

Baltic Sea nitrogen fixation estimated from the summer increase in upper mixed layer total nitrogen

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Abstract

We estimated nitrogen fixation from the increase in total nitrogen (N_2 gas excluded) in the upper 20 m during the summer biomass increase of heterocystous filamentous cyanobacteria at the off-shore Landsort Deep station (BY31, 5 yr) and at 10 more stations in all major basins of the Baltic Sea proper. Estimated fixation rates were 2.3–5.9 mmol $N\ m^{-2}\ d^{-1}$, within the range of reported direct measurements. Estimated total fixation in the Baltic Sea proper, 180–430 Gg $N\ yr^{-1}$ taking nitrogen settling loss and atmospheric deposition into account, was sufficient to sustain 30–90% of the June–August pelagic net community production. Filamentous cyanobacteria (mostly *Aphanizomenon* sp.) had low C:N and C:P ratios in spring 1998, indicating internal storage of both N and P. From early June, when their biomass growth started, ratios rose gradually to the biomass peak in August and early September, when the C:N ratio (6.5 mol/mol) was close to the Redfield ratio, but the C:P ratio reached 420, almost four times Redfield. The C:N ratio of the peak biomass was 1.5 times that in spring, and the C:P ratio was 13 times higher. The high C:P ratio indicates a smaller P demand by filamentous diazotrophs than expected from Redfield ratios. Only a few percent of the P mineralized daily is needed for filamentous cyanobacterial growth in summer. Filamentous cyanobacteria incorporated 16–41 mmol $N\ m^{-2}$ into biomass (C:N = 6.2) at BY31 in summer 1998. This was less than the estimated nitrogen fixation, suggesting fixed N leaks from growing diazotrophs.

Diazotrophic cyanobacteria are important providers of new nitrogen in many lakes (Howarth et al. 1988) and are increasingly recognized as such for tropical and subtropical oceans (Capone et al. 1997, Karl et al. 1997). Recent estimates suggest nitrogen fixation to equal vertical nitrate flux in nonupwelling regions of the tropical and subtropical North Atlantic (Capone et al. 1997) and to supply up to half of the N needed to sustain the annual particulate export in the oligotrophic northern Pacific Ocean (Karl et al. 1997).

The Baltic Sea is one of the few brackish water areas in the world where diazotrophic cyanobacteria, some of which are toxic, are an important component of the phytoplankton (Howarth et al. 1988). It is a large, semienclosed nontidal estuary comprised of a series of large basins where surface salinity decreases from 6–8 in the Baltic Sea proper (henceforth Baltic proper) to 5–6 in the Bothnian Sea and down to 2–3 in the northernmost parts of Bothnian Bay. Diazotrophs are generally restricted to areas with winter inorganic N/P ratios below the Redfield atom ratio of 16 (Redfield et al. 1963), that is, to the Baltic proper and the southern Bothnian Sea (Niemi 1979, Wasmund 1997).

In the Baltic proper, three cyanobacterial genera are com-

monly considered dominant in nitrogen fixation. *Aphanizomenon* sp., earlier identified as the freshwater species *Aphanizomenon flos-aquae* (L.) Ralfs (Janson et al. 1994) and *Nodularia spumigena* Mertens are the most abundant species (Wasmund 1997). *Anabaena*, the third genus, is represented by *A. lemmermannii* P. Richter and other species (e.g., Laamanen 1997) but is less common (Niemistö et al. 1989).

Monitoring data, although relatively scarce, indicate large-scale regional differences in the occurrence of *Aphanizomenon* and *Nodularia* (Wasmund 1997). Summer biomass of both genera tends to be higher in the southern and eastern Baltic proper (Niemistö et al. 1989). This is most pronounced for *Nodularia*, which was never one of the five species with the highest biomass in the western Baltic proper in 1979–1993 (HELCOM 1996).

The biomass of autotrophic plankton in the Baltic proper is rarely dominated by filamentous cyanobacteria. Their ability to regulate their buoyancy (Walsby et al. 1995) can, however, sometimes result in conspicuous surface accumulations, which can be concentrated along coasts and in bays by wind and currents (Niemistö et al. 1989). *Nodularia* usually dominates surface accumulations, whereas *Aphanizomenon* normally remains distributed in the water column (Niemistö et al. 1989).

Surface accumulations, most likely of filamentous cyanobacteria, were reported from the Baltic proper as early as the 19th century (review by Leppänen et al. 1988). The cyanobacterial pigment zeaxanthin and a low $^{15}N:^{14}N$ ratio, indicating substantial nitrogen fixation, have been found in sediment layers deposited in the Baltic proper as long ago as ca. 7000 B.P. (Bianchi et al. 2000). Thus, an abundance of nitrogen-fixing cyanobacteria seems to be natural to the Baltic Sea, but a recent increase in their occurrence has been suggested (Kahru et al. 1994) following an increased nutrient load during the 20th century (Larsson et al. 1985). Nitrogen fixation is considered the third largest source of new nitrogen

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Acknowledgment

We thank our technicians and students for collecting and analyzing an endless flow of samples from the Landsort Deep station with never-failing dedication and the Swedish Meteorological and Hydrological Institute (SMHI) for access to monitoring data collected within the Swedish Marine Monitoring Program. We also thank Hans Paerl and two reviewers for constructive criticism.

Funding was given by the European Union through BASYS within the MAST III program (MAS3-CT96-0058), the Swedish Foundation for Strategic Environmental Research (MISTRA: SUCOZOMA and MARE programs), and the Swedish EPA's Marine Monitoring Program.

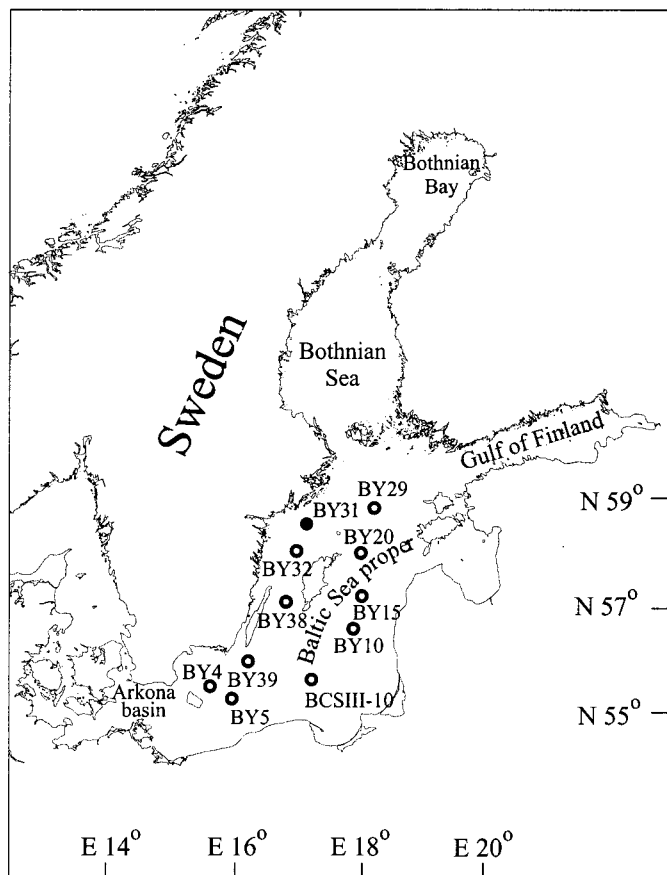


Fig. 1. Baltic Sea with sampling stations. Landsort Deep (BY31) indicated by filled circle.

to the Baltic proper after land run-off and atmospheric deposition (Larsson et al. 1985), and the risk that nitrogen fixation might counteract present international efforts to reduce the Baltic nitrogen load (Savchuk and Wulff 1999) is a major concern.

Recent nitrogen fixation estimates for the Baltic proper are uncertain and span more than an order of magnitude (Hübel and Hübel 1995: 18–186 Gg N yr⁻¹, northern Baltic proper excluded; Rahm et al. 2000: 30–260 Gg N yr⁻¹, western Arkona basin and northern Baltic proper excluded).

We here estimate nitrogen fixation during summer blooms of filamentous heterocystous cyanobacteria from 5 yr of total nitrogen measurements (gaseous dinitrogen excluded) in the upper mixed layer at the Landsort Deep station (BY31) in the northern Baltic proper, after correcting for atmospheric inputs and settling losses of combined nitrogen. We then relate the results to summer increases in total nitrogen at other Baltic stations to estimate total nitrogen fixation in the Baltic proper. In addition, we use cyanobacterial elemental composition to estimate their P demand and to indicate the likely cause of bloom termination.

Materials and Methods

Sampling stations—We sampled the Landsort Deep station (BY31, 58°35'N, 18°14'E; Fig. 1) weekly in spring, bi-

weekly in summer and autumn, and monthly in winter. We extracted monthly water chemistry data from the Swedish Marine Monitoring Program (funded by the Swedish Environmental Protection Agency) for 10 more stations in the Baltic proper from the SHARK database at the Swedish Meteorological and Hydrological Institute (SMHI). The stations were: Bornholm basin: BY4 and BY5; eastern Gotland basin: BCSIII-10, BY10, and BY15; northeastern Baltic proper: BY20 and BY29; western Gotland basin: BY32, BY38, and BY39 (Fig. 1, Gulfs of Finland and Riga not included in the Baltic proper).

Water chemistry—From 1994 to 1996, total nitrogen (TN, dinitrogen gas excluded, uncertainty $\pm 0.4 \mu\text{mol N L}^{-1}$ at $20 \mu\text{mol N L}^{-1}$) and phosphorus were determined separately according to Koroleff (1983, with slight modifications) in Landsort Deep (BY31) samples from every 5 m down to 30 m deep. From 1997, nitrogen and phosphorus were simultaneously oxidized using a modification of the method of Koroleff (1983), yielding a lower final pH. Standard flow injection analysis (QuikChem® 8000 Method 31-115-01-3-A, 31-107-04-1-A, and 31-107-06-1-A, Lachat Instruments) was used to measure dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN) ($\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$).

Phytoplankton—Phytoplankton was sampled with a plastic tube (inner diameter [ø] 2.5 cm), which was gently lowered to a depth of 20 m, stoppered at the upper end, retrieved, and emptied in a bucket. A 200-ml subsample, siphoned from the bucket while stirring and preserved with 0.8 ml of Lugol's iodine (I_2KI) solution supplemented with acetic acid, was counted in a settling chamber (10 to 50 ml) using a NIKON inverted microscope with phase contrast (HELCOM 1988). Microplankton was counted in diagonals or the half or whole chamber bottom at 150×. Biomass was estimated by multiplying the cell numbers with species-specific mean cell volumes, determined from measurements. A factor of 0.11 was used to convert volume to carbon (HELCOM 1988).

Phytoplankton primary production—Rates of ¹⁴C uptake were determined in 80-ml polycarbonate bottles, suspended horizontally at depths of 0, 1, 2, 4, 6, 8, 10, 12.5, 15, 20, and 25 m, with dark bottles at 0, 4, and 25 m. Each bottle received 4 μCi of carrier-free $\text{NaH}^{14}\text{CO}_3$. After incubation for ~4 h around noon, the water was immediately filtered through filters of 90, 40, 20, 10, 3, 1, and 0.2 μm , and the filtrate was collected. Filters $\geq 20 \mu\text{m}$ were custom-made from nylon net sheets; finer filters were Poretics® polycarbonate filters, all mounted in Swinlock filter holders (Millipore Inc.). After addition of a few drops of 1 N HCl, the filters were dried overnight at 60°C in plastic scintillation vials. Scintillation cocktail (7 ml; Filter Count, Packard Bioscience B.V.) was added before counting in a Tri-Carb 1600 TR (Packard Corp.). Rates of ¹⁴C uptake were also determined in 10-ml subsamples of unfiltered seawater and 0.2 μm filtrate in glass scintillation vials after adding 2 drops of 1 N HCl, bubbling with air for at least 30 min, and adding 10 ml of Lumagel Safe (Lumac LSC B.V.).

Carbon uptake was calculated according to Parsons et al. (1984). Dark uptake at incubation depths without dark bottles was calculated by linear interpolation and subtracted from the light uptake. Daily primary production was calculated by dividing by the fraction of total daily insolation received at Visby on the island of Gotland (100 km south of the sampling station) during the incubation. Integrated ^{14}C uptake rates were linearly interpolated over depth.

Filtration of ^{14}C samples after incubation results in an activity loss, which is proportional to the number of fractions (Larsson and Hagström 1982). To avoid underestimating ^{14}C uptake, we calculated the percentage uptake in separate size fractions in relation to the summed uptake of all fractions. Corrected uptake rates were calculated by applying the relative distribution of uptake rates from size-fractionated measurements to the uptake rate measured on intact seawater.

Elemental composition of filamentous cyanobacteria—Cyanobacteria were collected by vertical 90- μm WP2 (\varnothing 60 cm, HELCOM 1988) net hauls from the thermocline (when absent 15 m) to the surface. Zooplankters were removed in a light trap (a black funnel illuminated from the bottom), where they concentrated at the bottom, while buoyant cyanobacteria floated to the top. Cyanobacteria were then gently pipetted to another light trap, and the procedure was repeated until a clean sample of cyanobacteria was obtained. The cyanobacteria were rinsed in a 0.7% NaCl solution on a fine plankton net and residual water was removed from underneath the net with paper tissue. Subsamples of cyanobacteria were transferred to preweighed (Sartorius M3P microbalance, precision ± 0.001 mg) tin capsules for C and N analyses and to preweighed, acid-washed cover glasses for P analyses. Samples were dried to constant weight at 60°C (~ 3 d) before analysis using a Leco CHN-analyzer (CHN-900, 600-800-300, EDTA as standard). Samples on cover glasses were transferred to 15-ml glass tubes and combusted 2 h at 500°C before digestion in 6 ml persulfate solution ($50\text{ g L}^{-1} + 30\text{ mL L}^{-1} \text{H}_2\text{SO}_4$, 1 h, 120°C). Four milliliters of 1.6 M NaOH were added before analyzing for molybdate-reactive orthophosphate with the flow injection system, as above. Blanks and standards, prepared by adding stock phosphate solution to vials before digestion, were carried through the same procedure.

Results

Total nitrogen increase in the mixed layer at BY31—Each year, we found an increase in the concentration of total nitrogen (TN) in the near surface layer around the time of the major biomass increase of filamentous diazotrophic cyanobacteria (Fig. 2). The TN increase was calculated as the average concentration at 0, 5, 10, 15, and 20 m minus the mean below the summer pycnocline, at 25 and 30 m. The top 20 m was chosen because filamentous cyanobacteria, particularly *Aphanizomenon*, may have their maximum biomass as deep as 10 to 15 m (Niemistö et al. 1989, Hajdu et al. unpubl. data). Data from individual depths usually showed a total nitrogen increase in the top 10 m, whereas increases at 15 and 20 m commonly coincided with a deepening of the mixed layer (see Fig. 5c). By using the difference between

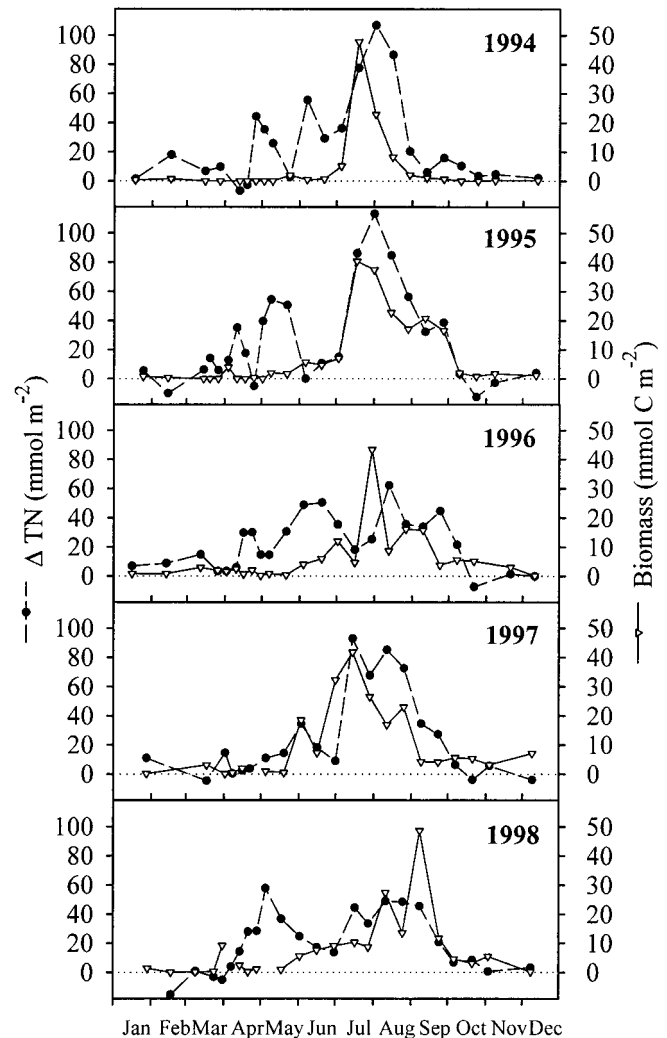


Fig. 2. Increase in average total nitrogen concentration in the top 20 m relative to the average concentration at depths of 25 and 30 m and biomass of heterocystous cyanobacteria in the top 20 m at station BY31 (Landsort Deep) in 1994 to 1998.

the surface layer and the subpycnocline concentration, we minimize effects of water exchange.

The estimated summer increase in TN at BY31 ranged from 35 to 100 mmol N m^{-2} (Table 1) and coincided with a rapid increase in diazotrophic filamentous cyanobacterial biomass, except in 1996, when it lagged 2 weeks after the biomass peak (Fig. 2). The increases in surface layer TN sometimes noted in spring were most likely due to nitrogen input from land by the spring flood.

Biomass of diazotrophic filamentous cyanobacteria—The summer biomass peak of diazotrophic filamentous cyanobacteria at BY31 (Fig. 2) ranged from 2 to 2.4 mmol C m^{-3} and was totally dominated by *Aphanizomenon* ($1.8\text{--}2.2\text{ mmol C m}^{-3}$) in all 5 yr (Fig. 3). Small amounts of *Aphanizomenon* were generally present also in other seasons, as reported by Kononen (1992), whereas *Nodularia* and *Anabaena* were found only in summer (peak range $0.12\text{--}0.82$ and $0.03\text{--}0.22\text{ mmol C m}^{-3}$, respectively). The maximum

Table 1. Estimated increase in average total nitrogen (TN, di-nitrogen gas excluded) concentration during summer growth of heterocystous filamentous cyanobacteria (*Aphanizomenon* + *Nodularia* + *Anabaena*) and their peak biomass in the upper 20 m at the Landsort Deep station BY31, Baltic proper.

Year	Sampling dates	TN increase (mmol N m ⁻²)	Peak biomass of heterocystous cyanobacteria (mmol C m ⁻²)
1994	05 Jul–02 Aug	79	48
1995	19 Jun–01 Aug	100	40
1996	16 Jul–13 Aug	44	43
1997	01 Jul–15 Jul	86	43
1998	30 Jun–11 Aug	35	48

biomass of diazotrophic filamentous cyanobacteria was found in July, except in 1998, when the peak was in early September. *Nodularia* usually co-occurred with *Aphanizomenon* during the peak, except in 1996, when *Nodularia* were sparse until September, and in 1997, when its biomass was exceptionally high in early-July before the *Aphanizomenon* peak.

A significant increase in *Aphanizomenon* biomass over that in winter and spring was normally first found 4 to 6

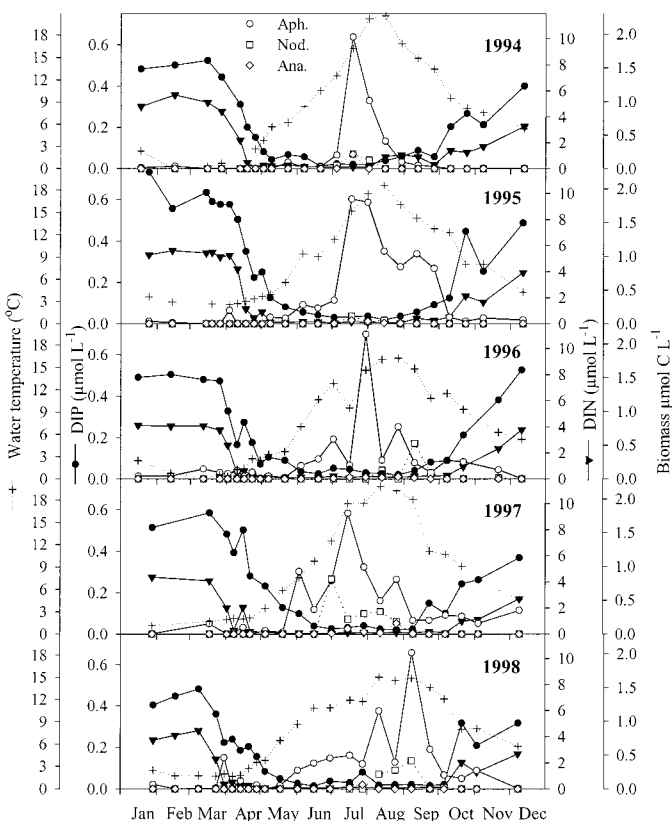


Fig. 3. Averages in the top 20 m of biomass of *Aphanizomenon* (Aph.), *Nodularia* (Nod.), and *Anabaena* (Ana.) and averages in the top 15 m of temperature and of concentrations of DIP and DIN at station BY31 (Landsort Deep) in 1994–1998. DIN and DIP axes are scaled 16:1.

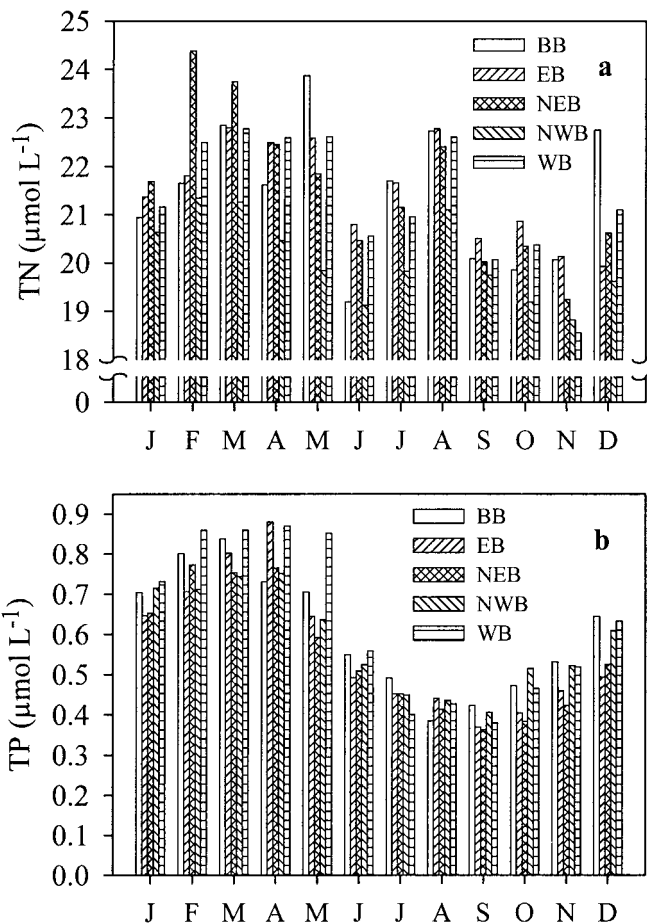


Fig. 4. Monthly average concentrations (0–15 m) of (a) total nitrogen (TN) and (b) phosphorus (TP) in five subareas of the Baltic proper based on monthly observations in 1994–1998. BB, Bornholm basin (two stations); EB, eastern Gotland basin (three stations); NEB, northeastern Baltic proper (two stations); NWB, northwestern Baltic proper (one station = BY31); and WB, western Gotland basin (three stations). Data from the Swedish Marine Environmental Monitoring Program.

weeks after inorganic nitrogen was depleted in the upper mixed layer (Fig. 3). Phosphate was usually still present in measurable concentration. *Nodularia* and *Anabaena* occurred irregularly in time, with large between-year variability in maximum biomass and showed no obvious connection to nutrient availability or surface layer temperature. Both genera were often found in periods of severely depleted phosphate, except when *Nodularia* peaked in early July 1997.

Increase in total nitrogen concentration in other subareas of the Baltic proper—Data from the top 15 m at 10 additional Baltic proper stations show the same pattern in all subareas (Fig. 4a). The average TN concentrations increased by $\sim 2 \mu\text{mol L}^{-1}$, except in the Bornholm basin, where the increase was $3.2 \mu\text{mol L}^{-1}$. The corresponding value at BY31 was $2.1 \mu\text{mol N L}^{-1}$.

In contrast, the concentration of total phosphorus (TP,

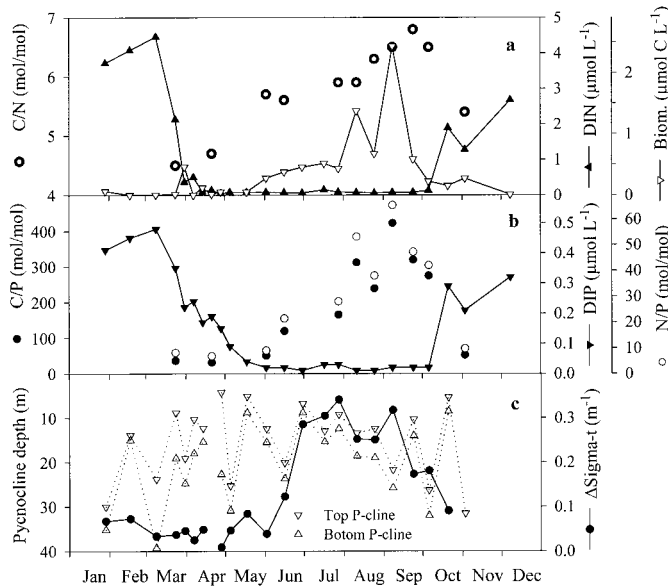


Fig. 5. Stoichiometric composition (mol/mol) of filamentous cyanobacteria, DIN and DIP concentrations (top 15 m), and depth and stability of the seasonal pycnocline at station BY31 (Landsort Deep) in 1998. (a) C:N, DIN and biomass of filamentous cyanobacteria. (b) C:P, N:P and DIP. (c) Top and bottom depth of pycnocline and density change $\Delta\text{Sigma-t}$ m^{-1} .

monthly averages for 1994–1998) in the mixed layer (0–15 m) decreased from June to August/September in all Baltic proper subareas (Fig. 4b). The average decrease was $0.14 \mu\text{mol L}^{-1}$, a loss of 25% of the mean June concentration. However, the greatest P loss occurred in spring prior to the onset of diazotrophic growth. Together, the concentration increase of TN and decrease of TP resulted in an average TN/TP ratio increase in the top 15 m, from ~ 30 at the end of the spring bloom to 38 in June and 53 in August.

Elemental composition of filamentous cyanobacteria at BY31 in 1998—The composition of filamentous cyanobacteria changed drastically over the 1998 growth season (Fig. 5). In spring samples (*Aphanizomenon* only, see Fig. 3), the C:N (Fig. 5a) and C:P (Fig. 5b) ratios were well below Redfield values ($\text{C}_{106}:\text{N}_{16}:\text{P}_1$), indicating internal storage of both P and N. From early June, when the *Aphanizomenon* biomass started to increase, the C:N and C:P ratios rose rather continuously to the biomass peak in August and early September (mixed *Aphanizomenon* sp. and *Nodularia spumigena*, Fig. 3). The C:P ratio of the peak population reached 420, almost fourfold the Redfield value and 13 times the spring value, while the C:N ratio, 6.5, was near Redfield and 1.5 times that in spring.

The C:N ratio started to increase as soon as DIN was depleted in the surface water. Even more clearly, the C:P ratio started to rise, just as DIP became depleted above the seasonal pycnocline, and returned to spring values as soon as DIP was mixed into the surface layer in autumn. Because the content of both N and P in the cyanobacterial cells decreased in relation to C, the seasonal change in N:P ratio

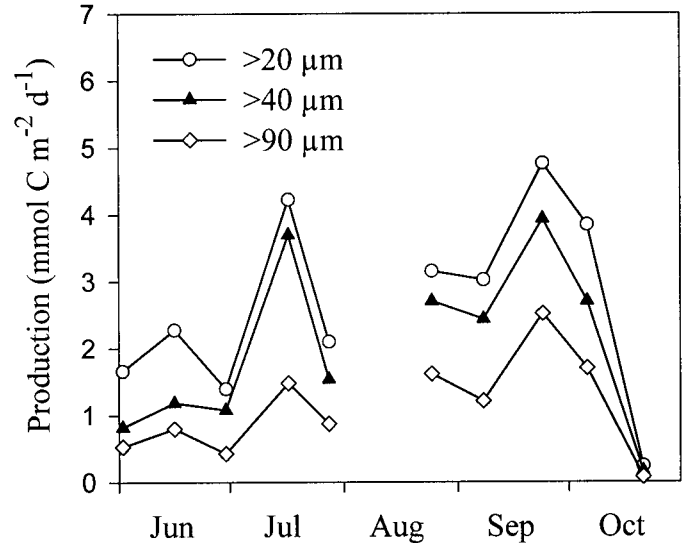


Fig. 6. Carbon uptake rates in size fractions $>20 \mu\text{m}$ at station BY31 (Landsort Deep), June–October 1998.

(Fig. 5b) was less than in the C:P ratio, but still about a factor of 10.

Figure 5c shows the top and bottom of the 1998 pycnocline and its stability (density change m^{-1}). The biomass of *Aphanizomenon* began to increase in early June before a strong pycnocline developed in late June. From late June to the biomass peak in early September, the depth of the pycnocline increased from ~ 10 to over 20 m, with little change in stability. The depth increase was likely a result of wind mixing (e.g., in August) and of water exchange, as indicated by increased mixed layer salinity in early September (data not shown).

Carbon-14 uptake rates—We used postfractionation of ^{14}C -incubated samples to estimate growth rates of phytoplankton >90 , 40 – 90 , and 20 – $40 \mu\text{m}$ in 1998 (Fig. 6). From the start of *Aphanizomenon* growth on 2 June to the biomass peak on 8 September, we estimated (linear interpolation) that 101, 93, and 58 mmol C m^{-2} was incorporated in the respective size fraction. Microscopic examination showed that phytoplankton retained by the 90 - μm net was almost entirely filamentous cyanobacteria. At times, they also were a major part of the phytoplankton biomass on the 40 - μm filter, and some were sometimes found on the 20 - μm filter. The lower bound estimate of primary production by diazotrophic filamentous cyanobacteria was then $0.10 (>90 \mu\text{m})$ and the upper bound was $0.25 \text{ mol C m}^{-2} (>20 \mu\text{m})$.

Discussion

Sources of total nitrogen—We found that an increase in TN concentration occurs each summer in the upper mixed layer of an open sea station in the northern Baltic proper and coincides with the build-up of diazotrophic (= heterocystous) filamentous cyanobacterial biomass. We interpret this increase as caused primarily by fixation of dissolved dinitrogen gas by diazotrophic cyanobacteria. Swedish mon-

Table 2. Total nitrogen (TN) increase (from Table 1), length of cyanobacterial growth period, atmospheric deposition, and particle N settling during the growth period, and resulting estimates of annual nitrogen fixation rates at the Landsort Deep station BY31 in 1994–1998.

Year	TN increase (mmol N m ⁻²)	Growth period (months)	Atmospheric deposition (mmol N m ⁻²)	Particle settling (mmol N m ⁻²)	Annual N fixation (mmol N m ⁻²)
1994	79	1	6	24–42	97–115
1995	100	1	6	24–42	118–136
1996	44	1	6	24–45	61–82
1997	86	1.5	9	36–63	113–140
1998	35	2	12	48–84	62–108

itoring data collected monthly since 1994 at 10 other stations from major Baltic proper subbasins show the same pattern.

Other factors may contribute to the increase in TN concentration. By using the difference in average concentrations between the surface layer and the water mass below the seasonal pycnocline, we have reduced the potential influence of upwelling water. We can rule out an increase due to an influence from the Bothnian Sea to the north since TN concentrations there are lower than in the northern Baltic proper (Sandén et al. 1991). Because we find a similar increase in TN in all subareas of the Baltic proper, while TP decreases, we consider large contributions from river run-off unlikely. This argument is supported by observations during the exceptional 1997 summer flood of the river Oder. Biological uptake effectively removed discharged nitrate near-shore, resulting in surplus phosphate being transported to the open sea (Humborg et al. 1998). The absence of a clear summer increase in total nitrogen in the Bothnian Sea (data not shown), where filamentous diazotrophic cyanobacteria are less common (Andersson et al. 1996), also supports this argument.

Wet and dry atmospheric deposition of inorganic and organic nitrogen compounds may stimulate algal growth (Paerl et al. 1999) and contribute to the nitrogen store above the seasonal pycnocline. Estimates of Baltic Sea wet and dry deposition of inorganic nitrogen range from 600 to 1,300 mg N m⁻² yr⁻¹ (Lindfors et al. 1993). Regional deposition patterns for the Baltic proper indicate lower deposition rates in the northern (~0.9 g N m⁻² yr⁻¹) than in the southern part (~1.1 g N m⁻² yr⁻¹), with clearly increasing deposition eastward in each subarea (Lindfors et al. 1993). We used 1 g N m⁻² yr⁻¹ as representative for the Baltic proper. This corresponds to an average monthly deposition of ~80 mg N m⁻² or 6 mmol N m⁻², disregarding seasonal signals, which vary between subareas (Lindfors et al. 1993).

The increase in TN concentration occurs in 6 weeks or less, suggesting that precipitation should contribute <10 mmol N m⁻² on average, although considerable variability between years is to be expected. Precipitation thus contributes only a minor fraction of the summer increase in TN concentrations in Table 1. New estimates of atmospheric deposition of inorganic nitrogen indicate somewhat lower rates of ~4 mmol N m⁻² month⁻¹ (Schulz et al. 1999). Because these deposition estimates do not include dissolved organic nitrogen (Cornell et al. 1995), we have used the higher value.

The summer increase of total nitrogen—Aphanizomenon sp. was usually the only cyanobacteria known to fix nitrogen present in the upper mixed layer before its TN concentration started to increase. We assume that nitrogen fixation at this time was low despite low ambient DIN concentrations because of internal nitrogen reserves in the cyanobacteria (Fig. 5 and below), as well as low temperature and weak stratification, which are unfavorable to diazotrophs (Hyenstrand et al. 1998). After the increase in filamentous diazotrophic cyanobacteria, a biomass of >0.4 mmol C m⁻³ usually persisted for 1.5–2.5 months (see Fig. 2). Its eventual decline generally coincided with a decrease in TN concentrations. Because the TN increase commonly took less than a month, a minimum nitrogen fixation estimate of 29–94 mmol N m⁻² can be obtained by subtracting an estimated 6 mmol N m⁻² month⁻¹ of atmospheric N deposition from the TN increase of 35–100 mmol N m⁻² (Table 2). We believe this estimate to be representative of Baltic proper conditions, considering the fairly uniform TN increase in all Baltic proper subbasins, except the Bornholm basin, where the data suggest higher nitrogen fixation rates.

*Rates of nitrogen loss from the mixed layer in summer—*Estimates based on TN increase minus N deposition will underestimate N fixation rates because nitrogen is also lost through settling out of organic matter from the mixed layer. We have attempted to estimate the rate of nitrogen loss due to settling particles, but it is a difficult task because of scarcity of data.

Organic carbon settling rates in sediment traps at 25 m (chloroform added, 2 weeks exposure time) in the Landsort Deep in July and August 1995 averaged 7 mmol C m⁻² d⁻¹ (210 mmol C m⁻² month⁻¹) (U. Larsson, unpubl. data). This is close to primary settling rates of 9 mmol C m⁻² d⁻¹ in a shallow (~50 m) open sea area at the mouth of the Gulf of Finland (Heiskanen and Tallberg 1999). Blomqvist and Larsson (1994) estimated primary settling rates in a northern Baltic coastal area in summer to average 11 mmol C m⁻² d⁻¹ (range 9–15 mmol C m⁻² d⁻¹) over 5 yr. Daily measurements of settling rate (no preservative) in the eastern Gotland basin in late July and early August of 2 yr gave averages of 8.7 and 12.5 mmol C m⁻² d⁻¹ and 1 and 1.2 mmol N m⁻² d⁻¹ (C:N, 8.6 and 10.2) (Olesen et al. unpubl.).

The organic carbon loss rates from sediment traps agree rather well with Stigebrandt (1991), who used oxygen sat-

uration to calculate average net primary production in July and August for the Arkona and Gotland basins to $12.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$. Over short periods, net production may overestimate export production because carbon can accumulate in the water, particularly when buoyant, unpalatable filamentous cyanobacteria are abundant.

A minimum N loss rate can also be estimated from the summer decrease in total phosphorus. On average (5 yr, 11 stations) $0.75 \text{ mmol P m}^{-2} \text{ month}^{-1}$ was lost from the upper 15 m during July and August. Settling particles in the open Baltic proper have N:P ratios (mol/mol) of around 13 (Olesen et al. unpubl.) to 22 (Tallberg and Heiskanen 1998) or 20–24 (Landsort Deep; Larsson, unpubl. data), similar to a 5-yr mean of 23 in the subtropical North Pacific Ocean (Karl et al. 1997). This yields basin-wide N settling rates of $10\text{--}18 \text{ mmol m}^{-2} \text{ month}^{-1}$ ($0.33\text{--}0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$) in summer, or about half the sediment trap estimates. This is likely to be an underestimate of the N loss rate because vertical mixing and thermocline erosion will introduce new phosphorus to the mixed layer due to relatively high P concentrations in and below the summer pycnocline (Niemistö et al. 1989).

Particulate settling rate estimates from deep, open, Baltic proper areas thus range from 7 to $12.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$, as do most observations from coastal areas, where imprecise corrections for resuspension are needed (Blomqvist and Larsson 1994, Tallberg and Heiskanen 1998). Assuming a C:N ratio of 9 (see above), we have calculated N export rates of $0.8\text{--}1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ during July and August that are in good agreement with an estimate of $0.8 \text{ mmol N m}^{-2} \text{ d}^{-1}$ from a coastal area at the entrance of the Gulf of Finland in summer (Heiskanen et al. 1998).

Estimates of nitrogen fixation—Compensating for loss of particulate N from the mixed layer from the start of TN increase to its first decline (see Fig. 2), we get nitrogen fixation rates of $60\text{--}140 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ (Table 2). These estimates are sensitive to assumed rates of N settling loss and to the growth period during which N fixation is assumed to occur, but rather insensitive to realistic variations in atmospheric N deposition rates. Assuming lower estimates of N settling loss ($0.33\text{--}0.6 \text{ mmol N m}^{-2} \text{ d}^{-1}$) will lower the calculated N fixation rates considerably. Such settling rates seem too low, however, because they imply that only a few percent of daily primary production settles out from the mixed layer in summer. Assuming higher settling rates will rapidly increase N fixation estimates to levels incompatible with recent Baltic proper nitrogen budgets (Wulff et al. 2001).

Because our data on TN and TP indicate that differences between subbasins are relatively small, at least when averaged over a 5-yr period, we consider the above estimate to be representative of the open Baltic proper north of the Bornholm basin. Extrapolation to the Baltic proper (Fig. 1, area at depths $>10 \text{ m}$, $1.96 \times 10^{11} \text{ m}^2$), except the Arkona basin, by assuming proportionally higher rates in the Bornholm basin, gives an estimated total annual nitrogen fixation of $170\text{--}390 \text{ Gg N}$. By assuming upper and lower bound estimates of 60 and $210 \text{ mmol N m}^{-2} \text{ yr}^{-1}$ in the Arkona basin (7% of the Baltic proper area), we get an estimate for the whole Baltic proper of $180\text{--}430 \text{ Gg N yr}^{-1}$. This is considerably

higher than earlier estimates of 100 Gg N yr^{-1} by Niemistö et al. (1989) and $20\text{--}190 \text{ Gg N yr}^{-1}$ by Hübel and Hübel (1995), the latter including also the Belt Sea but not the northern Baltic proper. Our estimate brackets a recent estimate by Wasmund et al. (in press) of 370 Gg N yr^{-1} . Recently, Rahm et al. (2000) used a biogeochemical approach to estimate N fixation at $30\text{--}260 \text{ Gg N yr}^{-1}$, excluding the Belt Sea and parts of the Arkona Sea as well as the northern Baltic proper. They based their estimate on the DIP pool remaining after depletion of the winter store of nitrate by the spring bloom, taking estimated external inputs of nitrate and DIP to the surface layer into account. They calculated N fixation as consumed DIP times 16 (the molar Redfield N:P ratio) and subtracted external DIN supply. However, our data indicate that substantial nitrogen fixation starts only after the formation of a pronounced summer pycnocline (Fig. 5c; Paerl 1990; Hyenstrand et al. 1998). This normally occurs in June, ~ 2 months after depletion of DIN. Much of the DIP remaining after the spring bloom is used up before the build-up of filamentous cyanobacterial biomass commences (Fig. 3), partly through internal storage by cyanobacteria, as indicated by their low N/P ratio before the start of rapid growth. We found that the N:P ratio of filamentous cyanobacteria then increases dramatically during their growth period, making the Redfield assumption unreliable.

Assuming no settling losses, the increase in total nitrogen suggests average nitrogen fixation rates of $2.3\text{--}5.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ during the initial phase of the growth period. Niemistö et al. (1989) measured N fixation rates of $0.4\text{--}2.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ in different Baltic proper areas over 3 yr. Wasmund et al. (in press) found $0.8\text{--}11 \text{ mmol N m}^{-2} \text{ d}^{-1}$ in the eastern Gotland basin in July/August, and Stal and Walsby (1998) found an average of $0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ for *Aphanizomenon* sp. alone in late July/early August. Wasmund et al. (in press) used an improved ^{15}N -tracer method, whereas the other estimates were obtained by the acetylene reduction method. Varying conversion factors (reduced acetylene to N fixation) and other methodological problems (e.g., loss of DO^{15}N from samples) may bias measured values (Moisander et al. 1996) and affect comparability. Our N fixation estimates are well within the range of earlier Baltic proper direct estimates, but considerably higher than most oceanic estimates ($<0.3 \text{ mmol N m}^{-2} \text{ d}^{-1}$, Capone et al. 1997).

We estimated growth of filamentous cyanobacteria at $100\text{--}250 \text{ mmol C m}^{-2}$ over the summer of 1998 (Fig. 6). The maximum biomass reached $2.4 \text{ mmol C m}^{-3}$ or 48 mmol C m^{-2} in the top 20 m of the water column. This suggests slow growth and low loss rates because 20–50% of the cyanobacterial production was present as accumulated biomass after 3 months. This is consistent with observations of generally low loss rates of filamentous cyanobacteria due to sedimentation (Heiskanen and Kononen 1994; Sellner 1997; but see Heiskanen and Olli 1996 for an exception) and grazing (Sellner 1997). The notoriously slow growth rate of *Trichodesmium* has been suggested to be an adaptation for exploiting the high-energy but low-nutrient environment of ocean surface waters (Capone et al. 1997).

Our carbon fixation rates ($1.4\text{--}4.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$) are lower than *Aphanizomenon* net photosynthesis rates over 9 d in July/August 1993 ($4.2\text{--}13.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$, assuming

a photosynthetic quotient of 1.0) given by Walsby et al. (1997). However, because their biomass estimates were considerably higher than ours, their production to biomass ratios were almost an order of magnitude lower.

Assuming an average C:N ratio of 6.2 (Fig. 5a), the recorded accumulation of cyanobacterial biomass corresponds to an incorporation of 16–41 mmol N m⁻² into biomass, provided no other nitrogen source is used (cf. Mulholland and Capone 1999). This is only a minor fraction of the estimated N fixation in 1998 but encompasses the estimated total nitrogen increase (Table 2). There are several possible reasons for the discrepancy between the estimates based on growth and on biogeochemistry. Filamentous cyanobacteria can release much newly fixed N₂, primarily as amino acids (Capone et al. 1994). If true also for Baltic cyanobacteria, this will cause growth to underestimate nitrogen fixation. Because we have used a uniform particulate settling rate and stoichiometric composition of settling material, interannual variability is not considered. This may bias estimates of nitrogen fixation rates, particularly in years with a long cyanobacterial growth period, as in 1998.

Nonheterocystous cyanobacteria, at times a significant part of the cyanobacterial biomass, and heterotrophic bacteria may also be suspected of fixing nitrogen (e.g., in microoxic conditions [Paerl 1990] or at night [Bergman et al. 1997]). Single and colonial picocyanobacteria may at times surpass the filamentous cyanobacteria in biomass, but a report that they are able to fix nitrogen (Mitsui et al. 1986) remains largely unconfirmed. Recently, however, Wasmund et al. (in press) reported observations of high nitrogen fixation rates at night in the Baltic proper, which was attributed to cyanobacteria <10 μm. Our biogeochemical nitrogen fixation estimate will include all forms of nitrogen fixation in the upper mixed layer.

Cyanobacterial P demand—The C:P ratio of ~400 (0.28% P of dry weight) at the biomass peak indicates that only 0.12 mmol P m⁻² was required for its formation. This is nearly equal to the 0.11 mmol P m⁻² stored in *Aphanizomenon* biomass (5.5 mmol C m⁻², C:P = 50) in early June 1998 early in the growth phase and before the increase in C:P ratio. The DIP was already virtually exhausted, indicating that if the P needed for growth of diazotrophic filamentous cyanobacteria in summer comes from DIP left over from the spring bloom, most has already been stored in *Aphanizomenon* biomass at the start of the intensive growth period. The external DIP used for *Nodularia* growth must come from mineralization of organic matter, from turbulent mixing (e.g., pycnocline erosion, see Fig. 5c), from upwelling (Kononen et al. 1996), or from P transport by vertical migration from below the summer pycnocline (cf. Hyenstrand et al. 1998). From the maximum estimated N fixation in Table 2 and the N:P ratio (65) at maximum biomass in Fig. 5b, we can estimate a maximum P demand by diazotrophic cyanobacteria in 1998 of 1.6 mmol P m⁻², of which ~0.1 mmol P m⁻² was initially present in biomass. Over a 70-d growth period, cyanobacteria must then on average acquire only ~0.02 mmol P m⁻² d⁻¹, which is most likely an overestimate, since our data suggest that much fixed N₂ is released and not incorporated into biomass.

Unlike *Aphanizomenon*, both *Nodularia* and *Anabaena* seem to lack early summer seed populations (Wasmund 1997). Once established, the rapid growth of *Nodularia spumigena* may be due to a competitive advantage over *Aphanizomenon* in a higher affinity for P (Wallström et al. 1992). Like *Nodularia*, lake isolates of *Anabaena* spp. have higher affinity for P than *Aphanizomenon* (De Nobel et al. 1997), but taxonomic difficulties suggest caution when extrapolating from studies of isolates of non-Baltic origin.

Cell stoichiometry indicates that the filamentous cyanobacteria are nitrogen-sufficient throughout their growth period (C:N ≤ 6.6), but that they successively develop severe P deficiency, culminating at the biomass peak. This is consistent with findings of Karl et al. (1992), who reported very high C:P ratios (twice ours) but similar C:N ratios in surface accumulations of *Trichodesmium* in the North Pacific Ocean. Later, Letelier and Karl (1998) reported high C:P ratios also in trichomes from various depths in the same area. Severely P-deficient cells grow only at a few percent of their maximum rate (Healey 1982). In view of this, our C:P data suggest a progressive decrease in growth rate to near zero at the biomass peak, which is consistent with the slow average increase in biomass.

Concluding remarks—To our knowledge, this is the first marine demonstration of a clear increase in TN concentrations in the whole upper mixed layer as a result of nitrogen fixation. Niemistö et al. (1989) noted increased TN concentrations in Baltic proper surface accumulations, and Karl et al. (1992) demonstrated significant enrichment of dissolved organic nitrogen in North Pacific Ocean surface water with dense accumulations of *Trichodesmium*.

Our estimates imply that nitrogen fixation sustains a considerable fraction of net community production in the Baltic proper in summer. Using an average C:N ratio of 7 in particulate matter (Walve and Larsson, unpubl. data), fixed N₂ may have contributed 0.4–1.0 mol C m⁻² during the 3 months of elevated TN concentrations in the mixed layer. If Stigebrandt's (1991) net plankton community production estimate of 375 mmol C m⁻² month⁻¹ in July and August is valid also for June, then fixed N₂ can sustain between a third and near 90% of the net plankton community production in summer. A similar importance of nitrogen fixation has recently been suggested by Karl et al. (1997) for the subtropical North Pacific Ocean and by Capone et al. (1998) for the central Arabian Sea. Consequently, new production (sensu Dugdale and Goering 1967) in summer seems to be driven largely by nitrogen fixation and, to a lesser extent, by atmospheric deposition and turbulent mixing of combined N (NH₄⁺ and NO₃⁻) through the seasonal pycnocline. This is consistent with very low concentrations of combined N in the water mass between the permanent halocline and seasonal pycnocline in summer. It also agrees with the observation of Rolff (2000) of low ¹⁵N:¹⁴N ratios, indicative of fixed atmospheric nitrogen, in all size fractions of Baltic proper plankton in late summer 1996.

That more nitrogen is fixed than is needed for the estimated growth of heterocystous cyanobacteria suggests that cyanobacteria release substantial amounts of fixed N₂. Land-sort Deep data from 1998, the year with the longest growth

period, indicate that several times more nitrogen may be fixed than incorporated in cyanobacterial biomass. Such a release of fixed N_2 may have several causes (cf. Paerl and Millie 1996), but its magnitude suggests the possibility of diazotrophy in organisms other than heterocystous cyanobacteria (Wasmund et al. in press).

Our data conclusively demonstrate that filamentous cyanobacteria deviate considerably from Redfield ratios during their seasonal development. Inclusion of this variability is needed for realistic representation of bloom development in oceanographic calculation models and most probably for development of prognostic models.

Putting Baltic proper nitrogen fixation into perspective, our estimate at the upper end is almost as large as the entire riverine load (480 Gg $N\ yr^{-1}$; natural plus anthropogenic, load to Gulf of Finland excluded) and twice the atmospheric load (~ 200 Gg $N\ yr^{-1}$; natural plus anthropogenic) (Elmgren and Larsson 2000). Despite this impressive fixation of N_2 , recent budget calculations (Wulff et al. 2001) support earlier conclusions (e.g., Granéli et al. 1990) of nitrogen as the main element controlling net plankton community production in the Baltic proper.

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Received: 26 April 2000
Amended: 15 January 2001
Accepted: 22 January 2001