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RESEARCH PAPER

Dynamics of dissolved nutrients among different macrophyte stands in a shallow lake

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Abstract Seasonally changing mechanisms affect the concentrations of dissolved inorganic nitrogen and soluble reactive phosphorus, which differ between the stands of different macrophyte life forms and open water in a eutrophic lake. Macrophytes that take nutrients up for their growth also shelter sediments from resuspension that brings nutrients back to the water and affect denitrification, which removes nitrogen from the water ecosystem. In this study the changes in nutrient concentrations were observed during the open-water period from April to November, and also denitrification rates were measured at different phases of the open-water season. The study was conducted at a shallow eutrophic lake where the effect of macrophytes on water quality is remarkable. The concentration changes of different nitrogen forms during the summer were very similar at the open-water and floating-leaved macrophyte (*Nuphar lutea* L.) stations. Nitrate was depleted faster among the submerged macrophytes (*Myriophyllum verticillatum* L.) than among floating-leaved plants or in open water. The decrease in the concentration of nitrate was so significant during the summer that it also affected the total nitrogen concentration in the water. Denitrification was highest in sediments among floating-leaved macrophytes (average 4.3 mg N m^{-2} d^{-1}) and lowest in sediments of submerged plants (average 1.5 mg N m^{-2} d^{-1}). Denitrification among submerged macrophytes was limited by low nitrate availability.

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Introduction

Nutrient dynamics in the vegetated littoral zone of lakes are complex because of the high variety of mechanisms by which, for example, macrophytes affect nutrient cycling. Macrophytes take nutrients up for their growth and release nutrients into their environment especially during decay (Granéli and Solander 1988; Lee and McNaughton 2004; Longhi et al. 2008). Macrophytes also affect resuspension, a process where sediment and nutrients are transported back to the water column because of physical (e.g., waves and currents) or biological (bioturbation) activity. Macrophyte beds attenuate wave action and increase the wind velocity needed for resuspension to occur (Madsen et al. 2001), thereby reducing the rate of sediment resuspension. Resuspension is often the most important transport mechanism of phosphorus (P) in shallow areas, and a decrease in resuspension also reflects on P concentrations (James et al. 2004; Gerhardt et al. 2010; Niemistö et al. 2011; Lawson et al. 2012). Also nitrogen (N) may be resuspended with particulate organic material or as dissolved compounds in the sediment porewater. The release of N from the sediment may be substantial and be responsible for the majority of the N requirement of phytoplankton (Cowan et al. 1996). Macrophytes may also promote aerobic P release as they increase water pH through intensive photosynthesis (Solim and Wanganeo 2009). Additionally, macrophytes transport oxygen (O_2) into the sediment and thus affect the redox state (Wigand et al. 1997). The O_2 dynamics are important to the P cycle, as internal P loading is often coupled with the

chemistry of iron (Fe) and O_2 conditions in the sediment (Christophoridis and Fytianos 2006).

The availability of O_2 is also important for the microbially mediated N cycle. Macrophytic O_2 transport enhances oxic nitrification and thereby also denitrification (Risgaard-Petersen and Jensen 1997), a natural N removal process, in which NO_x^-–N (combined nitrite–N and nitrate–N) is reduced to N_2 under anaerobic conditions. However, macrophytes also use ammonium–N (NH_4^+–N) and NO_x^-–N in their growth, thereby competing with nitrifying and denitrifying microbes for nutrients. On the other hand, macrophytes provide organic carbon for heterotrophic denitrifying bacteria and may thereby enhance denitrification (Karjalainen et al. 2001; Forshay and Dodson 2011).

A study by Nurminen and Horppila (2009) in shallow Lake Kirkkojärvi showed that different macrophyte life forms lowered the concentrations of total N (TN) and total P (TP) in the water by different mechanisms. Stands of floating-leaved *Nuphar lutea* (L.) Sibth. & Sm. had a reducing effect on P resuspension but no significant effect on N resuspension. The effect on P resuspension was due to strong root uptake by *Nuphar lutea,* reducing the P content of the sediment. Submerged plants reduced both N and P resuspension, but rather than lowering the sediment nutrient content, they diminished the overall sediment resuspension rate. The present study aims to clarify the availability of dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus (SRP) among the stands of different macrophyte life forms. The objective of the study was to focus especially on DIN and find out how fast and how large the variation in its concentration is during the growing season. Also the microbial N-cycling process denitrification was measured among different macrophytes in open water. The concentration of DIN and rate of denitrification were hypothesized to be smallest among the submerged macrophytes because of strong competition among primary producers and microbes.

Methods

The study site

Lake Kirkkojärvi (1.6 km^2, mean depth of 1.1 m, maximum depth of 3.5 m) (Fig. 1) is the most eutrophic basin of Lake Hiidenvesi in southwestern Finland (60°24′N, 24°16′E), having a summertime average TP concentration of 90 $\mu g\ l^{-1}$ and TN concentration of 1,250 $\mu g\ l^{-1}$ (Horppila 2005). The study was conducted during the 2010 open-water season at three different stations: among submerged (SUB) and floating-leaved (FLOAT) macrophytes and in the open water (OPEN) (Fig. 1). The area of each station was 20 × 20 m, each area including 3–6 sampling

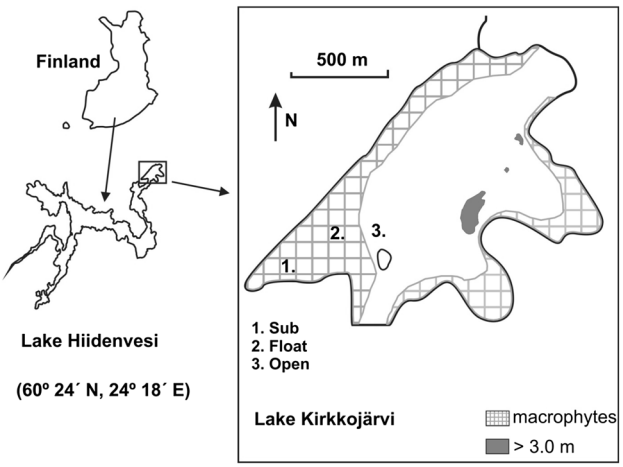

Fig. 1 Location of the study stations. The patterned area shows the maximum area covered by all macrophyte life forms together in late summer

points depending on the measured parameter. The vegetation at the SUB station was dominated by *Myriophyllum verticillatum* L. and the vegetation at the FLOAT station by *Nuphar lutea*. The stations were chosen to represent locations inhabited solely by submerged or floating-leaved plants. The water depths at the SUB, FLOAT and OPEN stations were 0.7, 1.2 and 1.7 m, respectively.

Macrophyte stands

Sampling on macrophytes was planned according to earlier studies on the seasonal development of macrophyte stands in Kirkkojärvi (Horppila and Nurminen 2001, 2003, 2005). The development of macrophyte stands was monitored from April to November 2010 with a 2–4 weeks sampling interval by measuring the percentage volume infested (PVI) by *Myriophyllum verticillatum* and *Nuphar lutea* in an area of 1 m^2 (6 randomly located replicates per station). The PVI percentage was calculated as plant coverage × plant height/water depth (Schriver et al. 1995).

Water column sampling

Water pH, temperature, turbidity and concentration of O_2 were measured at 2-week intervals (6 replicate measurement points at each station) in the water column using a YSI 6600V2 sonde (YSI Inc., Yellow Springs, OH, USA). Water samples (3 replicate samples from each station) were collected with a Limnos tube sampler (volume 2.8 l; Limnos, Ltd., Turku, Finland) with a 2-week sampling interval from the middle of the water column on each sampling date. The samples taken for dissolved nutrient concentrations (NO_x^-–N, NH_4^+–N and SRP) were immediately filtered in the field using polyethersulfone

membrane syringe filters (pore size 0.2 µm; VWR International). The concentrations of NO_x^-–N, NH_4^+–N and SRP were measured according to the methods of Grasshoff et al. (1983), Solorzano (1969) and Murphy and Riley (1962), respectively. The concentrations of TN and TP were measured using the method of Koroleff (1979). All nutrient concentrations were analyzed with a Lachat autoanalyzer (QuickChem Series 8000; Lachat Instruments (Hach Co.), Loveland, CO, USA). The concentration of chlorophyll *a* was analyzed spectrophotometrically after filtration on GF/C filters (nominal pore size 1.2 µm; Whatman) and extraction with ethanol (Finnish Standards Association 1993).

Sediment sampling

Denitrification rate in the sediment at the study stations was measured during four different phases of the open-water season 2010. The first measurements were taken in April just after the ice thawed, the second in June when the macrophyte beds had developed, the third in August at the peak of the growing season, and the last in November just before the lake froze over. Denitrification rates were measured using the isotope-pairing technique (IPT) (Nielsen 1992). Sediment samples were collected using an HTH corer (Renberg and Hansson 2008). The sediment was subsampled into smaller plastic cores (height 20 cm, Ø 2.5 cm), with about half of the core being filled with intact sediment and half with overlying water. The intact subsamples were closed with plastic caps and immediately incubated in the dark, at in situ temperature. At the beginning of the incubation $K^{15}NO_3$ (99 % ^{15}N, Cambridge Isotope Laboratories, Andover, MA, USA) was added to the samples to reach final concentrations of 600, 1,200 and 1,800 µg $^{15}NO_3^-$–N l^{-1} ($n = 2$ per concentration). During incubation the water on top of the sediment was gently stirred with small magnetic bars in the caps. The incubation was terminated after 4 h by carefully mixing the sediment with overlying water using a glass rod. The sediment was allowed to settle, and subsamples of 12 ml of water were transferred into gas-tight glass vials (Exetainers, Labco, Ltd., High Wycombe, Buckinghamshire, UK) containing 500 µl of 100 % (w/v) $ZnCl_2$ to terminate microbial activity. The isotopic composition of N_2 was analyzed by the National Environmental Research Institute in Silkeborg, Denmark, by using a Roboprep-G-Plus with Tracermass (Europa Scientific Ltd., Crewe, Cheshire, UK). The denitrification rate was calculated as the mean production of N_2 of the subsamples.

The organic content of the surface sediment (1 cm) was determined as the loss on ignition (LOI) by combustion for 2 h at 550 °C ($n = 3$ per site). The penetration of O_2 into the sediment was measured both during the peak of the growing season in August and at the end of the growing season in November from the intact sediment subsamples ($n = 3$ per site) using a Unisense Picoammeter PA2000 and a Unisense OX100 microelectrode (vertical resolution 200 µm; Unisense A/S, Aarhus, Denmark).

Statistical analyses

The between-station differences in water temperature, O_2, chlorophyll *a* and nutrient concentrations, sediment LOI, penetration of O_2 and denitrification rate in the sediment were statistically tested using analysis of variances for repeated measurements (ANOVAR, SAS 9.3 Statistical Software). The data sets were log-transformed before analysis to improve normality; LOI data were arcsin $\sqrt{x}$ transformed. Paired comparisons were performed using Bonferroni *t* tests. The results of the nutrient analyses were also sliced according to the sampling date.

Results

Macrophyte stands, background water quality parameters

In the beginning of June the PVI of submerged macrophytes was 1 %, while the PVI of floating-leaved macrophytes was 2 %. Floating-leaved macrophytes reached their highest PVI (43 %) in late July, while the highest PVI of submerged species (75 %) was observed in late August (Table 1).

The concentration of chlorophyll *a* was higher at the SUB station than at the other stations ($p < 0.01$). The concentration varied between 5 and 38 µg l^{-1} at the OPEN and 6–24 µg l^{-1} at the FLOAT station, and the difference was not statistically significant between FLOAT and OPEN (Fig. 2). At the SUB station, during the first 2 months the concentration was higher (30–65 µg L^{-1}) than at the other stations, but in June and August the concentration at the SUB station was lowest among the stations. From early September on, concentrations were again highest at the SUB station (Fig. 2).

Water pH was lowest (6.3–7.3) at the SUB station and varied between 6.8 and 8.5 at the FLOAT and OPEN stations (Table 2). Temperature was significantly lower at the SUB station than at the other two stations, and the FLOAT station showed the highest values ($p < 0.01$). Temperature differences between the stations were, however, on average less than 1 °C. The highest values were measured in July when the water temperature was 25 °C at the OPEN and FLOAT stations, and 23 °C at the SUB station (Table 2). The O_2 concentration in the water was constantly and significantly ($p < 0.01$) lower at the SUB station

Table 1 PVI of macrophytes at the different study stations during the study period

Station	28 April	18 May	31 May	14 June	29 June	12 July	26 July	9 August	23 August	7 September	28 September	8 November
SUB												
PVI (%)	0	nd	1 ± 1	23 ± 18	23 ± 21	nd	nd	38 ± 17	75 ± 15	48 ± 19	nd	nd
FLOAT												
PVI (%)	0	nd	2 ± 3	20 ± 12	20 ± 10	nd	43 ± 19	nd	43 ± 313	38 ± 19	nd	nd
OPEN												
PVI (%)	0	0	0	0	0	0	0	0	0	0	0	0

Each value is an average of six replicate measurements (±95 % confidence limits, nd = no data)

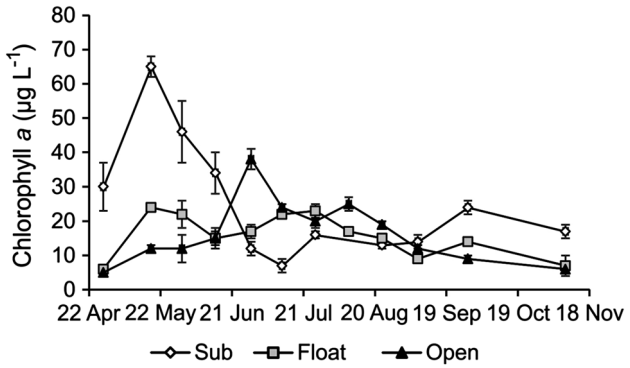

Fig. 2 Concentration of chlorophyll *a* at different study stations during April–November 2010 (±95 % confidence limits)

(0.6–8.1 mg l^{-1}) than at the other two stations (5.6–11.2 mg l^{-1}) (Table 2). The lowest O_2 concentrations at the SUB station were recorded during highest temperatures in July–August.

Nutrient concentrations in the water

In April–May, the concentration of NO_x^-–N was >600 µg l^{-1} at the FLOAT and OPEN stations (Fig. 3). In June, the concentration decreased steeply. At the SUB station, the concentration was significantly lower ($p < 0.01$) than at the other two stations and dropped from 360 µg l^{-1} in April to 100 µg l^{-1} in May. In July–August, NO_x^-–N was depleted (<2 µg l^{-1}) at all stations, and no statistically significant differences in NO_x^-–N concentrations were observed (Fig. 3, $p = 1.00$). In the autumn, the NO_x^-–N concentration was significantly lower ($p < 0.01$) at the SUB station (<100 µg l^{-1}) than at the other two stations (>600 µg l^{-1}).

The concentration of NH_4^+–N fluctuated between 30 and 150 µg l^{-1}, and the between-station differences were smaller than in NO_x^-–N. In May–June, the concentration of NH_4^+–N was significantly lower at the SUB station (20–30 µg l^{-1}) than at the other two stations (40–90 µg l^{-1}) (Fig. 3, $p < 0.01$), but in August the SUB station showed significantly higher ($p < 0.01$) concentrations of NH_4^+–N than the other stations. Between September–November, the NH_4^+–N concentration increased steeply at all stations, and no statistically significant differences between the stations were observed ($p = 0.681$).

The concentration of TN increased during the study period at all the stations, and except for July 12, the concentrations differed significantly between the stations (Fig. 3, $p < 0.01$). In April–June, the concentration was lowest at the SUB station, whereas in July–August the SUB station showed the highest values (Fig. 3).

SRP concentrations followed similar patterns at the OPEN and FLOAT stations, varying mostly between 10 and 23 µg l^{-1} and being highest in late July (Fig. 4). With few exceptions, the SRP concentration was lower at the SUB station than at the other stations, and it varied between 5 and 14 µg l^{-1} (Fig. 4, $p < 0.01$). In contrast, the average concentration of TP was highest at the SUB station, with an average of 95 µg l^{-1} (Fig. 4, $p < 0.01$). At the FLOAT and OPEN stations, the average concentration of TP was 73 µg l^{-1} (Fig. 4).

Denitrification, penetration of O_2 in sediment and LOI of surface sediment

Throughout the study, the rate of denitrification was significantly ($p < 0.01$) lower at the SUB station (average 1.48 mg N m^{-2} d^{-1}) than at the other stations (averages 4.29 and 4.19 mg N m^{-2} d^{-1}) (Table 3). No significant difference between FLOAT and OPEN stations was observed in the average denitrification rate ($p > 0.05$). The highest denitrification rate was recorded in the OPEN station in June (11.44 mg N m^{-2} d^{-1}), while at other sampling times, the FLOAT station showed the highest denitrification rates (Table 3). The penetration of O_2 in the sediment increased significantly ($p < 0.01$) from the SUB station to the FLOAT station and from the FLOAT station to the OPEN station. At all stations, the O_2 penetration depth increased from August to November (Table 3). The LOI of the surface sediment differed among the three stations statistically significantly throughout the study

Table 2 Water temperature, pH and O_2 at the different study stations

	Station	Temperature (°C)	pH	O_2 (mg l^{-1})	O_2 (%)
28 April	SUB	8.4 ± 0.2	6.5 ± 0.1	7.5 ± 0.3	64 ± 3
	FLOAT	8.0 ± 0.0	6.8 ± 0.0	9.9 ± 0.4	83 ± 3
	OPEN	7.4 ± 0.1	6.9 ± 0.2	10.3 ± 1.2	85 ± 9
18 May	SUB	19.6 ± 0.0	6.6 ± 0.0	4.0 ± 0.1	44 ± 1
	FLOAT	18.2 ± 0.0	7.1 ± 0.0	8.7 ± 0.0	92 ± 0
	OPEN	17.6 ± 0.0	7.1 ± 0.0	8.3 ± 0.0	87 ± 0
14 June	SUB	14.9 ± 0.0	6.7 ± 0.0	5.0 ± 0.2	49 ± 2
	FLOAT	15.4 ± 0.0	7.2 ± 0.0	7.9 ± 0.2	79 ± 2
	OPEN	15.4 ± 0.1	7.2 ± 0.0	7.6 ± 0.1	76 ± 1
12 July	SUB	23.0 ± 0.1	6.3 ± 0.0	0.6 ± 0.1	7 ± 1
	FLOAT	25.0 ± 0.1	7.2 ± 0.0	6.8 ± 0.1	83 ± 1
	OPEN	25.0 ± 0.1	7.2 ± 0.0	5.6 ± 0.2	68 ± 2
9 August	SUB	23.3 ± 0.2	6.7 ± 0.2	4.4 ± 1.0	51 ± 12
	FLOAT	24.5 ± 0.0	7.2 ± 0.0	6.3 ± 0.2	76 ± 2
	OPEN	23.9 ± 0.0	7.3 ± 0.0	7.5 ± 0.1	89 ± 1
7 September	SUB	12.3 ± 0.0	7.2 ± 0.1	6.2 ± 0.0	58 ± 0
	FLOAT	12.9 ± 0.1	7.5 ± 0.0	9.3 ± 0.2	88 ± 2
	OPEN	13.0 ± 0.0	8.1 ± 0.0	10.7 ± 0.0	101 ± 0
28 September	SUB	6.8 ± 0.1	7.3 ± 0.3	8.1 ± 0.1	66 ± 1
	FLOAT	9.1 ± 0.1	7.3 ± 0.0	9.7 ± 0.0	84 ± 0
	OPEN	9.3 ± 0.1	7.6 ± 0.0	9.5 ± 0.0	83 ± 0
8 November	SUB	nd	nd	nd	nd
	FLOAT	nd	nd	nd	nd
	OPEN	2.6 ± 0.1	8.5 ± 0.2	11.2 ± 0.0	82 ± 0

Each value is an average of six replicate measurements (±95 % confidence limits, nd = no data)

($p < 0.001$). The LOI was highest at the SUB station (26–31 %) and lowest at OPEN (9–12 %). LOI at the FLOAT was 13–15 % (Table 3).

Discussion

The concentrations of nutrients in the water

The concentrations of dissolved nutrients were generally similar at the OPEN and FLOAT stations, but lower at the SUB station. This can be explained by the different nutrient uptake mechanisms of the plants; *Nuphar* stands take nutrients from the sediment with their roots with less effect on water column concentrations, whereas *Myriophyllum* can also take nutrients up directly from the water (Best and Mantai 1978; Ciurli et al. 2009). The PVI of macrophytes was on the same level at both stations, but due to the life form differences, biomass in the water column was lower at the FLOAT station. If *Nuphar*- and *Myriophyllum*-type submerged plants have similar PVIs, then the biomass density of *Nuphar* is only one-third (Van Onsem et al. 2010). However, while *Myriophyllum* has <25 % of the summertime biomass in the roots, in *Nuphar* stands roots constitute to 50–80 % of the biomass (Smith and Adams 1986; Brock et al. 1987; Wetzel 2001). In June, when NO_x^-–N was depleted, with 25 % root biomass proportion for *Myriophyllum* and 75 % for *Nuphar*, the biomass difference between the two species was <10 %. Thus, differences in their effects on nutrient dynamics were attributed to the life form rather than differences in biomass. It must also be considered that vertical variations in physicochemical parameters can occur beneath submerged macrophytes (Herb and Stefan 2004; Obrador and Pretus 2013), while the samples were taken from the middle of the water column. However, the effect of such gradients on the results was probably small, because at the SUB station only a 10-cm water layer was left below and above the tube sampler. At the FLOAT station, steep vertical gradients were not likely to occur because of the simple underwater structures of the plants and consequent mixing of the water (Nurminen and Horppila 2009).

Submerged macrophytes effectively inhibit resuspension and also thereby affect the nutrient dynamics (James et al. 2004; Lawson et al. 2012). This has also been shown in Kirkkojärvi. Horppila and Nurminen (2003) showed that in early June the difference in resuspension

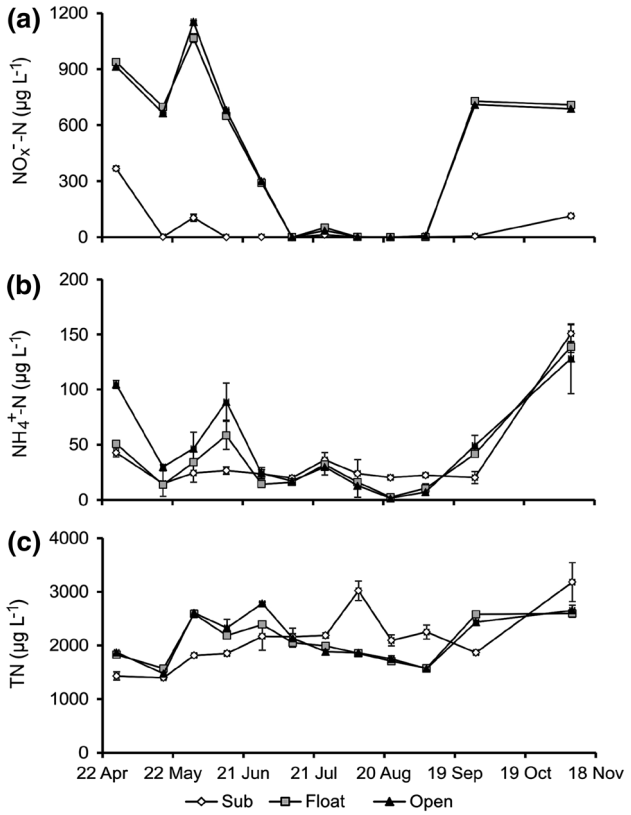

Fig. 3 Concentration of NO_x^-–N (**a**), NH_4^+–N (**b**) and TN (**c**) at different study stations during April–November 2010 (±95 % confidence limits)

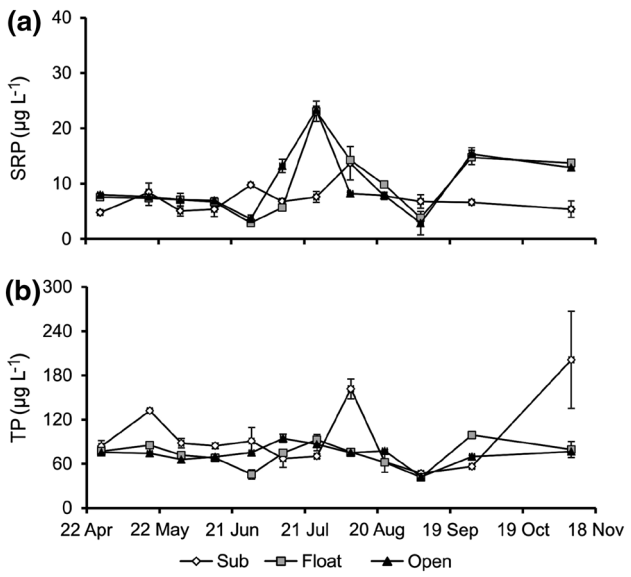

Fig. 4 Concentration of SRP (**a**) and TP (**b**) at different study stations during April–November 2010 (±95 % confidence limits)

rate between the open water and the sparse stand of submerged plants was <2 g dw m^{-2} d^{-1}, while in August with dense submerged vegetation (PVI 30 %) the difference was >10 g dw m^{-2} d^{-1}. Additionally, the sediment resuspension rate usually increases with decreasing depth because of increasing impact of wave action on the sediment (Hilton et al. 1986; Evans 1994). The seasonal development of macrophyte stands followed earlier findings in Kirkkojärvi (Horppila and Nurminen 2003; 2005). Thus, in early summer, before the development of macrophyte stands, resuspension was stronger at the SUB station than at the other two stations because of the lower water depth at SUB. As long as the coverage of plants was low, also TP concentration was higher at the SUB station than at the other two stations. The difference was mainly due to resuspended particulate P, because at the time no large differences in SRP or TN concentrations were observed. When the coverage of submerged plants increased over the course of the summer, resuspension decreased at the SUB station, and the differences in TP concentrations between the stations diminished. In late summer, with few exceptions, the TP concentration at the SUB station was lower than in the OPEN station. Compared with open water, the effect of macrophyte stands on the average TP concentration is usually pronounced, but a significant correlation between macrophyte coverage and TP concentration is not often found, because macrophytes have multiple effects on P dynamics and the importance of each mechanism varies seasonally (Granéli and Solander 1988; Stephen et al. 1997; Horppila and Nurminen 2001, 2003). Compared with TP, the effect of resuspension was not as clear for TN concentrations because of the large spatial and temporal variation of NO_x^-–N concentration, which comprised a significant part of TN at FLOAT and OPEN.

Table 3 Denitrification rate, LOI and penetration of O_2 in surface sediments of the SUB, FLOAT and OPEN stations (±95 % confidence limits, with the exception of O_2 in November at SUB station)

	SUB	FLOAT	OPEN
Denitrification rate (mg N m^{-2} d^{-1})			
28 April	2.43 ± 0.31	2.52 ± 1.11	0.71 ± 0.58
29 June	1.20 ± 0.28	8.08 ± 0.88	11.44 ± 4.17
9 August	1.42 ± 0.31	3.29 ± 0.92	1.62 ± 0.54
8 November	0.88 ± 0.27	3.27 ± 1.48	2.99 ± 1.28
O_2 penetration (mm)			
9 August	1.2 ± 0.23	1.2 ± 0.46	2.3 ± 0.69
8 November	2.3	4.8 ± 0.85	6.3 ± 1.41
LOI (%)			
28 April	27 ± 1	13 ± 0	9 ± 0
29 June	26 ± 0	14 ± 1	11 ± 0
9 August	26 ± 1	14 ± 0	11 ± 0
8 November	31 ± 1	15 ± 0	12 ± 0

Competition for available nutrients

During July and August, all stations were depleted of NO_x^-–N. At the SUB station, the depletion was probably accelerated by the uptake of the growing *Myriophyllum* stands, which could also be seen in the lower SRP concentrations, compared to the other two stations. Nutrient uptake by phytoplankton naturally had a role in the dynamics of NO_x^-–N, but cannot explain the between-station differences. In spring, the chlorophyll *a* concentration was high at the SUB station, because abundant epiphytic algae on the developing submerged macrophytes were suspended in the water during sampling and were included in the water samples. The lower initial NO_x^-–N concentration at SUB may be explained by the uptake of these algae. In July–August, however, the NO_x^-–N concentration did not differ between the stations, although the chlorophyll *a* concentration was significantly lower at the SUB station than at the other stations. Additionally, assuming a 1 % proportion of chlorophyll *a* of phytoplankton biomass (Vörös and Padisák 1991; Desortová 2007) and a 7.4 biomass:PVI relationship of submerged macrophytes (van Onsem et al. 2010), it can be shown that in July–August the biomass of macrophytes at the SUB station was >10 times higher than the phytoplankton biomass. Thus, uptake by the *Myriophyllum* stand was a factor behind the low mid-summer NO_x^-–N concentration at the SUB station. A low phytoplankton biomass among dense submerged macrophyte beds is a common phenomenon and explained by factors such as high biomass of herbivorous zooplankton occupying the refuge provided by the plants, competition for nutrients and allelopathic effects of macrophytes (van Donk and van de Bund 2002; Muylaert et al. 2010).

In addition to macrophytes and phytoplankton, also denitrifying bacteria compete for NO_x^-–N. During 2 weeks in July, N removal via denitrification was 87 μg l^{-1} at the OPEN station and 88 μg l^{-1} at the FLOAT station, which corresponded to 29 and 30 % of the NO_x^-–N loss, respectively. At the SUB station, NO_x^-–N was depleted already in May, but during 3 weeks in April–May, when submerged macrophytes were developing, denitrification removed 69 μg l^{-1}, which corresponded to 18 % of the change in NO_x^-–N concentration.

Factors affecting denitrification

The rate of sedimentary denitrification was highest at the OPEN and FLOAT stations in late June. At that time NO_x^-–N was still available, and the temperature was high. At the SUB station, the denitrification rate was maximal already in April, although the temperature increased until August. Taking into account the strong correlation between the denitrification rate and the concentration of NO_x^-–N (Risgaard-Petersen and Ottosen 2000; McCrackin and Elser 2010), it was likely that the low availability of NO_x^-–N restricted denitrification later in the summer. In November NO_x^-–N was again available at all stations, but the low temperature slowed down the denitrification rate.

The sediment denitrification rate usually decreases with increasing depth, which is attributed to decreasing temperature and the organic content of sediment (Christensen and Sørensen 1986; Saunders and Kalff 2001). Saunders and Kalff (2001) showed that in littoral sediment the denitrification rate can be negatively related to depth even within a 2 m depth range. In the present study, with a maximum 1-m depth difference between the stations, temperature differences between the stations were small. The difference between the SUB and OPEN stations, for instance, was on average 0.7 °C and mostly attributed to the diurnal change of temperature during sampling.

On the other hand, the organic content of sediment showed a clear decreasing trend with increasing depth, surface sediment LOI at the SUB station being on average 2.5 times higher than at the OPEN station. Despite this, sediment denitrification at the SUB station remained lowest among the three stations. With high availability of organic substrate, it is the availability of NO_x^-–N rather than organic C that limits the rate of denitrification (Forshay and Dodson 2011). On the other hand, our data demonstrated that in spring when NO_x^-–N was available at all stations, the rate of denitrification was higher in the organic-rich sediments of macrophyte sites than at the OPEN station.

In addition to denitrification, N can also be lost from the aquatic ecosystem in an anaerobic ammonium oxidation (anammox) process, in which NO_2^-–N and NH_4^+–N are combined to form N_2. However, our previous measurements at Lake Kirkkojärvi have shown no signs of this process (Holmroos et al. 2012), and it is likely that the nitrate formed in nitrification is used by primary producers and denitrifying bacteria.

Source of NO_x^- for denitrification

In addition to the external NO_x^-–N load in the lake, NO_x^-–N used in denitrification is also produced in lake sediments by the nitrification process that oxidizes NH_4^+–N. In Lake Kirkkojärvi, in another shallow and macrophyte-free station, located 600 m away from the current study, 98 % of denitrification that occurred in August was coupled with nitrification in the sediment (Holmroos et al. 2012). In May and November, the percentages were 38 and 24 %, respectively. Similar seasonality was likely in the present study, because the nitrate concentrations fluctuated in a similar manner in 2010 as in that seasonal study in 2009 (Holmroos et al. 2012).

Nitrate shortage in late summer highlights the importance of concomitant nitrification in feeding the removal process. In the present study, the concentration of NH_4^+–N in water decreased during the summer at the FLOAT and OPEN stations, and this may also have limited nitrification. At the SUB station the NH_4^+–N concentration did not decrease during the summer. This indicates high levels of mineralization, which is also supported by the low concentration of O_2 at the SUB station during high temperatures. Mineralization was probably so intensive that the NH_4^+–N remained available in the water while nitrification was limited by the low O_2 availability.

O_2 availability and organic matter in the surface sediment

By increasing O_2 penetration to the sediment, rooted macrophytes can raise the sediment redox potential (Soana and Bartoli 2014). On the other hand, high densities of submerged macrophytes can suppress the positive effects on the redox potential by reducing water mixing (Boros et al. 2011). In our study, the O_2 penetration depth in the sediment was higher at the OPEN than at the vegetated stations. At the OPEN station the wind induced sediment resuspension is able to oxidize the surface sediment resulting to deeper O_2 penetration. Additionally, the higher organic content of the sediments at the macrophyte stations may have decreased O_2 penetration (Caffrey et al. 1993). In November, the O_2 penetration depth was twice as high at the FLOAT as at the SUB station. This result is in line with the surface sediment LOI, the percentage of which was highest at the SUB station. The low O_2 penetration also affected the denitrification rate by restricting the coupled nitrification.

Concluding remarks

The study demonstrated that the seasonal nutrient dynamics differ in the various littoral zones. The concentration of phosphorus differed between the stations because of the sheltering effect of submerged macrophytes against resuspension, and the concentration of SRP was affected by uptake of macrophyte stands. Submerged macrophytes also lowered the amount of NO_x^-–N, which was depleted faster among submerged plants than among floating-leaved macrophytes or above the bare sediment. As a consequence, the natural N removal via denitrification was slowest among submerged plants. Denitrification was limited by NO_x^-–N availability especially during the summer months when the effect of temperature and the organic matter content of sediment remained secondary. Nitrification was limited by NH_4 availability among floating-leaved plants and in the bare sediments, but not among submerged plants. Variations in the structure of macrophyte communities can thus have substantial effects on nutrient cycling of lake ecosystems.

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