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Nitrification in marine ecosystems

Author(s) Enoksson, V.

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ENOKSSON V. 1980

Nitrification in marine ecosystems.

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## Introduction

The nitrification in the ocean is influenced by several environmental factors and the importance of these is more or less known. There are very likely many more to be discovered in the study of the interaction of nitrification bacteria and other micro-organisms in the ocean. Some of the factors to be considered will briefly be dealt with. Then we give the results of an incubation experiment in the Baltic Sea and from a detailed study in Gullmarn.

The nitrate production in the ocean is synonymous with the bacterial oxidation of ammonia to nitrate. The process occurs in two stages:

- 1)  $NH_3 + 1\frac{1}{2}O_2 = > HNO_2 + H_2O$
- 2)  $HNO_2 + \frac{1}{2}O_2 = > HNO_3$

Marine representatives of these two processes are (1) <u>Nitrosococcus</u> <u>oceanus</u> and (2) <u>Nitrococcus</u> <u>mobilis</u>. Both are chemoautotrophs i.e. they fix carbon dioxide.

#### Environmental factors

Oxygen: Nitrification bacteria are micro-aerophilic (Gundersen, 1966), i.e. they grow more quickly at low oxygen concentration. The oxygen starts to limit under 0.05 ml/l.

pH: NH<sub>4</sub> -oxydisers produce HNO<sub>2</sub> but not at such a rate that the pH of the ocean water is appreciably lowered.

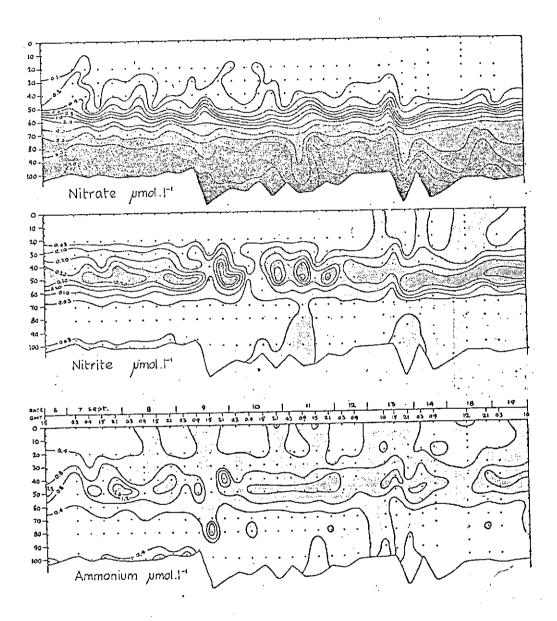
Redox- Nitrification is energy yielding if the Eh value is above potential c. 200 mV at a pH value of the oceanic water.

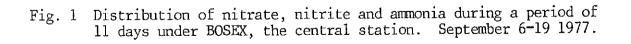
 $\operatorname{NH}_{4}^{+}$  High  $\operatorname{NH}_{2}^{+}$  - content is rarely found in oceanic waters; at the most a few  $\mu$ M. The nitrate formation in a water mass cannot exceed the NH<sub>2</sub> formation and it is therefore necessary to study the mineralisation.

NO,

Nitrite is an intermediary product both in nitrification and denitrification. Phytoplankton can furthermore reduce NO  $\frac{1}{3}$ to NO  $\frac{1}{2}$  in poor conditions of light. In the autumn of 1977 we found in the Baltic Sea a primary NO  $\frac{1}{2}$  -maximum at the thermocline, which in this case was much deeper than the photic zone (fig. 1). It coincided with a NH<sub>4</sub> -maximum and at the same depth the NO $\frac{1}{3}$  started to increase towards the bottom. Similar depth distribution of inorganic nitrogen can often be found in various oceans. gives little directional indication for the nitrification activity as it is used both for nitrogen assimilation and denitrification.

- 2 -





NO-3

## The Problems

Where does the primary  $NO_2$  maximum originate? A secondary maximum can occur at greater depths in the oceans and is believed to be derived from denitrification. Brandhorst suggested (1959) that nitrification gave rise to the primary nitrite maximum. Hattori and Wada (1971) gave denitrification as the explanation in the tropical southern part of the Pacific Ocean (fig. 2) and Gunderson <u>et al</u> (1972) gave the same explanation for Hawaii (fig. 3).

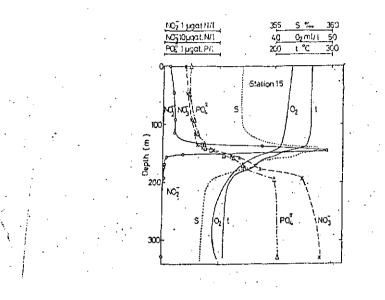


Fig. 2 Vertical profiles of nitrite, nitrate, phosphate, dissolved oxygen, temperature and salinity at station 15, Hakuho Maru KH-69-4 cruise (2°36'S, 154°53'W (Hattori and Wada 1971).

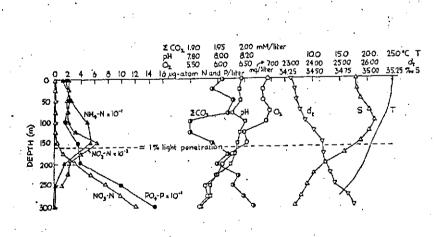


Fig. 3 Data for the uppermost 300m of a water column at station 17A outside Oahu. Data collected during the Bug Seafari cruise outside Hawaii (Gundersen <u>et al</u>, 1972). Kiefer <u>et al</u> (1976) (fig. 4) say that the NO  $\frac{1}{2}$  production from phytoplankton is sufficient to explain the primary NO  $\frac{1}{2}$  maximum in the central part of the Northern Pacific Ocean.

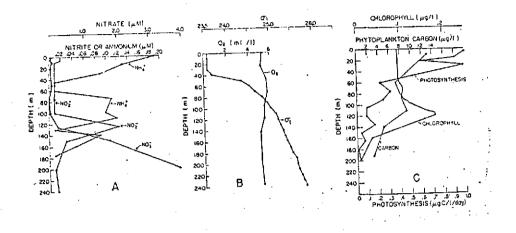


Fig. 4 The vertical distribution of nitrate, nitrite and ammonia (A), density and oxygen (B) and chlorophyll, plant biomass-C and primary production (C). The measurements were all made between August 29 and September 2 1973 near 27°57'N and 154°42'W. The biomass carbon was calculated from determinations of phytoplankton numbers (Kiefer <u>et al</u>, 1976).

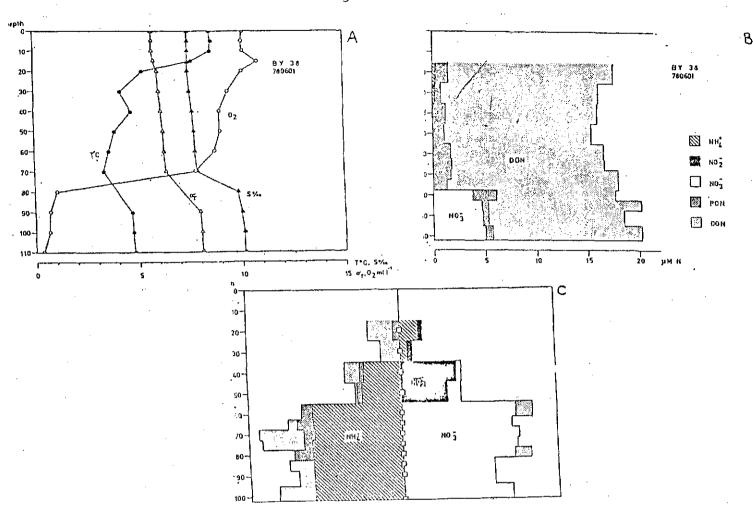
Attempts have been made to calculate the rate of nitrification in the ocean from the NO  $_3$  production per cell density in the ocean. The cell density in the water body studied was far from sufficient to explain the high nitrate concentrations of up to 40  $\mu$ M in the deep waters. One may speculate that this high nitrate was produced when the water was at another latitude than when measured. It is possible that a vital factor in the process has been ignored. Carlucci <u>et al</u> (1970) suggested that the rate can be larger in micro-environments, i.e. on plankton during the process of breaking down.

#### Sediment

Nitrification only takes place in the uppermost sediment layer, where oxygen is present. This has been confirmed by Billen (1976), who measured the autotrophic 14C incorporation in different types of sediment. In the sediment are often liberated large amounts of NH<sub>4</sub> during mineralisation, which would favour a quick nitrification as long as the oxygen available is sufficient. The distance between the aerobic and anaerobic environment is short, especially if anaerobic micro-environments are included. NO  $\frac{1}{3}$ can therefore easily diffuse to oxygen free zones where it is quickly denitrified. In the sediment bound nitrogen should thus effectively be released as N<sub>2</sub>. If the oxygen is depleted then the nitrogen accumulates as NH  $\frac{1}{4}$ . The denitrification is then moved out to the free water. Even water masses with low oxygen content have truly oxygen free micro-environments, though this is difficult to prove. Thus it is possible that nitrification and denitrification can exist side by side even in the free water.

### Methods

The methods used to study the nitrification activity consisted of incubation with several combinations of added materials. Incubation in bottles in situ or in the laboratory Incubation with or without the addition of NH  $\frac{+}{4}$ , NO  $\frac{-}{2}$ Incubation with or without inhibitors Incubation with tracers: 15<sub>N</sub>, 14<sub>C</sub> - 5 -



- Fig. 5 Nitrification (activity experiments), the Baltic Sea. Station BY 38 (Karlsö depth) June 1978.
  - A. Vertical distribution of temperature, salinity, density and oxygen.
  - B. Vertical distribution of the various nitrogen parameters presented as components of the total nitrogen content.
  - C. The nett increase resp. decrease of different nitrogen components after the addition of  $9\mu$ M of NH+<sub>4</sub> and following incubation of 3 months. Each point is the mean of two (duplicate) samples.
  - NB In B and C the quantities are given as lengths of horizontal columns, not as area.

<u>Results of incubation experiments with water from the Baltic Sea</u> Karlsö djupet (Karls Island depth) June 1978 (fig. 5)

The samples were incubated for 3 months with the addition of  $9\mu M NH_{L}$ .

- Fig. 5a: Hydrography. A thermocline between 10m and 30m depth. A halocline, which coincides with a thermocline at 70-80m. At the same depth, the oxygen content declines drastically.
- Fig. 5b: Original concentrations of the nitrogen components. (PON = particulate nitrogen. DON = dissolved organic nitrogen). The NO  $_2$ -and NH+ $_4$ -maxima found the previous autumn were not found again. Nitrate was the only inorganic nitrogen component found in rather high concentrations and then only below the halocline.
- Fig. 5c: Changes in the water during the incubation. The left hand side shows the utilisation and the right hand one the formation of nitrogen components.

The water column can be divided into three zones:

- 20 30m: Mineralisation but no nitrification.
- 40 50m: In one sample from each of the depths, all the NH  $\frac{4}{4}$  had been oxidised to NO  $\frac{1}{2}$  but not further on to NO<sub>3</sub>. There thus existed a potential for the NH+,-oxidation but not for the NO- $_2$ -oxidation. Even here a nett-mineralisation had occurred.
- 60 102m (bottom): Just about all the NH+<sub>4</sub> had been used up in all the 16 samples. Inorganic nitrogen reappeared as NO 3, including that formed by mineralisation.

The nitrification potential was thus largest at the depths where we found high NO  $\frac{1}{3}$  concentrations the previous autumn, i.e. under 60m. It may be coincidence that the samples which gave the NO  $\frac{1}{2}$  production had been taken from depths where the NO  $\frac{1}{2}$  maximum had been the previous autumn. Above 30m the nitrification potential is insignificant in spite of a good access to NH  $\frac{1}{2}$ .

This experiment very much indicates that the NO  $_{\overline{2}}$  maximum in the Baltic Sea originates from NH  $_{4}^{+}$  oxidation which has not been followed by NO  $_{\overline{2}}^{-}$  oxidation.

## Results from intensive studies in Gullmarn

At the end of October and beginning of November 1978, an intensive study was made in Gullmarn; two measurements per day for 5 days (fig. 6). Oxygen and nitrogen components were analysed along with measurements of flow, temperature and salinity which were done by Gary Shaffer (The Oceanographic Institute, Göteborg). We had hoped to find an answer to the question, 'How representative are individual measurements in Gullmarn?'

The sequence of events can most easily be explained for the first three days. On the fourth day the situation was complicated by strong winds.

- <10m: An inwards directed current was dominating. This period was preceded by a very dense autumn bloom and therefore nearly all the nitrogen organically bound.
- 10-20m An outwards directed current carried old water from Gullmarn, with a relatively low oxygen content, but a high NO 3 content.
- 20-50m This layer had entered over the threshold. The high NH  $\pm$  content had a connection with the preceding bloom. One can speculate that the water had been closer to the surface in Skagerak and it can therefore be considered to be not old or as surface water.
- 50m-bottom The threshold at 40m depth prevents the bottom water from being exchanged at the same rate as the layers above. The water is typically old, with relatively low concentrations of oxygen, NH  $_4^+$ , NO  $_2^-$ , and organic nitrogen but large amounts of NO  $_3^-$ .

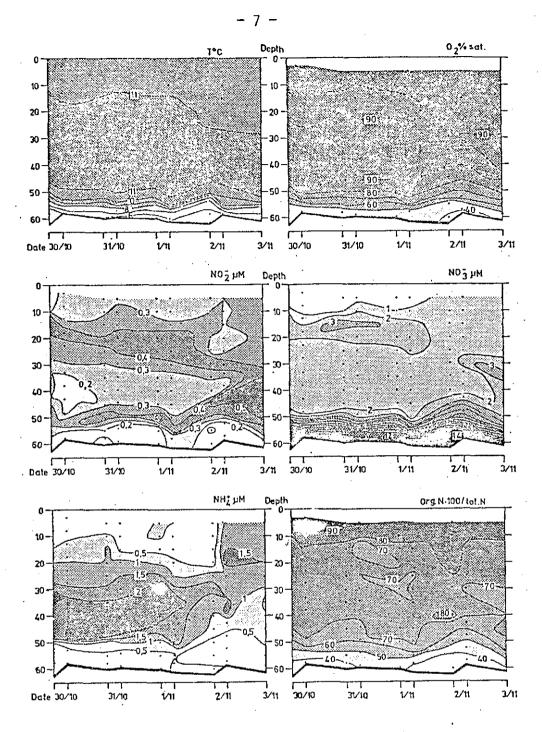


Fig. 6. Temperatur, syremättnad, nitrit-, nitrat och ammoniumhalt samt organískt kväve i procent av totalkvävet vid en station nära Småholmarna i Gullmarn under en 5-dagars period, hösten 1978. 9 mättillfällen, 12 mätdjup.

The distribution of NH  $\frac{1}{4}$ , NO  $\frac{1}{2}$  and NO  $\frac{1}{3}$  in Gullmarn during this period gives certain information about the nitrification activity. The large quantities of NH  $\frac{1}{4}$  between 20m and 50m indicate that the nitrification was slow in this water body. Both on top and below it was deliminated by old water which gave rise to two mixed zones. In both of these zones we found high concentrations of nitrite; this agrees well with the results from the incubation experiments with the Baltic Sea water. We still do not know why the NO  $\frac{1}{2}$  oxidation is inhibited more than the NH  $\frac{1}{4}$  oxidation in the mixed zones between the surface water and old water or why nitrification is nearly completly inhibited in the surface water. This unusual situation where we have a NO  $_3$  maximum near the surface and two NO  $_2$  maxima can be explained through our knowledge of the behaviour of the currents. We are continuing our intensive studies in Gullmarn in co-operation with other groups of the West Coast Project on the long term aspect of the nitrogen budget.

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# Notice

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