AGU PUBLICATIONS

Global Biogeochemical Cycles

RESEARCH ARTICLE
10.1002/2014GB005066

Key Points:
- Phytoplankton stoichiometry sets the deep-ocean N:P ratio but not its regulation
- Increased water column stratification will destabilize the deepwater N:P ratio

Supporting Information:
- Text S1
- Appendix S1
- Table S1

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Citation:
Augueres, A.-S., and M. Loreau (2015), Regulation of Redfield ratios in the deep ocean, *Global Biogeochem. Cycles*, *29*, doi:10.1002/2014GB005066.

Received 19 DEC 2014
Accepted 20 JAN 2015
Accepted article online 23 JAN 2015

Regulation of Redfield ratios in the deep ocean

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Abstract Biotic regulation of the environment at global scales has been debated for several decades. An example is the similarity between deep-ocean and phytoplankton mean N:P ratios. N and P cycles are heavily altered by human activities, mainly through an increase in nutrient supply to the upper ocean. As phytoplankton only access nutrients in the upper ocean, it is critical to understand (1) to what extent phytoplankton are able to regulate N and P concentrations as well as their ratio in the deep, inaccessible layer and (2) what mechanisms control the value of the deepwater N:P ratio and the efficiency of its biotic regulation. With a model of N and P cycles in the global ocean separated in two layers, we show that the value of the deepwater N:P ratio is determined by nonfixer's N:P ratio, recycling, and denitrification. Our model predicts that although phytoplankton cannot efficiently regulate deep nutrient pools, they can maintain nearly constant ratios between nutrients because compensatory dynamics between nonfixers and nitrogen fixers allows a control of deepwater chemistry through nutrient recycling. This mechanism could explain the near constancy of the deepwater N:P ratio, in agreement with Redfield's (1934, 1958) classical hypothesis. Surprisingly, N:P ratio of phytoplankton does not affect their ability to regulate the deepwater N:P ratio. Our model suggests that increased water column stratification as a result of global climate change may decrease the stability of the N:P ratio in the deep ocean over long temporal and spatial scales.

1. Introduction

Regulation of environmental conditions by organisms at global scale has been debated for several decades, especially concerning the controversial Gaia theory. This theory was originally developed to address the issue of the near constancy of physical and chemical properties of the atmosphere over long time scales [*Lovelock and Margulis*, 1974; *Margulis and Lovelock*, 1974]. The Gaia theory proposes that feedback mechanisms between organisms and their environment contribute to the restriction of variations in environmental conditions to a range that is habitable for life. This hypothesis was strongly criticized, as natural selection acts at the individual level to maximize the fitness of organisms in their local environment and does not necessarily promote stability and self-regulation of the global environment (see *Lenton* [1998] and *Free and Barton* [2007] for reviews). Redfield ratios in oceans provide another example of possible regulation by organisms of their environment at global scales.

The Redfield ratios are one of the key foundations of ocean biogeochemistry [*Falkowski*, 2000]. Although local limiting conditions and phytoplankton growth strategies can induce local variations in phytoplankton stoichiometry [*Arrigo*, 2005; *Franz et al*., 2012; *Martiny et al*., 2013], the mean value of phytoplankton C:N:P ratio is considered as relatively constant at large spatial and temporal scales [*Redfield*, 1934, 1958; *Karl et al*., 1993; *Anderson and Sarmiento*, 1994]. The issue of the biological meaning of the mean N:P ratio of 16:1 in phytoplanktonic cells has been a challenge for theoretical ecology in the last decade [*Klausmeier et al*., 2004, 2008; *Loladze and Elser*, 2011]. It has recently been shown theoretically that the balance between protein and rRNA synthesis leads to a homeostatic protein:rRNA ratio that corresponds to an overall cellular N:P ratio of 16 ± 3 [*Loladze and Elser*, 2011].

Redfield's fundamental insight into the chemistry of marine ecosystems was primarily related to the coupling between the N:P ratio of phytoplankton and that of seawater, regardless of a specific ratio per se. *Redfield* [1934] highlighted the similarity between the mean N:P ratio of phytoplanktonic cells and that of ocean deep waters. He proposed three hypotheses to explain this similarity: (1) it is a coincidence, (2) phytoplankton can adapt their stoichiometry to environmental conditions, or (3) phytoplankton control the chemical properties of their environment. The first hypothesis seems unlikely and thus was quickly rejected. The second hypothesis is relevant since consumption of N and P in a non-Redfield ratio is common in the ocean, depending on local limiting conditions and phytoplankton growth strategies [*Geider and La Roche*, 2002;

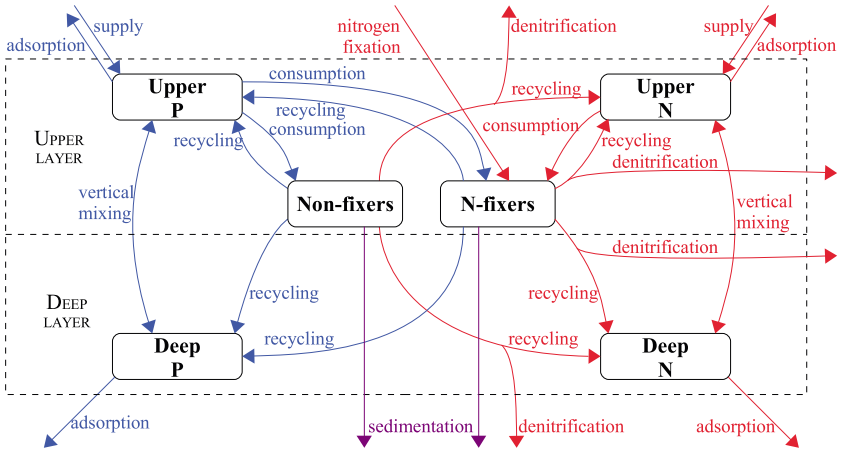

Figure 1. Nutrient stocks and flows in the model of coupled nitrogen and phosphorus cycles in the global ocean. Boxes represent stocks. Blue arrows are phosphorus flows, red arrows are nitrogen flows, and purple arrows are both nitrogen and phosphorus flows.

Franz et al., 2012]. Phytoplankton are thus able to adapt their stoichiometry to nutrient availability to a certain extent, depending on factors such as physiological constraints and the physical structure of ecosystems [*Hall et al*., 2005], which could explain part of the similarity between the mean N:P ratio of phytoplankton and that of deep waters. Adaptation of phytoplankton N:P ratio to environmental conditions should lead to a variability in the deepwater N:P ratio over time, as observed, for example, in the North Atlantic Ocean [*Pahlow and Riebesell*, 2000]. However, a recent study showed that the average N:P ratio of 16:1 in phytoplankton can be explained by the balance between protein and rRNA synthesis [*Loladze and Elser*, 2011]. Thus, the hypothesis that phytoplankton can adapt their stoichiometry to environmental conditions is inconsistent with the fact that phytoplankton N:P ratio may correspond to an optimum cell composition, independently of the composition of the growth medium. *Redfield* [1958] favored the third hypothesis, assuming that the intracellular content of phytoplankton could be central in the similarity observed between phytoplankton and deepwater N:P ratios. Phytoplankton could maintain this pattern through nitrogen fixation, denitrification, and recycling. The concentration of fixed inorganic nitrogen is indeed biologically controlled, whereas that of phosphate is set by the riverine inflows from continental sources and by the sedimentary outflows [*Karl et al*., 1997; *Tyrrell*, 1999; *Deutsch et al*., 2007]. When fixed inorganic nitrogen becomes limiting for phytoplankton, nitrogen fixation would increase the nitrogen inputs to the seawater [*Tyrrell*, 1999; *Lenton and Watson*, 2000; *Schade et al*., 2005].

Regulation of the deepwater N:P ratio is a major issue in marine ecology for several decades [*Falkowski*, 2000]. The biological basis of the mean N:P ratio in phytoplankton has received some attention [*Loladze and Elser*, 2011], but an important unknown question is whether phytoplankton can be expected to control deepwater composition from an ecological perspective. Nitrogen and phosphorus oceanic cycles are heavily affected by anthropogenic activities, mainly through an increase in N and P supply by rivers [*Benitez-Nelson*, 2000; *Gruber and Galloway*, 2008; *Seitzinger et al*., 2010] and in the atmospheric deposition of N [*Galloway*, 1998; *Duce et al*., 2008]. Phytoplankton have access only to the upper layer of the ocean, either because of the limited depth of the euphotic layer or because of the thermocline. Thus, it is critical to understand (1) to what extent phytoplankton are able to regulate the N:P ratio of the deep layer in human-altered marine systems and (2) what are the mechanisms that control the value of the deepwater N:P ratio and the efficiency of its regulation.

Our aim in this work is to clarify to what extent and by which way autotrophic organisms are able to control the chemistry of the deep ocean, to which they do not have a direct access. We address these two issues by building a model for the coupled N and P cycles in the ocean based on *Tyrrell* [1999], in which phytoplankton access nutrients only in the upper layer, and parametrize our model with existing data. Hereafter, the surface and deepwater N:P ratios refer only to the dissolved nutrients in the water. By performing a sensitivity analysis, we first determine the extent to which the different mechanisms involved in P and N cycles (e.g., denitrification, N fixation, and independent physical flows) control the value of the deepwater N:P ratio in the current

Table 1. Parameter Values Used in Simulations for the Model of Phosphorus and Nitrogen Cycles in the Global Ocean[a]

Symbol	Description	Units	Model Value	Literature Values
z_{tot}	Depth of the water column	m	3,730	
p_{za}	Fraction of the water column that corresponds to the upper layer		4.2×10^{-2}	4.2×10^{-2} [*Slomp and Van Cappellen*, 2006]
K	Vertical mixing coefficient	$m\ a^{-1}$	11.5	11.5 [*Slomp and Van Cappellen*, 2006][c]
S_N	Nitrogen supply (riverine and atmospheric)	$\mu mol\ N\ m^{-3}\ a^{-1}$	135	211 [*Codispoti et al.*, 2001][b,d] 132–198 [*Brandes et al.*, 2007][b,d] 172 [*Gruber and Galloway*, 2008][b,d]
S_P	Phosphorus supply (riverine)	$\mu mol\ P\ m^{-3}\ a^{-1}$	1.9	0.56–2.77 [*Benitez-Nelson*, 2000][d] 1.7 [*Slomp and Van Cappellen*, 2006][d]
q_N	Adsorption rate of nitrogen	a^{-1}	10^{-6}	
q_P	Adsorption rate of phosphorus	a^{-1}	10^{-5}	2.4×10^{-5} [*Slomp and Van Cappellen*, 2006]
R	P:N ratio of nonfixing phytoplankton	$mol\ P\ mol\ N^{-1}$	1:15	1:6–1:14 [*Sarthou et al.*, 2005] 1:5–1:19 [*Geider and La Roche*, 2002]
R_F	P:N ratio of N-fixing phytoplankton	$mol\ P\ mol\ N^{-1}$	1:50	1:5–1:150 [*LaRoche and Breitbarth*, 2005]
m	Mortality rate of phytoplankton (including grazing)	a^{-1}	85	55–321 [*Obayashi and Tanoue*, 2002] 73–657 [*Sarthou et al.*, 2005]
Rec_{tot}	Fraction of nutrient recycled in the water column		99.8×10^{-2}	99.8×10^{-2} [*Slomp and Van Cappellen*, 2006]
p_{Reca}	Fraction of total recycling that occurs in the upper layer		87.3×10^{-2}	87.3×10^{-2} [*Slomp and Van Cappellen*, 2006]
D_{tot}	Denitrification rate in the water column	a^{-1}	1.6×10^{-2}	1.7×10^{-2} [*Codispoti et al.*, 2001][e] $1.0–1.8 \times 10^{-2}$ [*Seitzinger et al.*, 2006][e] $0.9–1.1 \times 10^{-2}$ [*Brandes et al.*, 2007][e]
p_{Da}	Fraction of total denitrification that occurs in the upper layer	a^{-1}	22.5×10^{-2}	
μ	Maximum growth rate of nonfixing phytoplankton	a^{-1}	124	138–256 [*Obayashi and Tanoue*, 2002] 146–1 205 [*Sarthou et al.*, 2005] 124–299 [*Timmermans et al.*, 2005]
cost	Cost associated to N fixation (decrease in the maximal growth rate)	a^{-1}	4	growth rate of N fixers: 66–117 [*Masotti et al.*, 2007]
N_H	Half-saturation constant of growth of nonfixing phytoplankton for nitrogen	$\mu mol\ N\ m^{-3}$	1,500	1,429–14,290 [*Sterner and Grover*, 1998] 1,000 [*Palmer and Totterdell*, 2001] 1,600 [*Sarthou et al.*, 2005] 1,030–2,640 [*Timmermans et al.*, 2005]

[a]When units in the literature were different from those used here, we used the following assumptions to convert them.
[b]Molar weights of N and P are $14\ g\ mol^{-1}$ and $31\ g\ mol^{-1}$, respectively.
[c]The ocean surface is $361.10^{12}\ m^2$.
[d]The volume of the upper and deep layers are $54 \times 10^{15}\ m^3$ and $1.292 \times 10^{18}\ m^3$, respectively.
[e]Total oceanic primary production corresponds to $8800\ Tg\ N\ a^{-1}$.

ocean (section 3.1). We then analyze the potential for biotic regulation of N and P concentrations as well as of their ratio in the current ocean if either N or P supply is increased by anthropogenic activities (called hereafter "regulation efficiency," section 3.2). Finally, we perform a sensitivity analysis to assess which mechanisms drive the regulation efficiency of deepwater N:P ratio by autotrophic organisms.

2. Methods

2.1. Model Description

Our ocean model describes the biogeochemical cycles of N and P in the ocean (Figure 1 and Table 1) and includes two groups of phytoplankton, N fixers, and nonfixers [*Tyrrell*, 1999]. The water column, with depth z_{tot}, is separated in two layers, each of which is considered homogeneous. The upper layer, which corresponds to a fraction p_{za} of the water column, is accessible to phytoplankton. The deep layer is inaccessible to phytoplankton because of light limitation or water column stratification. N concentrations (N_a and N_i for the upper and deep layers, respectively) include nitrites, nitrates, and ammonium, and P concentrations (P_a and P_i) correspond to phosphates. The two inorganic pools are connected by physical processes—here diffusion and water vertical movements (i.e., upwellings and downwellings, governed by parameter K). Both layers have nutrient outflows to unrepresented parts of the Earth system, but only

the upper layer has nutrient inflows. N supply to the upper layer (S_N) includes atmospheric and riverine inflows [*Cornell et al.*, 1995], while P supply (S_P) includes only riverine inflow [*Benitez-Nelson*, 2000]. Nutrient outflows correspond to adsorption of inorganic nutrients [*Benitez-Nelson*, 2000; *Morse and Morin*, 2005]. We added adsorption to *Tyrrell*'s [1999] model to allow P to leave the system in the absence of organisms; this prevents the model from displaying the pathological behavior of indefinite P accumulation in the absence of organisms. Adsorption rates of dissolved P (q_P) and N (q_N) are considered constant in the water column. We assume that *Von Liebig*'s [1842] law of the minimum governs the growth of nonfixers, whose concentration in the upper layer is B. N fixers, whose concentration in the upper layer is B_F, consume phosphates in that layer. Nitrogen fixation is assumed to be the only source of N for N fixers, whose growth is limited by P because N_2 is in excess in the ocean. Phytoplankton have a traditional resource-dependent functional response to the accessible nutrient concentration. The functional response of nonfixers to P, $g(P_a)$, is distinguished from that of N fixers, $g_F(P_a)$. Their P:N ratio, R, is also assumed to be different from that of N fixers, R_F [*Lenton and Klausmeier*, 2007]; both ratios are supposed to be constant. Particle export from the upper to the deep layer is induced by sinking of dead organic matter as well as by grazing and vertical migrations of zooplankton. For the sake of simplicity, grazing is not explicitly taken into consideration and is included in the mortality rate of phytoplankton (m). Part of the organic matter is recycled by microorganisms, leading to a return of nutrients to the water column ($\mathrm{Rec_{tot}}$) [*Hood et al.*, 2006], with a fraction p_{Reca} to the upper layer. Lastly, denitrification of organic matter leads to a release of N_2 from the ocean to the atmosphere (D_{tot}) [*Hood et al.*, 2006], with a fraction p_{Da} from the upper layer. Mass balance is used to build a model that describes the dynamics of N and P masses. By dividing nutrient mass by the volume of the layer concerned, we then obtain a model in terms of nutrient concentrations (Figure 1):

$$
\begin{aligned}
\frac{\mathrm{d}N_a}{\mathrm{d}t} &= S_N + \frac{K}{z_{\mathrm{tot}}\,p_{za}}(N_i - N_a) - q_N N_a + m(\mathrm{Rec_{tot}}\,p_{\mathrm{Reca}} - D_{\mathrm{tot}}\,p_{Da})(B + B_F) - \min(g_N(N_a), g_P(P_a))B \\
\frac{\mathrm{d}P_a}{\mathrm{d}t} &= S_P + \frac{K}{z_{\mathrm{tot}}\,p_{za}}(P_i - P_a) - q_P\,P_a + m\,\mathrm{Rec_{tot}}p_{\mathrm{Reca}}(RB + R_F B_F) - \min(g_N(N_a), g_P(P_a))RB - g_{PF}(P_a)R_F B_F \\
\frac{\mathrm{d}N_i}{\mathrm{d}t} &= \frac{K}{z_{\mathrm{tot}}(1 - p_{za})}(N_a - N_i) - q_N N_i + \frac{p_{za}}{1 - p_{za}}\,m\,[\mathrm{Rec_{tot}}(1 - p_{\mathrm{Reca}}) - D_{\mathrm{tot}}(1 - p_{Da})](B + B_F) \\
\frac{\mathrm{d}P_i}{\mathrm{d}t} &= \frac{K}{z_{\mathrm{tot}}(1 - p_{za})}(P_a - P_i) - q_P\,P_i + \frac{p_{za}}{1 - p_{za}}\,m\,\mathrm{Rec_{tot}}(1 - p_{\mathrm{Reca}})(RB + R_F B_F) \\
\frac{\mathrm{d}B}{\mathrm{d}t} &= [\min(g_N(N_a), g_P(P_a)) - m]B \\
\frac{\mathrm{d}B_F}{\mathrm{d}t} &= [g_{PF}(P_a) - m]B_F
\end{aligned}
\tag{1}
$$

When necessary for numerical simulations, functional responses were modeled with a Michaelis-Menten function:

$$
\begin{aligned}
g_N(N_a) &= \frac{\mu N_a}{N_a + N_H} \\
g_P(P_a) &= \frac{\mu P_a}{P_a + RN_H} \\
g_{PF}(P_a) &= \frac{(\mu - \mathrm{cost})P_a}{P_a + RN_H}
\end{aligned}
\tag{2}
$$

N fixation is energetically more costly than mineral N uptake [*Vitousek and Field*, 1999; *Menge et al.*, 2008] and can be limited by iron [*Mills et al.*, 2004; *Weber and Deutsch*, 2012]. The maximal growth rate of N fixers is obtained by subtracting a given cost (cost) from the maximal growth rate of nonfixers (μ). N_H is the half-saturation constant of nonfixers for N. N fixers and nonfixers are considered to have the same half-saturation constant for P, which is fixed to $R \times N_H$ for consistency with the N:P ratio of nonfixers.

2.2. Regulation Coefficients

We calculated the strength of the regulation of the concentrations of a nutrient A with respect to changes in its supply:

$$
\rho_{x,y} = 1 - \frac{S_y}{A_x} \times \frac{\partial\, A_x}{\partial\, S_y} \tag{3}
$$

$\rho_{x,y}$ is defined as the regulation coefficient of the nutrient A concentration in pool x with respect to changes in the nutrient A supply to pool y. When $\rho_{x,y}=0$, there is no regulation (i.e., the proportional variation in nutrient A concentration in pool x is equal to that in nutrient A supply to pool y). At other extreme, when $\rho_{x,y}=1$, there is perfect regulation (i.e., there is no variation in nutrient A concentration in pool x as a result of that in nutrient A supply to pool y). When $0<\rho_{x,y}<1$, regulation is partial. Note that biota can sometimes overregulate the nutrient concentration in pool x, in which case $\rho_{x,y}>1$. Some cases where $\rho_{x,y}<0$ can also occur; regulation is then negative, i.e., organisms amplify variations in nutrient supply.

We also quantified the effect of changes in the supply of one nutrient A_1 on the concentrations of the other nutrient A_2 using the following equation:

$$\varepsilon_{A1x,A2y}=\frac{S_{A2,y}}{A_{1,x}}\times\frac{\partial A_{1,x}}{\partial S_{A2,y}} \tag{4}$$

$\varepsilon_{A1x,\,A2y}$ measures the effect of the supply of nutrient A_2 in pool y on the concentration of nutrient A_1 in pool x. This effect is positive when the supply of A_2 in pool y and the concentration of A_1 in pool x vary in the same direction, negative when they vary in opposite directions, and zero when the supply of A_2 does not affect the concentration of A_1.

We further quantified the strength of the regulation of the ratio between the two nutrients using the same principle as in equation (2). In this case, however, the elasticity of the ratio will change sign depending on whether the nutrient whose supply changes is in the numerator or in the denominator of the ratio. Therefore, to keep signs consistent, we calculated the regulation coefficient of the deepwater N:P ratio when N supply was modified and the regulation coefficient of the deepwater P:N ratio when P supply was modified. We obtain the following regulation coefficients for the N:P ratio of deep waters:

$$\begin{aligned}\rho_{(\mathrm{N:P})x,\,Na}&=\rho_{Nx,\;\;Na}+\varepsilon_{Px,\,Na}\\ \rho_{(\mathrm{P:N})x,\,Pa}&=\rho_{Px,\;\;Pa}+\varepsilon_{Nx,\,Pa}\end{aligned} \tag{5}$$

Lastly, we performed numerical simulations of the system when N fixers and nonfixers coexist, as it is observed in the ocean. We chose parameter values within the range of values found in the literature (Table 1) in order to be as realistic as possible. We increased nutrient supply by 50% after half of the simulation time to assess the strength of the regulation of nutrient pools in the current ocean.

2.3. Sensitivity Analysis

The sensitivity of a variable X to the parameter par ($\mathrm{sens}_{X,\mathrm{par}}$) can be measured as

$$\mathrm{sens}_{X,\;\mathrm{par}}=\frac{\mathrm{par}}{X}\times\frac{\partial\;X}{\partial\;\mathrm{par}} \tag{6}$$

$\mathrm{sens}_{X,\mathrm{par}}$ is negative when X and par vary in the opposite directions and positive when they vary in the same direction. The higher the absolute value of $\mathrm{sens}_{X,\mathrm{par}}$, the more sensitive X is to par.

Equation (6) gives information about local sensitivity. As values found in the literature for parameters often vary between studies (Table 1), we chose to calculate sensitivity over a range of parameter values. This avoids conclusions to be strongly dependent on the value chosen for numerical simulations. For each of the 17 parameters of the model, we thus used a set of 500 values uniformly distributed in an interval of 20% around the value used in numerical simulations. When necessary, we adjusted the bounds of the interval to be consistent with the possible values of the parameter. To assess which parameters have the strongest influence on the value and the regulation efficiency of the deepwater N:P ratio, we measured the sensitivity of (1) N_i/P_i (section 3.1), (2) $\rho_{(\mathrm{P:N})i,Pa}$ (section 3.3), and (3) $\rho_{(\mathrm{N:P})i,Na}$ (section 3.3) to the set of values for each parameter (see Table S1 in the supporting information).

3. Results

3.1. Which Mechanisms Control the Value of the Deepwater N:P Ratio?

Model (1) has six equilibria, depending on the nutrient that limits phytoplankton growth and on the presence or absence of either phytoplankton group. In this study, we focus on the case where N fixers and nonfixers coexist at equilibrium as it corresponds to the observations in the current ocean. We will first look at parameters and

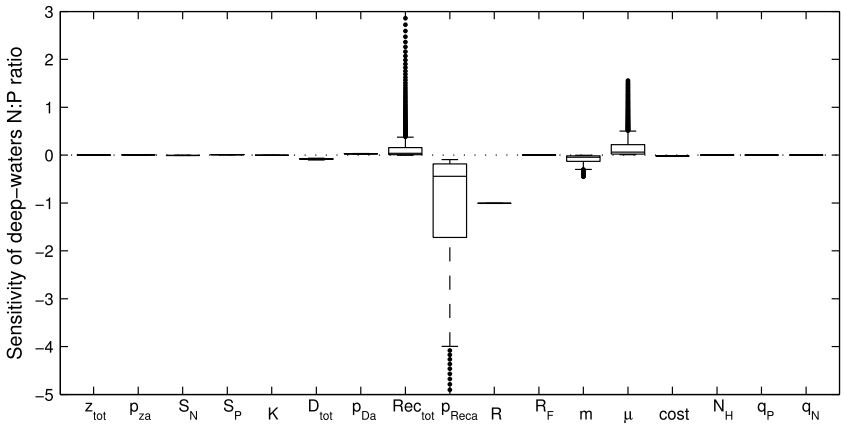

Figure 2. Distribution of the sensitivity of the deepwater N:P ratio (N_i/P_i). The sensitivity of a variable to a parameter is measured as the elasticity of the variable with respect to the parameter. For each parameter, the local sensitivity is calculated for 500 values uniformly distributed in an interval of ±20% around the value used for numerical simulations. The depth of the water column is z_{tot}, and the fraction that is accessible is p_{za}. S_N and S_P are supplies of N and P, respectively. K is the vertical mixing coefficient. D_{tot} and Rec_{tot} are the total denitrification and recycling rates, respectively. The fraction of denitrification and recycling in the upper layer, respectively, are p_{Da} and p_{Reca}. R and R_F are the P:N ratio of nonfixers and N fixers, respectively. The mortality rate is m, and the maximum growth rate of nonfixers is μ. The metabolic cost of N fixation is cost. N_H is the half-saturation constant for N. The adsorption rates of P and N, respectively, are q_P and q_N.

mechanisms that drive the value of the deepwater N:P ratio in the current ocean. In agreement with experimental data, the deepwater N:P ratio is near the one of the organisms in our numerical simulations (Figures 3c and 3f). The sensitivity of the deepwater N:P ratio to R is negative because R represents the P:N ratio of organisms, and thus, the two ratios vary in opposite directions. Changes in the deepwater N:P ratio follow almost perfectly those in phytoplankton N:P ratio, with the result that the absolute value of the sensitivity of the deepwater N:P ratio to phytoplankton P:N ratio is almost 1 for all the values of R tested (sensitivity of −1.01 whatever the value of R, Figure 2). Although the value of the deepwater N:P ratio is strongly dependent on nonfixer's N:P ratio, it is independent on that of N fixers (no sensitivity for all the values of R_F, Figure 2). This difference can be explained by the relative minority of N fixers at the scale of the global ocean compared to nonfixers (Figures 3d and 3h), and thus, their high N:P ratio has a negligible effect on the mean N:P ratio of phytoplankton in our numerical simulations.

The value of the deepwater N:P ratio depends on parameters related to the recycling of organic matter in the water column (Rec_{tot}, p_{Reca} and m). However, the effect of the fraction of organic matter recycled in the water column (p_{Reca}) and the mortality rate of phytoplankton (m) on the N:P ratio in the deep ocean strongly depend on the value of these two parameters, with almost no effect for more than half of the values tested (median sensitivities of 0.04 and −0.04 for Rec_{tot} and m, respectively, Figure 2). The distribution of sensitivity is particularly spread for Rec_{tot}, with 77 outliers corresponding to a sensitivity greater than 0.38. The deepwater N:P ratio will be higher when the fraction of recycling that occurs in the upper layer is low (median sensitivity of −0.44 for p_{Reca}, Figure 2). The intensification of recycling to deep waters (i.e., an increase in Rec_{tot} or a decrease in p_{Reca}) leads to an increase in their N:P ratio, since the mean N:P ratio of organisms is greater than that of deep waters. The maximal growth rate of nonfixers can also have a positive impact on the value of the deepwater N:P ratio but only for some values (median sensitivity of 0.06 and 62 outliers above 0.50, Figure 2). As expected, the total denitrification has a negative effect on the value of the deepwater N:P ratio (sensitivity of −0.10 for all the values of D_{tot}, Figure 2).

3.2. To What Extent Is Phytoplankton Able to Regulate the Deepwater N:P Ratio?

We now focus on understanding and quantifying the ability of phytoplankton to regulate the oceanic N and P cycles when nutrient supplies to the surface ocean are increased. Numerical simulations allow the strength of the regulation of N and P pools in the current ocean to be estimated quantitatively (Figure 3). An analysis of the flows between nutrient pools helps to better understand the results (Figure 4).

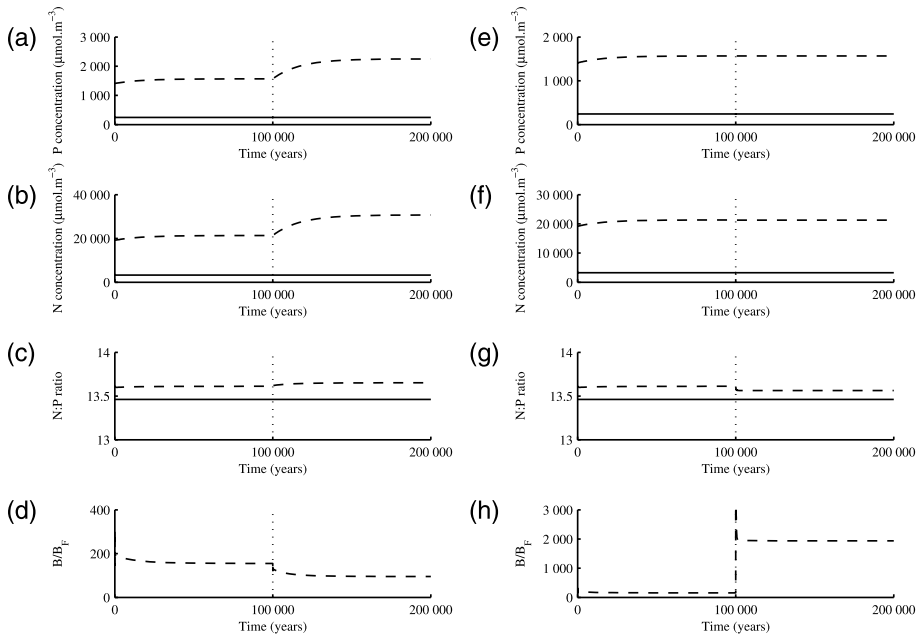

Figure 3. Regulation of N and P concentrations and the N:P ratio in the ocean. (a–d) P supply and (e–h) N supply are increased by 50% after 100,000 years. Simulations are performed with realistic parameter values. Bold lines are for the upper, accessible layer and dotted lines for the deep, inaccessible layer. Figures 3a and 3e show P concentrations ($\rho = 1$ and 0.13 in case of a 50% increase in P supply in the upper and deep layers, respectively, and $\varepsilon = 0$ in both layers in case of a 50% increase in N supply). Figures 3b and 3f show N concentrations ($\varepsilon = 0$ and 0.88 in case of a 50% increase in P supply in the upper and deep layers, respectively, and $\rho = 1$ and 1.01 in case of a 50% increase in N supply in the upper and deep layers, respectively). Figures 3c and 3g show N:P ratios ($\rho = 1$ in the upper layer and $\rho = 1.01$ in the deep layer in both cases). Figures 3d and 3h show the ratio of nonfixing over N-fixing phytoplankton (B/B_F).

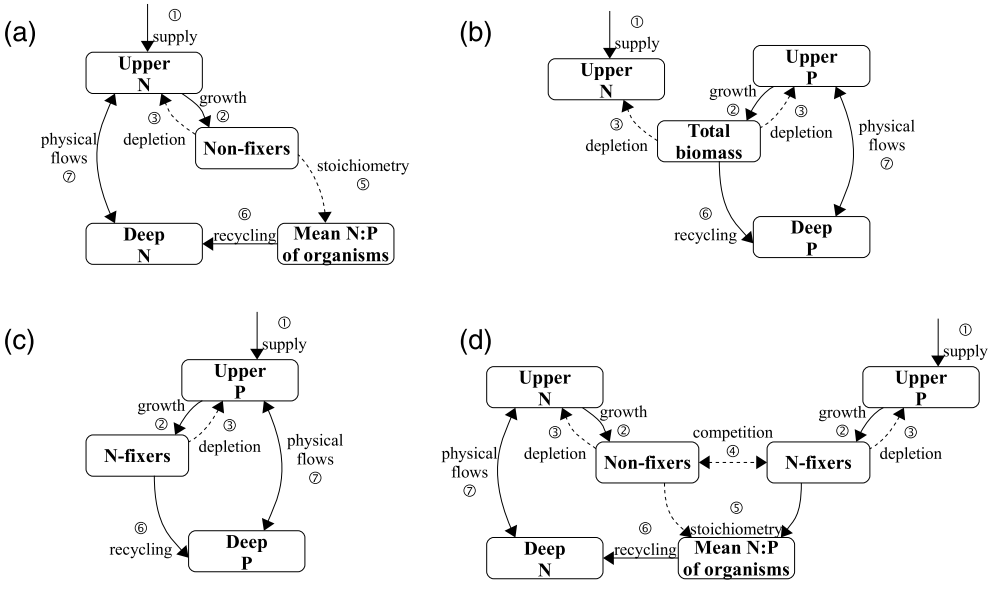

Figure 4. Regulation processes in the ocean model with N-fixing and nonfixing phytoplankton. (a) Impact of N supply on N pools. (b) Impact of N supply on P pools. (c) Impact of P supply on P pools. (d) Impact of P supply on N pools. Bold arrows indicate a direct relationship (e.g., an increase in accessible N concentration results in an increase in the biomass of nonfixers). Dashed arrows indicate an inverse relationship (e.g., an increase in biomass results in a decrease in accessible nutrient concentrations).

When the two phytoplankton groups coexist, P limits N fixers and N limits nonfixers. Any increase in the supply of a nutrient is consumed by those organisms whose growth is limited by that nutrient. Therefore, regulation in the upper layer is perfect, and there is no effect on the accessible concentration of the other nutrient (Figure 3). Perfect regulation is explained by strong negative feedback loops between phytoplankton and the accessible pools (paths 2–3 in Figure 4). Thus, regulation of surface N:P ratio by phytoplankton is perfect with respect to changes in both N and P supplies (Figures 3c and 3g).

Regulation of P concentration in deep waters is either partial or negative because deep P concentration varies in the same direction as P supply (paths 1-2-6 and 1–7, Figure 4c). In numerical simulations, regulation of deep P concentration against changes in P supply was found to be partial ($\rho_{Pi,Pa} = 0.13$, Figure 3b). Changes in N supply have no effect on accessible P concentration (Figure 3f) because they do not affect total biomass (no arrow from accessible N to total biomass in Figure 4b).

Changes in N supply affect the competition between the two phytoplankton groups, leading to changes in the mean N:P ratio of organic matter and in N outflow (arrows 5, Figures 4a and 4d). For example, an increased N supply is advantageous to nonfixers, resulting in a lower mean N:P ratio of organic matter; the N outflow to the deep layer is reduced, and the concentration of N in deep waters decreases. Since deep N concentration and N supply vary in opposite directions (path 1-2-5-6 in Figure 4a), this leads to an overregulation by organisms. In numerical simulations for the current ocean, this regulation was almost perfect ($\rho_{Ni,Na} = 1.01$, Figure 3e) because nonfixers are already dominant (Figure 3h), such that the mean N:P ratio of organic matter is little affected by the 50% increase in N supply. Changes in P supply have an opposite effect on the mean N:P ratio (paths 1-2-4-5 and 1-2-5 in Figure 4d). As a result, they have a positive effect on deep N concentration (Figure 3a).

The deepwater N:P ratio is always overregulated with respect to changes in N supply, because P concentration is not affected and N concentration is overregulated. In numerical simulation, regulation of the N:P ratio in the deep layer with respect to changes in N supply was almost perfect, because N concentration is almost perfectly regulated (Figure 3f). Regulation of deepwater N:P ratio with respect to changes in P supply cannot be deduced from the analysis of flows between nutrient pools. Even though deepwater nutrient concentrations are affected substantially by changes in P supply ($\rho_{Pi,Pa} = 0.13$ and $\varepsilon_{Ni,Pa} = 0.88$), regulation of the N:P ratio in the deep layer was high in numerical simulations ($\rho_{(P:N)i,Pa} = \rho_{(N:P)i,Na} = 1.01$, Figures 3c and 3g). Phytoplankton thus appear to efficiently regulate the deepwater N:P ratio with respect to changes in both N and P supplies in the current ocean.

3.3. Which Mechanisms Control the Regulation Efficiency of the Deepwater N:P Ratio?

Although N and P concentrations in deep waters vary with respect to changes in P supply, numerical simulations show that they vary in a nearly constant ratio ($\rho_{(P:N)i,Pa} = 1.01$, Figure 3c). The deepwater N:P ratio is indeed insensitive to both N and P supplies (S_P and S_N) over an interval of ±20% around the value found in the literature for both supplies (Figure 2). Regulation of the deepwater N:P ratio with respect to changes in P supply is thus almost perfect for this set of parameter values. It is important to understand the mechanisms that could explain the almost perfect biotic regulation of deepwater N:P ratio with respect to changes in nutrient supplies, as they can be different from those setting the value of the deepwater N:P ratio itself. In this section, we will no longer focus on the mechanisms driving the value of the deepwater N:P ratio but in the efficiency of its regulation when nutrient supplies change. The sensitivity analysis is thus performed on the regulation coefficient of the deepwater N:P ratio with respect to changes in P and N supplies.

The efficiency of this regulation appears to mainly be sensitive to recycling parameters. Regulation will be more efficient when the fraction of organic matter recycled in the water column and the mortality rate of phytoplankton are high (positive sensitivity of $\rho_{(P:N)i,Pa}$ to m and most of the values of Rec_{tot}, Figure 5a) and when the fraction of recycling that occurs in the upper layer is low (negative sensitivity of $\rho_{(P:N)i,Pa}$ to p_{Reca}, Figure 5a). The effect of these three parameters in the direction indicated seems intuitive since the intensification of recycling to deep waters leads to an increase in the control of deepwater chemistry by organisms. However, the importance of the sensitivity of $\rho_{(P:N)i,Pa}$ to these three parameters, and especially p_{Reca}, strongly depends on the parameter value (difference of 1.07 between the first and the ninth decile, Figure 5a). Regulation of the deepwater N:P ratio with respect to changes in P supply also appears to be sensitive to the maximal growth rate of nonfixers, μ, again with important variations depending on the value.

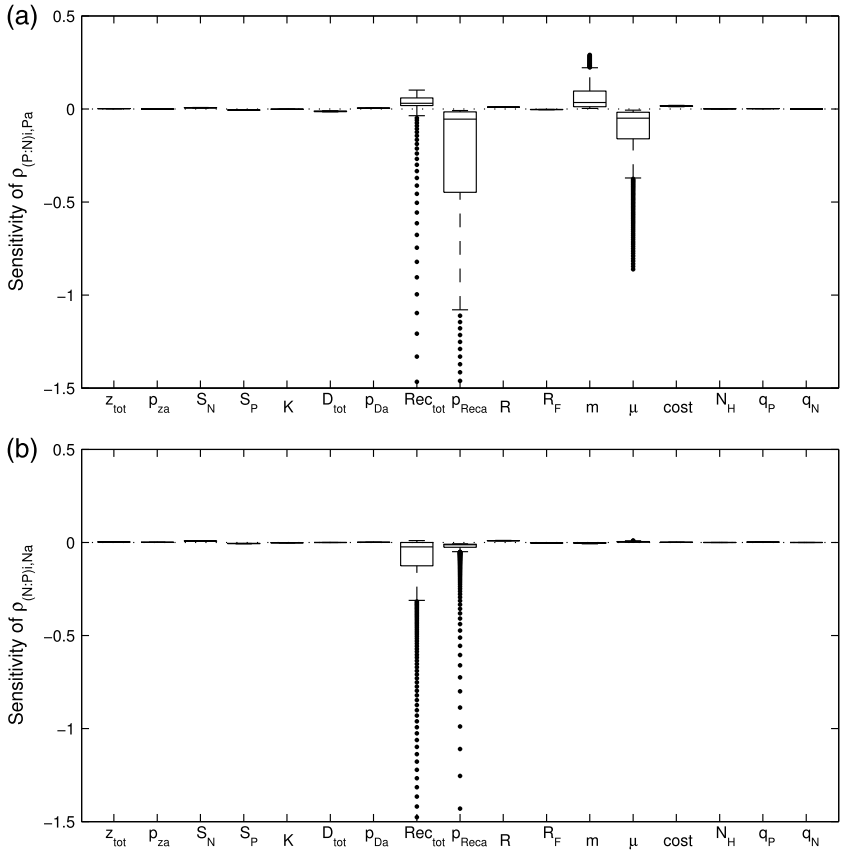

Figure 5. Distribution of the sensitivity of (a) regulation of deepwater N:P ratio with respect to changes in P supply ($\rho_{(P:N)i,Pa}$) and (b) regulation of deepwater N:P ratio with respect to changes in N supply ($\rho_{(N:P)i,Na}$). The sensitivity of a variable to a parameter is measured as the elasticity of the variable with respect to the parameter. For each parameter, the local sensitivity is calculated for 500 values uniformly distributed in an interval of ±20% around the value used for numerical simulations. The depth of the water column is z_{tot}, and the fraction that is accessible is p_{za}. S_N and S_P are supplies of N and P, respectively. K is the vertical mixing coefficient. D_{tot} and Rec_{tot} are the total denitrification and recycling rates, respectively. The fraction of denitrification and recycling in the upper layer, respectively, are p_{Da} and p_{Reca}. R and R_F are the P:N ratio of nonfixers and N fixers, respectively. The mortality rate is m, and the maximum growth rate of nonfixers is μ. The metabolic cost of N fixation is cost. N_H is the half-saturation constant for N. The adsorption rates of P and N, respectively, are q_P and q_N.

Surprisingly, the efficiency of this regulation appears to be insensitive to the N:P ratio of organisms for all the values used in our analysis (Figure 5a).

Variation in N supply is well absorbed in the deep layer, with the result that the deepwater N:P ratio is almost perfectly regulated ($\rho_{(N:P)i,Na} = 1.01$, Figure 3g). The strength of this regulation is insensitive to most of the parameters (no sensitivity of $\rho_{(N:P)i,Na}$ to 15 parameters for the intervals tested, Figure 5b). Although most of the values correspond to low sensitivities of $\rho_{(N:P)i,Na}$, regulation will be more efficient when the fraction of organic matter recycled in the water column and the fraction of recycling that occurs in the upper layer are low (negative sensitivity of $\rho_{(N:P)i,Na}$ to Rec_{tot} and p_{Reca}, Figure 5b). As changes in N supply modify the mean N:P ratio of organic matter and thus N outflow through recycling (Figure 4a), an intensification of recycling (i.e., an increase in Rec_{tot}) will further decrease the ability of organisms to regulate the deepwater N:P ratio, explaining the negative sensitivity of $\rho_{(N:P)i,Na}$ to Rec_{tot}.

4. Discussion

Our model of coupled N and P biogeochemical cycles in the ocean predicts that phytoplankton should perfectly regulate N and P concentrations in the upper layer because of its top-down control on the upper, accessible nutrient pools. These results are in agreement with chemostat and resource-ratios theories, which

predict that organisms consume as much of the limiting resources as possible at equilibrium [e.g., *Tilman*, 1980; *Smith and Waltman*, 1995]; as a result, they are expected to absorb any variation in the supply of a limiting nutrient in the accessible pool. As the nutrient supplied to the ocean occurs in the upper layer that is accessible to autotrophic organisms, we might expect perfect regulation of the concentration of P and N concentrations in both the upper and deep layers against changes in their supply. By contrast, we showed that variations in P and N supplies to the surface ocean impact nutrient concentrations in the deep, inaccessible layer. This occurs because biotic recycling of organic matter plays the role of a nutrient supply to the deep ocean, with the added complexity that the intensity of these biotic inflows depends on the biomass and N:P ratio of phytoplankton in the upper layer. Any change in the supply of either nutrient modifies the competition for P between nonfixers and N fixers. For example, the addition of P to the surface ocean results in an increase in the growth rate of N fixers and a decrease in that of nonfixers. The opposite occurs when N is added to the surface ocean, because the addition of N increases the growth rate of nonfixers and thus their absorption of P. The change in biomass induced by changes in the supply of either N or P then affects the intensity of nutrient recycling to the deep layer. Although nutrient concentrations in the deep layer are substantially affected by changes in P supply, as shown by numerical simulations, regulation of the nutrient ratio can be strong (Figure 3c).

Tyrrell [1999] showed that phytoplankton control the deepwater N:P ratio through the competition between nonfixers and N fixers. Nitrogen fixation thus adapts the concentration of N to the concentration of P in the surface waters, in a ratio that is transferred to the deep waters through recycling of organic matter. In his model, *Tyrrell* [1999] sets the same N:P ratio for nonfixers and N fixers; thus, the mean N:P ratio of the organic matter remained constant whatever the proportion of N fixers compared to nonfixers. However, the hypothesis that nonfixers and N fixers have the same N:P ratio could strongly influence the results as it decreases the ability of phytoplankton to regulate the deepwater N:P ratio. We thus included this differentiation in our model to avoid a possible bias in the quantification of the control of phytoplankton on the deepwater N:P ratio. Our model predicts that the value of the deepwater N:P ratio is mainly controlled by that of nonfixers, as well as, to a lesser extent, by the intensity of recycling of organic matter and denitrification. These predictions are in agreement with previous studies suggesting that the similarity of N:P ratio of both phytoplankton and deep ocean could be related to a balance between denitrification and N fixation [e.g., *Redfield*, 1958; *Tyrrell*, 1999; *Lenton and Klausmeier*, 2007]. In numerical simulations with realistic data for N and P flows, the N:P ratio of deep waters is slightly lower than that of nonfixing phytoplankton, as observed in the ocean [e.g., *Redfield*, 1934, 1958; *Karl et al*., 1993; *Anderson and Sarmiento*, 1994].

We also studied more deeply the parameters, and thus the mechanisms, that are involved in the regulation of deepwater N:P ratio. In sections 3.2 and 3.3, we focused on how the addition of N and P in the surface ocean by human activities affects the deepwater N:P ratio. Our detailed study of the mechanisms that control the regulation efficiency of deepwater N:P ratio allows us to better understand the observed near constancy of this ratio and to predict its expected changes in the context of global change. Both N and P supplies affect deep N concentration, but only P supply affects the deep P concentration. Competition between the two types of phytoplankton with different N:P ratios keeps the total amount of P stored in phytoplankton constant independently of N supply, and thus, P biotic flows are unaffected by variations in N supply. N concentration in deep waters also has a weak response to a 50% increase in N supply (Figure 3). Thus, variations in N supply are well absorbed in the deep layer, contrary to variations in P supply. This difference is due to the compensatory dynamics between N fixers and nonfixers, which makes the N cycle more adaptable than the P cycle [*Tyrrell*, 1999; *Deutsch et al*., 2007]. Surprisingly, our model predicts that competition between the two phytoplankton groups sets the efficiency of biotic regulation of the deepwater N:P ratio through recycling of organic matter, with no direct effect of the N:P ratio of phytoplankton and denitrification. This result is counterintuitive since one might expect the stoichiometry of phytoplankton to strongly influence their ability to regulate that of their environment.

In our model, we assume that *Von Liebig*'s [1842] law of the minimum governs the growth of nonfixers, which implies that the growth of organisms is limited by a single nutrient at a given time. However, phytoplankton growth is limited by multiple resources simultaneously in some regions of the world's ocean

[e.g., *Arrigo*, 2005; *Elser et al*., 2007]. In particular, colimitation of phytoplankton growth is commonly observed in oligotrophic oceanic regions [e.g., *Mills et al*., 2004; *Zohary et al*., 2005]. The use of colimitation instead of Liebig's law may alter our results by affecting the dynamics of phytoplankton populations [*Poggiale et al*., 2010; *Sperfeld et al*., 2012]. In our model, replacing Liebig's law by N and P colimitation for the growth of nonfixers may increase the strength of the competition with N fixers, and thus, the ability of phytoplankton to regulate nutrient pools might be strengthened.

In our model, we assumed different N:P ratios for the two phytoplankton groups considered (i.e., N fixers and nonfixers) but fixed ratios within each group. Yet the stoichiometry of phytoplankton can change depending on nutrient limitation conditions [e.g., *Geider and La Roche*, 2002]. Several models of phytoplankton stoichiometry allow N and P cell quotas to be adjusted depending on nutrient availability [*Klausmeier et al*., 2004, 2008; *Diehl et al*., 2005]. This plasticity of phytoplankton stoichiometry could alter their ability to control nutrient pools. Incorporating adaptable stoichiometry in the ocean model, however, leads to the same qualitative results as those presented in this paper (see Text S1 in the supporting information), which is why we did not consider this complication here. For the sake of simplicity, our model only considers two groups of phytoplankton? Nonfixers and N fixers are indeed two key functional groups in the nitrogen cycle. However, taking into account phytoplankton diversity more precisely might influence our predictions regarding the ability of phytoplankton to regulate N and P oceanic pools.

Global climate change is expected to increase water column stratification through increased sea surface temperature and decreased sea surface salinity [*Riebesell et al*., 2009; *Gruber*, 2011; *Rees*, 2012]. The degree of stratification is captured by parameter K, i.e., the mixing coefficient between the surface and deep layers. Our sensitivity analyses show that the strength of vertical mixing does not affect the value and the regulation efficiency of the deepwater N:P ratio (Figure 5). However, the decrease in the depth of the upper layer induced by increasing stratification is likely to intensify the recycling flow to the deep layer (associated with a decrease in the parameter p_{Reca}) because sinking particles will take less time to reach the deep layer [*Riebesell et al*., 2009]. Since the sensitivity of regulation coefficients of the deepwater N:P ratio to p_{Reca} is negative, the value of these regulation coefficients is then likely to increase, leading to a further enhancement of the current overregulation of the deepwater N:P and P:N ratios with respect to changes in N and P supplies, respectively. Thus, increasing water column stratification will likely result in stronger variability and lower stability of the N:P ratio in the deep ocean over long temporal and spatial scales.

We presented a simple compartment model for the global ocean. This model could also be useful to understand how regulation occurs spatially in the ocean, by integrating the dynamics of interactions between N fixers and nonfixers in a general circulation model. Although similar results might be expected at the scale of the global ocean, a general circulation model is likely to reveal interesting differences in the regulation of the deepwater N:P ratio among oceanic regions [e.g., *Pahlow and Riebesell*, 2000].

Acknowledgments
This work was supported by the TULIP Laboratory of Excellence (ANR-10-LABX-41). The model is parameterized with data found in the literature (see Table 1 for the complete list of references).

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