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# MEDDELANDE från HAVSFISKELABORATORIET · LYSEKIL

16

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On Nitrate and Ammonia in the Baltic Deep Water

by Stig H. Fonselius

(Contribution to ICES C.M. 1973/C:24 Copenhagen)

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International Council for the Exploration of the Sea

C.M. 1973/C:24 Hydrography Committee

#### On Nitrate and Ammonia in the Baltic Deep Water

by

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#### Abstract.

The atomic ratios of inorganic nitrogen and phosphorus are discussed and the deviation from the ratio in normal sea water, caused by the stagnant conditions in the Baltic are explained. Diagrams and tables are shown. Redfield et al. (1963) have shown that nutrient salts are accumulated in deep water in the same proportion as they are present in the plankton organisms. This means that if the plankton has an average composition (expressed in atoms) of C:N:P = 106:16:1 (Fleming 1940), the nutrient salt in the deep water should accumulate in the proportion (C:N:P) 106:16:1. Richards has investigated these factors in stagnant basins and he found a good agreement with his calculated values in the Black Sea and the Cariaco Trench (Redfield et al. 1963).

If we look at the conditions in the Baltic, we do not find this agreement at all (Fig. 1). In the surface water we have in winter a higher concentration of N and P than in summer. In summer both parameters may decrease to zero or values close to zero. The ratio N:P is somewhere between 10:1 and 20:1 ( $NO_3 + NH_4$ ):PO<sub>4</sub> but the concentrations are generally below 10 µg-at/l. The vertical convection brings during the winter nutrients down into the deep water as "preformed nutrients" (Redfield et al. loc.cit.). In addition nutrients are transported to the deep water through the Belts as another kind of "preformed nutrients". The amount is however, small because only 1/3 of the deep water is Kattegatt water (the salinity of the deep water is 1/3 of the salinity of the Kattegatt water). In the Kattegatt water we also have a N:P ratio fairly close to 16:1. Therefore these "preformed nutrients" do not change the N:P ratio in the deep water, if we assume that plankton in the Baltic has a normal C:N:P ratio = 106:16:1.

If we look at the actual N:P ratios in the deep water of the central Baltic, we find that it is about 2:1 indicating an enormous nitrogen deficit or as large a phosphorus excess (Table I). This may give the impression that plankton in the Baltic has another quite different composition than the plankton in the open sea, being on the starving limit regarding nitrogen. Nitrogen should therefore be the production limiting factor in the Baltic (Sen Gupta 1972).

A closer investigation shows that such N-deficits have never been created in laboratory tank experiments and in Nature large N-deficits have never been found (Strickland 1965). Richards (1965) has shown that  $NO_3^-$  is reduced to free N<sub>2</sub> gas in stagnant basins and that during nitrate reduction, released NH<sub>3</sub> is also transformed to N<sub>2</sub>. Only when

2.

the nitrate and all oxygen have disappeared from the water and  $H_2S$  formation begins,  $NH_3$  is formed instead of  $N_2$ . Therefore the relation N:P (inorganic salts) decreases below the halocline, when the oxygen content is only some tenths of a ml. Both parameters are of course accumulated in the deep water, but the denitrification is faster than the accumulation and the nitrate disappears completely, when all oxygen has been exhausted and hydrogen sulfide formation begins.

We have to observe that nitrogen gas values are not included in the tables. Only measurements of the Ar/N ratio by help of mass spectrometry, can show nitrogen gas increase in the water and such analyses can hardly be carried out on a routine basis. Volumetric analyses are not possible, because 10 µg-at/l of nitrate will only produce 0.1 ml of nitrogen and then the saturation value of nitrogen in sea water has to be known very exactly. Fig. 2 shows the vertical distribution of the nitrogen compounds except N, at the Gotland Deep in the Baltic. As we can see, nitrate first increases below the halocline due to accumulation, but soon it decreases down to zero. Also ammonia disappears almost completely, but begins to increase again in stagnant water, when H2S is formed. Fig. 3 shows the vertical distribution during oxidizing conditions, when no H<sub>2</sub>S is present in the water. Fig. 4 shows another vertical section in the Gotland basin. Here also phosphate is included in the figure. We can see how POA-P increases towards the bottom. This increase has been shown to be caused through dissolution of phosphate from the bottom sediments during reducing conditions (Fonselius 1963). This dissolution increases the amount of phosphate in the deep water, still more diminishing the ratio N:P. This effect has no importance in very deep and constantly stagnant basins as the Black Sea and the Cariaco Trech. During constantly stagnant conditions all phosphate remains in solution and we do not get abnormally high phosphate concentrations in the deep water, as is the case in shallow occasionally stagnant basins, where suddenly phosphate is released from the sediments when hydrogen sulfide is formed. When oxygen is present in the bottom water, phosphate is precipitated, probably in the form of ferriphosphate (Einsele 1938). During reducing conditions the iron is reduced to ferro-form and the phosphate is dissolved.

3.

There is still another process which may change the N:P ratio. When organic matter is oxidized in sea water, phosphate may be easier and faster released from the matter. This increases proportionally the amount of P in the water. We know that the slowly oxidable humus part of organic matter in the Baltic, contains 2.5 - 5% nitrogen but hardly any phosphorus.

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4.+

## Table I

The N:P relation at station BY 15A in the Baltic  $(NO_3 + NO_2 + NH_4) - N : P$ 

Depth m.	a 14.1.1971 N:P	b 2.3.1972 N:P	с 26.5.1972 N:Р	d 20.8.1972 N:P	e 31.10.1972 N:P						
						0	12.3:1	6.5:1	18.0:1	10,8:1	8.4:1
						5	14.7:1	7.3:1	27.9:1	8.3:1	6.9:1
10	17.0:1	9.0:1	17.5:1	5.5:1	7.7:1						
15	9.9:1	5.5:1	3.1:1	1.1:1	6.6:1						
20	9.6:1	6.4:1	6.9:1	0.7:1	7.5:1						
30	9.4:1	8.2:1	12.7:1	0.7:1	8.8:1						
40	8.2:1	5.3:1	9.2:1	0.5:1	5.7:1						
50	9.1:1	9.3:1	5.7:1	1.8:1	4.6:1						
60	7.0:1	7.0:1	5.3:1	0.8:1	3.5:1						
70	1.8:1	4.7:1	0.9:1	1.2:1	2.8:1						
80	1.7:1	2.8:1	3.8:1	ansa-ditati ettitik visias	1.8:1						
90	1.6:1	2.0:1	2.7:1	1.6:1	2.5:1						
100	2.3:1	1.8:1	2.3:1	2.1:1	2.5:1						
125	1.9:1	2.1:1	2.8:1	1.5:1	2.2:1						
150	2.0:1	0.6:1	0.7:1	1.0:1	1.2:1						
175	2.4:1	0.8:1	0.9:1	1.7:1	1.2:1						
200	2.1:1	1.0:1 H	S 1.0:1 H,	S 1.9:1	1						
225	2.2:1	1.0:1	1.0:1	2.1:1	1,9:1						
240	2.8:1	1.2:1	1.4:1	ssign-dator dates dives	2.2:1						







Fig. 3.



Fig. 4.

