

Autotrophy, nitrogen accumulation and nitrogen limitation in the Baltic Sea: A paradox or a buffer for eutrophication?

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[1] The autotrophic Baltic Sea acts as a sink for atmospheric CO₂, however it is also characterised by nitrogen limitation and nitrogen accumulation, the latter indicating heterotrophy. Physical and biogeochemical processes generate this paradox, since the developments of the seasonal thermocline, the spring bloom and the riverine nitrogen inputs start during early spring. The Baltic Intermediate Water (BIW) is separated from the above surface layer, i.e., from the euphotic zone preventing a significant amount of the former winter mixed layer nitrogen from being used by phytoplankton, which finally becomes nitrogen limited. The deepening of the mixed layer in autumn reintegrates the nitrogen constrained within the BIW into the surface layer. Nitrogen in turn accumulates over an annual time scale depending on the riverine nitrogen loads. The temporal nitrogen enclosure in the BIW buffers the potential impact of nutrient inputs on the Baltic Sea and its trophic state. **INDEX TERMS:** 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 4835 Oceanography: Biological and Chemical: Inorganic marine chemistry. **Citation:** Thomas, H., J. Pempkowiak, F. Wulff, and K. Nagel, Autotrophy, nitrogen accumulation and nitrogen limitation in the Baltic Sea: A paradox or a buffer for eutrophication?, *Geophys. Res. Lett.*, 30(21), 2130, doi:10.1029/2003GL017937, 2003.

1. Introduction

[2] During the last decade the important role of coastal and marginal seas in the global carbon cycle has become evident. High biological activity [Gattuso *et al.*, 1998; Falkowski *et al.*, 1998] leads to uptake of atmospheric CO₂ and subsequent transfer to the open ocean constituting the continental shelf pump [Tsunogai *et al.*, 1999; Liu *et al.*, 2000]. Moreover, coastal and marginal seas receive and buffer anthropogenic nutrient inputs, which have notable impacts on their ecosystems such as eutrophication or

oxygen depletion. In order to assess the coastal seas' trophic state and thereby their sink or source function for atmospheric CO₂ on a global scale, commonly the nutrient conditions are assessed [e.g., Buddemeier *et al.*, 2002]. Detailed carbon budgets have been established only for a few areas during the last years, amongst them the Baltic Sea (see below) or the East China Sea [Chen and Wang, 1999; Chen *et al.*, 2003; Chen, 2003].

2. The Paradox of the Baltic Sea

[3] Recent carbon cycle studies [Thomas and Schneider, 1999; Thomas *et al.*, 1999; Osterroht and Thomas, 2000] describe the Baltic Sea (Figure 1) as an autotrophic semi-enclosed sea. Typical for a brackish system, rivers and the adjacent basins Bothnian Sea and Gulf of Finland provide the largest part of the entire carbon imports to the Baltic Sea, but also the North Sea as a net carbon sink supplies a notable share. 13% of the overall imports are supplied by the atmosphere corresponding to 0.9 mol CO₂ m⁻² a⁻¹ (Table 1; Figure 2a). The overall carbon loss of the Baltic Sea is dominated by the export to the North Sea (92%) and only a minor fraction is buried into the sediments (8%). Net community production (NCP) is the driving factor for the transfer of atmospheric CO₂ into either the sediments or into the North Sea. The annual NCP amounts to 44% of the overall carbon fluxes into the Baltic Sea. In terms of carbon, 17% of NCP is exported to the sediments and 13% as dissolved inorganic carbon (DIC) to the North Sea. With regard to the CO₂ taken up from the atmosphere this means that 57% thereof is buried and 43% is exported to the North Sea constituting the continental shelf pump of the Baltic Sea.

[4] In contrast to the overall autotrophy, nitrogen as the limiting nutrient accumulates in the Baltic Sea [e.g., Sandén and Rahm, 1992]. This feature commonly serves as an indicator for heterotrophy. Despite this accumulation of nitrogen, biological activity is nitrogen-limited in wide areas of the Baltic Sea and moreover, nitrogen fixation has been observed [e.g., Leppänen *et al.*, 1988; Savchuk and Wulff, 2001]. The latter processes might also indicate a lack of nitrogen. The inorganic compounds, covering

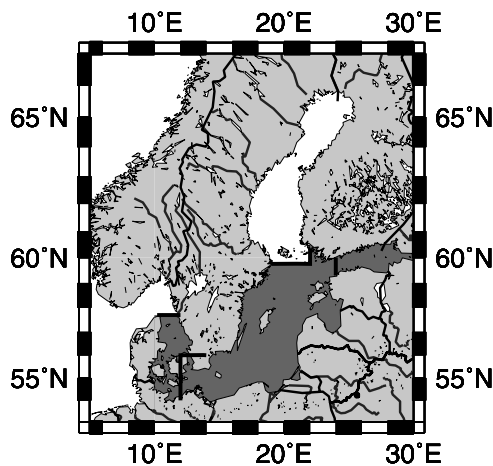


Figure 1. The shaded area indicates the budgeting area of the Baltic Sea according to Table 1. The Gulf of Finland is included in the Baltic Proper area for the nitrogen budgeting, whereas it is treated as individual source for the carbon budgeting.

approximately 65% of the entire nitrogen input (Table 1; Figure 2b), dominate the input of nitrogen into the Baltic Sea. In contrast to the input, the organic compounds provide the major output of nitrogen via sedimentation, denitrification in the sediments and via export to the North Sea. The rivers supply the majority of the nitrogen, but also the atmosphere and coastal or point sources (other than rivers) provide relevant inputs. The overall system accumulates approximately 11% of the nitrogen input into the Baltic Sea [Wulff *et al.*, 2001] (Table 1). A recent basin-wide estimate for the Baltic Proper [Thomas *et al.*, 1999] suggests that external inputs from rivers, the atmosphere and from nitrogen fixation provide $0.1 \text{ mol N m}^{-2} \text{ a}^{-1}$. The winter mixed layer provides $0.2 \text{ mol N m}^{-2} \text{ a}^{-1}$ (i.e., 66%) most notably as a consequence of organic matter remineralisation. The overall $0.3 \text{ mol N m}^{-2} \text{ a}^{-1}$ could finally be available to phytoplankton production.

[5] Concerning the carbon and nitrogen budgets, the paradox can be described by the following discrepancies.

Firstly, the carbon budget identifies the Baltic Sea as an autotrophic sea, which supports a net transport of atmospheric CO_2 to the sediments and to the North Sea. Secondly, the nitrogen budget provides evidence that nitrogen as the limiting nutrient accumulates, which could be seen as an indicator of heterotrophy. Thirdly, despite the accumulation of nitrogen, the Baltic Sea is well known to be a nitrogen-limited system [e.g., Savchuk and Wulff, 2001] with nitrogen fixation to some extent compensating the lack of nitrogen. This lack of nitrogen is thought to be partially caused by denitrification process [Rönnner, 1985].

3. Resolving the Paradox

[6] The solution to the obvious discrepancy between autotrophy and nitrogen accumulation is provided by the high inorganic nitrogen input from anthropogenic sources (Figure 2b). Organic matter, which has a C:N ratio of at least ≈ 4 (proteins) or higher, provides high organic carbon loads resulting in heterotrophy and/or carbon and nitrogen accumulation. Thus, organic matter input cannot serve as an explanation for the coincidence of nitrogen accumulation and autotrophy. High inorganic nitrogen input, however, enable nitrogen storage and accumulation without corresponding carbon storage. The system’s metabolic activities would then not change the genuine input balance of carbon and nitrogen compounds.

[7] The coincidence of nitrogen accumulation, on the one hand, and nitrogen limitation and nitrogen fixation, on the other hand, can be explained by the hydrochemical conditions in the surface layer of the Baltic Sea. A recent analysis [Thomas *et al.*, 1999; Osterroht and Thomas, 2000] provides evidence that these are governed by the seasonal pattern of the stratification. The halocline at about 60–80 m depth provides a permanent and strong barrier for the exchange of dissolved compounds. In addition, the Baltic Intermediate Water (BIW) is temporarily enclosed between the seasonal thermocline and the halocline during spring and summer. Note that the BIW does not exist during autumn and winter, since the mixed surface layer reaches down to the halocline thus comprising the BIW (Figure 3). Sinking particles can enter and also leave this enclosed

Table 1. Carbon and Nitrogen Budgets for the Baltic Proper (Figure 1)

C-budget: areas: Baltic Proper (incl. Kattegat), Gulf of Riga, (270750 km ²); Water: 14240 km ³				N budget: areas: Baltic Proper (excl. Kattegat), G. of Riga, G. of Finland (276000 km ²); Water: 14488 km ³		
C Sink/source	Water [km ³ a ⁻¹]	Input/output DIC/DOC [$\mu\text{mol l}^{-1}$]	C fluxes [$10^{12} \text{ mol a}^{-1}$]	N Sink/source	Water [km ³ a ⁻¹]	N fluxes [10^9 mol a^{-1}]
Atmosphere	26 (P-E)	$0.9 \text{ mol CO}_2 \text{ m}^{-2} \text{ a}^{-1}$	0.24	Atmosphere	26 (P-E)	16
Bothnian Sea	223	1341/321	0.37	Bothnian Sea	223	1
G. of Finland	112	1571/355	0.22	Rivers	260	34
Scandinavian rivers	18.1	174/360	0.01	Coastal/point sources		12
Continental rivers	128.9	2800/360	0.41			0
from the North Sea	238	2119/100	0.53	from the North Sea	238	4
to the North Sea	-746	2119/100	-1.66	to the North Sea	-746	-14
Sedimentation		$-0.51 \text{ mol m}^{-2} \text{ a}^{-1}$	-0.14	Sedimentation/Denitrification		-47
Unbalanced			-0.02 (1.2%)	Accumulation		7
ΣC Input:			1.78	ΣN Input:		68
ΣC Output			-1.8	ΣN Output		-61

Data sources for the C-budget: CO_2 air-sea exchange [Thomas and Schneider, 1999]; DIC: [Thomas and Schneider, 1999; Osterroht and Thomas, 2000]; DIC riverine inputs according to Figure 3 in [Thomas and Schneider, 1999]; DOC [Matthäus *et al.*, 2001; Nausch *et al.*, 2002]; sedimentation [Schneider *et al.*, 2000]; DOC output to North Sea: Thomas unpubl. data. (P-E) = Precipitation – Evaporation. Positive values indicate inputs and negative ones outputs, respectively. The uncertainty of the carbon budget is approximately 15% [Thomas *et al.*, 2003]. The uncertainty of the nitrogen budget, compiled after Wulff *et al.* [2001], is in the order of 5%.

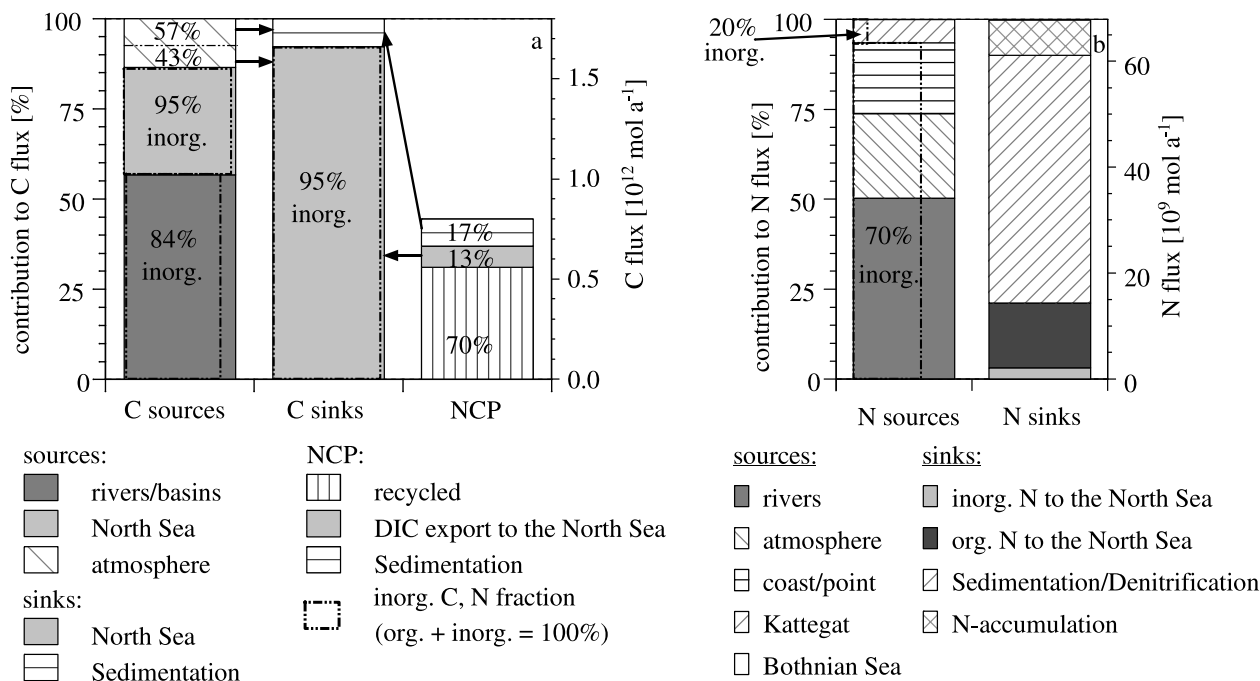


Figure 2. Carbon (a) and nitrogen (b) budgets for the Baltic Sea (Figure 1). The relative contributions of the inorganic and organic carbon and nitrogen sources are indicated. The percentages within the NCP bar [Thomas and Schneider, 1999] indicate the partitioning of the NCP between sedimentation, export to the North Sea and recycling.

water body, however dissolved compounds such as DIC and oxygen are known to accumulate or decrease, respectively, during the productive season without notable exchange with the above surface layer or the below-halocline deeper waters [Thomas *et al.*, 1999].

[8] The seasonal behaviour of NO_3 (Figure 3) in the waters above the halocline shows concentrations of about $5 \mu\text{M}$ NO_3 in the wintry mixed layer of 68 m, which corresponds to $340 \text{ mmol NO}_3 \text{ m}^{-2}$. At the end of the summer period, NO_3 is depleted in the surface layer because of the uptake by phytoplankton. Since the spring bloom period coincides with the rise of the thermocline, the NO_3 of the wintry mixed layer cannot be used entirely and a NO_3 residue of 102 mmol m^{-2} can be observed in the BIW below the thermocline at the end of summer. Alternatively, minor amounts of organic matter, generated during an early stage of the spring season, have been mineralised in the BIW and the corresponding nitrogen is not exploited by carbon fixation in the surface layer [Thomas *et al.*, 1999]. In both cases, the NO_3 residue hidden in the BIW is not available to phytoplankton thereby reducing the available nitrogen pool of the wintry mixed layer by 30%. Regarding the above overall nitrogen budget, this 30% reduction of the wintry mixed layer pool corresponds to a 20% reduction of the available nitrogen pool (0.3 mol m^{-2}). The enclosed nitrogen, which is controlled by the wintry mixed layer nitrogen concentration, is mixed back into the surface waters, when the deepening of the thermocline causes the BIW to vanish during autumn and winter.

[9] According to Wulff *et al.* [2001] approximately 11% of the annual external inputs accumulate in the Baltic Sea, supporting our conclusion of a nitrogen surplus in the Baltic Sea despite the known nitrogen limitation of the system. This 11% accumulation of the external nitrogen inputs

(0.1 mol m^{-2}) corresponds to 3.7% present in the wintry mixed layer and derived from external input (0.3 mol m^{-2}). This compilation provides evidence that the above annual nitrogen surplus is small and rather ineffective, since the NO_3 storage in the BIW (20% of the overall pool) out-

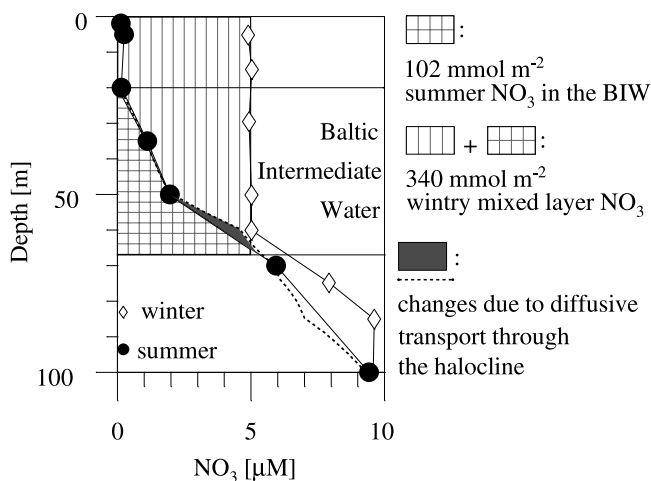


Figure 3. Nitrate profile observed at the central station of the Baltic Proper [Thomas *et al.*, 1999]. The hatched and crossed area indicated the NO_3 available in the wintry mixed layer above the halocline. The crossed area indicates the NO_3 residue in the Baltic Intermediate Water at the end of summer. The dashed line indicates diffusive inputs from below the halocline [Osterroht and Thomas, 2000] and the corresponding shaded area. The depth levels of the thermocline and halocline are approx. 20 m and 68 m, respectively.

numbers the nitrogen surplus by far. Moreover, the N-accumulation and the N-limitation are decoupled in time: During spring and summer, the temporal storage of nitrogen in the BIW prevents the nitrogen uptake by phytoplankton thereby causing the observed nitrogen limitation of the system. Additionally, the export of nitrogen to the sediments is prevented, since dissolved compounds cannot escape from the BIW. The nitrogen temporarily stored in the BIW is given back to the surface waters during autumn and winter, when phytoplankton are less active, finally contributing to the observed nitrogen accumulation in the surface waters. Similarly, this effective lack of nitrogen during the productive period likely serves as an explanation for the occurrence of nitrogen fixation, which supplies nitrogen to the system.

[10] The final question arises, whether the autotrophy of the Baltic Sea is caused by the anthropogenic nutrient inputs, or whether the system has already been autotrophic even before eutrophication started to increase the nutrient pools. From the above budget calculations it appears unlikely that those inputs could have caused a shift from heterotrophy to autotrophy, since the impact of eutrophication on the trophic state is strongly buffered by the nitrogen storage in the BIW. The high ratio of CO₂ uptake vs. nitrogen accumulation (CO₂ uptake: N-accum. = 30) (Table 1) rather implies that the Baltic Sea has been autotrophic even before eutrophication began, and that the inorganic nitrogen inputs might have further stimulated autotrophy. Efficient nutrient recycling mechanisms [Thomas *et al.*, 1999; Osterroht and Thomas, 2000] would still enable net-CO₂ drawdown from the atmosphere under past and future reduced nitrogen input conditions. The synergy of biogeochemical and physical processes thus provides an efficient buffer for anthropogenic nutrient inputs, which have probably not changed the general trophic state of the non eutrophicated system. In the global view, the coastal seas' role in absorbing atmospheric CO₂ has been largely underestimated hitherto, since most of the coastal seas, commonly classified as heterotrophic with respect to their nutrient budgets [Buddemeier *et al.*, 2002], are still autotrophic, i.e., still absorb atmospheric CO₂.

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References

- Buddemeier, R. W., S. V. Smith, D. P. Swaney, and C. J. Crossland (Eds.), The role of the coastal ocean in the disturbed and undisturbed nutrient and carbon cycles, *LOICZ Reports and Studies*, 24, 83 pp., LOICZ, Texel, The Netherlands, 2002.
- Chen, C. T. A., New vs. export production on the continental shelf, *Deep-Sea Res. II*, 50, 1327–1333, 2003.
- Chen, C. T. A., and S. L. Wang, Carbon, alkalinity and nutrient budget on the East China Sea continental shelf, *J. Geophys. Res.*, 104, 20,675–20,686, 1999.
- Chen, C. T. A., K.-K. Liu, and R. MacDonald, Continental margin exchanges, in *Ocean Biogeochemistry: A JGOFS synthesis*, edited by M. J. R. Fasham, Springer, 53–97, 2003.
- Falkowski, P. G., R. T. Barber, and V. Smetacek, Biogeochemical controls and feedbacks on ocean primary production, *Science*, 281, 200–206, 1998.
- Gattuso, J.-P., M. Frankignoulle, and R. Wollast, Carbon and carbonate metabolism in coastal aquatic ecosystems, *Annual Review of Ecology and Systematics*, 29, 405–433, 1998.
- Leppaenen, J. M., A. Niemi, and I. Rinne, Nitrogen fixation of cyanobacteria (blue-green algae) and the nitrogen cycle of the Baltic Sea, *Symbiosis*, 6, 181–194, 1988.
- Liu, K.-K., K. Iseki, and S.-Y. Chao, Continental margin carbon fluxes, in *The Changing Ocean Carbon Cycle*, edited by R. B. Hanson, H. W. Ducklow, and J. G. Field, Cambridge University Press, 2000.
- Matthäus, W., G. Nausch, H. U. Lass, K. Nagel, and H. Siegel, Hydrographisch-chemische Zustandseinschätzung der Ostsee 2000, in *The hydrographic-hydrochemical state of the western and central Baltic Sea in 1999/2000 and during the 1990s*, edited by W. Matthäus and G. Nausch, *Meereswiss. Ber. Warnemünde*, 45, pp. 27–88, 2001.
- Nausch, G., R. Feistel, H. U. Lass, K. Nagel, and H. Siegel, Hydrographisch-chemische Zustandseinschätzung der Ostsee 2001, *Meereswiss. Ber. Warnemünde*, 49, pp. 2–77, 2002.
- Osterroht, C., and H. Thomas, New production enhanced by nutrient supply from non-Redfield remineralisation of freshly produced organic material, *J. Mar. Sys.*, 25, 33–46, 2000.
- Rönnér, U., Nitrogen transformations in the Baltic Proper: Denitrification counteracts eutrophication, *Ambio*, 14, 1241–1243, 1985.
- Sandén, P., and L. Rahm, Nutrient trends in the Baltic Sea, *Environmetrics*, 4, 75–103, 1992.
- Savchuk, O., and F. Wulff, A Model of the Biogeochemical Cycles of Nitrogen and Phosphorus in the Baltic, in *A System Analysis of the Baltic Sea*, edited by F. Wulff, L. Rahm, and P. Larsson, Springer, Berlin Heidelberg, pp. 373–416, 2001.
- Schneider, B., K. Nagel, and U. Struck, Carbon fluxes across the halocline in the eastern Gotland Sea, *J. Mar. Sys.*, 25, 261–268, 2000.
- Thomas, H., and B. Schneider, The seasonal cycle of carbon dioxide in Baltic Sea surface waters, *J. Mar. Sys.*, 22, 53–67, 1999.
- Thomas, H., V. Ittekkot, C. Osterroht, and B. Schneider, Preferential recycling of nutrients—the ocean's way to increase new production and to pass nutrient limitation?, *Limnol. and Oceanogr.*, 44(8), 1999–2004, 1999.
- Thomas, H., J. Pempkowiak, F. Wulff, and K. Nagel, Carbon and nutrient budgets of the Baltic Sea, in *Carbon and nutrient fluxes in continental margins: A global synthesis*, edited by K. K. Liu, L. Atkinson, R. Quiñones, and L. Talaue-McManus, Springer, accepted, 2003.
- Tsunogai, S., S. Watanabe, and T. Sato, Is there a “continental shelf pump” for the absorption of atmospheric CO₂?, *Tellus*, B51, 701–712, 1999.
- Wulff, F., L. Rahm, A.-K. Hallin, and J. Sandberg, A Nutrient Budget model of the Baltic Sea, in *A System Analysis of the Baltic Sea*, edited by F. Wulff, L. Rahm, and P. Larsson, Springer, Berlin Heidelberg, pp. 354–372, 2001.

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