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Modelling of seasonal variation in nitrogen retention and in-lake concentration: A four-year mass balance study in 16 shallow Danish lakes

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Abstract. The mass balance for total nitrogen (N) was studied over a four-year period in 16 shallow mainly eutrophic 1st order Danish lakes. Water was sampled in the main inlet of each lake 18–26 times annually, and from the outlets and the lake 19 times annually. Water was also sampled from minor inlets, although less frequently. N input and output were calculated using daily data on discharge (Q), the latter being obtained either from the Q/H relationship based on automatic recordings of water level (H) for the main in- and outlet, or by means of Q/Q relationships for the minor inlets. Annual mean N retention in the lakes ranged from 47 to 234 mg N m^{-2} d^{-1}, and was particularly high in lakes with high N loading. Annual percentage retention ($N_{ret-y\%}$) ranged from 11 to 72%. Non-linear regression analysis revealed that hydraulic retention time and mean depth accounted for 75% of the variation in annual mean $N_{ret-y\%}$ and, in combination with inlet N concentration, accounted for 84% of the variation in the in-lake N concentration. $N_{ret\%}$ varied according to season, being higher in the second and third quarter than in the first and fourth quarter (median 18–19%). A simple model was developed for predicting monthly nitrogen retention (N_{ret-m}) on the basis of external N loading, the lake water pool of nitrogen N_{pool}, hydraulic loading and lake water temperature. Calibration of only two parameters on data from the randomly selected 8 out of 16 lakes rendered the model capable of accurately simulating seasonal dynamics of the in-lake N concentration and N_{ret-m} in all 16 lakes. We conclude that with regard to shallow, eutrophic lakes with a relatively low hydraulic retention time, it is now possible to determine not only annual mean nitrogen retention, but also the seasonal variation in N_{ret-m}. Prediction of seasonal variation in N loading of downstream N-limited coastal areas is thereby rendered much more reliable.

Introduction

The important role of lakes as a sink in the transport of nitrogen (total nitrogen; N) from the land to the sea is well documented (Andersen 1974; Seitzinger 1988; Jensen et al. 1991) and empirical models have been developed for predicting annual mean N retention (N_{ret-y}) and in-lake N concentration (N_{lake}) (OECD 1982; Bachmann 1984; Lijklema et al. 1989; Jensen et al. 1991). The general approach taken by these models is identical, N_{lake} being related to simple parameters such as inlet N concentration, hydraulic retention time and mean depth.

The models are capable of relatively precisely predicting the annual mean N_{lake} and hence N_{ret-y} in lakes with different morphometry and different external hydraulic and N loading (N_{load}). However, in order to evaluate how lakes influence nitrogen loading and thus the environmental quality of downstream coastal areas in critical periods during which phytoplankton growth is high, it is essential to be able to predict not only the average annual N_{ret-y}, but also the seasonal variation in N_{ret}. This is made difficult by the fact that seasonal dynamics of N_{ret} differs considerably from lake to lake. For example, in an eight-year study of shallow Lake Søbygård, Jensen et al. (1992), found percentage of N_{ret} in relation to external quarterly load to be low during the first quarter of the year (23%), three times higher during the third quarter and intermediate during the second and fourth quarters. In terms of absolute retention a similar seasonal pattern has been reported for Tegeler See by Ripl & Feibicke (1992) and by Gibson et al. (1992). In shallow lake Dümmer, in contrast, Ripl & Feibicke (1992) found retention to be maximum in early spring and low during summer (during which time there was a concurrent distinct reduction in the N_{load}), while Andersen (1974) and Bengtsson (1978) found no clear seasonal pattern in N_{ret} . The factors determining the difference in lake dynamics thus require further elucidation.

This paper presents the results of a comprehensive four-year mass balance study of 16 shallow Danish lakes. The aim was to elucidate the seasonal dynamics of N_{ret} in lakes differing in hydraulic and N loading. In addition, besides shown annual models we present the first simple model capable of accurately predicting seasonal variation in N_{lake} and N_{ret}.

Materials and methods

Study area

The 16 lakes included in the present study were shallow and mainly nutrient-rich (Table 1 and 2). Annual mean total phosphorus ranged from 92–1,127 $\mu g\ P\ l^{-1}$, being higher than 200 $\mu g\ P\ l^{-1}$ in 9 lakes. Chlorophyll *a* (chl*a*) was consequently high, and transparency low. Annual mean chl*a* ranged from 33 to 276 $\mu g\ l^{-1}$ and Secchi depth from 0.55 to 2.1 m, chl*a* being higher than 50 $\mu g\ l^{-1}$ and Secchi depth lower than 1.0 m in 11 of the 16 lakes. Although considerable seasonal variation was observed in some of the lakes, the annual hydraulic retention time (tw_y) was generally short, ranging from 0.02 to 0.7 years and being less than 0.22 years in 12 of the lakes.

Table 1. Mean depth (z), total phosphorus (TP), chlorophyll *a* (chl*a*), Secchi depth, total nitrogen (TN) and (NO_2-NO_3-N) for the 16 lakes. Annual means (±S.E.) are shown. n = number of years included.

Lake	Z (m)	TP (μg P l^{-1})	Chl*a* (μg l^{-1})	Secchi depth (m)	TN (mg N l^{-1})	$NO_2 + NO_3$ (mg N l^{-1})	n
Vesterborg Sø	1.4	241 (27)	105 (12)	0.70 (0.04)	5.21 (0.45)	3.70 (0.55)	4
Søgård Sø	1.6	272 (34)	153 (18)	0.58 (0.05)	6.69 (0.61)	4.67 (0.79)	4
Lemvig Sø	2.0	239 (11)	45 (4)	0.74 (0.05)	4.30 (0.48)	3.10 (0.36)	4
Hejrede Sø	0.9	123 (6)	75 (10)	0.65 (0.05)	4.34 (0.29)	2.18 (0.36)	4
Fuglesø	2.0	256 (22)	75 (4)	1.12 (0.03)	4.18 (0.37)	2.39 (0.41)	3
Fårup Sø	5.6	92 (5)	37 (4)	1.77 (0.08)	1.51 (0.05)	0.79 (0.02)	4
Lange Sø	3.1	279 (30)	62 (8)	1.24 (0.04)	3.80 (0.15)	2.39 (0.13)	4
Kilen	2.9	187 (17)	103 (22)	0.68 (0.09)	2.17 (0.07)	0.76 (0.06)	4
Jels Oversø	1.2	273 (26)	100 (12)	0.85 (0.05)	6.90 (0.18)	5.34 (0.26)	3
Ørn Sø	4.0	108 (2)	36 (2)	1.57 (0.05)	1.43 (0.04)	0.55 (0.02)	4
Hinge Sø	1.2	122 (3)	90 (9)	0.68 (0.03)	4.44 (0.20)	2.95 (0.17)	4
Dons Nørresø	1.0	216 (29)	251 (18)	0.56 (0.04)	5.05 (0.08)	3.05 (0.11)	4
Borup Sø	0.9	150 (10)	78 (9)	0.92 (0.04)	4.93 (0.46)	2.97 (0.36)	4
Gundsømagle Sø	1.2	1127 (130)	276 (15)	0.55 (0.02)	5.92 (0.42)	2.85 (0.44)	4
Store Søgård Sø	2.7	465 (53)	41 (1)	0.79 (0.05)	6.27 (0.32)	3.33 (1.65)	3
Bryrup Langsø	4.6	107 (7)	33 (4)	2.10 (0.10)	4.15 (0.11)	3.10 (0.11)	4

Sampling, analyses and calculations

Water was sampled in inlets and outlets according to the standardized guidelines of the Danish Nationwide Monitoring Programme (Kristensen et al. 1990; Kronvang et al. 1993). Thus the main inlet of each lake was sampled 18–26 times annually, depending on seasonal variation in discharge, while the minor inlets were sampled less frequently, depending on their relative contribution to the total hydraulic and nutrient loading. Epilimnetic water temperature was recorded and outlet samples and pooled epilimnetic lake water samples were collected fortnightly during summer and monthly during winter, i.e. 19 times annually. Total N was measured on unfiltered water as nitrite+nitrate after potassium persulphate digestion according to the method of Sol6rzano & Sharp (1980) and nitrite+nitrate after cadmium reduction.

Total discharge in the main inlets and most outlets (Q_m) was measured monthly with an OTT-propeller. The water level (H) was automatically and continuously recorded during the entire study period. Daily discharge (Q_d) was calculated by use of the relationship obtained for H and Q_m. In minor inlets and a few outlets discharge (q) was measured with an OTT-propeller and daily discharge values calculated from q/Q_d relationships.

Table 2. Annual hydraulic retention time (tw_y), inlet nitrogen concentration (N_{in}), external loading (N_{load}), nitrogen retention (N_{ret-y}) and percentage nitrogen retention ($N_{ret-y\%}$) for the 16 lakes included in the analysis. N_{in} is discharge weighted and $N_{ret-y\%}$ is calculated as the annual N_{ret-y} expressed as a percentage of annual N_{load}. Mean (±SE) for the 3–4 years (n) is shown. CV-N_{ret} and CV-N_{lake} are the coefficient of variation obtained when applying model 2 (Table 5) to the 36–48 monthly values (n_m) included in the analysis.

	tw_y (year)	N_{in} (mg N l^{-1})	N_{load} (mg N m^{-2} d^{-1})	N_{ret-y} (mg N m^{-2} d^{-1})	N_{ret-y} (%)	n	CV N_{ret-m}	CV N_{lake}	n_m
Vesterborg Sø	0.05 (0.01)	11.2 (1.0)	769 (125)	162 (40)	22 (5)	4	1.03	0.41	48
Søgård Sø	0.07 (0.01)	12.1 (0.9)	825 (155)	142 (26)	18 (2)	4	1.19	0.19	48
Lemvig Sø	0.08 (0.01)	8.7 (0.8)	671 (147)	179 (43)	26 (2)	4	0.73	0.18	48
Hejrede Sø	0.10 (0.03)	9.7 (0.8)	241 (43)	57 (5)	26 (5)	4	1.35	0.37	48
Fuglesø	0.14 (0.01)	11.1 (0.4)	435 (61)	234 (12)	56 (8)	3	0.48	0.40	36
Fårup Sø	0.49 (0.01)	3.8 (0.1)	120 (6)	68 (5)	57 (5)	4	0.72	0.21	48
Lange Sø	0.55 (0.04)	10.3 (1.0)	208 (32)	93 (12)	47 (6)	4	1.23	0.29	48
Kilen	0.69 (0.02)	7.8 (0.4)	92 (2)	67 (3)	72 (2)	4	0.62	0.11	48
Jels Oversø	0.02 (0.001)	11.0 (0.8)	1940 (180)	211 (25)	11 (2)	3	2.11	0.19	36
Ørn Sø	0.04 (0.001)	1.6 (0.1)	378 (19)	47 (10)	12 (2)	4	1.84	0.27	48
Hinge Sø	0.04 (0.002)	6.2 (0.5)	415 (45)	76 (3)	19 (3)	4	1.51	0.37	48
Dons Nørresø	0.05 (0.004)	7.8 (0.3)	406 (38)	100 (17)	24 (2)	4	0.73	0.18	48
Borup Sø	0.05 (0.01)	8.4 (0.6)	403 (46)	75 (20)	21 (8)	4	1.61	0.35	48
Gundsømagle Sø	0.08 (0.01)	12.8 (0.2)	468 (61)	173 (23)	38 (4)	4	0.75	0.32	48
St. Søgård Sø	0.17 (0.01)	12.0 (0.5)	513 (43)	147 (15)	29 (2)	3	1.05	0.22	36
Bryrup Langsø	0.25 (0.01)	8.9 (0.5)	445 (36)	217 (12)	49 (3)	4	0.45	0.16	48

Monthly water balances were calculated for each lake using the following equation:

$$Q_{in_m} + Q_{in_u} + \text{Prec} = \text{Vol}_{dif} + Q_{out_m} + Q_{out_u} + Evap \tag{1}$$

where Q_{in_m} and Q_{out_m} are the total discharge measured in inlets and outlets, respectively. Evap and Prec are mean monthly evaporation and precipitation obtained from meteorological stations situated in the vicinity of the lakes and Vol_{dif} is the monthly change in lake volume. Q_{in_u} and Q_{out_u} are the unmeasured input from the unmeasured catchment and output (seepage) from the lake, respectively. Q_{in_u} and Q_{out_u} was determined on a monthly basis by adjusting the mass balance, if vol_{dif} + Q_{out_m} + Evap > Q_{in_m} + Prec, then Q_{in_u} is equal to the difference; if the opposite is true Q_{out_u} is equal to the difference. Such an adjustment has not been made, however, if the water budget could be balanced by increasing or decreasing the water volume of the lake by up to 10%. In this case the water balance has been adjusted by changing Vol_{dif}. If above 10% Vol_{dif} was adjusted by the 10% and the budget thereafter balanced by increasing Q_{in_u}, if the left side of the equation (1) was lower than the right side, or else by adjusting Q_{in_out}. We have chosen to accept changes in Vol_{dif} of up to the 10% to take into account the uncertainty of the water balance and the fact that seasonal changes in the lake water volume often occur. The measured inlet, Q_{in_m}, accounted for more than 81% of the total input in 9 of the 16 lakes (max. 93%), and for more than 75% in an additional 3 lakes. In one lake Q_{in_m} accounted for only 22% of the input, groundwater input accounting for most of the remainder; however, data on the groundwater N concentration was available from springs in the catchment area of this lake making the mass balance of this lake more accurate than the 22% measured input may indicate.

Daily values for the various N concentrations were calculated by linear interpolation of observed values. N transport was then estimated as the product of daily water discharge and N concentrations.

The input and output of total N were determined using the monthly water balances, the assumption being made that the N concentration of the unmeasured discharges to and from the lake equalled the Q-weighted concentrations in the measured inlets and outlets. In cases where the input of ground water was considerable information on ground water N concentrations was applied. Atmospheric deposition was added using an average rate for Denmark of 15 kg N ha^{-1} $year^{-1}$ (Hovmand et al., 1993). For two of the lakes no outlet data were available and inlet Q and N_{lake} were therefore used instead. No information on nitrogen fixation was available.

Monthly nitrogen retention (N_{ret-m}) values were then calculated using the mass balance model of Messer and Brezonik (1978):

$$\begin{aligned}\text{Retention} = &\ \text{Total input (apart from N fixation)}\\ &+ \text{Storage} - \text{Total output} \qquad (2)\end{aligned}$$

Whether a 10% variation in Vol_{dif} was accepted or not did not result in a significant difference in lake retention (N_{ret-m} (10% Vol_{dif}) = 3.80($\pm$2.61) + 0.96($\pm$0.01) * N_{ret-m}(0%Vol_{dif}). Likewise the quarterly and annual nitrogen retention (N_{ret-qu} and N_{ret-y}, respectively) were calculated from formula (2) based on quarterly and annual data instead of monthly data on input, storage and output.

For estimating the parameters in the models developed the SAS GLM-package was used (SAS 1989) on log-transformed data, when not otherwise stated.

Results

The annual mass balances revealed major inter-lake variability (Table 2): the annual mean Q-weighted inlet concentration, N_{in} ranged from 1.6 to 12.8 mg N l^{-1}, while N_{ret-y} ranged from 47 to 234 mg N m^{-2} d^{-1}, and $N_{ret-y\%}$ from 11 to 72%. Annual mean $N_{ret-y\%}$ (Table 3) was highly related to tw_y, as was inter-annual variation in $N_{ret-y\%}$ (Fig. 1). In a simple non-linear model tw_y accounted for 74% of the variation in $N_{ret-y\%}$ (Table 3), a figure which could be significantly improved by also including mean depth (data not shown). An equally good relationship was obtained when using area-specific hydraulic loading (Q_s) together with mean depth (r^2 = 0.75). In contrast, with Q_s alone the relationship was comparatively weak (r^2 = 0.56). Annual mean N_{lake}could be related to tw and N_{in}, with the model accounting for 83% of the variation in N_{lake} (Table 3).

Marked seasonal variation in N_{load} was observed in all 16 lakes (Fig. 2). During the four-year period median N_{load} was high during the 1st quarter (418–920 mg N m^{-2} d^{-1}) coinciding with generally high N_{in} and Q_{in} (Q_{in-m} + Q_{in-u}). Following a decrease in N_{in} the median N_{load} declined markedly in the 2nd quarter to 115–322 mg N m^{-2} d^{-1} and to 72-137 mg N m^{-2} d^{-1} in the 3rd quarter. Thereafter N_{load} increased again to 383–734 mg N m^{-2} d^{-1} in the 4th quarter conçomitantly with increases in Q_s and N_{in}. The same seasonal pattern although somewhat attenuated was seen with the quarterly nitrogen retention(N_{ret-qu}), median values during the four years ranging from 100–180 mg N m^{-2} d^{-1} in the 1st quarter to 46–66 mg N m^{-2} d^{-1} in the 3rd quarter. $N_{ret-qu\%}$ was relatively low in the 1st quarter (11–21%)

Table 3. Non-linear models (annual values) relating in-lake total-N concentration (N_{lake}; mg N l^{-1}) to the inlet concentration (N_{in}; mg N l^{-1}), hydraulic retention time (tw_y; y) and mean depth (Z; m) and relating percentage N retention ($N_{ret-y\%}$) to tw, Z and area specific hydraulic loading (Q_s; m^3 m^{-2} y^{-1}). All variables are annual means.

Model	n	Parameter-estimates ± 95% C.L. a	b	c	r^2	p
1 $N_{lake} = a * N_{in} * tw_y^b$	61	0.32±0.04	−0.18±0.05		0.81	<0.0001
2 $N_{lake} = a * N_{in} * tw_y^b * Z^c$	61	0.27±0.06	−0.22±0.06	0.12±0.11	0.82	<0.0001
3 $^*N_{ret-y\%} = a * tw_y^b$	61	78±9	0.42±0.07		0.74	<0.0001
4 $N_{ret-y\%} = a * Q_s^b$	61	152±47	−0.56±0.13		0.58	<0.0001
5 $^*N_{ret-y\%} = a * Q_s^b * Z^c$	61	96±26	−0.48±0.10	0.34±0.11	0.75	<0.0001

* % of annual input

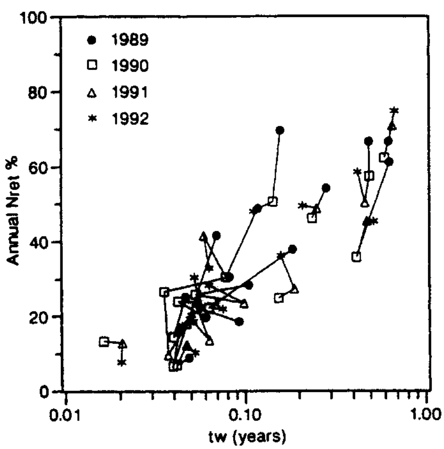

Figure 1. Annual mean percentage retention of nitrogen ($N_{ret-y\%}$) vs. hydraulic retention time (tw) for each of the 16 lakes for each of the four study years.

but increased significantly in the 2nd quarter (36–54%) (pairwise t-test, all data, $p<0.001$), thereafter to gradually decline to 17–24% in the 4th quarter. This was also confirmed by a pairwise t-test (2nd versus 3rd $p<0.007$ and 3rd versus 4th $p<0.0004$ respectively). There was no significant difference between $N_{ret-qu\%}$ in the 1st quarter and that in the 4th quarter ($p>0.46$).

A large inter-lake variation in seasonal dynamics was found as illustrated by the monthly mean values from the mass balances of three of the lakes studied (Fig. 3). In Lake Ørn the monthly values of Q_s and N_{in}, and hence of N_{load}, were relatively constant, Q_s being high (6.5–8.5 m $month^{-1}$) and N_{in} low (1.4–1.8 mg N l^{-1}). Nevertheless, there was marked seasonal variation in N_{ret}, from approx. 25 mg N m^{-2} d^{-1} in winter to 45–95 mg N m^{-2} d^{-1} in summer. $N_{ret-y\%}$ was low (6–13%). The constant input and the low $N_{ret-m\%}$

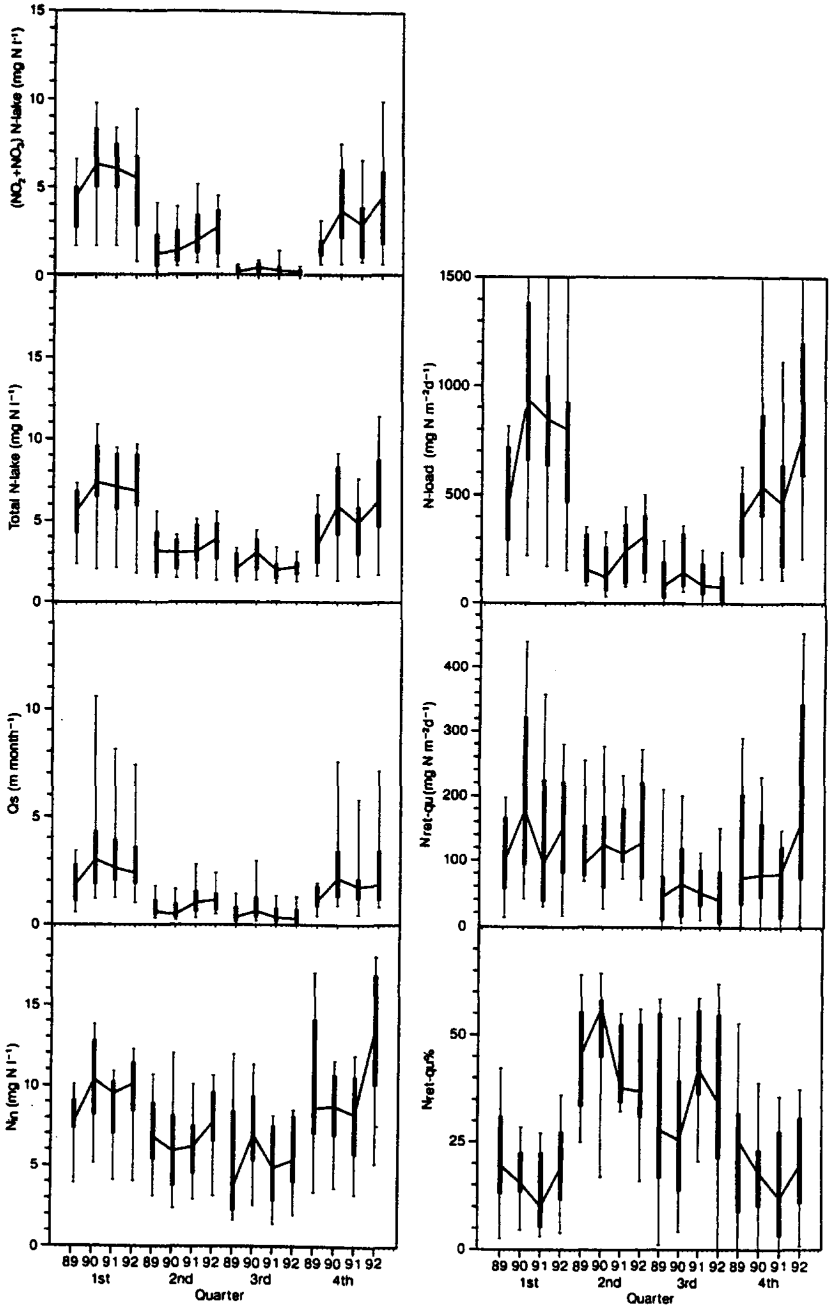

Figure 2. Seasonal variation in the in-lake concentration of nitrite + nitrate and total-N, area-specific hydraulic loading (Q_s), inlet concentration (N_{in}), external loading (N_{load}), retention (N_{ret-qu}) and percentage retention ($N_{ret-qu\%}$) of N in 16 shallow lakes during a four-year period (1989–1992). A line is drawn between medium values in each quarter. The thick bars represent the 25–75% quartiles and – marks the 10% and 90% quartiles, respectively. $N_{ret-qu\%}$is the quarterly retention expressed as a percentage of the sum of N_{load} and the total-N pool in the lake water at the beginning of the quarter.

resulted in N_{lake} being relatively constant throughout the season (1.3–1.6 mg N l^{-1}). Similarly, only minor variation was seen with nitrate (0.3–0.8 mg N l^{-1}). In Lake Bryrup Langsø annual mean N_{load} was almost identical to that in Lake Ørn. Q_s was much lower, however, (0.8–2.5 m month^{-1}), while N_{in} was higher (8.1–10.3 mg N l^{-1}). Seasonal variation was more pronounced, Q_s ranging from 0.8 to 2.5 m month^{-1}, and N_{load} from 200 to 820 mg N m^{-2} d^{-1}. Pronounced variation was also observed with N_{ret} and N_{lake}. In accordance with the lower Q_s, $N_{ret-y\%}$ was much higher (46–54%) than in Lake Ørn. N_{ret} ranged from 110–260 mg N m^{-2} d^{-1} during winter to 160–310 mg N m^{-2} d^{-1} during summer, and N_{lake} ranged from 1.9 to 6.4 mg N l^{-1} (Fig. 3). The more shallow Lake Hejrede showed roughly the same seasonal variation in the N variables and hydraulic loading as Lake Bryrup Langsø. However, N_{ret-m} had already started to decrease by the end of April, concomitant with an earlier and more marked decline in Q_s, N_{load} and lake water nitrate concentration (Fig. 3).

The annual budgets (Fig. 1), the quarterly data of all lakes (Fig. 2) and seasonal variation of lake Bryrup Langsø and Hejrede Sø (Fig. 3) indicate that much of the variation in N_{ret-m} may be attributed to changes in tw, N_{load}, and N_{lake}. However, seasonal variation in N_{ret} was also found in Lake Ørn despite relatively constant Q_s and N_{lake} (Fig. 3), possibly reflecting variation in lake water temperature or temperature-related processes. We therefore developed simple empirical models for predicting N_{ret-m} based only on data for tw (months), N_{load}, N_{lake} and water temperature (Table 4). The parameters were found by nonlinear regression (NLIN with Marquardt solution, SAS 1989) using data from half of the 16 lakes (randomly selected, upper 8 lakes in Tables 1 and 2). In the simplest of the four models (Model 1) we assumed that N_{ret-m} could be predicted from the maximum possible retention, $N_{retmax-m}$ (mg N m^{-2} day^{-1}), determined by adding the daily mean N_{load} for a given month (mg N m^{-2} d^{-1}) to the total N_{pool} of the lake (N_{lake} * mean depth * 1,000) (mg N m^{-2}) at the beginning of the month divided by the time step (number of days in the month (d)). The model accounted for 26% of the variation in N_{ret-m} in the 8 lakes and revealed that 14% of $N_{retmax-m}$ was retained in the lake. Inclusion of the surface water monthly average temperature markedly improved the model (r^2 = 0.41) (Van Hoff's equation, Model 2). This model predicts that 46% of $N_{retmax-m}$ is retained in the lake at 20°C, and that N retention decreases with a Q_{10} of 2.3. If instead tw was included in the model, improvements were also obtained (Model 3, r^2 = 0.32). No improvement was obtained by including both temperature and tw (Model 4, r^2 = 0.41) or N_{lake} in the model (not shown).

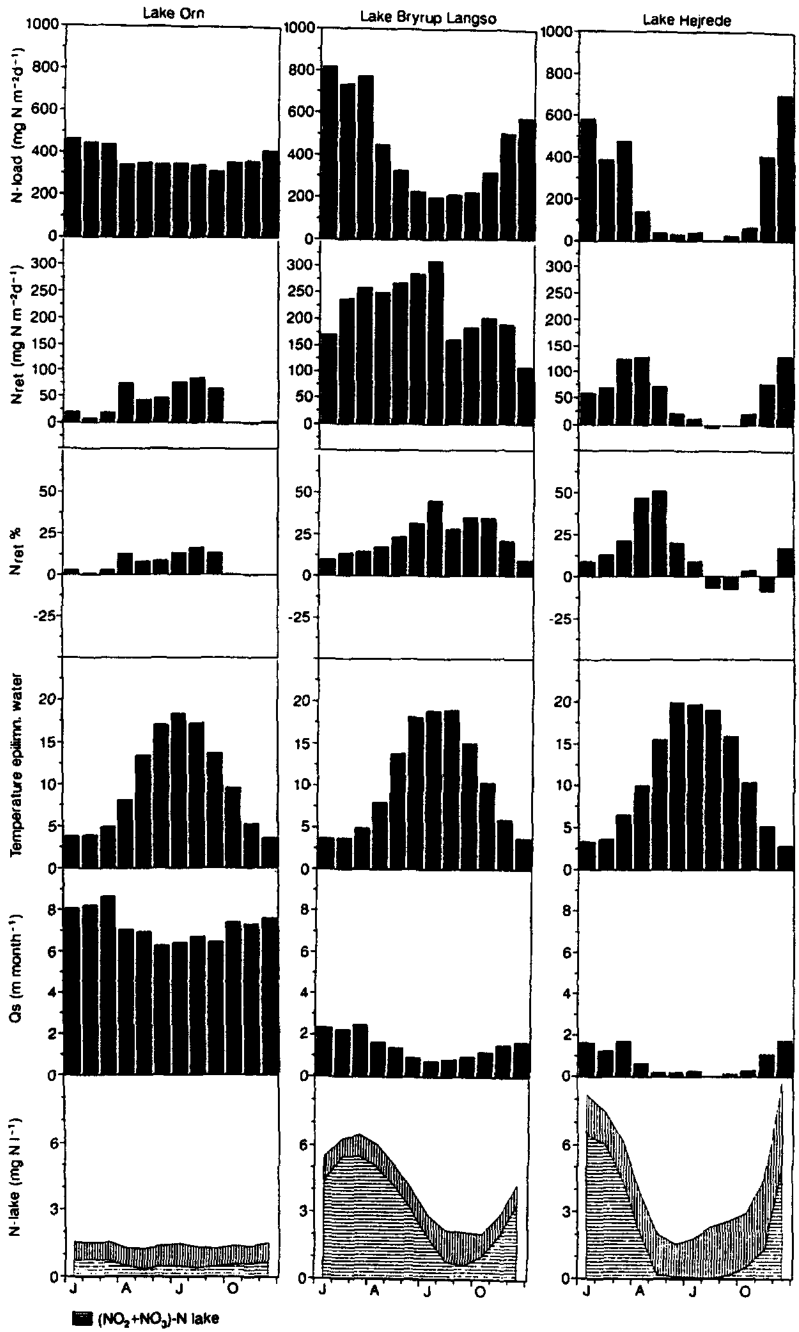

Figure 3. Seasonal dynamics of monthly mean external N loading (N_{load}), N retention rate (N_{ret-m}) and percentage ($N_{ret-m\%}$), surface water temperature, area-specific hydraulic loading (Q_s) and in-lake nitrogen concentrations (N_{lake} and NO_{2+3}-N) in three lakes with contrasting loading regimes. $N_{ret-m\%}$ is the monthly retention expressed as a percentage of the sum of N_{load} and the total-N pool in the lake water at the beginning of the month.

The calibrated version of model 2 (Table 4) was subsequently used for predicting N_{ret-m} (in units mg N m^{-2} d^{-1}) in the 8 lakes used for calibration and in the 8 test lakes.

$$N_{ret-m_{(t+1-t)}} = 0.455 * 1.087^{(Temp-mean(t+1-t)-20)} \cdot (N_{pool_t} + N_{load_{(t+1-t)}})/d \quad (3)$$

where d is the number of days in the month (month t to month t+1), N_{pool_o} is calculated as

$$N_{pool_t} = N_{lake_t} * Z_t * 1000\,(mg\ N\ m^{-2})$$

and temperature is the measured average temperature.

From Eq. 3 $N_{lake_{(t+1)}}$ (mg N l^{-1}) could then be calculated as

$$N_{lake_{(t+1)}} = \frac{(N_{load} - N_{ret-m})_{(t+1-t)}}{Z_{(t+1)1000}} + N_{lake(t)}\frac{Vol(t)}{Vol(t+1)} \quad (4)$$

where *Vol* is the lake volume. At time zero actual values of N_{lake} were used (N_{lake_o}) for calculating N_{pool_o}, otherwise succesively calculated N_{lake} and N_{pool} were used as input a time step later.

The model predictions were in reasonably close agreement with the observed N_{lake} and N_{ret}, both on an annual and on a quarterly basis (Fig. 4 and Fig. 5). In addition, the model closely simulated N_{ret-m} and N_{lake} (Fig. 6 and CV's in Table 2), irrespective of the level of tw, which ranged between 0.04 in Jels Oversø to approx. 0.25 y in Bryrup Langsø, and despite marked variations in N_{lake} (Table 2). It is noteworthy that simulated concentrations were in most cases far from the level that would have appeared if the retention had been fixed at zero. Thus close simulation of seasonal variation in N_{lake} does not simply depend on the variation in N_{in}. CV on N_{ret-m} ranged between 0.62 and 1.35 for the 8 lakes included in the calibration, and it was not significantly different from the CV of the test lakes (t-test, p>0.05) which ranges between 0.45 and 2.4. Model predictions are shown for selected lakes in Fig. 6. Model CV for N_{lake} was lower, ranging from 0.11 to 0.41 for the calibration data set to 0.16–0.37 for the test lakes (there being no significant difference between the two sets, t-test, p>0.05).

Discussion

Annual mean N_{ret} in the 16 lakes studied, although varying considerably (47–234 mg N m^{-2} d^{-1}, median 95 mg N m^{-2} d^{-1}), was comparable to that found in other mass balance studies from lakes in agricultural areas with

Table 4. Statistics and parameter estimates of models for monthly retention of total-N (N_{ret-m}, mg N m^{-2} d^{-1}). T is the monthly mean epilimnetic temperature (°C) and tw the hydraulic retention time (months). $N_{retmax-m}$ is the maximum retention = $N_{load} + \frac{N_{pool}}{d}$ (mg N m^{-2} d^{-1}), where N_{load} is mean daily external loading of total N in a given month (mg N m^{-2} d^{-1}), N_{pool} is total-N pool in the lake at the beginning of the month (mg N m^{-2}), and d is number of days in the month.

No.	Model	n	Parameter-estimates ±05% C.L.			r^2
			a	θ	c	
1	$N_{ret-m\%} = a * N_{retmax-m}$	371	0.141±0.013	–	–	0.30
2	$N_{ret-m\%} = a * \Theta^{(T-20)} * N_{retmax-m}$	371	0.455±0.074	1.087±0.014	–	0.41
3	$N_{ret-m\%} = a * \frac{1}{1+tw^c} * N_{retmax-m}$	371	0.332±0.030	–	−0.444±0.138	0.32
4	$N_{ret-m\%} = a * \Theta^{(T-20)} * \frac{1}{1+tw^c} * N_{retmax-m}$	371	0.880±0.197	1.084 ± 0.022	−0.025±0.150	0.41

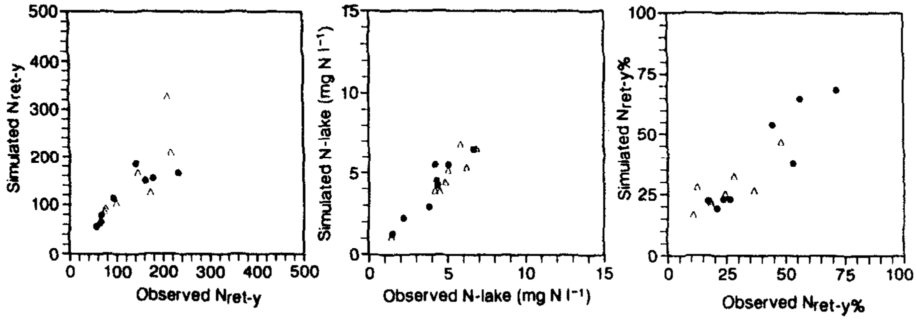

Figure 4. Simulated vs. measured annual N retention (N_{ret-y}), in-lake nitrogen concentration (N_{lake}) and percentage nitrogen retention ($N_{ret-y\%}$) in the 16 lakes (4 year means). Model 2 (Table 4) was used for the simulation. ● Lakes included in the calibration of parameters (upper 8 lakes in Tables 1 and 2). △ Other lakes.

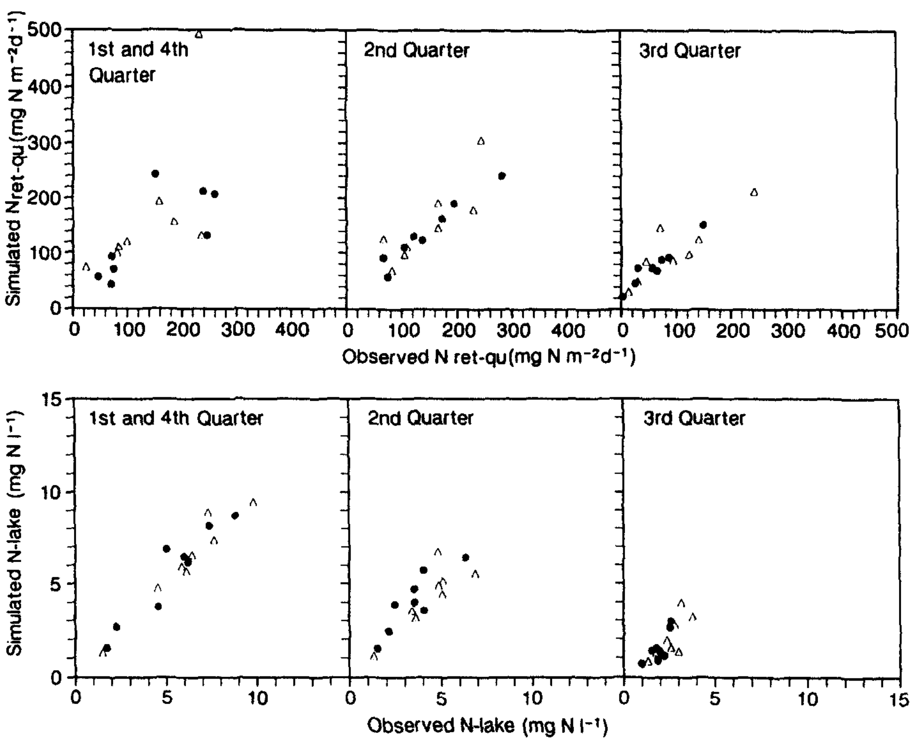

Figure 5. Simulated vs. measured N retention (N_{ret-qu}) and in-lake nitrogen concentration (N_{lake}) in the 16 lakes (4 years means) on a quarterly basis. Model 2 (Table 4) was used for the simulation. ● Lakes included in the calibration (upper 8 lakes in Tables 1 and 2). △ Other lakes.

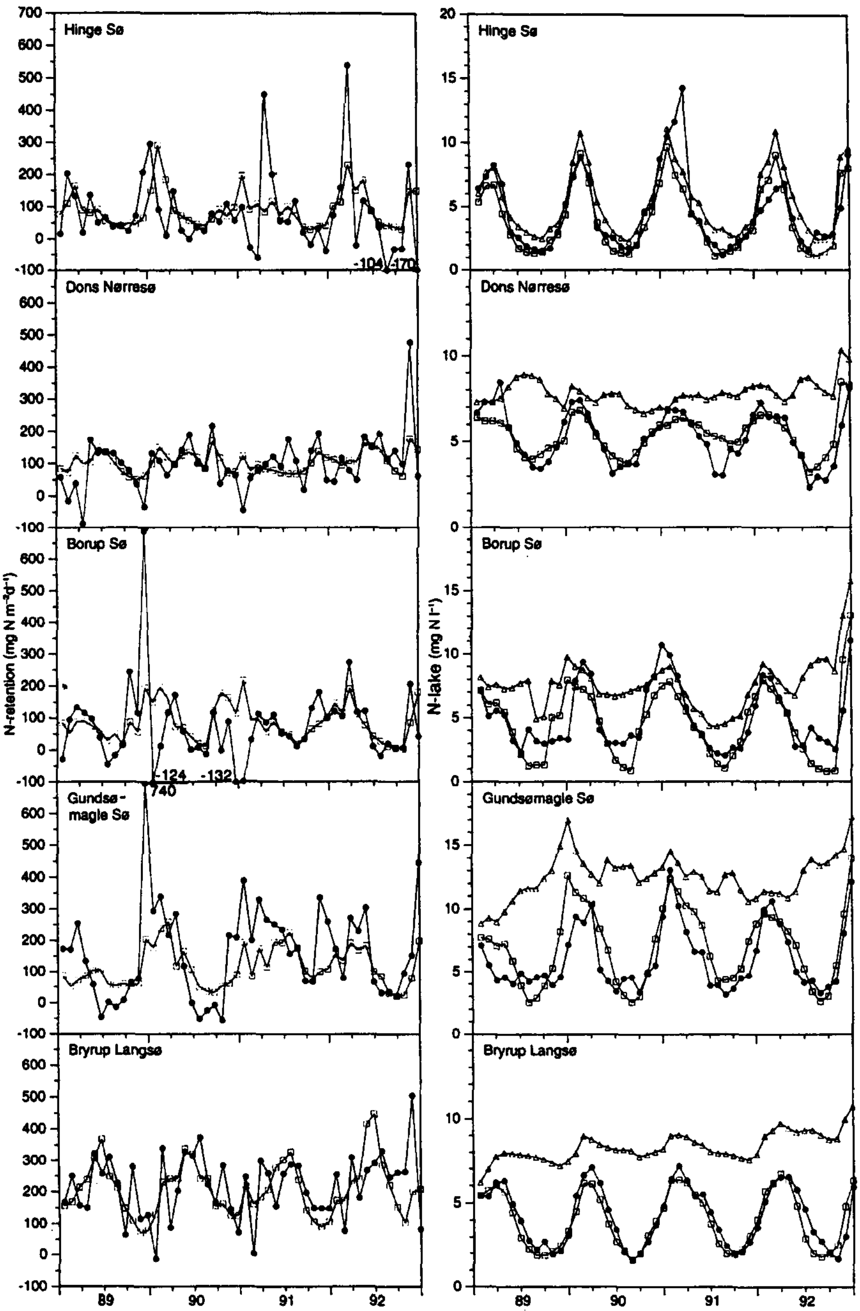

Figure 6. Seasonal dynamics (monthly means) of measured and simulated nitrogen retention (N_{ret-m}) and in-lake nitrogen concentration (N_{lake}) in five lakes with contrasting loading regimes. The lakes were not included in calibrations of the model. The figure also illustrates N_{lake} if nitrogen retention were zero (dilution curve). Model 2 (Table 4) was used for the simulation. Relevant characteristics of the lakes are given in Tables 1 and 2. ● Measured values □ simulated values, △ simulated values with N_{ret-m} set to zero.

relatively high N loading (Andersen 1974; Ripl & Feibicke 1992; Jensen et al. 1991), but they were high compared to rates obtained by less extensively N loaded lakes (Kelly et al. 1987; Seitzinger 1988; Molot & Dillon 1993).

The nitrogen retained in lakes is lost either by permanent burial in the sediment or by denitrification; other processes are of minor significance (Dudel and Kohl 1992). Using phosphorus as a conservative tracer, Jensen et al. (1991) estimated annual mean nitrogen burial in 69 mainly shallow Danish lakes to be 16 mg N m^{-2} d^{-1}, or 23% of the total N loss. In the present study we have not been able to determine burial as many of the lakes included in the investigation are in a transient state following a reduction in external phosphorus loading (Søndergaard et al. unpublished results) and hence subject to net internal phosphorus loading. In these lakes phosphorus cannot therefore be considered a conservative tracer. However, based on the study of Jensen et al. (1991) it can be expected that the major part of the nitrogen retained in the lakes included in the present study is also lost by denitrification. Even when applying a correction for burial of 23%, however, the remaining annual N_{ret} (estimated denitrification) was high in comparison with denitrification rates derived from most laboratory studies and *in vitro* experiments on lake sediment (Abdelmoneim et al. 1986; Seitzinger 1988) despite conservative mass balances because of exclusion of N fixation. Denitrification rates comparable to those we found have been reported in a few *in vitro* studies, however; e.g. 34–65 mg N m^{-2} d^{-1} in a shallow lake with short retention time (Rysgaard et al. 1993) and 17–154 mg N m^{-2} d^{-1} in a macrophyte-covered fish pond (Oláh & Szabó 1986). The observed difference between measured denitrification rates and mass balances may partly be explained by the fact that the commonly used acetylene method underestimates the actual denitrification because it does not include the coupled nitrification-denitrification process (Seitzinger et al. 1993). Nevertheless, denitrification rates obtained with the new ^{15}N technique (Nielsen 1992) supplemented by the improved method for ^{15}N analysis (Risgaard-Petersen et al. 1993) still seem to be lower than those obtained from mass balances corrected for burial. Thus Skaarup and Nielsen (1994) observed that denitrification measurements only amounted to approx. 20% of the mass balance estimations for Lake Søbygård, the discrepancy being particularly high in mid-summer, when the relative importance of the coupled nitrification-denitrification was greatest. Whether the difference between direct measurements and mass balance estimates can be ascribed to inadequate simulation of the physical conditions in the lakes by the laboratory setups commonly used remains to be elucidated.

Apart from N loading annual N_{ret} seems to be determined by hydraulic loading and average lake depth. Annual $N_{ret\%}$ ranged from 11–72% (Table 2), with the highest values being found in lakes with long hydraulic retention time and low mean depth (Tables 1 and 2), a finding in accordance with the empirical models of Lijklema et al. (1989), OECD (1982) and Jensen et al. (1991). In a mass balance study of 9 lakes, Molot and Dillon (1993) found a close inverse relationship between $N_{ret\%}$ and Q_s. In our study annual $N_{ret\%}$ was only weakly related to Q_s ($r^2 = 0.58$), although the relationship could be markedly improved by including mean depth ($r^2 = 0.75$) (Table 3). The importance of hydraulic loading/retention time is obvious: the shorter retention time the shorter the duration of contact between water and sediment and accordingly the lower the percentage lost by denitrification. At the same time the loss via the outlet of organic N increases which likewise results in decreasing $N_{ret\%}$. The importance of depth may be explained by various factors. At increasing depth the contact time between a given water volume and the sediment decreases and the possibility of sediment uptake of N and subsequent denitrification is reduced. Moreover, several of the deeper lakes in the present study were stratified which implies that only part of the water volume is in contact with the sediment. Nevertheless, the results show that shallow lakes even with a very short retention have a great potential to act as a sink of nitrogen. If the retention time is longer than, for instance, a month, annual $N_{ret\%}$ (according to model 4, Table 3) is greater than 27%.

Marked seasonal variations were found in $N_{ret\%}$ with generally high values during summer when temperature is high (Fig. 2) and vice versa during winter. $N_{ret\%}$ was only slightly lower in the 3rd than in the 2nd quarter, even though nitrate concentrations were markedly lower (0.18 versus 1.67 mg N l^{-1}, respectively, Fig. 3). If N_{ret} reflects denitrification, this indicates that denitrification is not solely related to lake water nitrate but that coupled nitrification-denitrification in the surface sediment also plays an important role, as has been reported previously (e.g. Jenkins and Kemp, 1984). That $N_{ret\%}$ can be high despite the nitrate concentration being low was also seen by Jensen et al. (1992) in their long-term study of shallow Lake Søbygård; $N_{ret\%}$ was not significantly influenced by a halving of the N_{load} and a consequent shift from a situation in which nitrate in the lake water was in surplus all year round (except a few days in summer) to one of prolonged period of nitrate depletion during the summer. Jensen et al. (1992) and Ripl & Feibricke (1992) found that N_{ret} was higher in the 4th quarter than in the 1st quarter despite similar temperatures. Jensen et al. (1992) argued that their results might reflect a high pool of labile, organic matter, i.e. the pool was assumed to increase during summer, when gross sedimentation of algae was extremely high, thereafter to decrease gradually as a result of mineralization during autumn and winter. Our data from less eutrophic lakes do not support these findings.

N_{ret} is probably underestimated as correction for lake nitrogen fixation was not possible. In a recent review Howarth et al. (1988) reported N fixation rates of 0–2.2 g N m^{-2} y^{-1} in temperate lakes, the rates being highest in eutrophic lakes. The highest value reported by Howarth et al. corresponds to 2.2% of the median N_{load} in the 16 lakes included in the present study, and to 10% of that in the lake in which N_{load} was lowest. It is therefore likely that the contribution made to the annual N budget by N fixation is low in these relatively fast-flushed shallow lakes. However, N fixation may potentially have a high impact during late summer in those of the lakes in which N_{load} and lake water nitrate concentration was low. Nevertheless, it is an open question whether this potential is realized in fully mixed eutrophic shallow lakes in which sediment release may be an important N source for phytoplankton growth (Leonardson 1984; Jensen et al. 1994). In concert with this view, non-heterocyst cyanobacteria or green algae rather than heterocystous cyanobacteria are dominant in late summer in shallow hypertrophic Danish lakes, even when the concentration of nitrate is low (Jensen et al. 1994). Moreover, it has been demonstrated by Levine & Schindler (1992) that N fixation is substantially less important in mesocosms with sediment than in those lacking sediment, and Dudel & Kohl (1992) have shown that N fixation makes only a minor contribution (0.004–4%) to the nitrogen input in shallow German lakes.

The present study demonstrates a simple relationship between N_{ret} on a monthly basis versus temperature and hydraulic retention time. The model developed is empirical, but also contains some causality. Hence, θ in Van Hoff's equation was calibrated to 1.08 ($Q_{10} \sim 2.3$), which is in close agreement with the values of 1.06–1.10 reported for lake denitrification by Lewandowski (1982). The regulating role of temperature is somewhat ambiguous. Whereas Andersen (1977) observed no significant effect of temperature on denitrification in a study of undisturbed sediment cores from six Danish lakes, Christensen et al. (1990) observed an indirect effect of temperature on denitrification in a nitrate-rich Danish stream (NO_3-N>4.5 mg N l^{-1}). In the latter study increased temperature resulted in a decline in the thickness of the diffusion layer to the denitrification zone and enhanced denitrification in the sediment. With regard to hydraulic retention time, the relationship found in our study between N_{ret-m} and tw implies that the simulated $N_{ret-m\%}$ decreases with increasing hydraulic loading, this being in concert with a number of other models of annual mean N_{ret} (Lijklema et al. 1989; OECD 1982; Jensen et al. 1991 and Fig. 1).

In the seasonal models developed in the present study no distinction was made between denitrification related to nitrate from the water phase and coupled nitrification-denitrification. Such an extension of the models would necessitate predicting not only N_{lake}, but also lake water nitrate concentrations, and would therefore require information on the processes decisive for phytoplankton uptake and loss (Kelly et al. 1987), i.e. phytoplankton production, respiration, loss by grazing and loss by sedimentation. This would make the models exceedingly complex and thereby reduce their value as simple management tools. The fact that we did not distinguish between the two types of retention and that N fixation was not included may explain why the final model sometimes overestimates N_{ret-m} in late summer (e.g. Lake Borup, Fig. 6), at which time N fixation is suggested to be of more importance because lake water nitrate concentration is often low at that time of the year (Fig. 2 and 3).

While the models developed accurately predict N_{ret} in the lakes included in the present study both on an annual and seasonal basis, it should be remembered that they were mainly highly N loaded shallow, nutrient-rich lakes with relatively short retention times. Moreover, because of the high eutrophication level the data set did not include lakes with extensive coverage of submerged macrophytes, N_{ret} in such lakes having been reported to be considerably higher than in lakes without macrophytes (Van Donk et al. 1990; Jeppesen et al. 1991). Finally, it has been found that major changes in the fish stock, e.g. by fish kill or biomanipulation, may markedly alter retention (E. Jeppesen et al. unpublished data). Such factors should be taken into consideration when applying the models to lake types other than that on which it is based.

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