Biochemical relationships and inorganic nitrogen equilibrium in semi-enclosed basins[1, 2]

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ABSTRACT

In anoxic basins the oxidation of organic matter has so far been represented taking only the reduction of sulphate into consideration. Theoretical studies, however, show that anaerobic bacteria reduces nitrate prior to the reduction of sulphate. Hence, in representing the total redox reactants, the inclusion of ammonia gives a better representation of its relation to the total phosphate regeneration in stagnant basins. An attempt is made to study the state of equilibrium of the inorganic nitrogen compounds from measurements of the concentrations of nitrate-, nitrite-, and ammonia-nitrogen, using the parameter pE. The systems $NO_2^- - NO_3^-$, $NH_4^+ - NO_3^-$, and $NH_4^+ - NO_2^-$ are applied for calculations. Studies are made of the variations of the three redox pairs in oxidising and in reducing environments. In narrow basins, under oxidising conditions, the system $NO_2^- - NO_3^-$ is found to approach equilibrium values. From the proximity of the calculated values to the equilibrium values the system $NO_3^- - NO_2^- - NH_4^+$ appears to exist at least in partial equilibrium, if not in total equilibrium conditions, in marine environments independent of the general equilibrium condition controlled by the system $H_2 - H^+ - H_2O$.

Biochemical relationships

In anaerobic basins the oxidation of organic matter has been represented by the following stoichiometric relationships (Richards & Vaccaro, 1956):

$$CH_2O + O_2 \rightleftharpoons CO_2 + H_2O$$

$$2CH_2O + SO_4^{2-} \rightleftharpoons 2CO_2 + S^{2-} + 2H_2O$$

and accordingly the total redox reactants have been represented as equivalent to $AOU^{(3)} + 4S^{2-}$, where $4S^{2-}$ is the amount of S^{2-} reduced from SO_4^{2-}, assuming that all S^{2-} originates from SO_4^{2-} and that SO_4^{2-} is equivalent to four oxygen atoms as oxidant. According to Mckinney & Conway (1957) the oxygen requirement of the anaerobic bacteria is provided by the selective removal of oxygen according to the following order of precedence:

$$O_2 > NO_3^- > SO_4^{2-} > CO_3^{2-}$$

Assuming that all NH_4^+ originates from NO_3^- and that nitrate as oxidant is equivalent to four oxygen atoms ($NH_4^+ + 2O_2 \rightleftharpoons NO_3^- + 2H^+ + H_2O$) the total redox reactants can better be represented as equivalent to $AOU + 4NH_4^+ + 4S^{2-}$. In these calculations the possible presence of intermediate products from the reductions of sulphate and nitrate as well as the hydrogen sulphide and ammonia which may originate directly from the decomposition of organic sulphur and nitrogen compounds respectively, have not been taken into account assuming the resulting error to be probably small.

This relation has been applied to measure-

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[2] Part of the thesis accepted for the degree of Filosofie Licentiat in Oceanography at Göteborgs Universitet.

[3] A.O.U. (apparent oxygen utilisation) $= 2(O_2' - O_2)$, where O_2 is the observed concentration of oxygen and O_2' the concentration of oxygen dissolved in the water having the observed salinity and temperature when in equilibrium with a water-saturated atmosphere (Redfield, 1942).

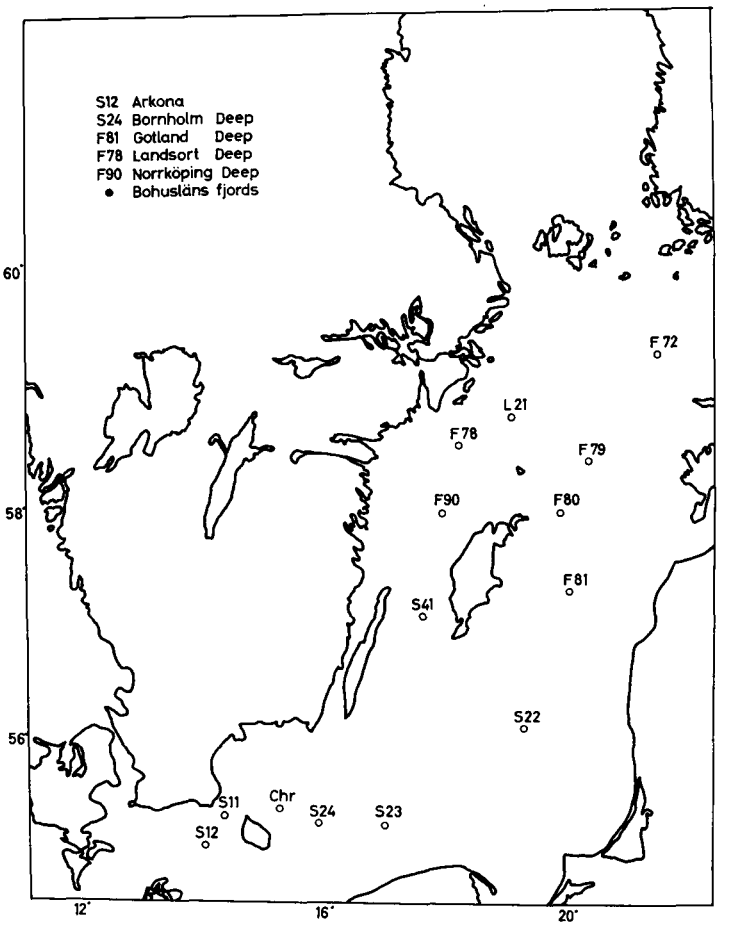

Fig. 1

ments from three stations in the Baltic (Gotland, Landsort and Norrköping deeps) and the Bohusläns fjords (fjords of the northern part of the Swedish west coast) (Fig. 1). Observations from a section round the Black Sea and one on the eastern North Atlantic from the Faroe Bank Channel to the northern slopes of the Bay of Biscay have also been considered for study.

The average values of all the parameters used in the calculations are given in Table 1. Literature data (Richards & Benson, 1961) for ammonia concentrations have been applied to the calculations for the Cariaco Trench (Gulf of Venezuela) and the Drammensfjord (Norway). The equations for the linear least square regression lines, with and without taking into consideration the ammonia concentrations, along with their coefficients of correlation, as calculated, are given in Table 2.

These equations show some characteristics. Taking the line for the eastern North Atlantic as a standard for oceanic environments, it can be seen from the values of the slopes that conditions for phosphate regeneration are almost the same in aerobic regions everywhere. The oxidation to phosphate regeneration ratio, as calculated from the equations, are 435, 305, 292, 191 and 246 for Gotland, Landsort, Norrköping deeps, eastern North Atlantic and the Cariaco Trench respectively. The corresponding values of the ratios without considering the contribution from ammonia are 476, 295, 292, 181 and 235 respectively for the stations mentioned above. It can be seen that, with the exception of

Table 1. *Average values of all parameters used in calculations*[a]

Values given per μg atom/l

Depth	Gotland deep (Nov. 1964 to Aug. 1966)					Landsort deep (Nov. 1964 to Aug. 1966)				
	AOU	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N	AOU	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N
0	31	0.13	0.46	0.15	4.96	−23	0.24	0.37	0.20	3.47
5	21	0.10	0.41	0.15	4.29	−34	0.22	0.55	0.17	3.77
10	40	0.12	0.52	0.16	4.06	−10	0.22	0.52	0.18	3.97
15	25	0.12	0.55	0.11	4.32	− 7	0.27	0.51	0.18	3.05
20	59	0.12	0.58	0.12	4.12	15	0.28	0.51	0.15	2.81
30	52	0.16	0.59	0.15	2.95	29	0.32	0.56	0.16	1.02
40	81	0.17	0.77	0.10	2.76	71	0.39	0.84	0.17	0.80
50	76	0.21	0.96	0.25	3.79	113	0.56	0.92	0.20	0.89
60	140	0.38	1.02	0.17	3.48	312	1.04	1.89	0.17	1.83
70	440	1.03	2.64	0.08	2.56	529	1.86	2.55	0.14	1.03
80	645	1.65	3.21	0.10	2.17	662	2.48	3.63	0.11	1.65
90	672	1.71	5.04	0.08	1.64	710	2.72	4.82	0.14	1.04
100	626	1.51	5.46	0.08	1.88	719	2.64	5.67	0.11	1.25
125	627	1.67	5.93	0.07	1.75	723	2.63	5.75	0.15	1.42
150	659	2.33	5.69	0.07	1.63	710	2.64	5.68	0.11	1.30
175	668[b]	2.81	5.72	0.11	1.95	—	—	—	—	—
200	675	2.56	5.99	0.07	1.97	716	2.60	5.77	0.12	1.16
225	674	2.27	6.41	0.13	1.46	—	—	—	—	—
245	678[b]	2.62	6.03	0.16	1.20	—	—	—	—	—
300	—	—	—	—	—	704	2.51	5.71	0.10	1.09
400	—	—	—	—	—	709	2 49	5.66	0.13	1.02
440	—	—	—	—	—	714	2.49	4.93	0.13	0.99

Depth	Black Sea (July–August, 1965: average of 17 stations)						Eastern North Atlantic (June–July, 1967: average of 8 stations)					
	AOU	H_2S	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N	AOU	pH	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N
0	8	0	0.11	0.41	0.07	2.56	46	8.15	0.11	3.29	0.17	3.00
10	2	0	0.11	0.52	0.21	3.25	23	8.20	0.30	2.78	0.12	5.42
20	18	0	0.11	0.51	0.18	2.30	—	—	—	—	—	—
30	53	0	0.11	0.69	0.27	4.11	—	—	—	—	—	—
50	81	0	0.21	0.52	0.50	2.68	9	8.19	0.32	4.41	0.23	5.61
75	312	0	0.82	2.09	0.24	1.78	—	—	—	—	—	—
100	456	0	1.15	2.60	0.28	0.95	41	8.17	0.44	7.41	0.16	0.55
125	582	0	1.10	2.15	0.34	2.62	—	—	—	—	—	—
150	610	7.3	2.63	0.87	0.35	5.23	45	8.16	0.76	7.72	0.11	0.93
200	634	43.0	4.56	0.62	0.26	11.46	48	8.16	0.70	8.35	0.03	5.67
250	645	82.4	4 87	0 48	0.22	17.98	—	—	—	—	—	—
300	642	145.3	5.20	0.45	0.22	18.80	50	8.16	0.82	8.89	0.02	1.94
400	652	213.3	5.79	0.41	0.24	19.64	52	8.19	0.75	8.21	0.06	3.69
500	640	345.4	6.41	0	0.24	19.77	62	8.17	0.88	8.81	0.03	3.94
600	—	—	—	—	—	—	88	8.16	0.82	9.57	0.02	3.75
700	—	—	—	—	—	—	108	8.15	1.04	9.96	0.14	2.19
750	637	468.0	7.15	0	0.47	21.18	—	—	—	—	—	—
800	—	—	—	—	—	—	146	8.15	1.02	11.19	0.07	2.00
1000	637	604.1	7.62	0	0.37	21.24	199	8.12	1.21	12.13	0.18	2.00
1100	—	—	—	—	—	—	198	8.13	1.28	13.23	0.16	2.05
1200	—	—	—	—	—	—	180	8.09	1.16	14.08	0.14	2.02
1250	637	631.3	7.84	0	0.44	22.11	—	—	—	—	—	—
1500	636	643.3	8.04	0	0.53	22.04	137	8.09	1.37	11.07	0.16	2.10
1800	—	—	—	—	—	—	140	8.12	1.33	12.53	0.19	0
2000	635	717.8	7.30	0	0.65	22.35	—	—	—	—	—	—
2100	—	—	—	—	—	—	148	8.12	1.44	13.28	0.23	0
2400	—	—	—	—	—	—	136	8.12	1.54	12.23	0.19	0

Table 1 (*cont.*)

	Norrköping deep (Nov. 1964 to Aug. 1966)					Bohuslän fjords (Dec. 1964 to Feb. 1965: average of 3 stations)						
Depth	AOU	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N	Depth	AOU	H_2S	PO_4^{3-}–P	NO_3^-–N	NO_2^-–N	NH_4^+–N
0	−28	0.21	0.24	0.09	3.25	20	605	0.3	3.3	0	0	13.8
5	59	0.23	0.34	0.11	3.13	25	643	50.0	5.7	0	0	18.3
10	−21	0.21	0.32	0.11	3.14	30	646	43.3	5.5	0	0	18.2
15	38	0.20	0.39	0.11	3.24	35	642	52.5	5.8	0	0	18.8
20	47	0.25	0.41	0.08	4.00	40	573	57.9	5.6	0	0	18.3
30	25	0.28	0.38	0.09	3.57	45	608	48.7	5.9	0	0	18.5
40	105	0.34	0.40	0.10	3.39	50	669	43.1	5.6	0	0	19.0
50	181	0.66	0.91	0.15	3.11	55	647	35.3	6.2	0	0	20.1
60	362	1.13	1.42	0.08	2.18							
70	604	1.82	2.31	0.06	1.10							
80	797	2.52	3.06	0.09	1.19							
90	899	2.87	3.63	0.06	3.15							
100	921	3.15	3.66	0.30	2.06							
125	928	3.28	4.04	0.51	1.96							
150	931	3.38	4.61	0.39	0.97							
175	928	3.62	4.93	0.99	0.62							

[a] Oxygen, phosphate and hydrogen sulphide values for the Baltic basins and the Bohuslän fjords have been taken from the records of the Hydrographic Department of the Royal Fishery Board of Sweden. Oxygen and phosphate values of the Black Sea stations have been taken from the cruise log of R.V. *John Elliott Pillsbury* and hydrogen sulphide values from the same cruise have been kindly permitted to be used for the article by Fil. lic. Stig Fonselius of the Fishery Board of Sweden.

[b] During August 1966 hydrogen sulphide was detected in the Gotland deep at depths of 175 and 245 metres and the concentrations were measured to be 4.2 and 5.3 μg at./l respectively. Simultaneously at these two depths no nitrate, only a trace amount of nitrite and quite a high concentration of ammonia were observed. The AOU values at those two depths were calculated as 788 and 805 μg at./l respectively. A detailed explanation of this phenomenon has been given elsewhere (Sen Gupta, 1967).

the Gotland deep, the inclusion of ammonia gives slightly higher values for the ratios. But, in general, the inclusion of ammonia certainly gives a better correlation between the different parameters, particularly for the stagnant basins, which can be seen from the coefficients of correlation (Table 2). With the exception of the Gotland deep all other values compare tolerably well with the theoretical value of 276 (Richards & Vaccaro, loc. cit.). The differences may be said to be due to variations in local conditions. The very high value at the Gotland deep has been explained by Fonselius (1967) to be due to the gradual overturning of the phosphate-rich stagnant waters from the bottom and also due to the effect of the higher ammonia concentrations at the surface layers (Table 1). Another fact that emerges out of the equations is that the *phosphate concentration is not a limiting factor for plant growth in marine environments* (positive values of the departures of the intercept in all the equations for aerobic regions). That the inclusion of the ammonia concentration is necessary to calculate the total redox reactants and gives a better representation can be seen from the two equations for the Cariaco Trench. The change in the sign of the departure of the intercept is significant in as much as it corroborrates the well-established fact stated above.

Conditions in the upper aerobic layer and the lower stagnant layer down to about 250 metres both in the Gotland deep and the Black Sea agree fairly well (Fig. 2). Values from the Drammensfjord and the Bohuslän fjords also lie within this range. This region for hydrogen sulphide production and phosphate regeneration appears to be characteristic for basins where stagnation is only a periodic phenomenon. This layer of increase may be termed as a "*transition layer*" for permanent anoxic basins because of the rapid increase of selective bacterial activity,

Table 2. *Total redox reactants in aerobic and anaerobic milieu*

Linear least-square regression lines

1. Gotland deep (Baltic) and Black Sea		
(i) Aerobic layer		
(*a*)	$PO_4^{3-}\text{-}P = 0.0023\ (AOU + 4\ NH_4^+) + 0.01$	$r^a = 0.997$
(*b*)	$PO_4^{3-}\text{-}P = 0.0021\ \ AOU + 0.06$	$r^a = 0.996$
(ii) Stagnant layer		
(*a*)	$PO_4^{3-}\text{-}P = 0.013\ (AOU + 4\ NH_4^+ + 4\ S^{2-}) - 6.62$	$r^a = 0.969$
(*b*)	$PO_4^{3-}\text{-}P = 0.011\ (AOU + 4\ S^{2-}) - 4.94$	$r^a = 0.916$
2. Black Sea (deeper stagnant layer)		
(*a*)	$PO_4^{3-}\text{-}P = 0.00117\ (AOU + 4\ NH_4^+ + 4\ S^{2-}) + 3.85$	$r^a = 0.959$
(*b*)	$PO_4^{3-}\text{-}P = 0.00118\ (AOU + 4\ S^{2-}) + 3.92$	$r^a = 0.959$
3. Landsort deep (Baltic)		
(*a*)	$PO_4^{3-}\text{-}P = 0.00328\ (AOU + 4\ NH_4^+) + 0.21$	$r^a = 0.973$
(*b*)	$PO_4^{3-}\text{-}P = 0.00339\ \ AOU + 0.16$	$r^a = 0.996$
4. Norrköping deep (Baltic)		
(*a*)	$PO_4^{3-}\text{-}P = 0.00343\ (AOU + 4\ NH_4^+) + 0.001$	$r^a = 0.993$
(*b*)	$PO_4^{3-}\text{-}P = 0.00342\ \ AOU + 0.03$	$r^a = 0.994$
5. Bohuslän fjords (Sweden)		
(*a*)	$PO_4^{3-}\text{-}P = 0.0096\ (AOU + 4\ NH_4^+ + 4\ S^{2-}) - 2.87$	$r^a = 0.914$
(*b*)	$PO_4^{3-}\text{-}P = 0.0102\ (AOU + 4\ S^{2-}) - 2.65$	$r^a = 0.896$
6. Eastern North Atlantic		
(*a*)	$PO_4^{3-}\text{-}P = 0.00524\ (AOU + 4\ NH_4^+) + 0.28$	$r^a = 0.858$
(*b*)	$PO_4^{3-}\text{-}P = 0.00554\ \ AOU + 0.37$	$r^a = 0.831$
7. Drammens fjord (Norway)		
(*a*)	$PO_4^{3-}\text{-}P = 0.0075\ (AOU + 4\ NH_4^+ + 4\ S^{2-}) - 1.62$	$r^a = 0.773$
(*b*)	$PO_4^{3-}\text{-}P = 0.00757\ (AOU + 4\ S^{2-}) - 1.58$	$r^a = 0.749$
8. Cariaco Trench (Gulf of Venezuela)		
(*a*)	$PO_4^{3-}\text{-}P = 0.00406\ (AOU + 4\ NH_4^+ + 4\ S^{2-}) + 0.003$	$r^a = 0.996$
(*b*)[b]	$PO_4^{3-}\text{-}P = 0.00426\ (AOU + 4\ S^{2-}) - 0.095$	$r^a = 0.959$

[a] r = Coefficient of correlation.

[b] From Richards & Vaccaro (1956).

resulting in sharp increases in ammonia and phosphate and a gradual increase in hydrogen sulphide concentrations. Below this depth, excepting the sulphur bacteria, most of the other forms are assumed to cease, with steep increase of hydrogen sulphide associated with a slow increase in phosphate and ammonia concentrations, as can be seen from the line for the deeper stagnant layers of the Black Sea (Fig. 2). It can be said, therefore, that conditions in periodic anoxic basins never go beyond that in the transition layer of permanent anoxic basins. But the line for the Cariaco Trench (Fig. 3), which is a permanent anoxic basin, does not show the same nature. Rather it appears to be in close proximity with those for aerobic regions. This

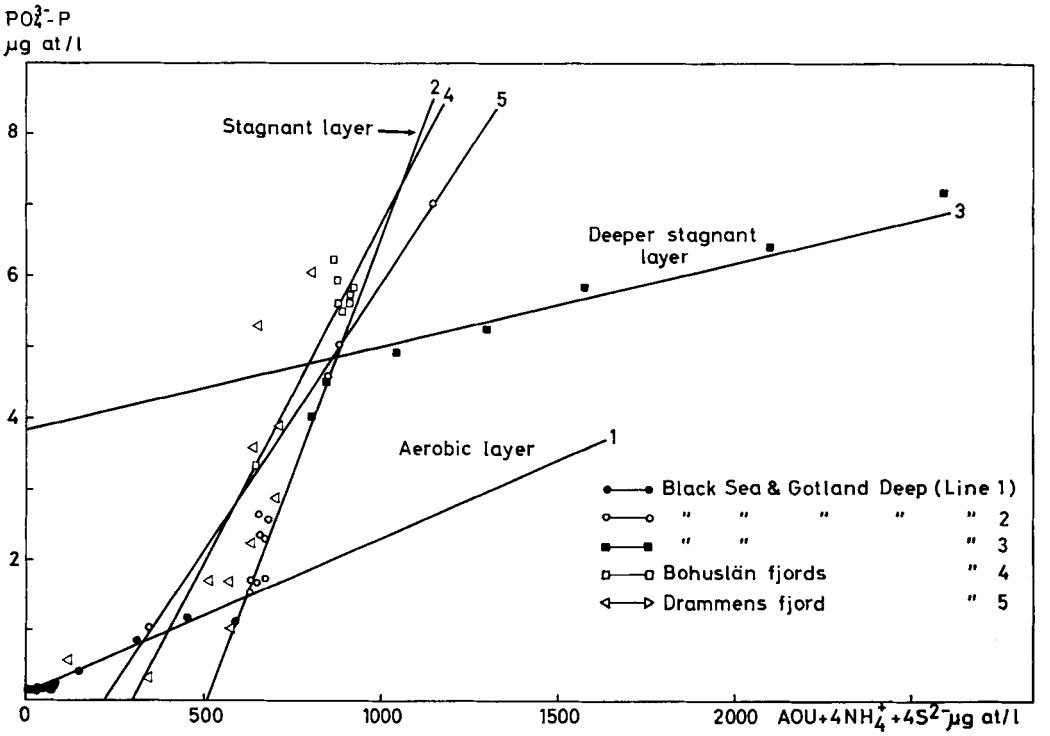

Fig. 2. Total redox reactants in anaerobic milieu.

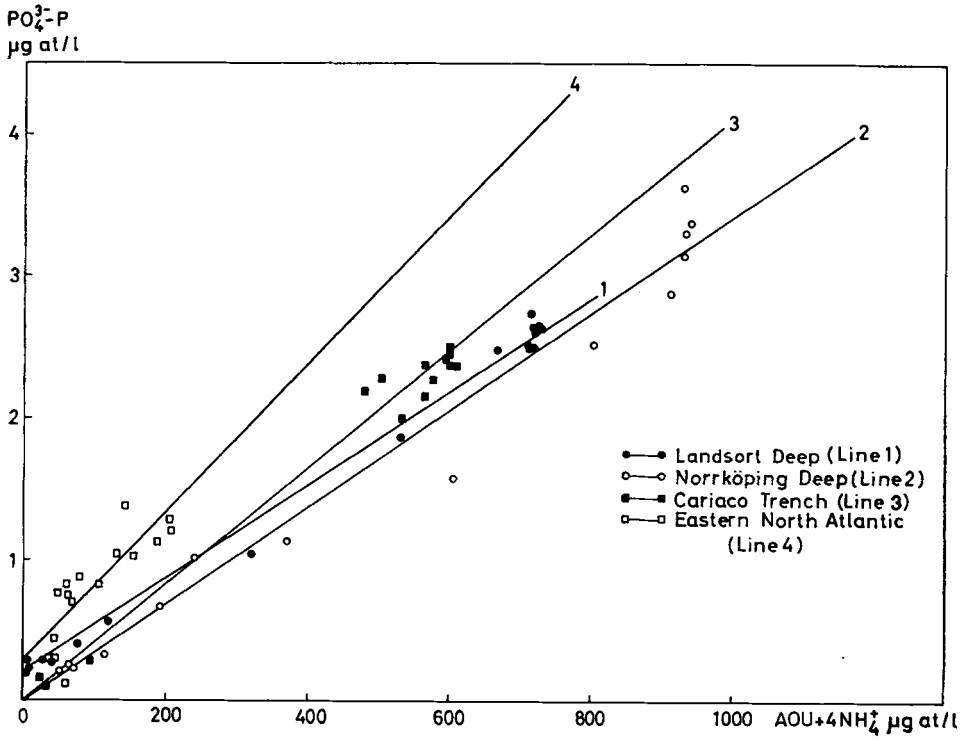

Fig. 3. Total redox reactants in aerobic milieu.

appears to be rather confusing. One probable reason may be that the values from the aerobic and the anaerobic regions have been represented by the same line and that is why it compares more with those for the aerobic milieu than with those for anaerobic milieu.

It is perhaps pertinent to mention here a characteristic of the "transition layer". In this layer there is almost always a sharp increase in phosphate concentration, whereas the increases in other parameters are relatively not so sharp. The mechanism for this process is not yet clearly understood. Richards & Vaccaro (loc. cit.) have suggested the more rapid decomposition of phosphatic organic compounds in the upper layers, permitting only residues low in phosphate to settle to greater depths, as a probable process. Olausson (1967) has suggested the dissolution of phosphorus from the bottom sediments with the lowering in pH as another probable process.

Inorganic nitrogen equilibrium

The conceptual meaning of a particular redox potential (electrode potential) is that it is the equivalent free energy, i.e., the free energy change per mole of electrons associated with a given reduction (Stumm, 1966). Although aqueous solutions do not contain free protons and electrons, it is possible to define a proton activity $pH = -\log \{H^+\}$ and an electron activity $pE = -\log \{e^-\}$. As pointed by Sillén & Martell (1964) pE is a convenient measure of the oxidising intensity of a system at equilibrium and is related to the reversible redox potential (E_H) by the factor $2.3RTF^{-1}$ (59.155 mV at 25°C). The measurement of E_H necesstates the use of a platinum electrode, which gets fouled in sulphide-bearing environments. Hence in a stagnant basin, if the necessary parameters are measured with sufficient accuracy, pE is a convenient means to express the activity intensity of the medium. Furthermore, pE makes calculations simpler. The relations as deduced from Sillén & Martell (loc. cit.) and used for the calculations are given in Table 3. For the Baltic and the Black Sea an average pH value of 7.8 ± 0.3 is assumed for the whole water column, while for the eastern North Atlantic the actually measured values are taken.

The areas selected for study are quite different from one another in hydrographic characteristics. Both the Baltic and the Black seas are semi-enclosed basins with narrow openings and shallow sill depths. In the Black Sea below about 150 metres there is permanent stagnation with the associated reducing conditions. In the Baltic, however, conditions are partly oxidising and partly reducing in the deeper waters. In the Gotland deep conditions below the sill depth vary, depending on the amount of the inflow. As long as not enough water flows in, stagnant or semi-stagnant conditions persist. But, in general, reducing conditions prevail. In the Landsort and the Norrköping deeps, however, below the sill depth conditions are absolutely oxidising. An area in the eastern North Atlantic has been investigated, since it has been suggested (L. H. N. Cooper, personnal communication) that the inorganic nitrogen system in oceanic environments may be expected to approach equilibrium conditions below 2000 metres.

The speed of production of life in the surface layers and in the shallow regions never allow any system in the sea to proceed towards equilibrium conditions. Further, it has been predicted (Sillén, 1966) that there exists in the top layers of the sea some organisms which probably can cause a nitrate-sink by transforming nitrate to nitrite and eventually to gaseous nitrogen even in the presence of excess oxygen. Therefore measurements from the Arkona and the Bornholm basins have been left out from detailed study and values only from the deep stations have been considered. The values of pE for the Gotland, Landsort and Norrköping deeps are plotted from the sill depth downwards, to study the conditions in those basins (Fig. 4). Values from the Black Sea for the same range of depth have been plotted in the same figure to attempt a comparison between different states of oxidation in the two environments. Values from the deeper regions of the Black Sea have been excluded from the diagram, since below about 400 metres NO_3^- totally disappears and the only redox pair that could be studied is NH_4^+/NO_2^- which does not show any appreciable variation with increasing depth, as could be seen from Table 3. The values for the system NO_2^-/NO_3^-, in general, increases with depth in the Gotland and the Landsort deeps, but show a sudden decrease at the bottom layers. This shows that conditions at the bottom layers of these two basins are, in general, reducing, but the degree

Table 3. *Equilibrium conditions of the inorganic nitrogen system calculated from pE values*

Definitions and relations used: $pE = -\log\{e^-\} = E_H/(2.3\,RTF^{-1}) = E_H/59.155$ mV at 25°C; $2\,pE = 28.4 - 2\,\text{pH} - \log\{NO_2^-/NO_3^-\}$; $8\,pE = 119.2 - 10\,\text{pH} - \log\{NH_4^+/NO_3^-\}$; $6\,pE = 90.8 - 8\,\text{pH} - \log\{NH_4^+/NO_2^-\}$. pH assumed for the Black Sea and the Baltic basins = 7.8 ± 0.3; for the eastern North Atlantic = actually measured values. { } denotes the molar concentration ratio of the two species

Calculated from ...	$\log\{NO_2^-/NO_3^-\}$					$\log\{NH_4^+/NO_3^-\}$					$\log\{NH_4^+/NO_2^-\}$				
Depth (m)	Gotland deep	Landsort deep	Norrköping deep	Black Sea	Eastern North Atlantic	Gotland deep	Landsort deep	Norrköping deep	Black Sea	Eastern North Atlantic	Gotland deep	Landsort deep	Norrköping deep	Black Sea	Eastern North Atlantic
50	—	—	6.79	—	6.65	—	—	5.08	—	4.66	—	—	4.51	—	3.98
60	6.93	6.97	7.02	6.41	—	5.08	5.15	5.17	5.06	—	4.52	4.56	4.49	4.61	—
70	7.16	7.03	7.19	—	—	5.15	5.19	5.19	—	—	4.48	4.59	4.52	—	—
75	—	—	—	6.87	—	—	—	—	5.15	—	—	—	—	4.59	—
80	7.15	7.16	7.17	—	—	5.19	5.19	5.20	—	—	4.51	4.54	4.55	—	—
90	7.30	7.17	7.29	—	—	5.20	5.23	5.16	—	—	4.51	4.59	4.44	—	—
100	7.32	7.26	6.94	6.89	6.86	5.20	5.23	5.17	5.20	4.83	4.51	4.56	4.59	4.65	4.15
125	7.34	7.19	6.85	6.80	—	5.21	5.22	5.23	5.13	—	4.51	4.57	4.69	4.59	—
150	7.36	7.25	6.94	6.60	6.96	5.21	5.23	5.20	5.05	4.82	4.51	4.55	4.61	4.54	4.10
175	7.26	—	6.75	—	—	5.20	—	5.26	—	—	4.53	—	4.77	—	—
200	7.37	7.24	—	6.59	7.05	5.21	5.23	—	5.00	4.72	4.49	4.57	—	4.46	3.87
225	7.25	—	—	—	—	5.21	—	—	—	—	4.56	—	—	—	—
245	7.19	—	—	—	—	5.23	—	—	—	—	4.59	—	—	—	—
250	—	—	—	6.57	—	—	—	—	4.95	—	—	—	—	4.41	—
300	—	7.28	—	6.53	7.36	—	5.24	—	4.94	4.70	—	4.56	—	4.42	3.91
400	—	7.22	—	6.51	7.34	—	5.24	—	4.93	4.71	—	4.58	—	4.42	3.92
440	—	7.19	—	—	—	—	5.23	—	—	—	—	4.59	—	—	—
500	—	—	—	—	7.38	—	—	—	—	4.73	—	—	—	4.42	3.95
600	—	—	—	—	7.36	—	—	—	—	4.75	—	—	—	—	3.99
700	—	—	—	—	7.27	—	—	—	—	4.79	—	—	—	—	4.08
750	—	—	—	—	—	—	—	—	—	—	—	—	—	4.46	—
800	—	—	—	—	7.15	—	—	—	—	4.81	—	—		—	4.08
1000	—	—	—	—	7.00	—	—	—	—	4.82	—	—		4.44	4.09
1100	—	—	—	—	7.03	—	—	—	—	4.83	—	—		—	4.11
1200	—	—	—	—	7.03	—	—	—	—	4.85	—	—		—	4.13
1250	—	—	—	—	—	—	—	—	—	—	—	—		4.45	—
1500	—	—	—	—	7.03	—	—	—	—	4.89	—	—		4.46	4.16
1800	—	—	—	—	6.99	—	—	—	—	—	—	—		—	—
2000	—	—	—	—	—	—	—	—	—	—	—	—		4.48	—
2100	—	—	—	—	6.96	—	—	—	—	—	—	—		—	—
2400	—	—	—	—	6.98	—	—	—	—	—	—	—		—	—

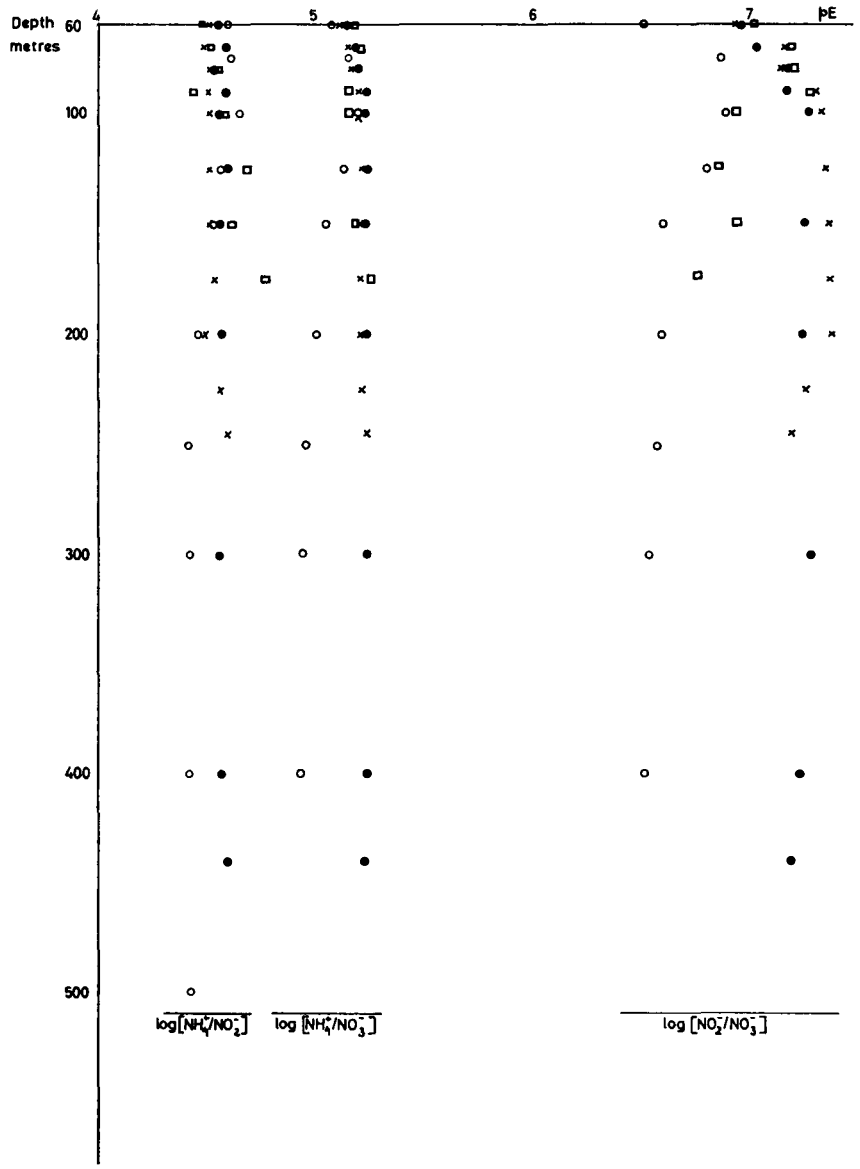

Fig. 4. Equilibrium conditions of nitrogen systems. ×, Gotland deep; ●, Landsort deep; ○, Black Sea □, Norrköping deep.

of reduction appears to be higher in the Gotland deep (7.37 at 175 m to 7.19 at 245 m) than in the Landsort deep (7.23 at 400 m to 7.19 at 440 m). But in the bottom layers of the Norrköping deep the values with respect to the system NO_2^-/NO_3^- decreases while those for the other two increases. This indicates oxidising conditions—the ammonia content in the process of being oxidised, is in the nitrite-stage. The values at the Black Sea show a sharp increase at the interface between the upper aerated and the lower stagnant layers (between 125 and 150 metres) and thereafter decreases gradually downwards. The higher values at the interface are probably due to the accumulation of organic matter just above the lower stable layer. This assumption has, later on, been confirmed by Prof. B. A. Skopintsev (personnal discussion).

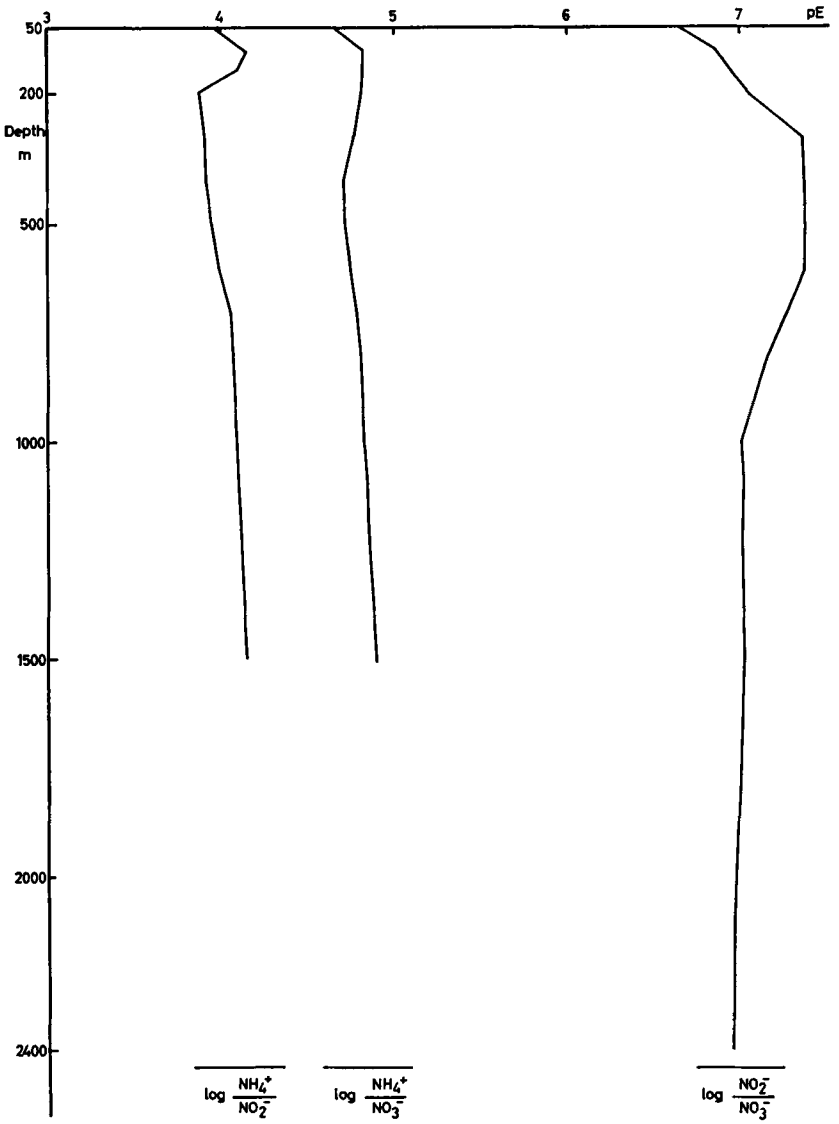

Fig. 5. Equilibrium conditions of inorganic nitrogen systems in the eastern North Atlantic.

In the eastern North Atlantic (Fig. 5) ammonia disappears below about 1500 metres, whereas all the parameters increase from the surface down to 600 metres. Below 600 metres, however, the values for the first pair decreases with depth while those for the other two increases till the disappearance of ammonia. This indicates that the organic matter, originating from the production at the surface, is fully oxidised at about 600 metres. below which depth the reduction process sets in which appears to cease at about 1500 metres. The almost constancy of the values below this depth, with respect to the first pair, indicates that the ammonia is in the nitrite stage of its oxidation to nitrate. In the deeper waters of the oceans the only probable inorganic nitrogen species appears to be nitrate, besides, of course, the gaseous nitrogen, which is postulated to exist in a state of saturation in the oceans, increasing to supersaturation under stagnant conditions.

The above values give rise to some interesting

problems. From the equations in Table 3 it can be calculated that the pE values at equilibrium of the three redox pairs between pH 7.8–8.0 lie between 6.4–6.2, 5.2–4.9, and 4.7–4.5 respectively and the calculations from the measured concentrations of nitrate, nitrite and ammonia leads approximately to the same results. Also the equilibrium constants have been used for 25°C whereas the average sea water is much colder; and calculating ΔH for the various reactions from the literature data it will not be surprising to find that there exists a difference. However, in general, this indicates the possibility that in marine environments the system $NO_3^- - NO_2^- - NH_4^+$ may proceed towards equilibrium independent of the general equilibrium conditions controlled by the $O_2 - H^+ - H_2O$ system.

The equations for the denitrification and nitrification processes may be represented as follows:

$$NO_3^- + 2H_2O \rightleftharpoons NH_3 + OH^- + 2O_2$$

$$\Delta G^\circ = 95.8 \text{ kcal}$$

$$NH_4^+ + 2O_2 + OH^- \rightleftharpoons NO_3^- + H^+ + 2H_2O$$

$$\Delta G^\circ = -83.1 \text{ kcal}$$

From informations available in literature (Cooper, 1937; Bongers, 1958) it is found that ΔG° values for the above two reactions are 73 and −77.4 kcal respectively. The present calculations have been made using the constants from Latimer (1952). The sum of these ΔG° values correspond of course to the equilibrium

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

which has a $\Delta G^\circ = 2.3RT \log K_{diss} = 12.7$ kcal. Perhaps the old calculations were made using some other constants.

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БИОХИМИЧЕСКИЕ СООТНОШЕНИЯ И РАВНОВЕСИЕ НЕОРГАНИЧЕСКОГО АЗОТА В ПОЛУЗАКРЫТЫХ БАССЕЙНАХ

В аноксических бассейнах окисление органической материи рассматривалось только при учете восстановления сульфата. Однако теоретические исследования показывают, что анаэробные бактерии восстанавливают нитрат скорее, чем сульфат. Следовательно, при рассмотрении всех окислительно-восстановительных реагентов учет аммония даст лучшее представление об их связи с полной регенерацией фосфата в непроточных бассейнах.

Делается попытка изучить состояние равновесия неорганических соединений азота из измерений концентраций нитрата, нитрата и аммония, используя параметр pE. При вычислениях рассматриваются системы $NO_2^- - NO_3^-$, $NH_4^+ - NO_3^-$, $NH_4^+ - NO_2^-$. Изучаются вариации этих трех оксилительно-восстановительных пар в восстановительных средах. В узких бассейнах при окислительных условиях найдено, что система, $NO_3^- - NO_2^-$ приближается к своим равновесным величинам. Из близости вычисленных величин к равновесным представляется, что система $NO_3^- - NO_2^- - NO_4^+$ находится, по крайней мере, в частичном, если не в полном, равновесии в морской среде независимо от условий полного равновесия, контролируемого системой $H_2 - H^+ - H_2O$.