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Heterotrophic denitrification vs. autotrophic anammox – quantifying collateral effects on the oceanic carbon cycle

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Abstract. The conversion of fixed nitrogen to N_2 in suboxic waters is estimated to contribute roughly a third to total oceanic losses of fixed nitrogen and is hence understood to be of major importance to global oceanic production and, therefore, to the role of the ocean as a sink of atmospheric CO_2. At present heterotrophic denitrification and autotrophic anammox are considered the dominant sinks of fixed nitrogen. Recently, it has been suggested that the trophic nature of pelagic N_2-production may have additional, "collateral" effects on the carbon cycle, where heterotrophic denitrification provides a shallow source of CO_2 and autotrophic anammox a shallow sink. Here, we analyse the stoichiometries of nitrogen and associated carbon conversions in marine oxygen minimum zones (OMZ) focusing on heterotrophic denitrification, autotrophic anammox, and dissimilatory nitrate reduction to nitrite and ammonium in order to test this hypothesis quantitatively. For open ocean OMZs the combined effects of these processes turn out to be clearly heterotrophic, even with high shares of the autotrophic anammox reaction in total N_2-production and including various combinations of dissimilatory processes which provide the substrates to anammox. In such systems, the degree of heterotrophy (ΔCO_2:ΔN_2), varying between 1.7 and 6.5, is a function of the efficiency of nitrogen conversion. On the contrary, in systems like the Black Sea, where suboxic N-conversions are supported by diffusive fluxes of NH_4^+ originating from neighbouring waters with sulphate reduction, much lower values of ΔCO_2:ΔN_2 can be found. However, accounting for concomitant diffusive fluxes of CO_2, the ratio approaches higher values similar to those computed for open ocean OMZs. Based on this analysis, we question the significance of collateral effects concerning the trophic nature of suboxic N-conversions on the marine carbon cycle.

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1 Introduction

The importance and relative proportion of processes removing combined nitrogen from the marine environment is currently under discussion. There is evidence supporting the long standing view that heterotrophic denitrification dominates oceanic N loss, but also autotrophic anaerobic ammonium oxidation (anammox) has been reported to make up for large shares, or even the bulk, in certain waters (e.g. Thamdrup et al., 2006; Ward et al., 2009). Both processes convert fixed nitrogen into N_2 (Ward et al., 2007; Devol, 2008) and reduce the oceanic nutrient inventory in this way. Temporal changes of the nitrogen removal flux in the past (on glacial/interglacial timescales), or from present to future, are thought to influence the level of oceanic production and associated CO_2 fluxes (Altabet et al., 1995; Ganeshram et al., 1995; Codispoti, 1995) by tightening or relaxing N-limitation of oceanic primary production and export. There are other aspects in which both processes differ (collateral effects, Voss and Montoya, 2009). One example is the formation of climate reactive gases, namely N_2O (Jin and Gruber, 2003), which is an intermediate of denitrification (Yoshinari and Knowles, 1976) but not known as one of anammox. Here we focus on collateral effects of the trophic status of nitrogen loss processes on the carbon cycle, as recently proposed by Voss and Montoya (2009).

Their argument is the following. Denitrification is a heterotrophic process during which organic matter is consumed and CO_2 is released to ambient waters. Pelagic denitrification thus effects a potential short-circuit in the biological pump by producing CO_2 from organic matter which otherwise might descend deeper into the ocean to be stored there for longer. In contrast, anammox is an autotrophic process potentially increasing the efficiency of the biological pump by fixing additional carbon in intermediate waters and thus reducing net CO_2 production in the water column. It appears to be of importance to the carbon budget whether it

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Table 1. Stoichiometric equations for (1) dissimilatory nitrate reduction to nitrite (DNRN), (2) denitrification, (3) anammox, and (4) dissimilatory nitrate reduction to ammonium (DNRA) for bulk organic matter with an average composition of $C_aH_bO_cN_dP_eS_f$. For simplicity and following Paulmier et al. (2009) we give the stoichiometric equations in non-ionic forms. We assume reaction of NH_3 and CO_2 with water and subsequent dissociation as well as dissociation of HNO_3, HNO_2, H_3PO_4, and H_2SO_4 according to seawater pH. For a more detailed discussion of the derivation of Eqs. (1), (2), and (3) see Paulmier et al. (2009).

	Bulk reaction stoichiometry	
(1)	$C_aH_bO_cN_dP_eS_f + xHNO_3 \rightleftharpoons aCO_2 + dNH_3 + eH_3PO_4 + fH_2SO_4 + yHNO_2 + zH_2O$ with $x = 2a + 0.5b - c - 1.5d + 2.5e + 3f$, $y = x$, $z = 0.5b - 1.5d - 1.5e - f$.	DNRN
(2)	$C_aH_bO_cN_dP_eS_f + x\ HNO_2 \rightleftharpoons aCO_2 + dNH_3 + eH_3PO_4 + fH_2SO_4 + yN_2 + zH_2O$ with $x = 4/3a + 1/3b - 2/3c - d + 5/3e + 2f$, $y = 2/3a + 1/6b - 1/3c - 0.5d + 5/6e + f$, $z = 2/3a + 2/3b - 1/3c - 2d - 2/3e$.	denitrification
(3a)	$xNH_3 + xHNO_2 \rightleftharpoons xN_2 + 2xH_2O$	anammox[a]
(3b)	$yHNO_2 + zCO_2 \rightleftharpoons zCH_2O_{0.5}N_{0.15} + wH_2O$	
(4)	$C_aH_bO_cN_dP_eS_f + xHNO_3 \rightleftharpoons aCO_2 + yNH_3 + eH_3PO_4 + fH_2SO_4 + zH_2O$ with $x = 0.5a + 0.125b - 0.25c - 0.375d + 0.625e + 0.75f$, $y = 0.5a + 0.125b - 0.25c + 0.625d + 0.625e + 0.75f = x + d$, $z = -0.5a + 0.375b + 0.25c - 1.125d - 2.125e - 1.75f$.	DNRA

[a] The energy gain from the anammox reaction (3a) is used to drive the fixation of CO_2 into organic matter (biomass of anammox bacteria). Here we follow the suggestion of Strous et al. (1998) and Kuenen (2008) that nitrite is used in this reaction as the electron donor of CO_2 fixation (Eq. 3b). Since the combined system of equations (3a, 3b) is underdetermined we are unable to provide a generic solution for x, y, z, and w. In our computations we use instead empirical values taken from the experimental work of Strous et al. (1998), i.e. z/x=0.066 mol CO_2:mol NH_4^+ and z/y=0.066/0.26 mol CO_2:mol NO_2^-. In the ΔCO_2:ΔN_2 ratios of Figs. 2a, 4b, and 6, these effects of autotrophic CO_2-fixation are included.

is a heterotrophic process or an autotrophic one which dominates nitrogen loss processes in the ocean's water column. In view of projected increases in the extent of oxygen minimum zones (Matear and Hirst, 2003; Oschlies et al., 2008; Hofmann and Schellnhuber, 2009), heterotrophy or autotrophy in relation to nitrogen losses taking place there would be of increasing importance, potentially providing a positive or negative feedback on the carbon cycle, respectively. In this short note we analyse the stoichiometries of suboxic nitrogen conversions and their effect on the carbon balance.

2 Heterotrophy vs. autotrophy of N_2 production in OMZs

2.1 Background and definitions

Nitrogen in the ocean occurs in seven oxidation states and there are transformations between all, oxidations and reductions. Nitrogen serves both as a constituent of organic matter and nitrogen compounds are used as oxidants and reductants in dissimilatory reactions. Historically, a number of terms, and varieties of definitions of some, have been in use for many of these reactions. We will in the following use only four reactions, all relevant to nitrogen loss in suboxic environments: (1) dissimilatory nitrate reduction to nitrite (DNRN); (2) denitrification, the production of N_2 from nitrite (denitrification sensu strictu; Zumft, 1997), this is a heterotrophic process consuming organic carbon; (3) anammox, the combination of nitrite and ammonia to produce N_2, which is an autotrophic process consuming CO_2; (4) dissimilatory nitrate reduction to ammonia (DNRA). Both DNRN and DNRA are heterotrophic. Formulas describing the bulk stoichiometries of these processes are given in Table 1. We use only these four definitions of suboxic nitrogen transformations to develop our points. There are numerous variations to these (incomplete reactions, shortcuts, combinations, by-reactions) which can be of interest in special environments. We confine the treatment to oxygen minimum zones (OMZ) which are the only pelagic realms in which nitrogen loss occurs (at $[O_2]<5\,mmol\,m^{-3}$; Devol, 2008). In the cores of OMZs, N transformations are based on the N inventory present plus anything which reaches them by sedimentation. It is these that we start with (Sects. 2.1 and 2.2). Later we shall consider the allochthonous supply of additional substrates by diffusion from the fringes of the OMZ, and other special situations encountered in the sea (Sects. 2.3 and 3).

The largest oxygen minimum zones (OMZ) meeting these low oxygen conditions are the intermediate to deep waters of the Arabian Sea and the Eastern Tropical South and North Pacific. Additional sites of suboxic nitrogen removal are enclosed seas like the Black Sea, the Baltic Sea and some fjords. While until recently all suboxic N_2-production in the ocean has been ascribed to denitrification, it is now known that a number of biotic and abiotic nitrogen transformations contribute to nitrogen loss (Hulth et al., 2005). At present denitrification and anammox are considered the most important ones for N_2 production (e.g. Thamdrup et al., 2006; Ward et al., 2009).

Already during early work on denitrification, it had been observed that this process cannot account for all observed nitrogen loss. Ammonia liberated from organic matter during its heterotrophic consumption by denitrification and DNRN should accumulate in an oxygen-free environment, but it does not (Thomas, 1966; Cline and Richards, 1972; Codipoti and Christensen, 1985). Therefore a reaction involving the combination of NO_3^- and NH_4^+ to produce N_2 has been invoked (Richards, 1965; Sen Gupta and Koroloff, 1973; Stumm and Morgan, 1996) and deduced from evolutionary and thermodynamical knowledge (Broda, 1977). Finally, a similar reaction has been observed in nature (Mulder et al., 1995; Thamdrup and Dalsgaard, 2002; Kuypers et al., 2003), the combination of NO_2^- and NH_4^+ to form N_2, which was called anaerobic ammonium oxidation (anammox).

During anammox NH_4^+ and NO_2^- react in an approximately equimolar ratio (Table 1). Since oceanic OMZs are extensive lenses of oxygen free water surrounded by oxygen rich waters above, below and at least towards the open sea, and since NH_4^+ and NO_2^- are usually scarce in these surrounding oxic waters (Zafiriou et al., 1992; Brzezinski, 1988), the major sources of the reactants of anammox must be autochthonous, i.e. NH_4^+ and NO_2^- must be produced in the suboxic water body itself. Anammox therefore depends on nutrient regeneration for the supply of both its substrates (NH_4^+ and NO_2^-) (Ward et al., 2009). In principle, NO_2^- can be supplied by DNRN (Table 1) and NH_4^+ may be liberated from organic matter broken down during DNRN or denitrification. The low production ratios of NH_4^+:NO_2^- of these reactions (compare Fig. 1b), however, allow only for a limited quantitative importance of anammox for N_2 production (see Sect. 2.2 for details). An alternative and additional autochthonous source of NH_4^+ may be dissimilatory nitrate reduction to ammonium (DNRA; Kartal et al., 2007; Lam et al., 2009) which is associated with heterotrophy as well.

In this paper, we will refer to the conversion of fixed nitrogen (i.e. the sum of NO_3^-, NO_2^-, NH_4^+, and organic nitrogen) to nitrogen gas (N_2) in suboxic waters as "suboxic N_2-production", irrespective of the pathways or agents (organisms) involved. Different stoichiometries of suboxic nitrogen conversions have been discussed in the literature, differing by the composition of the organic matter utilized and the fate of remineralised nitrogen (e.g. Richards, 1965; Canfield, 2006; Paulmier et al., 2009). In the following section we will present the bulk stoichiometries of two possible systems, one consisting of combinations of DNRN, denitrification and anammox (i.e. a system where heterotrophic denitrification necessarily dominates N_2 production) and an alternative system where DNRN, DNRA and anammox co-exist (i.e. a system where autotrophic anammox is the exclusive process forming gaseous nitrogen). We will also briefly discuss to what extent and under which specific conditions allochthonous sources of substrates can be relevant and evaluate their maximum effect on the trophic state of the suboxic

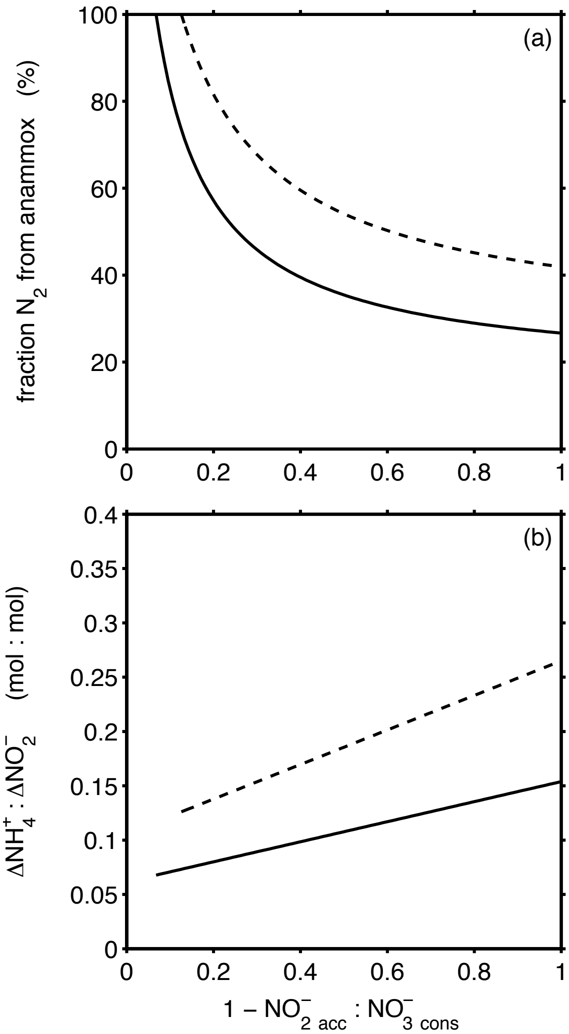

Fig. 1. Scenario I, assuming that suboxic N-conversions are due to a combination of DNRN, denitrification and anammox such that no NH_4^+ but variable fractions of NO_2^- accumulate. On the x-axes we plot the property "$1 - NO_{2\ \mathrm{accumulated}}^- : NO_{3\ -\mathrm{consumed}}^-$". We interpret this property as the efficiency of the overall N-conversion process where the value of one represents the condition of a fully efficient conversion of NO_3^- to N_2 (i.e. all NO_2^- is used up). Solid lines are for a mean composition of respired organic matter of $C_{106}H_{175}O_{42}N_{16}P$ (Anderson, 1995), dashed lines for respiration of pure proteins ($C_{3.83}H_{6.05}O_{1.25}N$, Laws, 1991; Anderson, 1995). **(a)** Fraction (in percent) of total N_2-production which is due to anammox. In the combined reactions of scenario I the remainder to 100 percent is due to denitrification. **(b)** Ratio of production rates of NH_4^+ and NO_2^- (mol:mol) during the coupled reactions of DNRN (providing NH_4^+ and NO_2^-) and denitrification (providing NH_4^+ only) for the given boundary conditions (no NH_4^+ accumulation) and the respective efficiencies of the overall N-conversion process (x-axes). Note that this ratio is always well below one, the stoichiometric ratio of NH_4^+ and NO_2^- in anammox, indicating NH_4^+ limitation of anammox.

layer. Our general subject will be to quantify the net ratio of CO_2 produced to molecular nitrogen formed ($\Delta CO_2:\Delta N_2$) given various combinations of the processes involved in suboxic N-conversions.

2.2 Stoichiometric constraints

First, let us consider the simple case that organic matter of standard oceanic composition ($C_{106}H_{175}O_{42}N_{16}P$; Anderson, 1995) is completely oxidized with nitrate to form CO_2, N_2 and water according to Reaction (R1) (Canfield, 2006).

$$C_{106}H_{175}O_{42}N_{16}P+104NO_3^- \rightleftharpoons 102HCO_3^-+4CO_2+60N_2 +HPO_4^{2-}+36H_2O \quad \text{(R1)}$$

Complete oxidation here refers to the boundary condition that neither NH_4^+ nor NO_2^- accumulate. This yields a ratio of organic carbon oxidized to nitrate consumed of close to 1 (106 C:104 NO_3^-) and a gross ratio of CO_2 produced to molecular nitrogen formed ($\Delta CO_2:\Delta N_2$) of +1.77 (106 C:60 N_2). In suboxic waters no NH_4^+ accumulates (Richards, 1965) and here we assume that the oxidation of NH_4^+ is due to anammox. In this reaction 1 mol of NH_4^+ combines with 1 mol of NO_2^- to form 1 mol of N_2 and water (Eq. 3a in Table 1). Each mol of NH_4^+ consumed supports the autotrophic fixation of about 0.07 mol of CO_2 (Strous et al., 1998; Tijhuis et al., 1993) yielding a molar $\Delta CO_2:\Delta N_2$ ratio of anammox of 0.07. The electron donor required for the reduction of CO_2 is not well known. In aerobic ammonium oxidation, NH_4^+ is the only reductant. In anammox, NO_2^- has been proposed as the electron donor resulting in NO_3^- as a product of CO_2 fixation (van de Graaf et al., 1996; Strous et al., 1998; Eq. 3b in Table 1). During experiments in a sequencing batch reactor of these authors the ratio $NO_{2\,\text{consumed}}^-$: $NH_{4\,\text{consumed}}^+$ differed significantly from the 1:1 ratio, which is usually assumed for marine anaerobic ammonium oxidation (e.g. Kuypers et al., 2003). About 20% of the nitrite was converted to nitrate and the $\Delta NO_2^-:\Delta NH_4^+$ ratio of the combined reaction (3a, 3b) was about 1.3:1. Under marine conditions, with substrate concentrations several orders of magnitude smaller than in the batch reactor experiments, a smaller $\Delta CO_2:\Delta NH_4^+$ is expected because of the energy requirements for maintainance. This results in a lower $\Delta NO_2^-:\Delta NH_4^+$ ratio of the combined reaction (3a+3b). Even when assuming the published $\Delta NO_2^-:\Delta NH_4^+$ ratio from batch reactor experiments to be valid for marine anammox, the effect on the nitrogen budget of the N-conversions is small. Consider the oxidation of a one mole P-equivalent of organic matter according to Reaction (R1) by DNRN+denitrification+anammox which consumes 104 mol of nitrate and implies the oxidation of 16 mol of NH_4^+ with 16 mol NO_2^- due to anammox. The associated CO_2 fixation should consume another 4 mol of nitrite and yield 4 mol nitrate, thus replenishing only about 4% of the nitrate consumed during DNRN+denitrification.

Using generic stoichiometric equations to describe the possible reactions which contribute to suboxic N_2-production (Table 1) we can quantify the proportions in which the individual reactions involved (DNRN, denitrification, anammox) are required for a variety of bulk organic matter compositions (Table 2) and for a range of boundary conditions (fraction of accumulating intermediate NO_2^-). For the mean organic matter composition given above, the condition of complete conversion of fixed nitrogen to N_2, is met if 1 mol P-equivalent of organic matter is remineralised through DNRN, 1.27 mol P equivalents of organic matter through denitrification and if the 2.27·16 mol NH_4^+ produced in these heterotrophic reactions are oxidized with NO_2^- to form N_2 via anammox. In this scenario about 73% of the N_2 produced is by denitrification and 27% by anammox (Table 2). The respective autotrophic CO_2 fixation is 2.54 (0.07·2.27·16) mol and the bulk $\Delta CO_2:\Delta N_2$ ratio for the combined heterotrophic and autotrophic processes changes to +1.75. This is, for all practical purposes, indistinguishable from the gross ratio (+1.77) which does not account for the autotrophic carbon fixation. The net $\Delta CO_2:\Delta N_2$ ratio for the complete conversion of fixed nitrogen to N_2 may vary between 1.58 and 1.90, depending on the composition of organic matter (Table 2).

Significantly higher contributions of anammox to N_2 production of up to 100% have been suggested from tracer experiments (Kuypers et al., 2005; Thamdrup et al., 2006; Hamersley et al., 2007). With a combination of DNRN, denitrification and anammox (scenario I, Figs. 1–3) this can be achieved if nitrite accumulates (Fig. 1a). Nitrite accumulation is a characteristic of the upper margin of oxygen minimum zones (Cline and Richards, 1972; Sen Gupta and Naqvi, 1984; Codispoti and Christensen, 1985). The ratio of nitrite accumulating to nitrate consumed denotes the inefficiency of suboxic N_2-production. We use the term "$1 - NO_{2\,\text{accumulated}}^- : NO_{3\,\text{consumed}}^-$", i.e. the efficiency of suboxic N_2-production, as the independent variable (x-axes) in Figs. 1–5. Contrary to expectations, a higher contribution of anammox to total N_2 production goes along with an increase (and not a decrease or even turn in sign) of the ratio of CO_2 produced to N_2 formed ($\Delta CO_2:\Delta N_2$, Fig. 2a). In the most extreme case (no denitrification, 100% anammox; high NO_2^- accumulation) the ratio is about +6.5, i.e. almost four times as high as for 100 percent efficient N_2-production (Fig. 2a). This effect is due to the increased contribution of organic nitrogen to produced N_2 (Fig. 2b). The higher the contribution from anammox the more inefficient the suboxic N-removal becomes.

Direct and indirect effects of autotrophic CO_2-fixation have a small impact on the integrated $\Delta CO_2:\Delta N_2$ – ratio (Fig. 3). The direct effect (from CO_2-uptake) is largest where the contribution of anmmox is highest. The indirect effect (i.e. the effect of NO_3^--production on the x-value) is largest at moderatly low x-axes values (Fig. 3a). Taken

Table 2. Bulk ratios for complete conversion of fixed nitrogen to N_2 (i.e. no accumulation of NO_2^- or NH_4^+) for different compositions of organic matter. Bulk ΔCO_2:ΔN_2 ratios include the effect of autotrophic CO_2 fixation (data for scenario I, with DNRN, denitrification and anammox, only).

	ΔCO_2:ΔN_2 mol:mol	Den:DNRN[a] mol:mol	N_2-anammox:total N_2-production, %	N_2 from org N %	ΔPO_4^{3-}:ΔN_2 mol:mol	ΔN_2-N:ΔNO_3^- mol:mol
$C_{106}H_{175}O_{42}N_{16}P$ Anderson (1995)	1.75	1.27	26.6	19.2	0.017	1.15
$C_{3.83}H_{6.05}O_{1.25}N$ Laws(1991)	1.58	1.10	41.9	28.8	0	1.27
$C_{106}H_{263}O_{110}N_{16}P$ Redfield et al. (1963)	1.9	1.25	29.0	20.7	0.018	1.17

[a] Ratio of denitrification to DNRN, in mol:mol of organic matter oxidized, respectively.

together, the combined effect is within ±1% of the uncorrected ΔCO_2:ΔN_2 (Fig. 3b).

Alternatively, OMZs may function as systems in which dissimilatory nitrate reduction to ammonium (DNRA) supplements the respiratory pathways of DNRN and denitrification in the production of ammonium to supply substrates to anammox (Lam et al., 2009; Eq. 4 in Table 1). In this case high shares of anammox in total N_2-production may be achieved even with no or little nitrite accumulation, i.e. with highly efficient nitrogen removal. Here (scenario II, Fig. 4) we assume combinations of DNRA (major NH_4^+ source), DNRN (prime source of NO_2^- and minor NH_4^+ source), and anammox as the only process producing N_2. Combining DNRA and DNRN in variable ratios yields a range of efficiencies of N_2-production (x-axes) accompanied by varying NO_2^--accumulation (again using the boundary condition that no NH_4^+ should accumulate).

Both DNRA and DNRN are heterotrophic. Figure 4a shows their relative contribution along the efficiency gradient expressed as the fraction of NH_4^+ provided via DNRA, to the total flux of NH_4^+ to anammox. High contributions of DNRA allow for highly efficient N-conversion while low efficiencies are found where NH_4^+ provision from DNRA falls below 50%. Although in this scenario 100 percent of N_2 production is from the autotrophic anammox reaction for all possible efficiencies, the overall process (i.e. the combined net effects of DNRA, DNRN, and anammox) is clearly heterotrophic (Fig. 4b), with ΔCO_2:ΔN_2 ratios almost indistinguishable from those given in Fig. 2a where DNRN, denitrification, and anammox co-exist.

Differences occur related to the quality of organic matter consumed during the N-conversions. Using protein instead of mean bulk organic matter, the ΔCO_2:ΔN_2 ratio is somewhat lower (Figs. 2a, 4b) and the yield of N_2-N produced per nitrate molecule consumed is larger (Fig. 5b) with maximum values of 2 in the case of very inefficient N-conversion. The major difference, however, is in the molar ΔPO_4^{3-}:ΔN_2 yield (Fig. 5a). For mean bulk organic matter of a composition commonly used in global biogeochemical models (Paulmier et al., 2009), the ΔPO_4^{3-}:ΔN_2 yield increases from about 0.02 mol P:mol N_2 (efficient N-conversion) to about 0.06 (highly inefficient N-conversion). If, however, mainly proteins were preferentially respired in OMZs as indicated by recent particle-flux and decay studies (van Mooy et al., 2002), the ΔPO_4^{3-}:ΔN_2 yield should be much smaller and even approach zero (Fig. 5a).

Assuming that autochthonous substrates to the anammox reaction dominate in typical open ocean OMZs, we find that although anammox itself is autotrophic, the sum of processes providing substrates for anammox and/or denitrification in all possible combinations of DNRN, denitrification, DNRA and anammox is heterotrophic. The degree of this heterotrophy depends on the efficiency of N_2-production. In a combination of DNRN, denitrification, and anammox it is actually positively correlated with the importance of anammox for N_2 production (Fig. 6).

2.3 Allochthonous substrate sources

So far we addressed a typical open-ocean OMZ bounded by oxic waters where substrates to anammox are autochthonous, i.e. produced within the OMZ. This is in particular relevant for NH_4^+, which appears to be limiting to anammox in a system characterized by DNRN, denitrification and anammox. Potential external sources of NH_4^+ are anoxic waters or sediments located below suboxic zones and the primary ammonia maximum at the base of the euphotic zone. In this section we discuss the potential effects of allochthonous substrate sources for ΔCO_2:ΔN_2 ratios.

In sediments or enclosed seas like the Black Sea, suboxic waters may sit on top of fully anoxic systems in which NH_4^+ has accumulated which has been produced from organic matter remineralised by sulphate reduction (Codispoti et al., 1991). Here, diffusive flux provides for additional NH_4^+ available to anammox in adjacent suboxic waters (Murray et al., 2005). Additionally, reactions of HS^-, another product of sulphate reduction, diffusing upwards combining

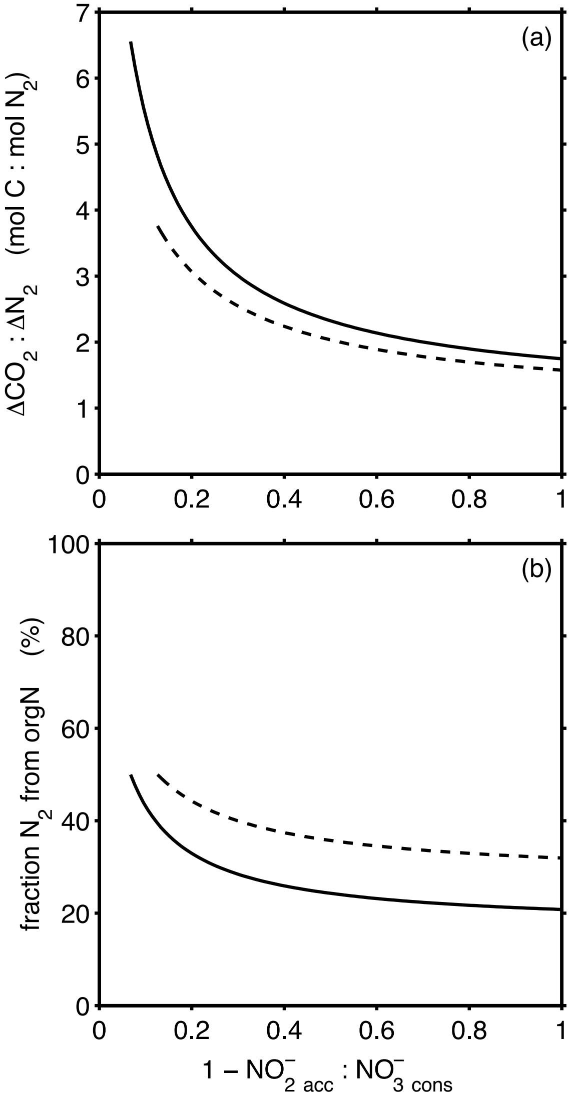

Fig. 2. Same N-conversion scenario as Fig. 1 (DNRN+denitrification+anammox; solid lines for OM composition of $C_{106}H_{175}O_{42}N_{16}P$; dashed lines for proteins). **(a)** The net ratio of CO_2 to N_2 release (ΔCO_2:ΔN_2, mol:mol) as a function of N-conversion efficiency. The ratios include a correction for autotrophic CO_2 fixation during anammox. **(b)** Percent fraction of N_2-production supported by nitrogen from respired organic matter.

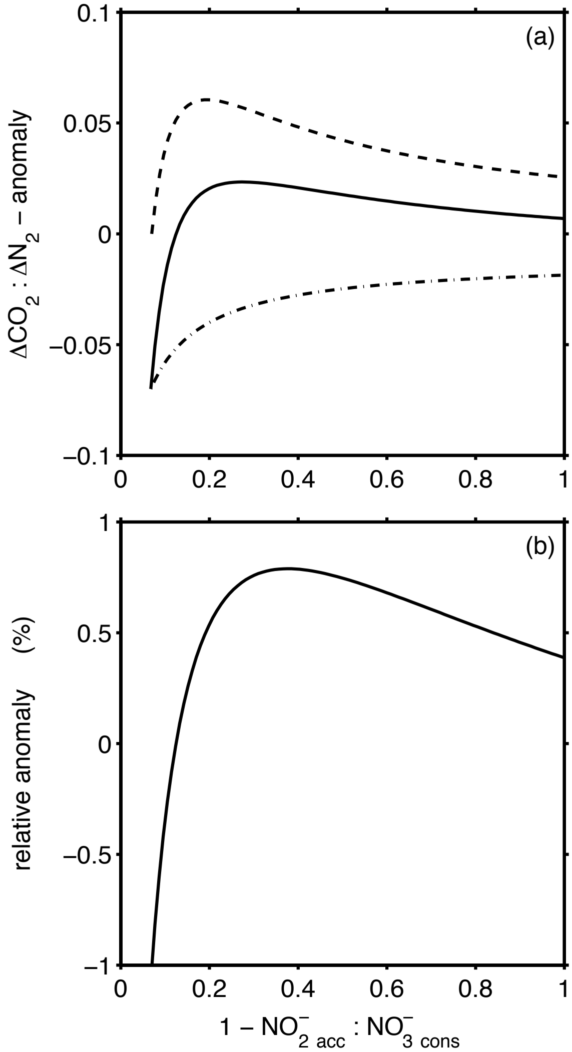

Fig. 3. Effects of autotrophic CO_2 fixation on ΔCO_2:ΔN_2 ratio (for scenario I). **(a)** Absolute anomalies (mol:mol). Dash-dotted line shows the direct effect of CO_2 fixation on ΔCO_2:ΔN_2 as difference between ΔCO_2:ΔN_2 (corrected for CO_2-fixation) and ΔCO_2:ΔN_2 (without this correction). Dashed line shows the indirect effect from NO_3^- production during anammox on ΔCO_2:ΔN_2 as difference between ΔCO_2:ΔN_2 (corrected for NO_3^--production) and ΔCO_2:ΔN_2 (without this correction). This indirect effect acts on values of the x-axes, not the ΔCO_2:ΔN_2 itself. The solid line gives the combination of both effects. **(b)** Plot shows the relative anomaly (%), i.e. the combined anomaly due to CO_2-fixation and NO_3^--production from (a) devided by the fully corrected ΔCO_2:ΔN_2 ratio times 100.

with nitrate diffusing downwards from overlying oxic waters may provide additional nitrite or ammonium (Konovalov et al., 2008) to support anammox and/or denitrification. In a system like the Black Sea such allochtonous sources of substrates may dominate (Fuchsman et al., 2008). Assuming DNRN as the sole NO_2^- source and diffusive NH_4^+ fluxes as the major NH_4^+ supply of anammox in the suboxic layers of the Black Sea, the net ΔCO_2:ΔN_2 ratio may be as low as 0.38 inside the suboxic layer. This is still heterotrophic, but to a much lesser degree than under the conditions discussed above. Heterotrophy may become even smaller when assuming HS^- to diffuse upward to combine with nitrate (Konovalov et al., 2008) producing NO_2^- by an autotrophic process. Under such conditions it is possible that all substrates for the anammox reaction are produced autotrophically. Also HS^- may combine with nitrate producing N_2 (chemolithotrophic denitrification; Hannig et al., 2007; Brettar and Rheinheimer,

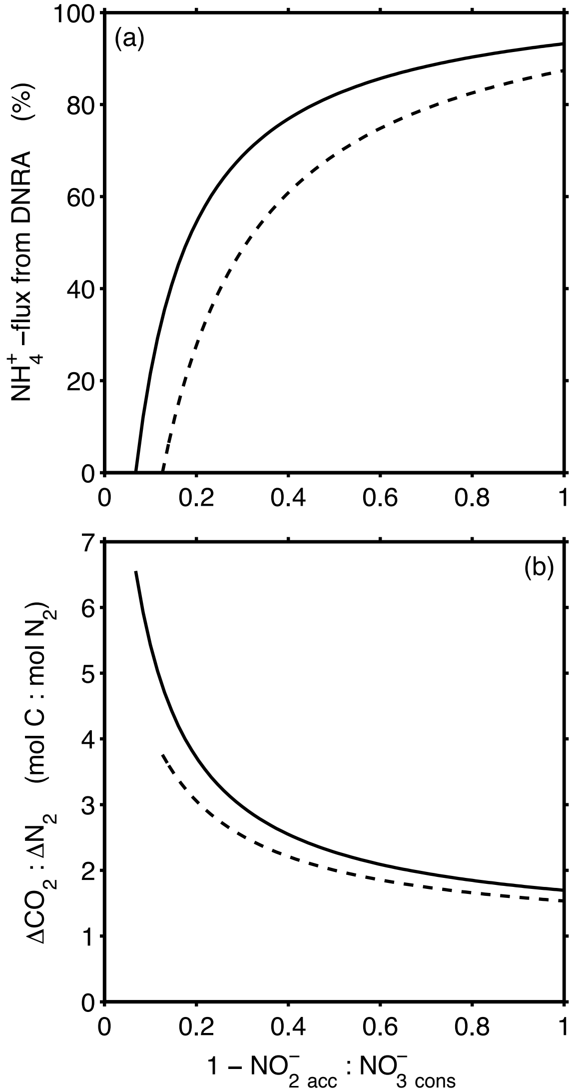

Fig. 4. Scenario II, assuming that suboxic N-conversions are due to a combination of DNRN, DNRA, and anammox. We assume that no NH_4^+, but variable fractions of NO_2^- accumulate (see description of x-axes in legend of Fig. 1). Solid lines are for bulk standard organic matter, dashed lines for proteins. **(a)** Percent fraction of NH_4^+ supply to the anammox reaction from DNRA. **(b)** ΔCO_2:ΔN_2 ratio for scenario II.

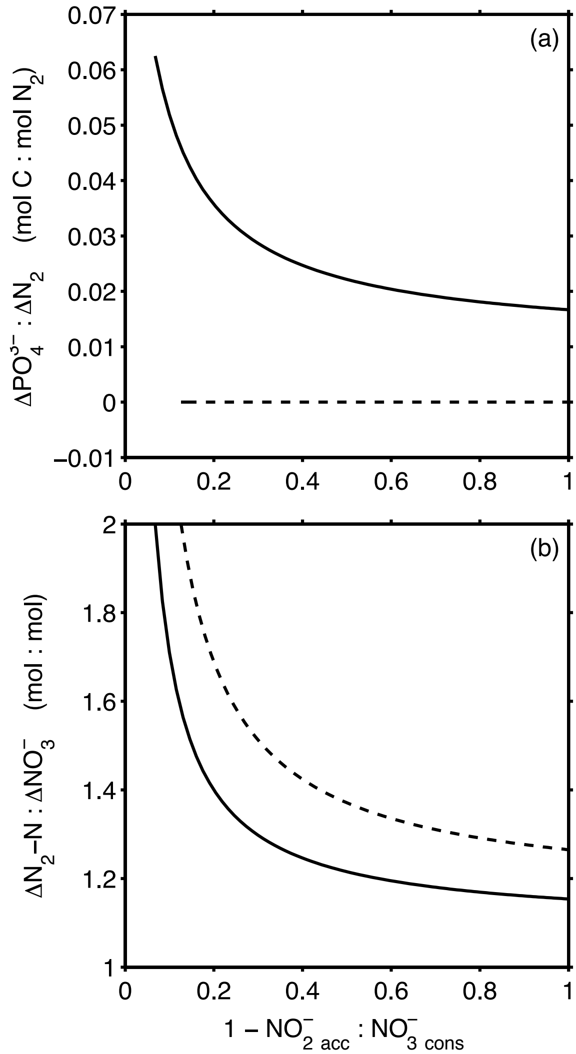

Fig. 5. Scenario I and II. Solid lines are for bulk organic matter composition, dashed lines for proteins. **(a)** The ratio of phosphate released per N_2 formed. **(b)** The molar ratio of N_2−N released to nitrate used during N-conversion.

1991). Hence suboxic N_2 production, supplied with substrates from outside, may locally become fully autotrophic. However, diffusion of reduced substrates is accompanied by diffusive CO_2-fluxes from the remote heterotrophic decomposition of organic matter by sulphate reduction, which drive the overall ΔCO_2:ΔN_2 back into the positive range.

While sulphate reduction can supply NH_4^+ to the suboxic layer from below, there is also the possibility of NH_4^+ entering from above. The primary NH_4^+ maximum at the base of the euphotic zone is a characteristic feature of open-ocean NH_4^+ distribution (Brzezinski, 1988). Where surface production and carbon turnover are high like in upwelling regions, NH_4^+ concentrations as high as 0.5 µmol/L have been observed in this layer (Gibb et al., 1999; Molina et al., 2005; Molina and Farías, 2009). It is under such conditions that also the lower slope of the primary NH_4^+ maximum and the oxycline coincide, and diffusive fluxes of NH_4^+ across the upper fringe of the OMZ may occur. Whether this is a significant NH_4^+ source for suboxic anammox may, however, be debated. On thermodynamic grounds (e.g. Brewer and Peltzer, 2009) it can be argued that, assuming similar energy yields for (oxic) nitrification (to NO_2^-) and (suboxic) anammox, nitrite concentrations larger than its oxygen equivalent (i.e. about 3/2* [O_2]) are needed for anammox to be more effective in oxidising NH_4^+ than nitrification. However, kinetics will matter as well. Nanomolar half saturation

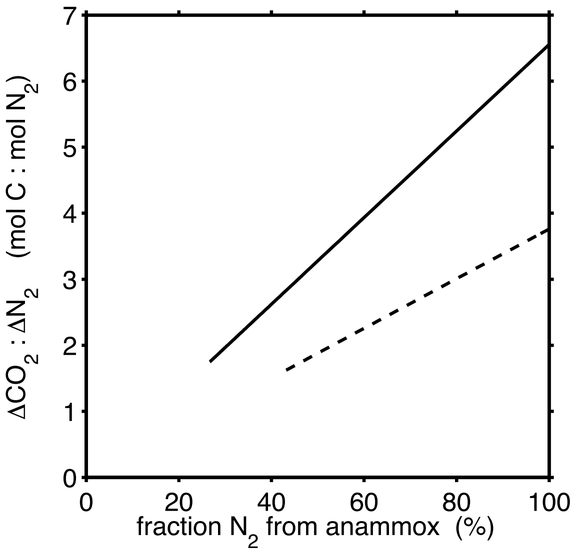

Fig. 6. ΔCO_2:ΔN_2 vs. percent fraction of N_2 produced by the anammox reaction for scenario I (DNRN+denitrification+anammox). Solid line is for bulk organic matter compositions, dashed line for proteins.

constants of aerobic ammonia oxidation and surge-uptake of substrate pulses have recently been observed in nitrifying archaea (Martens-Habbena et al., 2009). Unfortunately, 15N-isotope experiments of anammox studies have usually applied micro-molar tracer additions, often larger than the ambient substrate concentration, and therefore provide potential rather than in situ substrate uptake rates (Hamersley et al., 2007). It is therefore difficult to compare in situ kinetics of aearobic and anaerobic ammonium oxidation. From the thermodynamic argument given above we conclude that it appears more likely that low-oxygen nitrification stops at the NO_2^- level, providing NO_2^- rather than NH_4^+ to anammox (e.g. Schmidt et al., 2002) via diffusion of substrates into suboxic layers. Anyway, the NH_4^+ invading suboxic waters from above is of heterotrophic origin from the oxic remineralisation of organic matter and hence should be accompanied by diffusive fluxes of respiratory CO_2, similar as in an anoxic system underlying suboxic zones discussed above. This should drive the ΔCO_2:ΔN_2 ratio of the upper margin of the OMZ back towards values computed for autochthonous substrate sources of anammox.

3 Discussion

Considering autochthonous sources of NH_4^+ and NO_2^- to anammox and a coupled system with DNRN, denitrification and anammox, we find the somewhat counterintuitive relationship that the higher the contribution of autotrophic anammox to pelagic N_2-production, the more heterotrophic the system is (Fig. 6). Hence the feedback switch proposed by Voss and Montoya (2009) to the effect that expending OMZs (Stramma et al., 2008; Oschlies et al., 2008) will either act as positive or negative feedbacks in the carbon cycle depending on whether anammox or denitrification dominate N_2-production in OMZs does not exist. Including additional autochthonous NH_4^+ sources from DNRA does not change the picture significantly. Even when combining DNRA, DNRN, and anammox in scenarios with anammox always contributing 100 percent to N_2 production, the coupled system is always heterotrophic. What appears to be variable in both systems is the degree of heterotrophy, however, depending on the efficiency of N_2-production.

Allochthonous supply of NH_4^+ (or NH_4^+ and NO_2^-) may contribute to the substrate needs of anammox, as has been observed in the Black Sea (Murray et al., 2005; Fuchsman et al., 2008; Konovalov et al., 2008). In such a situation, ΔCO_2:ΔN_2 ratios in the suboxic layer are much lower than with autochthonous substrate supply, and hence the degree of heterotrophy is lower. However, the NH_4^+ diffusing from anoxic waters underlying a suboxic system is from organic matter remineralised via heterotrophic sulphate reduction, which has a concomitant CO_2 production. Hence NH_4^+ fluxes go along with CO_2 fluxes. NH_4^+ and total dissolved sulfide (S_T=H_2S+HS^-+S^{2-}) as well as S_T and total dissolved inorganic carbon (C_T) co-vary linearly over much of the anoxic water body of the Black Sea (Volkov and Rozanov, 2006). Averaging over anoxic waters from the upper 2000 m Volkov and Rozanov (2006) find S_T-NH_4^+ slopes of 4.29 and C_T-S_T slopes of 2.01, indicating an average C:N ratio of remineralisation of 8.6 which is close to that of bulk standard organic matter. Just below the suboxic layer, however, the HS^- to NH_4^+ slope is less (about 2) which if combined with the average C_T-S_T plot yields a C:N ratio of only 4.2. There is the possibility that this reduction in the apparent C:N remineralisation ratio can be explained as due to nitrogen-rich material (proteins) preferentially remineralised in the upper part of the anoxic layer. This has been suggested for other low oxygen waters by van Mooy et al. (2002). Alternatively, this difference in the apparent C:N ratio can be taken as another indication of the quantitative importance of anammox in close-by suboxic waters, providing a significant sink for NH_4^+ but not for CO_2, as evident from the observed low CO_2:NH_4^+ efficiency of the anammox reaction (Strous et al., 1998; Tijhuis et al., 1993). Though details will depend on the respective NH_4^+ supplies by diffusion or autochthonous sources, respectively, the overall ΔCO_2:ΔN_2 ratio should be larger than in the most extreme case computed above (ΔCO_2:ΔN_2=+0.38) and approach the autochthonous ratio (ΔCO_2:ΔN_2=+1.75).

Summarizing the above discussion, we find no simple relationship between the contribution of anammox to total N_2-production and the degree of heterotrophy. In particular, where autotrophic anammox contributes 100 percent to suboxic N_2-production, we find ΔCO_2:ΔN_2 yields varying between about +2 and +6 for open ocean OMZs.

Biogeochemically the system is clearly heterotrophic although autotrophic reactions are a vital element shaping the observed tracer distribution. Low, even negative, values of the $\Delta CO_2:\Delta N_2$ ratio can be computed where substrates are imported from anoxic domains and if associated diffusive CO_2 fluxes are ignored.

In Figs. 1–5 we use the property "1 – $NO_2^-{}_{\mathrm{accumulated}}:NO_3^-{}_{\mathrm{consumed}}$" as master variable in our discussion of suboxic nitrogen conversions. This property can vary between 0 and 1, reflecting a fully inefficient system where a large fraction of NO_2^- accumulates and a fully efficient system with no NO_2^- accumulation, respectively. In our model computations both numerator ($NO_2^-{}_{\mathrm{accumulated}}$) and denominator ($NO_3^-{}_{\mathrm{consumed}}$) are well constrained. When applying the results to the real ocean the denominator has to be estimated from observed data and a number of assumptions. One approach to quantify $NO_3^-{}_{\mathrm{consumed}}$ is the $NO_3^-{}_{\mathrm{deficit}}$-approach (Cline and Richards, 1972). In this approach the nitrate deficit is computed as the difference between expected and observed nitrate concentration, where the expected nitrate concentration can for example be computed from observed phosphate concentrations and a N:P ratio assumed or derived for the source waters of the OMZ. Including a correction for phosphate release during nitrate based oxidation of organic matter, a general form may be written

$$NO^-_{3\mathrm{def}}=(NO^-_{3\mathrm{exp}}-NO^-_{3\mathrm{obs}})/(1+r_{\mathrm{NO_3:PO_4}}/r_{\mathrm{NO_3:orgP}}), \qquad (1)$$

with $r_{\mathrm{NO_3:orgP}}$ as the ratio of nitrate consumed per P-equivalent of organic matter remineralised and $r_{\mathrm{NO_3:PO_4}}$ as the nitrate to phosphate ratio in the source water. The expected nitrate concentration can for example be computed from

$$NO^-_{3\mathrm{exp}}=PO^{3-}_{4\mathrm{obs}}\cdot r_{\mathrm{NO_3:PO_4}}. \qquad (2)$$

We use the Pacific subset of the GLODAP dataset (Key et al., 2004) to describe examplarily the vertical distribution of the N-conversion efficiency in low oxygen waters (Fig. 7). Values of "1 – $NO_2^-{}_{\mathrm{accumulated}}:NO_3^-{}_{\mathrm{consumed}}$" observed in the Pacific OMZs ($[O_2]<5\,\mathrm{mmol\,m^{-3}}$) range between 0.4 and 1, and 0.1 and 1, depending on the choosen form of Eq. (2) (see legend of Fig. 7 for details). In principle, the full range of N-conversion efficiencies theoretically possible is expressed in these real ocean data and we conclude that the full range of $\Delta CO_2:\Delta N_2$ may be found in the ocean as well.

Would the absence or presence of anoxic zones, or their extent, in the ocean have any collateral effects on the marine carbon balance at all? So far we emphazised that autotrophic anammox in OMZs depends on substrates (NH_4^+) provided by heterotrophic processes either locally, or from neighbouring water layers. Heterotrophic and autotrophic processes are similarly coupled also everywhere else in the aphotic oxic watersphere. Oxic remineralisation of organic matter there releases CO_2, PO_4^{3-} and NH_4^+

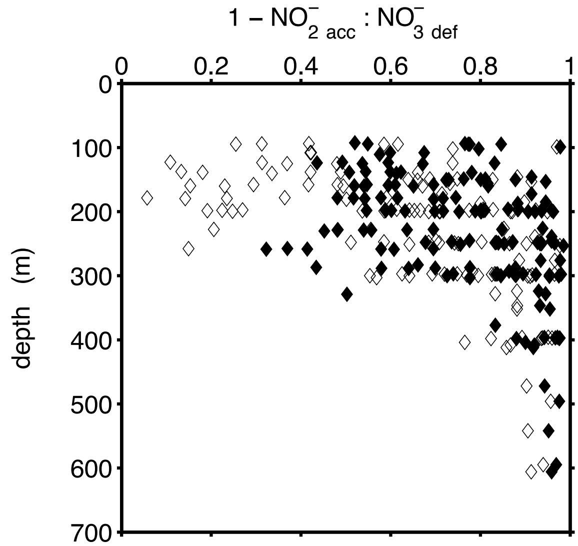

Fig. 7. Vertical distribution of the N-conversion efficiency (1 – $NO_2^-{}_{\mathrm{acc}}:NO_3^-{}_{\mathrm{exp}}$) in data from Pazific low oxygen waters (subset of GLODAP database, Key et al. (2004); $[O_2]<5\,\mathrm{mmol\,m^{-3}}$, $Z>80\,\mathrm{m}$). Results for two estimates of $NO_3^-{}_{\mathrm{exp}}$ are shown. Solid symbols: $NO_3^-{}_{\mathrm{exp}}$ is computed according to Eq. (2) with $r_{\mathrm{NO_3:PO_4}}$=16. Open symbols: $NO_3^-{}_{\mathrm{exp}}$ is computed as in Devol et al. (2006), i.e. $NO_3^-{}_{\mathrm{exp}}=14.89\cdot(PO_4^{3-}{}_{\mathrm{obs}}-0.28)$. The term "$1/(1+r_{\mathrm{NO_3:PO_4}}/r_{\mathrm{NO_3:orgP}})$" of Eq. (1), which in principle is a function of the N-conversion efficiency and the organic matter composition, is approximated with a constant value (0.87=1/(1+16/104)), which is based on the stoichiometry of Reaction (R1).

to ambient waters. NH_4^+ does not accumulate (Brezezinski, 1988) under oxic conditions but is subsequently oxidized autotrophically to nitrite and nitrate by nitrifying bacteria and archaea (Ward, 2008). The carbon fixation efficiency of nitrifyers is low ($\Delta CO_2:\Delta NH_4^+=0.03$ mol:mol, $\Delta CO_2:\Delta NO_2^-=0.01$ mol:mol) and generation times are in the order of 10 to 20 h (Ward, 2008). For mean C:N:P ratios of organic matter of 106:16:1 the gross carbon yield of the heterotrophic oxidation of organic matter is 106:1, the net yield, including the effect of autotrophic nitrification is 105:1 (106–16 · efficiency), i.e. at most 1 percent less. In fact, one may conclude in analogy to the fate of most phototrophic production in the surface ocean that most of the chemoautotrophic CO_2-fixation in the interior of the ocean will be recycled and respired in situ as well, bringing the overall $\Delta CO_2:\Delta P$ ratio back close to 106:1. Biogeochemically, also the oxic aphotic ocean is clearly heterotrophic although autotrophic reactions are a vital element shaping the observed tracer distribution, i.e. the accumulation of NO_3^- instead of NH_4^+. Making up a similar P-normalised budget for suboxic waters, we find that for both DNRN+denitrification+anammox and for DNRN+DNRA+anammox scenarios the net CO_2:P is constant (≈105:1) and basically indistinguishable from that of oxic conditions. Hence there is no significant difference between suboxic and oxic systems of the aphotic zone of the ocean concerning their trophic state.

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