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Variability of nutrient limitation in the Archipelago Sea, SW Finland

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Abstract

Eutrophication is the most acute environmental problem in the Archipelago Sea, SW Finland. When analysing the factors behind this escalating eutrophication the determination of limiting nutrient at a given time is essential. Besides experimentations, nutrient limitation of plankton has been extensively studied by direct chemical analyses. We used the latter approach in this work. Nutrient limitation was studied by calculating different nutrient ratios – total nitrogen:phosphorus, inorganic nitrogen:phosphorus, and nutrient balance ratio. Results showed that phosphorus usually limited primary production only near the coast line. In the middle zone of the Archipelago Sea the limiting factor varied temporally. Outer in the open sea nitrogen limited primary production during most of the year. Phosphorus limited phytoplankton growth especially in spring and in summer and nitrogen in late summer and in autumn. Our results suggested that nitrogen is an important limiting nutrient in the Archipelago Sea. In recent years when the eutrophication has proceeded there has been a shift from production limitation by both nutrients to limitation by nitrogen alone. But if we want to define and characterize the nutrient limitation of the entire ecosystem of the Archipelago Sea, budgets have to be calculated for both N and P and internal recycling must be taken into account as well as external supply of nutrients and loss processes.

Introduction

Nutrient enrichment and eutrophication are regarded as the most acute environmental problems in the Archipelago Sea, SW Finland (e.g. Jumppanen & Mattila, 1994) as in the whole Baltic Sea (e.g. Larsson et al., 1985; Wulff et al., 1990). When analysing the factors behind this escalating eutrophication the determination of limiting nutrient is essential. Several studies have shown that phosphorus (P) and nitrogen (N) are the nutrients potentially most limiting plankton growth in fresh and brackish waters (see e.g. Wetzel, 1983; Hecky & Kilham, 1988). It has been frequently stated that N limits phytoplankton growth in the sea and P in freshwater; consequently the question of which of them is limiting at intermediate salinities is receiving increasing attention (Paasche & Erga, 1988).

In the Archipelago Sea nutrient discharges from fish farming and diffuse loading have increased during the last 20–25 years. Although phosphorus load from industrial and municipal waste waters has decreased effectively (Pitkänen, 1994), total nitrogen load has remained high and environmental authorities must soon make decisions concerning nitrogen reduction in this area. Therefore it is important to know how the role of limiting nutrient varies in different parts of the Archipelago Sea.

The limiting nutrient concept was originally developed by Liebig (1855) as the ‘Law of the Minimum’. Simply paraphrased, it states that the yield of any organism will be determined by the abundance of the substance that, in relation to the needs of the organism, is least abundant in the environment (Wetzel, 1983).

Besides experimentation, nutrient limitation of plankton has been extensively studied by direct chemical analyses (Tamminen, 1990). This chemical evaluation is usually based on the comparison of observed nutrient ratios (inorganic, particulate or total) to corresponding Redfield ratios (Redfield et al., 1963) or local derivatives (Tamminen, 1990). The relative shortage – in relation to Redfield or others ratios – of a given nutrient is interpreted as indication of potential limitation by that nutrient (e.g. Forsberg et al., 1978).

In this study we analyse temporal and spatial variability of nutrient concentrations, describe long-term changes of water quality and finally evaluate the question of nutrient limitation in the Archipelago Sea. Thus, this paper summarizes a large number of chemical data from the coastal waters of southwestern Finland, but does not give any results of experiments for physiological nutrient limitation. Therefore, some limitations of our approach should be taken up here. Nutrient ratios cannot be taken as indicative of limitation if ambient nutrient concentrations are high. Yet nutrients control the algal growth rate only if supply falls short of demand over the timescale of cellular growth and reproduction (Harris, 1986), and thus low concentrations do not necessarily imply nutrient limitation. So in this – as in other similar investigations (eg. Paasche & Erga, 1988) – the word limitation has been used rather loosely to indicate a state where the lack of one nutrient elicits potential reduction in the algal growth rates.

Study area

The Archipelago Sea is located between the Baltic proper and the Bothnian Bay (See Figure 1). The Archipelago Sea is characterized by an enormous topographic complexity, including about 25 000 islands. The average water depth is only 23 m and the deepest trench reaches 146 m. The total coastal drainage area is about 8900 km^2 (of which lakes cover under 2% and fields 28%). The total area of the Archipelago Sea is 9436 km^2 and the water volume is 213 km^3. Water flows mainly from the Baltic Sea basin to the Bothnian Bay through the Archipelago Sea and back to the Bothnian Sea mainly along the Swedish coast. This means an eastward net transport in the south, northwards along the eastern coasts, and a southward transport along the western coast of the Baltic Sea (HELCOM, 1993). Eight rivers run to the Archipelago Sea. The mosaic morphology and the environmental gradients (salinity, temperature, exposure etc.) create several biotopes and complicated ecological webs (Blomqvist & Bonsdorff, 1993; von Numers, 1995). As the topography is complex, and the water shallow, the area acts as a buffer or filter between the coastline and the open sea, and also between the Baltic proper and the Bothnian Bay. A great deal of suspended matter and nutrients settles down to the bottom, but most part of the nutrients is used for primary production (Jumppanen & Mattila, 1994).

The archipelago is affected by nutrients coming from several sources; from industrial and municipal waste waters and as a diffuse load from agriculture and forestry. The coastal areas have been affected by a heavy nutrient load since the 1960s. Fish farming was introduced in the 1970s as a new source of nutrient load. Now the Archipelago Sea is the major fish farming area in Finland. In the 1990s the annual total phosphorus load from industrial and municipal waste waters, fish farming and agriculture and forestry has been about 500 t and the total nitrogen load about 7000 t.

Material and methods

The Southwest Finland Regional Environment Centre (SFREC) has monitored the water quality in the Archipelago Sea since the 1960s. In all, water samples have been collected at 24 monitoring stations 2–4 times a year in late winter and late summer. The monitoring station Seili (established in 1983) is the most intensively studied station in the Archipelago Sea having over twenty sampling times a year. Time series for this study were obtained from the Seili station and the stations Airismaa and Nötö (See Figure 1). We concentrate here on the samples taken during May–October since biological production mostly happens during the open water season. Spatial variability of water quality has been studied in May and in August at 50–60 monitoring stations covering the whole study area.

All samples used here were analyzed in the laboratory of the SFREC where all physical and chemical analyses have been performed using standard methods (Koroleff, 1976, 1979; National Board of Waters, 1981). Total phosphorus (TP), phosphate-phosphorus (DIP), total nitrogen (TN), ammonium-nitrogen (NH_4-N), nitrate- and nitrite-nitrogen (NO_2-N + NO_3-N) (NH_4-N and NO_2-N + NO_3-N together DIN) have been analyzed from discrete unfiltered samples (1, 5, 10, 20, 30 ... 1–2 m above the bottom). DIP has been analyzed by an ammonium molybdate method with ascorbic acid as the reducing agent. In TP determination the sample was digested by $K_2S_2O_8$ before it was analyzed with ammonium molybdate. NH_4-N has been analyzed colorimetrically with hypochlorite and phenol. The sum of NO_3-N and NO_2-N has been determined by reduction of NO_3 followed by NO_2-

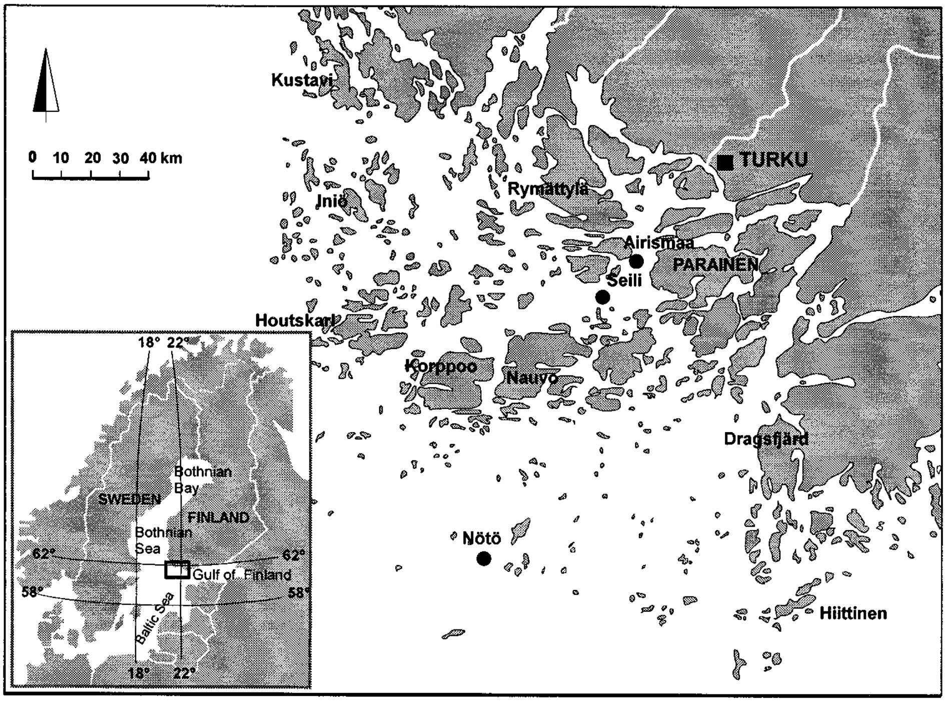


Figure 1. Study area.

N determination. TN has been analyzed as NO_3-N after the digestion of the sample with $K_2S_2O_8$. Filtrations for chlorophyll-*a* analyses were performed from composite samples (2∗Secchi depth collected at 2 m intervals). The algal pigments have been extracted with ethanol and chlorophyll-*a* concentration has been measured spectrophotometrically. Primary productivity has been estimated with ^{14}C technique.

The limits of detection in nutrient analyses have been determined in the SFREC by comparing to known concentrations following the guidelines given by the Environmental Agency of Finland (Mäkinen et al., 1996). These instructions are based on e.g. ‘Guide to Analytical Quality Control for Water Analysis’ (prENV ISO/CD 13530).

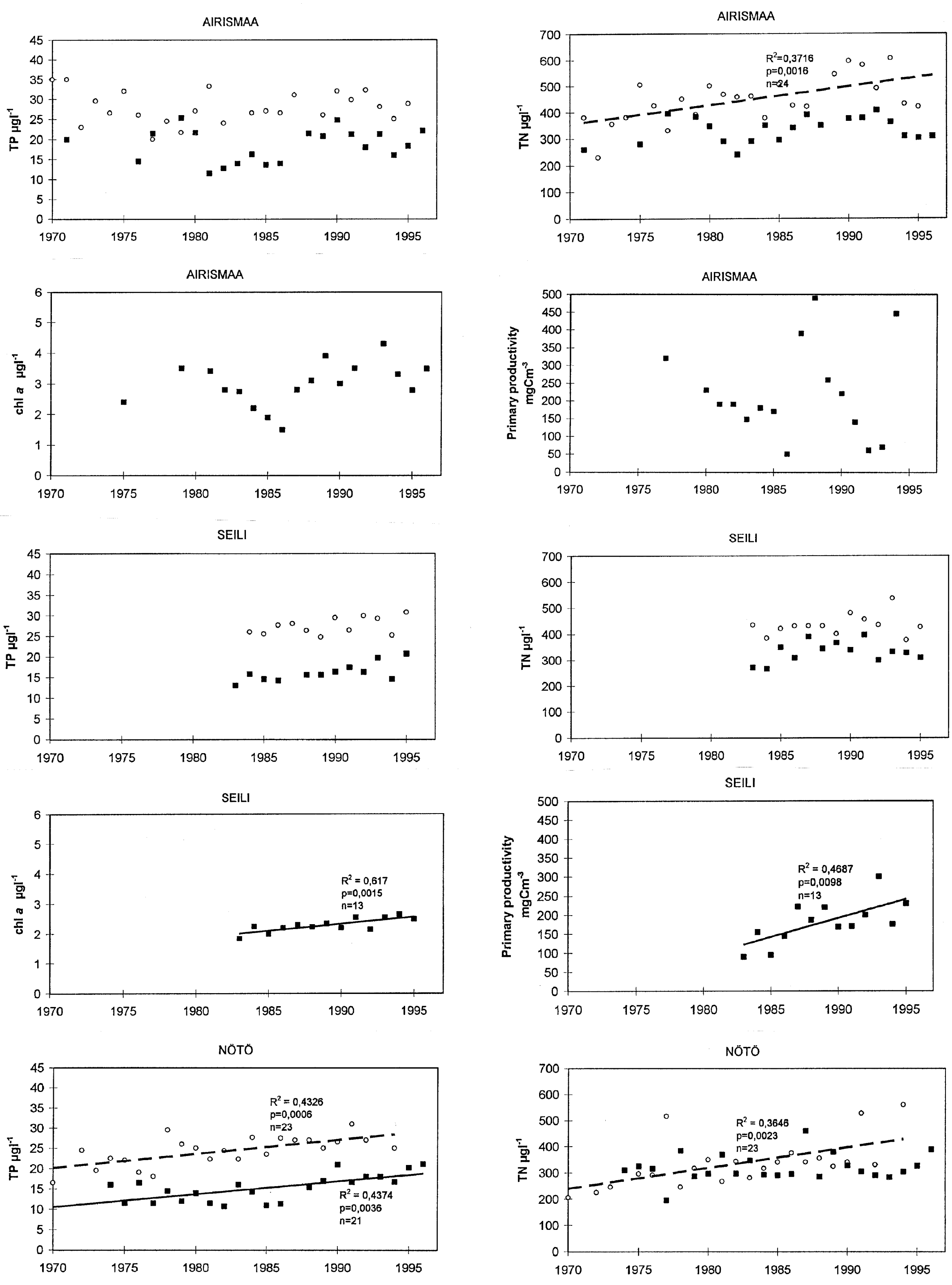
Here, nutrient limitation was studied by calculating different nutrient ratios in the surface layer (0–10 m): ratios between total nitrogen and phosphorus, between inorganic nitrogen and phosphorus, and finally between these two ratios, which is referred to as the ‘nutrient balance ratio’ according to Tamminen (1982). The following criteria were used to determine the limiting nutrient:

(1) If the total nutrient ratio TN:TP is over 7, phosphorus limits primary production and if TN:TP <7, nitrogen is the limiting factor (Redfield et. al., 1963).

(2) The inorganic nutrient ratio DIN:DIP has been evaluated according to two criteria. According to Forsberg et al. (1978) when DIN:DIP is below 5, nitrogen is the limiting factor and if the ratio is over 12, phosphorus limits primary production. If the ratio is between 5–12, the limiting factor may be either nitrogen or phosphorus or both. According to Ryther & Dunstan (1971) values below 10 represent situations where nitrogen is likely to be the principal limiting nutrient and values over 10 represent phosphorus limitation.

(3) Nutrient limitation has also been characterized by the nutrient balance ratio (Tamminen, 1982). If (TN/TP):[DIN/DIP]>1, nitrogen limits primary production and otherwise phosphorus is the limiting factor. The nutrient balance ratio compares the readily utilizable fractions of nutrients to respective total pool sizes (Tamminen, 1982).

Trend analyses were conducted by simple regression methods and probabilities (*p*) and coefficients of determinations (R^2) are given in figures, if *p*-values were statistically significant.


AIRISMAA
TP µgl-1
AIRISMAA
TN µgl-1
R2=0,3716
p=0,0016
n=24
AIRISMAA
chl a µgl-1
AIRISMAA
Primary productivity mgCm-3
SEILI
TP µgl-1
SEILI
TN µgl-1
SEILI
chl a µgl-1
R2 = 0,617
p=0,0015
n=13
SEILI
Primary productivity mgCm-3
R2 = 0,4687
p=0,0098
n=13
NÖTÖ
TP µgl-1
R2 = 0,4326
p=0,0006
n=23
R2 = 0,4374
p=0,0036
n=21
NÖTÖ
TN µgl-1
R2 = 0,3646
p=0,0023
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1970
1975
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Figure 2.

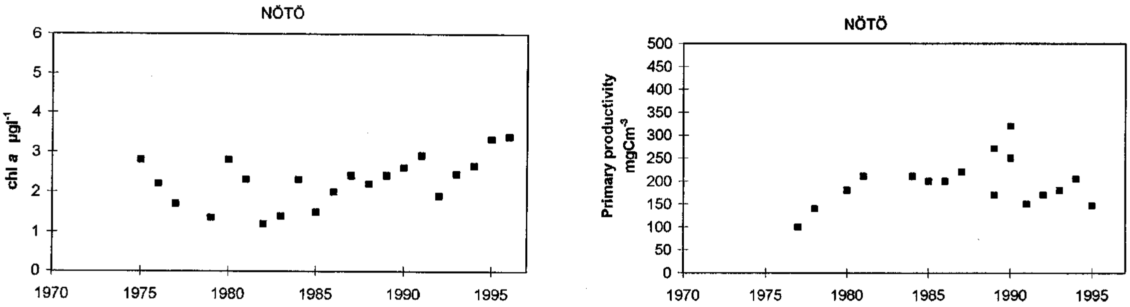

Figure 2. Total phosphorus (TP), total nitrogen (TN), chlorophyll-*a* (chl *a*) concentrations (μg l^{-1}) and primary productivity (mgC m^{-3}) in the Archipelago Sea 1966–1995 (black squares and solid regression line represent late summer values, circles and broken regression line represent winter values). Probabilities (p) and coefficients of determinations (R^2) are given in figures, if p-values are statistically significant.

Results

*Nutrient and chlorophyll-*a *concentrations and primary productivity*

Total phosphorus concentrations of sea water have clearly increased in the outer zone of the Archi- pelago Sea during the last two decades (see Figure 2, the monitoring station Nötö). The increase is especially apparent in the winter season data. The wintertime nutrient concentrations do not, however, directly affect the level of primary production of the following summer, because a large part of nutrients is transferred from the euphotic layer to deeper waters and to the bottom due to the vernal bloom (Pitkänen et al., 1993; Leppänen, 1988). At the monitoring station Seili, which represents the middle zone of the Archipelago Sea, the increase of the nutrient concentrations is not statistically significant. Near the coast, eg. at the monitoring station Airismaa, phosphorus concentrations decreased during the late 1960s and in the early 1970s due to notable improvements in sewage treatment techniques. After that phosphorus concentration has varied considerably.

Nutrient levels showed that the sea-areas near Turku, Rymättylä and Parainen are clearly eutrophied. Also Nauvo, Houtskari and Dragsfjärd-Hiittinen areas could be characterized as eutrophied. Other areas of the Archipelago sea are slightly eutrophied. In the late 1970s in summertime phosphorus concentrations over 20 μg l^{-1} were observed only in Rymättylä. Concentrations varied between 15-16 μg l^{-1} near the coast and 10-15 μg l^{-1} in the outer sea. In the 1990s values over 20 μg l^{-1} could be observed in more widespread areas nearby Iniö and Rymättylä sea-areas, and in Turku-Parainen-Nauvo-Korppoo sea-areas.

Total nitrogen concentrations have varied considerably, but an increasing trend has been obvious especially in winters. However, late summer concentrations have stayed at the same level (around 300 μg l^{-1}) during the last two decades.

Both the chlorophyll-*a* concentrations and the primary productivity have varied considerably at the Airismaa station and no trend can be observed. At the Seili station chlorophyll-*a* values and the primary productivity are clearly rising and the increase is statistically significant. Trends of chlorophyll-*a* and primary productivity seem to be rising also at the Nötö station, but the regressions are not statistically significant.

Nutrient limitation

When compared to the Redfield ratio, the total nutrient ratios (TN:TP) showed that there would exist phosphorus limitation in every analysed water sample. On the contrary, the ratios of inorganic nutrients, when compared to the criteria by Forsberg et al. (1978), showed that phosphorus usually limited primary production only near the coast line in August 1989 and during the earlier years (See Figure 3). In the middle zone of the Archipelago See the limiting factor varied temporally. Outer in the open sea nitrogen limited primary production during most of the year. If we compare the ratios of inorganic nutrient to the criteria by Ryther & Dunstan (1971), nitrogen seems to be the limiting factor also in the middle zone of the Archipelago Sea. In recent years, when the eutrophication has proceeded, there has been a shift from production limitation by both nutrients to limitation by nitrogen alone. For example, in August 1995, nitrogen limited the primary production in the whole study area.

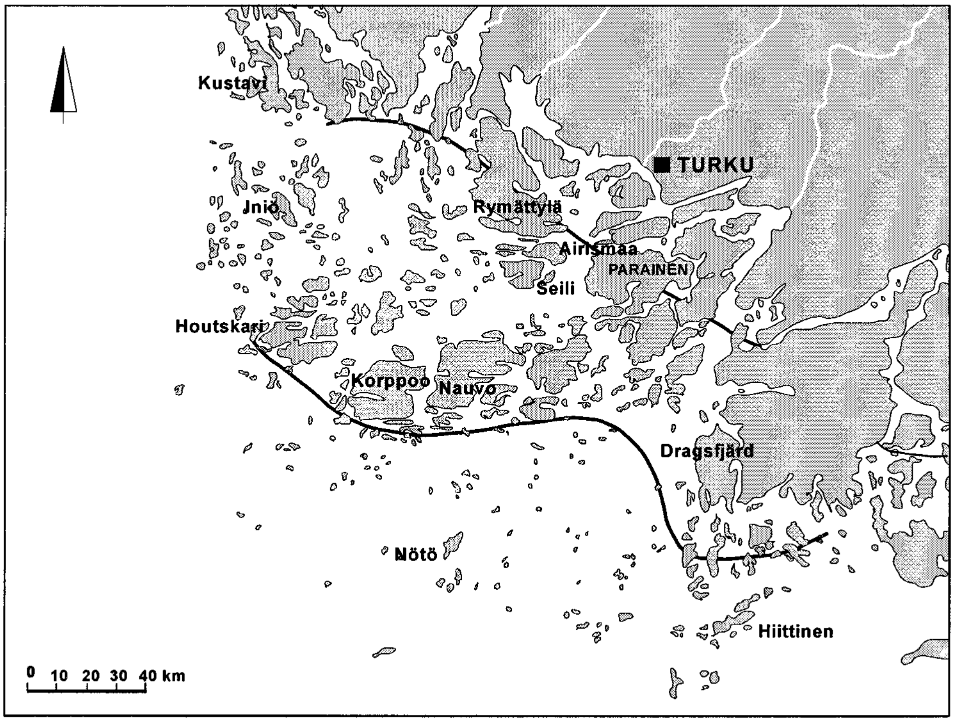

Figure 3. Inorganic nutrient ratios in August 1989. Inside the line near the coast DIN:DIP$>$12, between the two lines 5$<$DIN:DIP$<$12, outside the outer line DIN:DIP$<$5.

Frequently, a relatively sudden transition from limitation by one nutrient to limitation by the other occurs during open water seasons. According to the results (inorganic nutrients) of the monitoring station Seili, phosphorus limited phytoplankton growth especially in spring and in summer, while nitrogen was the limiting factor in late summer and in autumn when compared to the ratio by Ryther & Dunstan (1971). Results showed that there has been a change in nutrient limitation during the study period. After 1989 no phosphorus limitation could be found during the summer season (from July onwards) and in autumn (See Figure 4). When compared to the ratios presented by Forsberg et al. (1978), the DIN:DIP-ratio at the Seili station most often showed limitation situations in which the limiting factor may have been either nitrogen or phosphorus or both, especially in the 1980s. In the 1990s the DIN:DIP ratio showed mainly nitrogen limitation. The nutrient balance ratio has shown nearly exclusive nitrogen limitation during the whole monitoring period (See Figure 5). Moreover, in recent years all limitation cases by phosphorus alone were found in early May. Thus, during the 13 study years the proportion of the cases in which nitrogen was the limiting factor has increased (See Figures 4, 5a, b and c).

Discussion

Our results suggested that nitrogen is an important limiting nutrient in the Archipelago Sea. During the last decades the eutrophication has proceeded and phosphorus concentrations of the sea water have increased. At the same time a shift from production limitation by both nutrients to limitation by nitrogen alone has occured. Similar results have been found in other studies from the Archipelago Sea (e.g. Tamminen 1990). However, no general agreement on the question of the limiting nutrient at intermediate salinities has been found.

For example, ecosystem-level experiments in temperate coastal marine environments have shown significant responses to enrichment with nitrogen alone but not with phosphorus alone, indicating limitation by nitrogen (Oviatt et al., 1995; Taylor et al., 1995). In a simulated estuarine gradient bioassay, however, both inorganic nutrient concentrations and N:P ratios indicated that phosphorus was the limiting nutrient

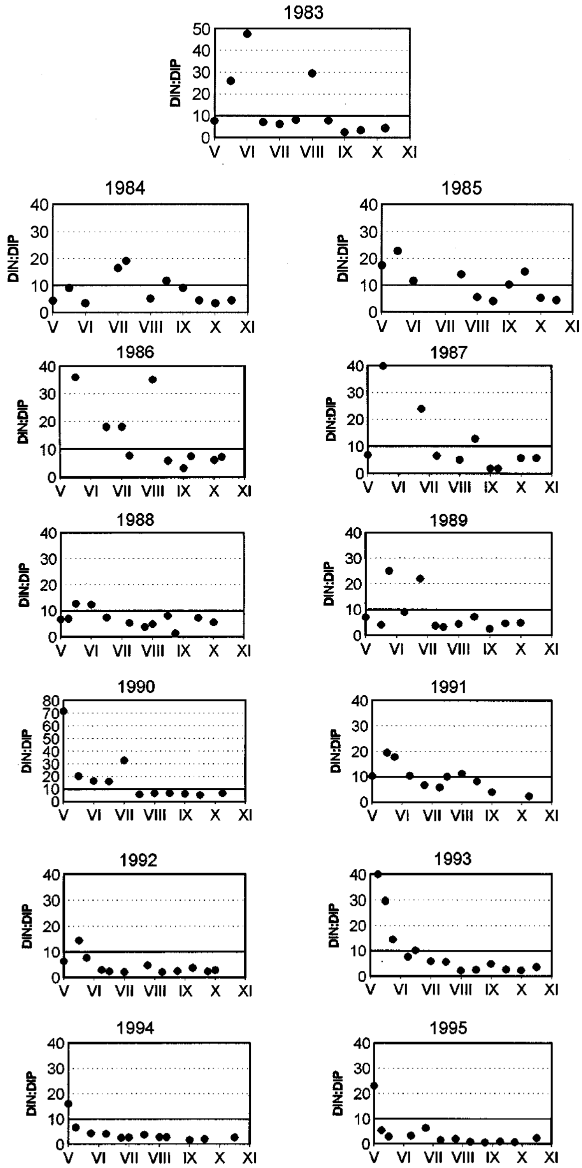

Figure 4. Inorganic nitrogen-phosphorus ratios at the station Seili in 1983–1995.

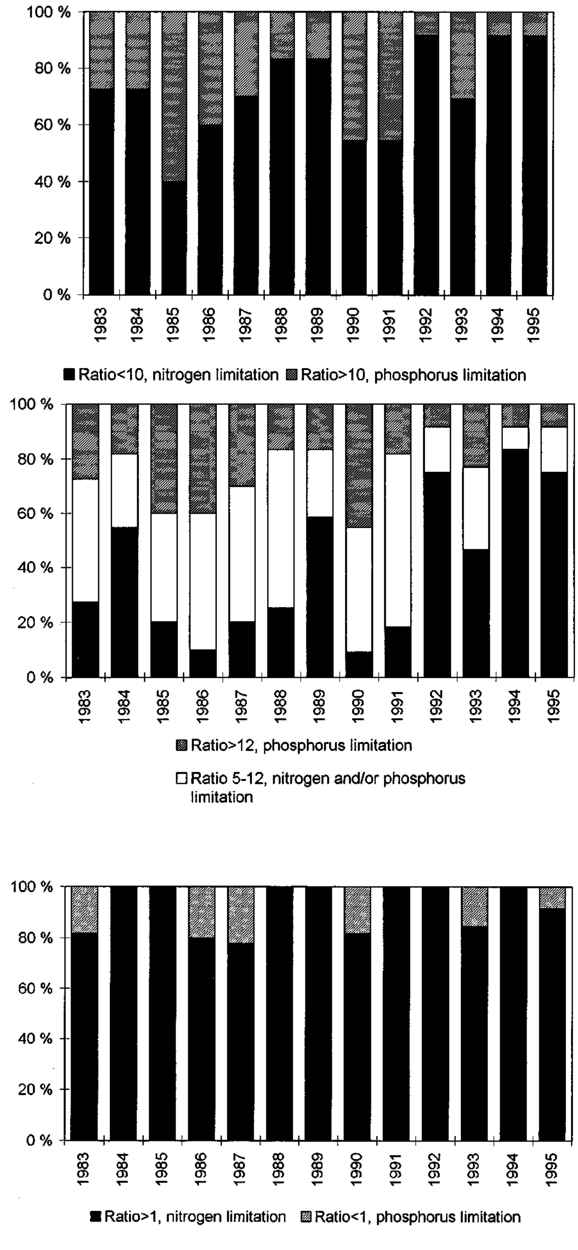

Figure 5. Proportion of cases when nitrogen, phosphorus or both are the limiting factors of primary production at the station Seili in 1983–1995. According to (a) criteria by Ryther & Dunstan (1971)(b) criteria by Forsberg (1978); (c) nutrient balance ratio; see page 119

at salinities lower than 10 ppt, while nitrogen was limiting at salinities of 25 ppt (Doering et al., 1995).

In the oceans, particulate C:N:P adheres to the Redfield ratio at which strong nutrient limitation by one element would not be expected (Hecky et al., 1993). The characterization of marine waters as N limited is based primarily on nutrient enrichment bioassays in bottles which may mispresent in situ conditions, and the N-limitation paradigm might require scrutiny (Hecky & Kilham, 1988). Elser et al. (1990) have also criticized enrichment assays and found that combined (N + P) enrichment enhanced algal growth much more frequently and more substantially than did single additions of N or P.

The use of nutrient ratios in evaluating the limiting factors has been widely criticized (e.g. Sakshaug & Olsen, 1986; Paasche & Erga, 1988). Different organisms have different requirements for essential elements and the Redfield ratio can be considered chiefly as a global mean (cf. Paasche & Erga, 1988). Tamminen (1982, 1990) has compared the N:P ratios (total, inorganic) as indicators of nutrient limitation in the brackish water and found that the TN:TP ratio was the most insensitive to the annual succession of the planktonic community. This is due to large compartments of dissolved organic nutrients, which are not readily utilizable for plankton (Tamminen, 1989). The DIN:DIP ratio was more sensitive to changes in the nutritional conditions of the plankton, but the nutrient balance ratio seemed to characterize spatial and temporal variations in nutrient limitation better than did the DIN:DIP ratio alone. Although these ratios showed good agreement with independent experimentation in the analysis of nutrient limitation (Tamminen, 1982), they are quite sensitive to analytical errors and imprecision especially in the summer periods when DIN- and DIP-concentrations are very low. We had in our study an opportunity to deal with precise analytical determinations. The limits of detection for the variables used in this study were the following: TP 0.9 μg l^{-1}, PO_4-P 0.6 μg l^{-1}, TN 10.3 μg l^{-1}, NH_4-N 1.1 μg l^{-1} and ($NO_2 + NO_3$)-N 1.4 μg l^{-1}. Only about 4% of the determinations of NH_4-N used in this study was near or under the detection limit, 9% of ($NO_2 + NO_3$)-N was under and 26% near the detection limit and about 7% of PO_4-P was near or under the detection limit.

One objection to the approach we have applied here has been that not all algae exhibit the same elemental ratio when grown in nutrient-replete medium, and this is further compounded by the fact that elemental ratios may vary through the natural light-dark cycle (Paasche et al., 1984; Brzezinski, 1985). Nutrient deficiency tends to be most pronounced when biomass reaches its culmination (Sakshaug & Olsen, 1986). In such situations nutrient demand greatly outstrips nutrient availability. Sakshaug and Olsen (1986) consider that conclusions based on nutrient status measurements are best when algal biomass is nearly monospecific. Balance point for N and P varies species by species (see e.g. Brzezinski, 1985; Paasche et al., 1984; Sakshaug & Olsen, 1986), which indicates that different species have different strategies for nutrient competition. Unfortunately, we have no detailed information on the composition of the algal biomass in the Archipelago Sea.

Natural phytoplankton populations are also continuously exposed to gradients of the limiting nutrients (Sakshaug & Olsen, 1986). This may include nutrient-rich pulses of different sizes, concentrations, and life times. In the Archipelago Sea, background load varies considerably especially during open water season, mainly because of highly variable wind conditions. Because these pulses have more P and N but lower N:P ratios (TN:TP = 16) than the waters in inner coastal zones (TN:TP = 20), rapid changes in phytoplankton species composition might emerge. Laboratory experiments (e.g. Sommer, 1984; Sakshaug & Olsen, 1986) have clearly demonstrated how such shifts occur. The absence of detailed phytoplankton data in our study may create some pitfalls in our interpretation because different phytoplankton species have different strategies for nutrient competition.

Paired N and P budgets including all sink and source elements would be useful when considering relative availability of these nutrient elements for plankton production (Paasche & Erga, 1988). In the Archipelago Sea only tentative estimations can be made because of the paucity of the data concerning for example the water inflow and outflow rates. Mean annual riverine fluxes of N and P to the Archipelago Sea were 5500 t and 491 t in 1986–1990 (TN:TP = 11). The inorganic N:P-ratio was 13 in the rivers discharging to the Archipelago Sea. The direct municipal inputs, including fish farming, of nitrogen and phosphorus to the Archipelago Sea were 1569 t a^{-1} of N and 89 t a^{-1} of P (TN:TP = 18) (Pitkänen 1994). The annual atmospheric input to the Archipelago Sea is about 4800 t a^{-1} of N and 82 t a^{-1} of P, thus the TN:TP ratio is 60 (Kirkkala, 1994).

In late summer the contribution of point-sources increases in relation to diffuse loading, because most of the agricultural areas are located in lake-poor coastal regions. Under normal hydrological conditions nutrient leaching from these areas mainly occurs during spring and late autumn. The average point-source inputs (including fish farming) are estimated as 60% of total N and 50% of total P for the Archipelago Sea. Point-sources contribute 74% of the summertime bioavailable N and 76% of the bioavailable P largely due to intensive fish farming, whereas the contribution of agriculture was estimated only as ca. 20% due to small leaching of nutrients from the fields in summer (Pitkänen, 1994).

Despite the fact that the Archipelago Sea receives a strong surplus of N there seems to be a trend towards low inorganic N:P ratios and even N deficiency, indicating important sinks for bioavailable N. Several coinciding internal processes, first of all denitrification of oxidized inorganic N, decrease the N:P ratios of the euphotic layer in coastal ecosystems (e.g. Seitzinger, 1988). There are also several other processes affecting N:P ratios like sedimentation, turbidity and light conditions (e.g. Pitkänen et al., 1994; Alasaarela, 1980).

So, if we want to define and characterize the nutrient limitation of the entire ecosystem of the Archipelago Sea, budgets have to be calculated for both N and P and internal recycling must be taken into account as well as external supply of nutrients and loss processes. We agree with Tamminen (1990) that definite results on nutrient limitation problems can be obtained by manipulating nutrient concentrations in carefully planned experiments. So far, in the absence of budget calculations and spatially and temporally representative field experiments, we can only utilize long-term monitoring data collected routinely by water authorities.

Acknowledgments

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