A closer look at nitrification in pelagic sediments

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Nutrient profiles in Southwest Pacific *interstitial solutions* suggest that in environments of oxic pelagic sedimentation microbially mediated nitrification is recognizable as a two-step process. During the first step partially oxidized nitrogenous intermediaries accumulate in distinctive ammonia and nitrite maxima along with nitrate. During the second step nitrification continues and all intermediate species are fully oxidized to nitrate. Both steps occur within a zone that corresponds in thickness to the biologically active surface layer. Similarly, *experimental nitrogen regeneration* from decomposition of plankton in seawater (VON BRAND and RAKESTRAW, 1941: VON BRAND *et al.*, 1942) suggests that each step corresponds to a distinct reaction in the microbially mediated transformation of N-org$\rightarrow$NH$_3$$\rightarrow$NO$_2$$\rightarrow$NO$_3$. The resolution of distinct reaction zones in pore water nutrient profiles possibly depends on the nature and mode of supply of the organic matter undergoing nitrification or reflects the spatial succession downcore of microbial populations capable of deamination, ammonium oxidation and nitrite oxidation, respectively. Finally, stoichiometric ratios of nutrients in the free *water column* - here demonstrated on published data from Saanich Inlet -- reflect the same two steps of nitrification as delineated by the dissolved pore water species. Future pore water studies should include dissolved oxygen measurements as well as accurate ΣCO_2, PO_4 and nitrogenous species profiles, to verify and better quantify these separate steps in nitrification mechanism of oxic pelagic sediments.

INTRODUCTION

Ever since the ratios among dissolved nutrients and metabolites in pore solutions of marine sediments were discovered to reflect different mechanisms of organic matter decomposition, a great number of decomposition models have been proposed (ALLER, 1977; BERNER, 1972; BALZER, 1978; HARTMANN *et al.*, 1976; MURRAY and IRVINE, 1895; MURRAY *et al.*, 1978; a.o.). This approach was further stimulated by the applicability of stoichiometric models developed by chemical and biological oceanographers for nutrient regeneration patterns in the free water column to those of interstitial solutions of marine sediments. Recently, it has been recognized that inorganic secondary reactions between metabolites and solid sediment phases greatly limit the nutrient regeneration models. It appears that only in environments of slow sedimentation, where secondary reactions are insignificant and metabolites simply accumulate, such models can be applied (BERNER, 1977; EMERSON, 1976; MARTENS *et al.*, 1978; FROELICH *et al.*, 1979; and SUESS, 1979).
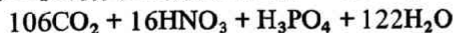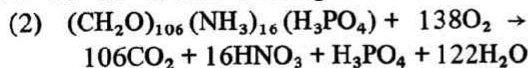
Oxic environments of slow pelagic sedimentation comprise the dominant areas of recent sediment accumulation in the oceans and hence the major sites of organic matter mineralization. BENDER *et al.* (1977) have first suggested that microbially mediated nitrification and denitrification are two prominent regeneration mechanisms at the sediment-water interface of pelagic sediments. We will extend those considerations with a closer look at nitrification in pelagic sediments and at selected water column data and experimental nitrification reactions.

Ideally, regeneration ratios in pore waters of oxygenated sediments should be:

(1) $-\Delta O_2 : \Delta NO_3 : \Delta PO_4 : \Delta \Sigma CO_2 =$

138 : 16 : 1 : 106

based on an overall decomposition reaction:

(2) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow$
$106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$

and the assumption that all NH_3 released by deamination is quickly oxidized to nitrate.

We present evidence here that this overall reaction may proceed in at least two resolvable steps with distinct steady state nutrient concentration patterns. During the first step partially oxidized nitrogenous intermediaries are formed and *not* immediately converted to nitrate as is generally assumed. Then during a second step they are fully oxidized.

This stepwise process in decomposition of organic matter by oxygen consumption is also evident in the primary ammonia and primary nitrite maxima of water column nutrients (COHEN, 1978) and in experimental nitrogen regeneration from decomposition of plankton in seawater (VON BRAND and RAKESTRAW, 1941; VON BRAND *et al.*, 1942). We develop our view of a stepwise nitrification process partially from such available water column nutrient and experimental data where overall nitrification is resolved into deamination, ammonium and nitrate oxidation and partially from our own measurements of regeneration products in pore waters of oxygenated near-surface sediments from the southwest Pacific.

RESULTS

The area of sampling in the Southwest Pacific and the core locations are shown in Fig.
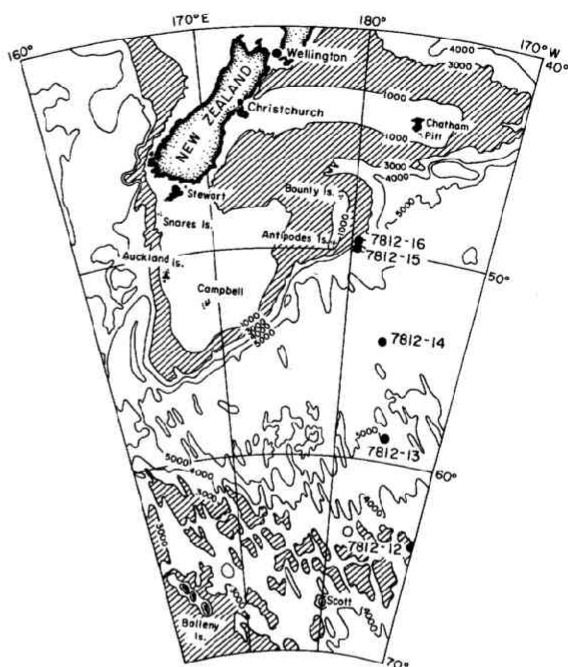

Fig. 1. SW Pacific station locations of three box cores (7812-12, 7812-14 and 7812-15) and two deep hydrocasts (7812-13 and 7812-16) for interstitial and bottom water chemical analyses.

1 and Table 1. The sediments there are oxygenated siliceous clays from the center of the SW Pacific Basin with manganese and iron oxides, carbonate silts from the Campbell Plateau and diatomaceous oozes from the north flank of the Pacific Antarctic Ridge. This ridge underlies the highly productive waters of the Circumpolar current.

The sediments were obtained with a Reineck-type box corer which ensures preservation of

Table 1. Station locations

Station No.	Latitude longitude	Water depth (m)	Remarks
7812-12	63° 19.3'S 169°43.8'W	2875	Diatomaceous ooze
7812-13	58° 27.3'S 174°33.0'W	4980	Bottom water
7812-14	54° 07.8'S 177°24.0'W	5446	Siliceous clay with Mn-nodules
7812-15	49° 38.1'S 179°33.3'W	3989	Calcareous silt with Mn-nodules
7812-16	49° 35.6'S 179°37.2'W	3560	Bottom water

the surface layers, and pore waters were separated by pressure filtration at *in situ* temperatures immediately after core recovery. All analyses were performed on board ship in less than 6 hours after coring. Aliquots for shore-based total dissolved organic carbon and nitrogen determinations were also taken immediately and sealed in glass ampoules. Analytical methods were those described by HARTMANN *et al.* (1976); BALZER (1978); GORDON *et al.* (1975); and SUESS (1976).

Figures 2a-c illustrate depth-concentration profiles of all dissolved constituents from diatomaceous ooze, siliceous clay and carbonate silt facies (Core 7812-12, Core 7812-14, Core 7812-15, respectively). Also included are concentrations of the same constituents in free bottom water samples; Stations 7812-13 and 7812-16.

All three sediment pore water profiles show increasing nitrification with increasing depth and well developed primary nitrite and ammonia maxima associated with the steepest gradient of nitrate increase. The profile from Core 7812-14 shows .further nitrite and ammonia maxima between 22 and 30cm of depth. All maxima are accompanied by high concentrations of other labile constituents; i.e. dissolved organic carbon (DOC), carbohydrates, organic nitrogen (DON) and urea (as μM-N), attesting to their transient and partially oxidized nature. The depths below the interface in which these
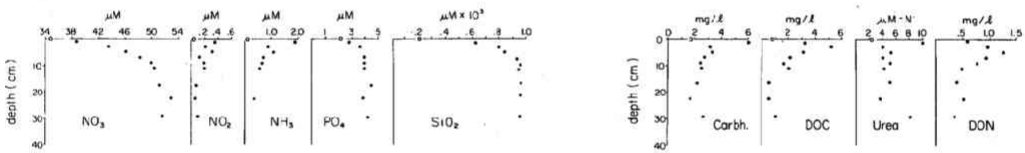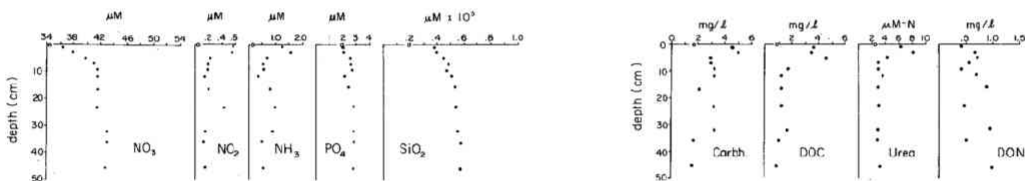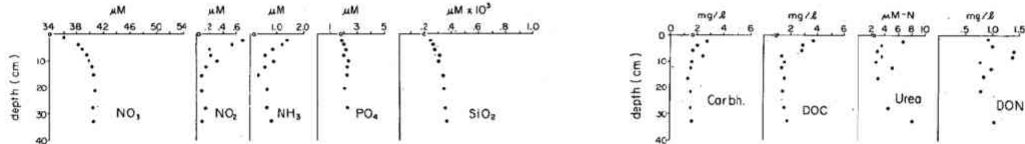

Fig. 2A
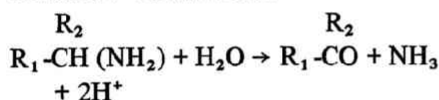
Fig. 2B

Fig. 2C

Fig. 2. Dissolved interstitial nutrients (SiO_2, NO_3, PO_4, NO_2, NH_3) and organic constituents (carbohydrates, dissolved organic carbon, urea and total dissolved organic nitrogen) in pore waters of SW Pacific oxic pelagic sediments and overlying bottom waters. Fig. 2A = diatomaceous ooze facies, Fig. 2B = siliceous clay facies, Fig. 2C = calcareous silt facies.

intermediary constituents are present in high concentrations is 5 cm for the diatomaceous ooze, 4 cm for the pelagic clay, and 10 cm for the carbonate silt and probably reflect the thickness of the biologically active surface layer or sediment permeability to oxygen. Dissolved SiO_2 and PO_4 gradually increase with depth, most likely reflecting simple accumulation. Dissolved SiO_2 appears to be controlled by the amount of opaline silica of the sediment or by a combination of silica input and rates of dissolution, diffusion and sedimentation as proposed by Schink and Guinasso (1980) rather than by the magnitude of the organic decomposition reaction.
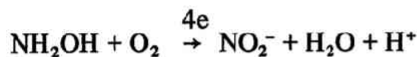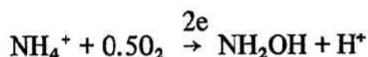
DISCUSSION

In general the following biochemical processes are involved in marine nitrogen metabolism according to Wada and Hattori (1971), Vaccaro (1965), Hooper (1978), Nicholas (1978) and Knowles (1978):

(3) Oxidative deamination

$$R_1\text{-CH}(NH_2) + H_2O \rightarrow R_1\text{-CO} + NH_3 + 2H^+$$

with R_2 groups.

(4) Oxidation of ammonia

$$NH_4^+ + 0.5O_2 \xrightarrow{2e} NH_2OH + H^+$$

$$NH_2OH + O_2 \xrightarrow{4e} NO_2^- + H_2O + H^+$$

(5) Oxidation of nitrite

$$NO_2^- + 0.5O_2 \xrightarrow{2e} NO_3^-$$

Whereby deamination is not accompanied by any significant energy yield; however, the free energy changes from oxidation of ammonia and nitrite are -59.4 kcal and -16.9 kcal, respectively.

In several experimental studies on decomposition of phytoplankton in seawater, von Brand and Rakestraw (1941) have shown that under controlled conditions of oxygen supply and in the absence of simultaneous phytoplankton growth bacterial nitrogen metabolism proceeds in sequential steps of deamination, followed by ammonium oxidation and finally by nitrite oxidation (Fig. 3). The sequence is suppressed when decomposable plankton matter was continuously supplied or had a "history" of earlier decomposition reactions. Hereby nitrate tended to dominate the metabolite concentrations suggesting concurrent reactions with nitrate formation being the fastest one.

In addition, similar experiments by Vaccaro (1965) with monitoring of PO_4 release, suggests that low PO_4 yields, i.e. $NO_3 : PO_4 = 16 : \ll 1$, is typical for decomposing phytoplankton and higher PO_4 yields for zooplankton. In summary then deamination accompanied by ammonium oxidation appears to be the first energy yielding reaction in microbial phytoplankton decomposition followed by nitrite oxidation; and these reactions are accompanied by low and non-stoichiometric PO_4 yields.

In water column nutrient distributions the assimilatory processes in phytoplankton growth within the euphotic zone dominate nitrogen
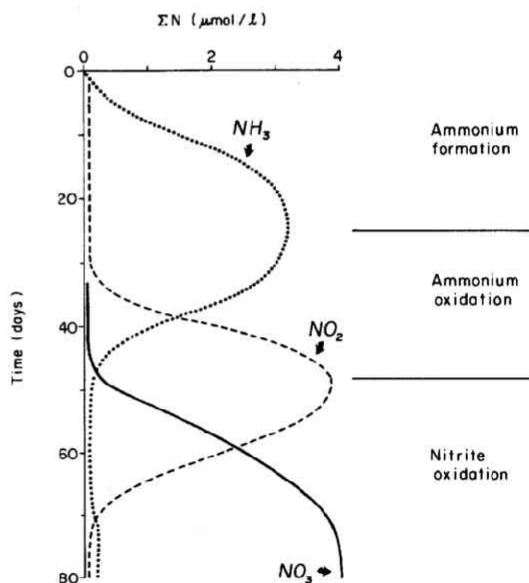

Fig. 3. Nitrogenous nutrient regeneration from phytoplankton in an experimental seawater system (after von Brand and Rakestraw et al., 1941; von Brand et al., 1942). Initially NH_3 is formed by deamination then it is oxidized to NO_2 and finally NO_3 is formed from the oxidation of NO_2.

metabolism. But similarities to pore water nutrient distribution patterns can be expected below the euphotic zone where only bacterial metabolism is active. Accordingly we propose that *oxidation of ammonia and oxidation of nitrite are two reactions in phytoplankton decomposition that may be encountered and compared in water column profiles below the euphotic zone and pore water profiles above the zone of denitrification.*

As a comparison then a depth-concentration profile for dissolved NO_3, NO_2, NH_3, O_2, PO_4 and H_2S from the Saanich Inlet water column is shown in Fig. 4. The data are from COHEN (1978), and are in general agreement with earlier work from the same area primarily by RICHARDS (1975) who pioneered stoichiometric modelling. Similar nutrient distribution patterns have been described from the N. Pacific and E. Atlantic (BRANDHORST, 1959; WADA and HATTORI, 1971; KIEFER *et al.*, 1976; HERBLAND and VOITURIEZ, 1979).

Our discussion of the Saanich Inlet data is *restricted to distribution patterns below* ~ 20 m of water depth where regeneration of nutrients exceeds consumption. Here nitrification is ac-

Fig. 4. Nutrient distribution in Saanich Inlet waters from COHEN (1978). Step (a) ammonia oxidation is characterized by NH_3 and NO_2 maxima; step (b) nitrite oxidation to NO_3 is characterized by the disappearance of NO_2 and NH_3.

companied by production of nitrogenous intermediaries (ammonia and nitrite) in a first step (between 20 and 50 m), whereas they are fully oxidized to NO_3 along with continued nitrification in a second step (between 50 and 75 m). This zone is followed by denitrification between 75-120 m and eventually by sulfate reduction > 130 m of water depth. The nutrient distribution patterns there are not pertinent to this discussion. We suggest that the two-step nitrification process is a general recognizable phenomenon. Nitrification as it proceeds in the water column of Saanich Inlet waters below the zone of production is then analogous to nitrification in the near-surface sediment layer of oxic, pelagic sediments from the SW Pacific or as experimentally induced in decomposing phytoplankton matter. Although vastly different in magnitude and nature of assimilatory and respiratory processes, the three environments are dominated by microbiological activity and we suppose that organic matter respiration may in all cases be reflected first by maxima of partially oxidized nitrogenous intermediaries (ammonium and nitrite) followed by complete oxidation to nitrate (nitrification *sensu strictu*).

Nutrient distributions in the waters from Saanich Inlet and oxygen consumption permit stoichiometric modelling by calculating regenerative ratios for the three decomposition reactions (Table 2).

For regenerative ratios various normalizing parameters were chosen. For the initial step the change in 16μM of all nitrogenous species with depth was used; for the subsequent step ratios were calculated with respect to oxidation equivalents of 138μM O_2 and for denitrification with respect to 138 (μM O_2 + $3/2$ NO_3). This scaling is based on the commonly accepted model reactions and allows direct comparison among the different reaction mechanisms. The results clearly indicate that within the initial step less O_2 is consumed and less nitrate produced than expected from total nitrogen- and PO_4-regeneration assuming conventional Redfield ratios. This, however, is not unreasonable since the nitrogenous intermediate
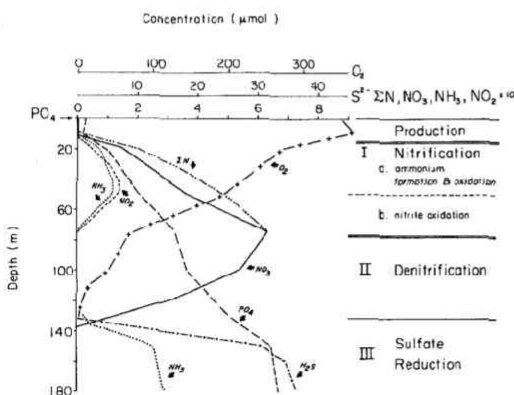
Table 2. Stoichiometry of nutrient regeneration in Saanich Inlet waters;
data from COHEN *(1978)*

Depth (m)	$\frac{\Delta O_2^{1)}}{\Delta x}$	$\frac{\Delta NO_3}{\Delta x}$	$\frac{\Delta \Sigma N}{\Delta x}$	$\frac{\Delta PO_4}{\Delta x}$	ΔO_2 :	ΔNO_3 :	$\Delta \Sigma N$:	ΔPO_4	Reaction[2]
20- 50	−2.57	0.356	0.476	0.0343	−86	12	<u>16</u>	1.15	Ia
50- 75	−5.00	0.545	−	0.0488	−138[3]	15	−	1.35	Ib
75-120	−1.38	−0.353	−	0.0300	−138[4]	−	−	2.10	II

1) *Change in concentration with depth in* $\mu Moles/\ell/m.$
2) *Ia = Nitrification with intermediaries;* NH_3 *and* NO_2.
    Ib = Nitrification sensu strictu; NO_2 *oxidation.*
    II = Denitrification; not observed in SW Pacific pore water profiles.
3) *Oxidation and nutrient equivalents normalized to species underlined.*
4) *Combined oxidation equivalents:* $\Delta O_2 + 3/2 \Delta NO_3.$

compounds are only partially oxidized.

On the other hand in the subsequent step where nitrification proceeds from oxidation of NO_2 without formation of intermediaries, the regeneration ratios are $15 \pm 0.5 \mu M$ of NO_3 and $1.35 \mu M$ of PO_4 for each $138 \mu M$ of oxidation equivalents. These relationships are very close to the ideal ratios and persist also through denitrification except for an increase in PO_4-regeneration with depth. Here $2.16 \mu M$ of PO_4 are regenerated from consumption of the combined oxidation equivalents of free oxygen and nitrate. Other nitrogenous end products of this reaction are presumably N_2O and N_2, whose combined total should be $\sim 16 \mu M$, but which are generally not determined. Not available from these hydrographic data are measurements of changes in CO_2-contents which should provide further support for our interpretations.

This interpretation then yields a consistent picture of organic matter decomposition in the upper water column and in the upper sediment column. We see its consistency in the predictable nitrogenous nutrient generation involving three different reaction mechanisms, i.e. deamination, ammonium oxidation and nitrite oxidation. The formation and persistence of nitrogenous intermediaries appear to be characteristic and measurable features of initial nitrification in this steady state process.

In attempting to apply the above model to the pore water data of the SW Pacific sediments, a convenient normalizing paramerer −

such as PO_4, O_2 or CO_2 − is not readily available. Changes in dissolved phosphate to be used here require a high analytical precision since the total magnitude of nutrient changes is rather small. Also PO_4 is known to readily undergo secondary reactions by sorption (BERNER, 1976) and furthermore the depletion in P-org of the decomposing phytoplankton matter makes use of the Redfield ratios as such a parameter slightly uncertain. On the other hand the largest changes in metabolic quantities affect the ΣCO_2. Here our data − although not very accurate − would allow sufficiently precise changes in ΣCO_2 to be used if it were not for the possibility of substantial losses in alkalinity due to effects of pressure release. MURRAY *et al.* (1980) have recently documented that alkalinity and pH measured *in situ* are systematically higher than values from deep sea samples obtained by box coring. They suggest that this is due to instantaneous precipitation of $CaCO_3$ induced by pressure release.

Nevertheless we have modelled the interstitial nutrient data of Core 7812-14 from the siliceous clay facies (Table 3) analogous to the distribution pattern of Saanich Inlet waters (Table 2). The changes in concentration with depth of nitrogenous species NO_3 and ΣN are normalized to those of PO_4. Again for the initial step − between 0-8 cm of depth − the observed change in NO_3 is smaller than predicted from the Redfield ratios i.e. <16, whereas total nitrogen generation approaches the value of 16,

Table 3. Stoichiometry of nutrient regeneration in pore waters from the siliceous clay facies (Core 7812-14) of the SW Pacific Basin

Depth (cm)	$\dfrac{\Delta NO_3{}^{1)}}{\Delta x}$	$\dfrac{\Delta \Sigma N}{\Delta x}$	$\dfrac{\Delta PO_4}{\Delta x}$	ΔNO_3	:	$\Delta \Sigma N$	:	ΔPO_4	Reaction[2]
0- 2	1.80	3.47	0.20	9		17		1[3]	
2- 4	1.11	1.77	0.10	11		17		1	
4- 6	1.06	1.21	0.08	12		16		1	Ia
6- 8	0.93	1.01	0.06	13		15		1	
8-10	0.78	0.85	0.06	14		15		1	
10-13	0.62	0.65	0.01(?)						
16-19	0.40	0.45	0.03	14		16		1	
22-25	0.29	0.35	0.02	14		16		1	Ib
31-34	0.26	0.29	0.02	14		16		1	
34-37	0.23	0.25	0.02	14		15		1	

1) *Change in concentration with depth in* $\mu Moles/\ell/cm$.
2) *Step (a) ammonium and nitrite formation.*
   Step (b) nitrite oxidation to NO_3.
3) *Nutrient equivalents normalized to* $PO_4 = 1$.

thus emphasizing NH_3 and NO_2 formation. In the subsequent reaction step — between 8-37 cm of depth — NO_2 is largely oxidized to NO_3 at the expected proportions relative to PO_4.

In summary then we propose hypothetical depth-concentration profiles of the chemical species involved in the two-step overall nitrification process (Fig. 5). The zone of nitrification is subdivided into an upper layer which is characterized by ammonia and nitrite formation and a lower layer characterized by nitrite oxidation to NO_3. These layers are also reflected in different oxygen distributions. The deepest layer is devoid of oxygen; it is characterized by denitrification. All nutrient concentration changes are normalized to a constant dissolved PO_4 increase downcore.

It is of great importance that in future pore water studies dissolved oxygen measurements be included, and provisions be made to obtain highly accurate ΣCO_2 and PO_4 profiles within the first 30 cm of the sediment water interface. Because, if once it is shown that nitrification proceeds in two steps as we suggest, then the distribution of the nitrogenous species alone can be used to precisely delineate zones of oxic diagenesis. Of these nitrogenous indicator species NO_3, NO_2, NH_3 and total DON are important and NH_2OH should be included as well. The zones of oxic diagenesis are thin,

being in the range of centimeters only, but surely exert a strong influence on the inorganic and organic chemical composition of the pelagic sediment record, and nutrient regeneration from the sediment-water interface.
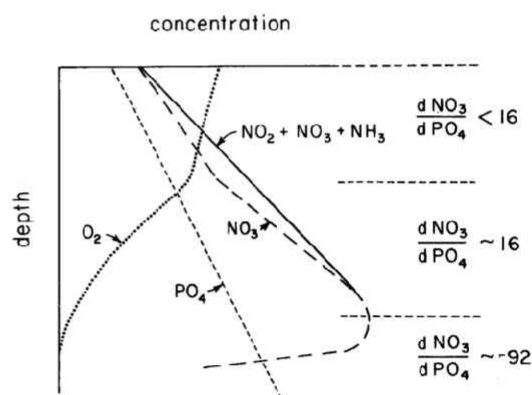

Fig. 5. Hypothetical nutrient distribution profile in oxic pelagic sediments. The zone of nitrification is subdivided into an upper layer which is characterized by formation of nitrite and ammonia and a lower layer characterized by nitrate formation. These layers are also reflected by particular oxygen distributions. Below these is a layer devoid of oxygen in which denitrification takes place. All nutrient concentration changes are normalized to a constant dissolved PO_4 increase downcore.

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