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Ecological stoichiometry of TN : TP : SRSi in freshwaters: nutrient ratios and seasonal shifts in phytoplankton assemblages

Katrin Teubner and Martin Dokulil

With 7 figures and 2 tables

Abstract: Our concept of the ‘balance of TN : TP : SRSi-ratios’ attempts to determine whether the seasonal succession of phytoplankton communities is influenced by or responds to nutrient stoichiometry. Because the molar average of TN : TP : SRSi = 20 : 1 : 17 for 118 measurements (7 lakes, 3 inflows, all seasons) was close to the marine optimum stoichiometric ratio, we used the ratio TN : TP : SRSi = 16 : 1 : 17 as a reference point for ecological stoichiometry. Triangular diagrams of TN : TP : SRSi ratios scaled in physiological proportions of 16 : 1 : 17 were used to identify seasonal fluctuation patterns of major phytoplankton nutrients. In lakes with ‘balanced nutrient ratios’ TN : TP : SRSi ratios vary evenly around the stoichiometric optimum of 16 : 1 : 17 within a year. Lakes with balanced nutrient ratios, however, were more the exception than the rule and only occurred in 2 of 7 lakes studied. Lakes with constant concentrations of one nutrient element in relation to those of the other two were common. Unbalanced nutrient ratios were associated with relatively constant concentrations of either SRSi, or TN or TP. The relative change in availability of soluble reactive silica was more affected by differences in lake morphometry than that of TN or TP. Ratios of TN : TP : SRSi have the advantage of synoptically presenting the relative nutrient availability for both diatoms and non-siliceous algae in phytoplankton communities. Shifts within the tripartite ratio correspond to successive substitution of phytoplankton groups, e.g. from diatoms to cyanobacteria.

Key words: N, P, Si, cyanobacteria, diatoms.

Introduction

Freshwater phytoplankton communities are comprised of siliceous and non-siliceous algae. Silica as well as nitrogen and phosphorus are, thus, of critical

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importance as macronutrients. Beside nutrient concentrations and their fluxes, the stoichiometric proportion between nutrients are key factors for algal growth in plankton communities (e.g. SAKAMOTO 1966, FORSBERG & RYDING 1980, SMITH 1982, 1983, SØNDERGAARD et al. 1999). In the present study, stoichiometric ratios between N, P and Si are evaluated in lakes along a trophic gradient using triangular diagrams (GIBBS 1878, VAN DAM et al. 1981, BAILEY-WATTS & KIRIKA 1987, SANDGREN 1988, PINTO & MORAIS 1994).

Variability in relative nutrient concentrations may be judged either by the relative change of a single element or by the stoichiometric ratios between available nutrients. Fluctuations in concentrations of a single element are important with respect to adaptation processes enabling organisms to detect relative rather than absolute changes (BRAY 1995). Cyanobacteria are able to adjust to external phosphate fluctuations by adaptive responses to threshold values and kinetic properties (WAGNER et al. 1995). Stoichiometric relations among elements are central to the theory of resource-ratio-competition between algae (TILMAN 1982, MAKULLA & SOMMER 1993, SOMMER 1993), consumer driven nutrient recycling (ELSER & URABE 1999) and perhaps food chain efficiency (STERNER et al. 1998).

Ecological stoichiometry of major phytoplankton nutrients is examined in our study using tripartite ratios between total nitrogen (TN), total phosphorus (TP) and soluble reactive silica (SRSi) and addresses the following questions:

What are the patterns of seasonal fluctuations of TN : TP : SRSi in meso- to hypertrophic lakes? Are elements with faster recycling times, such as phosphorus and nitrogen, less affected by lake type than the more slowly recycled Si? Can the Redfield ratio be generally applied to freshwater systems? Can the relative nutrient availability for phytoplankton assemblages be synoptically evaluated?

Materials and methods

In 1990-91, monthly samples were taken from a number of lakes in the vicinity of the city of Berlin [Langer See (LANS), Großer Müggelsee (MUES), Flakensee (FLAS) and Krumme Lake (KRUL)], and in the biological reserve 'Schorfheide-Chorin' in Brandenburg, to the north of Berlin [Parsteiner See (PARS), Rosinsee (ROSS) and Großer Plagesee (GPLA)]. In addition, the inlet waters of riverine lakes of a lowland lake system were sampled [inflows of Großer Müggelsee (MUEZ) and Flakensee (Woltersdorfer Schleuse FLZW, Löcknitz FLZL)]. Monthly sampling was continued for Langer See, Rosinsee and Parsteiner See into 1992. A biweekly interval was followed in Großer Müggelsee and Flakensee including their inlet waters (MUEZ, FLZL, FLZW) in 1992-93. Samples were integrated over the mixed surface layer during periods of thermal stratification.

Conductivity, TN, TP and SRSi were estimated using standard techniques (APHA 1992). Euphotic depth was calculated from under-water light attenuation using a 4 π quantum sensor (LI-COR). The biovolume of phytoplankton was estimated microscopically according to the Utermöhl method (1958). The mean value of the normal or the log-normal distribution was selected for abundance distribution (single cells, filaments or number of colonies) depending on which fitted better. For taxonomic details of diatoms refer to TEUBNER (1995, 1997), for other algae to TEUBNER (1996) and TEUBNER et al. (1997).

The step-wise extraction of limnological parameters was repeated in principal component analysis (PCA) until the first two components represented more than 80 % of the total variance (8 limnological variables in Fig. 2 B, cases: 10 waters represented by long-term averaged data, method: HENRION et al. 1988, HENRION & HENRION 1995). These limnological parameters extracted by PCA were included in the hierarchical cluster analysis (HCA, Fig. 2 C).

Triangular diagrams of nutrient ratios and phytoplankton structure

Triangular diagrams based on seasonal nutrient concentrations and phytoplankton biovolume (spring: March-May, summer: June-August, autumn: September-November, winter: December-February) were created in GRAPHER 4.0 for Windows, Golden Software, Inc.

In order to show the relative nutrient availability, the concentrations for total nitrogen (TN), total phosphorus (TP) and soluble reactive silica (SRSi) were used, based on the following arguments. In contrast to silicon which is recycled from organic matter at longer intervals (SOMMER 1988, BARKER et al. 1994), phosphorus and nitrogen are rapidly recycled. Algae have no storage capacity for silicon, but phosphorus and nitrogen can be intracellularly stored (e.g. polyphosphate bodies, cyanophycin granules); N and P from these stores can be mobilised and utilised for algal growth after external inorganic dissolved N and P pools are exhausted (DROOP 1973, GIBSON & FOY 1988). Consideration only of inorganic dissolved nitrogen and phosphorus thus would ignore the potential growth that can be driven by stored resources. The seasonality of total nitrogen and total phosphorus is closely paralleled by seasonal fluctuations of their dissolved inorganic fractions unless they become undetectable. Therefore TN and TP are better estimators of the total nutrient pool available for algal growth than the dissolved fractions alone. Moreover some components of dissolved organic nitrogen and dissolved organic phosphorus are available for algal growth (cf. REYNOLDS 1997, THOMPSON & RHEE 1994, MOSS et al. 1996, SOMMER 1999).

A scheme for simplifying the interpretation of triangular diagrams is shown in Fig. 1.

In triangular diagrams points represent the sum of three components equal to 100 %. If molar concentrations [$\mu\text{mol/l}$] of the three macronutrients are used as the three components to construct triangular graphs, it is possible to read the stoichiometric triple ratios directly (Fig. 1 A, 3). The corners of the triangle represent the concentration of one element only (100 %) and the absence of the remaining two nutrients. Following from $\text{SRSi} = 0$ and $\text{TN} : \text{TP} = 16 : 1$ by moles, the percentage ratio of TN : TP

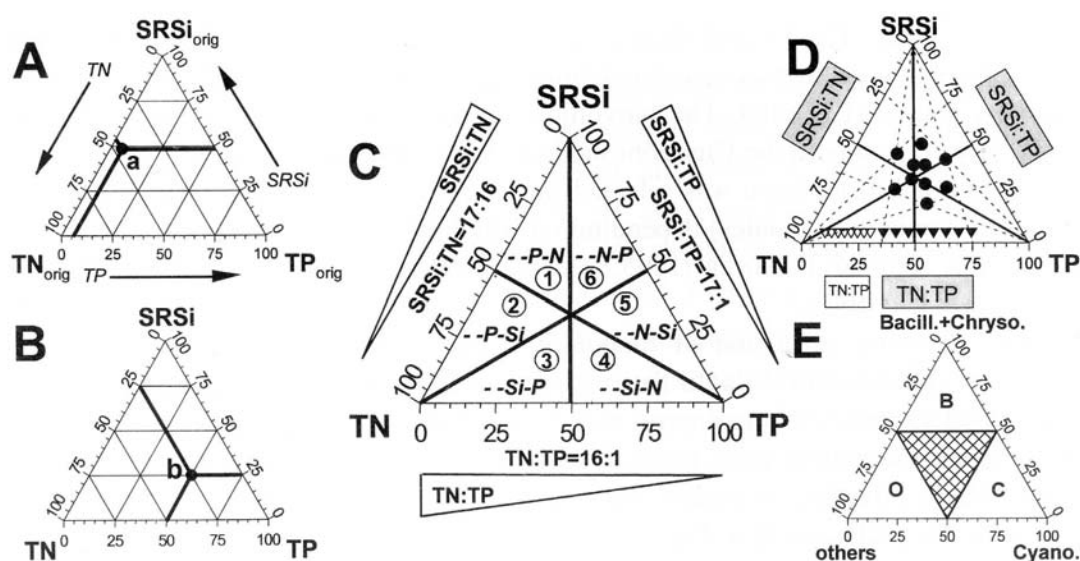


Fig. 1. Examples of how to read the triangles to evaluate nutrient ratios (A-D) and phytoplankton structure (E). **A:** Example for non-transformed nutrient ratios. Point 'a' represents the ratio of concentrations of $TN_{orig} : TP_{orig} : SRSi_{orig} = 45.71 : 5.71 : 48.57$. The sum of these three relative concentrations is 100. The arrows follow the scaling of axes. **B:** Example for normalised nutrient ratios. Point 'b' represents the ratio of concentrations of $TN : TP : SRSi = 25 : 50 : 25$. The sum of these three concentrations is 100. This normalised macronutrient ratio can be recalculated to the non-transformed $TN_{orig} : TP_{orig} : SRSi_{orig}$ ratio. For $TN = 25$ and $R_{TN} = 16$ is $TN_R = TN \cdot R_{TN} = 25 \cdot 16 = 400$, analogously for $TP_R = 50 \cdot 1 = 50$ and for $SRSi_R = 25 \cdot 17 = 425$. Dividing these three quantities by its sum ($TN_R + TP_R + SRSi_R = 875$) yields the original ratio $TN_{orig} : TP_{orig} : SRSi_{orig} = 48.57 : 5.71 : 45.71$. Therefore, the normalised ratio of concentrations of the point 'b' corresponds to the non-transformed ratio of the concentrations of the point 'a' in panel A. See Methods for reasons for normalisation. **C:** Lines and sectors in normalised nutrient triangles: Generally the bold lines mark the course of concentration of the element at the corner from 100 % to 0 % with a constant ratio of the remaining two nutrients. The point of intersection of the three bold lines (in the centre) indicate the molar ratio of $TN : TP : SRSi = 16 : 1 : 17$. The bold line $TN : TP = 16 : 1$ marks the constant $TN : TP$ ratio of 16 : 1 at variable $SRSi$. Analogously the other lines indicate the constant ratio of $SRSi : TP = 17 : 1$ at variable TN , of $SRSi : TN = 17 : 16$ at variable TP . For description of sectors 1-6 and preference of limitation symbolised as e.g. '-P -Si' see method and Table 2. **D:** Three idealised cases to illustrate patterns of $TN : TP : SRSi$ fluctuations for normalised nutrient triangles: i. weak variability (open triangles, ∇) of TN and TP at a constant $SRSi$; ii. strong variability (solid triangles, \blacktriangledown) of TN and TP at a constant $SRSi$; and iii. strong variation (solid circles, \bullet) for all three elements. Note that the weak case (∇) covers half the range of the strong cases ($\blacktriangledown, \bullet$) for $TN:TP$, but variations of strong case for all three elements (\bullet) are identical for all three axis ($TN : TP$, $SRSi : TP$, $SRSi : TN$). Dashed lines for ranges of variation (boxes on axes). **E:** All points in sector C indicate a contribution of at least 50 % cyanobacteria to total phytoplankton biovolume. Analogously sector B represents $\geq 50\%$ Bacillariophyceae and Chrysophyceae and sector O $\geq 50\%$ of other algae. The points on the shadowed area indicate that no single algal group exceed 50 % of total biovolume.

is 94.12 : 5.88 (TN + TP + SRSi = 16 µmol/l + 1 µmol/l + 0 µmol/l = 100 % = 94.12 % + 5.88 % + 0 %). This point is indicated by the intersection of the TN : TP = 16 : 1 line on the TN-TP-axis (Fig. 3). The TP scaling is from left to right (arrow in Fig. 1 A) and the TN scaling from right to left on this axis. All points on the bold line '16:1' represent ratios of constant TN : TP = 16 : 1 but variable concentrations of SRSi. Points on the left side of the line represent ratios of TN : TP > 16 and points on the right side represent TN : TP < 16. The problem with such diagrams is that points fall on a small area because the concentrations of these three macronutrients differ by several fold (Table 1). Therefore, concentrations were first normalised to the reference point of TN : TP : SRSi = 16 : 1 : 17 (see below), which is close to the mean value over the entire data set (TN_{mean} : TP_{mean} : SRSi_{mean} = 20 : 1 : 17 for n = 118 measurements, normalisation in Figs. 1 C-D, 4-6). For that scaling reason the normalised concentrations are calculated by

$$C_{TN} = \frac{C_{TN\ orig}}{R_{TN}}, C_{TP} = \frac{C_{TP\ orig}}{T_{TP}} \text{ and } C_{SRSi} = \frac{C_{SRSi\ orig}}{T_{SRSi}}$$

with $R_{TN} = 16$, $R_{TP} = 1$, and $R_{SRSi} = 17$ ($C_{TN\ orig}$, $C_{TP\ orig}$, $C_{SRSi\ orig}$ in µmol/l). In normalised triangular diagrams (Fig. 1 B, 4-6) a triple ratio is calculated as the sum of three normalised components equal to 100 %. As a consequence of that scaling the three optimum lines of TN : TP = 16 : 1, TN : SRSi = 16 : 17 and TP : SRSi = 1 : 17 are displayed in the triangles in the proportion 1:1 (50%:50%, Fig. 4-6). Points representing seasonal nutrient ratios become more scattered and are easier to distinguish. Original TN:TP:SRSi ratios, however, can be recalculated by reversing the normalisation procedure. The example in Fig. 1 A-B shows that the normalised TN:TP:SRSi ratio of point b corresponds with the non-transformed TN_{orig}:TP_{orig}:SRSi_{orig} ratio of point a.

For the present purposes we assume that the molar ratio N:P:Si=16:1:17 (recalculated from data in HARRIS 1986, p.63), which in a strict sense refers to cellular content only, reflects stoichiometric demand by the algal organisms. In this paper we call this ratio the 'optimum ratio' and use it as a reference point for ecological stoichiometry. The position of TN:TP:SRSi = 16:1:17 in the centre of the normalised triangles implies that the variations of TN, TP and SRSi are scaled in the physiological proportion of the optimum ratio. To put it simply, scattering of points extending an equal distance along each of the three lines (TN:TP=16:1, SRSi:TP=17:1 and SRSi:TN = 17:16 respectively, case iii in Fig. 1 D) shows physiologically equivalent proportional variations of TN, TP and SRSi. The dynamics of the three nutrients in the normalised triangular diagrams are therefore directly comparable (example for three idealised cases in Fig. 1 D) and have the same physiological relevance (Fig. 4-6). We emphasise that such normalised TN:TP:SRSi diagrams present the relative variability of physiologically scaled nutrient concentrations.

The sectors labelled with 1 to 6 in Fig. 1 C indicate six combinations of TN:TP, SRSi:TN and SRSi:TP ratios. Points which fall e.g. into sector 2 have simultaneous ratios of TN:TP > 16:1, SRSi:TP > 17:1 and SRSi:TN < 17:16, indicating that algal growth is primarily controlled by P and secondly by Si but not by N (strong P-limitation and weak SRSi-limitation, but no N-limitation symbolised as minus elements '-P -Si' in Fig. 1 C). The interpretation for the other sectors defined by three lines in Fig. 1 C follows the logic described above.

Triangular diagrams of phytoplankton structure are based on biovolumes of algal classes of single seasons (Fig. 7). By analogy to the TN:TP:SRSi diagrams the siliceous Bacillariophyceae and Chrysophyceae are arranged at the top (Fig. 1 E), the corner of high SRSi:TN and high SRSi:TP (1 C). Cyanobacteria, known for their frequent relationship to low N:P ratios, are assigned to the right-hand corner (TP) indicating low N:P-ratios. The remaining algae (others: Chlorophyta s.l., Cryptophyceae, Dinophyceae etc.) have been placed at the remaining corner of high TN:TP ratios and low silicon concentrations.

Results

Trophic and limnological characterisations of the investigated lakes are given in Figs. 2. The trophic levels of the waters ranged from meso- to hypertrophic, but the majority were hypertrophic (Fig. 2 A). Based on the limnological conditions in the various lakes, four discrete categories were distinguished (Fig. 2 B-C). The ‘hypertrophic riverine lakes’ (MUES, MUEZ, LANS) are shallow, turbulent mixed lakes (high ratio of mixed zone to maximum depth, $z_{\text{mix}}:z_{\text{max}}$) with high concentrations of chlorophyll-a, TP and SRSi. The ‘waters of moderate mineral content’ (FLAS, FLZL, FLZW) are characterised by a higher conductivity than other soft waters (Table 1) and a low TN:TP ratio because of low TN concentrations. The ‘dimictic, mesotrophic lakes’ (PARS, ROSS) are lakes with relatively shallow z_{mix} but high z_{max} and high TN:TP ratios caused by low concentrations of TP (Table 1). The combination of high TN:TP ratios and low conductivity accords with the character of the ‘dystrophic lakes’ (GPLA, KRUL). The high concentration of TOC at low alkalinity also distinguishes the last two lakes as being dystrophic (Fig. 2 D).

The molar average TN:TP:SRSi ratio over all seasons for the 7 lakes and 3 inflows is 20:1:17. The relationship among the three macronutrients in the four categories of lakes is shown in Fig. 3. The dimictic mesotrophic lakes and dystrophic lakes are marked by TN:TP ratios higher than 16:1 (points on the leftside of the bold line indicating TN:TP=16:1) and mainly had relatively low SRSi concentrations. In contrast the seasonal TN:TP ratios of the hypertrophic riverine lakes cluster around 16:1 at higher SRSi concentrations. The waters of moderate mineral content showed other patterns associated with varying SRSi concentrations usually at TN:TP lower than 16:1.

Since TN:TP:SRSi ratios in Fig. 4-6 are only mathematically transformed, the results described for Fig. 3 are also valid for Fig. 4-6. Each panel shows the seasonal normalised TN:TP:SRSi ratios for an individual lake category (Fig. 4) or for a single representative lake (Fig. 5-6). The phytoplankton composition for the four lake categories are shown in Fig. 7.

In the case of the hypertrophic riverine lakes, seasonal averages are scattered along all three optimum-ratio lines of TN:TP = 16:1, SRSi:TP = 17:1

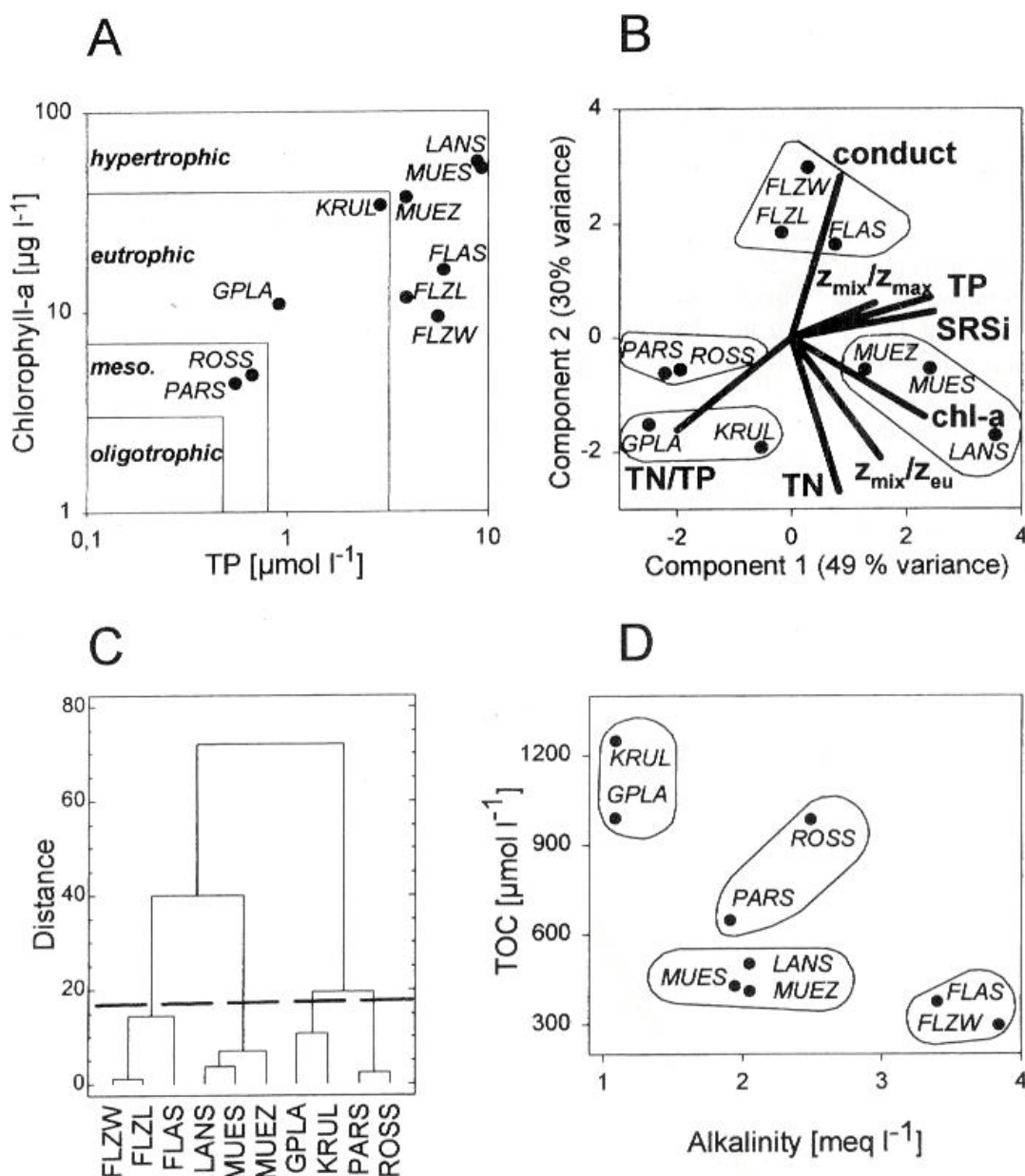


Fig 2. Overview of the limnology of the 10 investigated waters. **A:** Relationship between chlorophyll-a and TP concentration in the 10 waters. Trophic levels are indicated by the averaged data of the June-September period according to FORSBERG & RYDING (1980). **B:** Biplot of the second versus the first principal component for eight limnological variables (vectors) and distribution pattern of the waters (points). Waters assigned to four categories: -hypertrophic riverine lakes (MUES, MUEZ, LANS), -waters of moderate mineral content (FLAS, FLZL, FLZW), -dimictic, mesotrophic lakes (PARS, ROSS), -dystrophic lakes (GPLA, KRUL). **C:** Dendrogram of hierarchical cluster analysis. The broken line separates four categories of waters. Variables see B. Method: squared Euclidean distance, Ward linkage. **D:** Relation between alkalinity and TOC. Abbreviations of limnological parameters: conductivity (conduct), concentration of chlorophyll-a (chl-a), soluble reactive silicon (SRSi), total nitrogen (TN) and total phosphorus (TP), ratio of TN:TP (TN/TP), ratio mixed depth to euphotic depth ($z_{\text{mix}}/z_{\text{eu}}$) and to maximal water depth ($z_{\text{mix}}/z_{\text{max}}$), respectively.

Table 1. Morphometric and long term averaged limnological data for the 10 waters. Lake area and maximum depth from ANWAND 1973, retention time for MUES, LANS and FLAS (1992-93) from Kohl et al. (1994), for PARS, ROSS, GPLA and KRUL from SCHÖNFELDER ("Gewässerkataster und angewandte Gewässerökologie e. V. Brandenburg", pers. communication), Abbr. for lakes and years covered see method.

	KRUL	GPLA	PARS	ROSS	LANS	MUES	MUEZ	FLAS	FLZL	FLZW
conductivity [mS m^{-1}]	18.5	23.2	46.6	53.0	59.2	65.4	66.8	86.8	89.8	121.1
TN [$\mu\text{mol l}^{-1}$]	105.5	84.2	55.8	84.1	106.9	88.9	101.1	46.3	54.0	38.8
TP [$\mu\text{mol l}^{-1}$]	2.36	0.69	0.54	0.78	7.05	6.29	3.54	5.30	3.64	6.23
SRSi [$\mu\text{mol l}^{-1}$]	3.30	3.23	6.70	10.92	122.17	105.66	91.02	73.07	65.92	57.39
phytoplankton										
biovolume [$\text{mm}^3 \text{l}^{-1}$]	7.2	0.93	0.53	1.1	11.7	9.9	5.6	3.1	1.7	1.6
area [km^2]	0.15	0.78	11	0.2	1.53	7.7	inflow	0.73	inflow	inflow
max. depth [m]	4.8	5	27	9	7	7.5	5.0	4.5	8.5	3.8
euphotic depth [m]	2.3	4.4	10.2	7.1	2.4	3.5	3.3	4.8	4.9	6.2
mixing depth [m]	3.92	4.89	19.71	6.81	6.9	7.2	5.0	4.78	6.79	3.8
retention time	1 y	5 y	15 y	1.2 y	4.1 d	67.2 d		28.9 d		

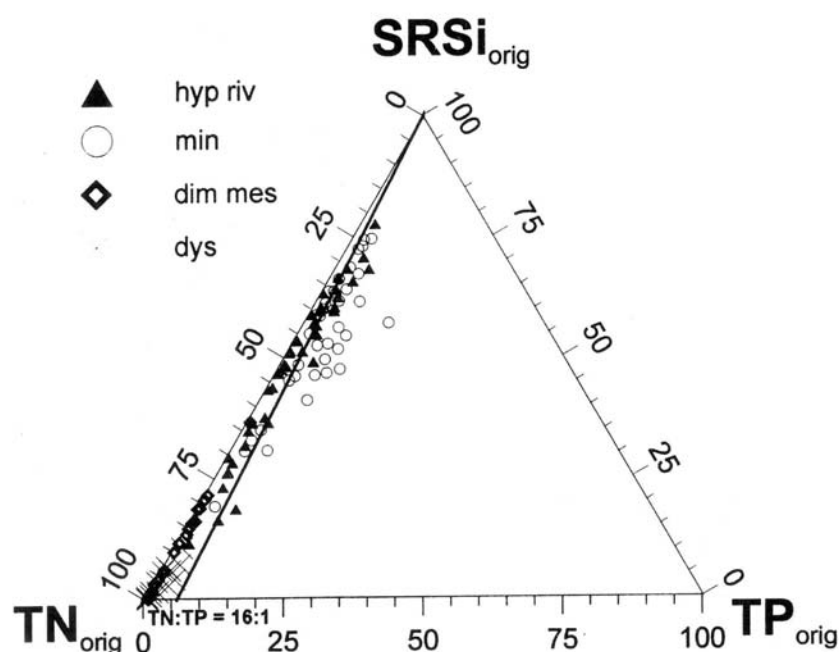


Fig. 3. Triangular diagrams of seasonal non-transformed $\text{TN}_{\text{orig}}:\text{TP}_{\text{orig}}:\text{SRSi}_{\text{orig}}$ ratios for the four categories of waters. The bold line marks the constant ratio of $\text{TN}:\text{TP}=16:1$ at variable SRSi (calculation of the intersection point of the line on axis see method, lake categories according to Fig.2 C-D: hyp riv - hypertrophic riverine lakes; min - waters of moderate mineral content; dim mes - dimictic, mesotrophic lakes; dys - dystrophic lakes).

and $\text{SRSi}:\text{TN}=17:16$ (Fig. 4 A). Nutrient ratios (i) circle around the optimum point 16:1:17 within a year and (ii) the $\text{TN}:\text{TP}$, $\text{SRSi}:\text{TP}$ and $\text{SRSi}:\text{TN}$ were highly fluctuating in the same range as indicated by the similar length of the

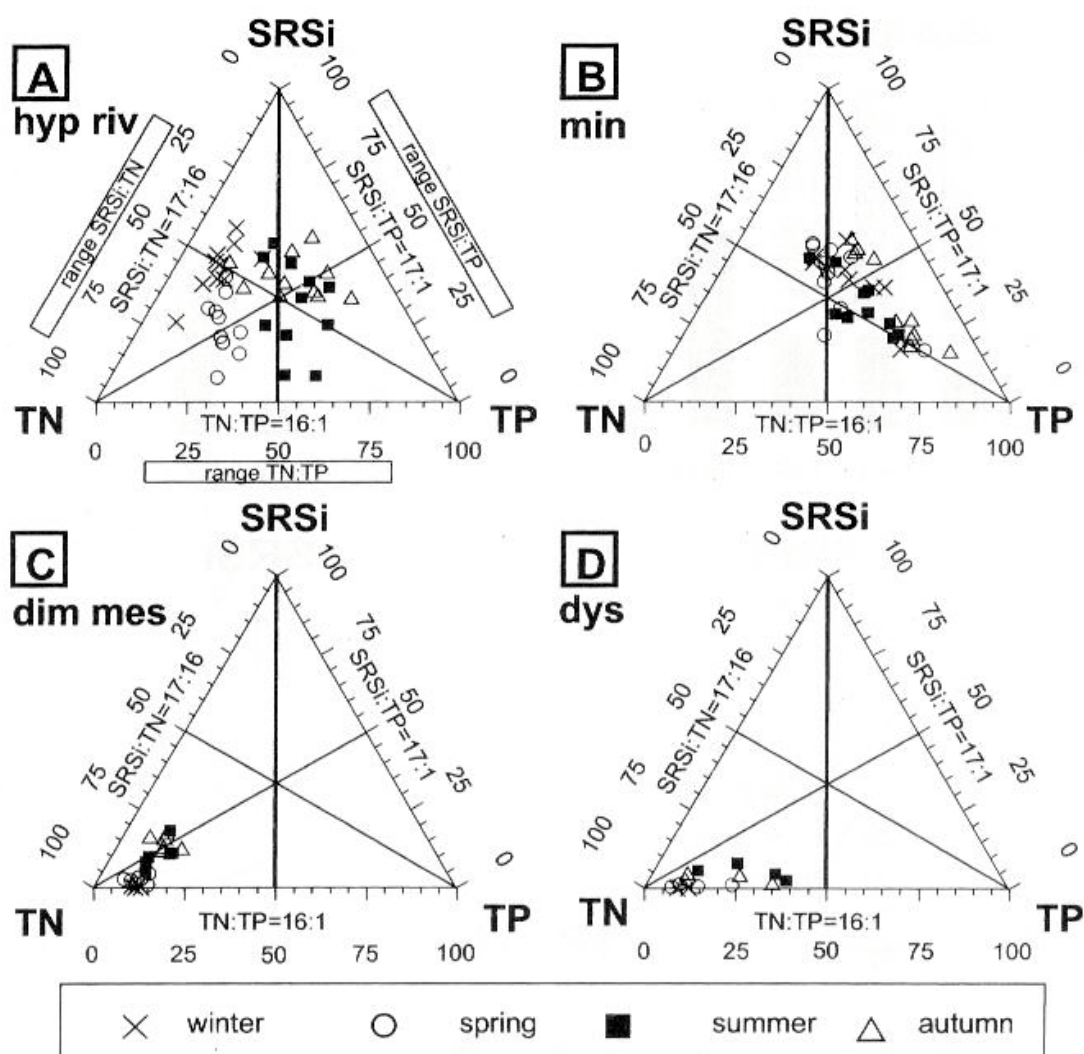


Fig. 4 A-D. Triangular diagrams of normalised TN:TP:SRSi ratios in the four categories of limnological similar waters. Every point represents an annual average of winter, spring, summer or autumn of a single water [lines and the intersection of the three lines of optimum ratios and patterns see Fig. 1 C-D; bars in A show the range of fluctuations of TN:TP, SRSi:TP and SRSi:TN as illustrated in Fig. 1 D; seasonal averaging for 10 waters (n=118) see method, water categories see Fig. 3].

bars on the three axis (see idealised case iii in Fig. 1 D). This implies a high seasonal interaction of TN, TP and SRSi in physiologically optimal proportions (see scaling method). Accordingly, the hypertrophic riverine lakes were termed '**balanced nutrient ratio lakes**'. The counterclockwise rotation of points around the optimum ratio of TN:TP:SRSi = 16:1:17 (Fig. 4 A) reveals a non-random pattern correlated to seasons. In winter, the TN:TP and SRSi:TP ratios were higher than the optimum, the SRSi:TN ratios scattered around 17:16 (compare sector 1-2 in Fig. 1 C with Fig. 4 A). From winter to spring, SRSi concentrations declined at TN:TP values higher than 16:1 (sector 2-3). The TN:TP ratio usually changes from higher than 16:1 to lower

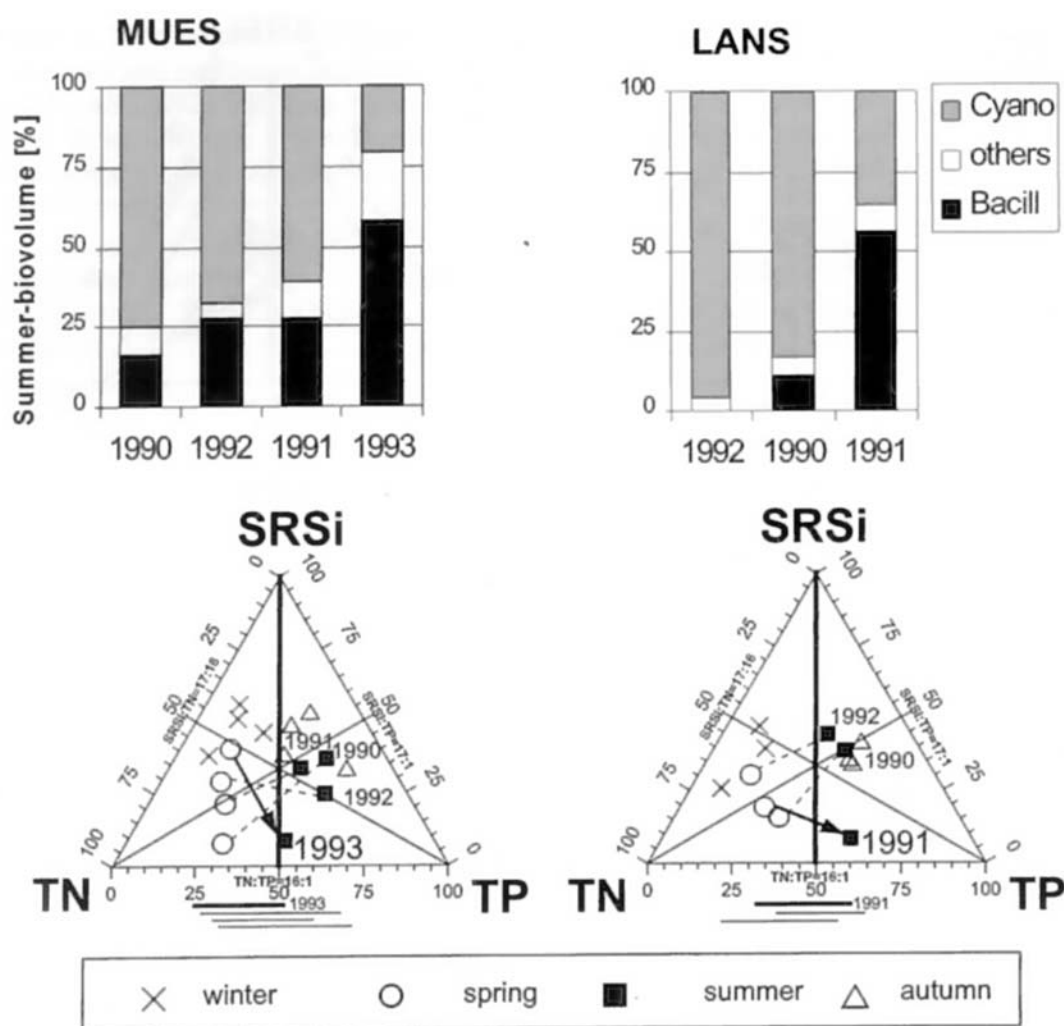


Fig. 5. Phytoplankton in summer (barcharts) and seasonal TN:TP:SRSi ratios for Großer Müggelsee (MUES) and Langer See (LANS) representative for the hypertrophic riverine lakes. Barcharts: Percentage of algal classes by total biovolume [$\text{mm}^3 \text{l}^{-1}$], Abbr.: Cyano = Cyanobacteria, Bacill = Bacillario- plus Chrysophyceae, other = the remaining algae. Triangular diagrams normalised as in Fig. 4. The arrows connect points for spring and summer of 1993 (MUES) and 1991 (LANS) while dashed lines connect those points for all other years. Bars below the TN:TP-axis indicate the variation of TN:TP for MUES 1993 and LANS 1991 (bold) in comparison to other years.

than 16:1 during the progression from spring to summer (sector 3-4). The relative increase of Si in the autumn is indicated by the increase of SRSi:TN and SRSi:TP with low TN:TP (sector 4-5). The TN:TP ratio changed back from <16:1 to >16:1 from autumn to winter. The strong nutrient interaction within a year is expressed by the dispersed cyclic pattern through all nutrient combinations (points join sectors 1-6, compare with Fig. 1 C and Table 2, idealised case iii in Fig. 1 D). These seasonal changes which generally occurred in the

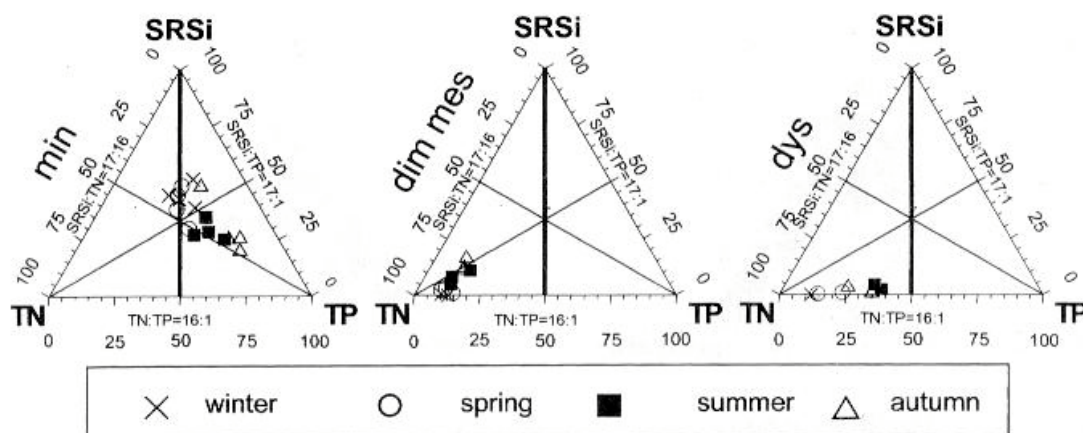


Fig. 6. Seasonal TN:TP:SRSi ratios for single lakes representative for waters of moderate mineral content (min: FLAS), dimictic mesotrophic lakes (dim mes: ROSS), dystrophic lakes (dys: KRUL). Normalisation and lines as in Fig. 4.

Table 2. TN:TP, SRSi:TN and SRSi:TP ratios for sectors in Fig. 1 C (see Methods).

sector	TN : TP = 16 : 1	SRSi : TP = 17 : 1	SRSi : TN = 17 : 16
1	higher	higher	higher
2	higher	higher	<i>lower</i>
3	higher	<i>lower</i>	<i>lower</i>
4	<i>lower</i>	<i>lower</i>	<i>lower</i>
5	<i>lower</i>	<i>lower</i>	higher
6	<i>lower</i>	higher	higher

hypertrophic riverine lakes are also characteristic for specific lakes of this category, the Großer Müggelsee and Langer See (Fig. 5).

The phytoplankton usually consisted of at least 50 % siliceous algae (mainly diatoms) or at least 50 % Cyanobacteria (nitrogen fixers: *Aphanizomenon flos-aquae*, *Anabaena flos-aquae*; non-nitrogen fixers: *Planktothrix agardhii*, *Microcystis* spp.; Fig. 5 and 7 A). Summer blooms with biovolume averages of 32 mm³/l in Großer Müggelsee and 25 mm³/l in Langer See were usually dominated by Cyanobacteria, whereas diatoms contributed only about 25 % (MUES: 1991-92, LANS: 1990, 1992, Fig. 5). Whenever summer phytoplankton composition shifted significantly towards diatom domination of more than 50%, concomitant changes in TN:TP:SRSi ratios occurred. As indicated by arrows downwards in the triangles a much stronger reduction of relative SRSi was clearly seen for 1993 in MUES and 1991 in LANS in comparison to other years indicated by dashed lines (Fig. 5). This decrease of SRSi:TP and SRSi:TN is usually coupled with a smaller change of TN:TP (see shortness of bold bars of respective years in comparison to other years on TN:TP-axis in Fig. 5).

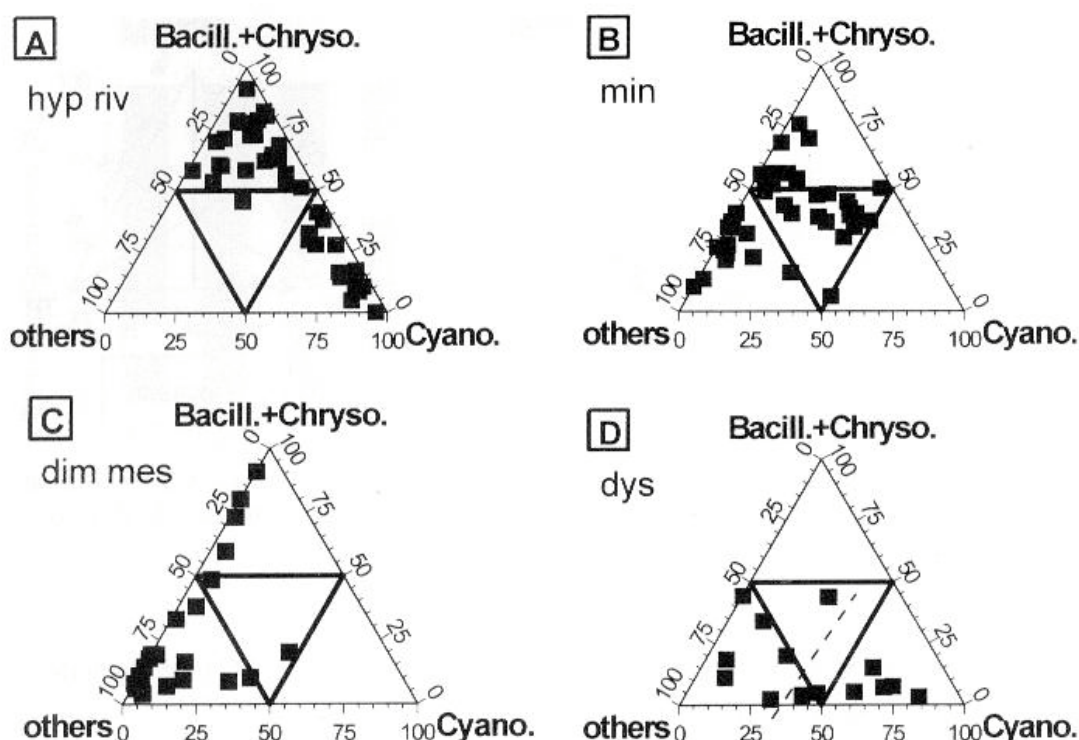


Fig. 7 A-D. Triangular diagram of phytoplankton structure for the four lake categories. Reasons for the arrangement of algal groups at the corners are given in the method. Dashed line in D separate GPLA (leftside) from KRUL (rightside). For easy reading see fig. 1 D. Abbr. of algal groups see Fig. 5, lake categories see Fig. 3.

In contrast to seasonal fluctuations of all the three elements in the hypertrophic riverine lakes, the seasonal variability in the other lakes mainly affected just two of the elements. Therefore, these are regarded as ‘**unbalanced nutrient ratio lakes**’. The arrangement of points parallel to an axis indicates strong variation between the two components of this axis with concentrations of the element on the opposite corner nearly constant. In dystrophic lakes, especially in the eutrophic dystrophic Krumme Lake (Fig. 2 A), with high variation in TN:TP relative to ‘constant’ SRSi (points arranged parallel to the TN:TP axis in Fig. 4 D and 6; idealised case ii in Fig. 1 D), the phytoplankton is dominated by either Cyanobacteria (e. g. nitrogen fixing: *Aphanizomenon skujae*, *Anabaena lemmermannii* and non-nitrogen fixing e.g. *Planktolytnbya subtilis*, *Snowella litoralis*, *Woronichia compacta*) or other non-siliceous algae, whereas diatoms have a negligible presence (Figs. 7 D). For the other dystrophic lake, Großer Plagesee, with a weaker variability of seasonal TN:TP ratios at ‘constant’ low SRSi, neither Cyanobacteria nor diatoms dominated (neither group ever exceed 50 % of total biovolume, Figs 4 D and 7 D, idealised case i in Fig. 1 D).

Deep dimictic mesotrophic lakes and shallow eu- to hypertrophic lakes with moderate mineral content showed weak seasonal variability in TN:TP ra-

tios but strong fluctuations in SRSi (Fig. 4 B-C). No increased likelihood of cyanobacterial dominance was evident (Fig. 7 B-C) although TN:TP ratios were lower than 16:1 in the Flakensee-group. In these lakes the phytoplankton was dominated by either diatoms or non-siliceous algae (excluding the Cyanobacteria) or by a balanced contribution from all three algal groups. Typical lakes from these two categories, however, showed the difference in the dynamic of TN:TP. Weak seasonal variations for TN:TP were caused in Rosinsee (dimictic mesotrophic lake) by variable TN concentrations with 'fixed' TP, while in Flakensee (water of moderate mineral content), TP concentrations varied with 'fixed' TN (Fig. 6, points parallel to the TN:SRSi-axis for Rosinsee but parallel to the TP:SRSi-axis for Flakensee).

Ratios in the lakes with unbalanced nutrient ratios deviated most from the reference point TN:TP:SRSi=16:1:17 by single elements as by nitrogen for FLAS (sector 5-6, - -N-P and - -N - Si), by phosphorus and silica for PARS (sector 2-3; - -Si - P and - -P - Si) and by silica for KRUL (sector 3; - -Si - P) as shown in Fig. 6 (sector description in Fig. 1 C and Table 2). No predominance for a single element limiting, however, was observed for lakes with balanced nutrient ratios as described above by points joining sectors 1-6.

Average TN:TP ratios were usually higher during winter/spring than during summer/autumn (Fig. 5-6). Different trends, however, were evident for SRSi concentrations in relation to TN:TP. Highest relative SRSi concentrations occurred (i) during summer/autumn for the dimictic mesotrophic lakes and the dystrophic lakes (Fig. 4 C-D, 6 (ROSS, KRUL)), (ii) during winter/spring in Flakensee (Fig. 6) and (iii) during autumn/winter in the hypertrophic riverine lakes (Fig. 4 A, 5).

Discussion

New approaches to ecological stoichiometry can show patterns otherwise not apparent. When the TN:TP:SRSi ratios are scaled to physiological proportions close to the optimum ratio, triangular ordination reveals different seasonal patterns of stoichiometric relationships among the nutrients. Nutrients might not necessarily vary in relation to each other throughout a given year. Lakes with constant concentration of one nutrient in relation to those of the other two seem to be more the rule than the exception. Lakes with unbalanced nutrient ratios are more common in the present data set than those with balanced nutrient ratios. These differences in nutrient ratio dynamics are the result of net-changes in the pool size of elements caused mainly by phytoplankton and lake type.

Dynamic of the N:P:Si ratio and phytoplankton structure

Since the classical study of REDFIELD (1958) on the elementary composition of marine plankton many investigations have focused on its application to freshwater and benthic communities (SMITH 1983, RHEE & GOTHAM 1980, HECKY et al. 1993, HILLEBRAND & SOMMER 1999). The relevance of the optimum ratio (REDFIELD 1958, RICHARDS 1958) for all the lakes investigated here derives from their close adherence of the mean TN:TP:SRSi ratio to 16:1:17. This holds true even for individual lakes having a balanced nutrient ratio dynamic (hypertrophic riverine lakes).

The importance of elemental ratios for phytoplankton has been studied in terms of relative nutrient availability (TILMAN 1982). Low N:P ratios favour the dominance of cyanobacteria during summer (e. g. SMITH 1983, STEINBERG & HARTMANN 1988, THOMPSON & RHEE 1994, SMITH & BENNETT 1999, BULGAKOV & LEVICH 1999), especially nitrogen-fixing species during the periods of nitrogen limitation (e.g. TRIMBEE & HARRIS 1984, SOMMER et al. 1986, DUDEL & KOHL 1991, DOKULIL & TEUBNER 2000). SRSi depletion in summer leads to a replacement of diatoms by other algae (e.g. cyanobacteria, SOMMER et al. 1986, TIPPMANN 1993). In all those studies nutrient ratios have been considered separately in pairs only, never as a tripartite ratio (SOMMER 1993). Hypertrophic riverine lakes with a balance between the three nutrients in principle illustrate, however, the rapid change in relative nutrient availability as reflected by yearly progression of the TN:TP:SRSi ratios within six stoichiometric regions separated by boundaries of optimal TN:TP, SRSi:TN and SRSi:TP. Changes in the TN:TP:SRSi ratio were reflected by the substitution of phytoplankton groups as can be exemplified by the lakes with balanced nutrient ratios. Years with stronger reduction of silica, implying a stronger decrease of SRSi:TP and SRSi:TN, were usually associated with a minor decline of TN:TP from spring to summer resulting in the replacement of cyanobacteria by diatoms (Fig. 5, for details about species see TEUBNER et al. 1999). By assuming that the optimum ratio 16:1:17 indicates average requirements of algae in the plankton communities, it is not surprising, that the lakes with balanced nutrient ratios reach highest algal biomasses as shown in Fig. 2 A. Other lakes in the same range of phosphorus concentration, retention time and euphotic depth but with unbalanced nutrient ratios are limited in algal growth as indicated by low chlorophyll (Fig. 2 B). Flakensee provides such an example of hypertrophic conditions which do not necessarily lead to a high dynamic of all macroelements resulting in low algal growth and hence low biomass.

In the past, nutrient ratios have been primarily viewed in a static way. Such an approach cannot explain the occurrence of cyanobacterial blooms at high TN:TP in one of the dystrophic lakes (KRUL) and the lack of cyanobacterial

dominance at low TN:TP ratios in the one hypertrophic lake (FLAS). In our opinion, TN to TP ratios lower than 16:1 are not always indicative of cyanobacterial dominance, but highly fluctuating TN:TP ratios appear to favour cyanobacteria. This hypothesis is substantiated by the high fluctuation in TN:TP associated with cyanobacterial dominance, as in the eutrophied dystrophic lake (KRUL) and the two hypertrophic riverine lakes. Long-term increase of nitrogen and phosphorus at low silica, as was observed in KRUL, caused dramatic shifts in the phytoplankton structure from diatoms to blue-green or green algae (e.g. SCHELSKE & STOERMER 1971, TILMAN 1982, SOMMER 1988, HUMBORG et al. 1997). Alternative blooming of either *Aphanizomenon flos-aquae* RALFS ex BORN. et FLAH. or *Planktothrix agardhii* (GOM.) ANAGN. et KOM. was induced by the timing of the critical TN:TP ratio of 16:1 in the hypertrophic riverine lakes as was previously shown by TEUBNER et al. (1999). In contrast, cyanobacteria were not dominant in lakes with weak TN:TP variation irrespective of their trophic state as observed in dimictic mesotrophic lakes (PARS, ROSS) and the rapidly flushed hypertrophic lake (FLAS), even if TN:TP ratios lower than 16:1 prevailed for several weeks. Highly variable SRSi concentrations at low seasonal variability of TN:TP indicated the favourable conditions for diatom blooms over cyanobacteria. The absence of cyanobacterial blooms even when conditions should be favourable because of low N:P ratios has been previously reported (e.g. SOMMER et al. 1986, SMITH & BENNETT 1999).

Fluctuations in TN:TP:SRSi are intimately linked to variable phytoplankton structure because of the particular Si-uptake and -accumulation by siliceous algae and the wide variability in their cellular composition with respect to nitrogen and phosphorus. The ability to store N and P intracellularly for later usage by some algal groups enhances the wide fluctuations of these elemental pools. Specifically for Großer Müggelsee, BEHRENDT (1990) has shown that the variation of elemental composition of seston samples is strongly affected by blooms of either diatoms or cyanobacteria. In contrast to the phytoplankton, the (meso)-zooplankton species maintain a relatively constant elemental composition even if they ingest food with an elemental composition much different from their body (ELSER & GEORGE 1993, VREDE 1998, CAPRILLO et al. 1996, GISMERVIK 1997, STERNER et al. 1998, ELSER & URABE 1999).

Beside nutrient ratios, temperature, light, or pulses of nutrients are important for resource competition (GOLDMAN 1986, TILMAN et al. 1986, WYNNE & RHEE 1986, SOMMER 1983, 1985, 1993, MAKULLA & SOMMER 1993). Therefore, the outcome of algal competition responds to a combination of nutrient ratios and co-varying environmental factors in lakes which can be designated by a template according to Reynolds (1998). Ratios of complex pools such as TN:TP seem to be driven by the match of processes ranging from environ-

mental factors, e.g. timing of temperature increase and mixing events, to food-web interactions. A previous study shows, that significant compositional changes in phytoplankton community occur only two times a year, i. e. from spring to summer and from autumn to winter and are therefore synchronised to the seasonal variation of the TN:TP in various lakes (TEUBNER 2000).

Lake type dependence of the N:P:Si ratio dynamic

Lake types, different in their trophic state and morphometry in this study, also reflect different seasonal dynamics in their nutrient ratios. The dynamic of the macroelements in these lakes is, to a large extent, a reflection of processes in the catchment (DOWNING AND MCCAULY 1992, PAERL 1997), of the proportion between external and internal nutrient load (LEVINE & SCHINDLER 1992, SØNDERGAARD et al 1999), and of the balance of autochthonous and allochthonous organic matter formation (HÅKANSON & PETERS 1995). Oxic cycling of nutrients can play a significant role in shallow polymictic lakes (REYNOLDS 1996) while the thermocline can remain an effective barrier in dimictic lakes (FEE 1979).

TN:TP decline from winter/spring to summer/autumn in all investigated lakes. In contrast, SRSi:TN and SRSi:TP varies individually in each lake. Thus, the relative change of silica seems to be more affected by lake type than by TN or TP (see also TEUBNER 2000). The epilimnetic cycle of Si runs much more slowly than the short-term cycles of phosphorus and nitrogen (SOMMER 1988). In lakes with very short retention times in the order of days to months (Table 1), the export of incorporated silica in diatoms through sedimentation and wash-out are largely replenished by the high silica concentrations in the inflow (BAILEY-WATTS et al 1989 a, b). The compensation of low internal cycling of silica by high external loading in hypertrophic riverine lakes is the crucial factor for the balance between Si and TN:TP supplies and is therefore essential for the variation of the three elements in physiological equivalent proportions to each other.

Dimictic mesotrophic and dystrophic lakes with long water renewal times and minimal inflows, however, depend almost entirely on internal silica recycling. Low silicon uptake in summer and reloading from the sediment associated with autumnal mixing (GIBSON et al. 2000) increase relative epilimnetic SRSi concentrations in the summer/autumn period. These lakes of unbalanced nutrient ratios are examples for directly related relative concentrations of silica and of phosphorus throughout the seasons. Concentrations of both elements are relatively high during summer/autumn and relatively low during winter/spring.

In contrast, the peak of relative SRSi concentration in winter/spring in the flushed lake with unbalanced ratios (Flakensee) indicates the delay in the de-

crease of silica at the beginning of the year because external loading makes up for the uptake by spring diatoms and the long turn-over time. In this lake relative concentrations of silica are inversely related to those of TP. An inverse relationship of silica and phosphorus is reported from long-term studies in stratified lakes elsewhere. Usually this is a consequence of P enrichment by eutrophication and hence accelerated silica depletion (SCHELSKE & STOERMER 1971, SCHELSKE et al. 1972, 1986).

Conclusions

To conclude, trophic situations were most commonly evaluated from concentrations of a single nutrient or a nutrient ratio, such as N:P. The basis of a more complex assessment is our concept of the 'balance of TN:TP:SRSi-ratios' in lakes. We used the ratio TN:TP:SRSi=16:1:17 as a reference point for ecological stoichiometry and call this the 'optimum ratio', in the sense of REDFIELD (1958) and HARRIS (1986) for plankton communities, but different from the definition by RHEE & GOTHAM (1980) for single species. Triangular diagrams have the benefit of presenting a synoptic picture of relative nutrient availability for phytoplankton communities and for evaluating multiple resource-ratio gradients. Nitrogen, phosphorus and silica are dynamically interrelated by non-random patterns correlated to seasons, phytoplankton community structure and lake types. These patterns indicate either a balanced or an unbalanced seasonal variation of TN, TP and SRSi. In lakes with balanced nutrient ratios TN:TP:SRSi ratios vary evenly around the stoichiometric optimum of 16:1:17 within a year. The unbalance is caused by seasonally constant TP, TN or SRSi relative to the remaining elements. In contrast to phosphorus and nitrogen, the more slowly recycled silica is more dependent on lake types differing in their water retention time and maximum depth. The Redfield ratio concept can be applied to freshwaters using 'optimum ratios' when a large number of systems are compared. Particular lakes, especially those having unbalanced ratios, deviate substantially from the optimum. Lakes with balanced nutrient ratios, however, show a close adherence to this classical ratio even for individual lakes (hypertrophic riverine lakes).

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Ecological stoichiometry of TN:TP:SRSi in freshwaters: nutrient ratios and seasonal shifts in phytoplankton assemblages

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With 7 figures and 2 tables

Abstract: Our concept of the 'balance of TN:TP:SRSi-ratios' attempts to determine whether the seasonal succession of phytoplankton communities is influenced by or responds to nutrient stoichiometry. Because the molar average of TN:TP:SRSi = 20:1:17 for 118 measurements (7 lakes, 3 inflows, all seasons) was close to the marine optimum stoichiometric ratio, we used the ratio TN:TP:SRSi = 16:1:17 as a reference point for ecological stoichiometry. Triangular diagrams of TN:TP:SRSi ratios scaled in physiological proportions of 16:1:17 were used to identify seasonal fluctuation patterns of major phytoplankton nutrients. In lakes with 'balanced nutrient ratios' TN:TP:SRSi ratios vary evenly around the stoichiometric optimum of 16:1:17 within a year. Lakes with balanced nutrient ratios, however, were more the exception than the rule and only occurred in 2 of 7 lakes studied. Lakes with constant concentrations of one nutrient element in relation to those of the other two were common. Unbalanced nutrient ratios were associated with relatively constant concentrations of either SRSi, or TN or TP. The relative change in availability of soluble reactive silica was more affected by differences in lake morphometry than that of TN or TP. Ratios of TN:TP:SRSi have the advantage of synoptically presenting the relative nutrient availability for both diatoms and non-siliceous algae in phytoplankton communities. Shifts within the tripartite ratio correspond to successive substitution of phytoplankton groups, e.g. from diatoms to cyanobacteria.

Key words: N, P, Si, cyanobacteria, diatoms.

Introduction

Freshwater phytoplankton communities are comprised of siliceous and non-siliceous algae. Silica as well as nitrogen and phosphorus are, thus, of critical

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importance as macronutrients. Beside nutrient concentrations and their fluxes, the stoichiometric proportions between nutrients are key factors for algal growth in plankton communities (e.g. SAKAMOTO 1966, FORSBERG & RYDING 1980, SMITH 1982, 1983, SØNDERGAARD *et al.* 1999). In the present study, stoichiometric ratios between N, P and Si are evaluated in lakes along a trophic gradient using triangular diagrams (GIBBS 1878, VAN DAM *et al.* 1981, BAILEY-WATTS & KIRIKA 1987, SANDGREN 1988, PINTO & MORAIS 1994).

Variability in relative nutrient concentrations may be judged either by the relative change of a single element or by the stoichiometric ratios between available nutrients. Fluctuations in concentrations of a single element are important with respect to adaptation processes enabling organisms to detect relative rather than absolute changes (BRAY 1995). Cyanobacteria are able to adjust to external phosphate fluctuations by adaptive responses to threshold values and kinetic properties (WAGNER *et al.* 1995). Stoichiometric relations among elements are central to the theory of resource-ratio-competition between algae (TILMAN 1982, MAKULLA & SOMMER 1993, SOMMER 1993), consumer driven nutrient recycling (ELSER & URABE 1999) and perhaps food chain efficiency (STERNER *et al.* 1998).

Ecological stoichiometry of major phytoplankton nutrients is examined in our study using tripartite ratios between total nitrogen (TN), total phosphorus (TP) and soluble reactive silica (SRSi) and addresses the following questions:

What are the patterns of seasonal fluctuations of TN:TP:SRSi in meso- to hypertrophic lakes? Are elements with faster recycling times, such as phosphorus and nitrogen, less affected by lake type than the more slowly recycled Si? Can the Redfield ratio be generally applied to freshwater systems? Can the relative nutrient availability for phytoplankton assemblages be synoptically evaluated?

Materials and methods

In 1990–91, monthly samples were taken from a number of lakes in the vicinity of the city of Berlin [Langer See (LANS), Großer Müggelsee (MUES), Flakensee (FLAS) and Krumme Lake (KRUL)], and in the biological reserve 'Schorfheide-Chorin' in Brandenburg, to the north of Berlin [Parsteiner See (PARS), Rosinsee (ROSS) and Großer Plagesee (GPLA)]. In addition, the inlet waters of riverine lakes of a lowland lake system were sampled [inflows of Großer Müggelsee (MUEZ) and Flakensee (Woltersdorfer Schleuse FLZW, Lößnitz FLZL)]. Monthly sampling was continued for Langer See, Rosinsee and Parsteiner See into 1992. A biweekly interval was followed in Großer Müggelsee and Flakensee including their inlet waters (MUEZ, FLZL, FLZW) in 1992–93. Samples were integrated over the mixed surface layer during periods of thermal stratification.

Conductivity, TN, TP and SRSi were estimated using standard techniques (APHA 1992). Euphotic depth was calculated from under-water light attenuation using a 4 π quantum sensor (LI-COR). The biovolume of phytoplankton was estimated microscopically according to the Utermöhl method (1958). The mean value of the normal or the log-normal distribution was selected for abundance distribution (single cells, filaments or number of colonies) depending on which fitted better. For taxonomic details of diatoms refer to TEUBNER (1995, 1997), for other algae to TEUBNER (1996) and TEUBNER et al. (1997).

The step-wise extraction of limnological parameters was repeated in principal component analysis (PCA) until the first two components represented more than 80 % of the total variance (8 limnological variables in Fig. 2 B, cases: 10 waters represented by long-term averaged data, method: HENRION et al. 1988, HENRION & HENRION 1995). These limnological parameters extracted by PCA were included in the hierarchical cluster analysis (HCA, Fig. 2 C).

Triangular diagrams of nutrient ratios and phytoplankton structure

Triangular diagrams based on seasonal nutrient concentrations and phytoplankton biovolume (spring: March–May, summer: June–August, autumn: September–November, winter: December–February) were created in GRAPHER 4.0 for Windows, Golden Software, Inc.

In order to show the relative nutrient availability, the concentrations for total nitrogen (TN), total phosphorus (TP) and soluble reactive silica (SRSi) were used, based on the following arguments. In contrast to silicon which is recycled from organic matter at longer intervals (SOMMER 1988, BARKER et al. 1994), phosphorus and nitrogen are rapidly recycled. Algae have no storage capacity for silicon, but phosphorus and nitrogen can be intracellularly stored (e.g. polyphosphate bodies, cyanophycin granules); N and P from these stores can be mobilised and utilised for algal growth after external inorganic dissolved N and P pools are exhausted (DROOP 1973, GIBSON & FOY 1988). Consideration only of inorganic dissolved nitrogen and phosphorus thus would ignore the potential growth that can be driven by stored resources. The seasonality of total nitrogen and total phosphorus is closely paralleled by seasonal fluctuations of their dissolved inorganic fractions unless they become undetectable. Therefore TN and TP are better estimators of the total nutrient pool available for algal growth than the dissolved fractions alone. Moreover, some components of dissolved organic nitrogen and dissolved organic phosphorus are available for algal growth (cf. REYNOLDS 1997, THOMPSON & RHEE 1994, MOSS et al. 1996, SOMMER 1999).

A scheme for simplifying the interpretation of triangular diagrams is shown in Fig. 1.

In triangular diagrams points represent the sum of three components equal to 100 %. If molar concentrations [$\mu\text{mol/l}$] of the three macronutrients are used as the three components to construct triangular graphs, it is possible to read the stoichiometric triple ratios directly (Figs. 1 A, 3). The corners of the triangle represent the concentration of one element only (100 %) and the absence of the remaining two nutrients. Following from SRSi = 0 and TN:TP = 16:1 by moles, the percentage ratio of TN:TP

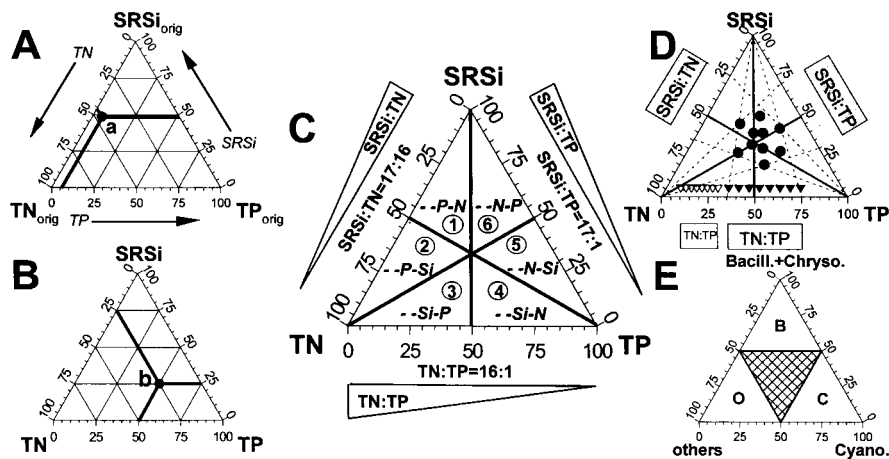


Fig. 1. Examples of how to read the triangles to evaluate nutrient ratios (A–D) and phytoplankton structure (E). **A:** Example for non-transformed nutrient ratios. Point ‘a’ represents the ratio of concentrations of TN_{orig} : TP_{orig} : $SRSi_{orig}$ = 45.71:5.71:48.57. The sum of these three relative concentrations is 100. The arrows follow the scaling of axes. **B:** Example for normalised nutrient ratios. Point ‘b’ represents the ratio of concentrations of TN : TP : $SRSi$ = 25:50:25. The sum of these three concentrations is 100. This normalised macronutrient ratio can be recalculated to the non-transformed TN_{orig} : TP_{orig} : $SRSi_{orig}$ ratio. For $TN = 25$ and $R_{TN} = 16$ is $TN_R = TN \cdot R_{TN} = 25 \cdot 16 = 400$, analogously for $TP_R = 50 \cdot 1 = 50$ and for $SRSi_R = 25 \cdot 17 = 425$. Dividing these three quantities by its sum ($TN_R + TP_R + SRSi_R = 875$) yields the original ratio TN_{orig} : TP_{orig} : $SRSi_{orig}$ = 48.57:5.71:45.71. Therefore, the normalised ratio of concentrations of the point ‘b’ corresponds to the non-transformed ratio of the concentrations of the point ‘a’ in panel A. See Methods for reasons for normalisation. **C:** Lines and sectors in normalised nutrient triangles: Generally the bold lines mark the course of concentration of the element at the corner from 100 % to 0 % with a constant ratio of the remaining two nutrients. The point of intersection of the three bold lines (in the centre) indicate the molar ratio of $TN:TP:SRSi = 16:1:17$. The bold line $TN:TP = 16:1$ marks the constant $TN:TP$ ratio of 16:1 at variable $SRSi$. Analogously the other lines indicate the constant ratio of $SRSi:TP = 17:1$ at variable TN , of $SRSi:TN = 17:16$ at variable TP . For description of sectors 1–6 and preference of limitation symbolised as e.g. ‘-P -Si’ see method and Table 2. **D:** Three idealised cases to illustrate patterns of $TN:TP:SRSi$ fluctuations for normalised nutrient triangles: i. weak variability (open triangles, ∇) of TN and TP at a constant $SRSi$; ii. strong variability (solid triangles, \blacktriangledown) of TN and TP at a constant $SRSi$; and iii. strong variation (solid circles, \bullet) for all three elements. Note that the weak case (∇) covers half the range of the strong cases (\blacktriangledown , \bullet) for $TN:TP$, but variations of the strong case for all three elements (\bullet) are identical for all three axis ($TN:TP$, $SRSi:TP$, $SRSi:TN$). Dashed lines for ranges of variation (boxes on axes). **E:** All points in sector C indicate a contribution of at least 50 % cyanobacteria to total phytoplankton biovolume. Analogously sector B represents ≥ 50 % Bacillariophyceae and Chrysophyceae and sector O ≥ 50 % of other algae. The points on the shadowed area indicate that no single algal group exceed 50 % of total biovolume.

is 94.12 : 5.88 (TN+TP+SRSi = 16 µmol/l + 1 µmol/l + 0 µmol/l = 100 % = 94.12 % + 5.88 % + 0 %). This point is indicated by the intersection of the TN:TP = 16 : 1 line on the TN–TP-axis (Fig. 3). The TP scaling is from left to right (arrow in Fig. 1A) and the TN scaling from right to left on this axis. All points on the bold line '16 : 1' represent ratios of constant TN:TP = 16 : 1 but variable concentrations of SRSi. Points on the left side of the line represent ratios of TN:TP > 16 and points on the right side represent TN:TP < 16. The problem with such diagrams is that points fall on a small area because the concentrations of these three macronutrients differ by several fold (Table 1). Therefore, concentrations were first normalised to the reference point of TN:TP:SRSi = 16 : 1 : 17 (see below), which is close to the mean value over the entire data set (TN_{mean}:TP_{mean}:SRSi_{mean} = 20 : 1 : 17 for n = 118 measurements, normalisation in Figs. 1C–D, 4–6). For that scaling reason the normalised concentrations are calculated by

$$C_{TN} = \frac{C_{TN\text{ orig}}}{R_{TN}}, C_{TP} = \frac{C_{TP\text{ orig}}}{R_{TP}} \text{ and } C_{SRSi} = \frac{C_{SRSi\text{ orig}}}{R_{SRSi}}$$

with $R_{TN} = 16$, $R_{TP} = 1$, and $R_{SRSi} = 17$ ($C_{TN\text{ orig}}$, $C_{TP\text{ orig}}$, $C_{SRSi\text{ orig}}$ in µmol/l). In normalised triangular diagrams (Figs. 1B, 4–6) a triple ratio is calculated as the sum of three normalised components equal to 100 %. As a consequence of that scaling the three optimum lines of TN:TP = 16 : 1, TN:SRSi = 16 : 17 and TP:SRSi = 1 : 17 are displayed in the triangles in the proportion 1 : 1 (50 % : 50 %, Figs. 4–6). Points representing seasonal nutrient ratios become more scattered and are easier to distinguish. Original TN:TP:SRSi ratios, however, can be recalculated by reversing the normalisation procedure. The example in Fig. 1A–B shows that the normalised TN:TP:SRSi ratio of point b corresponds with the non-transformed TN_{orig}:TP_{orig}:SRSi_{orig} ratio of point a.

For the present purposes we assume that the molar ratio N:P:Si = 16 : 1 : 17 (recalculated from data in HARRIS 1986, p. 63), which in a strict sense refers to cellular content only, reflects stoichiometric demand by the algal organisms. In this paper we call this ratio the 'optimum ratio' and use it as a reference point for ecological stoichiometry. The position of TN:TP:SRSi = 16 : 1 : 17 in the centre of the normalised triangles implies that the variations of TN, TP and SRSi are scaled in the physiological proportion of the optimum ratio. To put it simply, scattering of points extending an equal distance along each of the three lines (TN:TP = 16 : 1, SRSi:TP = 17 : 1 and SRSi:TN = 17 : 16, respectively, case iii in Fig. 1D) shows physiologically equivalent proportional variations of TN, TP and SRSi. The dynamics of the three nutrients in the normalised triangular diagrams are therefore directly comparable (example for three idealised cases in Fig. 1D) and have the same physiological relevance (Figs. 4–6). We emphasise that such normalised TN:TP:SRSi diagrams present the relative variability of physiologically scaled nutrient concentrations.

The sectors labelled with 1 to 6 in Fig. 1C indicate six combinations of TN:TP, SRSi:TN and SRSi:TP ratios. Points which fall e.g. into sector 2 have simultaneous ratios of TN:TP > 16 : 1, SRSi:TP > 17 : 1 and SRSi:TN < 17 : 16, indicating that algal growth is primarily controlled by P and secondly by Si but not by N (strong P-limitation and weak SRSi-limitation, but no N-limitation symbolised as minus elements '- -P -Si' in Fig. 1C). The interpretation for the other sectors defined by three lines in Fig. 1C follows the logic described above.

Triangular diagrams of phytoplankton structure are based on biovolumes of algal classes of single seasons (Fig. 7). By analogy to the TN:TP:SRSi diagrams the siliceous Bacillariophyceae and Chrysophyceae are arranged at the top (Fig. 1E), the corner of high SRSi:TN and high SRSi:TP (Fig. 1C). Cyanobacteria, known for their frequent relationship to low N:P ratios, are assigned to the right-hand corner (TP) indicating low N:P-ratios. The remaining algae (others: Chlorophyta s.l., Cryptophyceae, Dinophyceae etc.) have been placed at the remaining corner of high TN:TP ratios and low silicon concentrations.

Results

Trophic and limnological characterisations of the investigated lakes are given in Fig. 2. The trophic levels of the waters ranged from meso- to hypertrophic, but the majority were hypertrophic (Fig. 2A). Based on the limnological conditions in the various lakes, four discrete categories were distinguished (Fig. 2B–C). The ‘hypertrophic riverine lakes’ (MUES, MUEZ, LANS) are shallow, turbulent mixed lakes (high ratio of mixed zone to maximum depth, $z_{\text{mix}}:z_{\text{max}}$) with high concentrations of chlorophyll-*a*, TP and SRSi. The ‘waters of moderate mineral content’ (FLAS, FLZL, FLZW) are characterised by a higher conductivity than other soft waters (Table 1) and a low TN:TP ratio because of low TN concentrations. The ‘dimictic, mesotrophic lakes’ (PARS, ROSS) are lakes with relatively shallow z_{mix} but high z_{max} and high TN:TP ratios caused by low concentrations of TP (Table 1). The combination of high TN:TP ratios and low conductivity accords with the character of the ‘dystrophic lakes’ (GPLA, KRUL). The high concentration of TOC at low alkalinity also distinguishes the last two lakes as being dystrophic (Fig. 2D).

The molar average TN:TP:SRSi ratio over all seasons for the 7 lakes and 3 inflows was 20:1:17. The relationship among the three macronutrients in the four categories of lakes is shown in Fig. 3. The dimictic mesotrophic lakes and dystrophic lakes are marked by TN:TP ratios higher than 16:1 (points on the leftside of the bold line indicating TN:TP = 16:1) and mainly had relatively low SRSi concentrations. In contrast the seasonal TN:TP ratios of the hypertrophic riverine lakes cluster around 16:1 at higher SRSi concentrations. The waters of moderate mineral content showed other patterns associated with varying SRSi concentrations usually at TN:TP lower than 16:1.

Since TN:TP:SRSi ratios in Fig. 4–6 are only mathematically transformed, the results described for Fig. 3 are also valid for Fig. 4–6. Each panel shows the seasonal normalised TN:TP:SRSi ratios for an individual lake category (Fig. 4) or for a single representative lake (Fig. 5–6). The phytoplankton compositions for the four lake categories are shown in Fig. 7.

In the case of the hypertrophic riverine lakes, seasonal averages are scattered along all three optimum-ratio lines of TN:TP = 16:1, SRSi:TP = 17:1

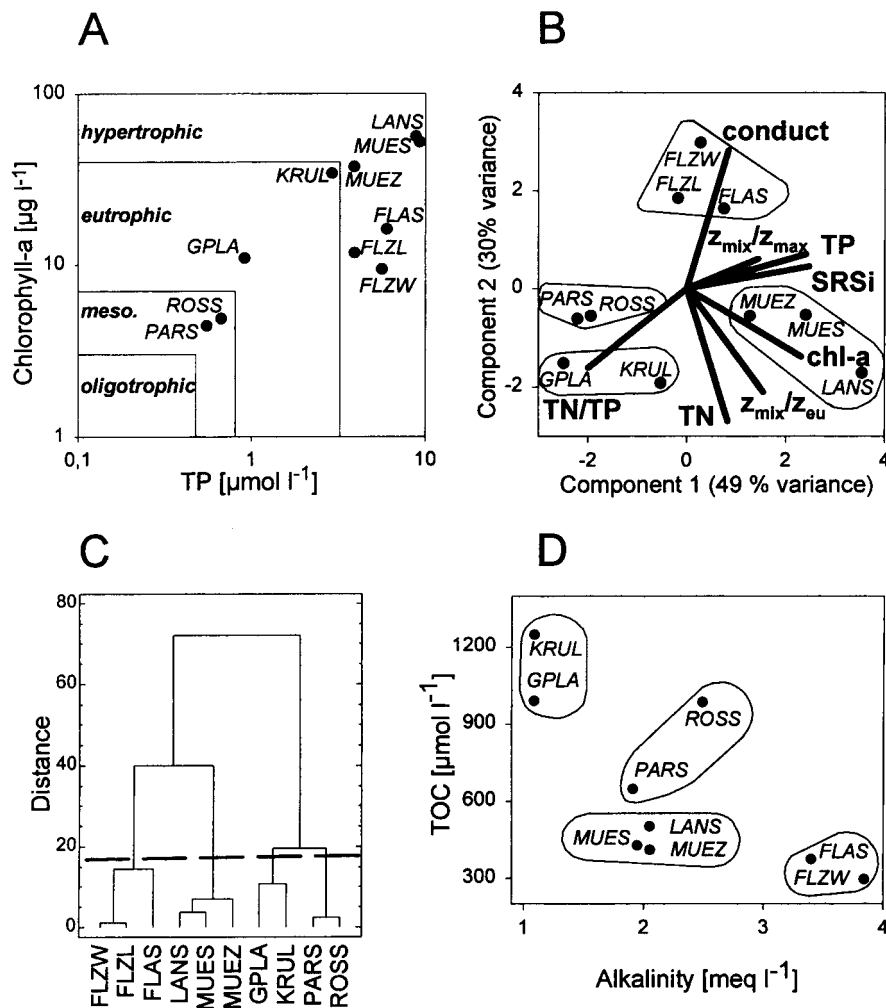


Fig. 2. Overview of the limnology of the 10 investigated waters. **A:** Relationship between chlorophyll-a and TP concentration in the 10 waters. Trophic levels are indicated by the averaged data of the June-September period according to FORSBERG & RYDING (1980). **B:** Biplot of the second versus the first principal component for eight limnological variables (vectors) and distribution pattern of the waters (points). Waters assigned to four categories: -hypertrophic riverine lakes (MUES, MUEZ, LANZ), -waters of moderate mineral content (FLAS, FLZL, FLZW), -dimictic, mesotrophic lakes (PARS, ROSS), -dystrophic lakes (GPLA, KRUL). **C:** Dendrogram of hierarchical cluster analysis. The broken line separates four categories of waters. Variables see B. Method: squared Euclidean distance, Ward linkage. **D:** Relation between alkalinity and TOC. Abbreviations of limnological parameters: conductivity (conduct), concentration of chlorophyll-a (chl-a), soluble reactive silicon (SRSi), total nitrogen (TN) and total phosphorus (TP), ratio of TN:TP (TN/TP), ratio mixed depth to euphotic depth ($z_{\text{mix}}/z_{\text{eu}}$) and to maximal water depth ($z_{\text{mix}}/z_{\text{max}}$), respectively.

Table 1. Morphometric and long term averaged limnological data for the 10 waters. Lake area and maximum depth from ANWAND 1973, retention time for MUES, LANS and FLAS (1992–93) from KOHL et al. (1994), for PARS, ROSS, GPLA and KRUL from SCHÖNFELDER (“Gewässerkataster und angewandte Gewässerökologie e. V. Brandenburg”, pers. communication), Abbr. for lakes and years covered see method.

	KRUL	GPLA	PARS	ROSS	LANS	MUES	MUEZ	FLAS	FLZL	FLZW
conductivity [mS m^{-1}]	18.5	23.2	46.6	53.0	59.2	65.4	66.8	86.8	89.8	121.1
TN [$\mu\text{mol l}^{-1}$]	105.5	84.2	55.8	84.1	106.9	88.9	101.1	46.3	54.0	38.8
TP [$\mu\text{mol l}^{-1}$]	2.36	0.69	0.54	0.78	7.05	6.29	3.54	5.30	3.64	6.23
SRSi [$\mu\text{mol l}^{-1}$]	3.30	3.23	6.70	10.92	122.17	105.66	91.02	73.07	65.92	57.39
phytoplankton										
biovolume [$\text{mm}^3 \text{l}^{-1}$]	7.2	0.93	0.53	1.1	11.7	9.9	5.6	3.1	1.7	1.6
area [km^2]	0.15	0.78	11	0.2	1.53	7.7	inflow	0.73	inflow	inflow
max. depth [m]	4.8	5	27	9	7	7.5	5.0	4.5	8.5	3.8
euphotic depth [m]	2.3	4.4	10.2	7.1	2.4	3.5	3.3	4.8	4.9	6.2
mixing depth [m]	3.92	4.89	19.71	6.81	6.9	7.2	5.0	4.78	6.79	3.8
retention time	1 y	5 y	15 y	1.2 y	4.1 d	67.2 d		28.9 d		

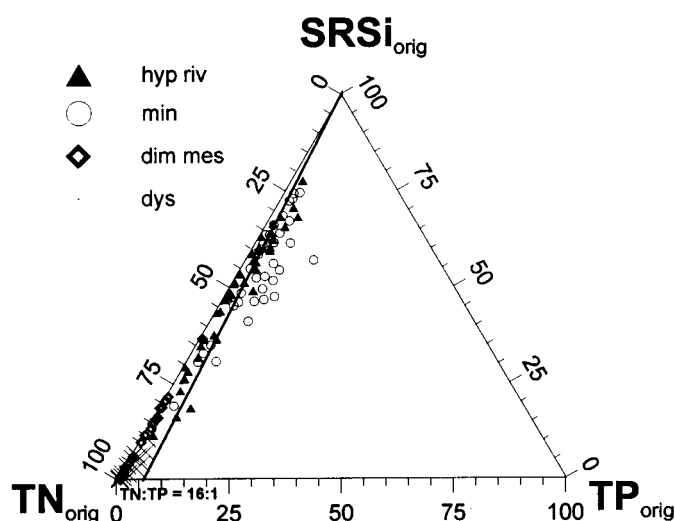


Fig. 3. Triangular diagrams of seasonal non-transformed $\text{TN}_{\text{orig}} : \text{TP}_{\text{orig}} : \text{SRSi}_{\text{orig}}$ ratios for the four categories of waters. The bold line marks the constant ratio of $\text{TN} : \text{TP} = 16 : 1$ at variable SRSi (calculation of the intersection point of the line on axis see method, lake categories according to Fig. 2 C–D: hyp riv – hypertrophic riverine lakes; min – waters of moderate mineral content; dim mes – dimictic, mesotrophic lakes; dys – dystrophic lakes).

and $\text{SRSi} : \text{TN} = 17 : 16$ (Fig. 4 A). Nutrient ratios (i) circle around the optimum point $16 : 1 : 17$ within a year and (ii) the $\text{TN} : \text{TP}$, $\text{SRSi} : \text{TP}$ and $\text{SRSi} : \text{TN}$ were highly fluctuating in the same range as indicated by the similar length of the

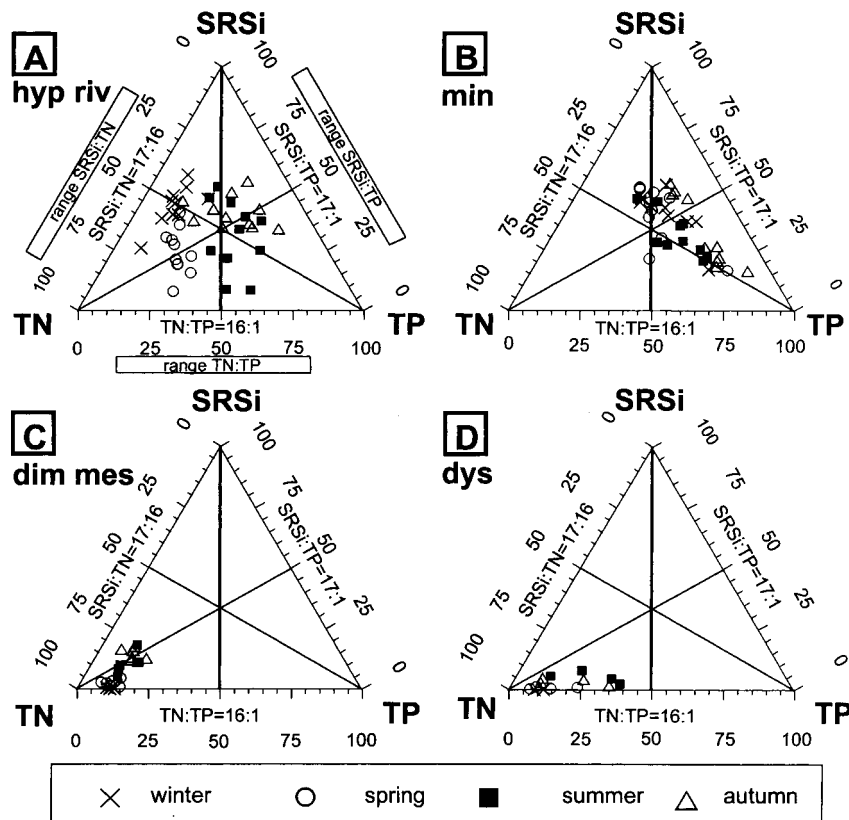


Fig. 4 A–D. Triangular diagrams of normalised TN:TP:SRSi ratios in the four categories of limnologically similar waters. Every point represents an annual average of winter, spring, summer or autumn of a single water [lines and the intersection of the three lines of optimum ratios and patterns see Fig. 1C–D; bars in A show the range of fluctuations of TN:TP, SRSi:TP and SRSi:TN as illustrated in Fig. 1D; seasonal averaging for 10 waters ($n = 118$) see method, water categories see Fig. 3].

bars on the three axis (see idealised case iii in Fig. 1D). This implies a high seasonal interaction of TN, TP and SRSi in physiologically optimal proportions (see scaling method). Accordingly, the hypertrophic riverine lakes were termed ‘**balanced nutrient ratio lakes**’. The counterclockwise rotation of points around the optimum ratio of TN:TP:SRSi = 16:1:17 (Fig. 4A) reveals a non-random pattern correlated to seasons. In winter, the TN:TP and SRSi:TP ratios were higher than the optimum, the SRSi:TN ratios scattered around 17:16 (compare sector 1–2 in Fig. 1C with Fig. 4A). From winter to spring, SRSi concentrations declined at TN:TP values higher than 16:1 (sector 2–3). The TN:TP ratio usually changed from higher than 16:1 to lower

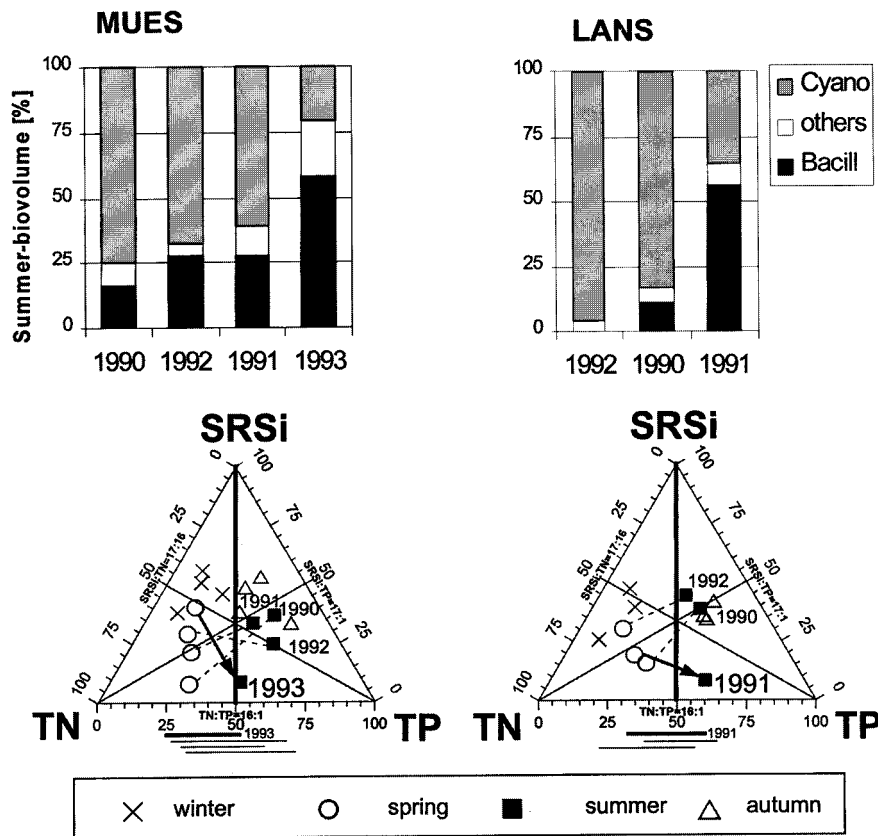


Fig. 5. Phytoplankton in summer (barcharts) and seasonal TN:TP:SRSi ratios for Großer Müggelsee (MUES) and Langer See (LANS) representative for the hypertrophic riverine lakes. Barcharts: Percentage of algal classes by total biovolume [$\text{mm}^3 \text{l}^{-1}$], Abbr.: Cyano = Cyanobacteria, Bacill = Bacillario- plus Chrysophyceae, other = the remaining algae. Triangular diagrams normalised as in Fig. 4. The arrows connect points for spring and summer of 1993 (MUES) and 1991 (LANS) while dashed lines connect those points for all other years. Bars below the TN:TP-axis indicate the variation of TN:TP for MUES 1993 and LANS 1991 (bold) in comparison to other years.

than 16:1 during the progression from spring to summer (sector 3–4). The relative increase of Si in the autumn is indicated by the increase of SRSi:TN and SRSi:TP with low TN:TP (sector 4–5). The TN:TP ratio changed back from <16:1 to >16:1 from autumn to winter. The strong nutrient interaction within a year is expressed by the dispersed cyclic pattern through all nutrient combinations (points join sectors 1–6, compare with Fig. 1C and Table 2, idealised case iii in Fig. 1D). These seasonal changes which generally occurred in the

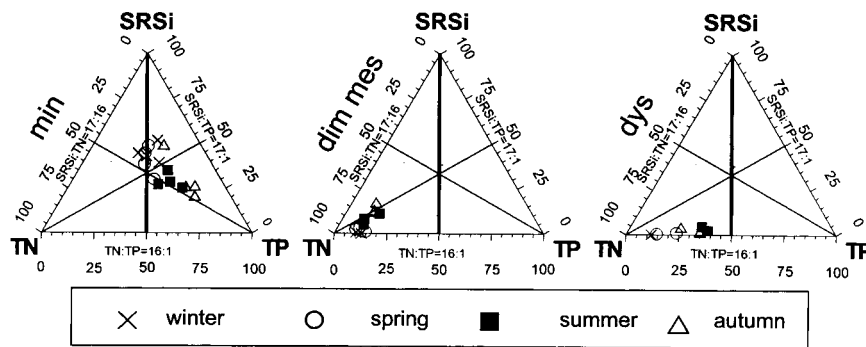


Fig. 6. Seasonal TN:TP:SRSi ratios for single lakes representative for waters of moderate mineral content (min: FLAS), dimictic mesotrophic lakes (dim mes: ROSS), dystrophic lakes (dys: KRUL). Normalisation and lines as in Fig. 4.

Table 2. TN:TP, SRSi:TN and SRSi:TP ratios for sectors in Fig. 1 C (see Methods).

sector	TN:TP = 16:1	SRSi:TP = 17:1	SRSi:TN = 17:16
1	higher	higher	higher
2	higher	higher	<i>lower</i>
3	higher	<i>lower</i>	<i>lower</i>
4	<i>lower</i>	<i>lower</i>	<i>lower</i>
5	<i>lower</i>	<i>lower</i>	higher
6	<i>lower</i>	higher	higher

hypertrophic riverine lakes are also characteristic for specific lakes of this category, the Großer Müggelsee and Langer See (Fig. 5).

The phytoplankton usually consisted of at least 50 % siliceous algae (mainly diatoms) or at least 50 % Cyanobacteria (nitrogen fixers: *Aphanizomenon flos-aquae*, *Anabaena flos-aquae*; non-nitrogen fixers: *Planktothrix agardhii*, *Microcystis* spp.; Fig. 5 and 7 A). Summer blooms with biovolume averages of 32 mm³/l in Großer Müggelsee and 25 mm³/l in Langer See were usually dominated by Cyanobacteria, whereas diatoms contributed only about 25 % (MUES: 1991–92, LANS: 1990, 1992, Fig. 5). Whenever summer phytoplankton composition shifted significantly towards diatom domination of more than 50 %, concomitant changes in TN:TP:SRSi ratios occurred. As indicated by arrows downwards in the triangles a much stronger reduction of relative SRSi was clearly seen for 1993 in MUES and 1991 in LANS in comparison to other years indicated by dashed lines (Fig. 5). This decrease of SRSi:TP and SRSi:TN is usually coupled with a smaller change of TN:TP (see shortness of bold bars of respective years in comparison to other years on TN:TP-axis in Fig. 5).

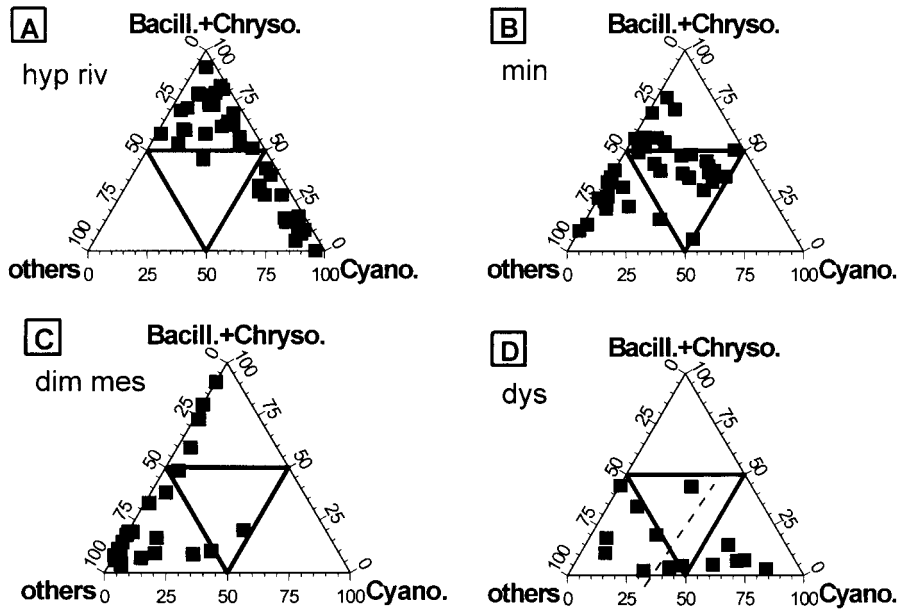


Fig. 7 A–D. Triangular diagram of phytoplankton structure for the four lake categories. Reasons for the arrangement of algal groups at the corners are given in the method. Dashed line in D separate GPLA (leftside) from KRUL (rightside). For easy reading see Fig. 1D. Abbr. of algal groups see Fig. 5, lake categories see Fig. 3.

In contrast to seasonal fluctuations of all the three elements in the hypertrophic riverine lakes, the seasonal variability in the other lakes mainly affected just two of the elements. Therefore, these are regarded as **‘unbalanced nutrient ratio lakes’**. The arrangement of points parallel to an axis indicates strong variation between the two components of this axis with concentrations of the element on the opposite corner nearly constant. In dystrophic lakes, especially in the eutrophic dystrophic Krumme Lake (Fig. 2 A), with high variability in TN : TP relative to ‘constant’ SRSi (points arranged parallel to the TN : TP axis in Fig. 4 D and 6; idealised case ii in Fig. 1 D), the phytoplankton was dominated by either Cyanobacteria (e.g. nitrogen fixing: *Aphanizomenon skujae*, *Anabaena lemmermannii* and non-nitrogen fixing e.g. *Planktolytnbya subtilis*, *Snowella litoralis*, *Woronichia compacta*) or other non-siliceous algae, whereas diatoms had a negligible presence (Figs. 7 D). For the other dystrophic lake, Großer Plagesee, with a weaker variability of seasonal TN : TP ratios at ‘constant’ low SRSi, neither Cyanobacteria nor diatoms dominated (neither group ever exceed 50 % of total biovolume, Figs. 4 D and 7 D, idealised case i in Fig. 1 D).

Deep dimictic mesotrophic lakes and shallow eu- to hypertrophic lakes with moderate mineral content showed weak seasonal variability in TN : TP ra-

tios but strong fluctuations in SRSi (Fig. 4 B–C). No increased likelihood of cyanobacterial dominance was evident (Fig. 7 B–C) although TN : TP ratios were lower than 16 : 1 in the Flakensee-group. In these lakes the phytoplankton was dominated by either diatoms or non-siliceous algae (excluding the Cyanobacteria) or by a balanced contribution from all three algal groups. Typical lakes from these two categories, however, showed the difference in the dynamic of TN : TP. Weak seasonal variations for TN : TP were caused in Rosinsee (dimictic mesotrophic lake) by variable TN concentrations with ‘fixed’ TP, while in Flakensee (water of moderate mineral content), TP concentrations varied with ‘fixed’ TN (Fig. 6, points parallel to the TN : SRSi-axis for Rosinsee but parallel to the TP : SRSi-axis for Flakensee).

Ratios in the lakes with unbalanced nutrient ratios deviated most from the reference point TN : TP : SRSi = 16 : 1 : 17 by single elements as by nitrogen for FLAS (sector 5–6, –N–P and –N–Si), by phosphorus and silica for PARS (sector 2–3; –Si–P and –P–Si) and by silica for KRUL (sector 3; –Si–P) as shown in Fig. 6 (sector description in Fig. 1 C and Table 2). No predominance of a single limiting element, however, was observed for lakes with balanced nutrient ratios as described above by points joining sectors 1–6.

Average TN : TP ratios were usually higher during winter/spring than during summer/autumn (Fig. 5–6). Different trends, however, were evident for SRSi concentrations in relation to TN : TP. Highest relative SRSi concentrations occurred (i) during summer/autumn for the dimictic mesotrophic lakes and the dystrophic lakes (Fig. 4 C–D, 6 (ROSS, KRUL)), (ii) during winter/spring in Flakensee (Fig. 6) and (iii) during autumn/winter in the hypertrophic riverine lakes (Fig. 4 A, 5).

Discussion

New approaches to ecological stoichiometry can show patterns otherwise not apparent. When the TN : TP : SRSi ratios are scaled to physiological proportions close to the optimum ratio, the triangular ordination reveals different seasonal patterns of stoichiometric relationships among the nutrients. Nutrients might not necessarily vary in relation to each other throughout a given year. Lakes with a constant concentration of one nutrient in relation to those of the other two seem to be more the rule than the exception. Lakes with unbalanced nutrient ratios are more common in the present data set than those with balanced nutrient ratios. These differences in nutrient ratio dynamics are the result of net-changes in the pool size of elements caused mainly by phytoplankton and lake type.

Dynamics of the N:P:Si ratio and phytoplankton structure

Since the classical study by REDFIELD (1958) on the elementary composition of marine plankton many investigations have focused on its application to freshwater and benthic communities (SMITH 1983, RHEE & GOTHAM 1980, HECKY et al. 1993, HILLEBRAND & SOMMER 1999). The relevance of the optimum ratio (REDFIELD 1958, RICHARDS 1958) for all the lakes investigated here derives from their close adherence of the mean TN:TP:SRSi ratio to 16:1:17. This holds true even for individual lakes having a balanced nutrient ratio dynamic (hypertrophic riverine lakes).

The importance of elemental ratios for phytoplankton has been studied in terms of relative nutrient availability (TILMAN 1982). Low N:P ratios favour the dominance of cyanobacteria during summer (e.g. SMITH 1983, STEINBERG & HARTMANN 1988, THOMPSON & RHEE 1994, SMITH & BENNETT 1999, BULGAKOV & LEVICH 1999), especially nitrogen-fixing species during the periods of nitrogen limitation (e.g. TRIMBEE & HARRIS 1984, SOMMER et al. 1986, DUDEL & KOHL 1991, DOKULIL & TEUBNER 2000). SRSi depletion in summer leads to a replacement of diatoms by other algae (e.g. cyanobacteria, SOMMER et al. 1986, TIPPMMANN 1993). In all those studies nutrient ratios have been considered separately in pairs only, never as a tripartite ratio (SOMMER 1993). Hypertrophic riverine lakes with a balance between the three nutrients in principle illustrate, however, the rapid change in relative nutrient availability as reflected by yearly progression of the TN:TP:SRSi ratios within six stoichiometric regions separated by boundaries of optimal TN:TP, SRSi:TN and SRSi:TP. Changes in the TN:TP:SRSi ratio were reflected by the substitution of phytoplankton groups as can be exemplified by the lakes with balanced nutrient ratios. Years with stronger reduction of silica, implying a stronger decrease of SRSi:TP and SRSi:TN, were usually associated with a minor decline of TN:TP from spring to summer resulting in the replacement of cyanobacteria by diatoms (Fig. 5, for details about species see TEUBNER et al. 1999). By assuming that the optimum ratio 16:1:17 indicates average requirements of algae in the plankton communities, it is not surprising, that the lakes with balanced nutrient ratios reach highest algal biomasses as shown in Fig. 2 A. Other lakes in the same range of phosphorus concentration, retention time and euphotic depth but with unbalanced nutrient ratios are limited in algal growth as indicated by low chlorophyll (Fig. 2 B). Flakensee provides such an example of hypertrophic conditions which do not necessarily lead to a high dynamic of all macroelements resulting in low algal growth and hence low biomass.

In the past, nutrient ratios have been primarily viewed in a static way. Such an approach cannot explain the occurrence of cyanobacterial blooms at high TN:TP in one of the dystrophic lakes (KRUL) and the lack of cyanobacterial

dominance at low TN:TP ratios in the one hypertrophic lake (FLAS). In our opinion, TN to TP ratios lower than 16:1 are not always indicative of cyanobacterial dominance, but highly fluctuating TN:TP ratios seem to favour cyanobacteria. This hypothesis is substantiated by the high fluctuation in TN:TP associated with cyanobacterial dominance, as in the eutrophied dystrophic lake (KRUL) and the two hypertrophic riverine lakes. Long-term increase of nitrogen and phosphorus at low silica, as was observed in KRUL, caused dramatic shifts in the phytoplankton structure from diatoms to blue-green or green algae (e.g. SCHELSKE & STOERMER 1971, TILMAN 1982, SOMMER 1988, HUMBORG et al. 1997). Alternative blooming of either *Aphanizomenon flos-aquae* RALFS ex BORN. et FLAH. or *Planktothrix agardhii* (GOM.) ANAGN. et KOM. was induced by the timing of the critical TN:TP ratio of 16:1 in the hypertrophic riverine lakes as was previously shown by TEUBNER et al. (1999). In contrast, cyanobacteria were not dominant in lakes with weak TN:TP variation irrespective of their trophic state as observed in dimictic mesotrophic lakes (PARS, ROSS) and the rapidly flushed hypertrophic lake (FLAS), even if TN:TP ratios lower than 16:1 prevailed for several weeks. Highly variable SRSi concentrations at low seasonal variability of TN:TP indicated the favourable conditions for diatom blooms over cyanobacteria. The absence of cyanobacterial blooms even when conditions should be favourable because of low N:P ratios has been previously reported (e.g. SOMMER et al. 1986, SMITH & BENNETT 1999).

Fluctuations in TN:TP:SRSi are intimately linked to variable phytoplankton structure because of the particular Si-uptake and -accumulation by siliceous algae and the wide variability in their cellular composition with respect to nitrogen and phosphorus. The ability to store N and P intracellularly for later usage by some algal groups enhances the wide fluctuations of these elemental pools. Specifically for Großer Müggelsee, BEHRENDT (1990) has shown that the variation of elemental composition of seston samples is strongly affected by blooms of either diatoms or cyanobacteria. In contrast to the phytoplankton, the (meso)-zooplankton species maintain a relatively constant elemental composition even if they ingest food with an elemental composition much different from their body (ELSER & GEORGE 1993, VREDE 1998, CAPRILLO et al. 1996, GISMERVIK 1997, STERNER et al. 1998, ELSER & URABE 1999).

Beside nutrient ratios, temperature, light, or pulses of nutrients are important for resource competition (GOLDMAN 1986, TILMAN et al. 1986, WYNNE & RHEE 1986, SOMMER 1983, 1985, 1993, MAKULLA & SOMMER 1993). Therefore, the outcome of algal competition responds to a combination of nutrient ratios and co-varying environmental factors in lakes which can be designated by a template according to REYNOLDS (1998). Ratios of complex pools such as TN:TP seem to be driven by the match of processes ranging from environ-

mental factors, e.g. timing of temperature increase and mixing events, to food-web interactions. A previous study shows, that significant compositional changes in phytoplankton community occur only two times a year, i.e. from spring to summer and from autumn to winter and are therefore synchronised to the seasonal variation of the TN:TP in various lakes (TEUBNER 2000).

Lake type dependence of the N:P:Si ratio dynamic

Lake types, different in their trophic state and morphometry in this study, also reflect different seasonal dynamics in their nutrient ratios. The dynamic of the macroelements in these lakes is, to a large extent, a reflection of processes in the catchment (DOWNING & MCCAULY 1992, PAERL 1997), of the proportion between external and internal nutrient load (LEVINE & SCHINDLER 1992, SØNDERGAARD et al. 1999), and of the balance of autochthonous and allochthonous organic matter formation (HÅKANSON & PETERS 1995). Oxidic cycling of nutrients can play a significant role in shallow polymictic lakes (REYNOLDS 1996) while the thermocline can remain an effective barrier in dimictic lakes (FEE 1979).

TN:TP decline from winter/spring to summer/autumn in all investigated lakes. In contrast, SRSi:TN and SRSi:TP varies individually in each lake. Thus, the relative change of silica seems to be more affected by lake type than by TN or TP (see also TEUBNER 2000). The epilimnetic cycle of Si runs much more slowly than the short-term cycles of phosphorus and nitrogen (SOMMER 1988). In lakes with very short retention times in the order of days to months (Table 1), the export of incorporated silica in diatoms through sedimentation and wash-out are largely replenished by the high silica concentrations in the inflow (BAILEY-WATTS et al. 1989 a, b). The compensation of low internal cycling of silica by high external loading in hypertrophic riverine lakes is the crucial factor for the balance between Si and TN:TP supplies and is therefore essential for the variation of the three elements in physiological equivalent proportions to each other.

Dimictic mesotrophic and dystrophic lakes with long water renewal times and minimal inflows, however, depend almost entirely on internal silica recycling. Low silicon uptake in summer and reloading from the sediment associated with autumnal mixing (GIBSON et al. 2000) increase relative epilimnetic SRSi concentrations in the summer/autumn period. These lakes of unbalanced nutrient ratios are examples for directly related relative concentrations of silica and of phosphorus throughout the seasons. Concentrations of both elements are relatively high during summer/autumn and relatively low during winter/spring.

In contrast, the peak of relative SRSi concentration in winter/spring in the flushed lake with unbalanced ratios (Flakensee) indicates the delay in the de-

crease of silica at the beginning of the year because external loading makes up for the uptake by spring diatoms and the long turn-over time. In this lake relative concentrations of silica are inversely related to those of TP. An inverse relationship of silica and phosphorus is reported from long-term studies in stratified lakes elsewhere. Usually this is a consequence of P enrichment by eutrophication and hence accelerated silica depletion (SCHELSKE & STOERMER 1971, SCHELSKE et al. 1972, 1986).

Conclusions

To conclude, trophic situations were most commonly evaluated from concentrations of a single nutrient or a nutrient ratio, such as N:P. The basis of a more complex assessment is our concept of the 'balance of TN:TP:SRSi-ratios' in lakes. We used the ratio $TN:TP:SRSi = 16:1:17$ as a reference point for ecological stoichiometry and call this the 'optimum ratio', in the sense of REDFIELD (1958) and HARRIS (1986) for plankton communities, but different from the definition by RHEE & GOTHAM (1980) for single species. Triangular diagrams have the benefit of presenting a synoptic picture of relative nutrient availability for phytoplankton communities and for evaluating multiple resource-ratio gradients. Nitrogen, phosphorus and silica are dynamically interrelated by non-random patterns correlated to seasons, phytoplankton community structure and lake types. These patterns indicate either a balanced or an unbalanced seasonal variation of TN, TP and SRSi. In lakes with balanced nutrient ratios TN:TP:SRSi ratios vary evenly around the stoichiometric optimum of 16:1:17 within a year. The unbalance is caused by seasonally constant TP, TN or SRSi relative to the remaining elements. In contrast to phosphorus and nitrogen, the more slowly recycled silica is more dependent on lake types differing in their water retention time and maximum depth. The Redfield ratio concept can be applied to freshwaters using 'optimum ratios' when a large number of systems are compared. Particular lakes, especially those having unbalanced ratios, deviate substantially from the optimum. Lakes with balanced nutrient ratios, however, show a close adherence to this classical ratio even for individual lakes (hypertrophic riverine lakes).

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