# Offsetting the radiative benefit of ocean iron fertilization by enhancing $N_2O$ emissions

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Received 19 August 2003; revised 14 October 2003; accepted 4 November 2003; published 18 December 2003.

[1] Ocean iron fertilization is being considered as a strategy for mitigating the buildup of anthropogenic CO<sub>2</sub> in the atmosphere. Assessment of this strategy requires consideration of its unintended consequences, such as an enhancement of ocean N2O emissions. This feedback could offset the radiative benefit from the atmospheric CO<sub>2</sub> reduction significantly, because N2O is a much more powerful greenhouse gas than CO2 itself. Our model results show that the magnitude of this offsetting effect is substantial, but is highly dependent on the location and duration of fertilization. We find the largest offsets (of the order of 100%) when fertilization is undertaken in the tropics, particularly when it is of limited duration and size. Smaller, but still substantial effects are found when fertilization is undertaken elsewhere and over longer periods. These results suggest that any assessment of ocean fertilization as a mitigating option is incomplete without consideration of the N<sub>2</sub>O feedback. INDEX TERMS: 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4842 Oceanography: Biological and Chemical: Modeling; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4808 Oceanography: Biological and Chemical: Chemical tracers; 3359 Meteorology and Atmospheric Dynamics: Radiative processes. Citation: Jin, X., and N. Gruber, Offsetting the radiative benefit of ocean iron fertilization by enhancing N<sub>2</sub>O emissions, Geophys. Res. Lett., 30(24), 2249, doi:10.1029/2003GL018458, 2003.

## 1. Introduction

[2] The ocean's biological pump plays a key role in regulating atmospheric CO<sub>2</sub>, as it shields a substantial fraction of the ocean inventory of carbon from contact with the atmosphere. This process does not operate at its full strength, however, as evidenced by regions with high macronutrients, but low chlorophyll concentrations ("High Nutrient Low Chlorophyll" (HNLC) regions). There is increasing evidence that the existence of these HNLC regions is a consequence of micronutrient limitation (mostly iron) [*Boyd et al.*, 2000], opening the possibility to increase the strength of this process by fertilizing these regions with iron [*Martin et al.*, 1991]. If successful, this would increase the export of organic carbon out of the surface ocean, lower surface CO<sub>2</sub> concentrations and consequently lower atmospheric CO<sub>2</sub> levels [*Joos et al.*, 1991].

[3] When organic matter is remineralized in the ocean's interior,  $N_2O$  is concomitantly produced by processes associated with the breakdown of organic nitrogen [*Capone*,

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1991]. One pathway is linked to the oxidation of ammonium to nitrate (nitrification), where it appears that about 1 ammonium molecule in 1000 is converted to N<sub>2</sub>O [Cohen and Gordon, 1979]. We refer to this mechanism as the "nitrification pathway". A second pathway appears to occur at low oxygen concentrations (<50  $\mu$ mol kg<sup>-1</sup>), in which a highly oxygen concentration dependent fraction of the original organic nitrogen is converted to N<sub>2</sub>O, resulting in high N<sub>2</sub>O yields [Law and Owens, 1990]. Although the exact mechanisms that lead to these high N<sub>2</sub>O yields are not fully understood [Capone, 1991], it appears that they involve interactions between nitrification and denitrification reactions [Codispoti et al., 1992]. We will refer to the suite of processes associated with N<sub>2</sub>O production at low O<sub>2</sub> concentrations as the "low oxygen pathway". The situation at low O<sub>2</sub> concentrations is made even more complex by the evidence that N<sub>2</sub>O gets consumed at O<sub>2</sub> concentrations below a few  $\mu$ mol kg<sup>-1</sup> [*Elkins et al.*, 1978]. [4] The drastically different sensitivities to the in situ O<sub>2</sub>

[4] The drastically different sensitivities to the in situ  $O_2$  concentrations lead to large differences in the spatial pattern of these two pathways. While the nitrification pathway occurs relatively uniformly within the ocean interior, the low oxygen pathway occurs only in a few localized regions where  $O_2$  is depleted, such as the tropical Pacific and Indian Ocean. The relative contributions of the two pathways to the oceanic emissions are believed to be about equal, although with uncertainties of the order of  $\pm 50\%$  [Suntharalingam et al., 2000; Nevison et al., 2003].

[5] A successful Fe fertilization will not only enhance the export of organic carbon out of the surface ocean, but will also increase remineralization in the interior ocean. This increase will lead to enhanced production of  $N_2O$  by both higher rates of nitrification and a general decrease of the ocean interior  $O_2$  concentration, increasing the  $N_2O$  yield in the low oxygen pathway. Although some of the newly produced  $N_2O$  is consumed in the ocean's interior, most of it will be emitted eventually into the atmosphere. As the radiative forcing for  $N_2O$  is nearly 300 times stronger per molecule than that for  $CO_2$  [*Ramaswamy et al.*, 2001], this feedback could substantially offset the radiative benefit of the atmospheric  $CO_2$  reduction stemming from the fertilization [*Fuhrman and Capone*, 1991].

#### 2. Model Setup and Simulations

[6] We investigate here this potentially important feedback using a suite of 3-D coupled physical-biogeochemical models [*Gnanadesikan et al.*, 2002], to which we added a model of the oceanic N<sub>2</sub>O cycle [*Suntharalingam et al.*, 2000] and an atmospheric box model. In order to separately analyze the response of the nitrification and low oxygen pathways as well

	100 year large-scale <sup>a</sup>			10 year large-scale <sup>a</sup>			10 year patch <sup>b</sup>
	Hi-Hi <sup>c</sup>	Lo-Lo <sup>c</sup>	HiSo-Lo <sup>c</sup> (Standard)	Hi-Hi <sup>c</sup>	Lo-Lo <sup>c</sup>	HiSo-Lo <sup>c</sup> (Standard)	HiSo-Lo <sup>c</sup> (Standard)
Tropics	47 (±28)	37 (±18)	40 (±20)	194 (±148)	71 (±77)	58 (±67)	115 (±34)
S. Ocean	6 (±4)	18 (±1)	13 (±6)	6 (±8)	11 (±13)	11 (±18)	$-7(\pm 40)$
N. Atlantic	10 (±4)	21 (±9)	18 (±7)	13 (±4)	23 (±10)	19 (±9)	19 (±12)
N. Pacific	4 (±4)	30 (±3)	32 (±5)	$-1(\pm 19)$	16 (±26)	$-5(\pm 31)$	-53 (±30)

Table 1. Magnitude of N<sub>2</sub>O Offsetting Effect (%) After 100 Years

<sup>a</sup>Tropics  $(18^{\circ}S - 18^{\circ}N; 1.20 \cdot 10^{14} \text{ m}^2)$ ; Southern Ocean (<31°S);  $1.06 \cdot 10^{14} \text{ m}^2$ ); North Atlantic (31°N – 76°N;  $0.24 \cdot 10^{14} \text{ m}^2$ ); North Pacific (31°N – 67°N;  $0.24 \cdot 10^{14} \text{ m}^2$ ).

<sup>b</sup>Tropical patch (116.2°W–105°W; 8.9°S–4.4°N; 0.018  $\cdot$  10<sup>14</sup> m<sup>2</sup>); Southern Ocean patch (150°W–138.8°W; 57.8°S–44.5°S; 0.012  $\cdot$  10<sup>14</sup> m<sup>2</sup>); North Atlantic patch (26.2°W–15°W; 48.9°N–62.2°N; 0.010  $\cdot$  10<sup>14</sup> m<sup>2</sup>); North Pacific patch (168.8°E–180°E; 40°N–53.3°N; 0.013  $\cdot$  10<sup>14</sup> m<sup>2</sup>).

<sup>c</sup>Hi-Hi: Model with high vertical and high isopycnal mixing everywhere; Lo-Lo: Model with low vertical and low isopycnal mixing everywhere; HiSo-Lo: Model with low vertical and low isopycnal mixing everywhere, except for the Southern Ocean (see *Gnanadesikan et al.* [2002] for details).

as to assess a whole range of relative contributions of the two pathways, we consider two separate N<sub>2</sub>O tracers in our simulations. One follows the nitrification pathway, while the second N<sub>2</sub>O tracer follows the low oxygen pathway. Both tracers are consumed in the anoxic zones of the ocean. As the tracer equation is linear, we can combine the results of these two extreme cases to obtain any intermediate case. We regard the average of the two cases as our "central estimate" and the 25% and 75% percentile between the two extreme cases as our uncertainty range. We assume that the relative contribution of the two processes to the total production remains constant over time. This does not imply, however, that the two processes are constrained by each other. Rather, each of them is permitted to respond individually to the perturbation. Our assumption is justified by the fact that these relative contributions are mechanistically linked to the N2O yield during the transformation of nitrogen in the respective processes, which we expect not to change. For the spinup, we constrain the global N<sub>2</sub>O emissions of the model to 3.6 TgN yr<sup>-1</sup> [Nevison et al., 1995]. The oceanic emissions are permitted to evolve freely thereafter.

[7] In order to assess the offsetting effect in terms of net changes in radiative forcing [*Ramaswamy et al.*, 2001], we use a well-mixed box model of the atmosphere, which simulates the evolution of the atmospheric CO<sub>2</sub> and N<sub>2</sub>O concentrations in response to the fertilization. We assess the robustness of our results with regard to uncertainties in the modeled ocean circulation by using three configurations of the same physical model with rather different circulation pattern and rates [*Gnanadesikan et al.*, 2002]. We consider the HiSo-Lo model as our standard case (see Table 1) based on its superior agreement with observations.

[8] We model export production by restoring the model simulated surface phosphate toward the observed values. The effect of iron fertilization is then simulated by setting the observed phosphate concentration to zero [*Gnanadesikan et al.*, 2003]. We conduct fertilization experiments in the tropics, the Southern Ocean, the North Pacific and the North Atlantic, considering two temporal and two spatial scenarios: In the first temporal scenario, we fertilize continuously for 100 years, whereas in the second temporal scenario, the fertilization is stopped after 10 years, but the model integration is continued for another 90 years (Table 1).

## 3. Results and Discussion

[9] Our model simulations suggest that the N<sub>2</sub>O feedback is substantial and in a few cases could actually outweigh the

radiative benefit from the  $CO_2$  drawdown. Our central estimates of the offsetting effect range from a few percent to more than 100% with the magnitude depending on (in decreasing importance) location, duration, and areal extent of the fertilization (Table 1). In contrast, we find relatively little sensitivity to the ocean circulation model. The largest offsets are found when fertilizing in the tropics (40% to 115%), whereas they are generally smaller for the Southern Ocean, despite larger absolute increases in oceanic N<sub>2</sub>O emissions. The offsets for the North Pacific and the North Atlantic are in between these two regions. Given the large differences in the magnitudes of the N<sub>2</sub>O feedback, it behooves us to understand the factors controlling the ocean N<sub>2</sub>O response to fertilization.

[10] We start with the long-term, large-scale Southern Ocean fertilization case, as this region has the largest potential for drawing down atmospheric CO<sub>2</sub> [Sarmiento and Orr, 1991]. Complete fertilization in this region results in a large increase in the oceanic uptake of  $CO_2$  from the atmosphere (Figure 1b), leading to an atmospheric CO<sub>2</sub> reduction of more than 60 ppm over 100 years. At the same time, the oceanic emissions of N<sub>2</sub>O increase substantially (Figure 1a), leading to a nearly 23 ppb increase in atmospheric N<sub>2</sub>O. As shown in Figure 1a, the fertilization induced emissions stem mostly from an increase in the N<sub>2</sub>O production associated with the nitrification pathway, while those from the low oxygen pathway remain low, except for the second half of the 21st century. The magnitude of the offsetting effect increases substantially with time (Figures 1c and 1d). This is because the fertilization induced CO<sub>2</sub> fluxes decrease rapidly after an initial pulse, while the oceanic N<sub>2</sub>O emissions tend to remain high.

[11] It is very instructive to contrast the temporal evolution in the Southern Ocean with that exhibited when the tropical areas are fertilized (Figures 1e to 1h). While the temporal evolutions appear overall similar in both regions, the roles of the nitrification and low oxygen pathways are reversed. In the tropical fertilization case, most of the increase in the oceanic  $N_2O$  emissions is a consequence of a strong stimulation of the low oxygen pathway, while the emissions by the nitrification pathway decrease below the initial levels after an early spike.

[12] The factors controlling the strong regional dependence become more evident by inspecting Figure 2. When the Southern Ocean is fertilized, export production in this region increases manifold (Figures 2a and 2b). As this exported organic material is remineralized in the interior ocean,  $N_2O$  production by the nitrification pathway is



**Figure 1.** Time series of the response of oceanic and atmospheric  $N_2O$  and  $CO_2$  to long-term (100yr) and large-scale fertilizations. Shown are the changes in response to fertilization (a–d) in the Southern Ocean (south of 31°S) and (e–h) in the Tropics (18°S–18°N) relative to control simulations. (a) and (e): Fertilization induced  $N_2O$  emissions from the ocean surface. (b) and (f): Fertilization induced  $CO_2$  uptake by the ocean surface. (c) and (g): Fertilization induced changes in atmospheric radiative forcing. (d) and (h): Magnitudes of the  $N_2O$  offsetting effect. The blue and red lines indicate the emissions induced by the nitrification and low oxygen pathways, respectively. The green line represents our central estimate, with the uncertainties indicated as a gray band. All solid lines show global changes, while the dashed lines represent the fluxes integrated over the fertilized areas only. The results are from the HiSo-Lo model.

similarly increased in this region (Figure 2f). At the same time, oxygen concentrations start to drop, increasing the volume of waters that have oxygen concentrations in the range critical for producing very high N<sub>2</sub>O yields (<50 µmol kg<sup>-1</sup>) (Figure 2d). This leads to an increase of the N<sub>2</sub>O production by the low oxygen pathway. This latter increase is nearly entirely

offset, however, by a decrease in the  $N_2O$  production by this pathway outside of the Southern Ocean (Figure 2f). This is a consequence of the fact that fertilization in the Southern Ocean tends to decrease export production in the low latitudes (Figure 2b), as the preformed nutrients that used to be transported to the low latitudes by the large-scale



**Figure 2.** Plots of zonally integrated properties controlling the marine production of  $N_2O$  and their changes in response to fertilization. (a) Zonally integrated export production in the control simulation (without fertilization). (b) Changes in zonally integrated export production as a result of fertilization in the Southern Ocean (dark gray) and in the tropics (light gray). (c) Zonally integrated volume of water that has oxygen concentration lower than 50  $\mu$ mol kg<sup>-1</sup>, i.e., O<sub>2</sub> concentrations that give raise to a high yield of N<sub>2</sub>O (d) Changes in the zonally integrated volume of water with critical oxygen concentrations. (e) Zonally and depth integrated production of N<sub>2</sub>O by the nitrification (blue) and low oxygen (red) pathways. (f) Changes in the zonally and depth integrated N<sub>2</sub>O production. The results are from the HiSo-Lo model.

circulation and fueled production there, are now consumed in the Southern Ocean and exported into the deep ocean [*Sarmiento and Orr*, 1991]. As a consequence, the volume of critical  $O_2$  concentrations in the low latitudes shrinks (Figure 2d), decreasing  $N_2O$  formation by the low oxygen pathway there (Figure 2f). By contrast, fertilization in the tropics does not show a similar compensation, so the effect of the oxygen decrease (Figure 2d) is fully expressed in the low oxygen pathway response (Figure 2f).

[13] More importantly, fertilization in the tropics tends to increase the volume of critical oxygen concentrations in an area that already has very low oxygen concentrations to start with (Figure 2c), leading to a 28% increase in the global volume of critical oxygen concentrations with a global increase in export production of only 1%. By contrast, fertilization in the Southern Ocean actually leads to a global decrease in the volume of critical oxygen concentrations of 6%, while almost doubling export production. In summary, the oxygen concentration of the waters underlying the fertilization areas play a crucial role in determining the magnitude of the N<sub>2</sub>O feedback, while changes and shifts in ocean export production lead to modulations of this response.

[14] The complexities in the processes that produce the  $N_2O$  and  $CO_2$  fluxes have also strong implications for where the changes in the air-sea fluxes occur. As shown in Figure 1, the global  $N_2O$  emissions and  $CO_2$  uptake are quite different from their corresponding local components. For example, if the benefit of fertilization in the tropical oceans was assessed only by measuring  $CO_2$  and  $N_2O$  fluxes over the area of the actual fertilization, the  $CO_2$  benefit as well as the  $N_2O$  offset would be overestimated by about 347% and 28%, respectively, leading to an overall overestimation of the radiative benefit by more than 500%. Therefore, verifications of the benefits of ocean fertilization require essentially global-scale assessments, which are very difficult to obtain given the small signals and the presence of natural variability [*Gnanadesikan et al.*, 2003].

[15] Will these conclusions also hold if we conduct the fertilizations over limited periods and over much smaller areas? As it turns out, after 100 years, the magnitudes of the N<sub>2</sub>O feedbacks in the 10 year fertilization scenarios are generally similar to those of the 100 year fertilizations, except for the tropics, where the offsetting effect in our central estimate is even larger (Table 1). If fertilizations are conducted over regions of a few 100 km<sup>2</sup> and over limited periods, the offsetting effects tend to get even larger (Table 1). Both responses are mainly driven by the large-scale and long-term decrease in the ocean's interior oxygen concentration, which leads to enhanced N<sub>2</sub>O production even when the CO<sub>2</sub> benefit is small or has stopped.

# 4. Conclusions

[16] Our model results demonstrate that the magnitude of the  $N_2O$  offsetting effect is substantial and particularly large in regions that are underlain by waters with low  $O_2$  con-

centrations. Therefore, this potential feedback needs to be taken into account when assessing the benefits and problems associated with the use of ocean iron fertilization as a  $CO_2$  mitigation option [*Chisholm et al.*, 2001]. Similarly, effects of changes in the magnitude and pattern of ocean productivity [*Gnanadesikan et al.*, 2003], ecosystem structure, fisheries, and the production of other trace gases [*Lawrence*, 2002] need to be considered.

[17] Acknowledgments. This study was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG03-00ER63010. We thank Jorge L. Sarmiento and Anand Gnanadesikan for providing us the Princeton Ocean Biogeochemistry Model. We greatly appreciate the modeling support by Rick Slater and Hartmut Frenzel. We enjoyed the very stimulating discussions with Cynthia Nevison as well as her insightful review. We thank a second reviewer for his helpful comments to improve the paper.

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