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Stoichiometries of remineralisation and denitrification in global biogeochemical ocean models

A. Paulmier^{1,*}, I. Kriest¹, and A. Oschlies¹

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Correspondence to: A. Paulmier (apaulmier@ifm-geomar.de)

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BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ◀ ▶I

Full Screen / Esc

Close

Back

Printer-friendly Version



¹Leibniz-Institute of Marine Sciences IFM-GEOMAR, Düsternbrooker Weg 20, 24105 Kiel, Germany

now at: Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany

Abstract

Since the seminal paper of Redfield (1934), constant stoichiometric elemental ratios linking biotic carbon and nutrient fluxes are often assumed in marine biogeochemistry, and especially in coupled biogeochemical circulation models to link the global oxygen, carbon and nutrient cycles. However, when looking in more detail, some deviations from the classical Redfield stoichiometry have been reported, in particular with respect to remineralization of organic matter changing with depth or with ambient oxygen levels. We here compare the assumptions about the stoichiometry of organic matter and its remineralization that are used explicitly and implicitly in common biogeochemical ocean models. We find that the implicit assumptions made about the hydrogen content of organic matter can lead to inconsistencies in the modeled remineralization and denitrification stoichiometries. It is suggested that models explicitly state the chemical composition assumed for the organic matter, including its oxygen and hydrogen content.

1 Introduction

The relative success of coupled biogeochemical circulation (BGC) models in simulating the oceanic component of the global carbon cycle relies to a large extent on the assumption of constant stoichiometric ratios linking biotic carbon and nutrient fluxes (Redfield, 1934). On average, the "Redfield picture" seems to work relatively well for net biotically induced fluxes in the upper ocean. Some deviations from the classical Redfield stoichiometry become apparent at greater depths (Anderson and Sarmiento, 1994; Schneider et al., 2003) and in oxygen minimum zones (OMZs: Paulmier et al., 2008), in particular with respect to changes in the carbon to nutrient ratios of organic matter and the oxygen demand associated with its remineralisation. As a result, different biogeochemical models focusing on different time and depth scales sometimes use different factors to convert from nutrients to carbon. By using phosphorus rather than

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I◀ ▶I

Full Screen / Esc

Printer-friendly Version

Close

Back



nitrogen as chemical reference element, most first-generation biogeochemical models could also avoid the explicit consideration of oxygen-sensitive non-Redfield processes like denitrification or anammox. Although there is no agreement concerning the threshold in oxygen that defines the extent of the denitrification and anammox area (Paulmier and Ruiz-Pino, 2008), these processes are limited to very low oxygen concentrations and lead to a loss of fixed nitrogen. There is evidence that the intensity of this nitrogen loss has varied in concert with the extension of suboxic waters in the past (Altabet et al., 1982; Ganeshram et al., 2002), and there is concern that the recent decline of oxygen levels in the tropical oceans (Stramma et al., 2008) may lead to a substantial increase in denitrification during this century (Oschlies et al., 2008).

So far, relatively little emphasis has been put on suboxic areas simulated by biogeochemical circulations models. A cursory look at recently published results of various biogeochemical climate models reveals that all models seem to have considerable difficulties getting the extent and intensity of the main oceanic oxygen minimum zones (OMZs) right. Typically, simulated OMZs have too large extensions, both in the horizontal and in the vertical direction. Subsurface oxygen levels are too low along the equatorial Pacific and in the Bay of Bengal, whereas global models generally fail to reach observed suboxic conditions in the Arabian Sea (e.g. Meissner et al., 2005; Moore and Doney, 2007; Schmittner et al., 2008).

The general tendency of too large extensions of the suboxic or even anoxic regions is expected to lead to overestimates in denitrification rates and the associated loss of fixed nitrogen. Potential explanations for this apparently systematic deficiency across various different models include possible errors in the physical transport terms (too low ventilation, too low mixing), in the euphotic zone processes (too high export production), and in the aphotic processes (too high remineralisation/respiration rates). This note aims at a better understanding of the relevant assumptions used by the different biogeochemical models to simulate oxic and suboxic remineralisation processes. We will discuss what the different biogeochemical models have in common and how they differ and how this could impact on the simulated distributions of oxygen and other

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ◀ ▶I

■ Back Close

Full Screen / Esc

Printer-friendly Version



biogeochemical tracers. To this extent we focus on four global BGC models:

- the HAMOCC 5.1 model (HAMburg Ocean Carbon Cycle; Six and Maier-Reimer, 1996; Maier-Reimer et al., 2005);
- the PISCES model (Pelagic Interaction Scheme for Carbon and Ecosystem Studies; Aumont, 1998; Aumont and Bopp, 2006);
- the BEC model (Biogeochemical Elemental Cycling; Moore et al., 2002; Moore and Doney, 2007);
- the SCHMITTNER model (Schmittner et al., 2008).

HAMOCC is a global ocean biogeochemistry model that simulates biogeochemical tracers in the water column and in the sediment. It has been developed at the Max Planck Institute for Meteorology (Germany). PISCES is an ecosystem and carboncycle model, with fixed O₂/C/N/P ratios, based on 24 prognostic variables which describe the carbon, nitrogen, silicon, and iron cycles. It has been developed at the Laboratoire d'Oceanographie DYnamique et de Climatologie (LODYC, France). The Biogeochemical Elemental Cycling (BEC) model simulates the biogeochemical cycling of C, O, N, P, Fe, Si and alkalinity and four phytoplankton functional groups (diazotrophs, diatoms, pico/nano-plankton, and coccolithophores). It was originally developed at the National Center for Atmospheric Research in Boulder (USA). The SCHMITTNER ecosystem/biogeochemical model is an expanded NPZD (nutrient, phytoplankton, zooplankton, detritus) ecosystem model, with a parameterization of fast nutrient recycling due to microbial activity that emerged from a North Atlantic data assimilation study (Schartau and Oschlies, 2003). It is implemented into the University of Victoria (UVic) Earth System model (Weaver et al., 2001), and has been developed at the College of Oceanic and Atmospheric Sciences (Oregon, USA).

Referring to these models we will in this note examine the specific assumptions about the C/P, N/P, $-O_2$ /P and $-NO_3$ /P ratios used in the respective models, and how

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.



Printer-friendly Version



these differ among the different models. We will also diagnose and discuss the implicit choices these models make about the C/H and H/O ratios of particulate organic matter, as these ratios impact on the oxidant requirements during aerobic and anaerobic remineralization. In this paper we will not consider dissolved organic matter, which can have stoichiometries very different from the standard Redfield picture. Instead we employ the term "organic matter" as synonym for particulate organic matter, which is usually considered to be relatively well represented by the Redfield stoichiometry. As we will see below, large variations in the oxidant requirements during remineralization can occur even for the assumed narrow C:N:P ranges of particulate organic matter, mainly as a result of different implicit assumptions on the hydrogen and oxygen content of the organic matter.

The paper is organized as follows: The following section gives a brief historical overview over stoichiometric relationships used to represent organic matter in the ocean. Section 3 then focuses on the stoichiometric description of aerobic and anaerobic remineralisation processes. The explicit and implicit assumptions made by the different biogeochemical models are discussed in Sect. 4, before Sect. 5 concludes the short note with a discussion of the possible impacts of using different stoichiometric assumptions in different biogeochemical models.

2 Organic matter stoichiometries

2.1 Classical notation

The classical expression for the composition of organic matter (OM), proposed by Richards (1965), assigns specific components to the different chemical elements, e.g. carbohydrates to the C-component, ammonia (NH $_3$) to the N-component, and H $_3$ PO $_4$ to the P-component:

$$_{5}$$
 $(CH_{2}O)_{x}(NH_{3})_{y}H_{3}PO_{4}$ (1)

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.



Full Screen / Esc

Close

Back

Printer-friendly Version



2.1.1 Phosphorus

Phosphorus is contained in cells among others as nucleic acids, phospholipids, phosphoproteins, or inorganic phosphate. Making no assumption about the species of phosphorus assimilated or released (see also Brewer and Goldman, 1976) traditional notations assumed it in the form of H₃PO₄ in water as well as in OM, without any change during remineralisation (e.g. Richards, 1965).

2.1.2 Nitrogen

Likewise, OM nitrogen has been described in amino form (NH₃). When it is released into water during remineralisation, at mean oceanic pH (\approx 8) it dissociates into NH₄⁺ and OH⁻. The ammonia released is then oxidized during the (autotrophic) nitrification to nitrite and nitrate.

2.1.3 Cell compounds in carbon and hydrogen, and the oxygen demand for remineralisation

The classical works by Richards (1965) and Redfield (1963) used CH_2O for the composition of organic matter, i.e., they referred to organic matter that consisted mainly of carbohydrates (monosaccharides) However, in reality carbohydrates (not necessarily monosaccharides) only constitute about 5–41% of the biomass (Anderson, 1995). The remainder consists of proteins (47–63%), lipids (5–31%), and a small amount of nucleic acids (1–7%). Especially lipids, but also proteins can drive the H/O ratio of organic matter towards higher values (e.g. Anderson, 1995; Fraga et al., 1998). The oxidation of this "excess" hydrogen (implying more reduced carbonated and/or nitrogeneous compounds for OM) increases the oxygen demand that is required to oxidize one mole of organic phosphorus. While the "classical" value for oxygen demand is 138 mole oxygen per mole organic phosphorus, calculations based on the different constituents of phytoplankton cells suggested an oxygen demand of 149–150 (Anderson, 1995; Fraga

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ◀ ▶I

■ Back Close

Full Screen / Esc





et al., 1998), and calculations from inorganic dissolved seawater properties resulted in oxygen demands of about 165–178 per mole organic phosphorus (Takahashi et al., 1985; Anderson and Sarmiento, 1994). Boulahdid and Minster (1989) found a variation of the oxygen demand between 108–200 per mole organic phosphorus for different isopycnals. Note that most of these calculations from dissolved inorganic constituents implicitly include nitrification (i.e., they include the complete oxidation of organic nitrogen to nitrate), and that accounting for this process has an effect on the estimated oxygen demand (see below).

2.2 General notation

Denoting the ratio of nitrogen to phosphorus in organic matter as y, and the ratio of carbon to phosphorus in organic matter as x, the above considerations lead to the modified notation of organic matter:

$$C_x (H_2O)_w (NH_3)_v H_z H_3 PO_4$$
 (2)

where w denotes the amount of water in organic matter (more precisely: the H and O atoms that can be combined in a ratio of 2 to form water), while z denotes "excess" hydrogen (e.g., from lipids, polysaccharides or proteins). Using this notation, remineralisation of OM under oxic conditions can then be expressed as

$$C_x (H_2O)_w (NH_3)_y H_z H_3PO_4 + \left(x + \frac{1}{4}z\right) O_2 \longrightarrow x CO_2 + y NH_3 + H_3PO_4 + \left(w + \frac{1}{2}z\right) H_2O$$
 (3)

This equation immediately shows that the amount of oxygen required to remineralise one mole phosphorus depends on the excess hydrogen, i.e., on the proportion of lipids, proteins, polysaccharides, etc. With increasing z, the oxygen demand for remineralisation increases. For the special case of w=x and z=0, we recover Eq. (1).

An alternative notation of the composition of organic matter is not explicitly based on the assumptions about the different molecules in OM, but on the bulk chemical

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.



Abstract

Introduction

Conclusions

References

Tables

Figures

I∢

►I

4



Back

Close

Full Screen / Esc

Printer-friendly Version



composition of OM. Allowing an easy access to estimates of bulk OM composition this notation has been used by Anderson (1995) and Fraga et al. (1998) and also by other approaches, e.g. by Takahashi et al. (1985). In this notation, OM is described by

$$C_a H_b O_c N_d P (4)$$

5 The indices relate to the those of relation 2 via:

$$W = c - 4$$

 $X = a$
 $Y = d$
 $Z = b - 2c - 3d + 5$ (5)

where a, b, c and d are the (measureable) stoichiometric ratios of particulate organic matter (in relation to one mole P), and may vary between $a \approx 80-108$ and $d \approx 16-18$ (Copin-Montegut and Copin-Montegut, 1983; Anderson, 1995), including the classical Redfield values of 106 and 16 for carbon and nitrogen, respectively (see also Table 1).

The latter notation 4 provides immediate insight into the elemental ratios and is often used by modelers, although most models explicitly prescribe only $C_a N_d P$. As we will see below, the models do, however, make implicit assumptions about $H_b O_c$ via the parameterization of the OM remineralization processes.

3 Stoichiometry of remineralisation processes

This section describes the different heterotrophic and autotrophic remineralisation processes that take place in the water column. In our approach, as well as in the models discussed lateron, any bacteria involved in the aerobic and the anaerobic processes are assumed to act simply as catalysts and to not change their biomass nor their composition (dB/dt=0). The stoichiometry is formulated as described above, accounting

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

_

▶I

- ■

•

Back

Close

Full Screen / Esc

Printer-friendly Version



for organic matter that consists of an unspecified mixture of compounds like carbohydrates, lipids, and proteins.

3.1 Aerobic remineralisation

Aerobic remineralisation will take place under oxic conditions. The exact oxygen thresholds for the transition from aerobic to anaerobic remineralisation processes are not well known (e.g. Paulmier and Ruiz-Pino, 2008) and, in biogeochemical models, are generally assumed to be near $4\,\mu\text{M}\,\text{O}_2$. The detailed formulations used by the different models investigated here are illustrated in Fig. 1.

3.1.1 Heterotrophy: remineralisation of OM

Aerobic remineralisation of OM is a heterotrophic process that produces ammonia. The rate of this process is denoted as v_1 :

$$C_a H_b O_c N_d P + \left(a + \frac{1}{4}b - \frac{1}{2}c - \frac{3}{4}d + \frac{5}{4}\right) O_2 \xrightarrow{\nu_1} a CO_2 + d NH_3 + H_3 PO_4 + \left(\frac{1}{2}b - \frac{3}{2}d - \frac{3}{2}\right) H_2 O(6)$$

3.1.2 Autotrophy: nitrification of ammonia to nitrate

This is a two step process: first oxidation of ammonia to nitrite, then oxidation of nitrite to nitrate. These proceed at rates v_2 and v_3 for the oxidation of ammonia to nitrite, and nitrite to nitrate, respectively. Thus, the d moles of ammonia obtained by heterotrophic remineralisation of OM (Eq. 6) are nitrified as follows:

$$d NH_3 + \frac{3}{2} d O_2 \xrightarrow{\nu_2} d HNO_2 + d H_2 O$$
 (7)

$$d \text{ HNO}_2 + \frac{1}{2} d \text{ O}_2 \xrightarrow{\nu_3} d \text{ HNO}_3$$
 (8)

Summing up the two equations yields

$$d \text{ NH}_3 + 2 d \text{ O}_2 \longrightarrow d \text{ HNO}_3 + d \text{ H}_2 \text{O}$$
 (9)

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I∢



4



Back

Close

Full Screen / Esc

Printer-friendly Version



3.1.3 Hetorotrophy+autotrophy: a shortcut for remineralisation of OM

Combining Eqs. (6 to 9) provides a shortcut for the immediate remineralisation of OM to nitrate, called "Complete" aerobic Remineralisation (CR):

$$C_a H_b O_c N_d P + \left(a + \frac{1}{4}b - \frac{1}{2}c + \frac{5}{4}d + \frac{5}{4}\right) O_2 \longrightarrow a CO_2 + d HNO_3 + H_3 PO_4 + \left(\frac{1}{2}b - \frac{1}{2}d - \frac{3}{2}\right) H_2 O (10)$$

This relationship is essentially the same as Eq. (3) of Anderson (1995).

The following two paragraphs show two examples for the classical Redfield stoichiometry, as well as for a stoichiometry that accounts for more realistic OM composition:

Redfield stoichiometry: Consider a=106, d=16. Assuming that the OM consists mainly of monosaccharides, NH₃ and H₃PO₄, b=2a+3d+3=263 and c=a+4=110. Then the equation for OM remineralisation and instantaneous, complete nitrification is:

$$C_{106}\,H_{263}\,O_{110}\,N_{16}\,P + \left(\frac{4\times106+263-2\times110+5\times16+5}{4}\right)\,O_2 \longrightarrow 106\,CO_2 + 16\,HNO_3 + H_3PO_4 + \left(\frac{263-16-3}{2}\right)\,H_2O\,\,\textbf{(11)}$$

i.e., 138 moles of oxygen are required to remineralise one mole of organic phosphorus to carbon dioxide, nitrate and 122 moles of water. Note, that the C/N/P stoichiometries of the two examples are identical as are the remineralization products that contain C, N, and P. For biogeochemical models that focus on these chemical elements, results would therefore be undistinguishable. The examples differ, however, in the O and H content of organic matter and, as a results, in the oxygen demand during remineralization.

"Empirical" stoichiometry: Consider a=106, b=175, c=42 and d=16. This refers to the composition given by Anderson (1995), calculated from observed constituents of organic matter. Then the equation for OM remineralisation and instantaneous, complete nitrification is:

$$C_{106} H_{175} O_{42} N_{16} P + \left(\frac{4 \times 106 + 175 - 2 \times 42 + 5 \times 16 + 5}{4}\right) O_2 \longrightarrow 106 CO_2 + 16 HNO_3 + H_3 PO_4 + \left(\frac{175 - 16 - 3}{2}\right) H_2 O \quad (12)$$
2548

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I∢

١

4



Back

Close

Full Screen / Esc

Printer-friendly Version



i.e., 150 moles of oxygen are required to remineralise one mole of organic phosphorus to carbon dioxide, nitrate and 78 moles of water.

3.2 Anaerobic conditions

These processes will take place under suboxic conditions, i.e. for ambient oxygen concentrations smaller than about $4 \mu M O_2$.

3.2.1 Heterotrophy: remineralisation of OM by denitrification

Anaerobic remineralisation (denitrification) of OM is a heterotrophic process that may involve several oxidation states of nitrogen. Here only nitrate, nitrite, and molecular nitrogen are considered. The oxidation of organic matter further produces ammonia (contained in OM). First, there is reduction of nitrate to nitrite rate proceeding at rate V_4 .

$$C_{a} H_{b} O_{c} N_{d} P + \left(2 a + \frac{1}{2} b - c - \frac{3}{2} d + \frac{5}{2}\right) HNO_{3} \xrightarrow{\nu_{4}} a CO_{2} + d NH_{3} + H_{3} PO_{4} + \left(\frac{1}{2} b - \frac{3}{2} d - \frac{3}{2}\right) H_{2}O + \left(2 a + \frac{1}{2} b - c - \frac{3}{2} d + \frac{5}{2}\right) HNO_{2}$$
(13)

Then, nitrite is reduced to molecular nitrogen with the rate constant v_5 .

$$C_{a} H_{b} O_{c} N_{d} P + \left(\frac{4}{3} a + \frac{1}{3} b - \frac{2}{3} c - d + \frac{5}{3}\right) HNO_{2} \xrightarrow{\nu_{5}} a CO_{2} + d NH_{3} + H_{3} PO_{4}$$

$$+ \left(\frac{2}{3} a + \frac{2}{3} b - \frac{1}{3} c - 2 d - \frac{2}{3}\right) H_{2} O + \left(\frac{2}{3} a + \frac{1}{6} b - \frac{1}{3} c - \frac{1}{2} d + \frac{5}{6}\right) N_{2}$$
 (14)

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I∢

►I

4

•

Back

Close

Full Screen / Esc

Printer-friendly Version



Note that while Eq. (13) yields (2a+1/2b-c-3/2d+5/2) moles nitrite per mole organic phosphorus remineralised, Eq. (14) requires (4/3a+1/3b-2/3c-d+5/3) moles nitrite to remineralise one mole organic phosphorus.

Summing up the two equations – more precisely: 2/5 times Eq. (13) plus 3/5 times Eq. (14) – yields the "net" equation for denitrification:

$$C_{a} H_{b} O_{c} N_{d} P + \left(\frac{4}{5} a + \frac{1}{5} b - \frac{2}{5} c - \frac{3}{5} d + 1\right) HNO_{3} \longrightarrow a CO_{2} + d NH_{3} + H_{3} PO_{4}$$

$$+ \left(\frac{2}{5} a + \frac{3}{5} b - \frac{1}{5} c - \frac{9}{5} d - 1\right) H_{2}O + \left(\frac{2}{5} a + \frac{1}{10} b - \frac{1}{5} c - \frac{3}{10} d + \frac{1}{2}\right) N_{2} (15)$$

Richards (1965) and others have further assumed an immediate, complete oxidation of the ammonia released from organic matter during denitrification:

$$_{10}$$
 $d NH_3 + \frac{3}{5} d HNO_3 \longrightarrow \frac{4}{5} d N_2 + \frac{9}{5} d H_2 O$ (16)

Adding this process to Eq. (15) yields the equation for Complete Denitrification (CD):

$$C_{a} H_{b} O_{c} N_{d} P + \left(\frac{4}{5} a + \frac{1}{5} b - \frac{2}{5} c + 1\right) HNO_{3} \longrightarrow a CO_{2} + H_{3} PO_{4}$$

$$+ \left(\frac{2}{5} a + \frac{3}{5} b - \frac{1}{5} c - 1\right) H_{2}O + \left(\frac{2}{5} a + \frac{1}{10} b - \frac{1}{5} c + \frac{1}{2} d + \frac{1}{2}\right) N_{2}$$

$$(17)$$

3.2.2 Autotrophy: anammox

Ammonia and nitrite can be combined in an autotrophic process called "anaerobic ammonium oxidation" (anammox) (V_6) with rate v_6 to molecular nitrogen:

$$d \text{ NH}_3 + d \text{ HNO}_2 \xrightarrow{\nu_6} d \text{ N}_2 + 2 d \text{ H}_2\text{O}$$

$$2550$$

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I∢ ►I

→

Back Close

Full Screen / Esc

Printer-friendly Version



The ammonia required may have been produced either by anaerobic oxydation of OM during denitrification or DNRA (Dissimilatory Nitrate Reduction to Ammonium), or by aerobic remineralisation and subsequent transport into the low-oxygen "anammox region". In both cases, the ammonia will come from the decomposition of organic matter. Thus, as for nitrification, organic matter (particulate or dissolved) is required to feed this process. The nitrite required in the anammox reaction will either come from the first (aerobic) nitrification step (with subsequent transport to the "anammox" environment), or it may be produced as an intermediate product of denitrification (i.e., a heretotrophic process).

However, as none of the models which will be discussed below explicitly considers anammox, for now we will skip further consideration of the stoichiometric relation of anammox with the two different steps of denitrification.

3.3 Implications

3.3.1 A stoichiometric oxygen switch

Equations (6–17) present the process equations for aerobic and anaerobic remineralization processes and their stoichiometries in terms of the composition of organic matter, as specified by the subscripts a, b, c, and d. The stoichiometric relationships between the different processes can be easily expressed by the amount of oxygen that is required to remineralise one mole organic phosphorus during aerobic remineralisation. According to Eq. (6) this amount is given by $R_0 = a + 1/4 b - 1/2 c - 3/4 d + 5/4$. This is used to express the stoichiometric ratios of the different processes in Table 1.

Making use of term R_0 , we now can easily evaluate stoichiometric relationships especially between the different processes and their requirements in the oxix and suboxic zones:

First, assume that all organic matter is remineralized to CO₂, H₃PO₄, water and NH₃ under suboxic and oxic conditions (cf. Eqs. 15 and 6). In this case the relation between

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Int

Conclusions Re

Tables F

Back

Close

Introduction

References

Figures

Full Screen / Esc

Printer-friendly Version



nitrate demand (suboxic) to oxygen demand (oxic) is expressed by

$$R_{\text{HNO}_3:O_2}^* = \frac{4/5R_0}{R_0} = \frac{4}{5} \tag{19}$$

i.e. 0.8 mole nitrate replace one mole oxygen. This is equivalent to the classical assumption that 1 mole of NO₃ can accept 5e⁻ while 1 mole of O₂ can accept only 4e⁻.

As an example, Richards (1965) evaluates 106 mole oxygen demand for the aerobic remineralisation to NH₃, and 84.4=0.8×106 mole nitrate demand for denitrification (of organic matter to NH₃).

However, the notations e.g. by Richards (1965) and Anderson (1995), as well as many models proceed by immediate nitrification of the released ammonia to nitrate under oxic conditions (Eq. 9), or by immediate oxidation of ammonia to N_2 under suboxic conditions (Eq. 16). In this case, the right hand sides of the oxic and suboxic processes differ (both in terms of products as well as in oxidation states of nitrogen). As a consequence the relationships between nitrate vs. oxygen requirement deviate from the classical 4/5 ratio. For example, the relationship between "Complete" Denitrification (CD i.e., denitrification with immediate oxidation of the ammonia released from organic matter to N_2 which, according to Eq. (17), needs $4/5\,R_0+3/5\,d$ moles of nitrate) and aerobic remineralisation with subsequent nitrification (CR which, according to Eq. 10 consumes $R_0+2\,d$ moles of oxygen) gives:

$$R_{\text{HNO}_3:O_2} = \frac{4/5R_0 + 3/5d}{R_0 + 2d} \tag{20}$$

For example, Richards (1965) evaluates 138 mole oxygen demand for complete remineralisation (to nitrate) under oxic conditions, and $94.4=(0.8\times106+0.6\times16)$ mole nitrate demand under suboxic conditions, the ratio thus being ≈0.7 . Note, that if one wanted to have 1 mol HNO₃ on the right hand side of the CD Eq. (17), this would require $4/5R_0+3/5d+d=4/5(R_0+2d)$ moles HNO₃, and the classical ratio of 4/5 would be recovered.

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

l∢ ≻l

Back Close

Full Screen / Esc

Printer-friendly Version



Via R_0 the ratio given by Eq. (20) depends on the amount of "excess" hydrogen (R_0 =a+z/4: see Eq. 5) and increases with increasing excess hydrogen. Thus, the more hydrogen-rich substances (lipids, polysaccharides, proteins) the organic matter contains, the higher the nitrate demand of denitrification becomes in comparison to oxic remineralisation. In the theoretical limit of $R_0 \rightarrow \infty$ we obtain $R_{\text{HNO}_2; O_2} \rightarrow 4/5$.

3.3.2 How much fixed N is removed during denitrification?

The above considerations provide some insight into the dependence of fixed N (as organic matter, ammonia, nitrate or nitrite) removal on the supply of organic matter to the deep ocean: taking the "Complete" Denitrification (CD as of Eq. 17, i.e., assuming the "Richards" approach to anaerobic ammonia oxidation), and relating it to the amount of organic nitrogen denitrified, yields the ratio

$$R_{\text{N:N}_{\text{org}}} = 2 \frac{2/5R_0 + 4/5d}{d} \tag{21}$$

That is, per mole organic N (N_{org}) denitrified, ≈ 7 atoms fixed N are lost from the system. On long time scales, for the global oceanic nitrogen inventory to be in equilibrium the fixed nitrogen lost via denitrification would have to be supplied again to the system either via nitrogen fixation or atmospheric deposition. Interestingly, such a supply does not automatically lead to an increase in fixed nitrogen: if the newly fixed N is transformed into organic matter above suboxic areas and, upon sinking into the suboxic environment, is denitrified, an addition of new nitrogen at the ocean surface could generate an even greater loss of fixed nitrogen in the suboxic areas below.

3.3.3 How much N_2 is produced during denitrification?

In the above comparison of "Complete" aerobic Remineralisation (AR: remineralisation plus nitrification) and "Complete" Denitrification (CD: denitrification with oxidation

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ◀ ▶I

■ Back Close

Full Screen / Esc

Printer-friendly Version



of the ammonia), we assumed that during both aerobic and anaerobic remineralisation ammonia is immediately oxidized to nitrate and dinitrogen, respectively. In this case, models considering only dissolved inorganic nitrogen would induce the same biogeochemical effect associated with the remineralisation mechanisms as models that explicitly distinguish between nitrate and ammonia. Nevertheless, the coupling and decoupling between different processes or intermediate steps, mainly depends on the speed of the different process rates v_i . Resolving these rate dependencies requires the separate consideration of at least two pools of inorganic nitrogen (ammonia and nitrate).

In the "Complete" Denitrification, the moles of N produced in form of N_2 (i.e., 2 moles of N_2) versus moles of HNO₃ consumption can be calculated from:

$$R_{\text{N}_2:\text{HNO}_3} = 1 + \frac{d}{4/5R_0 + 3/5d} \tag{22}$$

(see also Table 1). Considering the stoichiometry range for the organic matter composition (see Table 1), the N_2 production (in moles of N) versus HNO $_3$ consumption ranges between +113% (a=108; b=263; c=42; d=16) and +133% (a=80; b=171; c=110; d=18). However, it has recently been reported that the excess N_2 measured in the Arabian Sea (Devol et al., 2006) may exceed the nitrate deficit by more than a factor 2. If this excess N_2 estimated from observations is confirmed, one explanation is that denitrification does not follow the stoichiometries reported in Table 1. In support of this notion, results by Van Mooy et al. (2002) suggest that denitrifying bacteria in the OMZ core of the Eastern Tropical North Pacific preferentially attack amino acids with C/N ratio of 4 (by atoms) versus the ratio of 6.6 "Redfieldian" organic matter.

4 Parameterisation of stoichiometry in global models

Using the above considerations about the relation between organic matter stoichiometry and the stoichiometries of the different aerobic and anaerobic processes, we now

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Full Screen / Esc

Close

Back

Printer-friendly Version

Interactive Discussion



2554

aim to examine the parameterisation in four different global biogeochemical models: HAMOCC (in the setup presented in Wetzel, 2004; Maier-Reimer et al., 2005), PISCES (after Aumont, 1998; Aumont and Bopp, 2006), BEC (as described in Moore et al., 2002; Moore and Doney, 2007) and SCHMITTNER (as in Schmittner et al., 2008).

We would like to note that our investigation refers to specific setups of the different models; the exact parameterisation (e.g. C/P ratio, oxygen demand of remineralisation) may differ in later experiments and be subject to change in the future. Therefore, the model structures as described here should not be regarded as static, but mainly as examples for numerical simulation of oceanic biogeochemistry. Thus, our findings should be considered as an attempt to point towards possible sources of inconsistencies the implicit assumptions of ocean biogeochemical models, and as an encouragment to use full stoichiometric descriptions of organic matter in model formulation and description.

4.1 Process parameterisations

In all models aerobic remineralisation is a function of both particulate and dissolved organic matter, except for the SCHMITTNER model, where only particulate organic matter remineralisation is considered. In addition, remineralisation is a function of depth (PISCES) or a function of temperature (BEC, SCHMITTNER). All four models explicitely simulate denitrification, although its parameterisation differs from that of the aerobic remineralization in their substrate requirements (e.g., in HAMOCC's suboxic zones only particulate matter is subject to anaerobic degradation). For denitrification, the maximum rates are always lower than for aerobic remineralisation, between a factor of ≈ 1 (PISCES) and 5 (SCHMITTNER model). The oxygen threshold, below which denitrification and nitrate consumption start, is typically set to values between 4 μ M (e.g. BEC) and 5 μ M (e.g. SCHMITTNER). The different formulations of the remineralisation and denitrification rates as a function of ambient oxygen levels are illustrated in Fig. 1.

Among the models considered, N_2 production is modeled explicitly only in HAMOCC model. N_2 O production is also considered in HAMOCC as well as in unpublished ver-

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Full Screen / Esc

Close

Back

Interactive Discussion

Printer-friendly Version



sions of PISCES and the SCHMITTNER model. None of the models considered here includes anammox. With the exception of HAMOCC, they do not include sedimentary denitrification, which would provide a large and possibly less climate-sensitive sink for fixed nitrogen. Nitrification is taken into account explicitly in PISCES and BEC, and implicitly in HAMOCC and SCHMITTNER, as these two latter models consider only dissolved inorganic nitrogen (usually interpreted as nitrate) but not ammonium.

Nitrogen fixation, being the counterpart (on long enough time scales) to the removal of fixed N via denitrification, is considered in all models with different levels of complexity, from a simple relaxation towards fixed stoichiometric ratios of nitrate and phosphate, to explicit consideration of diazotroph physiology.

4.2 Parameterization of OM stoichiometry and remineralization

The four BGC models considered in this study all use the same N/P ratio of 16, but differ with respect to the C/P ratio (see Table 2). Whereas C/P are similar (\approx 120) in the HAMOCC, PISCES and BEC models, the OM contains less carbon (C/P=112) in the SCHMITTNER model. This indicates that the SCHMITTNER model considers an OM with less carbohydrates and therefore relatively more nitrogeneous reduced matter (e.g. proteins), as considered by Redfield (1963) and Anderson (1995).

Whereas the $-O_2/P$ ratio for aerobic remineralisation is similar (≈ 170) for HAMOCC, PISCES and BEC, the SCHMITTNER model assumes that about 20% more O_2 is consumed during aerobic remineralisation of organic matter. Further, the nitrate requirement for denitrification varies widely among the models, from 98 (PISCES) to 163.3 (SCHMITTNER).

Comparing aerobic remineralisation and denitrification, model descriptions often state the ratio of nitrate consumption during denitrification to oxygen consumption during aerobic demineralization. In the case of the SCHMITTNER mode, this is given as 0.8, for HAMOCC it is 0.6, whereas PISCES and BEC use a ratio of 0.7 similar to that of Redfield (1963) and Anderson (1995). Closer inspection of the model code shows, however, that the equation for denitrification in the SCHMITTNER model adds HNO₃ to

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

→

Back Close

Full Screen / Esc

Printer-friendly Version



both sides of our Eq. (17). As a result, the ratio of 0.8 is not identical to the one given by our relation 20 which we will diagnose for the SCHMITTNER model below as 0.72.

- 4.3 Implicit assumptions about OM stoichiometry imposed by aerobic remineralisation
- In numerical biogeochemical models, the C/P (our *a*) and N/P (our *d*) ratios of organic matter are generally prescribed as explicit input parameters. In contrast, the H excess (determining H/P and O/P ratios modulo H₂O) is often determined implicitely through the choice of the -O₂/P ratio for the aerobic remineralisation (and, as we will see below, the choice of -HNO₃/P for denitrification).

To evaluate the implicit assumptions about organic matter composition from the assigned stoichiometric ratios of aerobic remineralisation (usually a, d and oxygen demand), we here refer to the "excess" hydrogen, (i.e., the hydrogen atoms that cannot be combined in a ratio of 2 with oxygen; z of Eq. 2).

Equation (3) shows that the oxygen demand for aerobic remineralisation depends on the carbon content (x=a, see Eq. 5) and on z via $R_0=a+0.25\,z$. The models parameterise "complete remineralisation", i.e. remineralisation plus nitrification (R_0^{CR}), the endproduct being nitrate. Using

$$R_0^{CR} = R_0 + 2d = a + 2d + 0.25z (23)$$

(see Table 1), we can express the excess hydrogen that provides the substrate for oxic remineralisation in terms of the models' prescribed oxygen demand for complete remineralisation, R_0^{CR} , their C/P (a) and N/P (d) ratio:

$$z^{CR} = 4R_0^{CR} - 4a - 8d (24)$$

The value of z^{CR} thus indicates the implicitly assumed organic matter composition in the models that can be diagnosed from the N/P and C/P ratios of organic matter in combination with the oxygen demand of aerobic remineralization. Table 2 reveals that

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I∢



■



Back

Close

Full Screen / Esc

Printer-friendly Version



for the models considered here, z^{CR} varies between 72 and 256 and is always much higher than the value that we evaluate analogously from the organic matter composition compiled by Anderson (1995).

4.4 Implicit assumptions on OM stoichiometry imposed by denitrification

The nitrate demand of complete denitrification, $R_0^{CD} = 0.8 R_0 + 0.6 d$ (Table 1) can be expressed in terms of the oxygen demand of complete remineralisation (R_0^{CR} , see Eq. 23 above):

$$R_0^{CD} = 0.8 R_0^{CR} - d = 0.8(a + 2d + 0.25z) - d$$
 (25)

The models usually prescribe the nitrate demand for denitrification, R_0^{CD} . Like for aerobic processes, from this value, the C/P ratio a and the N/P ratio d we can derive the excess hydrogen of organic matter that served as substrate for complete denitrification as a function of R_0^{CD} :

$$z^{CD} = 5R_0^{CD} - 4a - 3d (26)$$

Note, that in the case of the SCHMITTNER model, R_0^{CD} is not prescribed. Instead, only $R_0^{CD} + d = 0.8 R_0^{CR}$ is given, which yields

$$R_0^{CD} + d = 0.8 R_0^{CR} = 0.8(a + 2d + 0.25z)$$
 (27)

and

$$z^{CD} = 4R_0^{CR} - 4a - 8d (28)$$

That is, for the SCHMITTNER model, we automatically have $z^{CR} = z^{CD}$, which would be required for a consistent stoichiometry – i.e., assuming that organic matter decomposition is the same everywhere, regardless whether in oxic or suboxic zones. Evaluation

BGD

6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I₫







Back



Full Screen / Esc

Printer-friendly Version



of z^{CD} from a, d and the prescribed nitrate demand for denitrification, R_0^{CD} , among the different models shows, that among the other models only BEC fulfills this requirement. PISCES and HAMOCC implicitly assume that the organic matter supplied to and degraded in the suboxic zones contains less "excess" hydrogen.

A too low excess hydrogen content results in a too low nitrate consumption. Taking the OM composition as implicitly defined via R^{CR} and d, from Eq. (25), we can evaluate the theoretical nitrate demand for a stoichiometrically consistent nitrate requirement (Table 2). Comparing this theoretical value to the nitrate requirements prescribed in the models shows, that in the HAMOCC and PISCES models, nitrate consumption by denitrification is too low by 23 and, respectively, 24 moles HNO $_3$ per mole organic phosphorous supplied. Thus, differences in the implicit OM composition not only exist between the models, but in some cases also between the different remineralization pathways considered in a model, the effect of which has yet to be investigated. Given the large variability (and uncertainty; see above) in the parameterisation of sedimentation and remineralisation rate, however, the effect of these differences might turn out to have a relatively low impact on simulated tracer fields.

5 Conclusions

The specific assumptions made about the elemental composition of organic matter simulated in biogeochemical models have consequences for the simulated fluxes of oxygen, nutrients, and carbon. Assuming organic matter rich in hydrogen (H excess), such as lipids or proteins (also rich in nitrogen), implies more consumption of O_2 during aerobic remineralisation, and also more consumption of O_2 and more loss of fixed nitrogen as O_2 by denitrification, but less production of O_2 per O_3 consumption.

All models considered in this study implicitly assume an efficient coupling between the aerobic remineralisation and nitrification, without any rate limitation of these processes. In addition, the biogeochemical models do not consider the coupling and/or decoupling between the aerobic (aerobic remineralisation, nitrification) and anaerobic

BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

.00.00

Figures

I∢



•



Back



Full Screen / Esc

Printer-friendly Version



(denitrification, anammox, DNRA) processes, which can largely affect the stoichiometry of the resulting total remineralisation. Indeed, this coupling and/or decoupling between the aerobic and anaerobic processes is only taken into account by an O₂ threshold, still not very well defined, but do not take into account the coupling and/or decoupling due to the intermediate compounds such as nitrite.

Even in this simplified picture, biogeochemical models may implicitly assume a composition of organic matter that differs for aerobic remineralization and anaerobic denitrification. It is not impossible that such differences in the remineralization stoichiometry exist in reality. Models may help to investigate the possible relevance of such differences. In order to do so, however, the explicit and implicit assumptions used by such biogeochemical models must be clearly stated. This note is one attempt to do so.

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BGD

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

Back Close

Full Screen / Esc

Printer-friendly Version



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6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Full Screen / Esc

Close

Back

Printer-friendly Version



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6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

l∢ ⊳l

•

Back Close

Full Screen / Esc

Printer-friendly Version



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6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.



Table 1. Stoichiometric ratios of organic matter and its remineralisation. C_{org} , H_{org} , O_{org} , N_{org} and P_{org} denote C, H, O, N and P contained in organic matter, respectively. (1) Stoichiometric ratios of organic matter composition from Redfield (1963), Copin-Montegut and Copin-Montegut (1983), Anderson (1995) and Fraga et al. (1998). (2) $NH_3/P_{org}=d$ for all specific processes. To minimize the number of parameters, the values of the processes have been expressed in terms of R_0 whenever possible.

Equation	Ratio	Name	Value				
	Organio	matter	composition (1)				
4 C_{org}/P_{org} $a \approx 80-108$							
4	$H_{\text{org}}/P_{\text{org}}$		≈ 171–263				
4	O _{org} /P _{org}		≈ 42–110				
4	$N_{\text{org}}/P_{\text{org}}$		≈ 16–18				
	Sp	ecific pr	ocesses (2)				
Oxic: Rem	nineralisation						
6	$-O_2/P_{ora}$	R_0	a + 1/4b - 1/2c - 3/4d + 5/4				
Suboxic: L	Denitrification I	U	, , , , , , , , , , , , , , , , , , , ,				
13	$-HNO_3/P_{org}$		2 <i>R</i> ₀				
13			2 R ₀				
Suboxic: [Denitrification II		Ü				
14	$-HNO_2/P_{org}$		$4/3R_0$				
14	N_2/P_{org}		2/3 <i>R</i> ₀				
Suboxic: [Denitrification I-	<i>⊦11</i>	, 0				
15	$-HNO_2/P_{org}$		$4/5R_0$				
15	N_2/P_{org}		2/5 R ₀				
		Bulk pro	ocesses				
Oxic: Rem	nineralisation pl	lus nitrific					
10	$-O_2/P_{org}$		$R_0 + 2d$				
10	HNO ₃ /P _{org}		d				
Suboxic: L		+II+oxida	ation of NH $_3$ by HNO $_3$				
17	-HNO ₃ /P _{org}		$4/5R_0 + 3/5d$				
17	N_2/P_{org}		$2/5R_0 + 4/5d$				

6, 2539-2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I ◆ ▶I

◆ Back Close

Full Screen / Esc

Printer-friendly Version



Table 2. Stoichiometry for 1 mole of P in main BGC models: HAMOCC (from Wetzel, 2004; Maier-Reimer et al., 2005), PISCES (from Aumont and Bopp, 2006), BEC (from Moore et al., 2002, 2004; Moore and Doney, 2007); SCHMITTNER (from Schmittner et al., 2008) with organic matter ($C_aH_bO_cN_dP$), complete aerobic remineralisation (CR: cf. Eq. 10) and complete denitrification (CD: cf. Eq. 17) as considered in Table 1. Stoichiometry from Redfield (1963) and Richards (1965), and from Anderson (1995) are called RR and AN, respectively. For the SCHMITTNER model, values in brackets refer to the set-up used by Oschlies et al. (2008).

	HAMOCC	PISCES	BEC	SCHMITTNER	RR	AN				
Organic matter ratios										
C/P (a)	122	122	117	112 (112)	106	106				
N/P (<i>d</i>)	16	16	16	16 (16)	16	16				
H excess (z), aerobic ¹	72	72	84	256 (102.4)	0	48				
H excess (z), anaerobic ²	-43	64	84	256 (102.4)	0	48				
Process ratios										
-O ₂ /P for CR	172	172	170 ³	208 ⁴ (169.6)	138	150				
HNO ₃ /P for CR ⁵	16	16	16	16 (16)	16	16				
−HNO₃/P for CD	99 ⁶	98 ⁷	120	150.4 (119.68) ⁸	94.4 ⁸	104 ⁸				
(-HNO ₃ /P) for CD, theor. ⁹	122	122	120	150.4 (119.68)						
N ₂ /P for CD	57 ⁶	68 ⁸	68	83.2 (67.8) ⁸	55.2 ⁸	60 ⁸				
$-2 N_2/N_{\rm org}$ for CD ¹⁰	7.1	8.5	8.5	10.4 (8.5)	6.9	7.5				
Excess of N ₂ / -HNO ₃ 11	+15%	+39%	+13%	+11% (+13%)	+17%	+15%				
$-HNO_3/-O_2^{12}$	0.58	0.57	0.71	0.72 (0.71)	0.68	0.69				

 1 Calculated from Eq. (24); 2 Calculated from Eq. (26); 3 from OM stoichiometry according to Anderson and Sarmiento (1994); 4 from O/N=13 and N/P=16; 5 From line c=N/P; 6 From 172*2/3–16 for nitrate consumption, and 172*1/3 for N₂ production; subject to change, E. Maier-Reimer, personal communication; 7 Deduced from N/C ratio of 0.8 for denitrification multiplied by a=C/P; 8 Calculated from Eq. (17) or Table 1; 9 Calculated from Eq. (25), using the model's prescribed O₂ demand, C/P and N/P.; 10 Calculated from N₂/(P×d); for RR and AN this corresponds to Eq. (21); 11 Calculated from (2 N₂/P)/(HNO₃/P)-1; for RR and AN this corresponds to Eq. (22); 12 Calculated from (HNO₃/P)/(O₂/P); for RR and AN this corresponds to Eq. (20).

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6, 2539–2566, 2009

Stoichiometry of remineralization

A. Paulmier et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

I

I

I

Back Close

Printer-friendly Version

Full Screen / Esc



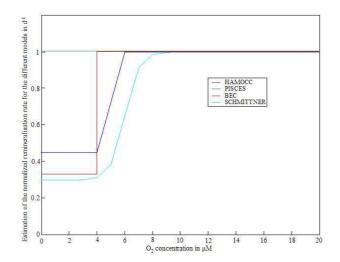


Fig. 1. Plot of the remineralisation, normalized to 1 at high oxygen levels, rate versus O_2 concentration, illustrating the different formulations used in HAMOCC, PISCES, BEC and SCHMITTNER BGC models. A threshold in O_2 implicitely separates the rate corresponding to the aerobic remineralisation (CR) and to the denitrification (CD), for the higher and lower O_2 concentration, respectively. For HAMOCC, the illustration of the slope (here between 4 and 6 μM) corresponds to a case with sufficiently detritus (DET) and Dissolved Organic Matter (DOM) for CR, and DET and nitrate for CD (no limitation of the remineralisation by the organic matter). For PISCES, the total aerobic and anaerobic remineralisation does not depend on O_2 , but below 6 μM a fraction is remineralised by denitrification, increasing when O_2 becomes lower (100% for O_2 =0 μM). The CR and CD rates vary with depth and DOM, and also depend on the bacterial activity, parameterised as a function of zooplankton. For BEC, the CR and CD rates depend on temperature, and on nitrate, turning off CD when nitrate concentration is higher than 32 μM. For the SCHMITTNER model, the CR and CD rates depend on temperature. The threshold in O_2 for the onset of denitrification is 5 μM, but it is a "smooth" transition mediated by the tanh function.

6, 2539–2566, 2009

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