

# A modeling study of oceanic nitrous oxide during the Younger Dryas cold period

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[1] The marine production, cycling, and air-sea gas exchange of nitrous oxide ( $\text{N}_2\text{O}$ ) are simulated in a coupled climate-biogeochemical model of reduced complexity. The model gives a good representation of the large-scale features of the observed oceanic  $\text{N}_2\text{O}$  distribution and emissions to the atmosphere. The transient behavior of the model is tested for the Younger Dryas (Y-D) cold period (12,700–11,550 BP), which is simulated by releasing a freshwater pulse into the North Atlantic, causing a temporary collapse of the model's Atlantic thermohaline circulation (THC). A temporary drop in atmospheric  $\text{N}_2\text{O}$  of about 10 ppb results, while ice-core measurements show a total drop of 25 to 30 ppb. This suggests that terrestrial changes have also contributed to the observed variations. The main cause of the modeled reduction in atmospheric  $\text{N}_2\text{O}$  is increased oceanic storage in the short-term and a reduction of new production in the long-term due to increased stratification.

**INDEX TERMS:** 1620 Global Change: Climate dynamics (3309); 4850 Oceanography: Biological and Chemical: Organic marine chemistry; 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 3337 Meteorology and Atmospheric Dynamics: Numerical modeling and data assimilation. **Citation:** Goldstein, B., F. Joos, and T. F. Stocker, A modeling study of oceanic nitrous oxide during the Younger Dryas cold period, *Geophys. Res. Lett.*, 30(2), 1092, doi:10.1029/2002GL016418, 2003.

## 1. Introduction

[2] Nitrous oxide is an important contributor to the greenhouse effect, ranking third in radiative forcing strength of the well-mixed greenhouse gases [Ehhalt *et al.*, 2001]. It also plays an active role in the destruction of stratospheric ozone [Minschwaner *et al.*, 1993; Wennberg *et al.*, 1994]. Atmospheric  $\text{N}_2\text{O}$  concentration has increased from around 270 ppb in pre-industrial times to 317 ppb today due to the use of fertilizers, industrial production, and the burning of fossil fuels [Kroeze *et al.*, 1999]. Natural sources stem from microbial activity and consist of around 4 TgN/yr being produced in the ocean and 6 TgN/yr on land, adding up to about the same magnitude as the anthropogenic emissions [Nevison *et al.*, 1995; Kroeze *et al.*, 1999]. The main sink of  $\text{N}_2\text{O}$  is photodissociation in the stratosphere, leading to an atmospheric lifetime of around 120 years.

[3] The abrupt cooling events of the last glacial may serve as a testbed for the transient behavior of physical-

biogeochemical climate models. We set our focus on the Younger Dryas (Y-D) cold period, which lasted from around 12,700 yr BP to 11,550 BP [Johnsen *et al.*, 1992] and is associated with a slowdown of the North Atlantic THC, thought to have been caused by a release of freshwater from ice sheets [Broecker *et al.*, 1985; Clark *et al.*, 2002]. The concentration of atmospheric  $\text{N}_2\text{O}$  trapped in the GRIP ice core (Greenland) during the Y-D drops by 25 to 30 ppb [Flückiger *et al.*, 1999]. Changes of up to 50 ppb have been recorded for other abrupt climate changes during glacial periods, such as Dansgaard/Oeschger events and the transition to the Bølling/Allerød warm period [Flückiger *et al.*, 1999].

[4] The response of the carbon cycle and atmospheric  $\text{CO}_2$  to the Younger Dryas perturbation has been investigated in earlier studies applying the same model as used here [Marchal *et al.*, 1999a, 1999b]. Modeled atmospheric  $\text{CO}_2$  varies by about 10 ppm during the Younger Dryas event, in agreement with ice core data.

[5] The purpose of this study is to gain insight into the oceanic contribution to past variations in atmospheric  $\text{N}_2\text{O}$  concentrations, which is crucial for understanding future changes. We have implemented a formulation for production, transport, and outgassing of  $\text{N}_2\text{O}$  in a well-tested model for paleoclimate studies and examine the effects leading to changes in  $\text{N}_2\text{O}$  concentrations.

## 2. Model Description

[6] For this study, the three-basin latitude-depth ocean circulation model of Wright and Stocker [1992] is used, coupled to a one-dimensional, zonally and vertically averaged energy balance model of the atmosphere [Stocker *et al.*, 1992] with an active hydrological cycle [Schmittner and Stocker, 1999]. The marine biogeochemistry model of Marchal *et al.* [1998] is used to represent the new production/remineralization cycle of organic material as well as calcite precipitation and dissolution. Detailed model descriptions are given by Schmittner and Stocker [1999] and Marchal *et al.* [1998].

[7] The production of  $\text{N}_2\text{O}$  is parameterized according to the observed correlation between apparent oxygen utilization (AOU) and excess nitrous oxide ( $\Delta\text{N}_2\text{O}$ ). The latter is defined as the difference between the saturation concentration (with respect to the atmospheric partial pressure) and the in situ concentration of  $\text{N}_2\text{O}$ :

$$\Delta\text{N}_2\text{O} = [\text{N}_2\text{O}] - [\text{N}_2\text{O}]_{\text{sat}}$$

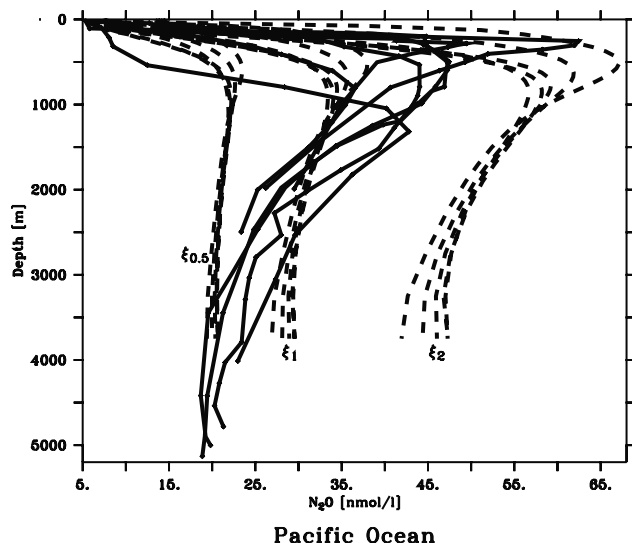
Measurements from ship cruises show a linear correlation between  $\Delta\text{N}_2\text{O}$  and AOU, which has led to the prevailing

view that nitrification during the decomposition of organic material in the ocean is the main source for oceanic  $\text{N}_2\text{O}$  [Yoshinari, 1976; Elkins et al., 1978; Butler et al., 1989; Kim and Craig, 1990; Oudot et al., 1990]. Data summarized by Suntharalingam and Sarmiento [2000] yield a range from  $0.33$  to  $3.1 \cdot 10^{-4}$  mol  $\Delta\text{N}_2\text{O}$  per mol AOU, with an intercept ranging from  $-49.4$  to  $+2.3$  nmol  $\Delta\text{N}_2\text{O}$  for an AOU of zero. In the model base case  $\xi_1$ , we assume that one molecule of  $\text{N}_2\text{O}$  is produced per 10,000 molecules of oxygen that are consumed during remineralization of organic material.  $\text{N}_2\text{O}$  production in the euphotic zone is assumed to be zero. For sensitivity studies, the  $\text{N}_2\text{O}$  production ratio is varied within the observed boundaries with the reference cases  $\xi_2$  (doubled  $\text{N}_2\text{O}$  production ratio) and  $\xi_{0.5}$  ( $\text{N}_2\text{O}$  production cut in half). The process of denitrification, which is both a source and a sink for oceanic  $\text{N}_2\text{O}$ , is not considered because it depends heavily on local oxygen levels, which are not resolved in the model.

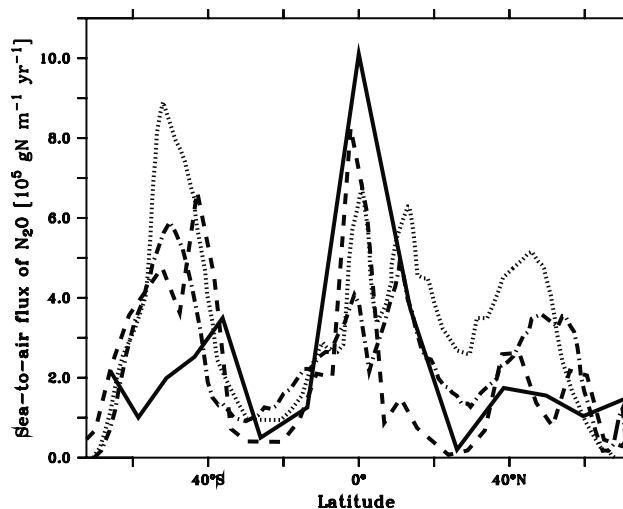
[8] The ocean model is spun up from rest by relaxation to modern-day surface salinity and temperature for the physical component and phosphate concentrations for the biological component. Atmospheric  $\text{N}_2\text{O}$  is set to 270 ppb and its lifetime to 120 years. After 12,000 years, the ocean is coupled to the atmosphere. After another 7,000 years, marine  $\text{N}_2\text{O}$  production is diagnosed from the net export production out of the euphotic zone, and the size of the terrestrial  $\text{N}_2\text{O}$  source is determined to balance the atmospheric sink and the oceanic emissions. Then, the marine biology is switched to prognostic mode [Marchal et al., 1998] and the atmospheric  $\text{N}_2\text{O}$  is allowed to evolve freely for another 1,000 years before transient simulations are started.

### 3. Model Validation

[9] Figure 1 compares model output with observed  $\text{N}_2\text{O}$  depth profiles in the Pacific. The model output reflects the general course of the measured depth profiles, but does not



**Figure 1.** Depth profiles of nitrous oxide in the Pacific Ocean. Ship measurements are marked with crosses [Cohen and Gordon, 1979; Yoshida et al., 1989; Butler et al., 1987]. The smooth profiles are the corresponding model results obtained with  $\text{N}_2\text{O}$  production ratios of  $\xi_1$ ,  $\xi_{0.5}$ , and  $\xi_2$ .



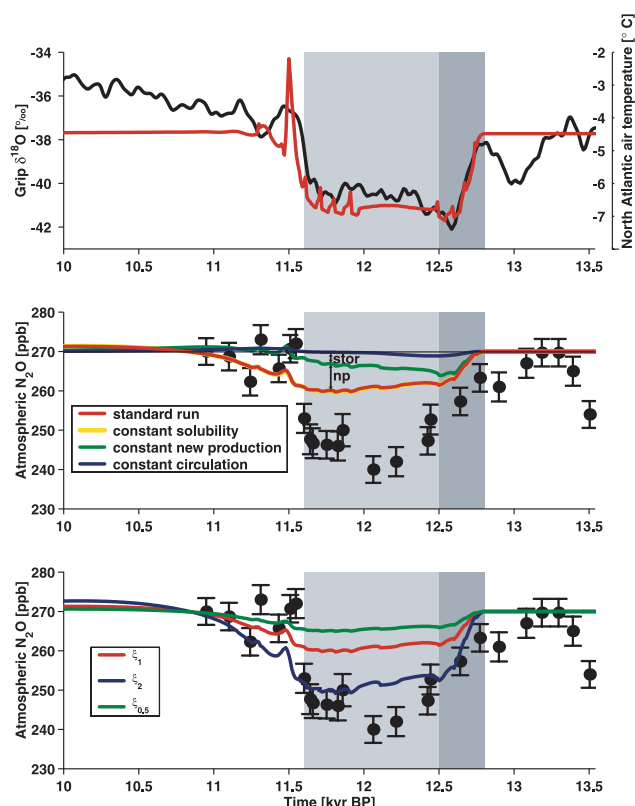
**Figure 2.** Sea-to-air flux of  $\text{N}_2\text{O}$  for ocean circulation models and calculations based on  $\Delta p\text{N}_2\text{O}$  measurements. The solid line is from this study, the dashed line from the 3D model in Suntharalingam and Sarmiento [2000]. The dotted and dash-dotted lines are from calculations based on  $\Delta p\text{N}_2\text{O}$  measurements by Nevison et al. [1995] and Suntharalingam and Sarmiento [2000], respectively.

capture the observed vertical gradients. Cruise data show a steeper increase and subsequent decrease in  $\text{N}_2\text{O}$  concentration with depth. The main cause of the smooth depth profiles in the model is the coarse resolution. The model works with zonal averages, whereas the data show local concentrations. Averaging out a series of varying local profiles with large depth gradients yields a smoothed average profile.

[10] Model results give global oceanic  $\text{N}_2\text{O}$  emissions of  $4.2$  TgN/yr, ranging from  $2.1$  to  $8.4$  TgN/yr for  $\text{N}_2\text{O}$  production ratios of  $\xi_2$  and  $\xi_{0.5}$ , respectively. This is in good agreement with studies based on surface partial pressure difference ( $3.8$  ( $1.2$ – $6.8$ ) TgN/yr [Nevison et al., 1995]) and other modeling studies ( $3.85$  ( $2.7$ – $8.0$ ) TgN/yr [Suntharalingam and Sarmiento, 2000]). Agreement with these studies is also seen in the trimodal meridional distribution of  $\text{N}_2\text{O}$  sea-to-air flux, with maxima in the tropics and at high latitudes. The model, however, underestimates outgassing at high latitudes, and overestimates outgassing in the tropics (see Figure 2).

### 4. Younger Dryas Simulation

[11] Ice core data show that atmospheric  $\text{N}_2\text{O}$  was lower by about 30 ppb during the Younger Dryas cold period [Flückiger et al., 1999], and ocean sediment and ice core records suggest that the North Atlantic THC was collapsed during that time. A freshwater flux into the North Atlantic, causing a temporary breakdown of the THC, is used in the model to mimic Younger Dryas conditions. The release rate is assumed to rise linearly to a maximum at the middle of the release period and then to decrease again linearly until the end of the freshwater release. Duration and volume of the freshwater pulse are chosen to most closely match the temperature variation inferred from the  $\delta^{18}\text{O}$  record of the GRIP ice core (Figure 3, top). A simulated freshwater volume of  $3.0 \cdot 10^{15}$   $\text{m}^3$  released during 300 years shows the best match. Recon-



**Figure 3.** Younger Dryas data and model output. Top: GRIP  $\delta^{18}\text{O}$  record plotted against North Atlantic air temperatures for a freshwater pulse simulating the Y-D cold event. Middle: GRIP  $\text{N}_2\text{O}$  record [Flückiger et al., 1999] plotted against modeled atmospheric  $\text{N}_2\text{O}$  partial pressures for different model runs, each keeping a certain mechanism leading to  $\text{N}_2\text{O}$  reduction in constant steady state. The effect due to increased storage is marked with “stor”, the effect due to the decrease in new production with “np”. The small solubility effect is seen in the difference between the standard run and the run with constant solubility, as well as in the difference between the baseline and the run with constant circulation. Bottom: GRIP  $\text{N}_2\text{O}$  record plotted against modeled atmospheric  $\text{N}_2\text{O}$  partial pressures for different production ratios in nitrification. The dark shading shows the period of freshwater release, the light shading the Y-D cold period. Error bars on the measurements represent 1 $\sigma$  deviation.

structions of Laurentide Ice Sheet melting by Clark et al. [2002] yield freshwater fluxes of the same order of magnitude in both volume and duration.

[12] Modeled atmospheric  $\text{N}_2\text{O}$  dropped only by about 10 ppb for the base case  $\xi_1$ . The magnitude of the drop is proportional to the chosen  $\Delta\text{N}_2\text{O}/\text{AOU}$  ratio: the ratio of  $\xi_{0.5}$  leads to a 5 ppb drop,  $\xi_2$  to 20 ppb (Figure 3, bottom). The model underestimates the magnitude of the atmospheric  $\text{N}_2\text{O}$  drop. However, emissions from the terrestrial biosphere are kept constant and only marine changes are considered in the model.

[13] We separate three different effects leading to the  $\text{N}_2\text{O}$  drop in the model. A decrease in new production, due to more stable layering when deep water formation is

reduced, leads to a decrease in atmospheric  $\text{N}_2\text{O}$ . With an increased stratification, less nutrients upwell into the euphotic zone, causing a decrease in new production. When less organic material is available for remineralization, the nitrification rate decreases in the model and less  $\text{N}_2\text{O}$  is formed. An increased storage of  $\text{N}_2\text{O}$  in the ocean temporarily reduces the atmospheric  $\text{N}_2\text{O}$  concentration. With reduced circulation and vertical mixing, the residence time of  $\text{N}_2\text{O}$  in the ocean increases and the ocean inventory increases. This leads to a temporary reduction in outgassing and atmospheric  $\text{N}_2\text{O}$  until the ocean inventory has reached its new equilibrium. An immediate response of the model to a freshwater pulse is due to the haline solubility effect. Nitrous oxide is more soluble in fresh water and is therefore taken up by the ocean when a freshwater pulse reduces the salinity of the northern Atlantic. As the freshwater mixes down, the effect is subdued. Solubility decreases with decreasing temperatures. Changes in the modeled sea surface temperature, showing strong cooling in the North Atlantic region and warming in the Southern Hemisphere, can also affect atmospheric  $\text{N}_2\text{O}$  by changing the interplay between sea water chemistry, air-sea exchange, and marine transport and production of  $\text{N}_2\text{O}$ .

[14] To examine the contribution of each effect to the modeled drop in atmospheric  $\text{N}_2\text{O}$ , we assume, in turn, solubility, ocean circulation (plus new production), and new production only to remain constant during the Younger Dryas climate variation (Figure 3, middle). Changes in solubility due to freshening and temperature changes have almost no effect on the atmospheric  $\text{N}_2\text{O}$  concentration. The increased storage of  $\text{N}_2\text{O}$  in the ocean in response to the THC breakdown has a significant effect on the atmospheric  $\text{N}_2\text{O}$  concentration in the first 300 years after the start of the freshwater pulse. This storage effect diminishes over time, and atmospheric  $\text{N}_2\text{O}$  approaches its initial value towards the end of the simulated Y-D period when new production is kept constant. While the storage effect dominates the short-term response to the THC changes, the long-term response is dominated by changes in new production and, hence,  $\text{N}_2\text{O}$  production. It takes several centuries, the typical time scale for surface-to-deep ocean exchange, until lowest atmospheric  $\text{N}_2\text{O}$  values are reached. It also takes several centuries until atmospheric  $\text{N}_2\text{O}$  has reached its initial value again after the North Atlantic THC has recovered.

## 5. Conclusions

[15] The model gives a good representation of oceanic  $\text{N}_2\text{O}$  distribution and outgassing to the atmosphere. Simulations of a Y-D-type cold period show a drop of 10 (5–20) ppb in modeled atmospheric  $\text{N}_2\text{O}$  concentrations, whereas ice core measurements show a drop of 25–30 ppb. The rise at the end of the Y-D is abrupt in measurements; in the model, the rise takes place over about 1000 years. These discrepancies suggest that changes in oceanic emissions are not solely responsible for the observed reduction of atmospheric  $\text{N}_2\text{O}$  during the Y-D. Changes in the terrestrial biosphere are also likely to have had a major influence. In the model, the effects leading to the drop in atmospheric  $\text{N}_2\text{O}$  are a reduction in sea-to-air flux due to decreased overturning in the short-run and a reduction of marine  $\text{N}_2\text{O}$  production in the long-run.

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