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Satu Maaria Karjalainen

IDENTIFICATION OF PROCESSES LEADING TO LONG-TERM WASTEWATER PURIFICATION IN NORTHERN TREATMENT WETLANDS

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IDENTIFICATION OF PROCESSES LEADING TO LONG-TERM WASTEWATER PURIFICATION IN NORTHERN TREATMENT WETLANDS

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Abstract

Treatment wetlands (TW) constructed on natural wetlands potentially perform efficient purification of wastewater, but the longevity of TWs at northern latitudes is not well known. This thesis examined processes affecting nutrient and suspended solids (SS) retention in TWs during their lifetime. In total, 15 TWs were studied using water and peat quality and gas flux data for different TW life lengths, the longest period being 18 years.

The TWs commonly retained nutrients and suspended solids efficiently, even after 18 years of wastewater loading. For nitrogen (N) removal, sedimentation, nitrification-denitrification and plant uptake were efficient processes in the wetlands studied. However, emissions of nitrous oxide (N_2O) from TWs are not a major contributor to climate change due to the small total surface area of TWs. The significance of anaerobic ammonium oxidation (anammox) and other newly discovered nitrogen processes in TWs remains to be clarified. Phosphorus (P) adsorption capacity in TWs remained efficient over a 12-year study period, the process being continuous when surfaces for adsorption were available or freed up through alternating absorption/desorption/ adsorption. Phosphorus accumulation by peat accretion was low, but has not been well assessed in northern TWs receiving nutrient-rich waters. Iron (Fe) and aluminium (Al) in peat extraction runoff and purified wastewater from sewage treatment plants were of great importance for precipitation of P in TWs. Filtration and sedimentation of organic humic substances with Fe- or Al-bound P were other probable P retention pathways. In peat extraction runoff, Fe was more significant than Al for P retention, but Fe-bound P is susceptible to desorption in anaerobic environments, whereas Al-bound P is more strongly retained. Suspended solids were generally retained well, although there was great variation in percentage retention in individual TWs in different years and different seasons. Changes in discharge affected SS transportation and retention. SS were retained by sedimentation, the rate of which was affected by particle size. It is plausible that smaller particles from old peat extraction areas where the extracted peat has a high humification degree erode more easily than poorly humified particles in surface peat. Weakened SS retention may also have been caused by development of preferential flow areas (PFA) in TWs, changes in sediment delivery characteristics and sampling involving too few samples to show SS transportation sufficiently accurately for estimating SS retention.

Thus TWs are potentially ideal for purification of wastewater and can have high purification efficiency even after long-term use in northern regions. They are also more widely applicable as long as their limitations are understood.

Keywords: nutrients, organic matter, peat extraction, retention, suspended solids, treatment wetland, wastewater

Karjalainen, Satu Maaria, Pohjoisten kosteikkopuhdistamoiden pitkäaikaiseen toimintakykyyn johtavien prosessien tunnistaminen.
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Tiivistelmä

Kosteikkopuhdistamot, jotka on rakennettu luonnonkosteikoille, voivat tehokkaasti vähentää erilaisten maankäyttömuotojen ja pistekuormituslähteiden vesistökuormitusta. Niiden käyttöikää pohjoisilla alueilla ei kuitenkaan tunneta hyvin. Tässä väitöskirjassa tarkastellaan kosteikkopuhdistamoissa tapahtuvia biologisia, kemiallisia ja fysikaalisia prosesseja, joilla on vaikutusta ravinteiden ja kiintoaineen pidättymiseen. Yhteensä 15 eri-ikäisen kosteikkopuhdistamon toimintaa tutkittiin veden ja turpeen laadun sekä kasvihuonekaasumittausten avulla. Näistä vanhinta kosteikkoa oli tutkimusta tehdessä käytetty 18 vuotta turvetuotannon valumavesien puhdistukseen.

Tyypillisesti kosteikkopuhdistamot pidättivät ravinteita ja kiintoaineita tehokkaasti jopa 18 vuoden käytön jälkeen. Typenpoistossa sedimentaatio, nitrifikaatio-denitrifikaatio ja kasvien ravinteidenotto olivat tutkituilla kosteikoilla tehokkaita prosesseja. Kosteikkopuhdistamoiden typpioksiduulipäästöt (N_2O) ilmaan eivät kuitenkaan ole merkittäviä ilmastonmuutoksen aiheuttajia, koska tällaisten kosteikkopuhdistamoiden kokonaispinta-ala on pieni. Anammox- (anaerobic ammonium oxidation) ja muiden viimeaikoina muissa tutkimuksissa havaittujen typpiprosessien merkitys kosteikoilla tulisi vielä selvittää. Fosforin adsorptiokyky kosteikkopuhdistamoilla pysyi tehokkaana 12 vuoden tutkimusjaksolla, koska niissä adsorptiopintoja oli joko vapaana tai niitä vapautui absorptio- ja desorptioprosessien seurauksena. Kosteikkopuhdistamolla fosforin kertyminen turpeen muodostuksessa arvioitiin vähäiseksi, tosin kertymistä ei ole tarkkaan määritetty pohjoisilla kosteikkopuhdistamoilla, joihin tulee ravinteikasta vettä. Turvetuotannon valumavesissä ja jätevedenpuhdistamoilta tulleissa vesissä orgaanisten humusaineiden rautaan ja alumiiniin sitoutuneen fosforin suodattuminen ja sedimentoituminen olivat muita todennäköisiä fosforin pidättymismekanismeja kosteikoilla. Turvetuotannon valumavesissä rauta oli alumiinia merkittävämpi tekijä fosforin pidättymisessä. Rautaan sitoutunut fosfori on kuitenkin altis desorptiolle hapettomissa olosuhteissa, kun taas alumiiniin sitoutunut fosfori pidättyy pysyvämmin. Kiintoaines pidättyi kosteikkopuhdistamoissa yleensä hyvin, vaikka pidättyneen aineen osuudessa kokonaiskuormituksesta oli suurta vaihtelua yksittäisissä kosteikkopuhdistamoissa eri vuosina ja eri vuodenaikoina. Muutokset virtaamissa vaikuttivat kiintoaineksen kulkeutumiseen ja pidättymiseen. Kiintoaines pidättyy sedimentaatiossa, jonka suuruuteen vaikuttaa kiintoaineen partikkelikoko. On todennäköistä, että vanhojen turvetuotantoalueiden korkean humusasteen pienikokoiset turvepartikkelit erodoituvat helpommin kuin pintaturpeen vähemmän hajonneet partikkelit. Heikentynyt kiintoaineen pidättyminen saattaa aiheutua myös kosteikkopuhdistamoiden oikovirtauksien kehittymisestä, muutoksista sedimentin kulkeutumistavoissa ja liian harvoista näytteenotoista, jolloin ei pystytä riittävän tarkasti arvioimaan kiintoaineksen pidättymistä.

Kosteikkopuhdistamot voivat olla ideaalisia jätevesien puhdistamiseen ja ovat osoittaneet hyvää puhdistustehokkuutta myös pitkäaikaisessa käytössä pohjoisissa olosuhteissa. Siten ne ovat laajasti sovellettavissa, kunhan niiden käyttömahdollisuuksien rajoitteet on otettu huomioon.

Asiasanat: jätevesi, kiintoaines, kosteikkopuhdistamo, orgaaninen aines, pidättyminen, ravinteet, turvetuotanto

To the memory of my parents

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Oulu, May 2016 Satu Maaria Karjalainen

Abbreviations

anammox	anaerobic ammonium oxidation
CEC	cation exchange capacity
C_{in}	concentration in the TW inlet
C_{out}	concentration in the TW outlet
CW	constructed wetland
FFP	free floating plant-type wetland
FWS	free water surface-type wetland with emergent plants
HAMW	high apparent molecular weight
HSSF	horizontal subsurface flow type wetland
NA	not assessed
OFA	overland flow area
PE	peat extraction
PFA	preferential flow area
PFP	preferential flow path
Q	discharge
R	water purification efficiency
TW	treatment wetland

Original publications

This thesis is based on the following publications, which are referred throughout the text by their Roman numerals:

I Karjalainen SM, Huttunen JT, Liikanen A, Väisänen TS, Kløve B, Ylitolonen A, Heikkinen K & Martikainen PJ (2005) Nitrous oxide emissions from constructed boreal wetlands used to polish municipal wastewater. Verh. Internat. Verein. Limnol. 29: 612–617.

II Liikanen A, Huttunen JT, Karjalainen SM, Heikkinen K, Väisänen TS, Nykänen H, Martikainen PJ (2006) Temporal and seasonal changes in greenhouse gas emissions from a constructed wetland purifying peat mining runoff waters, Ecol. Eng. 26: 241–251.

III Postila H, Saukkoriipi J, Heikkinen K, Karjalainen SM, Kuoppala M, Marttila H & Kløve B (2014) Can treatment wetlands be constructed on drained peatlands for efficient purification of peat extraction runoff? Geoderma 228–229: 33–43.

IV Karjalainen SM, Heikkinen K, Ihme R & Kløve B (2016) Long-term purification efficiency of a wetland constructed to treat runoff from peat extraction. J Environ Sci Health A 51(5): 393–402.

V Karjalainen SM, Ronkanen A-K, Heikkinen K & Kløve B (2016) Long-term accumulation and retention of Al, Fe and P in peat soils of northern treatment wetlands. Ecol Eng 93: 91–103.

The author's contributions to the publications:

I: Planned the work together with the project team, was responsible for field sampling, analysed the water and gas data and wrote the paper. The co-authors commented on the paper.

II: Planned the work together with the project team, participated in field sampling and in writing of the paper.

III: Planned the work together with the project team, participated in field sampling, participated in data analysis and writing of the paper.

IV: Planned the work together with the project team, was responsible for field sampling, analysed the data and wrote the paper with the co-authors.

V: Planned the work together with other writers of existing data, participated in data analysis and wrote the paper with the co-authors.

Contents

1 Introduction

Nutrients and organic matter are essential substances for supporting life in different ecosystems. However, changes in land use also typically increase the amount of leaching substances, potentially causing eutrophication of water bodies and silting up of river and lake beds when water pollution control is not sufficient. Despite increased attention being paid to water quality and water pollution control in recent decades, deterioration of surface waters still continues, including in Finland (Putkuri *et al.* 2013). This has increased government regulatory pressure to improve the status of water bodies, based on European (Council of the European Union 2000) and national goals (Mäenpää & Tolonen 2011).

For water pollution control, especially in remote areas but also in cities, wetlands have proven useful. If available, natural wetlands are often used, as they provide a cost-effective treatment solution (see Kadlec & Knight 1996, Vymazal 1998, Scholz & Lee 2005, and references therein). Constructed wetlands (CW) include various types of systems from natural wetlands to filter systems (Johansson Westholm 2006, Vymazal 2007, Vohla *et al.* 2011), where wastewater flows either horizontally or vertically depending on the structural configuration. Use of wetlands, natural or constructed, has become common practice worldwide for treating e.g. municipal wastewater (e.g. Nichols 1983, Mitchell 1996, Yates *et al.* 2012, Hayward *et al.* 2014), arable field runoff (Hill *et al.* 2000, O'Geen *et al.* 2010, Vymazal & Březinová 2015) and industrial wastewater (Mitchell 1996, White *et al.* 2000, Närhi *et al.* 2012, Schaller *et al.* 2013). In Finland, treatment wetlands (TWs) are used to purify runoff from peat extraction areas, arable land and peatland forestry and stormwater (Ihme 1994, Heikkinen *et al.* 2002, Koskiaho & Puustinen 2005, Nieminen *et al.* 2014, Sänkiaho & Sillanpää 2012, Wahlroos *et al.* 2015). TWs are also used to polish sewage water (Ronkanen & Kløve 2009) and industrial process water such as mining effluent (Räisänen *et al.* 2001, Palmer *et al.* 2015).

Filter materials such as sand, gravel, leca and limestone (Vohla *et al.* 2011) are typically used in constructed TWs. In regions where peatlands are abundant, i.e. areas in the boreal zone and tropics, peat is a common substrate in TWs. Peat can provide an effective medium for retention of nitrogen (N), phosphorus (P) and suspended solids (SS) (Couillard 1994, Heikkinen *et al.* 1995a and b, Bulc *et al.* 1997, Kieckbusch & Schrautzer 2007), dissolved metals (aluminium, iron, nickel) (Brown 2000, Räisänen *et al.* 2001), heavy metals (Couillard 1994 and references therein), metalloids such as arsenic (Palmer *et al.* 2015), pesticides (Roseth & Haarstad 2010), oils and odours (Couillard 1992).

1.1 Processes affecting purification in TWs

The processes occurring in TWs vary depending on the quality and quantity of load entering the TW and soil type, hydraulics, biota and physicochemical properties of the wetland (Kadlec & Knight 1996). Substances which need to be retained include contaminants harmful to biota in recipient waterways (e.g. heavy metals, pesticides, pharmaceuticals, faecal bacteria) and pollutants affecting ecosystems by modifying the environment (e.g. nutrients, inorganic, organic matter) (e.g. Couillard 1992, 1994, Mander & Mitsch 2009, Roseth & Haarstad 2010). The removal and retention of nutrients, which cause eutrophication of surface waters, and of organic matter, which causes siltation of the base of water bodies, are the processes most widely studied in TWs (e.g. Nichols 1983, Couillard 1992, Vymazal 2007 and references therein).

Nitrogen retention and removal in TWs are based on several different processes (Fig. 1), which are affected by biotic factors (e.g. vegetation, microbiota) and abiotic factors (e.g. temperature, pH, soil type, availability of carbon, presence of oxygen (O_2), redox potential) (Vymazal 2007, Faulwetter *et al.* 2009 and references therein). Physicochemical transformations and processes mitigated by microbes change one N species to another, resulting in retention or removal of N in TWs.

Important soluble forms of N in wetland processes are ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-). Ammonia (NH_3) in water can be transformed to gaseous ammonia through volatilisation, to gaseous dinitrogen (N_2) through anaerobic ammonium oxidation (anammox) or to nitrite through partial nitrification (nitritation) and further to nitrate through nitrification, or it can be assimilated by vegetation or microbes to form organic N (Couillard 1994, Vymazal 2007). Ammonia may be formed through fixation of gaseous N_2, ammonification of organic N and nitrate-ammonification of reduced nitrate (Couillard 1994, Vymazal 2007). NH_4^+ ions may also be adsorbed through cation exchange reaction with detritus, inorganic sediments or soils (Heikkinen 1995a, Vymazal 2007). In denitrification (heterotrophic and sulphur based autotrophic, Shao *et al.* 2010, Chen *et al.* 2014), nitrate is reduced to nitrite and further to nitric oxide (NO), N_2 or nitrous oxide (N_2O). Nitrite together with ammonium may be transformed to N_2 in anammox (van de Graaf *et al.* 1995). In decaying organic material, organic nitrogen is buried through peat formation and thus becomes unavailable for nutrient cycling (Couillard 1994, Vymazal 2007). The significance of these N retention and removal processes in various types of CWs has been estimated by Vymazal (2007), with the results demonstrating high variability in permanent N removal potential in different

TWs (see also Ligi *et al.* 2014). Through these processes, N is permanently removed from TWs by ammonia volatilisation, anammox, denitrification, ammonium adsorption, plant uptake (if vegetation is harvested) and burial of organic nitrogen including microbes and plants. Among these processes, anammox and denitrification occur only in anaerobic conditions and involve bacteria as does nitrite-dependent anaerobic methane oxidation (Hu *et al.* 2014), but its significance for N removal is not well known. Ammonia volatilisation has been found to be insignificant in flooded soils and sediments with pH below 7.5 (Reddy & Patrick 1984). Ammonium adsorption is most effective in soils with a high amount of sorption sites, e.g. in clays (Vymazal 2007).

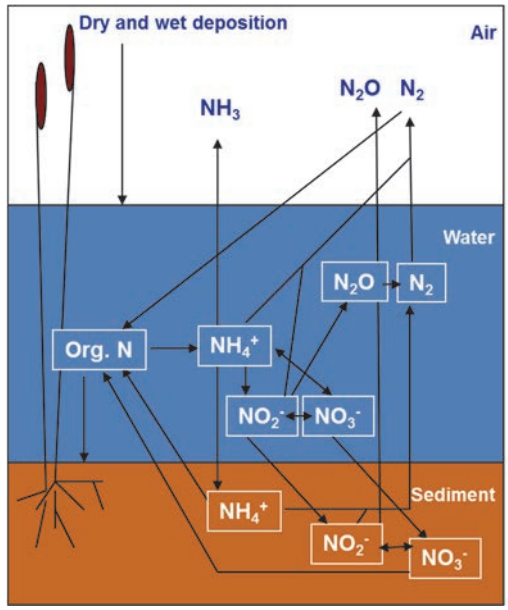

Fig. 1 Nitrogen processes in wetlands.

Phosphorus retention processes in TWs include (ad)sorption, plant and microbial uptake, peat/soil accretion including sedimentation, filtration, precipitation and formation of phosphine (PH_3) (Kadlec & Knight 1996, Vymazal 2007) (Fig. 2). Of these processes, sorption and plant uptake capacity are considered saturable (Dunne and Reddy 2005). Precipitation is effective when material providing the capacity for P sorption is not limited. Biological uptake by plants has been shown to play a

minor role for P removal (Huttunen *et al.* 1996, Vymazal 2007). In general, vegetation serves mainly as a short-term P sink if the biomass is not harvested (Richardson 1985). Nichols (1983) found that microbes may be important in P immobilisation in the initial phase of applying wastewater to peat, but that continuous application of wastewater with low C/P ratio soon saturates the P demand of microbes. However, Silvan *et al.* (2003) noted that the soil microbial community grows slowly in environments with low pH, immobilising nutrients for a longer time than in soils with higher pH. Overall, accretion of peat or soil is regarded as the only continuous long-term sink for P (Vymazal 2007), but it should be noted that peat accretion is effective only if biomass production is high. PH_3 is generally present at very low and greatly variable concentrations in the atmosphere (Gassmann *et al.* 1996). However, PH_3 fluxes have been found to rise in high air temperature and increased vegetation. Thus vegetation expedites the release of PH_3 from soils, whereas water coverage may hinder the fluxes from soils and sediments to the atmosphere (Han *et al.* 2011). Soil type in general greatly affects the adsorption of P depending also on the soil content of Fe, Al, Ca and Mg (Vymazal 2001). However, P adsorption by Fe is susceptible to release when anoxic conditions occur, e.g. through watertable fluctuations (e.g. Meissner *et al.* 2008, Niedermeier and Robinson 2009). The P retention processes in TWs are also controlled by other hydraulic, chemical and physical properties, such as pH, cation exchange capacity (CEC), hydraulic conductivity, porosity and surface area (Heikkinen *et al.* 1995b, Vymazal 1998). However, according to Drizo *et al.* (1999) these properties play only minor roles in estimated P adsorption capacity in different wetland substrates, highlighting the complex nature of P processes in P retention in wetlands.

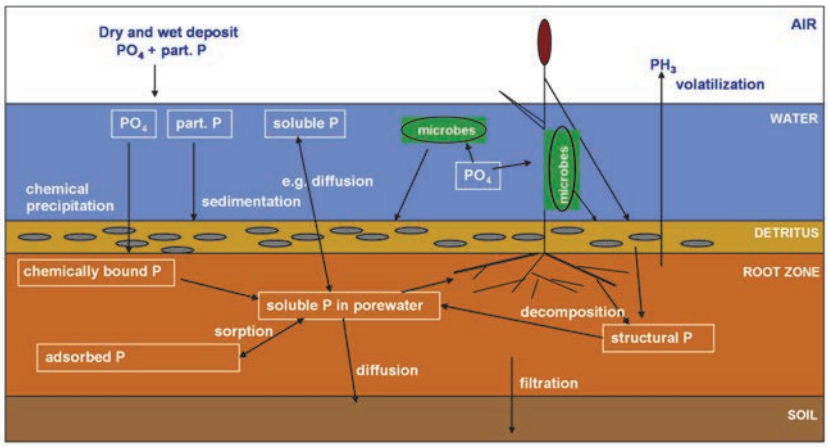

Fig. 2 Phosphorus processes in wetlands.

The retention processes for suspended solids (SS) in TWs are sedimentation and filtration (Brix 1993). In addition, the organic fraction of SS is affected by microbial degradation. Along with these SS retention processes, nutrients and pathogens are also retained (Brix 1993). Sedimented particles may, however, be returned to the water column by resuspension from sediment. Braskerud (2001) described how macrophytes can enhance retention of sediment by reducing resuspension in shallow TW ponds. Vegetation enables shorter particle settling distance, as it increases the hydraulic efficiency by reducing short-circuit or preferential flow.

1.2 Long-term purification in TWs: Objectives and hypotheses

Previous long-term studies on the function of wetlands are rare and include work carried out in the Everglades wetlands in Florida (e.g. Reddy *et al.* 1993, Craft & Richardson 1993), in riverine wetlands (Mitsch *et al.* 2012) and in horizontal subsurface flow wetlands in Czech Republic (Vymazal 2011, Vymazal & Březinová 2014). In Finland, Heikkinen *et al.* (2002) and Ronkanen & Kløve (2009) have previously studied Kompsasuo and Puutiosuo TWs extensively for periods of at least 10 years.

In a TW constructed on peat and purifying peat extraction runoff, the P adsorption capacity of the peat has been estimated to be 20 to 25 years (Heikkinen *et al.* 1995b). This is long time compared with e.g. CWs with sand or gravel as a

substratum, where saturation conditions can be reached after few years of operation (Mann & Bavor 1993, Arias *et al.* 2001).

For wetlands treating different types of runoff, the hydraulic load to TWs is seldom constant and depends greatly on the climate, particularly variations in precipitation and air temperature. In wetlands designed for point source pollution removal, the hydraulic load is more controlled and depends on the activity of systems used (e.g. sewage treatment in ski resorts, industrial processes in mining). It is also possible that the quality of load changes over time, thus changing the retention processes in a treatment plant. The properties of TWs may also change over time due to changes in: 1) quality and quantity of load, 2) substance saturation, 3) hydraulics, 4) biota, and 5) physico-chemical properties of the TW. Both the load and TW properties thus affect the purification results. For example, changes in the structure of free water surface (FWS)- and overland flow area (OFA)-type TWs differ under long-term loading processes (Fig. 3), as do the P and N processes in those wetland types (Vymazal 2007).

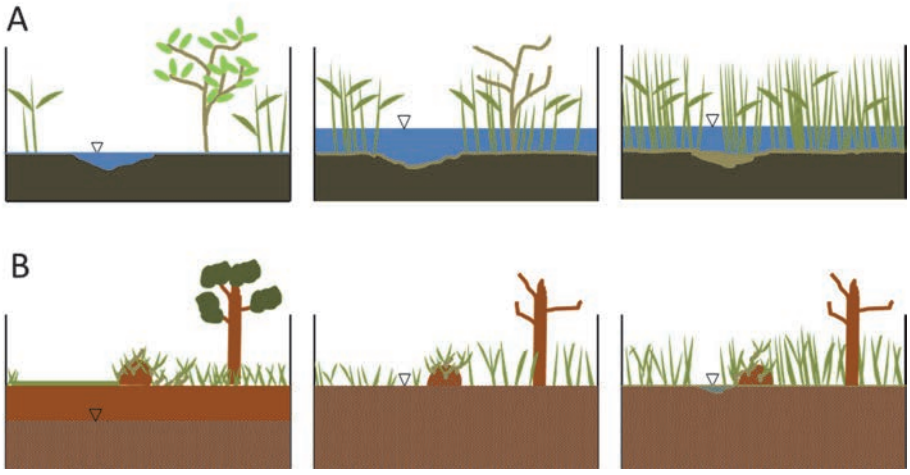

Fig. 3 Changes in A) free water surface -type and B) overland flow area-type treatment wetlands during long-term use for water treatment.

The overall objective of this study is to identify the processes involved in long-term runoff and wastewater purification in TWs of northern region. The hypotheses tested in this thesis were that:

- TWs constructed on drained peatland may also function well for a long period if soil properties, vegetation and runoff quality enable this (III)
- retention efficiency may change in different phases of TW lifetime (III, IV), but TWs constructed on pristine peatland retain and/or remove P, N and SS for a long time after establishment (IV, V),
- N_2O emissions are not a significant concern for the treatment wetlands of the boreal zone (I, II),
- precipitation of P by metals in inflow is an important retention mechanism in TWs treating peat extraction runoff (III, IV, V),
- processes affecting nutrient retention differ in TWs constructed on different soils and receiving wastewater of differing quality (I, II, III, IV, V).

2 Materials and methods

2.1 Study wetlands

The TWs studied in this thesis are situated in northern Finland, in the zone from Central Ostrobothnia to Lapland (Fig. 4). Most of the TWs are constructed on peatlands, either pristine or drained, but Lakeus TW is constructed on pristine coastal reed vegetation on clay soil. Most of the TWs purify peat extraction runoff, but two polish wastewater from sewage treatment plants (Table 1).

Ruka sewage treatment plant mechanically and chemically purifies wastewater from the Ruka ski resort area. A characteristic of Ruka TW, which is constructed on peatland, is that it receives its highest hydraulic load during the skiing season in spring time and its lowest hydraulic load in August (Ronkanen & Kløve 2008). Lakeus central treatment plant purifies municipal wastewater, treating the sewage water chemically and biologically. Lakeus TW is constructed on pristine reed vegetation area on the shore of the Bay of Bothnia and was the only FWS-type wetland (Vymazal 1998) studied here. The other TWs studied can be divided into OFA types (Ihme 1994) which have both horizontal surface and subsurface flow (Ronkanen & Kløve 2005), and those constructed on drained peatlands (III). The TWs are presented in more detail in Tables 1 & 2.

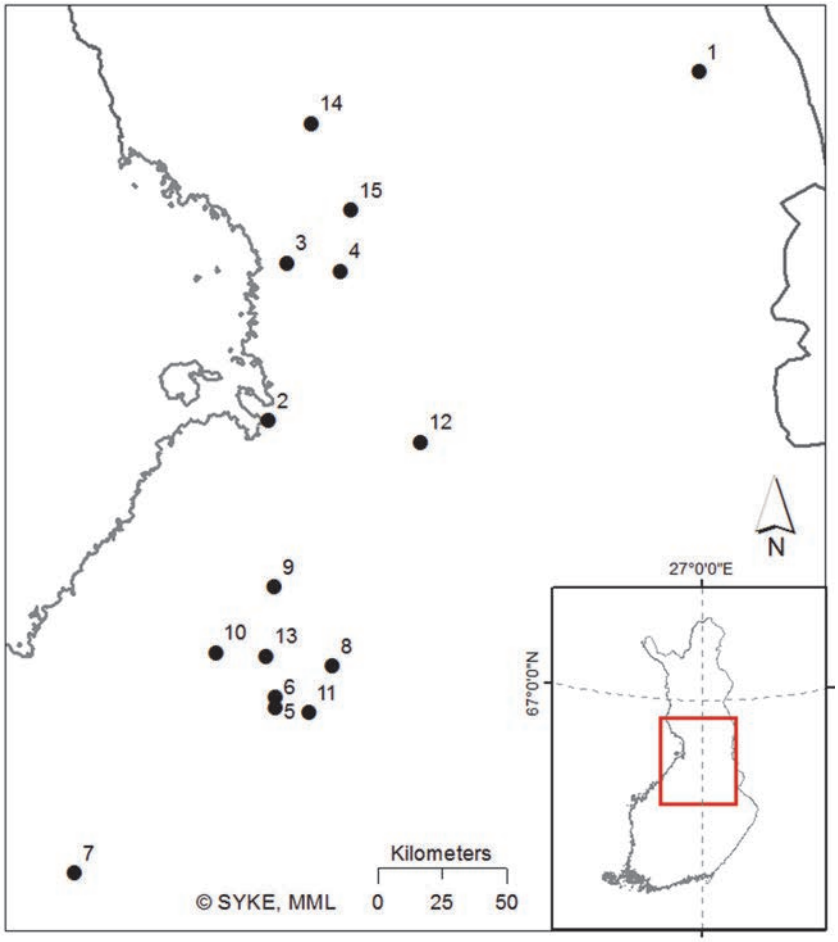

Fig. 4 Location of the treatment wetlands (TWs) studied in this thesis. Numbers indicate the respective TWs listed in Tables 1 and 2.

Table 1. Details of the 15 treatment wetlands (TWs) studied.

No.	Wetland	Latitude	Longitude	Type of load	Start of peat extraction	TW type	Year of TW establishment	Age of TW at study (y)
1	Ruka	66º10'10"	29º07'28"	Polished sewage water	-	OFA[1]	1995	7
2	Lakeus	64º53'78"	25º27'80"	Polished sewage water	-	FWS[2]	1996	7
3	Kompsasuo	65º44'43"	25º57'80"	PE[3] runoff	(1988), 1992–1995	OFA	1986–1989	4, 5, 15, 17
4	Puutiosuo	65º42'	26º03'	PE runoff	1994[4]	OFA		6, 18
5	Hankilaneva 1	63°56'22"	25°34'9"	PE runoff	1994	Drained peatland	1992	18
6	Hankilaneva 2	63°54'8"	25°33'57"	PE runoff	1994	Drained peatland	1992	18
7	Kapustaneva	63°18'13"	24°2'48"	PE runoff	2008	Drained peatland	2008	1, 2
8	Luomaneva	64°2'59"	26°0'48"	PE runoff	1992	Drained peatland	1998	11, 12
9	Savaloneva	64°19'12"	25°32'7"	PE runoff	2009	Drained peatland	2005	4, 5
10	Äijönneva	64°5'13"	25°4'56"	PE runoff	2010	Drained peatland	2009	0, 1
11	Iso-Lamminneva	63°53'10"	25°49'48"	PE runoff	2011	Drained peatland	2010	1
12	Itäsuo	64°49'45"	26°42'14"	PE runoff	1979	Drained peatland	1995	16
13	Kuljunneva	64°4'45"	25°28'50"	PE runoff	2010	Drained peatland	2009	2
14	Lumiaapa 2	65°55'49"	25°45'39"	PE runoff	1977	Drained peatland	1996	15
15	Pohjoinen Latvasuo	65°37'55"	26°6'41"	PE runoff	1996	Drained peatland	1994	17

[1]OFA = overland flow area

[2]FWS = free water surface

[3]PE = peat extraction

[4]Heikkinen *et al.* (2002)

Table 2. Characteristics of the 15 treatment wetlands (TWs) studied. Degree of humification refers to the von Post (1924) scale for surface peat. Sampling indicates: 1 = water quality, 2 = peat, and 3 = gas sampling in the TW.

No.	Wetland	Hydraulic load (mm d^{-1})	TW area (ha)	TW area/ catchment area (%)	Degree of humification	Sampling	Paper
1	Ruka	44[1]	0.82	-	H1–H6	1, 2, 3	I
2	Lakeus	82[2]	4.4	-	-	1, 2, 3	I
3	Kompsasuo	15[3]	2.4/2.2[4]	4.8/4.4[4]	H1–H4	1, 2, 3	II, IV, V
4	Puutiosuo	18[3]	6	6.6	H1–H3[5]	1, 2	V
5	Hankilaneva 1	NA	8.9	8.9	H6	1, 2	III
6	Hankilaneva 2	NA	7.8	3.5	H7	1, 2	III
7	Kapustaneva	NA	6.9	4.6	H4	1, 2	III
8	Luomaneva	NA	3.2	2.8	H5	1, 2	III
9	Savaloneva	NA	6.1	7.4	H5	1, 2	III
10	Äijönneva	NA	5.8	5.6	H5	1, 2	III
11	Iso-Lamminneva	NA	1.6	4.1	H4	1, 2	III
12	Itäsuo	NA	12	6.3	H3	1, 2	III
13	Kuljunneva	NA	5.8	6.6	H5	1, 2	III
14	Lumiaapa 2	NA	9.5	5.1	H4	1, 2	III
15	Pohjoinen Latvasuo	NA	2.8	1.8	H5	1, 2	III

[1]Ronkanen & Kløve (2009).

[2]In 2002–2003 (I).

[3]In period from May to October (V).

[4]Intial size measured in 1986 (II, IV), confirmed size measured in 2002 (V).

[5]Heikkinen *et al.* (2002).

2.2 Sampling and analyses

Water, peat and gas samples were taken in the TWs. The peat samples were taken in summer and the water and gas samples in different seasons.

At the TWs receiving treated sewage water, discharge was continuously measured and recorded at the sewage treatment plant. Discharge to and from TWs receiving runoff from peat extraction areas was measured for those TWs where there was appropriate measuring equipment, such as a triangular Thompson's V-notch measuring weir equipped with a graphic water level recorder or a pressure probe (Kompsasuo and Puutiosuo TWs) or a recording water level sensor (Savaloneva TW). In TWs where runoff is pumped through pipes to the wetland, discharge at the inlet was measured with the EHP-Ultrasonic Measurement System Fluxus ultrasonic device (EHP-Tekniikka Ltd.) (Kapustaneva, Luomaneva and

Äijönneva TWs). However, at the outlet of these TWs there was also a measuring weir equipped with a recording water level sensor.

At some TWs (Ruka, Lakeus and Kompsasuo), water level, soil temperature, pore water temperature and redox potential were measured *in situ*.

Vegetation was studied at 3-6 points, each measuring 2 m x 2 m, in six TWs constructed on drained peatland (Hankilaneva I and II, Kapustaneva, Luomaneva, Savaloneva and Äijönneva TWs). Tree stands were estimated visually in all TWs constructed on drained peatlands. The methods used are presented in Paper III and in Postila *et al.* (2011).

Calculation of loads was generally performed using the water discharge measured at the upper and lower measuring weir and water quality data from the inlet and outlet. However, if the lower measuring weir at the outlet was not functioning reliably, as was the case for Kompsasuo TW, the outgoing loads were calculated based on the discharge from the upper measuring weir. The loads were calculated with the period method (Tattari *et al.* 2014), in which the mean daily discharge of days prior to and following the water quality sampling day are used to calculate mean discharge. For the drained TWs, however, the mean discharge was counted from the previous days of water quality sampling, as done in operational monitoring of peat extraction in northern Finland (Postila *et al.* 2011).

The reduction in the load of different substances was calculated as the difference between mean load of substance at the inlet and outlet of Kompsasuo TW. Percentage retention for a given period was calculated from daily loads for spring-autumn and monthly loads for winter as:

$$x = \{ \Sigma [(QC_{in})_i - (QC_{out})_i] / \Sigma (QC_{in})_i \} * 100 \quad (1)$$

where:

x is the percentage reduction (%)

C_{in} is the concentration at the inlet of TW

C_{out} is the concentration at the outlet of TW

Q is the inflow discharge calculated for spring-autumn from the mean of 7-day average inflow discharge (determined as a moving average from daily discharge three days before and after the water quality measurement day), and for winter from the water quality measurement day.

Water purification efficiency (R) was calculated for the drained wetlands constructed on peatland using the mean substance concentrations of incoming and outgoing water of the TW as:

$$R = [(C_{in} - C_{out}) / C_{in}] * 100\% \quad (2)$$

where:

C_{in} is mean substance concentration in incoming water

C_{out} is mean substance concentration in outgoing water.

2.2.1 Water sampling (I, II, III, IV, V)

Water samples were taken at the inflow and outflow of TWs and from groundwater and surface water, peat pore water, soil and gas chambers. Water sampling of inflow and outflow was typically conducted once a month in winter, and every two weeks in spring, summer and autumn. Other water samples were taken when different studies were conducted.

In all TWs studied, for estimation of inflow and outflow water quality and for calculation of substance loads and retention, water samples were taken at the inlet and outlet of the TW. In general, these samples were analysed for different species of P and N, suspended solids (SS), loss on ignition (LOI), pH, chemical oxygen demand (COD_{Mn}) and Fe. In addition, for some TWs electrical conductivity (EC), biological oxygen demand (BOD_7), total organic carbon (TOC), dissolved organic carbon (DOC), sulphate (SO_4) and/or water colour were analysed in the water samples, while water temperature, pH and/or oxygen concentration were measured onsite. SS was determined as total SS and LOI represented organic SS, and thus the ignition residue represented inorganic SS. To obtain data on dissolved organic fractions in humic waters, COD_{Mn}, total P and total Fe were also analysed after sample filtration through Whatman® GF/C glass microfibre filters with pore size ~1.2 µm. COD_{Mn} was taken as a measure of total organic matter (TOM) and COD_{Mn} in the filtered water sample as a measure of dissolved organic matter (DOM). Water sampling and analysis methods are described in more detail in Papers I-V.

In the Ruka, Lakeus and Kompsasuo TWs, water samples were also taken from the aluminium frames used for gas measurements. In addition, water samples were taken around the gas sampling plots in Ruka and Lakeus TWs (see section 2.2.3 Gas sampling). These samples were filtered for analysis of total N, ammonium N (NH_4-N), nitrite and nitrate N (NO_2+NO_3-N) and TOC (Paper I).

Peat pore water was obtained by squeezing water from peat taken from the surface layer (0-20 cm) and a deeper peat layer (30-40 cm) at different parts of Kompsasuo and Puutiosuo TWs. These samples were analysed for total P, phosphate P (PO_4-P), Fe and Al. The choice of sampling sites in TWs is described in detail in Paper V.

Sampling, sample pre-treatment and transportation were performed according to the guidelines of the laboratory quality manual, based on the SFS-EN ISO/IEC 17025 standard.

2.2.2 Peat sampling (III, V)

In Kompsasuo and Puutiosuo TWs and their reference peatlands (areas 50-150 m away from the TW and not affected by peat extraction), peat samples were taken from 0-50 cm depth. Sampling was done with an auger of cross-section 8 cm x 8 cm and length 70 cm. The peat samples were analysed for total Al, total Fe and ammonium oxalate-extractable Al (Al_{ox}) and Fe (Fe_{ox}). Al_{ox} and Fe_{ox} were determined using a method modified according to Niskanen (1989). Oxygen concentration, redox potential and pH were measured *in situ* in boreholes 10 cm below the surface layer.

For estimation of the P adsorption capacity of Kompsasuo TW, adsorption isotherms for peat from the wetland and its reference area were determined by a common batch-test procedure. The procedure was performed according to Heikkinen *et al.* (1995b) to avoid any problems when comparing newer measurements with old measurements reported by those authors. The measurements were made on peat samples (4-6 g, three replicates) in their natural state of humidity. For each isotherm, a set of six samples to which 40 mL of standard KH_2PO_4 solution of varying strength (0, 8, 100, 300, 500, 1000 mg P L^{-1}) were added, was processed. The samples were filtered through 1.2 µm (Schleicher & Schuell GF52) and 0.2 µm (Nuclepore) membranes. The samples were then preserved with H_2SO_4 and PO_4-P was measured using a molybdenum blue-ascorbic acid method. All orthophosphate lost from the liquid phase was assumed to be adsorbed. Adsorption to peat was calculated in mg P g^{-1} dry material. For this calculation, the dry weight of the wet peat samples was determined by drying the soils for approximately four days at 105°C. The relationship between the equilibrium PO_4-P concentration in solution and the PO_4-P amount sorbed on the peat was described by adsorption isotherms with Freundlich equations as delineated in Heikkinen *et al.* (1995b).

Peat P in four TWs constructed on drained peatland (Hankilaneva 1, Kapustaneva, Savaloneva and Äijönneva) was fractionated from 3-5 replicates into: 1) loosely bound and water-soluble P, 2) Fe- and Al-bound P, 3) Ca-bound P, and 4) organic P including humic and fulvic acids. Sequential extraction was performed according to Golterman (1996).

2.2.3 Gas sampling (I, II)

Fluxes of CH_4, CO_2 and N_2O were measured with a static chamber technique (Crill *et al.* 1991, Nykänen *et al.* 1995) using aluminium frames covering an area of 60 cm x 60 cm. In Kompsasuo TW, initial gas measurements had been conducted in summer 1992. They were repeated from August 2001 to August 2002. In Ruka and Lakeus TWs, measurements were conducted during the snow-free period in 2002 and in wintertime once in Ruka (February 2002) and twice in Lakeus (March 2002 and February 2003).

In Kompsasuo and Ruka TWs, the sampling plots were located at different distances from the distribution ditch and each contained 1-4 frames inserted into the peat. In Lakeus TW, the three sampling plots were located at different distances from the inlet: in the pool near the inlet of the wetland (upper pool), next to the intermediate dam within the reed vegetation (vegetated area) and in the pond near the outlet of the wetland (pond). In summer, three floating chambers (Huttunen *et al.* 2002) were placed in both the upper pool and pond plots, and three aluminium frames were assembled in the vegetated area plot. In winter, in addition to these plots with 2-3 chambers, two floating chambers were placed in open water in the vegetated area.

For flux measurements, a chamber was placed in the water-filled groove of the frame, and four gas samples were taken from the chamber headspace with polypropylene syringes equipped with three-way stopcocks during 24-28 min measuring periods in summer and 60 min periods in winter. In Ruka and Kompsasuo TWs, the chamber was placed directly on the peat and sealed with snow for measurements in winter.

Gas samples from the chambers were analysed within 24 hours of sampling using a gas chromatograph (Hewlett Packard [Palo Alto, CA] 5890 Series II) equipped with a flame ionisation detector for CH_4, a thermal conductivity detector for CO_2 and an electron capture detector for N_2O (Nykänen *et al.* 1995). The fluxes were calculated from the increase/decrease in gas concentration in the chamber

over time using the chamber/frame surface area. More detailed descriptions of field samplings and gas measurements are presented in Papers I and II.

2.3 Statistical analyses

The data were tested statistically using the SPSS statistical package. Correlations between watertable level, water quality and peat parameters were tested with Spearman's rank correlation (r_s), as the parameters were typically not normally distributed (I, III, IV, V). However, Pearson correlation coefficient (r_p) was used for gas fluxes, gas concentrations in TW water, watertable levels and surface soil and air temperature in Kompsasuo TW (II). Differences in the inlet and outlet gas concentrations of Kompsasuo TW were tested with Student's *t*-test, which was also used to compare the gas fluxes in two different years (II). Variations in gas fluxes between sub-sites in Kompsasuo TW were tested with analysis of variance (ANOVA) using Tukey's *b post hoc* test. Differences in water quality between seasons were estimated for Kompsasuo TW with one-way analysis of variance (IV). If the variances of seasons differed significantly, the Welch or Brown-Forsythe test was used. To compare the medians of peat P concentrations from the dataset taken in different years in the middle line of Kompsasuo treatment peatland, the Sign test was used (V). Linear regression was used to estimate P concentration by Al and Fe in peat and pore water, and Al_{ox} and Fe_{ox} in peat (V). In Paper V, differences in the concentrations of P, Al, Fe, Al_{ox} and Fe_{ox} between the wetlands and reference areas were also examined using a two-way ANOVA with area (wetland and reference area) and sampling depth (0-20 cm and 30-40 cm) as fixed factors. For this, separate analyses were performed for Kompsasuo and Puutiosuo TWs. To study the interaction of significant area and depth, a simple effect test was conducted to examine differences in concentrations separately for the two levels of each factor. Results were taken to be significant at the 5% level ($p<0.05$). Variances were again tested using Levene's test and logarithm transformations were applied when needed for normal distribution of variables.

3 Results and discussion

3.1 Hydrology and hydraulics at the TWs (III, IV)

The hydraulic loads and discharge from peat extraction area were found to vary between years due to changes in hydrology (e.g. precipitation, evaporation and evapotranspiration). The highest inflow values were measured in spring, after snowmelt, but also after wet periods or heavy rainfall events in summer and autumn. In some years the hydraulic load and precipitation showed high seasonality, as was the case in Kompsasuo TW in 1988 and 2002 (Paper IV).

Water residence time and effective flow depth in the wetland had a great impact on the success of wastewater treatment in TWs. Estimated water residence time in the wetlands studied varied from less than 1 day in Luomaneva TW to more than 11 days in Kapustaneva TW. In Ruka TW, water residence time was 1-2 days, in Lakeus TW 1.5-4 days, in Äijönneva TW less than 3 days, in Savaloneva TW more than 3 days and in Kompsasuo TW 6-11 days, (Karjalainen *et al.* 2005a, Ronkanen & Kløve 2009, III). In the studied TWs, the effective flow depth varied greatly. In OFA-type TWs, runoff/polished sewage water flowed mainly in the upper 40 cm depth: in Puutiosuo TW down to 20 cm (Ronkanen & Kløve 2008), in Ruka TW down to 30 cm and in Kompsasuo TW down to 40 cm (Ronkanen & Kløve 2005). In TWs constructed on drained peatlands, however, there was more variation in effective flow depth: in Luomaneva TW it was only down to 10 cm depth and in Kapustaneva, Savaloneva and Äijönneva TWs it was down to 20 cm, but in Itäsuo TW it was down to 40 cm depth and in Kuljunneva, Lumiaapa 2, Pohjoinen Latvasuo and Hankilaneva 1 and 2 TWS it was even down to 60-70 cm depth (III). In Iso-Lamminneva TW, median hydraulic conductivity decreased between 20 and 30 cm depth, but increased again in deeper peat layers (III).

3.2 Nitrogen (I, II, III, IV)

Mean total N concentration in the runoff from peat extraction areas varied from 0.78 to 6.3 mg L^{-1}. The concentration of inorganic N was higher in sewage water (variation in seasonal average 27.7-72.2 mg N L^{-1}; Karjalainen *et al.* 2005a, b) than in peat extraction runoff (average 0.2-2.3 mg N L^{-1}). Inorganic N was mostly in the form of NH_4-N in the TWs studied (Postila *et al.* 2011, I, III, IV) except in Hankilaneva 1 TW. In general, at the outlet of TWs inorganic N occurred mainly

as NH_4-N except in Kompsasuo TW, where inorganic N constituted 71% of NO_2+NO_3-N in periods with no ground frost (IV). The concentration of NO_2+NO_3-N was higher at the outlet than at the inlet only in Ruka and Lakeus TWs in winter (I). In Kompsasuo TW the concentration of NO_2+NO_3-N was high (mean 0.15 mg L^{-1} in summer-autumn 2002) at the outlet.

High concentrations of NH_4-N at the outlet of TWs can indicate insufficient CEC in the wetland peat/soil. In Lakeus TW, NH_4^+ reserved only 0.27% of measured CEC sites in the inlet pond (Karjalainen *et al.* 2005a), whereas Heikkinen *et al.* (1995a) estimated that in Kompsasuo TW NH_4^+ could occupy 4.6-5.8% of CEC sites. Taking into account the NH_4-N loads into Kompsasuo TW, this indicates NH_4^+ retention potential for less than 6 months in the top 15 cm surface layer of peat (Heikkinen *et al.* 1995a). However, their results also showed that the adsorption capacity of Kompsasuo TW was actually longer than estimated. This may be due to new CEC sites recently released by nitrification-denitrification and biological assimilation (Heikkinen *et al.* 1995a).

Lack of oxidation in wetland substrates can also lead to increased concentrations of NH_4-N at the outlet of TW, thus indicating deficient nitrification. This can be caused by e.g. short residence time in the TW. Long residence time is needed for efficient oxygen transport and aeration of wetland substrate. Residence time and temperature are key factors for N removal in cold climates (Ronkanen & Kløve 2009). The water residence time is longer in Kompsasuo TW than in Ruka and Lakeus TWs, indicating that there are other possible factors causing ineffective nitrification.

In winter, the air temperature is typically below 0°C in the study region, leading to frost in the wetlands. If soil frost occurs before there is a snow cover on the wetland or the cover is only thin, ground frost goes deeper into TW soil and remains longer in spring. This may weaken the performance of the TW. If there is a proper snow cover before low temperatures occur, snow may prevent the peat from freezing, thus enabling retention processes to continue. In Lakeus and Ruka TWs, the water temperature was between 0.1 and 6.2°C and in Kompsasuo TW between 0.1 and 3.5°C in winter/spring (I, IV). At these temperatures, there are some contradictory observations on whether nitrifying bacteria can act: some studies have observed significant activity between 0 and 5°C, while in other studies nitrification has been observed to be inhibited by water temperatures below 10°C and to fall drastically below 6°C (Herskowitz *et al.* 1987, Sundblad & Wittgren 1991, Xie *et al.* 2003, Sundberg *et al.* 2007a). Cookson *et al.* (2002) therefore suggested that nitrifying communities may adapt to temperature changes by

maintaining their activity through metabolic adaptation at lower temperatures. Hence in addition to summer, nitrification activity seems to be probable in winter. However, the optimal temperature range for the nitrification process (28-36°°C in Faulwetter *et al.* 2009, 30-40°C in Vymazal 2007) is seldom reached in northerly regions.

In addition to water residence time and temperature, redox potential, pH and certain plant species are also reported to affect N removal mitigated by microbes (e.g. Bremner & Shaw 1958, Faulwetter *et al.* 2009). Those authors also reported that in TWs with low redox potential, plant oxygen release may not compensate for the demands of nitrification. This can be the case especially in horizontal subsurface TWs for domestic wastewater high in organic carbon (Faulwetter *et al.* 2009). It could also be the case in TWs constructed on peatlands for treating peat extraction runoff or polished sewage water. In such TWs, the nitrification process needs a longer time to move across the treatment wetland area. Plants are important in soil oxidation through their roots, thus enabling e.g. nitrification by microbes (Faulwetter *et al.* 2009). However, in preferential flow areas (PFA) there can be sub-areas with no vegetation, especially in preferential flow paths (PFP) along which the water flows fastest, as was the case for Kompsasuo and Ruka TWs.

High concentrations of NO_2+NO_3-N in the outlet can indicate inadequate denitrification to remove N in the TW, but the high concentration observed at the outlet of Kompsasuo TW could also be caused by weak nitrification efficiency near the inlet of TW, and thus occurring only near the outlet. Continuous flow feeding of wastewater in horizontal subsurface type wetlands (as is the case in Kompsasuo and Ruka TWs) results in lower redox potential than batch flow and intermittent flow feed (Stein *et al.* 2003, Caselles-Osorio & Garcia 2007). As low redox potential does not support nitrification, continuous flow may impair nitrification more at the inlet than in the outlet areas of Kompsasuo and Ruka TWs. Redox potential generally rises from the inlet to the outlet due to progressive biotic degradation of pollution and filtration of SS (Garcia *et al.* 2003, Headley *et al.* 2005, Faulwetter *et al.* 2009). In addition, Nurk *et al.* (2005) observed higher potential nitrification near the outlet in comparison with the inlet, which may have been caused by the decrease in organic carbon and/or toxic substances during treatment in the wetland. Sundberg *et al.* (2007b) observed that ammonium removal in subsurface flow wetlands is low when they are permanently flooded. Lakeus TW, purifying carbon-rich water, is a FWS-type wetland which is usually regarded as anoxic, with a thin aerobic layer at the water surface due to passive aeration (IWA 2000). It thus also has weaker possibilities to transform ammonium to nitrate in

nitrification during wastewater treatment. The studied TWs constructed on drained peatland seemed to have better nitrification activity. This is probably partly due to intermittent flow feeding by pumping runoff to the TW.

In Lakeus and Ruka TWs, it is also possible that the nitrification process occurred effectively, but due to short water residence times in winter there was no time or temperatures were not high enough (0.2-5.8°C) for the N removal process to be concluded with denitrification by microbes. In Kompsasuo TW the residence time is longer than in Lakeus and Ruka TWs and in summer-autumn water temperature does not hinder the denitrification process.

As the denitrification process releases N_2O, which unlike N_2 can easily be measured, N_2O concentration has been used as a proxy to assess the variation in N removal, even if the major product of denitrification is generally N_2 (Paul & Clark 1989). In Lakeus and Ruka TWs, N_2O emissions were responsible for only 0.2-0.6% of annual inorganic N removal (I). In Kompsasuo TW, N_2O emissions did not increase over a period of 10 years and comprised less than 2.2% of N removed from the TW (II). However, the proportion of loaded N transformed to N_2O-N in the Kompsasuo TW was higher than that reported by Johansson *et al.* (2003) for two other TWs treating nutrient-rich wastewaters (0.3-1.1% and 0.02-0.53%, respectively) (II). Nevertheless, the values of Kompsasuo TW corresponded those presented by Intergovernmental Panel on Climate Change (IPCC 2014) and Mander *et al.* (2014) as average for HSSF-type wetlands (N_2O/total N 0.79%).

Vymazal (2007) summarised the environmental factors having an impact on denitrification. Among those factors, carbon is needed in denitrification for microbial growth. In TWs constructed on peatland or receiving sewage water there is no lack of carbon, but according to Burchell *et al.* (2007), at winter temperatures (7.5°C) denitrification activity shows no response to organic carbon addition. Nevertheless, Bremner and Shaw (1958) found that denitrification can proceed below 5°C, although more slowly than at higher temperatures, but Bailey (1976) found no denitrification at 5°C. The major low temperature (6-15°C) products in denitrification are NO and N_2O according to Bailey (1976). Fluxes of N_2O were observed in Kompsasuo TW (II), where mean air temperature is generally below 5°C from October to April, and in Ruka and Lakeus TWs at air temperatures below 0°C. The pH range in peat is often lower than the optimal range (pH 6-8; Paul & Clark 1989) for the denitrification process. This is the case for Kompsasuo TW, where the pH ranges from 2.3 to 6.1 (IV). The oxidation-reduction potential in Kompsasuo TW (-17 to 151 Eh mV) is also at the lower end of the variation required for efficient denitrification at 100-350 Eh mV (Vymazal 2007).

The characteristics of Kompsasuo TW that have an impact on the rate of denitrification can also be extrapolated to other TWs constructed on peatlands, as they are typically high in moisture, acidic, anoxic or anaerobic where overlying water exists (especially in PFA) in a climate with only a few months of air temperatures above 5°C. However, if the wetland is constructed on drained peatland with old drainage ditches still existing, the conditions in peat pore water and overlying water are changed. Consequently, these TWs are more aerobic or oxic and thus nitrification could function better if the water residence time is long enough. In some TWs constructed on drained peatlands the old ditches also reach into the mineral soil (III). With their lower carbon content, these ditches are probably areas with less active nitrification-denitrification processes than those in peatlands. This was also observed for Lakeus TW, which is constructed on sand, where N_2O fluxes were substantially lower than those in Ruka TW, which is constructed on peat (-186 to 5100 and 79 to 63000 $\mu g\ m^{-2}\ d^{-1}$, respectively) (I).

Besides denitrification, "partial nitrification-denitrification" or anaerobic ammonium oxidation (anammox) are possible processes for N removal in anoxic environments. In "partial nitrification-denitrification" in anoxic environments, ammonium (NH_4^+) is transformed to nitrite (NO_2^-) rather than nitrate (NO_3^-) (Bernet *et al.* 2001). Nitrite is then directly denitrified to nitric oxide (NO), nitrous oxide (N_2O) and/or dinitrogen (Vymazal 2007). Ammonium together with nitrite also forms dinitrogen in anoxic conditions in the anammox process (Mulder *et al.* 1995). The significance of these processes could not be evaluated here, as the nitrite was determined together with nitrate in the laboratory. However, their role could be important in northern boreal wetlands, as Alleman (1985) observed that nitrite accumulated in cold temperatures.

Nitrogen load was estimated only for Kompsasuo TW, where measurements of hydraulic load above the TW were made (IV). The loads of all N species were high in the beginning of peat extraction when ditch excavation was still being carried out. High N loads after ditch excavation have also been observed by others (Manninen 1998, Vassiljev & Blinova 2012) and are probably caused by oxidation of peat and fresh organic matter recently opened to the air (Kløve 2001). Despite the high N loads, at that time Kompsasuo TW retained more than half of total N and more than 70% of inorganic N (IV), and only organic N was retained less efficiently (27%). Ihme (1994) observed weak retention of organic N or leaching of N from northern wetlands which were exceptionally wet, because their TW area/catchment area ratio was only 1.5%. In some of the TWs on drained peatland studied here, leaching of N was observed immediately after TW construction (II).

Retention of organic N (calculated from loads) generally varied from 10% to 79% in these TWs (Postila *et al.* 2011). Plant and microbial assimilation of N transforms inorganic N into organic N. NH_4-N, NO_3-N and NO_2-N are used by plants (Vymazal 2007, Kotur *et al.* 2013), but NH_4-N is preferred over NO_3-N for assimilation as it is more reduced energetically (Kadlec & Knight 1996). Organic nitrogen retained permanently in TW is stored in belowground parts of vegetation or buried (e.g. through peat formation) (Vymazal 2007). Nitrogen fixation, where gaseous N_2 is transformed to NH_4, can also occur biologically in aerobic and anaerobic environments, but is probably negligible in TWs receiving N-rich wastewater (Vymazal 2007).

3.3 Phosphorus (III, IV, V)

The mean total P concentration in the peat extraction runoff of TWs varied between 32-226 µg L^{-1} and PO_4-P concentrations between 7-75 µg L^{-1}. In the inflow of TWs treating polished sewage water, the P concentrations were much higher, with the mean of winter and summer seasons being 560 and 450 µg L^{-1} for total P and 410 and 320 for µg L^{-1} for PO_4-P in Lakeus and Ruka TWs, respectively (Karjalainen *et al.* 2005a, b). Mean particulate P in TWs purifying peat extraction runoff varied between 20 and 85 µg L^{-1}, while in the two TWs polishing sewage water (Lakeus and Ruka) it was 570 and 330 µg L^{-1}, respectively (Karjalainen *et al.* 2005a, b). Thus particulate P comprised from 25 to almost 100% of total P in the inflow of TWs.

The P loads to Lakeus and Ruka TWs were 0.7 and 0.2 kg ha^{-1} d^{-1}, respectively, for total P and 0.5 and 0.1 kg ha^{-1} d^{-1}, respectively, for PO_4-P. For TWs purifying peat extraction runoff, the corresponding values were 0.007-0.014 kg total P ha^{-1} d^{-1} and 0.002-0.008 kg PO_4-P ha^{-1} d^{-1} in Kompsasuo TW (Ihme 1994, Heikkinen *et al.* 2002, IV), while they were 0.004-0.05 kg total P ha^{-1} d^{-1} and 0.0007-0.01 kg PO_4-P ha^{-1} d^{-1} for drained TWs (Postila *et al.* 2011) in periods with no ground frost. The highest P loads in peat extraction runoff were estimated for Kompsasuo TW in spring (0.2 kg total P ha^{-1} d^{-1} and 0.05 kg PO_4-P ha^{-1} d^{-1}), when hydraulic load was also highest (IV). However, for exact estimation of spring loads from peat extraction areas, the water quality should be measured continuously during the measurement of hydraulic load increments.

The TWs of sewage treatment plants were able to retain 57-91% total P and 62-100% PO_4-P on average all year round (Karjalainen *et al.* 2005a, b). In TWs for extraction runoff, the mean retention of P loads varied from 47% to 64% for total

P and from 47% to 68% for PO_4-P in periods with no ground frost (Postila *et al.* 2011, IV). TWs with an intact peat layer can retain P (Ihme 1994, Heikkinen *et al.* 2002, IV), but P retention capacity in TWs constructed on drained peatlands can vary from retention to release of P in the same TW in different years (Postila *et al.* 2011). In TWs on drained peatland, PO_4-P was retained only in Kapustaneva TW when calculated from P loads (Postila *et al.* 2011). However, PO_4-P was found to be retained in other TWs constructed on drained peatlands (Hankilaneva 1, Hankilaneva 2, Lumiaapa 2 and Pohjoinen Latvasuo) (III).

The highest P retention was achieved in Ruka TW, where Al and Fe concentrations in the treated sewage water were high after a chemical activated sludge treatment step. In Lakeus TW too, Al in water increased the percentage retention. In the peat of the drained Kapustaneva TW, 33% of total P was bound by Fe and Al (III), whereas in the other drained TWs studied for their peat P pools, Ca-bound P comprised 17-25% of total P. The P retention processes involving Al are more straightforward than those with Fe and Ca, which are more susceptible to changes in the environment.

In the TWs of sewage treatment plants, PO_4-P was retained by Al via precipitation, sedimentation and/or (ad)sorption, and remained at the inlet of the TWs (Ronkanen & Kløve 2009, Karjalainen *et al.* 2005a, b). In contrast, Fe was observed to move further down in the surface peat in the hydraulic pathway and to accumulate near the outlet in Kompsasuo TW (V). In humic runoff and natural waters, Fe is mainly carried in oxygenated water by dissolved organic matter (DOM), with high apparent molecular weight (HAMW) DOM being preferred by Fe (Ghassemi & Christman 1968, Koenings & Hooper 1976, Heikkinen 1990, Heikkinen & Ihme 1995, III). In the HAMW-Fe complex, PO_4-P associates with the organic fraction (Heikkinen & Ihme 1995) thus forming dissolved organic Fe-P colloids. Shapiro (1964) and Wartiovaara (1978) reported that increased Fe content in DOM makes it more responsive to precipitation and sedimentation. Retention of P by Fe is, however, susceptible to changes in Fe oxidation state; if anaerobic conditions occur in the peat, Fe appears as the bivalent (Fe^{2+}) soluble form of Fe. Hence in highly loaded peat surface layers near TW inlets where groundwater level is high (e.g. in Ruka, Kompsasuo and Puutiosuo TWs) reducing conditions are prevailing, and therefore trivalent Fe is reduced to soluble bivalent Fe. This soluble Fe then moves farther down in the surface peat of TW and changes to trivalent form in more oxidised parts of the TW, e.g. outside the PFA or near the outlet, retaining Fe-P complexes through precipitation and/or (ad)sorption (Karjalainen *et al.* 2005b, IV, V). Calcium binds P when the environment is alkaline

(pH >8) (Richardson 1999). This can occur in peatlands with a high content of Ca, but if runoff entering the TW is acid, leaching of Ca-bound P from peat is possible (III).

3.4 SS and organic matter (I, II, III, IV)

Mean total SS concentration in peat extraction runoff at the inlet of Kompsasuo TW varied seasonally, being lowest in periods with no ground frost (4.1 mg L^{-1}) and highest in winter (6.4 mg L^{-1}) in 2002. The value obtained for periods with no ground frost did not differ from that recorded in 1988. However, the values observed in period with no ground frost in 2002 were lower than the mean for 1988-1996 in Kompsasuo TW (6.3 mg L^{-1}) and for 1990-1995 in Puutiosuo TW (10.4 mg L^{-1}). In TWs polishing sewage water, there were also slightly lower means for incoming total SS concentrations in summer (10.0 and 11.4 mg L^{-1}) than in winter (11.8 and 14.5 mg L^{-1}) for Lakeus and Ruka TWs, respectively (Karjalainen *et al.* 2005a, b). Mean total SS concentration in the runoff to the drained TWs constructed on peatland varied greatly, from 5 to 158 mg L^{-1}. In Kompsasuo TW, mean inorganic SS concentration (1.2 mg L^{-1}) was lower than mean organic SS concentration (2.9 mg L^{-1}) in periods with no ground frost in 2002. This was also the case in winter and spring. Organic SS thus comprised from 59% to 71% of total SS. In the TWs polishing purified sewage water, this relationship was similar (72% in Ruka TW and 75% in Lakeus TW). The mean concentration of organic SS was, however, approximately three-fold higher in the polished sewage water than in the peat extraction runoff entering Kompsasuo TW (Karjalainen *et al.* 2005a, b).

Mean TOC concentration in the peat extraction runoff to Kompsasuo TW was 16.4 mg L^{-1} in periods with no ground frost, 9.3 mg L^{-1} in winter and 12.2 mg L^{-1} in spring in 2002. The mean concentrations in the peat extraction runoff to the drained TWs were substantially higher, 30-48 mg L^{-1}, of which most (92-98%) consisted of DOC (Postila *et al.* 2011). In the purified sewage water, mean summer and winter TOC concentrations and BOD_7 and COD_{Mn} values were slightly higher in Lakeus TW (19-30 mg TOC L^{-1}, 8.5-13 mg BOD_7 L^{-1} and 17-18 mg COD_{Mn} L^{-1}) than in Ruka TW (7.8-18 mg TOC L^{-1}, 5.8-9.0 mg BOD_7 L^{-1} and 13-15 mg COD_{Mn} L^{-1}). The TOC concentrations at the inlet were similar all year round, but BOD_7 and COD_{Mn} values were naturally higher in summer than in winter due to warmer conditions for biological activity. Mean TOC concentrations in different parts of Lakeus and Ruka TWs resembled the outlet concentrations. In the peat extraction runoff mean COD_{Mn} values varied greatly, from 15 to 97 mg L^{-1}, being

lowest in Pohjoinen Latvasuo TW three years after its establishment and highest in Itäsuo TW in the year this wetland was established. DOM comprised most (89-91%) of the TOM (i.e. COD_{Mn}) at the inlet of Kompsasuo TW and also Lakeus and Ruka TWs (Karjalainen *et al.* 2005a, b).

In summer, mean SS loads from peat extraction areas to drained TWs constructed on peatland (0.92-11.5 kg ha^{-1} d^{-1}) varied from those in Kompsasuo TW (0.7 kg ha^{-1} d^{-1}) . The higher loads to drained TWs could be due to calculation method, as hydraulic load data were only available for the sampling days. However, the SS load from the peat extraction area to Kompsasuo TW in 2002 was similar to that at TW establishment when the peatland was drained for peat extraction in 1988, with similar mean hydraulic loads. Ihme (1994) showed that those TWs receiving a hydraulic load of 560 m^3 ha^{-1} d^{-1} or more had high SS loads (4.5-8.6 kg ha^{-1} d^{-1}). This may be partly caused by the different years of action: the longer the duration of peat extraction, the finer and more humified the peat extracted, and hence peat quality (particle size and humification degree) in the peat extraction area is altered. In addition, more advanced water pollution control methods such as runoff control dams in recently established peat extraction areas may have reduced high discharges and thus lowered hydraulic load to the TW. Installing a sedimentation basin(s) before the TW is also important in reducing SS in the water at the inlet of TW (Ihme 1994, Kløve 1997). Mean SS load to Lakeus and Ruka TWs below the sewage treatment plant was 9 and 5.6 kg ha^{-1} d^{-1}, respectively (Karjalainen 2005a, b). This was similar to that in TWs which received the highest SS loads from peat extraction. Organic SS load did not differ greatly in Kompsasuo TW in 1987-1992 and 2002 (0.7 kg ha^{-1} d^{-1} (Ihme 1994) and 0.5 kg ha^{-1} d^{-1}, respectively).

Mean BOD_7 load from sewage treatment plants to Lakeus and Ruka TWs was 13 kg ha^{-1} d^{-1} and 2.8 kg ha^{-1} d^{-1}, respectively. Mean TOM load to Kompsasuo TW in 2002 (4.2 kg ha^{-1} d^{-1}) was half that reported by Ihme (1994) for 1987-1992 (8.2 kg ha^{-1} d^{-1}). Drained TWs received even less TOM, with mean TOM load varying between 0.2 and 0.6 kg ha^{-1} d^{-1} in summer (Postila *et al.* 2011). Mean TOC load varied from 0.2 to 0.5 kg ha^{-1} d^{-1} and mostly consisted of the dissolved fraction (Postila *et al.* 2011). As TOM is mostly composed of the dissolved fraction in peat extraction runoff (Ihme 1994), the DOM load was nearly as high as the TOM load to Kompsasuo TW. Mean TOC load to Kompsasuo TW was 3.1 kg ha^{-1} d^{-1}, thus comprising 74% of TOM. In Kompsasuo TW, the highest SS, TOC, TOM and DOM loads occurred in spring due to high hydraulic loads.

Total SS retention was 31% in Kompsasuo TW in summer and autumn 2002. In Lakeus and Ruka TWs, SS retention was 53% and 80%, respectively. In the

drained TWs, water purification efficiency of SS varied greatly, from 4% to 96%. This large variation is possibly partly due to low number of samples: two at a minimum and six on average. The drained Savaloneva TW was the only one which leached SS, despite the larger number of samples (5 and 17). However, SS retention was generally at the same level (50-80%) as in TWs constructed on pristine peatland (Heikkinen *et al.* 2002, Kløve *et al.* 2012, Tuukkanen *et al.* 2012). Organic and inorganic SS retention in Kompsasuo TW was at the same level as total SS retention (34% and 30%). BOD7 was reduced on average by 44% and 63% in Lakeus and Ruka TWs. TOM was reduced by 16% in Kompsasuo TW in 2002, and it contained mostly (70%) DOM. TOM retention in Kompsasuo TW was at the same level as in other well-functioning TWs constructed on pristine peatland (Ihme 1994, Heikkinen *et al.* 2002). TOM was mostly leached from TWs constructed on drained peatland when calculated from water purification efficiency, and was estimated to be mainly the dissolved fraction. Such leaching of organic matter has also been observed for drained peatlands which have been restored or rewetted (Koskinen *et al.* 2011). Low organic matter retention is typical in TWs constructed on peatland, as peat decomposition continuously releases humic substances to runoff.

There were substantial differences in the variation in TOM concentrations between the three different study periods in 2002. The results showed that SS concentrations in the inlet water of Kompsasuo TW were lowest during summer and autumn and highest in winter. The concentrations of TOC were highest in summer and autumn, probably due to biological elements such as microbes being present in higher numbers in warmer seasons.

Snowmelt in spring is the key event for total loads and runoff, e.g. the spring load represented 90-99% of the total annual load to Kompsasuo TW in 2002. In particular, SS and organic matter (TOM, TOC) had high loads during spring, but during periods with no ground frost (i.e. summer and autumn) the loads were more similar, although double those observed in winter.

The reduction in organic substances (TOC and TOM) was lower in winter and spring than in summer-autumn. Total SS was retained in all seasons, at retention rates varying from 20% to 33%. TOM was not retained in the wetlands in winter or spring in 2002. In winter, DOM formed about 30% of the TOM leached.

Fluxes of CH_4 from Kompsasuo TW varied greatly in different seasons, being highest in autumn (4320 mg CH_4 m^{-2} d^{-1}) and lowest in winter (0.4 mg CH_4 m^{-2} d^{-1}). The wetland water CH_4 concentration was correlated with those fluxes (r_p=0.4, p=0.004). The CH_4 fluxes and concentrations were higher in the sampling plot near

the inlet than in that farthest away. These sampling plots with higher CH_4 emissions had 25-53% more plant biomass than that near the outlet. Substantially more CO_2 was released in Kompsasuo TW in summer (33 660 mg CO_2 m^{-2} d^{-1}) than in winter (90 mg CO_2 m^{-2} d^{-1}), and release was correlated with surface soil and air temperature (r_p=0.757, p<0.001 and r_p=0.6, p<0.001, respectively). The free CO_2 concentration in wetland water was also correlated with CO_2 release (r_p=0.341, p=0.012). In contrast to CH_4, free CO_2 concentrations in water and CO_2 release rates were similar in the three sampling plots.

3.5 Long-term nutrient, SS and organic matter retention

Drainage for peat extraction created the highest loads of N in summer and autumn. In Kompsasuo TW, the N concentration of inflow, and hence also the N load, was higher during initial drainage of the peat extraction area than later, when peat was extracted from deeper layers. However, N was retained at the same level in Kompsasuo TW (IV). On TWs constructed on drained peatlands, N leaching occurred mostly just after TW construction (III), while later on these TWs generally retained N. Thus, it is important to construct a TW that is efficient at N removal already before ditch digging and site preparation for peat extraction, in order to remove initial N loads.

Achieving good N removal during the initial phase after TW construction is challenging, whether the wetland type is OFA or FWS. At this stage, the limited net biological growth limits N uptake by vegetation, but after some years the importance of vegetation increases (Couillard 1994, III). However, N retention by microbial activity has been recorded to be as high as 90% from wastewater during the second and third year of operation of a peat-sand filter bed (Nichols & Boelter 1982). Silvan *et al.* (2003) reported that the soil microbial community grows slowly in environments with low pH, thus immobilising N for longer than in soils with higher pH. In the TWs constructed on peatlands examined in this thesis, the pH in inflow/outflow ranged between 4.3 and 7.2 and in peat between 3.0 and 5.4, thus overlapping the mean soil water pH range (4.0-4.5) reported by Silvan *et al.* (2003). Thus nutrient immobilisation by microbes in the TWs studied here is probable.

In the beginning of TW use, NH_4^+ in solution may occupy free cation exchange sites through adsorption. Clay and humic substances generally sorb NH_4^+, which is loosely bound and can be desorbed easily and used e.g. in nitrification in oxidised conditions (Vymazal 2007). Thus these cation exchange sites are released and re-occupied throughout the life time of TWs.

Due to limitations in N removal caused by initial environmental conditions on pristine wetlands, a long water residence time and oxidation of surface peat or sediment in the TW are crucial for efficient N removal by nitrification-denitrification. It has been noted for wastewater treatment systems that at dissolved oxygen concentrations below ~2.5 mg L^{-1} NO_2 oxidation is inhibited, and thus nitrite is accumulated (Paredes *et al.* 2007). This may enhance the possibilities for the anammox reaction, where NO_2^- acts as an electron acceptor for NH_4^+ if bacteria performing the reaction are present (Schmid *et al.* 2000, Sliekers *et al.* 2002).

Later on, when vegetation has grown intensively with increasing nutrient addition, there are more suitable sites for microbes in TWs due to increased root systems in the soil. However, root oxygen release varies between macrophyte species (Brix 1997, Stottmeister *et al.* 2003). Thus, where possible, plant species should be selected carefully according to their suitability to the wetland type and effectiveness in oxygen release for efficient nitrification. Moreover, oxygen transport by vegetation may be too slow for efficient treatment considering the relatively short residence time of wastewater. Nitrification may be reduced if several PFPs or a PFA is created on the TW surface, thus reducing the water residence time considerably. Ronkanen (2009) demonstrated that large potential nutrient retention areas are not used in TWs constructed on peatlands, and thus maintenance of the TW to obtain good hydraulic efficiency is crucial. Organic N in vegetation and microbes may be retained from the nitrogen cycle by burial in FWS-type TWs and by peat formation in OFA-type TWs in all phases of TW use. However, as vegetation appropriate to its TW increases over time in suitable environmental conditions, N burial may be higher in older TWs. Planting of TWs constructed on drained peatlands, as was done for Kapustaneva TW, may also help create suitable environmental conditions for peat oxidation and nutrient uptake.

Denitrification seems to occur at a similar level in the beginning of TW use and 10 years later (II). However, if nitrification is hindered due to e.g. shortened water residence time in the TW, lack of nitrate may limit denitrification. Thus maintaining the TW in good condition, i.e. with no PFA, is essential for processes to continue later on.

When a TW is constructed there is water-soluble P present in the peat (III). This P may be leached when excess water is conducted to the TW, e.g. for purification of wastewater or restoration of the wetland (Vasander *et al.* 2003, III). However, depending on the season and the water residence time in the TW, soluble P may be retained by means such as precipitation with metals and subsequent sedimentation and filtration (Couillard 1994, Giesler *et al.* 2005), (ad)sorption

(Heikkinen *et al.* 1995b) and uptake by microbes and vegetation (Richardson 1985, Vymazal 2007, Yousefi & Mohseni-Bandpei 2010). However, Huttunen *et al.* (1996) noted that P uptake by vegetation is only of minor importance for P retention in Kompsasuo TW. Vegetation thus acts mainly as a short-term sink for P if the biomass is not harvested (Richardson 1985), which is normally possible only in certain types of TWs such as FWS- and free floating plant (FFP)-types (Vymazal 2007). Microbial uptake also generally immobilises P for a short period and at very low magnitude (Vymazal 2007), although in the acidic conditions of the TWs studied here longer immobilisation is possible according to Silvan *et al.* (2003), as discussed earlier for N. In addition, at more oligotrophic sites, microbial uptake may store more P than at eutrophic sites (Richardson *et al.* 1997)

Peat or soil accretion is regarded as the only continuous long-term sink for P, yet it is efficient only with high biomass production (Vymazal 2007). At northern latitudes peat accumulation is typically slow (Borren *et al.* 2004), and thus P accumulation by peat accretion is also low (0.005-0.22 g P m^{-2} a^{-1}) at these latitudes (Nichols 1983). According to Vymazal (2007), soil accretion varies from high in FWS-type to zero in HSSF-type TWs. In the OFA-type TWs receiving peat extraction runoff studied here, peat accretion was estimated to bury between 0.002-0.028 g P m^{-2} yr^{-1}, which constitutes only 0.5-7% of their annual P retention (V).

In addition to peat accretion, P adsorption in soil is also considered to control the long-term P sink (Richardson & Marshall 1986), especially if the substrate has high sorption capacity, as exhibited by clay and minerals in soil (Vymazal 2007). However, sorption is a process with restricted capacity (Dunne & Reddy 2005), but even soils saturated with adsorbed PO_4 may recover their adsorption capacity in 2-3 months due to occlusion and precipitation of adsorbed PO_4 (Ellis 1973, Sawhney & Hill 1975). In Kompsasuo TW, the P sorption capacity did not change in 12 years, yet the maximum sorption capacity of peat seems to have been reached according to the peat P concentration (V). Heikkinen *et al.* (1995b) estimated that this TW would have P adsorption capacity in peat for 20-25 years. However, even if adsorption may not be regarded as a permanent sink of P, as it is at least partly reversible (Nichols 1983), occlusion, precipitation and desorption of P may give possibilities for adsorption repeatedly even after 25 years of TW use.

In TWs where a substantial part of the P in inflow is in particulate form, sedimentation and filtration may be important in P retention, especially in OFA-type TWs, for a long time, until e.g. the organic fraction is reutilised through decomposition by microbes.

Dissolved organic P prefers to be attached to the organic fraction of HAMW Fe in DOM (Heikkinen & Ihme 1995). In the older TWs constructed on drained peatland studied in this thesis, peat P was mostly bound to Fe and Al humates (III). However, Ca-bound P comprised up to 25% of studied P forms in TW peat. Precipitation of P as a retention process occurs not only through binding to wetland soil components such as clay or metals, but also metals in the inflow (III, IV). As TW soil may contain material providing only restricted capacity for P precipitation, induced material may prolong this capacity and make the TW a possible long-term sink for P. These metal-based retention mechanisms are not susceptible to changes when metals are added actively by a treatment plant, e.g. in chemical water treatment of peat extraction runoff or sewage treatment plant effluent, and can thus be regarded as long-term retention mechanisms. However, in the case of Fe, conditions in the TW have to remain oxidised for continuous retention by precipitation.

In peat extraction runoff, the concentration and oxidation state of metals in inflow are dependent on environmental circumstances such as climate effects (e.g. precipitation quantity and regime, air temperature) and peat quality in the peat extraction area (e.g. metal and P concentrations, pH and degree of humification). If Fe is the metal partly responsible for P retention, it is important that oxidation conditions are suitable for soluble Fe to be oxidised into Fe^{3+} form for P precipitation/sorption in the TW. Leaching of P is also possible from wetland soil when the water level fluctuates, which can cause anoxia and release of Fe-bound P (Meissner *et al.* 2008, Niedermeier & Robinson 2009). The acidity of the inflow also affects the capacity of metals to sorb P in TWs. If Ca is responsible for P sorption in TW soil, changing neutral inflow water to acidic water induces leaching of P (III), whereas Fe and Al could still sorb P. Nevertheless, in the TWs studied here, precipitation with metals introduced to the TW by inflow seems to be an important reason for P retention in the long term, as the percentage retention is high even after nearly 20 years of loading.

Differences between years in SS and organic matter loads depend on fluctuations in runoff quantity and substance concentrations. A comparison between 1988 and 2002 for Kompsasuo TW showed that there was no great difference in total SS loads, but high TOM loads were present in 1988, more than twice those in 2002. As the hydraulic discharge was similar in the two years, the difference in loads was due to the TOM concentration. In 1988, the Kompsasuo peat extraction area was still the site of drainage activities and this was apparent as high TOM loads. Total SS loads to Kompsasuo TW remained at same level over

the 14-year study period from 1988 to 2002, but the retention capability decreased (IV). This is not easy to explain, as the hydraulic regime differed in the study years even if the hydraulic load was similar: in 1988 there was higher discharge in autumn than in 2002, while in 2002 there was higher discharge in summer than in 1988.

Total SS was retained very well (73%) during initial use of Kompsasuo TW in summer and autumn. However, the retention decreased to 31% after 15 years. This is close to the level in TWs reported by Ihme (1994) as not functioning well. Respective differences occurred also in inorganic and organic SS. However, TOM and DOM loads were only slightly lower in 2002 than in 1988. As SS is removed by settling, it is possible that these finer particles are eroded from older mires with higher humification degree, and thus potentially smaller particle sizes. There may also be sediment available in ditches for transport after the drainage stage, when peat extraction begins (Kløve 1998). The development of PFPs in the TW also shortens the water residence time, which may have weakened SS retention. In 2002 there were also fewer water samples (n=9) than in 1988 (n=20), which may have affected recorded changes in sediment delivery characteristics.

Although the TOM load decreased to less than half from 1988 to 2002, retention of TOM declined only slightly. As most of the TOM was dissolved, it could probably only be removed from the TW by filtration and microbial uptake. CH_4 emissions and CO_2 release from wetlands can have an effect on TOM retention, through the associated increase in vegetation and microbial activity. Over the years of TW use, higher hydraulic and nutrient loads than in natural wetlands enhance the growth of vegetation biomass and change the plant species present in TWs (Kaasinen 2003, Karjalainen *et al.* 2005a, b). An increase in vascular plants such as reeds, the aerenchyma of which act as conduits directly from anoxic peat to the atmosphere (Bubier & Moore 1994), also increases the CH_4 emissions.

The extent of future climate change, with predicted increases in precipitation and air temperature, will affect the removal and retention mechanisms in TWs in different seasons. Leaching of nutrients from TWs may possibly be enhanced in winter, as then there is no assimilating vegetation, low temperature limits the activity of microbes and water residence time is short due to reduced evapotranspiration. In contrast, the loads in spring may diminish if the amount of snow declines due to milder winters in which part of the precipitation occurs not as snow, but as rain. Thus operational monitoring should react to these potential changes in seasons, with possibly increased sampling in winter. However, it is possible that long-term water quality monitoring does not provide a realistic view

of e.g. P retention if the TW experiences flooding from a nearby river (as in Kompsasuo TW) (V).

4 Conclusions

The purpose of this thesis was to identify the processes which affect retention of nutrients and suspended solids during long-term use of TWs. Treatment wetlands are constructed on different soil types and thus the importance of soil materials for long-term retention were also studied, as was the quality of wastewater entering the TW.

The TWs studied generally retained nutrients and SS well, even after 18 years of wetland use, if the wetland functioned well at the start. The most important pathway of N removal in the long term is probably through denitrification and perhaps also anammox when suitable anoxic conditions and microbes are available. However, the significance of anammox, sulphur based autotrophic denitrification and nitrite-dependent anaerobic methane oxidation in TWs needs to be studied in more detail. Vegetation also retains nitrogen in the growing season and when the vegetation is harvested, if possible, this nitrogen is removed from the TW. However, winter is challenging for any nitrogen removal mechanism which is very dependent on biota, since in addition to vegetation microbes are greatly affected by low temperatures and are thus less active in winter than in summer. Nevertheless, in TWs receiving wastewater from indoor sewage treatment plants, microbial activity for N_2O emissions may be as high as summer emissions in TWs receiving peat extraction runoff. However, N_2O emissions from TWs have no great importance as a greenhouse gas due to the small surface area of TWs.

The P adsorption capacity of the TWs studied did not change in a 12-year-period, as the process of adsorption can be continuous through alternation of P desorption, occlusion, precipitation and adsorption in TWs. Phosphorus accumulation through peat accretion did not seem to be of pronounced importance in the northern cold climate studied, although this has not been well studied in TWs receiving nutrient-rich waters or water containing SS. For runoff from peat extraction areas and effluent from the sewage treatment plants studied here, Fe and Al were important in precipitation of P in TWs. It is probable that P entering the TWs was organically bound in Fe and Al humates, and thus filtration and sedimentation are also possible means of P retention. In peat extraction areas Fe is more important for P retention than Al, but as P bound to Fe is subject to chemical reduction in anaerobic conditions, Al is a more permanent retention mechanism for P. Calcium present in TW peat was also found to be unstable for P precipitation, as its retention capability is susceptible to changes in inflow acidity.

Water quality monitoring for almost 20 years reliably estimated the quantity of P retained in the surface peat of a TW. However, if the TW experiences exceptional hydraulic events, such as flooding by a nearby river, it is probable that part of the P retained in the TW will be leached. In such an event, it is also likely that SS retained in the TW will be leached. In general, TWs retained SS even after many years of wetland use, but there were large variations between years. This is probably mainly caused by differing volume of discharge, which greatly affects the transport and retention of SS. In addition, SS is removed by sedimentation, which depends on particle size. It is probable that smaller particles from old peat extraction mires which have high humification degree are eroded more easily than surface peat particles with low humification degree. In addition, SS retention may have been weakened by the development of preferential flow areas in the TW during use, causing shorter water residence time and thus weaker SS retention. Changes in sediment delivery characteristics and the sampling procedure, with too few samples to show SS transportation accurately, may also have had an effect on the SS retention results.

The potential to use TWs for a long time is an advantage not only for the operator releasing runoff/wastewater into the TW, but also for the environment and especially water bodies downstream. It is also important to recognise that the processes affecting the potential of TWs to retain nutrients and SS change in response to changes in the quality of the incoming wastewater.

For estimation of long-term retention in TWs, it is essential to have high quality data on different parameters. Currently, the parameters studied in research projects are not always covered in operational monitoring. Sparse sampling of TWs also increases the uncertainty in assessment of TW processes.

In future studies, the potential for using automatic measurement equipment in wetland process studies should be examined, particularly for the period from November to March. This period was formerly regarded as winter, with ice/snow cover on TWs, and thus water quality sampling was scaled back. However, climate change has already increased precipitation and air temperature in the study region, resulting in more rain in winter and thus increasing hydraulic loads at a time there is no active biota in the TW to retain and remove the nutrients and organic matter in sufficient quantities.

List of references

Arias CA, Del Bubba M & Brix H (2001) Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Res 35: 1159–1168.

Alleman JE (1985) Elevated nitrite occurrence in biological waste-water treatment systems. Water Sci Technol 17 (2/3): 409–419.

Bailey LD (1976) Effects of temperature and root on denitrification in a soil. Can J Soil Sci 56: 79–87.

Bernet N, Dangcong P, Delgenes J-P, Moletta R (2001) Nitrification at low oxygen concentration in biofilm reactor. J Environ Energy 127: 266–71.

Borren W, Bleuten W & Lapshina ED (2004) Holocene peat and carbon accumulation rates in the southern taiga of western Siberia. Quat Res 61: 42–51.

Braskerud BC (2001) The influence of vegetation on sedimentation and resuspension of soil particles in small constructed wetlands. J Environ Qual 30: 1447–1457.

Bremner JM & Shaw K (1958) Denitrification in soil. II. Factors affecting denitrification. J Agric Sci 51: 40–52.

Brix H (1993) Wastewater treatment in constructed wetlands: system design, removal processes, and treatment performance. In: Moshiri GA (ed) Constructed Wetlands for Water Quality Improvement. Lewis publishers, Boca Raton, Florida: 9–22.

Brix H (1997) Do macrophytes play a role in constructed treatment wetlands? Water Sci Technol 35 (5): 11–17.

Brown PA, Gill SA & Allen SJ (2000) Metal removal from wastewater using peat. Water Res 34: 3907–3916.

Bubier JL & Moore TR (1994) An ecological perspective on methane emissions from northern wetlands. Tree 9: 460–464.

Bulc T, Vrhovšek D & Kukanja V (1997) The use of constructed wetlands for landfill leachate treatment. Water Sci Technol 35: 301–306.

Burchell II MR, Skaggs RW, Lee CR, Broome S, Chescheir GM & Osborne J (2007) Substrate organic matter to improve nitrate removal in surface-flow constructed wetlands. J Environ Qual 36: 194–207.

Caselles-Osorio A & Garcia J (2007) Impact of different feeding strategies and plant presence on the performance of shallow horizontal subsurface-flow constructed wetlands. Sci Total Environ 378: 253–262.

Chen Y, Wen Y, Zhou Q & Vymazal J (2014) Effects of plant biomass on nitrogen transformation in subsurface-batch constructed wetlands: a stable isotope and mass balance assessment. Water Res 63: 158–167.

Cookson WR, Cornforth IS & Rowarth JS (2002) Winter soil temperature (2–15◦C) effects on nitrogen transformations in clover green manure amended or unamended soils; a laboratory and field study. Soil Biol Biochem 34: 1401–1415.

Couillard D (1992) Appropriate wastewater management technologies using peat. J envir Syst 21: 1–19.

Couillard D (1994) The use of peat in wastewater treatment. Water Res 28: 1261–1274.

Council of the European Union (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off. J. Eur. Communities L327: 1–72.

Craft CB & Richardson CJ (1993a). Peat accretion and phosphorus accumulation along a eutrophication gradient in the northern Everglades. Biogeochemistry 22: 133–156.

Crill PM, Harriss RC & Bartlett KB (1991) Methane fluxes from terrestrial wetland environment. In: Rogers JE & Whitman WB (eds) Microbial production and consumption of greenhouse gases: methane, nitrogen oxides and halomethanes. Washington DC, American Society for Microbiology: 91–110.

Drizo A, Frost CA, Grace J & Smith KA (1999) Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. Water Res 33: 3595–3602.

Dunne EJ& Reddy KR (2005) Phosphorus biogeochemistry of wetlands in agricultural watersheds. In: Dunne EJ, Reddy R & Carton OT (eds) Nutrient management in agricultural watersheds: a wetland solution. Wageningen, Wageningen Academic Publishers: 105–119.

Ellis BG (1973) The soil as a chemical filter. In: Sopper WE & Kardos LT (eds) Recycling treated municipal wastewater and sludge through forest and cropland. Penn. State Univ. Press: 46–70.

Faulwetter JL, Gagnon V, Sundberg C, Chazarenc F, Burr MD, Brisson J, Camper AK & Stein O (2009) Microbial processes influencing performance of treatment wetlands: A review. Ecol Eng 35: 987–1004.

Garcia J, Ojeda E, Sales E, Chico F, Piriz T, Aguirre P & Mujeriego R (2003) Spatial variations of temperature, redox potential, and contaminants in horizontal flow reed beds. Ecol Eng 21: 129–142.

Gassmann G, van Beusekom JEE & Glindemann D (1996) Offshore atmospheric phosphine. Naturwissenschaften 83(3): 129–131.

Ghassemi M & Christman RF (1968) Properties of the yellow organic acids in natural waters. Limnol Oceanogr 13: 583–597.

Giesler R, Andersson T, Lövgren L & Persson P (2005) Phosphate sorption in aluminum- and iron-rich humus soils. Soil Sci Soc Am J 69: 77–86.

Golterman HL (1996) Fractionation of sediment phosphate with chelating compounds: a simplification, and comparison with other methods. Hydrobiologia 335: 87–95.

Han C, Geng J, Hong Y, Zhang R, Gu X, Wang X, Gao S & Glindemann D (2011) Free atmospheric phosphine concentrations and fluxes in different wetland ecosystems, China. Environ Pollut 159(2): 630–635.

Hayward J, Jamieson R, Boutilier L, Goulden T & Lam B (2014) Treatment performance assessment and hydrological characterization of an arctic tundra wetland receiving primary treated municipal wastewater. Ecol Eng 73: 786–797.

Headley TR, Herity E & Davison L (2005) Treatment at different depths and vertical mixing within a 1-m deep horizontal subsurface-flow wetland. Ecol Eng 25: 567–582.

Heikkinen K (1990) Nature of dissolved organic matter in the drainage basin of a boreal humic river in northern Finland. J Environ Qual 19: 649–657.

Heikkinen K & Ihme R (1995) Retention of organic Fe-P-colloids from peat mining water in an overland flow wetland treatment system in northern Finland. Arch Hydrobiol 134: 547–560.

Heikkinen K, Ihme R & Lakso E (1995a). Contribution of cation exchange property of overflow wetland peat to removal of NH_4^+ discharged from some Finnish peat mines. Appl Geochem 10: 207–214.

Heikkinen K, Ihme R, Osma A-M & Hartikainen H (1995b). Phosphate removal by peat from peat mining drainage water during overland flow wetland treatment. J Environ Qual 24: 597–602.

Heikkinen K, Savolainen M, Ihme R & Lakso E (2002) The use of overland flow wetland treatment system for the purification of runoff water from peat mining areas – the service life of the system. In: Mander Ü & Jenssen PD (eds) Natural wetlands for wastewater treatment in cold climates. Boston, WIT Press: 29–45.

Herskowitz J, Black S & Sewandowski W (1987) Listowel artificial marsh treatment project. In: Reddy KR & Smith WH (eds) Aquatic plants for water treatment and resource recovery. Orlando, Magnolia Publishing Co: 247–254.

Hill CM, Duxbury J, Geohring L & Peck T (2000) Designing constructed wetlands to remove phosphorus from barnyard runoff: a comparison of four alternative substrates. J Environ Sci Health Part A-Toxic/Hazard Subst Environ Eng 35: 1357–1375.

Hu B-L, Shen L-D, Lian X, Zhu Q, Liu S, Huang Q, He Z-F, Geng S, Cheng D-Q, Lou L-P, Xu X-Y, Zheng P & He Y-F (2014) Evidence for nitrite-dependent anaerobic methane oxidation as a previously overlooked microbial methane sink in wetlands. Proc Natl Acad Sci USA 111(12): 4495–4500.

Huttunen, A., Heikkinen, K. & Ihme, R. (1996) Nutrient retention in the vegetation of an overland flow treatment system in northern Finland. Aquat. Bot. 55: 61–73.

Huttunen JT, Väisänen TS, Hellsten SK, Heikkinen M, Nykänen H, Jungner H, Niskanen A, Virtanen MO, Lindqvist OV, Nenonen O & Martikainen PJ (2002) Fluxes of CH_4, CO_2 and N_2O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland. Global Biogeochem Cycles 16: 1–17, doi: 10.1029/2000GB001316.

Ihme R (1994) Use of the overland flow wetland treatment system for the purification of runoff water from peat mining areas. VTT Julkaisuja 798: 1–140.

IPCC (2014) 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands, Hiraishi T, Krug T, Tanabe K, Srivastava N, Baasansuren J, Fukuda M & Troxler TG (eds). Switzerland, IPCC: 1–354.

IWA (2000) Constructed wetlands for pollution control: processes, performance, design and operation. London, IWA Publications: 1–156.

Johansson AE, Klemedtsson AK, Klemedtsson L & Svensson BH (2003) Nitrous oxide exchanges with the atmosphere of a constructed wetland treating wastewater. Tellus 55B: 737–750.

Johansson Westholm L (2006) Substrates for phosphorus removal – Potential benefits for on-site wastewater treatment? Water Res 40: 23–36.

Kaasinen E (2003) Kompsasuon pintavalutuskentän kasvillisuuden muutoksista (Changes in the vegetation of Kompsasuo overland flow area) M.Sc. thesis. University of Oulu, Department of Biology: 1–42.

Kadlec, RH & Knight RL (1996) Treatment Wetlands. Boca Raton, Lewis Publishers: 1–893.

Karjalainen SM, Ronkanen A-K, Huttunen J, Kilpeläinen E, Koskiaho J, Liikanen A, Kløve K, Heikkinen K, Väisänen T & Ylitolonen A (2005a) Lakeuden keskuspuhdistamon jälkikäsittelykentän toiminta – PRIMROSE-projektin tulokset. In: Karjalainen SM & Ronkanen A-K (eds) Kosteikot Lakeuden keskuspuhdistamolta ja Rukan puhdistamolta tulevien vesien jälkikäsittelyssä – PRIMROSE-projektin (2001–2003) tulokset. Alueelliset ympäristöjulkaisut 401: 5–45.

Karjalainen SM, Ronkanen A-K, Huttunen J, Kilpeläinen E, Pohjola T, Liikanen A, Kløve K, Heikkinen K, Väisänen T & Ylitolonen A (2005b) Rukan puhdistamon jälkikäsittelykentän toiminta – PRIMROSE-projektin tulokset. In: Karjalainen SM & Ronkanen A-K (eds) Kosteikot Lakeuden keskuspuhdistamolta ja Rukan puhdistamolta tulevien vesien jälkikäsittelyssä – PRIMROSE-projektin (2001–2003) tulokset. Alueelliset ympäristöjulkaisut 401: 47–96.

Kieckbusch JJ & Schrautzer J (2007) Nitrogen and phosphorus dynamics of a re-wetted shallow-flooded peatland. Sci Total Environ 380: 3–12.

Kløve B (1997) Settling of peat in sedimentation ponds. J Environ Sci Health Part A-Toxic/Hazard Subst Environ Eng 32: 1507–1523.

Kløve B (1998) Erosion and sediment delivery from peat mines. Soil Till Res 45: 199–216.

Kløve B (2001) Characteristics of nitrogen and phosphorus loads in peat mining wastewater. Water Res 35: 2353–2362.

Kløve B, Saukkoriipi J, Tuukkanen T, Heiderscheidt E, Heikkinen K, Marttila H, Ihme R, Depre L & Karppinen A (2012) Pre-estimation of loading on water bodies from peat production and new pollution control methods (TuVeKu). The Finnish Environment 35: 1–31.

Koenings JP & Hooper FF (1976) The influence of colloidal organic matter on iron and iron-phosphorus cycling in an acid bog lake. Limnol Oceanogr 21: 684–696.

Koskiaho J & Puustinen M (2005) Function and potential of constructed wetlands for the control of N and P transport from agriculture and peat production in boreal climate. J Environ Sci Health A Tox Hazard Subst Environ Eng 40: 1265–1279.

Koskinen M, Sallantaus T & Vasander, H (2011) Post-restoration development of organic carbon and nutrient leaching from two ecohydrologically different peatland sites. Ecol Eng 37: 1008–1016.

Kotur Z, Siddiqi YM & Glass ADM (2013) Characterization of nitrite uptake in Arabidopsis thaliana: evidence for a nitrite-specific transporter. New Phytol 200: 201–210. doi: 10.1111/nph.12358

Ligi T, Truu M, Oopkaup K, Nõlvak H, Mander Ü, Mitsch WJ & Truu J (2015) Genetic potential of N_2 emission via denitrification and ANAMMOX from the soils and sediments of a created riverine treatment wetland complex. Ecol Eng 80: 181–190.

Mander Ü, Dotro G, Ebie Y, Towprayoon S, Chiemchaisri C, Nogueira SF, Jamsranjav B, Kasak K, Truu J, Tournebize J & Mitsch WJ (2014) Greenhouse gas emission in constructed wetlands for wastewater treatment: a review. Ecol Eng 66 : 19–35.

Mander Ü & Mitsch WJ (2009) Pollution control by wetlands. Ecol Eng 35: 153–158.

Mann RA & Bavor HJ (1993) Phosphorus removal in constructed wetlands using gravel and industrial waste substrata. Water Sci Technol 27(1): 107–113.

Manninen P (1998) Effects of forestry ditch cleaning and supplementary ditching on water quality. Boreal Environ Res 3: 23–32.

Meissner R, Leinweber P, Rupp H, Shenker M, Litaor MI, Robinson S, Schlichting A & Koehn J (2008) Mitigation of diffuse phosphorus pollution during rewetting of fen peat soils: a trans-European case study. Water Air Soil Pollut 188: 111–126.

Mitchell C (1996) Overview of constructed wetland applications and research in Australia. In: Staudemann, J, Schonborn A & Etnier C (eds) Recycling the resource: proceedings of the second international conference on ecological engineering for wastewater treatment. Environmental Research Forum 5-6: 397–399.

Mitsch WJ, Zhang L, Stefanik KC, Nahlik AM, Anderson CJ, Bernal B, Hernandez M & Song K (2012) Creating wetlands: Primary succession, water quality changes, and self-design over 15 years. Bioscience 62(3): 237–250.

Mulder A, van de Graaf AA, Robertson LA & Kuenen JG (1995) Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiol. Ecol. 16: 177–184.

Mäenpää M & Tolonen S (eds) (2011) The summary of the river basin district's river basin management plans until 2015. The Finnish Environment 23: 1–118.

Nichols DS (1983) Capacity of Natural Wetlands to Remove Nutrients from Wastewater. J Water Pollut Control Fed 55: 495–505.

Nichols DS & Boelter DH (1982) Treatment of secondary effluent with a peat-sand filter bed. J Environ Qual 11: 86–92.

Niedermeier A & Robinson JS (2009) Phosphorus dynamics in the ditch system of a restored peat wetland. Agric Ecosyst Environ 131: 161–169.

Nieminen M, Kaila A, Koskinen M, Sarkkola S, Fritze H, Tuittila E-S, Nousiainen H, Koivusalo H, Laurén A, Ilvesniemi H, Vasander H & Sallantaus T (2014) Natural and restored wetland buffers in reducing sediment and nutrient export from forested catchments: Finnish experiences. In: Vymazal J (ed) The role of natural and constructed wetlands in nutrient cycling and retention on the landscape. Switzerland, Springer International Publishing. DOI 10.1007/978-3-319-08177-9_5

Niskanen R (1989) Extractable aluminium, iron and manganese in mineral soils: II Extrability by oxalate and pyrohosphate. J Arric Sci Finl 61: 79–87.

Nurk K, Truu J, Truu M & Mander Ü (2005) Microbial characteristics and nitrogen transformation in planted soil filter for domestic wastewater treatment. J Environ Sci Health 40: 1201–1214.

Nykänen H, Alm J, Lång K, Silvola J & Martikainen PJ (1995) Emissions of CH_4, N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland. J Biogeogr 22: 351–357.

Närhi P, Räisänen ML, Sutinen M-L, Sutinen R. (2012) Effect of tailings on wetland vegetation in Rautuvaara, a former iron–copper mining area in northern Finland. J Geochem Explor 116–117: 60–65.

O'Geen AT, Budd R, Gan J, Maynard JJ, Parikh SJ & Dahlgren RA (2010) Mitigating nonpoint source pollution in agriculture with constructed and restored wetlands. Adv Agron 108: 1–76.

Palmer K, Ronkanen A-K & Kløve B (2015) Efficient removal of arsenic, antimony and nickel from mine wastewaters in Northern treatment peatlands and potential risks in their long-term use. Ecol Eng 75: 350–364.

Paredes D, Kuschk P, Mbwette TSA, Stange F, Muller RA, Köser H (2007) New aspects of microbial nitrogen transformations in the context of wastewater treatment—a review. Eng Life Sci 7 (1): 13–25.

Paul EA & Clark FE (1989) Soil microbiology and biochemistry. San Diego, Academic Press Inc.

Postila H, Heikkinen K, Saukkoriipi J, Karjalainen SM, Kuoppala M, Härkönen J, Visuri M, Ihme R & Kløve B (2011) Turvetuotannon valumavesien ympärivuotinen käsittely – TuKos-hankkeen loppuraportti. Suomen ympäristö 30: 1–155.

Putkuri E, Lindholm M & Peltonen A (2013) Ympäristön tila Suomessa 2013. SYKEn julkaisuja 1: 1–116.

Reddy KR, DeLaune RD, DeBusk WF & Koch MS (1993) Long-Term Nutrient Accumulation Rates in the Everglades. Soil Sci Soc Am J 57:1147–1155.

Reddy KR & Patrick WH (1984) Nitrogen transformations and loss in flooded soils and sediments. CRC Crit Rev Environ Control 13: 273–309.

Richardson CJ (1985) Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228: 1424–1427.

Richardson CJ (1999) The role of wetlands in storage, release, and cycling of phosphorus on the landscape: a 25-year retrospective. In: Reddy KR, O'Connor GA & Schelske CL (eds) Phosphorus biogeochemistry in subtropical ecosystems. Boca Raton, CRC Press.

Richardson CJ & Marshall PE (1986) Processes controlling movement, storage, and export of phosphorus in a fen peatland. Ecol Monogr 56: 279–302.

Richardson CJ, Qian SS, Craft BC & Qualls RG (1997) Predictive models for phosphorus retention in wetlands. Wetlands Ecol Manag 4: 159–75.

Ronkanen A-K & Kløve B (2005) Hydraulic soil properties of peatlands treating municipal wastewater and peat harvesting runoff. Suo – Mires and peat 56(2): 43–56.

Ronkanen A-K & Kløve B (2008) Hydraulic and flow modelling of water treatment wetlands constructed on peatlands in Northern Finland. Water Res 42(14): 3826–3836.

Ronkanen A-K (2009) Hydrologic and hydraulic processes in northern treatment petlands and the significance for phosphorus and nitrogen removal. Acta Univ Oul C 321. University of Oulu, Oulu, Finland: 1–67.

Ronkanen A-K & Kløve B (2009) Long-term phosphorus and nitrogen removal processes and preferential flow paths in Northern constructed peatlands. Ecol Eng 35(5): 843–855.

Roseth R & Haarstad K (2010) Pesticide runoff from greenhouse production. Water Sci Technol 61: 1373–1381.

Räisänen ML, Lestinen P & Kuivasaari T (2001) The retention of metals and sulphur in a natural wetland – preliminary results from the old Otravaara pyrite mine, eastern Finland. In: Proceeding of International Conference on Mining and the Environment, Skellefteå, Sweden, The Swedish Mining Association 2: 662–670.

Sawhney BL & Hill DE (1975) Phosphate sorption characteristics of soils treated with domestic waste water. J Environ Qual 4: 342–346.

Schaller J, Vymazal J & Brackhage C (2013) Retention of resources (metals, metalloids and rare earth elements) by autochthonously/allochthonously dominated wetlands: A review. Ecol Eng 53: 106–114.

Schmid M, Twachtmann U, Klein M, Strous M, Juretschko S, Jetten M, Metzger J, Schleifer KH, Wagner M (2000) Molecular evidence for genus level diversity of bacteria capable of catalyzing anaerobic ammonium oxidation. Syst Appl Microbiol. 23: 93–106.

Scholz M & Lee B (2005) Constructed wetlands: a review. Int J Environ Studies 62: 421–447.

Shao MF, Zhang T, Fang HH-P (2010) Sulfur-driven autotrophic denitrification: diversity, biochemistry, and engineering applications. Appl Microbiol Biotechnol 88(5): 1027–1042.

Shapiro J (1964) Effect of yellow organic acids on iron and other metals in water. J. Am. Water Works Assoc. 56: 1062–1082.

Silvan N, Vasander H, Karsisto M, Laine J (2003) Microbial immobilisation of added nitrogen and phosphorus in constructed wetland buffer. Appl Soil Ecol 24: 143–149.

Sliekers AO, Derwort N, Campos Gomez JL, Strous M, Kuenen JG, Jetten MSM (2002) Completely autotrophic nitrogen removal over nitrite in one single reactor. Water Res 36: 2475–2482.

Stein OR, Hook PB, Biederman JA, Allen WC & Borden DJ (2003) Does batch operation enhance oxidation in subsurface constructed wetlands? Water Sci Technol 48(5): 149–156.

Stottmeister U, Wiessner A, Kuschk P, Kappelmeyer U, Kastner M, Bederski O, Muller RA, Moormann H (2003) Effects of plants and microorganisms in constructed wetlands for wastewater treatment. Biotechnol Adv 22: 93–117.

Sundberg C, Stendahl JSK, Tonderski K & Lindgren PE (2007a) Overland flow systems for treatment of landfill leachates—potential nitrification and structure of the ammonia-oxidizing bacterial community during a growing season. Soil Biol Biochem 39: 127–138.

Sundberg C, Tonderski K & Lindgren PE (2007b) Potential nitrification and denitrification and the corresponding composition of the bacterial communities in a compact constructed wetland treating landfill leachates. Water Sci Technol 56(3): 159–166.

Sundblad K & Wittgren HB (1991) Wastewater nutrient removal and recovery in an infiltration wetland. In: Etnier C & Guterstam B (eds) Ecological engineering for wastewater treatment. Göteborg, Bokskogen: 190–198.

Sänkiaho L & Sillanpää N (eds) (2012) STORMWATER project – Final report. Tiede+Teknologia 4: 1–60.

Tattari S, Koskiaho J & Kosunen M (2014) Turvetuotannon kuormituslaskentasuositus ja perustelut sen käyttöönotolle. Report of TASO project. Helsinki, Finnish Environment Institute: 1–45.

Tuukkanen T, Kløve B, Marttila H, Heikkinen K & Karppinen A (2012) Processes and site characteristics controlling nutrient and sediment runoff loads from peat harvesting sites. Extended abstract No 312, 14th International Peat Congress.

van de Graaf AA, Mulder A, de Bruijin P, Jetten MSM, Robertson LA & Kuenen JG (1995) Anaerobic oxidation of ammonium is a biologically mediated process. Appl Environ Microbiol 61: 1246 –1251.

Vasander H, Tuittila E-S, Lode E, Lundin L, Ilomets M, Sallantaus T, Heikkilä R, Pitkänen M-L & Laine, J (2003) Status and restoration of peatlands in northern Europe. Wetl Ecol Manag 11: 51–63.

Vassiljev A & Blinova I (2012) The influence of drained peat soils on diffuse nitrogen pollution of surface water. Hydrol Res 43: 352–358.

Vohla C, Kõiv M, Bavor HJ, Chazarenc F & Mander Ü (2011) Filter materials for phosphorus removal from wastewater in treatment wetlands – A review. Ecol Eng 37: 70–89.

von Post L (1924) Das Genetische System der Organogenen Bildungen Schwedens (Genetic Classification for the Organic Soils of Sweden). Comité Intemational de Pédologie IV Communication 22: 287–304.

Vymazal J (1998) Introduction. In: Vymazal J, Brix H, Cooper PF, Green MB & Haberl R (eds) Constructed wetlands for wastewater treatment in Europe. Leiden, Backhuys Publishers: 1–15.

Vymazal J (2001) Nutrient removal and transformation mechanisms in constructed wetlands. In: Vymazal J (ed) Transformations of nutrients in natural and constructed wetlands. Leiden, Backhuys Publishers: 1–92.

Vymazal J (2007) Removal of nutrients in various types of constructed wetlands. Sci Total Environ 380: 48–65.

Vymazal J (2011) Long-term performance of constructed wetlands with horizontal sub-surface flow: Ten case studies from the Czech Republic. Ecol Eng 37: 54–63.

Vymazal J & Březinová T (2014) Long term treatment performance of constructed wetlands forwastewater treatment in mountain areas: Four case studies from the Czech Republic. Ecol Eng 71: 578–583.

Vymazal J & Březinová T (2015) The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: a review. Environ Int 75: 11–20.

Wahlroos O, Valkama P, Mäkinen E, Ojala A, Vasander H, Väänänen V-M, Halonen A, Lindén L, Nummi P, Ahponen H, Lahti K, Vessman T, Rantakokko K & Nikinmaa E (2015) Urban wetland parks in Finland: improving water quality and creating endangered habitats. Int J Biodivers Sci, Ecosyst Serv Manag 11(1): 46–60, DOI: 10.1080/21513732.2015.1006681

Wartiovaara J (1978) Phosphorus and organic matter discharged by Finnish waters to the Baltic Sea. Publications of the Water Research Institute 29: 1–42.

White JS, Bayley SE & Curtis PJ (2000) Sediment storage of phosphorus in a northern prairie wetland receiving municipal and agro-industrial wastewater. Ecol Eng 14: 127–138.

Xie S, Zhang X & Wang Z (2003) Temperature effect on aerobic denitrification and nitrification. J Environ Sci 15: 669–673.

Yates CN, Wootton BC & Murphy SD (2012) Performance assessment of arctic tundra municipal wastewater treatment wetlands through an arctic summer. Ecol Eng 44: 160–173.

Yousefi Z & Mohseni-Bandpei A (2010) Nitrogen and phosphorus removal from wastewater by subsurface wetlands planted with *Iris pseudacorus*. Ecol Eng 36: 777–782.

Original publications

I Karjalainen SM, Huttunen JT, Liikanen A, Väisänen TS, Kløve B, Ylitolonen A, Heikkinen K & Martikainen PJ (2005) Nitrous oxide emissions from constructed boreal wetlands used to polish municipal wastewater. Verh. Internat. Verein. Limnol. 29: 612–617.

II Liikanen A, Huttunen JT, Karjalainen SM, Heikkinen K, Väisänen TS, Nykänen H, Martikainen PJ (2006) Temporal and seasonal changes in greenhouse gas emissions from a constructed wetland purifying peat mining runoff waters, Ecol. Eng. 26: 241–251.

III Postila H, Saukkoriipi J, Heikkinen K, Karjalainen SM, Kuoppala M, Marttila H & Kløve B (2014) Can treatment wetlands be constructed on drained peatlands for efficient purification of peat extraction runoff? Geoderma 228–229: 33–43.

IV Karjalainen SM, Heikkinen K, Ihme R & Kløve B (2016) Long-term purification efficiency of a wetland constructed to treat runoff from peat extraction. J Environ Sci Health A 51(5): 393–402.

V Karjalainen SM, Ronkanen A-K, Heikkinen K & Kløve B (2016) Long-term accumulation and retention of Al, Fe and P in peat soils of northern treatment wetlands. Ecol Eng 93: 91–103.

Original publications are not included in the electronic version of the dissertation.

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