{3-} were occasionally higher in the water outflow of the buffer than in the water inflow (Table 3 and Fig. 7a–b, 8a–b). The poor retention of P observed in our buffers contrasts with the results reported from fertilization experiments with high P loads where high retention has been observed (e.g. Silvan et al. 2003; Liikanen et al. 2004, Silvan et al. 2004; Väänänen et al. 2008). The P concentrations in our inflow waters were clearly lower than those reported from fertilization experiments (see e.g. Silvan et al. 2003; Liikanen et al. 2004; Silvan et al. 2004; Väänänen et al. 2008). This may partly explain the higher P outputs than inputs: when the P concentration is high, more P will be adsorbed to the particles (Vought et al. 1994). In addition, redox potential, pH, temperature, the amount of already adsorbed P, and the reaction time may affect P adsorption (Vought et al. 1994). After the most common forestry operations, such as harvesting and soil preparation, the increased P load during the ten year period after operations is about 0.251 kg ha^{-1} in mineral soils and 0.638 kg ha^{-1} in peat soils (Finér et al. 2010). In nutrient addition experiments, the amount of added P was $10–50 \text{ kg P ha}^{-1}$ during a 5–8 day period (Väänänen et al. 2008) or 30 kg P ha^{-1} during one growing season (Silvan et al. 2003). Thus, high P retention associated with high P loads has no practical application in Finnish forestry except after P fertilization. Increased P loading after fertilization is only 1.35 kg ha^{-1} , integrated over 10 years in peat soils according

Table 3. The minimum and maximum concentrations of P_{TOT} , $PO_4\text{-P}$, Fe and Al in the spruce swamp in inflowing and outflowing waters and concentrations of P_{TOT} and $PO_4\text{-P}$ in the spruce-pine mire buffer in inflowing water. It was not possible to take water samples from the water outflow in the spruce-pine mire buffer.

Site	Water inflow		Water outflow	
	P_{TOT} , $\mu\text{g l}^{-1}$	$PO_4\text{-P}$, $\mu\text{g l}^{-1}$	P_{TOT} , $\mu\text{g l}^{-1}$	$PO_4\text{-P}$, $\mu\text{g l}^{-1}$
Spruce swamp	22–150	7–77	40–110	27–81
Spruce-pine mire	8–316	0–290		
	Fe, $\mu\text{g l}^{-1}$	Al, $\mu\text{g l}^{-1}$	Fe, $\mu\text{g l}^{-1}$	Al, $\mu\text{g l}^{-1}$
Spruce swamp	220–4400	190–810	840–3200	280–630
Spruce-pine mire, sedimentation pond	122	111		

to Finér et al. (2010). The utility of buffers as binders of low concentrations should be evaluated correctly as our measurements did not include flow rates. Our study sites indicated that peatland buffers probably could not trap P if concentrations are low. Evapotranspiration is probably not a marked component of the water balance of the catchment and thus an explanation for higher P concentrations in outflowing waters may be because the buffer areas are so small and tree stands are partly dead. In dry summer times, the water table level was deeper in the soil than during the colder spring and autumn time when evapotranspiration is lower. The role of vegetation in evaporation is most significant in summer time when vegetation is most abundant.

The concentrations of Fe and Al, the metals which may bind PO_4^{3-} from soil solution (see e.g. Vought et al. 1994; Heikkinen et al. 1995; Nieminen et al. 2008) varied only a little between the study sites. Overall, the concentrations of Fe^{3+} in the vadose waters were similar to those of boreal minerotrophic mires (Table 3, Fig. 7d and 8d; see Bragazza et al. 2005). The concentrations of Al^{3+} were also typical for northern minerotrophic mires (Table 3, Fig. 7c and 8c; see Bragazza et al. 2005) but more than 7 times lower than in a podsol soil in the same region (Pirainen et al. 2007). The PO_4^{3-} binding capacity of Fe and Al in peatland buffers is typically lower than in podzol soils. Buffers are usually constructed just before water courses, and these are often lakeside or riparian peatlands. Construction of numerous but smaller buffers in the upper catchments could utilise areas of podsol soils for buffer construction, which would likely enhance P retention; however, these areas are typically forested and so the costs of water protection would be higher than when utilizing treeless peatlands.

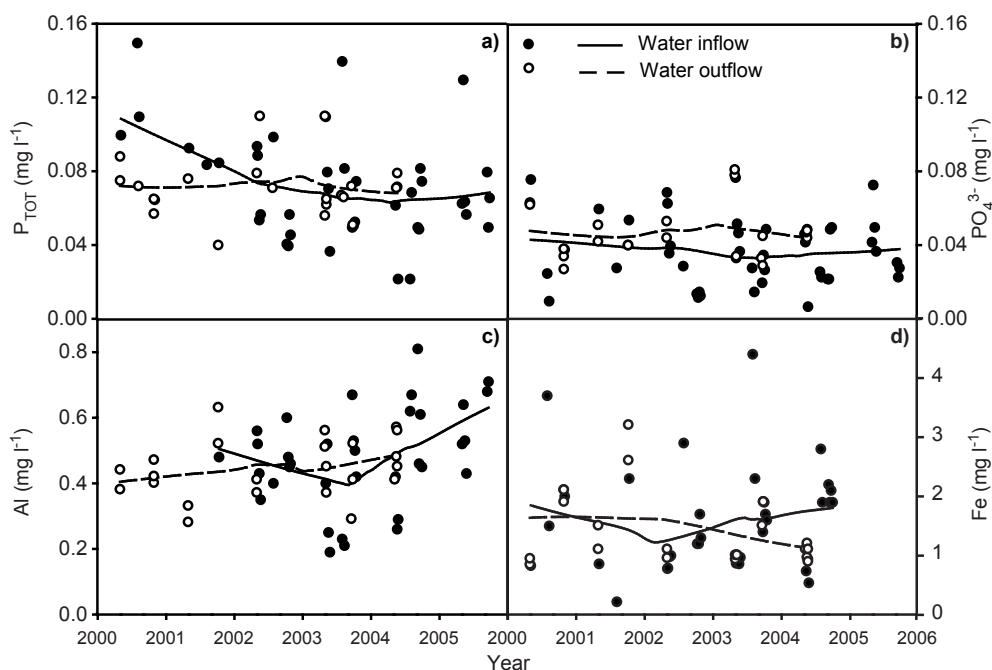


Figure 7. The concentrations of P_{TOT} , PO_4^{3-} , Al and Fe of the water inflow and outflow in the spruce swamp.

Vegetation may bind more nutrients in the plant biomass if the proportion of the below ground biomass increases or perennial species override annual species in the buffer (IV). Peat chemical and physical properties vary e.g. according to vegetation composition, hydrological conditions and nutrient fluxes in different mire types. Thereby, potential P retention capacity varies between possible buffer areas. In addition, buffer construction, with a higher water table level, may release earlier bound P to vadose water and flush nutrients into the watercourses. Furthermore, water table levels may cause changes in the tree stand. For example, in the spruce swamp, the proportion of the oxic peat profile was decreased by a higher water table level after buffer construction and anoxic conditions in the soil killed the trees (IV). About 40% of the trees died on the wettest transect 1 and 35, 19 and 20% on transects 2, 3, and 4, respectively and only 4% in transect 5 outside the buffer. Decomposed biomass potentially released P and N bound in the trees. Based on the dead tree biomass, the estimated release of P was more than 4 kg in the buffer (ca. 13 kg ha⁻¹), and that of N was over 50 kg (about 150 kg ha⁻¹, IV). Furthermore, the live tree stand takes up 2.5–3.4 kg ha⁻¹ of P annually on peatland forests (Finér 1989). P uptake from the soil by the tree stand reduces with a decrease in the live tree stand. The tree biomass was highest in transect 5 outside the buffer, where old stumps remaining from earlier thinnings were not found as in the buffer area. This (i.e. no cuttings in transect 5) may partly explain the higher biomass and P content of trees on transect 5 compared to transects 1–4. Although the dying and decomposing tree stand may be the main reason for the nutrient release in the spruce swamp buffer, harvesting would be problematic as forest machines disturb the soil surface, enhancing by-pass flows and solid loads, and by reducing the capacity of the soil and vegetation to bind nutrients.

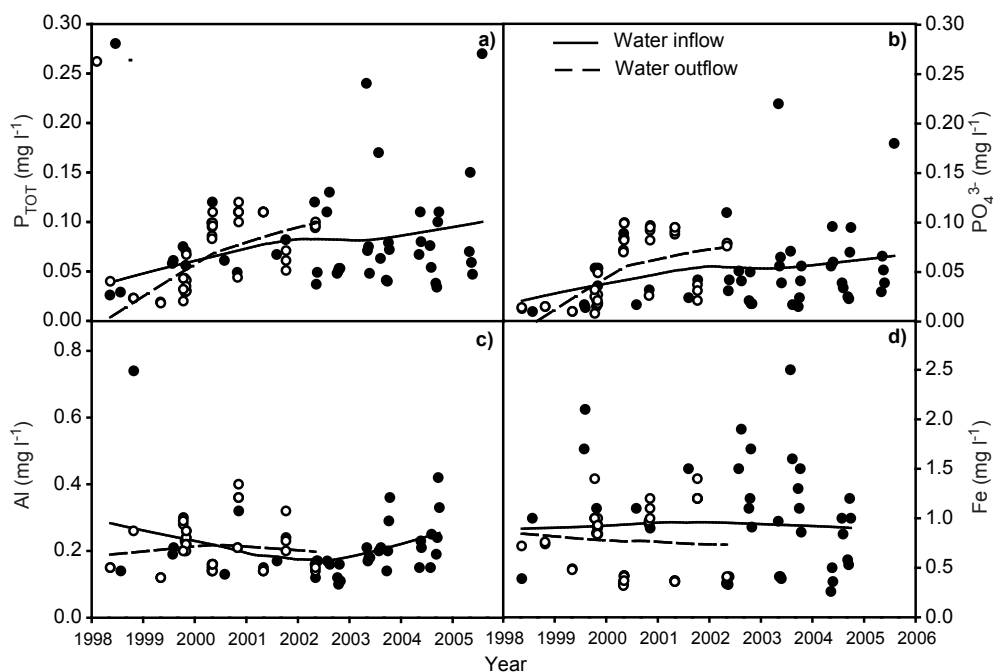


Figure 8. The concentrations of P_{TOT} , PO_4^{3-} , Al and Fe of the water inflow and outflow in the brook margin meadow.

CONCLUSIONS

The role of peatland buffers in nutrient binding with a low nutrient load from forestry operations may be smaller than estimated according to fertilization experiments (c.f. Silvan et al. 2003 and 2004; Väänänen et al. 2008). In our study sites, marginal amounts of inorganic N were released to the atmosphere through denitrification as N_2O in the buffers and sedimentation ponds, and that pathway may be negligible due to the low N load. With high inorganic N loads, N_2O emissions would be higher than our field observations as our laboratory experiments with the same soil demonstrated. Although peatlands with a high N content are potential sources of N_2O (Regina et al. 1996), N is mainly in an organic form and not usable for denitrification. In addition, a high water table level does not allow for nitrification, which could modify organic N to an inorganic form and a suitable reactant for denitrification. This may explain the low N_2O emissions.

The dynamics of labile C concentrations in a soil solution seemed to be connected to the development of the biomass of decomposers in the clear-cut area and thus connected to the dynamics of N in the logging residues. As Smolander et al. (2013) note, logging residues may stimulate processes in C and N cycling in the organic layer in Scots pine stands at least within a few years. The presence of low molecular weight DOC, regardless of the total amount of DOC, may be a significant controller of N_2O effluxes after clear-cutting and site preparation. The growth of decomposer biomass in the logging residues and detritus from the degenerating ground vegetation may result in a temporary immobilization of N. During that phase, the fraction of low molecular weight DOC was nearly absent and net N_2O -uptake into the soil was observed. Soil net N_2O -uptake with the absence of the low molecular weight DOC in soil solution could indicate a temporary immobilization of N by the biomass of decomposers. The lowered availability of low molecular weight DOC possibly limited the growth of microbes later and caused a subsequent decrease of microbial biomass, releasing again some low molecular weight DOC fractions and supporting N_2O emissions.

Under hypoxic conditions favorable for denitrification, the P bound by iron under oxic conditions may be dissolved. Higher PO_4 -P concentrations were measured in the outflow compared to the incoming waters in the two aged buffers, which may indicate PO_4 -P release in the buffer. However, it has been assumed (e.g. Sallantausta et al. 1998; Braskerud et al. 2005; Väänänen et al. 2008) that buffers release nutrients such as PO_4 -P immediately after construction, but bind nutrients over the long term. The fact that phosphate is released under hypoxic conditions and the lag in the development of the nutrient binding capacity reduces the effectiveness of the buffers as the highest P load is released during the 1-3 years after forestry operations (Nieminen 2003; Piirainen et al. 2007) since the nutrient binding capacity in buffers is lowest when the need for nutrient binding is highest. Dying and decomposing tree stands, saturation of nutrient binding sites, overland water flows, floods and the small size of the buffer may be reasons for nutrient leaching and even net nutrient release from our small buffers.

We did not find high N release in gaseous form as N_2O in our buffers, which may indicate a low N load to the peatland buffers from forestry operations similar to that estimated by Finér et al. (2010). Although we did not find significant N retention in our buffers either, sedimentation ponds and buffers apparently decrease the load of solids to the water courses (see Joensuu et al. 1999; Nieminen et al. 2005a). Solids and humic compounds often constitute a more significant problem for water courses than the relatively low nutrient loads released by forestry operations. Even small buffers may be better binders of solids than the

sedimentation bonds (c.f. Sallantausta et al. 1998; Joensuu et al. 1999; Nieminen et al. 2005a and b) and should be recommended (see also Joensuu et al. 2012). Filtering through a peat layer is a more effective method than sedimentation of suspended solids in sedimentation ponds or constructed wetlands. Thus, more information would be needed in regard to the capacity of small buffer areas to bind solids and more attention should be paid to the loading of solids and various humic compounds in forestry. The loading of solids and humus should also be taken into account in the statements of public authority, environmental permits and legislation and more research is needed in regard to the amounts of nutrients bound by solids. In addition, the role of DOM and its quality in the nutrient binding capacity of the buffers is still unclear.

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