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On the seasonal nitrogen dynamics of the Baltic proper biogeochemical reactor

by Kari Eilola[1] and Anders Stigebrandt[1]

ABSTRACT

During the last decade it has become increasingly obvious that the turnover of dissolved organic nitrogen DON in marine environments is quite vigorous. This paper quantifies the turnover of DON in the Baltic proper regarded as a biogeochemical reactor. In a nitrogen model for the reactor, dissolved inorganic nitrogen DIN, DON and molecular N, fixed by cyanobacteria, can be used for plant production. The decomposition of particulate organic matter is assumed to produce DON and DIN as end products in the proportions $(1 - \eta)$ to η $(0 \leq \eta \leq 1)$. The model includes two internal sink processes, denitrification and sequestering in the bottom sediments and accounts for external sources and sinks by import and export of DIN and DON.

The annual net production in the Baltic proper is about 12.8 10^6 ton C (50 gC m^{-2}) requiring about 2.3 10^6 ton N. However only about 1.0 10^6 ton N are available as DIN and the deficit has to be covered by an uptake of N from DON and/or fixed molecular nitrogen. The results of the model depend on the value of η. With $\eta = 1$ the use of DON for primary production is at a minimum (0.19 10^6 ton N) while there are maxima for nitrogen fixation (1.0 10^6 ton N) and denitrification (1.5 10^6 ton N). However, both these values are considered unrealistically large. A more likely value of η is determined from the model in such a way that the annual rate of nitrogen fixation in the Baltic proper is in accordance with a recent estimate from the literature (0.11 10^6 ton N). This gives $\eta = 0.55$ implying that about 0.67 10^6 ton N is denitrified, and 1.10 10^6 ton DON is used for net production, and 0.91 10^6 ton DON is produced by decomposition of particulate organic matter and the turnover time for DON is about 4 years.

The finding that there is a vigorous turnover of DON on the reactor level has important consequences. *Firstly,* earlier estimates of denitrification rates were based on budgets for oxygen and DIN and overlooked the DON decomposition pathway, why denitrification rates are severely overestimated, often by a factor of 2 or greater. *Secondly,* the extensive use of DON for primary production in the Baltic proper in combination with abundance of DON, challenge the widely accepted opinion that nitrogen is the production-limiting nutrient on the systems (reactor) level in the Baltic proper.

1. Introduction

The concept that any natural water body may be looked upon as a complex biogeochemical reactor was introduced by Wulff and Stigebrandt (1989). They were guided by successful empirical studies of large-scale ecological processes in limnology which, for

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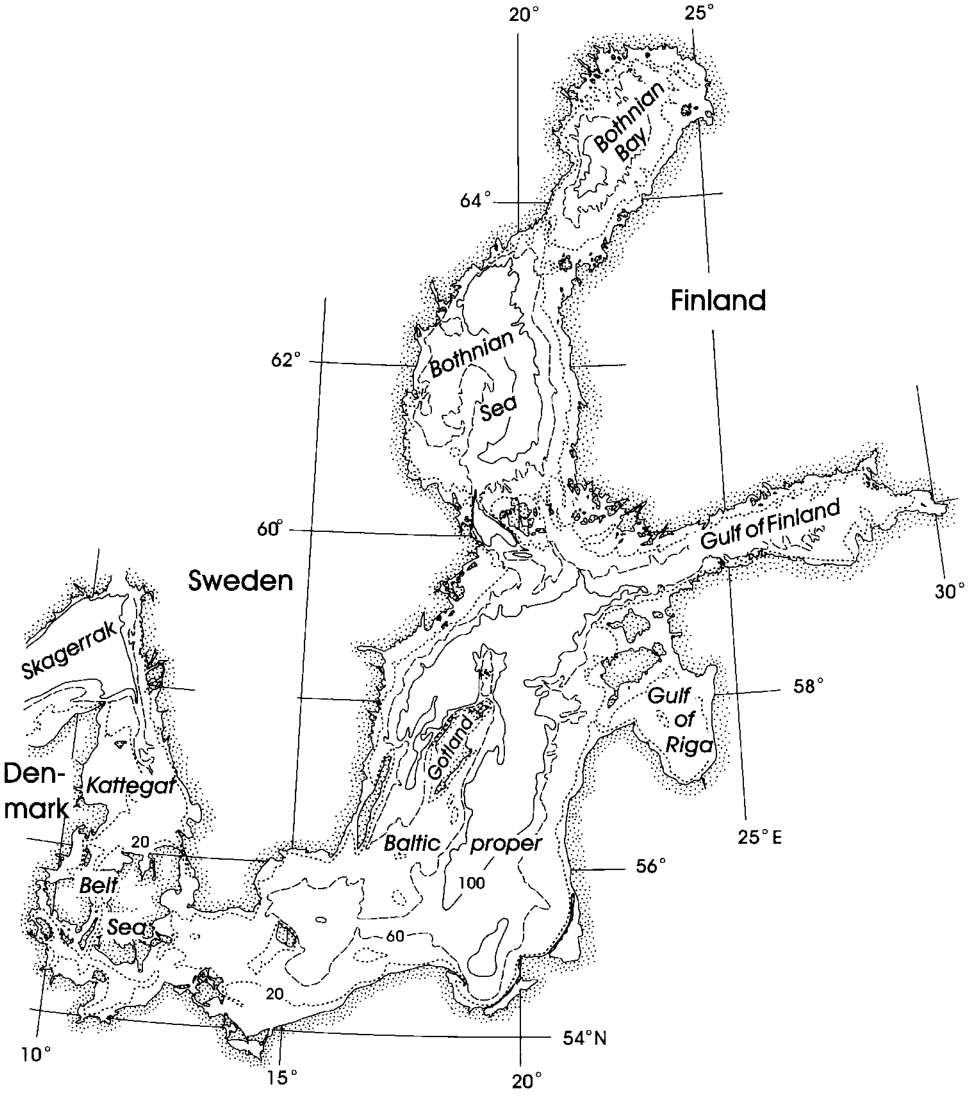

Figure 1. Map of the Baltic Sea. The maximum sill depth between Kattegat and the Baltic proper is about 18 m.

instance, showed simple relationships between winter surface concentrations of nutrients and biogeochemical sinks in lakes (Vollenweider, 1969). The great success of the limnological studies, and also the success of studies in the Baltic Sea (Fig. 1), lies in the relative ease with which external boundaries and transfers of energy and material across these are determined. The intention of the reactor approach is to reveal how qualitative and quantitative measures of the state of the water body depend on a few critical biogeochemical processes, the supplies of nutrients, organic matter and energy, and physical transports within the system. This is not only of scientific interest but also a prerequisite for making quantitative estimates of effects of changes of external supplies of nutrients upon the water quality of the Baltic as measured by, e.g. the volume of anoxic deepwater, the extent of summer blooms of the often toxic blue-green algae and the transparency of surface water and the associated state of shallow water benthic communities.

The aim of the present paper is to formulate a budget model which can be used to describe the seasonal cycling of nitrogen and quantify the use of different nitrogen compounds for the seasonal net production of organic matter in the reactor. The model is used in a diagnostic mode and applied to the present (around 1980) Baltic proper using robust estimates of bulk properties to constrain ranges of different fluxes and to test postulated dynamics.

a. The Baltic biogeochemical reactor

Phosphorus and nitrogen are lost from the Baltic Sea reactor by net export to external and internal sinks. The latter may be due to sequestering in the bottom sediments and transformation to a biochemically "inert" state; e.g., to molecular nitrogen by the process of denitrification. For long-term steady state of the reactor the supply of nutrients must equal the removal. From earlier long-term budgetary work we know that most of the nitrogen and phosphorus supplied to the Baltic ends up in internal sinks; only relatively small amounts ($\sim$10%) are exported through the mouth to the Belt Sea/Kattegat (Wulff and Stigebrandt, 1989). This implies that with respect to nutrients, the Baltic is an almost closed, i.e., slowly flushed, system. Wulff and Stigebrandt (1989) used a data set covering the period 1977–1981 and computed monthly means of nutrient concentrations and salinity. From these they computed annual means and used continuity equations to estimate the exchange of water and nutrients between the sub-basins of the Baltic Sea. The specific internal nutrient sinks (sink per horizontal unit surface area) were found to differ between the major basins of the Baltic Sea. The ratio between the specific internal sinks of P and Si was, however, quite similar in all basins, suggesting a similar sink mechanism for P and Si, in accordance with observed sequestering in the sediments (Jonsson and Carman (1994) and Eilola (1998)). The nitrogen sink was found to be more efficient due to denitrification.

To study the cycling of nitrogen on a seasonal basis we will take a closer look into the functioning of the Baltic biogeochemical reactor which produces organic matter and is driven by solar energy and carbon and plant nutrients. The concentration of particulate organic matter, a multidimensional time-dependent function, is a fundamental state variable of the reactor. For the reactor approach, however, the dimension of this function should be strongly reduced by aggregation of species to only a few classes. The high latitudes of the Baltic means that solar radiation is strong enough for production of organic matter in the upper layers during only a half-year-long production season centered around summer. Topographical characteristics and physical transport and mixing processes regulate the vertical stratification and modify the functioning of the reactor.

If the production of organic matter by the Baltic reactor is measured, the result depends on the time-scale considered. The net amount of organic matter produced by the reactor during the production season is here denoted the net production NP. Much of this is exported to deeper layers, beneath the productive upper layer, where most of it is oxidized thereby decreasing oxygen concentrations and increasing nutrient concentrations. Eventually, a small fraction of NP, however, becomes part of the sediment.

b. The net production NP

The net production NP of the reactor is controlled by the amount of nutrients supplied to the sun-lit, photic, production compartment of the reactor during the production season. Due to vertical convection, the Baltic proper is well mixed down to the perennial halocline at about 60 m depth in winter. The seasonal vertical stratification developing in the upper layers in spring (Fig. 2) impedes vertical transports of nutrients from lower layers to the sun-lit surface layers. Because of this, the winter concentrations in the slowly flushed reactor largely determine the availability of nutrients which in turn determines the net production NP. There is also a continuous production of organic matter during the production season using N and P regenerated by the decomposition of fresh organic matter in the surface layers. However, this production does not increase the seasonal NP. Shortage of one of the essential nutrients (phosphorus and nitrogen) may limit the net production. To investigate whether or not this is the case, one may make inventories of nutrients available for NP. If it turns out that one of the nutrients is less available than the other relative to the needs of plants, one would expect that this less available nutrient should limit NP. It is relatively easy to estimate the inventory of available phosphorus. However, to estimate the inventory of available nitrogen is a more difficult task because nitrogen has dynamic internal sources and sinks mentioned earlier in this paper.

c. The pool and turnover of DON

It has been argued by many authors, e.g. Rosenberg *et al.* (1990) and Granéli *et al.* (1990), that nitrogen is limiting the production in the Baltic proper because the ratio DIN/DIP of inorganic nitrogen (DIN) and phosphorus (DIP) in the winter water is lower than the 16:1 molar-ratio required by primary producers (Redfield *et al.,* 1963). However, it was shown by Jackson and Williams (1985) that an inclusion of the dissolved compounds of nitrogen (DON) and phosphorus (DOP) in oligotropic waters improved the Redfield argument that organisms control the nutrient concentrations and their distributions. As further discussed below, it has become increasingly obvious during the last decade that the turnover of DON in marine environments is quite vigorous and that DON has to be considered in discussions about nutrients available for biological production of organic matter.

The pool of DON consists of low-molecular-weight (LMW) compounds; e.g., urea and amino acids, which contain appreciable amounts of nitrogen expected to be biologically labile and high-molecular-weight (HMW) "humus"-like compounds with low contents of

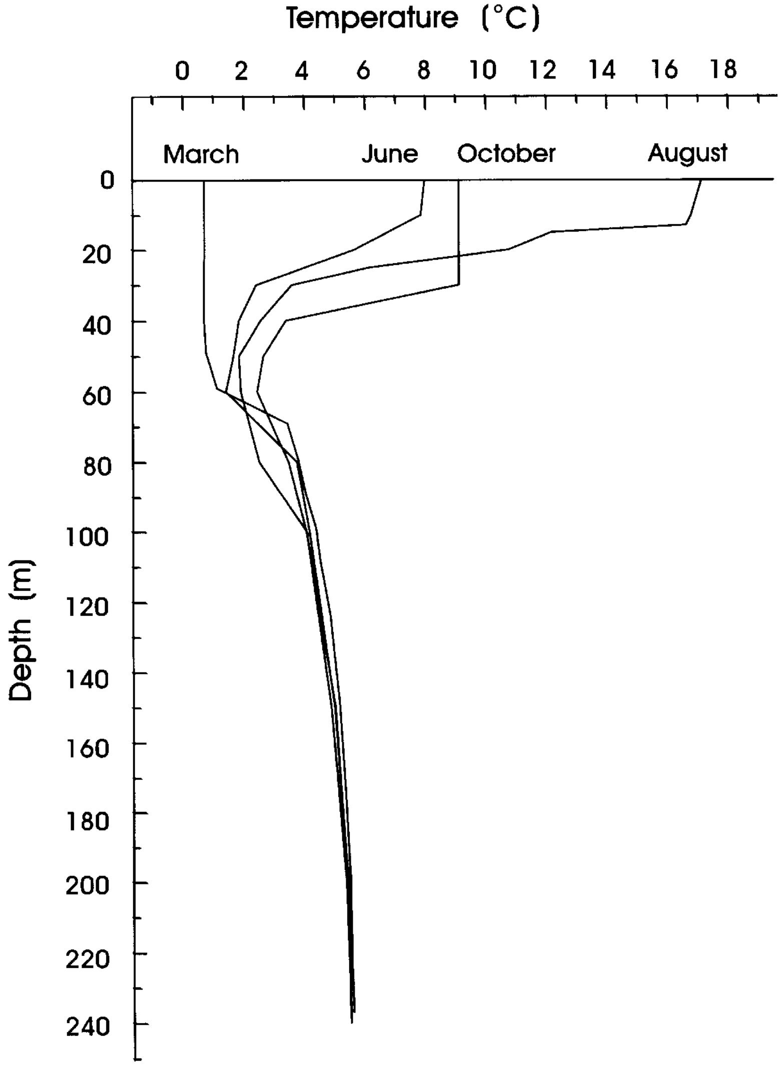

Figure 2. An example of vertical profiles of temperature from the central Baltic proper in March, June, August and October 1986. Data provided by the Department of Systems Ecology, Stockholm University.

nitrogen. However, as pointed out by Schnitzer (1985) a major part (~75%) of the nitrogen in humic substances seems to be contained in LMW compounds which are loosely held or adsorbed by humic substances. UV-light breaks down DON into smaller molecules (Kieber *et al.*, 1989). A major part of DON may thus be available for biological production (see the review by Antia *et al.* (1991)), and recently it has been shown that the HMW fraction is much coveted by bacteria (Amon and Brenner, 1994). In winter, the surface water of the

Baltic proper has DON concentrations (defined as DON = TotN-DIN) of about 20μM and a DON to DIN ratio in the range 3–4, e.g. Wulff and Stigebrandt (1989). For comparison, it may be mentioned that at depths greater than 100 meters in the open ocean DON ~ 3μM and DON/DIN ~ 0.1 (Sharp, 1983).

In later years it has become obvious that DON is a highly dynamic nitrogen compound in marine environments. Wulff and Stigebrandt (1989) noted that DON increases in concentration and changes in character from the Bothnian Bay to the Baltic proper, with probably a higher percentage of labile organic matter in the latter. Their nitrogen budget showed that about 2/3 of the net nitrogen sink in the Bothnian Sea should emanate from DON. Bronk *et al.* (1994) report that in oceanic, coastal and estuarine environments an average of 25 to 41 percent of the DIN taken up by phytoplankton is released as DON. Measurements of benthic nitrogen fluxes, using both *in situ* benthic chambers and incubation of sediment cores, at several places in Skagerrak and around Svalbard (Hulth, 1995, Blackburn *et al.,* 1996), in Kattegat (Enoksson, 1993) and in the Gullmar Fjord on the Swedish Skagerrak coast (Hall *et al.,* 1992; Landén *et al.,* 1999) show that DON often is a significant, and sometimes even dominating, species of the nongaseous benthic nitrogen flux to the water column. Because DON apparently constitutes an important part of the nitrogen released at decomposition of particulate organic matter there must also be processes in the reactor consuming DON at mean rates about equally large.

Grasshoff and Voipio (1981) pointed out that DIN may not be the only nitrogen compound of importance in the Baltic marine ecosystem because urea, found in significant amounts in the upper layers of the Baltic, might be a potential source of nitrogen for primary producers, particularly when other sources have been exhausted. Hagström and Öqvist (1983) showed a possible pathway from dissolved organic nitrogen via microbial activity. Carlsson *et al.* (1993, 1995) found in experiments with riverine humic substances that estuarine bacteria may use 30 to 60 percent of humic nitrogen. Seitzinger and Sanders (1997) found from experiments with estuarine bacteria that average DON content in river water entering estuaries had decreased by 40–72 percent after about 2 weeks. Palenik and Morel (1990) have shown that some phytoplankton have cell-surface enzymes allowing them to utilize DON in a way similar to the well-known cell-surface phosphatases making organic forms of phosphorus available for phytoplankton. Today it is evident that both bacteria and phytoplankton may use DON and DIN simultaneously for growth. The fact that usage of DON for primary production has been ignored earlier is mainly due to the analytical problems involved in measuring these compounds in sea water at environmental concentrations (Antia *et al.,* 1991).

Hence, several pathways making DON available for phytoplankton have been suggested, like direct uptake of DON by phytoplankton or indirect uptake after degradation and/or remineralization of DON either by the phytoplankton or by the aid of other micro organisms (see Carlsson and Granéli, 1998). However, no quantitative estimates of large-scale primary production based on DON seem to be available. In the present paper

Table 1. Horizontal areas at different depths and partial volumes of the Baltic proper, including Gulf of Finland, as determined from a topographical data base with the resolution 2′ × 1′ (Seifert and Kayser, 1995).

	Volumes (km^3)	Depth (m)	Area (km^2)
Box 1 (0 m–15 m)	3580	0	256700
Box 2 (15 m–60 m)	7120	15	217300
Box 3 (60 m–depth)	4190	60	106300

we will estimate the turnover of DON and thereby obtain a measure of its importance as a nitrogen source for the Baltic marine ecosystem.

To quantify the use of different nitrogen compounds for the net production NP we formulate (Section 2) a model appropriate for studies of the seasonal cycling of nitrogen in the Baltic proper with particular emphasis on the roles played by DON, N-fixation and denitrification. An application of the model to the present day Baltic proper is done in Section 3. The model results are discussed in Section 4. Finally the paper is concluded in Section 5.

2. Seasonal nutrient dynamics

A simple model for the seasonal nitrogen dynamics in the Baltic proper biochemical reactor is developed in this section. The bulk properties of the Baltic proper reactor used in the model are the magnitudes of nutrient import and export and the seasonal net production NP and the amount of DIN in the Baltic proper before the onset of the spring bloom. The model comprises the whole reactor but for model evaluation we need to estimate the availability of nutrients for primary production during the production season which, among other things, depends on vertical stratification. Roughly, the Baltic proper is composed of three homogeneous layers (boxes) occupying the depth intervals 0–15 m, 15–60 m and 60 m to greatest depths. The boxes are denoted Box 1 to Box 3 and their volumes are V_1 to V_3, see Table 1 for volumes and horizontal surface areas. The rationale of this partition is as follows. There is a seasonal thermocline at about 15 m depth in the summer season (cf. Fig. 2) so Box 1 contains essentially the seasonally heated water and, in addition, the depth of the euphotic zone happens to be about 15 meters. At about 60 m depth there is a permanent strong halocline below which the deep water resides. Due to cooling and strong wind-forced mixing during autumn, the waters in Boxes 1 and 2 become merged. This state persists throughout the winter and early spring. During this period the perennial halocline is eroded whereby deep water (from Box 3) is entrained into the upper layer. In spring when the seasonal thermocline becomes established, the water above the halocline again becomes separated into two layers. For a description of the annual stratification cycle in the Baltic proper see Figure 2 and Stigebrandt (1985).

Primary production takes place in the uppermost layer in summer. However, the spring bloom starts already when the depth of the upper layer is equal to or less than the so-called critical depth (Sverdrup, 1953), see Stigebrandt and Djurfeldt (1996) for seasonal varia-

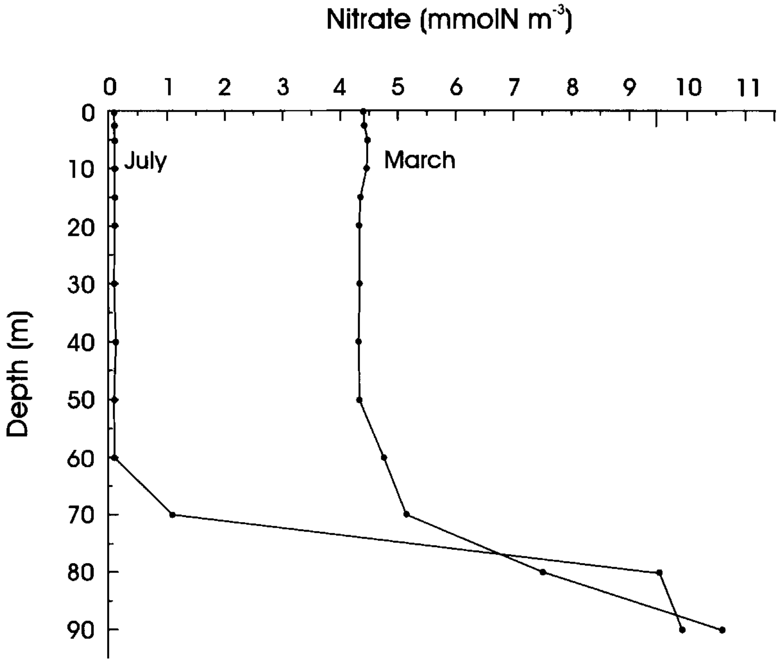

Figure 3. An example of vertical profiles of nitrate concentrations in March and July 1994 from the central part of the Baltic proper. Data provided by the Department of Systems Ecology, Stockholm University.

tions of the critical depth and the upper pycnocline in the Baltic proper. During this initial phase of the production season nutrients from both Box 1 and 2 are used (c.f. Fig. 3) as discussed in Stigebrandt and Wulff (1987). The use of nutrients from Box 2 may also be due to intermittent deepening of the upper layer before the seasonal pycnocline has become well established as suggested by these authors. Diffusive fluxes of nutrients from below 60 m to the photic zone are, therefore, neglected in the present model because they should be small due to the stable stratification developing in the spring (cf. Fig. 2). Organic matter sinks down into the water below the surface box where it is broken down or sequestered in the bottom sediments.

Oxygen budgets for both the surface layer (Stigebrandt, 1991) and for deeper layers (Eilola, 1998) in the Baltic proper indicate that in the late 1970s the seasonal net production NP was about 50 gC m^{-2}yr^{-1}, or 12.84 Mton C yr^{-1} (1 Mton = 10^6 ton) (Table 2) if integrated over the whole Baltic proper with the horizontal surface area as given in Table 1.

Table 2. Net production of organic matter. The figures below are based on the Redfield ratios.

Production	C (Mton yr^{-1})	P (Mton yr^{-1})	N (Mton yr^{-1})
Spring	8.21	0.20	1.44
All Seasons	12.84	0.31	2.26

Table 3. Nutrients (in Mton) available in the well mixed surface layer (0–60 m) in late winter. Nutrient concentrations were taken from Wulff and Stigebrandt (1989) and the volume used is from Table 1.

DIP_A	DOP_A	TOTP	DIN_A	DON_A	TOTN
0.18	0.09	0.27	0.75	2.70	3.45

This is also well in accordance with the oxygen consumption in lower layers estimated by Rahm (1987) and with estimates of the gross production GP by Elmgren (1984) if the so-called *f*-ratio is 0.3. To produce this amount of organic matter, 2.26 Mton N yr^{-1} and 0.31 Mton P yr^{-1} are needed if organic matter produced by primary producers is composed according to the so-called Redfield ratios, i.e., C:N:P = 106:16:1. From where are these nutrients taken?

As mentioned above, the spring bloom is able to utilize nutrients down to the perennial halocline; i.e., the nutrients in Box 1 and 2 (cf. Fig. 3). With a mean winter concentration of total phosphorus of 0.8 μM (Wulff and Stigebrandt, 1989), Box 1 and 2 contain 0.27 Mton P (Table 3). In addition there is an annual external supply of about 0.05 Mton P yr^{-1} (Table 4). Maybe half of this enters during the production season. It thus seems that the amount of available phosphorus is accurately what is needed for the estimated net production NP. This is probably not just a coincidence but rather an indication of phosphorus being the nutrient controlling the net production NP. With a mean winter concentration of 5 μM DIN (mainly nitrate) (Wulff and Stigebrandt, 1989) Boxes 1 and 2 contain 0.75 Mton DIN. Where does the rest of the nitrogen come from; i.e., 1.5 Mton, used for the seasonal net production NP? Some DIN is supplied by external sources during the production season, probably some 0.3 Mton as discussed below, but still there is a deficit of more than 1 Mton N ($2.26 - 0.75 - 0.3$). There is a large pool of about 2.7 Mton DON in Box 1 and 2 which most probably is used by plant plankton, possibly via microbial activity. Here we have defined DON = TotN-DIN using a winter concentration of total nitrogen of 23 μM (Wulff and Stigebrandt, 1989). Another potential nitrogen source is molecular nitrogen that may be fixed by cyanobacteria.

Nutrient supplies to the Baltic proper are given in Table 4. The external nutrient loading to the Baltic proper was computed using the loading from atmospheric and point sources (both assumed inorganic) presented by Larsson *et al.* (1985) and the riverine loading estimated by Stålnacke (1996) who used statistical methods to remove inconsistent or incorrect data and to fill gaps in the time series. Finally he computed flow-normalized nutrient loads to the sub-basins of the Baltic Sea. It is believed that the riverine loading

Table 4. Nutrient supplies and net export of nutrients to the Gulf of Bothnia and Kattegat.

	Nitrogen (Mton yr^{-1})			Phosphorus (Mton yr^{-1})		
	DIN	DON	TotN	DIP	DOP	TotP
Ext. Load	0.61	0.31	0.92	0.033	0.016	0.049
Net Exp.	0.01	0.12	0.13	0.005	0.005	0.010

Table 5. Water exchange ($km^3\ yr^{-1}$) between the Baltic proper and adjacent seas. Here we used the geostrophic baroclinic outflow from the Gulf of Bothnia computed by Eilola and Stigebrandt (1998). The corresponding inflow was obtained using the annual freshwater supply to the Gulf of Bothnia referred to in Eilola and Stigebrandt (1998) and budgets of volume conservation. The water exchange with the Belt Sea/Kattegat was computed from salt and volume budgets by Wulff and Stigebrandt (1989).

To *From*	Baltic proper	Bothnian Sea	Belt Sea/Kattegat
Baltic proper	—	1390	1000
Bothnian Sea	1600		
Belt Sea/Kattegat	500		

given by Stålnacke (1996) is less uncertain than previous estimates. Nitrogen fixation is (of course) not included in the external loading in Table 4. The total loadings are about equal to the figures from Larsson *et al.* (1985) which were used by Wulff and Stigebrandt (1989), though, the loading of phosphorus is lower by about 0.01 Mton yr^{-1} and the loading of nitrogen is higher by about 0.1 Mton yr^{-1}. To compute the net nutrient export we used the geostrophic baroclinic water exchange with the Gulf of Bothnia computed by Eilola and Stigebrandt (1998) and the water exchange with the Belt Sea/Kattegat computed from salt and volume budgets by Wulff and Stigebrandt (1989), see Table 5. Nutrient concentrations used in the computations (Table 6) were taken from Wulff and Stigebrandt (1989). In the present paper, the Gulfs of Finland and Riga are included in the Baltic proper.

a. The nitrogen model

Here we formulate annual nitrogen budgets for the Baltic proper biogeochemical reactor to investigate the roles played by DIN, DON, N fixation, denitrification and the pathways of N in the decomposition of organic matter. The N requirements for the net production NP, denoted NPN, are thought to be covered by the following sources; DIN_p which is DIN stored in the water when the spring bloom starts and DIN supplied from external sources during the production season, DON_p taken from the pool of DON, and molecular nitrogen

Table 6. Annual mean nutrient concentrations used for computations of import and net export of nutrients to the Baltic proper. The annual mean DIN_m, $TotN_m$, $TotP_m$ and winter concentrations DIN_W and DIP_W are from Wulff and Stigebrandt (1989). No values of DIP_m were presented. For simplicity here we define $DOP_m = 0.5 \cdot TotP_m$ and $DIP_m = 0.5 \cdot TotP_m$. The figures are believed to be accurate enough for the purpose of the present paper. We also define $DON_m = TotN_m - DIN_m$.

	Nitrogen (μM N)			Phosphorus (μM P)		
	DIN_m	DON_m	$TotN_m$	DIP_m	DOP_m	$TotP_m$
South Bothnian Sea	1.34	14.6	15.9	0.185	0.185	0.37
North Baltic proper	1.93	17.5	19.4	0.270	0.270	0.54
South Baltic proper	1.08	19.1	20.2	0.350	0.350	0.70
Belt Sea-Kattegat	1.94	23.1	25.0	0.525	0.525	1.05

NF fixed by cyanobacteria. Thus,

$$\mathrm{NPN} = \mathrm{Din}_P + \mathrm{Don}_P + \mathrm{NF} \tag{1}$$

Here $\mathrm{DIN}_P = \mathrm{DIN}_A + \frac{1}{2}\mathrm{DIN}_{EXT}$ where DIN_A is DIN stored in the water when the spring bloom starts and used during the production season and DIN_{EXT} is the supply from external sources, by runoff and from the atmosphere and waste water outlets, during one year. Half of DIN_{EXT} is assumed to be supplied and used during the production season. Thus, according to this model the net production NP is produced using partly DIN and partly DON and molecular N fixed by cyanobacteria (NF).

As discussed in the introductory section of this paper, DON seems to be an important product from decomposition processes operating on organic matter. We, therefore, assume that there are two pathways for nitrogen in decomposition processes. One is to DIN and the other to DON and these are produced at the rates DIN_K and DON_K, respectively. We assume that the net result of all decompositional processes, i.e. both pelagic and benthic, during the production season is such that DON and DIN are produced in the ratio $(1 - \eta)/\eta$ $(0 \leq \eta \leq 1)$ where η thus is the fraction of N regenerated as DIN. It is also assumed that the fraction $(1 - \alpha)$ of the net production is decomposed while the fraction α is buried in the bottom sediments, thus

$$\mathrm{DIN}_K = \eta(1 - \alpha)\mathrm{NPN} \tag{2}$$

$$\mathrm{DON}_K = (1 - \eta)(1 - \alpha)\mathrm{NPN} \tag{3}$$

The DIN balance for the reactor reads

$$\frac{d}{dt}\mathrm{DIN} = \mathrm{DIN}_{EXT} + \mathrm{DIN}_K - \mathrm{DIN}_D - \mathrm{DIN}_{EXP} - \mathrm{DIN}_P \tag{4}$$

Here d/dt(DIN) is the long-term (year to year) rate of change of DIN content in the reactor, DIN_D is the rate of denitrification and DIN_{EXP} is the net export of DIN to the Belt Sea/Kattegat and the Gulf of Bothnia. According to this model the Baltic proper thus obtains DIN by external supplies and by decomposition of organic matter in proportion to the net production NP.

The DON balance for the reactor is

$$\frac{d}{dt}\mathrm{DON} = \mathrm{DON}_{EXT} + \mathrm{DON}_K - \mathrm{DON}_P - \mathrm{DON}_{EXP} \tag{5}$$

Here d/dt(DON) is the long-term rate of change of DON content in the reactor and DON_{EXP} is the net export of DON to the Belt Sea/Kattegat and the Gulf of Bothnia. According to the model, the Baltic proper obtains DON not only by external supplies but also by decomposition of organic matter in proportion to the net production.

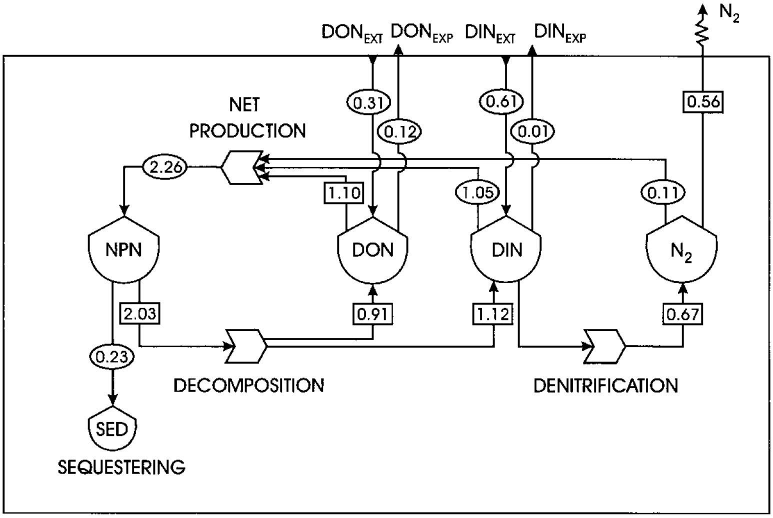

Figure 4. Flow chart for nitrogen in the Baltic proper biogeochemical reactor according to our model. As further explained in the text, numbers (in Mton N yr^{-1}) in ovals are considered known and numbers in squares are computed by the model using $\eta = 0.55$.

Just to check the overall nitrogen balance for the reactor Eqs. (4) and (5) may be added. With the help of Eqs. (1), (2) and (3) one then obtains

$$\frac{d}{dt}\text{totN} = \text{DIN}_{\text{EXT}} + \text{DON}_{\text{EXT}} + \text{NF} - \alpha\text{NPN} - \text{DIN}_{\text{D}} - \text{DIN}_{\text{EXP}} - \text{DON}_{\text{EXP}} \qquad (6)$$

This equation describes the expected overall nitrogen balance for the whole reactor with supplies by import of DIN and DON and by nitrogen fixation and losses by burial of organic matter, denitrification and export. A flow chart of nitrogen in the Baltic proper biogeochemical reactor according to our model is shown in Figure 4.

The corresponding budget for total phosphorus totP is

$$\frac{d}{dt}\text{totP} = \text{DIP}_{\text{EXT}} + \text{DOP}_{\text{EXT}} - \alpha\text{NPP} - \text{DIP}_{\text{EXP}} - \text{DOP}_{\text{EXP}} \qquad (7)$$

where DIP and DOP are the dissolved inorganic and organic phosphorus compounds. NPP is the P requirement for net production of organic matter.

One important difference between the budgets for N and P is that there are no degrees of freedom for the regulation of sources and sinks in the P budget. The net supply of phosphorus to the Baltic reactor at a steady state has to become buried with some of the organic matter exported to the sediments (Wulff and Stigebrandt, 1989; Carman and Wulff, 1989; Eilola, 1998). Thus, in a steady-state reactor the net production must support the phosphorus sink by $\alpha\text{NPP} = \text{DIP}_{\text{EXT}} + \text{DOP}_{\text{EXT}} - \text{DIP}_{\text{EXP}} - \text{DOP}_{\text{EXP}}$ as can be shown from Eq. (7). Hence, when regarding the cycling of phosphorus the forcing of NP in the model is quite severe through the benthic retention coefficient α in the model. The actual concentrations of P in the reactor are therefore determined by the physical and biological processes which make P available for NP during the production season. The nitrogen budget model on the other hand has degrees of freedom whereby the sources and sinks of nitrogen may become regulated and balanced in the reactor. Thus, if the supply of nitrogen is greater than the internal sinks, the reactor will begin to leak nitrogen, as gas to the atmosphere through DIN_D and/or as export to external areas (DIN_{EXP}, DON_{EXP}). However, if more nitrogen is needed for biological production in the reactor, nitrogen may be assimilated from the atmosphere through NF. The overall roles of NF and DIN_D in the Baltic reactor are, however, poorly known and described at present.

In the next section we will use the model to study how nitrogen fixation NF, denitrification DIN_D and use of DON for production DON_P depend on η in the present day Baltic proper where we know NPN, DIN_P, DIN_{EXT}, DIN_{EXP}, DON_{EXT}, DON_{EXP}. For simplicity, we will also assume that $d/dt = 0$; i.e., we assume steady state on the annual time scale.

3. Application to the present day Baltic proper

The external supply of DIN is about 0.61 and the export is about 0.01 so the net supply, $DIN_{EXT} - DIN_{EXP}$ equals about 0.60 Mton yr^{-1} (Table 4). The total content of DIN in Boxes 1 and 2 just before the spring bloom starts is 0.75 Mton (Table 3) so DIN_A equals 0.75 Mton yr^{-1} if all DIN in Boxes 1 and 2 at the start of the spring bloom is used for biological production and $DIN_P = DIN_A + \frac{1}{2}DIN_{EXT} = 1.05$ Mton yr^{-1}. Using the figures from Table 4, DON_{EXT} is about 0.31 Mton yr^{-1} and the net export to Kattegat and the Gulf of Bothnia DON_{EXP} is about 0.12 Mton yr^{-1}. These known nitrogen fluxes are shown by the figures in ovals in the flow chart describing our nitrogen model (Fig. 4). Eilola (1998) estimated from oxygen budgets that α equals 0.12 which should be valid for carbon. This is close to the figure 0.14 that can be derived from the sink of total phosphorus 0.039 (Table 4) if all the phosphorus in Box 1 and 2 (0.27) (Table 3) is used for net production. Here we use $\alpha = 0.1$ for nitrogen.

Using the model in the previous section and the independent observations above, valid for the present day Baltic proper, we will study the relationships between η and NF, DIN_D and DON_P.

Using $d/dt = 0$, $DON_{EXT} - DON_{EXP} = 0.19$ and Eq. (5) we find that

$$DON_P - DON_K = 0.19. \tag{8}$$

If this is used together with Eq. (3), with $\alpha = 0.1$ and $NPN = 2.26$, we get

$$DON_P = 2.22 - 2.03\eta. \tag{9}$$

From Eq. (1) with $NPN = 2.26$ and $DIN_P = 1.05$ we get

$$DON_P + NF = 1.21. \tag{10}$$

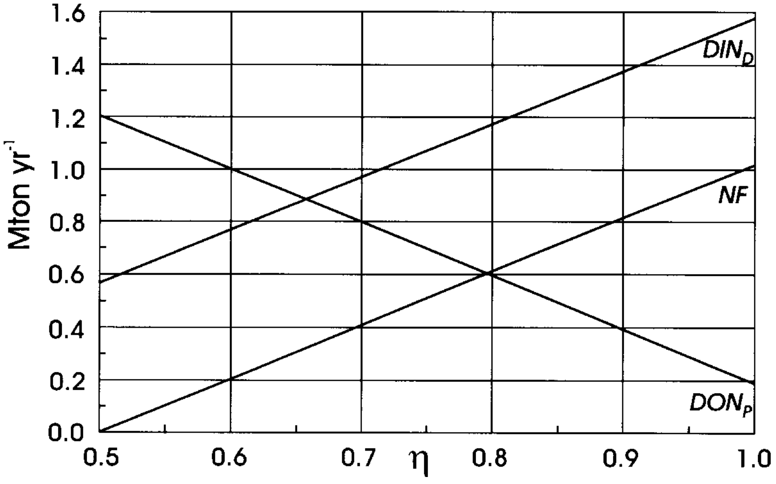

Figure 5. Model results showing DON_P, NF and DIN_D versus η.

Inserting Eq. (9) in Eq. (10) we get

$$NF = 2.03\eta - 1.01. \tag{11}$$

Since NF cannot be negative the fraction η of the decomposed net production entering the water column as DIN is thus at minimum 0.50 but may be larger if there is nitrogen fixation (NF), cf. Eq. (11). By obvious reasons, η cannot be greater than one so Eq. (11) also shows that NF $\leq$ 1.02 Mton yr^{-1}.

Finally, using Eq. (4) with $d/dt = 0$, $DIN_{EXT} - DIN_{EXP} = 0.60$ and $DIN_P = 1.05$ and DIN_K evaluated from Eq. (2) with $\alpha = 0.1$ and $NPN = 2.26$ we obtain the following expression for the rate of denitrification

$$DIN_D = 2.03\eta - 0.45. \tag{12}$$

In Figure 5 we have plotted DIN_D, NF and DON_P versus η. As shown by Eq. (10) the sum of NF and DON_P is constant and equals 1.21 Mton yr^{-1}. In the model the relative magnitude of NF and DON_P is regulated by η and both DIN_D and NF increase with η while DON_P decreases. Furthermore, we notice that the rate of denitrification in the reactor decreases with increasing turnover of DON.

η has been constrained to the interval $0.50 < \eta \leq 1$ which means that $0 \leq NF \leq 1.02$ Mton yr^{-1}, $1.21 \geq DON_P \geq 0.19$ Mton yr^{-1} and $0.57 \leq DIN_D \leq 1.58$ Mton yr^{-1}. There is, so far, no estimate of η for the Baltic proper biochemical reactor. However, an independent estimate of either DON_P, NF or DIN_D may be used to determine η. At present there is no estimate of DON_P. Leppänen *et al.* (1988) estimated that NF equals 0.11 Mton yr^{-1} which gives $\eta = 0.55$ from Eq. (10). Using Eqs. (9) and (11) one then obtains $DIN_D = 0.67$ Mton yr^{-1} and $DON_P = 1.10$ Mton yr^{-1}. This estimate of NF may be uncertain. It seems still harder, however, to estimate η using estimates of DIN_D.

Another way to calculate η is to apply a model for phosphorus (DIP and DOP) similar to that developed in Section 2. Using the information in Tables 3 and 4 one may then obtain the single value $\eta = 0.63$, which is rather close to the η-value estimated above from the nitrogen budget with the observed NF from Leppänen *et al.* (1988). (With $\eta = 0.63$, Eq. (11) gives NF $= 0.27$ Mton yr^{-1}.) This suggests that the inorganic and organic nitrogen and phosphorous compounds regenerated from organic matter in the Baltic proper are products of similar degradation processes. In fact, DOP is considered as biologically available in the Baltic Sea (Granéli *et al.,* 1990) and the results of the present study suggest that DON should be an equally dynamic participant in biological primary production.

The regeneration ratio η was about 0.71 in experiments with undisturbed coastal sediments to which fresh organic matter (molar C/N-ratio = 6.4) was added (Enoksson, 1993). From these experiments we estimated η from $\eta = 1/(1 + \mathrm{DON_K/DIN_K})$ using the reported mean values of net sediment to water nitrogen fluxes for a period of 19 days after the algal addition, 17.9 μmolNm^{-2}h^{-1} ($\mathrm{DON_K}$), 49.0 μmolNm^{-2}h^{-1} (NH_4^+) and -4.4 μmolNm^{-2}h^{-1} (NO_3), ($\mathrm{DIN_K} = NH_4^+ + NO_3$). The benthic oxygen consumption in the same period was 540 μmol(O_2)m^{-2}h^{-1}. Enoksson also suggested that the release of DON is regulated by the oxygen conditions since much of the DON disappeared from the pore water and the release of DON ceased when the overlying water turned anoxic. However, these results may be questioned since Hall *et al.* (1992) did not see this effect in their observations. The DON released by phytoplankton reported by Bronk *et al.* (1994) (see Section 1) corresponds to η in the range 0.59–0.75.

Shaffer and Rönner (1984) estimated denitrification in the Baltic proper deepwater in Box 3 to be about 0.47 Mton yr^{-1}. They estimated oxygen consumption and nitrate production rates using a natural coordinate conservation method. Oxygen consumption was then transformed to nitrification rates using a stoichiometric model of the organic matter decomposing in the deep water. Finally they computed the rate of denitrification from the difference between estimated and observed nitrate production rates, thus implicitly assuming that $\eta = 1$. However, if on average 45% of the decomposed matter is regenerated as DON and thus not denitrified nitrate, we conclude that the total denitrification in the deep water should be much less than estimated by Shaffer and Rönner. According to the results of the present paper (cf. Fig. 4) $\mathrm{DIN_D} = 0.67$ Mton yr^{-1}. To obtain a first estimate of the distribution among the boxes, one may assume that this is proportional to the bottom area of the boxes. If so, since Box 3 has about 40% of the bottom area (Table 1) it has 40% of the denitrification; i.e. $0.4 \cdot 0.67 = 0.27$ Mton yr^{-1} which is only about half of the denitrification estimated by Shaffer and Rönner (1987). The denitrification in Box 1 and 2 should then amount to about 0.4 Mton yr^{-1}. Our estimate require a mean specific rate of denitrification of about 2.5 ton km^{-2} yr^{-1}. However, to the best of our knowledge there are no other independent estimates of denitrification in the Baltic proper; thus, our figure for $\mathrm{DIN_D}$ cannot be verified at present. The fluxes computed by the model and constrained by the estimated NF are shown by the numbers in squares in Figure 4. The only model result that we have not commented upon is the net flux of nitrogen gas out of the reactor, 0.56 Mton yr^{-1}, which balances the import minus export of DON and DIN minus the sequestering of particulate nitrogen in sediments. Measurements of the N_2 flux from the Baltic proper may thus be used to check this balance. To the best of our knowledge there is no published estimate of nitrogen fluxes out of the Baltic based on measurements.

4. Discussion of model results

In qualitative reasonings of the functioning of the Baltic proper biogeochemical system on the reactor level, it is usually assumed that N fixation is the process supplying the system with nitrogen when DIN has been used up (although, of course, there still may be primary production driven by nitrogen regenerated in the production layer). According to the model in the present paper this implies that $\eta = 1$ and with the net production NPN used here the nitrogen contribution from cyanobacteria should be 1.02 Mton yr^{-1} which is a factor of nine larger than estimated from field measurements by Leppänen *et al.* (1988). This large discrepancy together with evidence for bioavailability of DON presented in the introductory section as well as our model results, suggest that DON is the major non-DIN nitrogen source for the production of organic matter in the Baltic proper.

In the model there are two different pathways for nitrogen in the decomposition processes with DIN and DON as the end products. The parameter η gives the DIN fraction and the remainder becomes DON. The value of η in the model indirectly determines the relative amounts of nitrogen for net production that comes from DON and nitrogen fixation, respectively, c.f. Eqs. (9) and (11). Thus, the model describes the average magnitude of blooms of blue green algae (cyanobacteria). One may assume that this may change over longer time scales in response to fluctuations in summer weather conditions. For instance, a period with several warm summers should give an increase in NF and by that a corresponding decrease of DON_P while DON_K should not be affected. This should lead to an increase of the DON content in the Baltic proper reactor. On the other hand, a series of cold summers should lead to a decrease in NF and a corresponding increase of DON_P leading to a reduction of the DON content in the reactor. So far there are no data to check this prediction.

For our computations we used the value 0.1 for the burial parameter α. The model results are not sensitive to small changes of this value. If we put $\alpha = 0$, the maximum value of NF (i.e., for $\eta = 1$) does not change at all. However, changes to large values of α should certainly have a substantial effect. For the evaluation of the model we assumed long-term steady state in the Baltic proper. There has been an accumulation of totN as reported in Wulff and Rahm (1988). However, accounting for this increase causes only small changes to our results. Our estimate of the nitrogen demands for the net production NPN depends on the composition of the produced organic matter. We have assumed that the composition is according to the so-called Redfield ratios.

Our model indicates that DON may supply nitrogen for about half of the net production NP meaning that supplies of DON should be counted when external nitrogen loading is estimated. This is in line with general conclusions drawn for estuaries and coastal waters by Seitzinger and Sanders (1997). However, in slowly flushed systems it is still more important that DON is produced in the reactor by processes decomposing particulate organic matter. Accumulation of DON in the water column becomes especially evident in productive shallow waters, like in the Baltic Sea, where the benthic production of DON may become important. Our model with $\eta = 0.55$ suggests that the rate of DON production (DON_K) in the Baltic proper equals 0.91 Mton yr^{-1} while the net import of DON ($DON_{EXT} - DON_{EXP}$) is only about 0.19 Mton yr^{-1}. The supply of DON is, therefore, dominated by the internal DON production. The storage of DON in the Baltic proper is about 4 Mton so the turnover time of DON, computed as the storage divided by the rate of supply, is about 4 years in this specific reactor.

It would be interesting to use the model developed in the present paper together with the corresponding phosphorus model in the time-dependent mode to compute the long-term response of the Baltic to changing nutrient loading in the spirit of Wulff and Stigebrandt (1989). For this we should be able to express the rate of denitrification and the values of α and η as functions of the state of the Baltic reactor. It seems that the rate of denitrification in inland lakes is a function of the organic loading (Hellström, 1996). The burial factor α may be a function of oxygen conditions and sedimentation rates as discussed by Eilola (1998) who estimated changes in NP in the Baltic from historic oxygen data. He suggested that α probably has increased by a factor 3–5 during the present century due to an increased sequestering of organic matter in sediments, a conclusion supported by sediment data by Jonsson and Carman (1994). As mentioned above, the value of η might possibly be a function of oxygen conditions as suggested by Enoksson (1993).

5. Concluding remarks

In this paper we have put together a logical and seemingly realistic model for the cycling of nitrogen in the Baltic proper biogeochemical reactor. Model results are confined using independent robust estimates of the net production NP, net external nutrient supplies and the amount of DIN available for the seasonal production. The model clearly shows that DON is a major nitrogen component of both production and decomposition of organic matter in the Baltic proper.

The finding in this paper, that a substantial part of degraded organic matter ends as DON ($\sim$45%), implies that earlier estimates of denitrification rates, based on budgets for DIN and oxygen and implicitly assuming the $\eta = 1$ nitrogen decomposition pathway, are seriously in error. The rate of denitrification estimated for the deep water of the Baltic proper by Shaffer and Rönner (1984) is probably overestimated by about a factor 2 due to the neglect of the DON decomposition pathway.

The application of our model shows that several important large-scale properties of the Baltic biogeochemical reactor still remain to be better investigated. The list of urgent research items includes: (1) quantification of processes consuming and producing DON, (2) the rate of denitrification as function of, among others, organic loading, (3) the magnitude of N fixation by cyanobacteria under different conditions, (4) monthly inventories of different nutrient species in the reactor, (5) processes influencing sequestering of nutrients in bottom sediments, (6) the average composition of organic matter produced in the reactor. These research items are all quite important to achieve better understanding of the Baltic proper biogeochemical reactor.

It has been postulated that the magnitude of the spring bloom is determined by the available amount of DIN (Elmgren, 1989). However, the production compatible with the winter storage of DIN is only 0.75 Mton yr^{-1} (Table 3). The net production for the spring period ending in June, as determined by an oxygen budget for the surface layer of the Baltic proper in Stigebrandt (1991), is ca. 32 gC m^{-2} or 1.44 Mton N yr^{-1} (Table 2). Even if supplies by runoff from land and from the atmosphere contribute some DIN during the spring period, this is not enough to explain the estimated net production and why another nitrogen source is needed. Nitrogen fixation by cyanobacteria is generally believed to require rather high temperatures (16° or higher) to be efficient (see Wasmund, 1997). Such temperatures do not generally occur in the Baltic during the spring bloom while DON should be the main additional nitrogen source for net production during spring and early summer.

The absence of generally accepted quantitative models for the nutrient dynamics of the Baltic proper on the reactor (basin-wide) scale allows free scope for diverse opinions regarding effects of removal of different nutrient species upon quantity and quality of the plant production. It has been postulated that (i) most of the input of oxygen-consuming organic material to the bottom sediments in the Baltic comes with the spring bloom and (ii) the spring bloom is limited by DIN, (see also interview with R. Elmgren in Moffat, 1998). If this is true, the oxygen conditions in deeper parts of the Baltic may be improved by decreasing the availability of DIN in spring; e.g., by nitrogen removal from anthropogenic outlets. These arguments, scrutinized in the following paragraph, have had large impact on Swedish decision makers and expensive nitrogen removal is now required from even quite small municipalities.

The argument that the spring bloom is DIN-limited does not seem to hold as shown above. Furthermore, the argument that only the DIN-supported production sinks to deeper layers is not in accordance with the oxygen budgets for the deeper layers of the Baltic proper by Eilola (1998) and Rahm (1987) showing that almost all of the net production NP sinks to the bottom even in deep waters. The present model shows that DON and nitrogen fixation may supply enough nitrogen so the net production NP should be limited by phosphorus, a conclusion also drawn by Hellström (1996) based on results from a study of a number of similarly functioning lakes. This may also be concluded from a detailed biogeochemical process model for the Baltic proper, with DIN and fixed molecular nitrogen as N sources, by Savchuk and Wulff (1998). They found that a reduction of the phosphorus content will likely lead to a basin-wide scale reduction of productivity without an adverse promotion of cyanobacteria blooms. These authors also found that reduced nitrogen loads might lead to increased production by cyanobacteria. In the light of the model results of the present paper, however, one may suspect that a decreased nitrogen load does not necessarily lead to increased production by cyanobacteria as long as DON is abundantly available. Rather, the occurrence of massive blooms of cyanobacteria might depend on the occurrence of good conditions for such blooms. There appear to be no scientifically valid arguments for a general reduction of the nitrogen load to the Baltic proper. To decrease the net production in the Baltic proper, and thereby generally improve water quality, it seems obvious that the phosphorus load has to be decreased.

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REFERENCES

Amon, R. M. W. and R. Benner. 1994. Major role for high-molecular weight dissolved organic matter in the marine carbon cycle. Nature, *369,* 549–552.

Antia, N. J., P. J. Harrison and L. Oliveira. 1991. The role of dissolved organic nitrogen in phytoplankton nutrition, cell biology and ecology. Phycologia, *30,* 1–89.

Blackburn, T. H., P. O. J. Hall, S. Hulth and A. Landén. 1996. Organic-N loss by efflux and burial associated with a low efflux of inorganic N and with nitrate assimilation in Arctic sediments (Svalbard, Norway). Mar. Ecol. Prog. Ser., *141,* 283–293.

Bronk, D. A., P. M. Glibert and B. B. Ward. 1994. Nitrogen uptake, dissolved organic nitrogen release and new production. Science, *265,* 1843–1846.

Carlsson, P. and E. Granéli. 1998. Utilization of dissolved organic matter (DOM) by phytoplankton, including harmful species, *in* Physiological Ecology of Harmful Algal Blooms, Anderson *et al.,* eds., NATO ASI Series, vol G. *41,* 509–524.

Carlsson, P., E. Granéli, P. Tester and L. Boni. 1993. Influences of riverine humic substances on bacteria, protozoa, phytoplankton and copepods in a coastal plankton community. Mar. Ecol. Prog. Ser., *127,* 213–221.

Carlsson, P., A. Z. Segatto and E. Granéli. 1995. Nitrogen bound to humic matter of terrestrial origin—a nitrogen pool for coastal phytoplankton? Mar. Ecol. Prog. Ser., *97,* 105–116.

Carman, R. and F. Wulff. 1989. Adsorption capacity of phosphorus in Baltic Sea sediments. Estuar. Coastal Shelf Sci., *29,* 447–456.

Eilola, K. 1998. Oceanographic studies of the dynamics of freshwater, oxygen and nutrients in the Baltic Sea, Ph.D. thesis, Dept. of Oceanography, Göteborg University, Sweden, 81 pp.

Eilola, K. and A. Stigebrandt. 1998. Spreading of juvenile freshwater in the Baltic proper. J. Geophys. Res., *103,* C12, 27795–27807.

Elmgren, R. 1984. Trophic dynamics in the enclosed, brackish Baltic Sea. Rapp. P. V. Réun. Cons. Int. Explor. Mer, *183,* 152–164.

—— 1989. Man's impact on the ecosystem of the Baltic Sea: Energy flows today and at the end of the century. Ambio, *18*, 326–332.

Enoksson, V. 1993. Nutrient recycling by coastal sediments: effects of added algal material. Mar. Ecol. Progr. Ser., *92,* 245–254.

Granéli, E., K. Wallström, U. Larsson, W. Granéli and R. Elmgren. 1990. Nutrient limitation of primary production in the Baltic Sea area. Ambio, *19,* 142–151.

Grasshoff, K. and A. Voipio. 1981. Chemical Oceanography, *in* The Baltic Sea, A. Voipio, eds., Elsevier Oceanography Series, *30,* 183–218.

Hagström, Å. and G. Öqvist. 1983. Algal and bacterial production in a coastal area (Norrbyn) of the northern Bothnian Sea, Rep. PM 1618, Natl. Swed. Env. Prot. Board, Stockholm, 227–234.

Hall, P. O. J., O. Holby, S. Kollberg and M-O. Samuelsson. 1992. Chemical fluxes and mass balances in a marine fish cage. IV. Nitrogen. Mar. Ecol. Prog. Ser., *89,* 81–91.

Hellström, T. 1996. An empirical study of nitrogen dynamics in lakes. Water Environ. Res., *68,* 55–65.

Hulth, S. 1995. Mineralization of biogenic debris in continental shelf and slope sediments, Ph.D. thesis, Dept. of Analytical and Marine Chemistry, Göteborg University, 312 pp.

Jackson, G. A. and P. M. Williams. 1985. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. Deep Sea Res., *32,* 223–235.

Jonsson, P. and R. Carman. 1994. Changes in deposition of organic matter and nutrients in the Baltic Sea during the twentieth century. Mar. Poll. Bull., *28,* 417–426.

Kieber, D. J., J. McDaniel and K. Mopper. 1989. Photochemical source of biological substrates in sea water: implications for carbon cycling. Nature, *341,* 637–639.

Landén, A., P. O. J. Hall and S. Hulth. 1999. Seasonal variation of dissolved organic matter and of nitrogen and carbon recycling rates in a coastal marine sediment. J. Mar. Res., (submitted).

Larsson, U., R. Elmgren and F. Wulff. 1985. Eutrophication of the Baltic Sea: Causes and consequences. Ambio, *14,* 9–14.

Leppänen, J.-M., Å. Niemi and L. Rinne. 1988. Nitrogen fixation of cyanobacteria (blue-green algae) and the nitrogen cycle of the Baltic Sea. Symbiosis, *6,* 181–194.

Moffat, A. S. 1998. Global nitrogen overload problem grows critical. Science, *279,* 988–989.

Palenik, B. and F. M. M. Morel. 1990. Amino acid utilization by marine phytoplankton: a novel mechanism. Limnol. Oceanogr., *35,* 260–269.

Rahm, L. 1987. Oxygen consumption in the Baltic proper. Limnol. Oceanogr., *32,* 973–978.

Redfield, A. C., B. H. Ketchum and F. A. Richards. 1963. The influence of organisms on the composition of sea-water, *in* The Sea, 2 N. Hill, ed., Interscience, NY, 26–77.

Rosenberg, R., R. Elmgren, S. Fleischer, P. Jonsson, G. Persson and H. Dahlin. 1990. Marine eutrophication case studies in Sweden. Ambio, *19,* 102–108.

Savchuk, O. and F. Wulff. 1999. Modelling regional and large-scale responses of the Baltic Sea ecosystems to nutrient reductions. Hydrobiologia (in press).

Schnitzer, M. 1985. Nature of nitrogen in humic substances, *in* Humic Substances in Soil, Sediment and Water. Geochemistry, Isolation and Characterization, G. R. Alken, D. M. McKnight, R. L. Wershaw and P. Macarthy, eds., Wiley, NY, 303–328.

Seifert, T. and B. Kayser. 1995. A high resolution spherical grid topography of the Baltic Sea. Institute für Ostsee Forschung, Warnemünde. Marine Science Reports.

Seitzinger, S. P. and R. W. Sanders. 1997. Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. Mar. Ecol. Prog. Ser., *159,* 1–12.

Shaffer, G. and U. Rönner. 1984. Denitrification in the Baltic proper deep water. Deep-Sea Res., *31,* 197–220.

Sharp, J. H. 1983. The distribution of inorganic nitrogen and dissolved and particulate organic nitrogen in the sea, *in* Nitrogen in the Marine Environment, E. G. Carpenter and D. G. Capone, eds., Academic Press, 1–35.

Stålnacke, P. 1996. Nutrient loads to the Baltic Sea. Linköping Studies in Arts and Science, Ph.D thesis, The Institute of Tema Research, Linköping Univ., Sweden, 191 pp.

Stigebrandt, A. 1985. A model for the seasonal pycnocline in rotating systems with application to the Baltic proper. J. Phys. Oceanogr., *15,* 1392–1404.

—— 1991. Computations of oxygen fluxes through the sea surface and the net production of organic matter with application to the Baltic and adjacent seas. Limnol. Oceanogr., *36,* 444–454.

Stigebrandt, A. and L. Djurfeldt. 1996. Control of the production of organic matter in the ocean on short and long terms by stratification and remineralization. Deep-Sea Res. II, *43,* 23–35.

Stigebrandt, A. and F. Wulff. 1987. A model for the dynamics of nutrients and oxygen in the Baltic proper. J. Mar. Res., *45,* 729–759.

Sverdrup, H. U. 1953. On conditions for vernal blooming of phytoplankton. J. de Conseil Permanent International pour l'Exploration de la Mer, *18,* 287–195.

Vollenweider, R. A. 1969. Possibilities and limits of elementary models concerning the budget of substances in lakes. Arch. Hydrobiol., *66,* 1–36.

Wasmund, N. 1997. Occurrence of cyanobacterial blooms in the Baltic Sea in relation to environmental conditions. Int. Revue ges. Hydrobiol., *82,* 169–184.

Wulff, F. and L. Rahm. 1988. Longterm, seasonal and spatial variations of nitrogen, phosphorus and silicate in the Baltic: An overview. Mar. Environ. Res., *26,* 19–32.

Wulff, F. and A. Stigebrandt. 1989. A time-dependent budget model for nutrients in the Baltic Sea. Global Biogeochem. Cycles, *3,* 63–78.

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