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Design parameters for nitrogen removal by constructed wetlands treating mine waters and municipal wastewater under Nordic conditions

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Abstract

Nitrogen (N) loads from municipal and mine wastewater discharges typically increase N concentrations in recipient water bodies which should get more attention especially in cold-climate regions. This study compared N removal efficiency of six constructed wetlands (CWs) treating mine waters and three CWs polishing municipal wastewater. There were clear impacts of point source N loading to recipient water bodies in all cases studied and more than 300-fold increase in N was seen in some cases. First-order N removal coefficient was determined for seven of these CWs. All CWs studied were observed to remove N efficiently during the warm growing season but the amount of N released increased significantly during the cold season. Although some year-round purification was achieved by both peat-based and pond-type CWs, removal of nitrate+nitrite-N ($(\text{NO}_3^- + \text{NO}_2^-)\text{-N}$) was low during winter. The first-order N removal coefficient varied from $4.9 \cdot 10^{-6}$ to $1.9 \cdot 10^{-3} \text{ d}^{-1}$ and showed that peat-based CWs were slightly more efficient in N removal than pond-type CWs. However, purification efficiency was steadier and higher for pond-type CWs, as lower hydraulic load or longer water residence time compensated for purification performance. Pond-type CWs showed mean removal efficiency of 59% and 46% for ammonium-N ($\text{NH}_4^+\text{-N}$) and $(\text{NO}_3^- + \text{NO}_2^-)\text{-N}$, respectively, whereas peatland-type CWs had lower removal efficiency for $\text{NH}_4^+\text{-N}$ (mean of

26%) and in many cases negative removal for $(\text{NO}_3^- + \text{NO}_2^-)\text{-N}$. Correlation analysis revealed no clear, systematic relationship between temperature and N removal. However, in some CWs the highest correlation was between temperature and $(\text{NO}_3^- + \text{NO}_2^-)\text{-N}$, reflecting lower denitrification rate at lower temperature. More than 50% removal was found to require a hydraulic load below 10 mm d^{-1} . In order to achieve 70% of $\text{NH}_4^+\text{-N}$ removal, N_{tot} load lower than $75 \text{ g m}^{-2} \text{ year}^{-1}$ and a residence time longer than 80 d are needed in CWs in cold-climate regions.

Keywords: Passive treatment; Removal kinetics; Mine emissions; Nitrogen load; Recipient water body

Introduction

Terrestrial and aquatic ecosystems, especially naturally oligotrophic water bodies, are sensitive to nutrient load. Phosphorus (P) is typically the limiting nutrient in base production in inland waters (e.g., rivers and lakes), while nitrogen (N) is generally the limiting nutrient in many oceanic and coastal waters, such as the Baltic Sea. This means that increased N load can lead to enhanced ecosystem production and to subsequent eutrophication of oceanic and coastal water systems (Guildford and Hecky, 2000; Danielsson et al., 2008). In the Arctic region, there are also some valuable pristine lake and river ecosystems where N has been found to control growth of phytoplankton (e.g., Levine and Whalen, 2001; Bergström et al., 2005). High N concentration typically leads to oxygen deficiency due to increased biomass production in waters, but also has direct toxic effects on water organisms (Pommen, 1983; Forsyth et al., 1995; Stumm and Morgan, 1996). High N concentrations have also observed to reduce species diversity (James et al., 2005; Barker et al., 2008) and the growth of macrophytes in some lake ecosystems (Yu et al., 2015).

Input of N and P have been reduced in many countries through improved wastewater treatment and more efficient use of fertilizers. However, deterioration of surface water bodies continues (Blaas and Kroeze, 2016). Much attention has been paid to reducing the P load from municipalities and agriculture, or loads of harmful substances such as nickel, antimony, and sulfate from metal mines (Younger et al., 2002; Räisänen, 2009; Nordstrom, 2011; Kauppila et al., 2011; Palmer et al., 2015). However, less attention has been paid to N loads coming from municipalities and mines, although both are important local N sources (Chlot, 2011). The N content in sewage

waters is typically high, while mine drainage waters often contain high amounts of N due to the use of N-based explosives. In general, the amount of N released from different rock-blasting explosives varies between 20-30% of the weight of the explosive, depending on its type and solubility (Morin and Hutt, 2009; Chlot, 2011) and on the success of explosion (Forsyth et al., 1995; Revey, 1996). Besides explosives, certain mineral processing activities, including pH regulation, use of cyanide in gold extraction, and use of ammonia as a lixiviant, can generate significant N loads to the environment (Morin and Hutt, 2009; Jermakka et al., 2014). Annual discharges to recipient water bodies have been reported to vary from tens to hundreds of tons of total N at some large Nordic mines (Mattila et al., 2007; Lindeström, 2012; Maikkula, 2013), and municipalities can supply even higher annual N loads to surface waters (Pietiläinen et al., 2008).

Nitrogen is typically removed from wastewater by biological processes in bioreactors and active barriers (Mattila et al., 2007; Vymazal, 2007; Jermakka et al., 2014). In addition, membrane separation processes (Mattila et al., 2007) and methods based on ion exchange (Hekmatzadeh et al., 2012), reverse osmosis (Wang et al., 2016), adsorption (Bhatnagar and Sillanpää, 2011), electrocoagulation (Kuokkanen et al., 2013), or freeze crystallization (Maekawa et al., 1995) have been used to decrease N concentrations in wastewaters. However, these conventional methods used in industry are not cost-effective for the treatment of mine waters in Nordic climate regions, due to the massive volume of water generated during mining operations (Jermakka et al., 2014) and to the high maintenance requirements of the methods. The need to treat large water volumes also means that these conventional methods are not suitable for N removal in small municipalities either. Thus, alternative methods to reduce N loads to water bodies are needed.

At mines, removal of N is commonly based on passive water treatment by recycling, especially for process water, via tailings ponds or by using constructed wetlands (CW), where the water flow is delayed and a large filtration network is available with many adsorptive surfaces on plant roots or soil particles (Younger et al., 2002; Kadlec and Wallace, 2009). By working as buffer zones between the point source and the recipient water bodies, CWs are widely used to polish process and drainage waters at mines and efficiently remove harmful metals and metalloids from those waters (Wieder, 1989; Younger et al., 2002; Yang et al., 2006; Räisänen, 2009; Palmer et al., 2015). Different types of CWs, including pond-type CWs (Al-Isawi et al., 2017), are well-known to reduce the N load

from municipal and industrial waters (e.g., Vymazal, 2011; Ronkanen and Kløve, 2009), and the N load in runoff coming from different land uses such as agriculture and forestry (Koskiahio et al., 2003; Vikman et al., 2010). Although CW systems can be suitable and cost-effective for N removal, the Nordic climate with its low annual and winter temperatures is challenging for efficient year-round purification, as N removal processes are largely temperature-dependent. In addition to low temperature, N removal processes may be restricted by lack of readily biodegradable carbon sources (Mattila et al., 2007; Jermakka et al., 2014).

Nitrogen compounds of wastewaters to be purified are involved in various physical, chemical and biological processes including filtration, sedimentation, volatilization, plant/microbial uptake, ammonia adsorption, anaerobic ammonium oxidation (Anammox), nitrification, and denitrification in CWs (e.g., Vymazal, 2007, Heikkien et al., 2018). The extent to which each of these processes occurs depends on many variables, e.g., biological activity, pH, oxygen availability, and redox conditions in the system (Vymazal, 2007; Morin and Hutt, 2009; Jermakka et al., 2014). In addition to this, also the type of CW plays an essential role in controlling dominant purification mechanism in CWs. In peatland-type CWs (Karjalainen et al., 2016), the vegetation has been found to play a role in N removal by plant uptake (Silvan et al., 2004) but also by creating more nitrification and denitrification interfaces further down in lower peat layers via oxygen transportation through the root system (Heikkinen et al., 2018). In pond-type CWs, nitrification has been found to occur on surfaces in the water column and denitrification in the sediment (Bastviken, 2006).

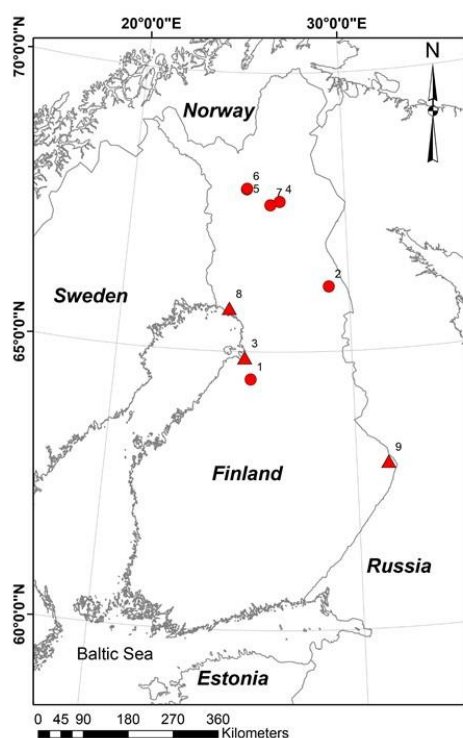
The design of CWs in Nordic climate conditions needs to be optimized taking into account environmental conditions at the site, rate of removal required, and inflow water quality, in order to provide sustainable and efficient year-round N removal. Although CWs are widely used and designing parameters for peat extraction runoff waters have been generated (Heikkinen et al., 2018), guidelines on CW designing for mine and municipal wastewaters in cold-climate regions are still lacking. This means that in these cases, CWs are typically planned based only on the land type and area available. Thus, the aims of the present study were to (i) investigate the N removal efficiency of pond-type and peatland-type CWs treating wastewater from municipalities or mining operations, (ii) apply well-established first-order reaction kinetics to determine the N removal coefficient for these two types of CWs, and (iii) assess the impact of nitrogen loads from point source on recipient water bodies when

different type of CWs are applied. Based on the results obtained factors such as temperature, dissolved oxygen concentration, hydraulic load etc. influencing nitrogen removal in CWs were identified, which would allow for improved design of CWs in future applications of municipal and mine wastewaters under Nordic climate condition.

METHODS

Study sites

The two different types of CWs included in this study (pond-type and peatland-type; Table 1) represent the most commonly used CW types in Finland. Three of the CWs (two peatland-type, one pond-type) are used to purify municipal wastewaters and six (four peatland-type, two pond-type) to purify mine waters with different water quality (Table 1). All CWs are located at latitudes higher than 62°N (Fig. 1) and in an arctic climate. Long-term mean annual temperature at the sites ranges from -0.4°C to 3.5 °C, while mean annual precipitation is more than 500 mm at all sites (Table 1; data from 2000 to 2015 provided by Finnish Meteorological Institute).



Location of the CWs:

1. Siikalatva wastewater treatment plant
2. Ruka wastewater treatment plant
3. Lakeus wastewater treatment plant
4. Kevitsa mine
- 5/6. Kittilä mine
7. Pahtavaara mine
8. Kemi mine
9. Pampalo mine

Fig. 1. Location of constructed wetlands (CWs) investigated in this study. The CWs are numbered as in Table 1. Pond-type CWs are indicated by red triangles and peatland-type CWs by red circles.

Table 1. Main characteristics of the nine constructed wetlands (CWs) investigated in this study

CW number	CW type	Point source type	Size (ha)	Established year	t_d (d)	t_p (d)	H (mm/d)	Q (m ³ /d)	T (°C)	P (mm)	Peat thickness (m)
1	Peatland	WW	24.5	2007	35	62–75	6	1575	3.4	537	n.a.
2*	Peatland	WW	0.6/1.1	1995	1–2	4–11	50	290	0.6	554	0.5–1.5
3	Pond	WW	17.1	1996	7	7.1	45	7700	3.5	606	-
4	Peatland	MW	13	2012	n.a.	3	65	6466	0.6	555	0.2–1.7
5	Peatland	MW	17	2006	n.a.	1–36	38	6500	-0.4	532	1–2
6	Peatland	MW	44	2010	n.a.	7–42	6.1	2700	-0.4	532	1–2
7	Peatland	MW	30	1997	n.a.	n.a.	12	3600	0.6	555	n.a.
8	Pond	MW	193	1969	n.a.	225	1.2	2300	1.4	500	-
9	Pond	MW	26.1	2011	n.a.	n.a.	11	2800	3.2	634	-

* For study period 2011–2015, the size of the CW changed; WW= municipal wastewater; MW = mining water; t_d = measured residence time of water; t_p = potential residence time of water calculated by dividing water volume by inflow rate; H = mean hydraulic load; Q = mean inflow rate; T = annual mean temperature; P = annual precipitation; n.a. = data not available

The mine sites produce metal ores (chromium and gold) and had been running 5 to 50 years at the start of this study (2016) and CWs have been worked nearly same time (Table 1). Mining at these sites have been started as open-pit mining and changed progressively to underground mining. The CWs in the sites work as passive treatment units and are treating either drainage water, mine dewatering water or excess waters from the ore beneficiation processes. The process waters are treated by conventional methods (e.g. precipitation), and further polished by CWs. At CW8, about 63% of the outflow water from the CW is circulated back into the mine processes and only 37% of the water is discharged to the downstream water body. The peatland-type of CWs (4-7) are common poor fens with mosses (e.g. *Sphagnum* sp.), *Eriophorum angustifolium*, *Carex* sp. and *Trichophorum cespitosum* whereas pond-type of CWs are open, free water clarification pond of the tailing management facility.

The municipal wastewater treatment plants are conventional chemical activated sludge treatment plants (CW2, CW3) with no biological nitrogen removal steps but the CW1 polish the municipal wastewaters after traditional biorotor plant (Table 1). The oldest wastewater treatment plant has been in operation since 1996, the youngest since 2004. The CW treatment is always the final treatment step, after which the purified wastewater is discharged to the downstream water body. The peatland-type CW2, which treats municipal wastewaters, represents the

common pristine peatland type in the region where different *Carex* species are dominant, whereas CW1 was partly constructed on pristine peatland and partly on extracted peatland. The pond-type CW polishing municipal wastewater (CW3) consists of three separated free-water surface ponds with common local vegetation (e.g. *Phragmites communis*).

Purification efficiency of CWs

Available monitoring data on the composition of inflow and outflow waters from CWs treating mine or municipal wastewaters were compiled from a) monitoring data supplied directly by the mining companies or the operators of the municipal wastewater treatment plants, and from b) water quality data collected by environmental authorities. In both cases, water samples were analyzed by accredited laboratories using standard methods. Sampling intervals varied a lot depending the site and the year. The most intensive sampling (nearly every day for specific years) was done in the mine site of CW5 and 6 but sampling interval has been longer (1 to 2 months) in some municipal wastewater treatment plants. The number of samples are reported in the Table 6. From the final dataset, the data available for the period 2010-2016 were selected for further analysis. For CW2, data for the period 1996-2003 were also included, as they included the results of N removal kinetics analysis, but the size of CW2 changed for the period 2011-2015, so the data from that site were handled separately for these two periods. Purification efficiency for total N, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ was calculated based on the difference between the inflow and outflow concentrations as:

$$\text{Purification efficiency (\%)} = \frac{[\text{Inflow}] - [\text{Outflow}]}{[\text{Inflow}]} \cdot 100\% \quad (1)$$

Annual and seasonal averages of both loads and purification efficiencies were calculated separately. The seasonal periods were as defined by Finnish Meteorological Institute (2017), based on their average duration in Finland and used in official comparisons of climate data. The seasons comprise the following months: Spring = March, April, May; Summer = June, July, August; Autumn = September, October, November; Winter = December, January, February.

Nitrogen removal kinetics

In order to determine N removal rates in the different CWs, surface water samples were taken from seven CWs in separate sampling campaigns and different N fractions were analyzed (Table 2). The samples were stored in cold, dark conditions prior to analysis. The sampling campaign was repeated in different months, representing cases of different hydraulic loads and different temperatures. The water samples were analyzed using standard methods in accredited laboratories.

Table 2. Water sampling for nitrogen (N) removal kinetics in the nine constructed wetlands (CWs) studied. Total N, ammonium-N ($\text{NH}_4^+\text{-N}$), and nitrate+nitrite-N ($\text{NO}_3^-+\text{NO}_2^-\text{-N}$) were determined, unless otherwise indicated

CW	No. of sampling points	No. of sampling occasions	Sampling year(s)
1	4	10	2011
2	3–8	7 ^a	1995, 2002, 2004
3	4	10	2011
4	5	20	2014
5	6–9	5	2013, 2015, 2016
6	4–20	12	2013–2016
7	-	-	not included
8	4	8	2012–2014
9	-	-	not included

^a On three occasions only total N was determined

General first-order reaction kinetics based on completely mixed systems (also known as homogeneous batch reactors or continuously stirred tank reactors) are widely used to model pollutants in water bodies (Chapra, 1997). Since there is a free watertable in CWs, first-order reaction kinetics can be applied to CW systems such as pond- and peatland-type CWs (Chavan and Dennett, 2008; Ronkanen and Kløve, 2009). The model combines all processes in which N is removed from the water (Kadlec and Wallace, 2009). In order to compare N removal efficiencies of different purification systems under different environmental conditions during the frost-free period, a first-order areal model was fitted to the measured N data from the water flowing through the seven CWs for which N removal kinetics were studied:

$$C_N = c_0 + ae^{-k_*x} \quad (2)$$

where C_N is N concentration in mine water or wastewater at distance x from the inlet [g m^{-3}]; c_0 is background N concentration in the area [g m^{-3}]; a is a site-specific constant [g m^{-3}] that can be also defined as $c_{\text{IN}} - c_0$, where c_{IN}

is the N concentration in inlet water; k_* is the first-order reaction rate [m^{-1}] that can be defined as k/H , where k is reaction coefficient [d^{-1}] and H is hydraulic loading rate [m d^{-1}]; and x is distance from the inlet [m].

Nitrogen load to recipient waters

The impact of point sources on downstream water bodies was assessed by comparing N concentrations upstream and downstream of two mine sites and two municipal wastewater treatment plants. Selection of downstream water bodies was based on availability of monitoring data. Data on total N (N_{tot}), NO_3^- -N+ NO_2^- -N, and NH_4^+ -N concentrations were provided by Finnish Environmental Institute and were downloaded from the Hertta database (Hertta database, 2016). Most of these data have been collected in the monitoring program of the companies, as part of their environmental impact monitoring required by the Finnish environmental authorities. The longest dataset available was for the river Siikajoki, where samples have been collected three to 31 times a year since 1962. Sampling locations in recipient water bodies for the point sources studied were decided by the Finnish environmental authorities and are specified in the environmental permits of the mines and treatment plants. Sampling points selected for this study were located a few hundred meters before and after the outflow point of the studied point source.

RESULTS

Nitrogen in recipient water bodies

Before the point sources (mines or wastewater plants), the N concentrations in recipient rivers were generally low, with median N_{tot} ranging from 120 to 885 $\mu\text{g L}^{-1}$, NH_4^+ -N from 3 to 31 $\mu\text{g L}^{-1}$ and NO_3^- + NO_2^- -N from 3 to 94 $\mu\text{g L}^{-1}$ (Table 3). These concentrations can be taken to represent the natural variations in N concentrations in rivers without the impact of a point source. The highest concentrations were found in the recipient river for CW1 (Siikajoki), where agriculture is one of the largest land uses in the catchment. In general, NH_4^+ -N concentrations upstream of the point sources were highest during the winter/spring months February-March and lowest in July, August, and September. The water quality in the rivers studied is representative of that in Finnish rivers in Central

and Northern Finland (Niemi and Raateland, 2007; Niemi, 2010). Typically, the N concentrations in Finnish rivers are clearly lower than in many European or Chinese rivers, where N concentrations can be 10- to 100-fold higher than in this study (e.g., Xu et al., 2014; Yang et al., 2006). Intensive land use and different types of pollution problems are the main reasons for high N loads (Omernik, 1976; Foley et al., 2005; Bussi et al., 2017).

Table 3. Nitrogen concentrations (mg L⁻¹) in the recipient rivers of two constructed wetlands (CWs) receiving mine water and two CWs receiving municipal wastewater. Values shown are median with the range (minimum-maximum values) of concentrations measured upstream and downstream of the point source during the period 2010-2016.

Recipient river	CW No/ water type	Upstream			Downstream		
		N _{tot}	NH ₄ -N	NO ₃ ⁻ +NO ₂ ⁻ - N	N _{tot}	NH ₄ -N	NO ₃ ⁻ +NO ₂ ⁻ - N
Siikajoki n=22	1/WW	885 (660–4000)	31 (16–3500)	94 (27–313)	855 (660–1600)	41 (6–340)	230 (96–383)
Kesäjoki n=18	2/WW	415 (300–520)	26 (6–130)	20 (3–180)	5050 (1500–35000)	3950 (870–36000)	580 (130–3000)
Seurujoki n=206	5 and 6/MW	120 (25–650)	3 (2–110)	10 (2–74)	465 (95–2900)	57 (2–1700)	240 (8–1100)
Kemijoki n=72	8/MW	630 (260–1500)	15 (2–230)	3 (1–490)	1300 (460–7800)	200 (2–1400)	340 (3–5700)

n = number of samples; WW = municipal wastewater; MW = mining water

Table 4. Characteristics of the recipient rivers of two constructed wetlands (CWs) receiving mine water and two CWs receiving municipal wastewater. Information on catchment area and flow volumes (average 2010-2016) was obtained from the Hertta database, information on land use was obtained from the Corine landcover database (2012).

Recipient river	Catchment area (km ²)	Average flow (m ³ s ⁻¹)	Main land use type
Siikajoki	4320	49.7	Forest 78% Agriculture 9.6% Wetlands 8.5% Settlements & Industry 1.6% Water bodies 2.3%
Kesäjoki	19.8	0.265	Forest 77.2% Agriculture 3% Wetlands 9.2% Settlements & Industry 6.9% Water bodies 3.7%
Seurujoki	300	3.73	Forest 76.6% Agriculture 0.1% Wetlands 21.8% Settlements & Industry 1.0% Water bodies 0.4%
Kemijoki	50600	604	Forest 75.3% Agriculture 0.7% Wetlands 18.6% Settlements & Industry 0.8% Water bodies 4.6%

An impact of the point source on the N concentration in recipient water bodies was clearly visible in all four cases studied (Fig. 2, Figs. S1-S4). However, the magnitude of the effect on downstream water quality was variable (Table 3). In Siikajoki and Kemijoki, which have large catchments and land use like agriculture (Table 4), N_{tot} were 1 or 2 times higher at downstream just after the point source effluent place compared to the concentration at upstream before the point source. In Seurujoki and Kesäjoki, which have smaller catchments, the increase in N_{tot} concentration was much more pronounced (5-10 times higher concentrations at downstream after the point source). Furthermore, the dominant N species observed in the recipient water bodies differed based on the type of point source. In rivers receiving mine waters, $\text{NO}_3^- + \text{NO}_2^- - \text{N}$ was the major contributor to the N load. For example, the concentration of $\text{NO}_3^- + \text{NO}_2^- - \text{N}$ was on average 32-fold higher in the river Seurujoki and 320 higher in the river Kemijoki after the point source (Table 3, Fig. 2 and Suppl. Figs. S3 and S4). In the rivers receiving effluent from municipal wastewater treatment plants, the $\text{NH}_4^+ - \text{N}$ concentrations were somewhat higher than the $\text{NO}_3^- + \text{NO}_2^- - \text{N}$ concentrations (Table 3, Suppl. Figs. S1 and S2). The N concentrations in the recipient river for CW2 (Kesäjoki) were actually 300-fold higher after, compared with before, the treated wastewater discharge point.

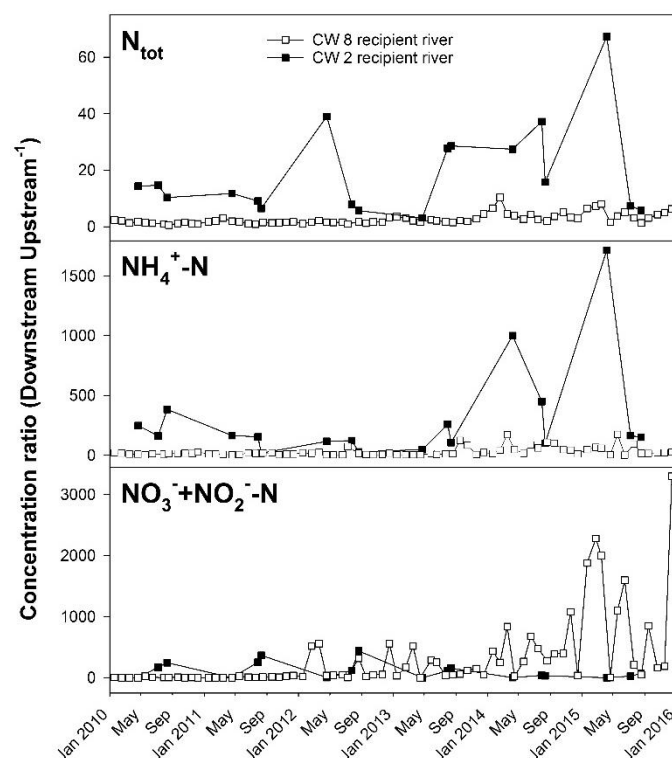


Fig. 2. Effect of point source discharge on nitrogen (N) fractions in the recipient water body. The concentration ratios were calculated for constructed wetland CW2 (municipal wastewater) and CW8 (mine wastewater). A ratio close to 1 indicates no clear impact of the point source on N content in the river, while ratios greater than 1 indicate more pronounced impacts.

The results showed that specific N treatment prior to the CW is beneficial for the recipient water body. In cases where the CW was the only means of N removal (CW2, CW4-7), a 29-390 fold increase in N concentration was observed in the recipient river after the point source. In the case of CW1, a specific treatment for N removal is applied prior to discharging the water into the CW and its effect was seen in a clearly lower impact of the point source on N concentrations in the river, with only two-fold higher N concentrations after the point source. However, it is also important to take into account the flow rate of the recipient river in relation to the amount of wastewater discharged from point sources. CW1 outflow is only about 0.04% of the Siikajoki river water and the outflow of CW8 only 0.004% of the Kemijoki river water. This explains why the impact of point source is not that clear in these two cases compared to the others (Kesäjoki and Seurujoki) where the point source water amount (outflow from CW2, CW5/6) represents 1.3-2.0% of the river waters. Despite of this, the results reveal the fact that, from the viewpoint of the recipient water body, a CW as the only purification step for N removal is not sufficient or that the CWs currently in place are poorly designed for N removal purposes. Additional treatment

steps or improved CW design are needed to reduce the N load to recipient waters. The results also highlight the difficulties in achieving year-round effective purification to meet targets based on watershed perspective as required by the European Union's Water Framework Directive (WFD0 (European Commission, 2012).

Nitrogen loads to the CWs and removal efficiencies

In CWs receiving pre-treated municipal wastewater, $\text{NH}_4^+\text{-N}$ was the main N species in the inflow water, accounting on average for 85% of N_{tot} (Table 5). In contrast, $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ was the main N species in the inflow water of CWs receiving mining wastewaters, accounting on average for 57% of N_{tot} (Table 5). It is well known, that nitrogen originating from explosives usually appears as NO_3^- and $\text{NH}_4^+/\text{NH}_3$, while the amounts of NO_2^- and organic N are comparatively low in mine waters (Morin and Hutt, 2009; Bailey et al., 2013; Jermakka et al., 2014; Karlsson and Kauppila, 2015). NO_2^- and organic N are however typical components in municipal wastewaters. This means that also the efficiency of biological N-removal in CWs is crucially influenced by the type of N load, as N is removed by coupled nitrification-denitrification processes. Thus municipal and mine wastewaters have different requirements for effective N removal. Wastewaters with high $\text{NH}_4^+\text{-N}$ content require CWs with oxic zones to enable aerobic nitrification to take place, converting NH_4^+ to $\text{NO}_3^-/\text{NO}_2^-$, followed by anaerobic denitrification in more anoxic zones of the CW. On the other hand, wastewaters with high $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ content can be purified under anoxic conditions during anaerobic denitrification and do not require any oxic zones in the CW.

The N load to the CWs ranged from 10 to more than $1000 \text{ g m}^{-2} \text{ year}^{-1}$, which is high compared with that in other studies on natural wetlands as a purification unit for municipal wastewaters (e.g., Nichols, 1983). However, the studied CWs removed 10 to 90% of the N_{tot} load (Table 6). The highest purification efficiencies were observed in pond-type CWs receiving mine wastewaters, while the lowest purification efficiencies were observed in peatland-type CWs receiving mine wastewaters (Table 6). In most cases, the removal efficiencies were higher for NH_4^+ (30-92%) than for $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ (from leaching to 80% removal). However, it should be borne in mind that only net removal of $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ was assessed. Part of the low $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ purification efficiency can be explained by nitrification in waters with high NH_4^+ loads, as part of the NH_4^+ is transformed to $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ as water flows through the CW, thus replenishing the $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ pool.

Table 5. Percentage of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$), nitrate + nitrite nitrogen ($\text{NO}_3^-+\text{NO}_2^-\text{-N}$) and organic nitrogen (N_{org}) in the inflow water of the nine constructed wetlands (CWs) in different seasons

	Water type	N-fraction (%)	Average	Winter	Spring	Summer	Autumn
CW1	Municipal	$\text{NH}_4^+\text{-N}$	85	97	79	80	86
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	0.2	0.3	0.1	0.1	0.5
		$\text{N}_{\text{org}}^{\text{a}}$	14	2	21	20	14
CW2 ^b	Municipal	$\text{NH}_4^+\text{-N}$	75/81	89/84	88/97	71/86	59/55
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	18/14	12/8	2/2	24/8	31/40
		N_{org}	7/5	0/8	10/1	5/6	10/5
CW3	Municipal	$\text{NH}_4^+\text{-N}$	94	104	99	95	76
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	6	2	1	3	22
		N_{org}	0	0	1	2	2
CW4	Mine	$\text{NH}_4^+\text{-N}$	23	26	23	25	20
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	53	46	45	68	59
		N_{org}	24	28	33	8	21
CW5	Mine	$\text{NH}_4^+\text{-N}$	22	29	24	12	18
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	76	67	77	86	77
		N_{org}	2	3	0	1	5
CW6	Mine	$\text{NH}_4^+\text{-N}$	65	68	67	66	59
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	26	23	24	25	34
		N_{org}	9	9	9	9	7
CW7	Mine	$\text{NH}_4^+\text{-N}$	18	22	24	5	5
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	74	84	70	63	74
		N_{org}	8	0	6	32	20
CW8	Mine	$\text{NH}_4^+\text{-N}$	19	19	n.a.	18	17
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	74	74	n.a.	75	75
		N_{org}	7	7	n.a.	7	8
CW9	Mine	$\text{NH}_4^+\text{-N}$	20	20	28	16	23
		$\text{NO}_3^-+\text{NO}_2^-\text{-N}$	78	80	72	78	77
		N_{org}	2	0	0	6	0

^aCalculated as $\text{N}_{\text{org}} = \text{N}_{\text{tot}} - (\text{NH}_4^+\text{-N}) - (\text{NO}_3^-+\text{NO}_2^-\text{-N})$; n.a. = data not available. For CW2, the values for 1995-2003 and 2011-2015 are reported separately.

Table 6. Annual and seasonal mean concentrations and removal efficiencies of total nitrogen (N), ammonium-N, and nitrate + nitrite N in inflow and outflow waters and removal efficiencies of the nine constructed wetlands (CWs) in different seasons. For CW2, concentrations and removal efficiencies at different study periods are shown, as the size of that CW differed in those periods

CW	Season	Total N ($\mu\text{g L}^{-1}$)			Ammonium-N ($\mu\text{g L}^{-1}$)			Nitrate + Nitrite-N ($\mu\text{g L}^{-1}$)			Period	No. of samplings
		Inflow	Outflow	Removal-%	Inflow	Outflow	Removal-%	Inflow	Outflow	Removal-%		
CW1	Annual	37279	18207	51	31844	14180	55	84	1497	-1682	2011-	54–61 (8) ^a
	Winter	39769	23069	42	38769	25500	36	119	1498	-1162	2015	13 (2)
	Spring	38000	23909	37	30091	20645	31	33	n.a. ^b	n.a.		11 (0)
	Summer	37895	12833	66	30368	5842	81	19	260	-1247		15-19 (3)
	Autumn	34389	15187	56	29470	8533	71	158	2733	-1634		15-18 (3)
CW2	Annual	46277/ 55446	35525/ 49447	23/ 11	34875/ 44911	24365/ 42211	30/ 6	8242/ 7814	8313/ 4778	-1/ 39	1995- 2003/ 2011- 2015	126/ 38–56 ^c
	Winter	60847/ 67154	53181/ 63938	13/ 5	54093/ 56154	44293/ 54688	18/ 3	7399/ 5483	9382/ 5563	-27/ -1		25/8-13
	Spring	50526/ 49143	48577/ 53077	4/ -8	44196/ 47571	40374/ 49538	9/ -4	1005/ 1119	3670/ 1108	-265/ 1		20/13
	Summer	38128/ 50467	22215/ 41556	42/ 18	26921/ 43400	12651/ 37000	53/ 15	9217/ 4089	7089/ 3249	23/ 21		47/9-15
	Autumn	45619/ 52615	33321/ 37938	27/ 28	26829/ 28923	15209/ 23688	46/ 18	14143/ 21215	13797/ 11675	3/ 45		34/ 8-15
CW3	Annual	69459	60148	13	65230	54082	17	4475	3277	27	2011-	61
	Winter	75200	70000	7	78267	68000	13	1442	1546	-7	2015	15
	Spring	67133	62333	7	66133	62333	13	434	1872	-332		15
	Summer	71688	55000	23	68063	48000	30	2189	2079	5		16
	Autumn	63667	53600	16	48267	43000	11	13987	7693	45		15
CW4	Annual	4906	2141	56	1121	802	28	2598	974	63	2013-	74–952 ^c
	Winter	5238	2557	51	1343	1184	12	2416	941	61	2016	21-310
	Spring	6092	2487	59	1380	1120	19	2719	963	65		12-158
	Summer	3754	1409	62	933	372	60	2540	686	73		24-262
	Autumn	4641	2136	54	921	524	43	2730	1322	52		17-222

CW5	Annual	13805	12370	10	2985	1645	45	10507	10203	3	2013-	75-83
	Winter	14635	13744	6	4296	3822	11	9701	9843	-1	2016	23-26
	Spring	13124	12337	6	3215	1200	63	10122	10473	-3		14-17
	Summer	13183	9961	24	1640	15	99	11359	9695	15		22-23
	Autumn	14059	14325	-2	2571	2068	20	10775	11016	-2		16-17
CW6	Annual	30942	15857	49	20168	7901	61	8096	6952	14	2013-	92-659
	Winter	29139	21611	26	19810	14578	26	6626	6560	1	2016	26-194
	Spring	33119	18821	43	22254	12792	43	7841	4528	42		16-119
	Summer	31116	8573	72	20516	1268	94	7804	6560	16		23-190
	Autumn	29859	15593	48	17705	4754	73	10011	9703	3		27-156
CW7	Annual	7406	4129	44	1327	568	57	5512	2757	50	2009-	64
	Winter	10964	7560	31	2421	1615	33	9160	6044	34	2015	19
	Spring	11056	5752	48	2691	1041	61	7756	3884	50		11
	Summer	3351	1503	55	162	17	89	2102	931	56		15
	Autumn	4911	3581	27	269	222	18	3654	2019	45		19
CW8	Annual	22340	2375	89	4191	281	93	16603	1417	91	2012-	9
	Winter	18320	2800	85	3546	670	81	14514	1700	88	2013	2
	Spring	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.		
	Summer	24213	2425	90	4334	170	96	18119	1608	91		4
	Autumn	18350	2150	88	3151	325	90	13814	1053	92		3
CW9	Annual	31059	21163	32	6188	2138	65	24176	19318	20	2012-	17
	Winter	32250	21150	34	6500	2875	56	25750	18275	29	2016	4
	Spring	21500	14500	33	6000	2850	53	15500	11650	25		2
	Summer	31857	23000	28	5000	1833	63	25000	21571	14		7
	Autumn	33250	21750	35	7750	1500	81	25500	20250	21		4

^a Nitrate-nitrite-N in outflow only from 2011 (no. of nitrate outflow samples given in parentheses); ^b n.a. = data not available; ^c Inflow sampled more frequently than outflow

Nitrogen removal kinetics

The N_{tot} concentration in inflow water to the CWs ranged from 2.5 to 85 mg L⁻¹ during water sampling for the N kinetics studies (Suppl. Figs. S5-S11). The highest N_{tot} values were found for CW3, treating municipal wastewater, and the lowest for CW4, treating mine water. The N_{tot} concentration decreased within the CWs with increasing distance from the inlet (Suppl. Figs. S5-S11). The outflow concentration ranged from 0.9 mg L⁻¹ (CW8) to 56 mg L⁻¹ (CW3). First-order removal kinetics explained the N_{tot} removal in most datasets ($R^2 \geq 0.8$). Areal rate constant weighted by hydraulic load (k) ranged from $4.9 \cdot 10^{-6}$ to $1.9 \cdot 10^{-3}$ d⁻¹ (Fig. 3). No clear correlation was observed between k and inflow water temperature or oxygen concentration for individual sites in most cases (Fig. 3, Table 7). However, a positive correlation was observed between water temperature and k in CW1 and CW5 ($r = 0.69$ and $r = 0.95$, respectively), a positive correlation between oxygen concentration and k in CW3 ($r = 0.40$), and a negative correlation between oxygen concentration and k in CW5 and CW8 ($r = -0.90$ and $r = -0.89$, respectively). These CWs treat mine waters and $\text{NO}_3^- + \text{NO}_2^-$ -N comprises 74-76% of total N load to the sites (Table 5).

The NH_4^+ -N concentration in inflow water ranged from 0.6 to 82 mg L⁻¹ (Suppl. Figs. S5-S11). As was the case for N_{tot} , the highest inflow concentrations were generally in CW3 and the lowest in CW4. Like N_{tot} concentrations, NH_4^+ -N concentrations decreased along the CWs with increasing distance from the inlet (Suppl. Figs. S5-S11), and outflow concentrations ranged from 0.2 mg L⁻¹ (CW4) to 60 mg L⁻¹ (CW3). First-order removal kinetics explained NH_4^+ -N removal in most cases (Supplemental Figures 5-11). Generally, k ranged from $2.5 \cdot 10^{-6}$ to $8.6 \cdot 10^{-4}$ d⁻¹ (Fig. 3). A positive correlation was observed between inflow water temperature and k in CW1, CW2, CW5, and CW6 ($r = 0.68$, $r = 0.74$, $r = 1.00$, $r = 0.45$, respectively). A negative correlation was observed between inflow oxygen concentration and k in CW3 and CW6 ($r = -0.72$ and $r = -0.40$, respectively) (Table 7).

The $\text{NO}_3^- + \text{NO}_2^-$ -N concentration in inflow water ranged from 0.2 to 31 mg L⁻¹. The highest inflow concentrations were observed in CW3 and the lowest in CW1 (Suppl. Figs. S5-S11) treating municipal wastewater after a biorotor treatment step. First-order retention kinetics explained $\text{NO}_3^- + \text{NO}_2^-$ -N concentrations well only in CW8, CW4, CW3, and CW6. In the other CWs, $\text{NO}_3^- + \text{NO}_2^-$ -N concentrations were either similar all along the CW (CW2, CW5) or there was an increase in concentration with increasing distance from the wastewater inlet (CW1; Supplementary Figures 5-11). Also previous studies have found that in large pond type CWs, N removal processes

can be complex and the simple first-order retention kinetics does not describe satisfactorily N transformation (Bastviken, 2006). Areal rate constant k for further analysis of this study was calculated only in cases where first-order retention kinetics provided a good fit ($R^2 \geq 0.8$) and its value ranged from $2.5 \cdot 10^{-8}$ to $6.9 \cdot 10^{-3} \text{ d}^{-1}$ (Fig. 3). No clear correlation was observed between k and water temperature or oxygen for most CWs. There were positive correlations between k and inflow water temperature in CW2 and CW6 ($r = 1.0$ and $r = 0.5$, respectively) and between k and inflow water oxygen concentration in CW3 ($r = 1.0$) (Table 7). There was a negative correlation between inflow water oxygen concentration and k in CW4 and CW8 ($r = -0.48$ and $r = -0.41$, respectively).

Table 7. Pearson correlation (r) between reaction coefficient k for removal of total nitrogen (N), ammonium-nitrogen ($\text{NH}_4^+\text{-N}$), and nitrate + nitrite nitrogen ($\text{NO}_3^-+\text{NO}_2^-\text{-N}$) and inflow temperature, air temperature, and oxygen. Data were tested for normality using the Shapiro-Wilk test. Significant correlations are indicated in bold. Significance level: * $p<0.1$; ** $p<0.05$; *** $p<0.01$

Site	Total N			$\text{NH}_4^+\text{-N}$			$\text{NO}_3^-+\text{NO}_2^-\text{-N}$		
	Temperature			Temperature			Temperature		
	Inflow	Air	Oxygen	Inflow	Air	Oxygen	Inflow	Air	Oxygen
CW 1	0.69	0.69	0.05	0.68*	0.56	0.06	n.d. ^a	n.d.	n.d.
CW 2	-0.49	-0.05	n.d.	0.74	-0.09	n.d.	0.99**	0.40	n.d.
CW 3	0.41	0.43	0.40	0.24	0.31	-0.72	0.18	0.05	0.99**
CW 4	0.19	0.26	0.13	-0.15	-0.11	-0.03 ^b	-0.09	-0.07	-0.48
CW 5	0.95	0.92	-0.90	n.d.	0.99*	0.38	n.d.	n.d.	n.d.
CW 6	0.33	0.50	-0.13	0.45	0.42	-0.40	0.50	0.49	-0.08 ^b
CW 8	-0.61	0.46	-0.89***	-0.08	-0.06	-0.22	0.00 ^b	0.07	-0.41

^a n.d. = not determined (when number of available k vs. temperature/oxygen pairs <3). ^b not normally distributed.

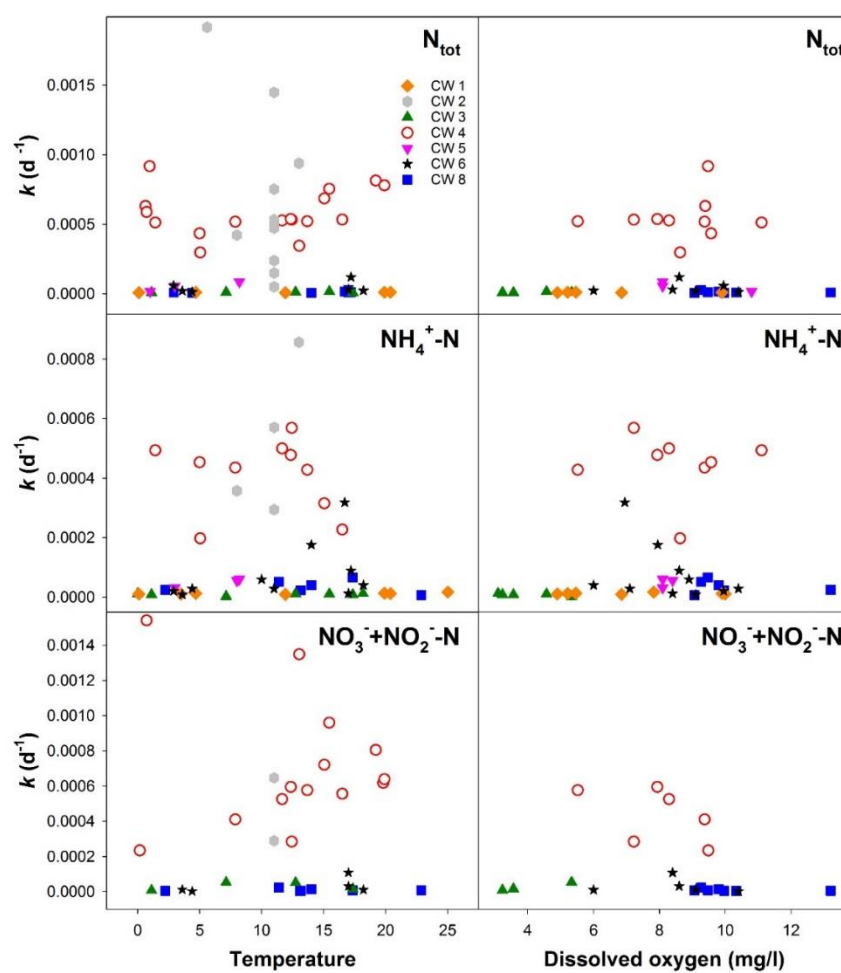


Fig. 3. Effect of temperature and dissolved oxygen on areal rate constant weighted by hydraulic load (k) in the seven constructed wetlands (CWs) in which reaction kinetics were studied. For CW2, no oxygen data were available.

DISCUSSION

Seasonal variation in N removal rate

The incoming N loads to the CWs and the relative abundance of different N species varied with season (Tables 4 and 5). The highest N_{tot} loads were encountered in winter in most CWs (five out of nine), while the highest $NO_3^-+NO_2^--N$ load season varied. The abundance of NH_4^+-N also did not follow a clear seasonal pattern, as in some CWs (CW1, CW2, CW5, CW6, CW7) it was higher in winter and spring than in summer and autumn, whereas there was no seasonal difference in the relative abundance of NH_4^+-N in the other CWs.

In CWs, most N is typically removed from the water by nitrification/denitrification and plant uptake (e.g. Silvan et al., 2004; Hallin et al., 2015). Nitrification and denitrification are both biological processes, with increased rates of reaction at higher temperatures (Dawson and Murphy, 1972; Cameron et al., 2010), while plant growth is also accelerated at higher temperatures (Morison and Lawlor, 1999; Loveys et al., 2002). Thus, N removal can be expected to be higher in summer months when air and water temperatures are higher, as is typical in cold-climate regions. This was clearly seen in the N_{tot} removal efficiencies of CW2, CW5, CW6, and CW7 (all peatland-type CWs), and in the $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ removal efficiencies of most CWs. Summer air temperatures varied from 0.4 to 25.8 °C and summer water temperatures from 5.6 to 25.0 °C, providing good conditions for biological removal processes. However, within these summer temperature ranges, there was no clear impact of temperature on N removal kinetics. In fact, some CWs showed similar N_{tot} removal efficiencies throughout the year (CW1, CW3, CW4, CW8, CW9), and CW8 showed the highest $\text{NH}_4^+\text{-N}$ removal efficiencies in autumn. The most pronounced seasonal differences in removal efficiency were observed for $\text{NO}_3^- + \text{NO}_2^-\text{-N}$, which three CWs (CW2, CW5, CW6) removed only in the summer months, while there was either no net removal or even an increase in concentration during the rest of the year. Leaching of $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ was always observed from CW1, where the inflow concentration was extremely low compared with that in other CWs (Table 5). The other CWs showed intermediate net removal during the autumn to spring months. However, note that only net $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ removal is observable. In CWs with high $\text{NH}_4^+\text{-N}$ removal, NO_3^- and NO_2^- are continuously produced during nitrification and thus not only the $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ in the inflow water but also that newly produced during nitrification have to be removed by denitrification. The results in this study indicate that denitrification restricts N removal during winters in most cases. This can be partly explained by snow and ice cover preventing inflow water flowing through the peat layer in peatland-type CWs, and by the active water volume being reduced by snow and ice and low water temperature decreasing the activity of denitrifying microorganisms in pond-type CWs (e.g. Saleh-Lakha et al., 2009).

The decreased removal efficiency of CWs in winter is also reflected in the load to the recipient water bodies. In the streams receiving waters from CW5, CW6, and CW8, treating mine waters, the increase in N concentrations downstream of the point sources was more pronounced in winter/spring than in summer months. In the stream receiving water from CW2 this trend was less pronounced and in the stream receiving water from CW1, which

polishes municipal wastewater, no such effect was observed. As noted earlier, background N concentrations in this stream (Siikajoki) are already quite high, and possible seasonal differences in load caused by the discharge from CW1 might go unnoticed.

Comparison of pond-type and peatland-type CWs

There was no clear pattern of differences in N removal efficiency between pond-type and peatland-type CWs. In general, slightly higher removal efficiencies for N_{tot} were observed in pond-type than in peatland-type CWs (Table 5). The difference was even more pronounced for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^- + \text{NO}_2^-\text{-N}$, for which pond-type CWs showed average removal efficiencies of 59% and 46%, respectively, while peatland-type CWs showed lower removal efficiencies for $\text{NH}_4^+\text{-N}$ (on average 26%) and in many cases negative removal of $\text{NO}_3^- + \text{NO}_2^-\text{-N}$, i.e., $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ production (Table 5). This was especially pronounced in CW1, CW2, and CW5 (Table 5). However, the first-order reaction coefficient k for all N compounds in the frost-free period was lower for the pond-type than the peatland-type CWs (Fig. 5), indicating slower decrease of nitrogen from the inlet to the outlet. The difference in k between the CW types was not as significant for $\text{NH}_4^+\text{-N}$, reflecting the fact that the rate of oxygen demand for the nitrification process is quite similar in both CW types. In peatland-type CWs, most of the water flow occurs as free water flow or in surface layers, while infiltration into deeper soil layers is low (Ronkanen and Kløve, 2008; Palmer et al., 2015). Oxygen diffusion into the free-flowing water and upper soil layers is high, likely also aided by oxygen transport along plant roots (Brix, 1993; Stein and Hook, 2005). Under oxic conditions, nitrification can occur and NH_4^+ and NO_2^- are thus oxidized to NO_3^- . Denitrification is an anaerobic process, so it is less likely to occur in the layers into which oxygen can diffuse and is thus restricted to the lower, more anoxic soil layers (e.g., Kadlec and Wallance, 2009; Heikkinen et al. 2018). Based on the results of the present study, it seems that anaerobic layers are more available in peatland-type CWs than in pond-type, since k for removal of $\text{NO}_3^- + \text{NO}_2^-\text{-N}$ was clearly higher for peatlands. Previous studies have pinpointed that denitrification processes typically occur in pond sediment (Bastviken, 2006) which partly explain differences between these two type of CWs. However, the hydraulic load to the peatland controls this, as infiltration rates into deeper soil layers are typically low and

denitrifiers in deeper soil layers thus do not receive NO_3^- , so part (or sometimes most) of the NO_3^- produced by nitrification is not removed by denitrification.

In both types of CWs, lower hydraulic load increased NH_4^+ -N removal (Fig. 4A), but no relationship was observed between removal of other N compounds and hydraulic load. The results also indicated slightly higher NH_4^+ removal at higher hydraulic loads in peatland-type CWs compared with pond-type (Fig. 4A). Based on the regression equations obtained for N_{tot} load to CWs considering all CWs together ($R^2=0.53$), more than 70% removal would be achieved for N_{tot} loads $<75 \text{ g m}^{-2} \text{ year}^{-1}$ ($207 \text{ mg m}^{-2} \text{ d}^{-1}$) (Fig. 4). This is higher than the previously reported load of $0.10 \text{ mg m}^{-2} \text{ d}^{-1}$ for treatment peatlands, based on one-site studies (Ronkanen and Kløve, 2009). Considering only pond-type CWs, regression analysis ($R^2=0.99$) indicates a design load of max. $3.2 \text{ mg m}^{-2} \text{ d}^{-1}$ to achieve 70% N_{tot} removal.

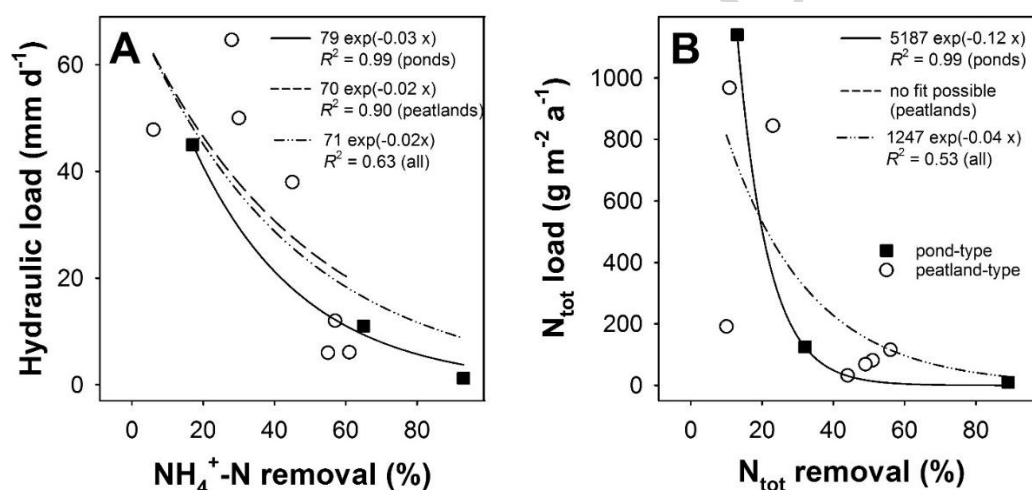


Fig. 4. Regression analysis for A) mean hydraulic load to constructed wetlands (CWs) and ammonium-nitrogen (NH_4 -N) removal efficiency; and B) annual total nitrogen (N_{tot}) load to the CWs and N_{tot} removal efficiency. The regressions for pond-type CWs, peatland-type CWs, and all CWs combined are shown as solid lines, dashed lines, and dashed-dotted lines, respectively.

It can be concluded that the pond-type CWs studied were lightly more consistent in their removal efficiencies than peatland-type CWs, but that N removal rate was slightly faster in peatland CWs. In particular, NH_4^+ -N removal via nitrification was somewhat higher in the pond-type CWs, while $\text{NO}_3^- + \text{NO}_2^-$ -N removal via denitrification was

higher in some of the peatland-type CWs. One reason could be that typically organic carbon, restricting denitrification, is more readily available in peatlands.

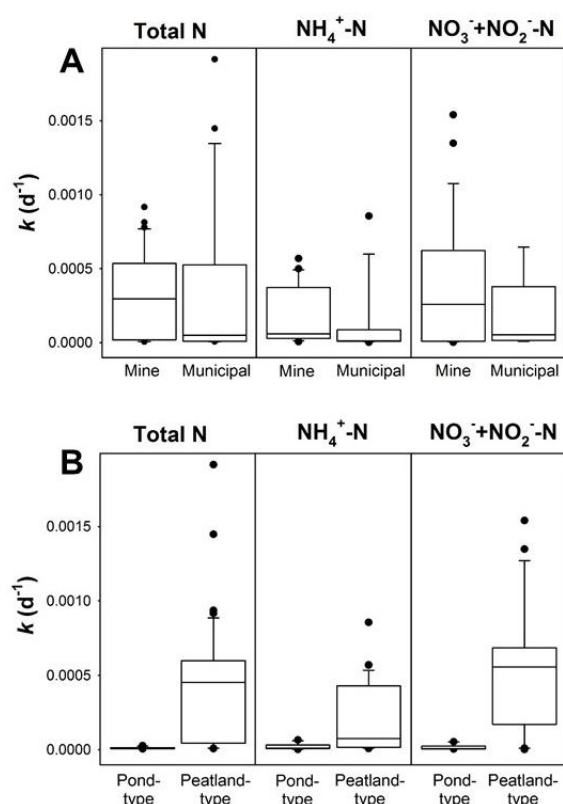


Fig. 5. Influence of A) water type (mine water, municipal wastewater) and B) wetland type (peatland, pond) on nitrogen (N) removal kinetics in constructed wetlands.

The N removal efficiency of CWs is controlled by a variety of environmental parameters, e.g., temperature, oxygen availability, water residence time, and availability of carbon sources. Water residence time is tightly linked to oxygen availability, as longer residence times allow efficient diffusion of oxygen into the surface water. On the other hand, if the residence time is too long and areas of standing water occur, anoxic zones are likely to develop. Moreover, longer residence times allow more time for processes to purify the waters, so total removal might be high even though process rates are low. Longer residence times are mostly found in large CWs with moderate hydraulic loads, e.g., CW1, CW6, and CW8. In fact, moderately high oxygen concentrations ($5\text{-}10 \text{ mg L}^{-1}$) were measured in the surface water of those three CWs on selected sampling occasions. The amount of oxygen available

potentially affects nitrification efficiency in CWs. During nitrification, NH_4^+ is converted stepwise via NO_2^- to NO_3^- . Thus, oxygen-rich conditions are especially important in those CWs, in which NH_4^+ is the major N load, here CW1, CW2, CW3, and CW6 (Table 4). CW1, CW6, and CW8 had rather good N_{tot} and NH_4^+ -N removal efficiency, indicating that there is a sufficient oxygen supply to maintain nitrification and sufficient time for processes to occur. On the other hand, NH_4^+ -N removal efficiencies were rather low in CW2 and CW3, indicating that nitrification is not working optimally, perhaps due to lack of oxygen.

Temperature is a crucial parameter in N removal (Huang et al., 2013; Mietto et al., 2015). In the nine CWs studied here, N removal processes are mainly governed by the temperature of the incoming water, the soil and air temperature, and the water residence time. With long residence times, water temperature is more likely to be determined by soil and air temperature than by the temperature of the incoming water. In CW1, which has a rather long residence time of water, incoming water temperature was relatively constant throughout the year (measured in 2011), while temperatures measured in the surface water of the CW showed a clear seasonal trend (near 0°C in winter, $>20^\circ\text{C}$ in summer), thus reflecting air temperature rather than incoming water temperature.

Carbon availability influences denitrification of NO_3^- or NO_2^- to gaseous nitrogen forms and thus their removal from water. Easily available carbon can be derived from e.g., municipal wastewaters with high biological oxygen demand (BOD) or it can be generated in the CW itself during degradation of organic matter (e.g., litter, dead plants) via oxidative and fermentative processes. During degradation, sugars (e.g., glucose), alcohols (e.g., ethanol), and short-chain fatty acids (e.g., acetate) are formed, and can be used to fuel denitrification. Denitrification in natural peatland systems is often carbon-limited, as carbon stored in plants is often recalcitrant and thus not available for denitrifiers.

The residence time in the CW is another important factor in N removal, with longer residence times leading to better removal of N_{tot} and NH_4^+ (Fig. 6). This can also be seen as longer water flow routes, which have been found to positively correlate with N removal efficiency (Heikkinen et al. 2018). Sufficient residence time can also compensate for slower N removal rate, e.g., in this study clearly smaller k values but higher N removal efficiencies were observed for pond-type CWs. As NH_4^+ removal is typically an aerobic process (Vymazal, 2007) and continuous aeration is needed while wastewater is flowing through the CW, the open free water in pond-type CWs

likely allows for more efficient oxygen transportation from air to water. When 70% removal of $\text{NH}_4\text{-N}$ is the target, this will require a residence time of longer than 80 days in CWs located in cold-climate regions.

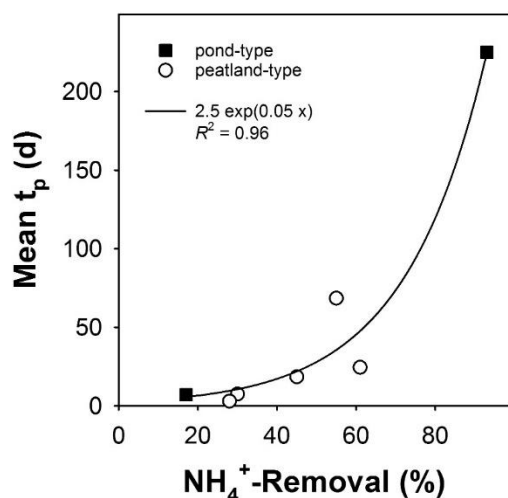


Fig. 6. Effect of mean potential residence time on ammonium (NH_4^+) removal in the nine constructed wetlands (CWs). For total nitrogen (N_{tot}) removal, a very similar pattern was observed (data not shown).

Conclusions

Nitrogen removal by pond-type and peatland-type CWs is strongly controlled by hydraulic load and, for more than 50% removal efficiency, the hydraulic load must be below 10 mm d^{-1} . Furthermore, $\geq 70\%$ N removal would require an N_{tot} load lower than $75 \text{ g m}^{-2} \text{ a}^{-1}$ and a residence time longer than 80 d in CWs under Nordic climate conditions. Correlation analysis revealed no clear, systematic relationship between temperature and N removal, although in some individual CWs high correlations were found between temperature and $\text{NO}_3^- + \text{NO}_2^- \text{-N}$, indicating lower denitrification rate at lower temperature. Moreover, high variation in reaction coefficient k was found for all N compounds, especially in peatland-type CWs. Year-round purification efficiency was achieved in both CW types, but $\text{NO}_3^- + \text{NO}_2^- \text{-N}$ removal by denitrification was low during winter. The quality of the water controlled wintertime performance of the CWs more than CW type. However, those CWs with the lowest hydraulic load (about 6 mm/d) achieved N removal rates of 29-72% in wintertime. An impact of point source N loading to recipient waters was highly visible in all cases and in some cases the N load increased by more than 300-fold

compared with the level before the point source. It is possible to decrease this load in a CW, provided that a specific N removal units is used before the CW, but more attention should be paid to N load and environmental permit limits on mine waters.

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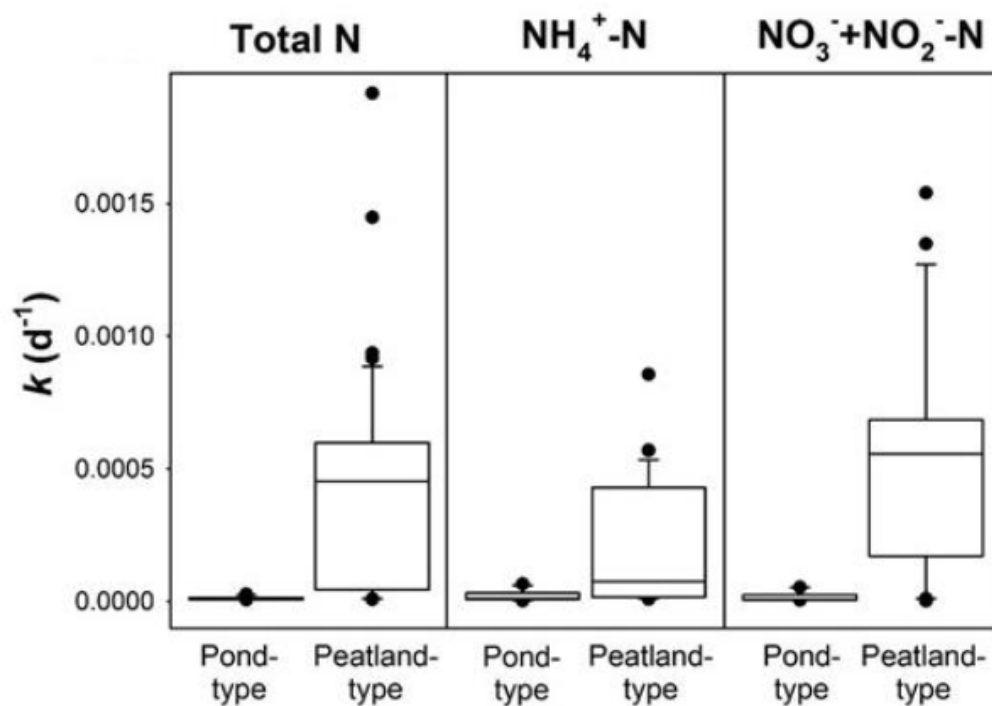
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Graphical abstract



Studied peat-based constructed wetlands were slightly more efficient in N removal than pond-type of constructed wetlands

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Highlights

- Impact of mine water on recipient water systems were investigated.
- Peat-based and pond-type constructed wetlands were found to decrease the N load to recipient waters but still clear impacts of point source on recipient water bodies were observed.
- The study is the first attempt to find designing parameters for nitrogen removal by constructed wetland under Nordic condition: The first-order nitrogen removal coefficient was determined for seven constructed wetlands.
- More than 50% removal efficiency was found to require a hydraulic load below 10 mm d⁻¹

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