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Nitrous oxide in the deep waters of the world's oceans

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Abstract. We present a compilation and analysis of N_2O data from the deep-water zone of the oceans below 2000 m. The N_2O values show an increasing trend from low concentrations in the North Atlantic Ocean to high concentrations in the North Pacific Ocean, indicating an accumulation of N_2O in deep waters with time. We conclude that the observed N_2O accumulation is mainly caused by nitrification in the global deep-water circulation system (i.e., the "conveyor belt"). Hydrothermal and sedimentary N_2O fluxes are negligible. We estimate the annual N_2O deep-water production to be 0.3 ± 0.1 Tg. Despite the fact that the deep sea below 2000 m represents about 95% of the total ocean volume, it contributes only about 3–16% to the global open-ocean N_2O production. A rough estimate of the oceanic N_2O budget suggests that the loss to the atmosphere is not balanced by the deep-sea nitrification and pelagic denitrification. Therefore an additional source of 3.8 Tg N_2O yr^{-1} attributed to nitrification in the upper water column (0–2000 m) might exist. With a simple model we estimated the effect of changes in the North Atlantic Deep Water (NADW) formation for deep-water N_2O. The upper water N_2O budget is not significantly influenced by variations in the N_2O deep-water formation. However, the predicted decrease in the NADW formation rate in the near future might lead to an additional source of atmospheric N_2O in the range of about 0.02–0.4 Tg yr^{-1}. This (anthropogenically induced) source is small, and it will be difficult to detect its signal against the natural variations in the annual growth rates of tropospheric N_2O.

1. Introduction

Nitrous oxide (N_2O) is an atmospheric trace gas which significantly influences, directly and indirectly, Earth's climate. In the troposphere it acts as a greenhouse gas, and in the stratosphere it is the major source for NO radicals, which are involved in one of the main ozone reaction cycles [*Prather et al.*, 1996].

Recently published source estimates indicate that the world's oceans play a major, but not dominant, role in the global budget of atmospheric N_2O [*Bouwman et al.*, 1995; *Khalil and Rasmussen*, 1992; *Prather et al.*, 1996]. Most of the world's ocean surface layer is near gas-exchange equilibrium with the atmosphere [*Nevison et al.*, 1995], whereas a subsurface N_2O accumulation is generally associated with the oxygen minimum, indicating that nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) is responsible for N_2O production [*Butler et al.*, 1989; *Cohen and Gordon*, 1979; *Yoshinari*, 1976]. In intermediate layers with extreme oxygen depletion (i.e., suboxic conditions), as found in the Arabian Sea and the eastern tropical Pacific Ocean, N_2O is also produced in considerable amounts by denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$) [*Codispoti and Christensen*, 1995]. Recent dual-isotope measurements of $\delta^{15}N$ and $\delta^{18}O$ brought some new insights. *Dore et al.* [1998] suggested that nitrification is the dominant N_2O production pathway in surface waters of the subtropical Pacific Ocean. Additionally, *Naqvi et al.* [1998] speculated about a coupling of nitrification and denitrification in the surface layer of the Arabian Sea. Measurements of N_2O in deep waters are sparse, and the mechanism of the N_2O production in deep waters is still under debate [*Kim and Craig*, 1990; *Yoshida et al.*, 1989].

Here we present a compilation of N_2O measurements from water depths below 2000 m in order to evaluate the global distribution of N_2O in deep waters of the world's oceans. On the basis of this data set, an estimate of the magnitude of N_2O deep-water production and a discussion about its role for the global N_2O budget are presented. With a simple model we evaluate the implications of possible changes in the North Atlantic Deep Water (NADW) formation for the global N_2O budget.

2. Data Compilation

In Table 1 we present an overview of N_2O data from deep waters below 2000 m. The boundary of 2000 m was chosen to gain a most representative data set for N_2O in the deep waters. Three points led to our choice:

1. In order to investigate the N_2O distribution in the deep waters, we have to exclude the effects of the thermocline circulation, which could reach down to about 1000–1500 m [*Broecker and Peng*, 1982].

2. As mentioned in section 1, N_2O is mainly produced in the oxygen minimum zone (OMZ), whose lower boundary is found down to about 1200 m in the world's oceans [*Broecker and Peng*, 1982]. Since N_2O is produced in considerable amounts in the OMZ, there is usually a decreasing N_2O gradient toward deep-water layers. A check of the available data sets for N_2O gradients revealed that the choice of 2000 m minimizes a possible bias due to N_2O gradients at the top of the deep-water layer (see also discussion of diapycnal mixing in section 4).

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Table 1. Compilation of N_2O Data in Deep Waters Below 2000 m.

Latitude, °N or °S[a]	Longitude, °W[a] or °E	Date	Depth interval, m	Mean N_2O, nmol L^{-1}	SD[b] nmol L^{-1}	Minimum, nmol L^{-1}	Maximum, nmol L^{-1}	Samples	Calculated[c] (C) or Estimated[c] (E)	Reference
						North Atlantic				
65	−1.5	Aug. 1976	2100–2500	11.0	2.6	7.4	14.7	8	C	*Hahne* [1977]
64	0	Aug. 1976	2000–2800	12.2	1.4	10.0	15.6	13	C	*Hahne* [1977]
39.1	−62.4	May, July 1972	2000–5000	16	0.5	15	16	7	E	*Yoshinari* [1976]
35.9	−63.7	June 1972	2000–5000	15	0.7	14	16	14	E	*Yoshinari* [1976]
						South Atlantic				
−36	−45.1	Oct. 1994	2000–5000	16	1	14	17	8	E	*Butler et al.* [1995]
						North Indian				
24.3	58.2	Sept. 1986	2000–2700	25.3		24.0	26.6	2	C	*Law and Owens* [1990][d]
23.7	59.1	Sept. 1986	2000–2750	17.4	4.7	12.5	21.9	3	C	*Law and Owens* [1990][d]
22.7	60.7	Sept. 1986	2000–3000	23.5	4.4	20.1	28.5	3	C	*Law and Owens*, [1990][d]
21.8	64	April–May 1994	2000–2750	27	5.5	22	33	3	E	*Lal et al.* [1996]
21.3	63.3	Sept. 1986	2000–3000	20.7	4.1	16.6	24.7	3	C	*Law and Owens* [1990][d]
20	65.8	May 1997	2000–3150	18.8		14.4	23.2	2	C	Bange et al., submitted manuscript [1999]
19	67	Sept. 1986	2000–3200	15.3	2.2	13.0	17.5	3	C	*Law and Owens* [1990][d]
19	64	April–May 1994	2000–3000	26	6.1	20	33	3	E	*Lal et al.* [1996]
18	69	Dec. 1988	2000–3000	25	1.1	24	26	3	E	*Naqvi and Noronha* [1991]
18	58	Aug. 1995	2600–3200	16.5	1.8	14.8	18.3	3	C	Bange et al., submitted manuscript [1999]
17.5	59.1	July 1997	2000–3600	20.8	4.0	16.4	24.2	3	C	Bange et al., submitted manuscript [1999]
17.2	59.8	July 1995	2900–3900	16.5	1.0	16.0	17.5	3	C	Bange et al., submitted manuscript [1999]
16.3	61.4	Aug. 1995	2000–3900	17.2	3.7	12.2	24.8	10	C	Bange et al., submitted manuscript [1999]
16.2	60.3	May 1997	2500–4100	16.7	3.5	12.9	21.7	4	C	Bange et al., submitted manuscript [1999]
16	62	July 1997	2000–3950	18.5	3.4	14.4	22.4	4	C	*Law and Owens* [1990][d]
16	62	July 1995	2500–3900	17.9	1.0	16.3	18.8	5	C	*Law and Owens* [1990][d]
15.6	68.6	May 1997	3000–3900	18.3	3.1	16.1	21.8	3	C	Bange et al., submitted manuscript [1999]
14.5	65	July 1995	2000–4000	12.3	5.1	8.1	21.0	5	C	Bange et al., submitted manuscript [1999]
14.5	64.6	May 1997	2000–4000	18.3	1.9	15.7	20.4	5	C	Bange et al., submitted manuscript [1999]
14.4	66.9	Sept. 1986	2500–3900	22.4	2.3	19.3	23.5	4	C	Bange et al., submitted manuscript [1999]
12	67	Sept. 1986	2250–4200	13.5	1.5	11.2	14.4	4	C	Bange et al., submitted manuscript [1999]
11	64	May–July 1994	2000–3000	24	5.4	20	30	3	E	*Lal et al.* [1996]
10.1	64.7	May 1997	2000–4050	16.2	1.3	15.5	18.0	5	C	Bange et al., submitted manuscript [1999]
10	65	July 1995	2250–4400	15.7	2.2	12.7	19.6	7	C	Bange et al., submitted manuscript [1999]
8	67	Sept. 1986	2000–4500	11	1.3	9.1	11.8	4	C	*Law and Owens* [1990][d]
6	65	July 1995	2050–4400	20.4	1.7	18.2	22.4	6	C	Bange et al., submitted manuscript [1999]
4	67	Sept. 1986	2000–3050	10.3		7.5	13.0	2	C	*Law and Owens* [1990][d]
3	65	July 1995	2000–2800	19.1	2.3	16.5	21.5	5	C	Bange et al., submitted manuscript [1999]
						South Indian				
-27.63	90	June 1987	2000–3000	22.0		20.5	23.4	2	C	*Butler et al.* [1988]

Table 1.

Latitude, °N or °S[a]	Longitude, °W[a] or °E	Date	Depth interval, m	Mean N_2O, nmol L^{-1}	SD[b], nmol L^{-1}	Minimum, nmol L^{-1}	Maximum, nmol L^{-1}	Samples	Calculated (C)[c] or Estimated (E)[c]	Reference
						North Pacific				
48.4	155.6	May 1987	2500–3100	28.6		25.9	31.3	2	C	*Butler et al.* [1988]
48	156.0	May 1987	3900–5900	22.2	0.8	21.7	23.1	3	C	*Butler et al.* [1988]
47.7	156.3	May 1987	2000–4600	21.6	4.0	16.1	25.6	4	C	*Butler et al.* [1988]
47.5	156.5	May 1987	2000–3900	22.6		21.6	23.6	2	C	*Butler et al.* [1988]
47.1	157.0	May 1987	2500–4600	24.6	1.4	23.6	26.2	3	C	*Butler et al.* [1988]
46.8	157.1	May 1987	2500–4900	22.0	1.5	20.4	24.1	4	C	*Butler et al.* [1988]
46.8	−126.8	July 1977	2000–2500	25		24	26	2	E	*Cohen and Gordon* [1979]
46.6	157.3	May 1987	2950–4500	23.2	1.2	21.8	24.1	3	C	*Butler et al.* [1988]
46.4	157.5	May 1987	2950–4900	22.4	1.0	21.6	23.5	3	C	*Butler et al.* [1988]
46.2	157.7	May 1987	2500–4900	23.1	1.8	21.6	25.0	3	C	*Butler et al.* [1988]
46.0	157.9	May 1987	2500–5100	21.1	2.7	18.9	24.8	4	C	*Butler et al.* [1988]
45.8	158.1	May 1987	2500–5000	20.8	3.0	18.7	25.2	4	C	*Butler et al.* [1988]
45.5	158.4	May 1987	2950–3900	22.5		20.9	24.0	2	C	*Butler et al.* [1988]
45.2	160.3	Aug.–Sept.1983	2000–4800	24	3.8	19	30	11	E	*Yoshida et al.* [1989]
28.1	152.9	Aug.–Sept.1983	2500–4000	26	3.4	22	29	3	E	*Yoshida et al.* [1989]
22.4	170.1	Oct.–Dec. 1993	2000–5000	22.5	4.0	19	28	4	E	*Usui et al.* [1998]
22.8	−158.1	Oct.–Dec. 1993	2000–5000	22	3.0	20	26.5	4	E	*Usui et al.* [1998]
22.8	−148.0	Sept.–Oct. 1996	2000–3000	25.5		23	28	2	E	*Dore et al.* [1998]
22.6	−107.7	Dec. 1993	2250–2500	25	1.1	24	26	3	E	*Yoshinari et al.* [1997]
15.1	−105.9	Jan. 1977	2000–2750	18		17	19	2	E	*Cohen and Gordon* [1979]
10.8	−111.9	Jan. 1977	2000–2500	18		16	19	2	E	*Cohen and Gordon* [1979]
0.1	−159	Oct.–Dec. 1993	2500–5000	20	1.4	18	20	3	E	*Usui et al.* [1998]

[a] West longitudes and south latitudes are given as negative values.

[b] SD stands for standard deviation.

[c] Calculated (C) indicates that the values are based on data listed in reports. Estimated (E) indicates that the values are estimated from figures in the given reference.

[d] Original data set provided by C. S. Law.

Table 2. Overview of the data used in Figures 1 and 2.

	N_2O,[a] nmol L^{-1}	Age of Deep Water at 3000 m,[b] years
North Atlantic Ocean	13.6 ± 2.3 (4)	153 ± 66 (6)
South Atlantic Ocean	16 (1)	465 (1)
North Indian Ocean	18.7 ± 4.4 (28)	1227 ± 43 (5)
South Indian Ocean	22.0 (1)	1250 (1)
North Pacific Ocean	22.7 ± 2.5 (22)	1759 ± 176 (19)

Data are given as mean ± standard deviation. The number of profiles used for averaging is given in parentheses.

[a] Based on the data compilation in Table 1.

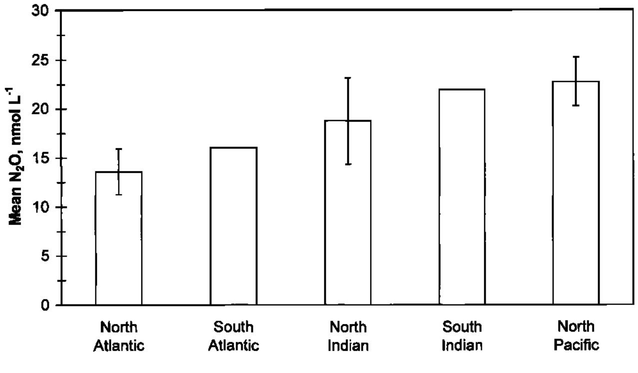
[b] Based on the data set by *Broecker et al.* [1988].

3. The choice of a 3000-m boundary would reduce the available data considerably, making an interpretation more difficult.

Unfortunately, only a few data are available as data reports, and thus we had to include data extracted from figures which are associated with an enhanced error for the extracted data. In order to keep the data uncertainties as small as possible, we generally did not consider N_2O data presented as contour plots, and we considered only depth profiles with more than one point below 2000 m. N_2O concentrations are usually given in nmol L^{-1} or ng L^{-1}. References reporting saturation values (in %) or excess N_2O (i.e., ΔN_2O in nmol L^{-1}), which require a correction introducing further uncertainties, were therefore not considered. Unfortunately, there are no data from the South Pacific and the Southern Oceans which match our criteria, and only a single profile was found for both the South Atlantic and the south Indian Oceans (Table 1). The very early N_2O measurements from the South Pacific Ocean reported by *Craig and Gordon* [1963] and from the North Atlantic Ocean reported by *Junge et al.* [1971] appear to be biased by analytical problems and thus are not included in Table 1. Despite our rigorous selection criteria, we were able to tabulate mean N_2O values from 56 depth profiles, providing for the first time an overview of the N_2O distribution in deep waters of the world's ocean.

3. Results

The N_2O data listed in Table 1 vary between 7 and 33 nmol L^{-1}. Surprisingly, the range for the data from the north Indian Ocean, which exclusively consists of data from the Arabian Sea, is exceptionally high. The reason for this variability is unknown (but see also section 4). From the mean values of each profile we calculated overall mean N_2O concentrations for the major ocean basins (Table 2). The highest mean N_2O value (22.7 ± 2.5 nmol L^{-1}) was found for the north Pacific Ocean, whereas the lowest mean N_2O value (13.6 ± 2.3 nmol L^{-1}) was found for the North Atlantic Ocean (Figure 1). Because the deep waters of the North Atlantic, north Indian, and North Pacific Oceans represent the major starting and turning points of the global deep-water circulation system (i.e., the so-called conveyor belt system), we might argue that the observed N_2O differences are caused by an accumulation on the two flow paths from the deep North Atlantic to the deep North Pacific Oceans and from the Weddell Sea to the north Indian Ocean [*Broecker*, 1991; *Schmitz*, 1995; *You*, 1999]. To test this hypothesis, we considered the mean age of the deep waters at 3000-m depth in each ocean basin (Table 2) [*Broecker et al.*, 1988]. We found a good correlation between the mean ages of the deep waters and the mean N_2O concentrations, indicating that N_2O in the deep waters is accumulating with time (Figure 2). The slope of the linear regression (5.7 ± 1.0 nmol m^{-3} yr^{-1}) in Figure 2 can be set equal to an annual N_2O accumulation rate. With the volume of about 1.15×10^{18} m^3 for the depth range from 2000 to 6000 m [*Menard and Smith*, 1966] we estimate an annual N_2O accumulation of 0.29 ± 0.05 Tg yr^{-1}.



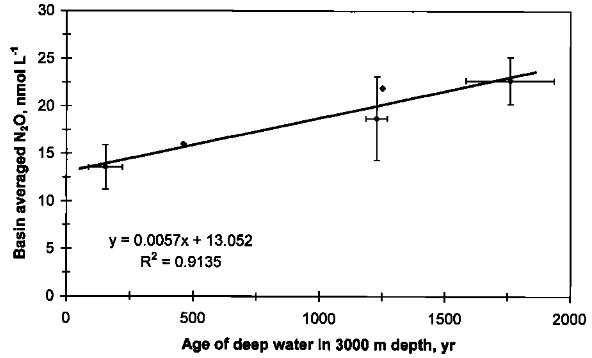


Figure 2. Basin-averaged N_2O concentrations in deep waters below 2000 m versus basin-averaged ages of the deep waters in 3000 m.

4. Discussion

What causes the observed N_2O accumulation? There are several possibilities:

First, mixing of waters with different N_2O concentrations may play a role. Transport of N_2O into the deep waters is mainly driven by diapycnal diffusivity along N_2O concentration gradients at the upper boundary of the deep-water layer (i.e., 2000 m). The diapycnal flux F_d of N_2O can be parameterized as

$$F_d = -K\, dN_2O / dz = -K\, [(N_2O)_h - (N_2O)_z] / (h - z),$$

where K is the diapycnal eddy diffusivity, dN_2O/dz is the concentration gradient, $(N_2O)_h$ stands for the N_2O concentration in depth h (above 2000 m), and $(N_2O)_z$ stands for the concentration in depth z (below 2000 m). Mean N_2O concentration gradients are listed in Table 3. N_2O gradients in the North Atlantic Ocean are close to zero, whereas the steepest N_2O

Table 3. Overview of the Calculated N_2O Concentration Gradients Across 2000 m.

Ocean Basin	Mean dN_2O/dz, µmol m^{-4}	SD,[a] µmol m^{-4}	Profiles	Data Set Used[b]
North Atlantic				
	0.001		1	*Hahne* [1977]
	> −0.001[c]		4	*Yoshinari* [1976]
South Atlantic				
	−0.010[c]		1	*Butler et al.* [1995]
North Indian				
	−0.011	0.009	19	Bange et al., submitted manuscript [1999]
	−0.013	0.010	9	*Law and Owens* [1990]
South Indian				
	−0.007	0.003	4	*Butler et al.* [1988]
North Pacific				
	−0.009	0.002	12	*Butler et al.* [1988]
Mean	−0.007			

Negative gradients indicate that $(N_2O)_h$ (i.e., above 2000 m) is greater than $(N_2O)_z$ (i.e., below 2000 m).

[a] SD stands for standard deviation.

[b] See also Table 1.

[c] Estimated from figure in the given reference.

gradients were observed for the north Indian Ocean (i.e., the Arabian Sea). The Arabian Sea appears to be the site of pronounced cross-isopycnal and dianeutral mixing processes [*Brandes et al.*, 1998; *You*, 1999]. Mixing effects in connection with very high N_2O values (up to 110 nmol L^{-1}) as found in the oxygen minimum zone (150–1200 m) of the Arabian Sea [*Law and Owens*, 1990] might be the reason for the observed wide range of N_2O concentrations of the Arabian Sea data listed in Table 1. With a mean N_2O gradient (dN_2O/dz) of about −0.01 µmol m^{-4}, a mean diapycnal diffusivity K for deep water of 0.1 x 10^{-4} m^2 s^{-1} [*Polzin et al.*, 1997], and an ocean area of 290 x 10^{12} m^2 (i.e., the ocean area with water depths deeper than 2000 m [*Menard and Smith*, 1966]), we estimate a diapycnal flux of about 0.04 Tg N_2O yr^{-1}. This is about 13% of the N_2O accumulation in the deep waters, indicating a small contribution by vertical transport of N_2O.

Second, N_2O may be emitted into deep waters through hydrothermal vents. The few measurements of N_2O concentrations in the hydrothermal vent waters of the Galapagos spreading center (0.8°N, 86.0°W) range from about 10 nmol L^{-1} to about 110 nmol L^{-1} [*Lilley et al.*, 1982]. The observed good linear correlations of the N_2O vent concentrations with silica showed either positive or negative slopes. Thus *Lilley et al.* [1982] speculated that N_2O might be consumed or produced in hydrothermal vents depending on the local redox potential. With the recent estimate of the global hydrothermal input of 0.15 ± 0.11 Tmol Si yr^{-1} [*Tréguer et al.*, 1995] and the observed N_2O to Si molar ratios of −0.034 x 10^{-3} and 0.178 x 10^{-3} [*Lilley et al.*, 1982], we estimate the global N_2O input by hydrothermal vents to range from −0.0002 to 0.001 Tg N_2O yr^{-1}. Thus we conclude that the contribution of hydrothermal systems to the deep-water accumulation of 0.3 Tg N_2O yr^{-1} is negligible.

Third, N_2O is produced in sediments by denitrification and/or nitrification and can be subsequently released into the water column above [*Seitzinger*, 1990, *Usui et al.*, 1998]. Unfortunately, only a few N_2O fluxes from deep-sea sediments of the equatorial Pacific and the subtropical North Pacific have been reported [*Usui et al.*, 1998]. On the basis of the flux data by *Usui et al.* [1998] (which range from 0.17 to 0.23 nmol N m^{-2} h^{-1}) and by applying a deep ocean area of 290 x 10^{12} m^2 (i.e., the ocean area with water depths deeper than 2000 m [*Menard and Smith*, 1966]), we extrapolate an annual N_2O release of 0.010 to 0.013 Tg. The sedimentary flux represents about 3–4% of the N_2O deep-water accumulation of 0.3 Tg N_2O yr^{-1} indicating that the N_2O flux across the sediment–water column interface in the deep sea is of minor importance.

Fourth, N_2O could be produced in situ in the deep water. In most studies of oceanic N_2O a positive linear correlation between excess N_2O (ΔN_2O = N_2O(observed) − N_2O(saturated)) and the apparent oxygen utilization (AOU = O_2(saturated) − O_2(observed)) was observed. This led to the prevailing view that during decomposition of organic material in the ocean, nitrification is the main source for oceanic N_2O [*Butler et al.*, 1989; *Cohen and Gordon*, 1979; *Yoshinari*, 1976]. Since most studies on oceanic N_2O focus on the upper water column, only a few ΔN_2O–AOU relationships including deep-water data are available [*Butler et al.*, 1989; *Cohen and Gordon*, 1979; *Law and Owens*, 1990; *Naqvi and Noronha*, 1991; H. W. Bange et al., Nitrous oxide cycling in the Arabian Sea, submitted to *Journal of Geophysical Research*, 1999 (hereinafter referred to as Bange et al., submitted manuscript)]. The good correlations of the ΔN_2O–AOU relationships found for the Pacific Ocean (Table 4) indicate that N_2O in deep waters of the Pacific Ocean is produced by nitrification. Nitrification in the Arabian Sea deep waters seems to be biased by another process as indicated by the low correlation coefficient [Bange et al., submitted manuscript, 1999]. We speculate that down-mixing of water affected by denitrification might be the reason for the observed low correlation [Bange et al., submitted manuscript, 1999] (see also above discussion about diapycnal mixing).

The unexpected finding of the considerable ^{15}N enrichment in deep-water N_2O caused a controversy about the prevailing production mechanism in deep waters. *Yoshida et al.* [1989] proposed that denitrification in particulate organic matter is the major process, whereas *Kim and Craig* [1990] argued that N_2O is produced by nitrification, which might be associated with a

Table 4. ΔN_2O–AOU Relationships Which Include Deep-Water Data.

Ocean Area	Slope (ΔN_2O/AOU)	Intercept	R^2 / Samples	Depth Range, m	Reference
Eastern tropical North Pacific	0.152 ± 0.013	–31.33	0.916 / 14	700–3000[b]	*Cohen and Gordon* [1979]
Northeastern Pacific	0.218 ± 0.026	–46.25	0.976 / 5	1000–2500[b]	*Cohen and Gordon* [1979]
Western Pacific, eastern Indian	0.125+0.00993 t[a]	–13.5	not given	0–5900	*Butler et al.* [1989]
Arabian Sea	0.1066+0.00455 t[a]	3.20	not given	0–3500[b]	*Naqvi and Noronha* [1991]
Arabian Sea	AOU<197: 0.033	5.5	significant at the	0–3500	*Law and Owens* [1990]
	AOU>197: 0.31	–49.4	1% level		
Arabian Sea	0.0910	–15.0	0.14 / 46	2000–4500	Bange et al., submitted manuscript [1999]
	0.0672	–11.0	0.25 / 15		
	0.3363	–68.4	0.55 / 5		

AOU, apparent oxygen utilization. ΔN_2O is given in nmol L^{-1}, and AOU is given in μmol L^{-1}.

[a] t stands for temperature in °C.

[b] Without data affected by denitrification.

subsequent consumption by denitrification in the interior of organic particulates. In a recent study on nitrate respiration in aggregates in the bottom waters of the northeast Pacific Ocean, *Wolgast et al.* [1998] found that denitrification could occur in microzones of the aggregates. The observations by *Wolgast et al.* [1998] suggest strongly that (strictly anaerobic) denitrification can occur in (well-oxygenated) deep-sea environments, implying that denitrification could be potentially involved in N_2O production or consumption in deep waters. However, no N_2O formation rates were measured by *Wolgast et al.* [1998]; therefore the question of whether nitrification or denitrification is the main N_2O formation process in deep waters requires further experimental efforts.

On the basis of the above discussion, we conclude that N_2O accumulation in the deep ocean is resulting mainly from nitrification processes; however, denitrification cannot be excluded definitely. There also might be a small contribution by down mixing of N_2O from upper layers. Hydrothermal and sedimentary N_2O sources are most probably negligible.

In Table 5 we present an overview of the current open-ocean N_2O budget. The deep-water nitrification is about 12–16% of the global oceanic N_2O produced by pelagic denitrification and about 3–16% of the N_2O loss from the open ocean to the atmosphere (Table 5). Obviously, the sum of the N_2O produced in the deep-water and pelagic denitrification zones does not balance the N_2O loss to the atmosphere, implying an unrealistically high loss of oceanic N_2O. Assuming steady state for the oceanic N_2O cycle, we can speculate that the missing N_2O source of about 3.8 Tg yr^{-1} is attributable to production by pelagic nitrification in the upper water column (above 2000 m). This sums up to an overall oceanic nitrification of 4.1 Tg N_2O yr^{-1} (i.e., deep-water plus upper water nitrification). Considering the considerable uncertainties of the fluxes listed, we conclude that our estimate is only slightly higher than the recent estimate of 2.4 Tg N_2O yr^{-1} produced by nitrification in the open ocean [*Capone,* 1996]. In *Capone*'s [1996] estimate, pelagic denitrification (6.7 Tg N_2O yr^{-1}) is the dominating open-ocean N_2O source. In contrast, we conclude that nitrification could be the dominating source for N_2O in the open ocean. This is in line with the results of *Dore et al.* [1998], who suggested that nitrification as the dominant N_2O production pathway could explain the observed isotopic signature of N_2O in the troposphere.

Table 5. Global Budget for Oceanic N_2O in the Open Ocean.

	Average Tg N_2O yr^{-1}	Range Tg N_2O yr^{-1}	Reference
Sources			
Deep-water nitrification	0.3 ± 0.1		this paper
Net production via pelagic denitrification[a]	2.2	1.9–2.5	
Sink			
Loss to atmosphere	6.3	1.9–10.7	*Nevison et al.* [1995]
ΣSources - Sink	–3.8		

[a] Estimated on the basis of the global pelagic denitrification of 60–80 Tg N yr^{-1} [*Codispoti and Christensen,* 1985; *Gruber and Sarmiento,* 1997], assuming that 2% is transformed to N_2O as observed in the Arabian Sea [Bange et al., submitted manuscript, 1999; *Mantoura et al.,* 1993].

5. Model

Besides the observed N_2O deep-sea accumulation, another question arises: what are the consequences of possible climatically induced changes in the pattern of the deep-sea circulation (i.e., the "conveyor belt" system)?

With a simple box model we estimated the time variation of the N_2O concentration in deep water (below 2000 m) in the period 1903–2065 A.D.:

$$dC_{N_2O}/dt = (\beta x' V_{NADW}) + S - C_{deep} V_{upw},$$

where x' is the atmospheric N_2O dry mole fraction in ppb, V_{NADW} is the volume flow of the NADW formation in 10^6 m^3 s^{-1}, β is the solubility function for N_2O in seawater, S stands for the observed N_2O accumulation in deep waters, V_{upw} is the deep-water upwelling flow (which is equal to V_{NADW}), and C_{deep} is the mean N_2O deep-water concentration.

5.1. Input Parameters

The deep-water N_2O accumulation S was set to 0.3 Tg N_2O yr^{-1}. The 1903 start value for x' was set to 278.8 ppb N_2O [*Battle et al.,* 1996] and 18×10^6 m^3 s^{-1} for the North Atlantic Overturning [*Sarmiento et al.,* 1998]. Annual decrease rates of

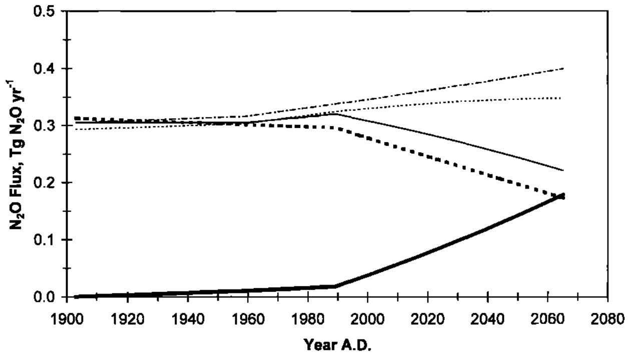


Figure 3. Model results of the temporal development of the N_2O fluxes in the deep sea: the dashed-dotted line represents F_{control}, the thin solid line represents F_{NADW}, the thick solid line represents ΔF, the thin dashed line represents N_2O accumulation in the deep sea, and the thick dashed line stands for F_{upw}.

0.01×10^6 m^3 s^{-1} (1903–1990) and 0.1×10^6 m^3 s^{-1} (1990–2065) for the North Atlantic Overturning were adapted from *Sarmiento et al.* [1998]. In a control run the overturning was set to a constant value of 18×10^6 m^3 s^{-1}. Annual tropospheric N_2O growth rates were set to 0.6% yr^{-1} (1903–1958) and 0.22% yr^{-1} (1959–1990) [*Battle et al.*, 1996]. The annual N_2O growth rate for the period 1990–2065 was modified to include an N_2O feedback effect due to changes in the uptake N_2O by NADW formation. We did not account for interhemispheric differences resulting from the fact that the annual growth rates were derived from South Pole snowpack and NADW formation takes place in the Northern Hemisphere. However, since the annual growth rates for both the Southern and Northern Hemispheres seem to be in phase for the period considered, the small interhemispheric difference of about 1–1.5 ppb N_2O [*Weiss*, 1994] is negligible. Dissolved N_2O concentrations were calculated with the solubility equation given by *Weiss and Price* [1980], assuming that the N_2O concentration in the North Atlantic is always equal to the equilibrium concentration (neglecting seasonal variations of N_2O in the North Atlantic surface water). This assumption appears to be reasonable since N_2O surface concentrations from the North Atlantic Ocean are mainly driven by the seasonality of the sea surface temperature (SST), implying a mean annual N_2O concentration equal to the equilibrium value [*Nevison et al.*, 1995]. Moreover, we did not account for long-term trends of the SST and sea surface salinity (SSS) of the North Atlantic surface waters (in the model they are fixed at 2°C and 35‰, respectively), because sensitivity studies of our model indicated that temporal changes in SST and SSS result in negligible changes of the annual N_2O fluxes.

5.2. Results

The resulting fluxes are presented in Figure 3. The model results are given as N_2O fluxes such as F_{control} (i.e., constant North Atlantic Deep Water formation), F_{NADW} (i.e., temporal modulated formation of NADW), F_{upw} (i.e., the N_2O flux out of the deep-sea into the intermediate layers), and ΔF (i.e., $F_{\text{control}} - F_{\text{NADW}}$). ΔF is a measure for the amount of N_2O which is not "buried" in the deep sea, representing an indirect source for atmospheric N_2O. F_{upw} shows a maximum of 0.31 Tg N_2O yr^{-1} at the beginning of the century and, consequently, decreases when the NADW formation is reduced. Assuming that the N_2O production in the upper water layer at the beginning of the century was about the same as today (3.8 Tg N_2O yr^{-1} for nitrification and 2.2 Tg N_2O yr^{-1} for denitrification; see Table 5), we estimate that N_2O upwelled into the upper water layers contributes less than 5% to the N_2O sources in the upper water column. Thus the N_2O surface distribution and, consequently, the N_2O air–sea exchange are not significantly influenced by variations in the deep-water formation of N_2O.

The results for ΔF show a slight increase from 1903 until 1990 correlating with the variations in the deep-water formation. The change in the annual atmospheric N_2O growth rate in 1959 results in an increase of F_{NADW}, which does not yield a decrease of the rate of ΔF. From 1990 on, the accelerated slowing of the North Atlantic Overturning results in an accelerated increase of ΔF (Figure 3). The mean ΔF was calculated to be 0.017 Tg N_2O yr^{-1} for 1990. This shows that the indirect N_2O source by reduced NADW formation represents only about 0.4% of the annual N_2O growth rate of about 5.6 Tg in 1990. An arbitrarily introduced, complete shutdown of the North Atlantic Overturning (which is theoretically predicted to take place at a flow rate of approximately 10×10^6 m^3 s^{-1} [*Rahmstorf*, 1998], a threshold value which will be reached in the year 2065, according to the model by *Sarmiento et al.* [1998]) will result in a maximal atmospheric N_2O source of 0.40 Tg yr^{-1}. This is about 5.8% of the modeled annual N_2O growth rate of 6.9 Tg for the year 2065.

Our simple estimate does not include changes of the deep-water formation in the Southern Ocean (e.g., in the Weddell Sea). A recent estimate yielded a flow rate of about 15×10^6 m^3 s^{-1}, indicating that deep-water formation in the Southern Ocean is of the same magnitude as the North Atlantic Overturning [*Broecker et al.*, 1998]. Thus we conclude that the N_2O fluxes presented in Figure 3 are conservative and could increase when including temporal changes in the deep-water formation in the Southern Ocean.

6. Conclusions

Despite the fact that the deep-water zone of the world's oceans represents about 95% of the total ocean volume, it contributes only about 3–16% (i.e., 0.3 Tg N_2O yr^{-1}) to the global open-ocean N_2O production. This emphasizes the role of the upper ocean for the cycling of oceanic N_2O.

A rough estimate of the oceanic budget N_2O suggested that the loss to the atmosphere could be balanced only by an additional source of 3.8 Tg N_2O yr^{-1} attributed to nitrification in upper waters (0–2000 m).

The predicted decrease in the NADW formation rate in the near future will lead to an additional source of atmospheric N_2O in the range of about 0.02–0.4 Tg yr^{-1}, amplifying the annual N_2O growth rate, which in turn increases possible climatic changes via an enhanced greenhouse warming effect and thus might lead again to changes in the NADW formation. However, the signal of this (anthropogenically induced) feedback mechanism is small and will be very difficult to detect against the natural variations in the annual growth rates of tropospheric N_2O.

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References

Battle, M., et al., Atmospheric gas concentrations over the past century measured in air from firn at the South Pole, *Nature*, *383*, 231–235, 1996.

Bouwman, A.F., K.W. Van der Hoek, and J.G.J. Olivier, Uncertainties in the global source distribution of nitrous oxide, *J. Geophys. Res.*, *100*, 2785–2800, 1995.

Brandes, J.A., A.H. Devol, T. Yoshinari, D.A. Jayakumar, and S.W.A. Naqvi, Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles, *Limnol. Oceanogr.*, *43*, 1680–1689, 1998.

Broecker, W.S., and T.-H. Peng, *Tracers in the Sea*, 690 pp., Eldigio, Palisades, N.Y., 1982.

Broecker, W.S., The great ocean conveyor, *Oceanography*, *4*, 79–89, 1991.

Broecker, W.S., M. Andree, G. Bonani, W. Wolfli, H. Oeschger, M. Klas, A. Mix, and W. Curry, Preliminary estimates for the radiocarbon age of deep water in the glacial ocean, *Paleoceanography*, *3*, 659–669, 1988.

Broecker, W.S., et al., How much deep water is formed in the Southern Ocean?, *J. Geophys. Res.*, *103*, 15,833–15,843, 1998.

Butler, J.H., J.W. Elkins, C.M. Brunson, K.B. Egan, T.M. Thompson, T.J. Conway, and B.D. Hall, Trace gases in and over the west Pacific and east Indian Oceans during the El Niño–Southern Oscillation event of 1987, NOAA Data Report ERL ARL-16, Air Resour. Lab., Silver Spring, M.D., 1988.

Butler, J.H., J.W. Elkins, T.M. Thompson, and K.B. Egan, Tropospheric and dissolved N_2O of the west Pacific and east Indian Oceans during the El Niño Southern Oscillation Event of 1987, *J. Geophys. Res.*, *94*, 14,865–14,877, 1989.

Butler, J.H., J.M. Lobert, S.A. Yvon, and L.S. Geller, The distribution and cycling of halogenated trace gases, in *Reports on Polar Research No. 168 – The expedition ANTARKTIS XII of RV "Polarstern" in 1994/95: Reports of legs ANT XII/1 and 2*, edited by G. Kattner and D.K. Fütterer, pp. 33–40, Alfred Wegener Inst. for Polar and Mar. Res., Bremerhaven, Germany, 1995.

Capone, D.G., A biologically constrained estimate of oceanic N_2O flux, *Mitt. Int. Ver. Limnol.*, *25*, 105–113, 1996.

Codispoti, L.A., and J.P. Christensen, Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific, *Mar. Chem.*, *16*, 277–300, 1985.

Cohen, Y., and L.I. Gordon, Nitrous oxide production in the ocean, *J. Geophys. Res.*, *84*, 347–353, 1979.

Craig, H., and L.I. Gordon, Nitrous oxide in the ocean and the marine atmosphere, *Geochim. Cosmochim. Acta*, *27*, 949–955, 1963.

Dore, J.E., B.N. Popp, D.M. Karl, and F.J. Sansone, A large source of atmospheric nitrous oxide from subtropical North Pacific surface waters, *Nature*, *396*, 63–66, 1998.

Gruber, N., and J.L. Sarmiento, Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cycles*, *11*, 235–266, 1997.

Hahne, A., Messungen atmosphärischer Spurengase im Meerwasser, *Ber. der Kernforschungsanlage Jülich 1444*, 58 pp., Kernforschungsanlage Jülich GmbH - Institut für Chemie, Jülich, Germany, 1977.

Junge, C., B. Bockholt, K. Schütz, and R. Beck, N_2O Measurements in air and seawater over the Atlantic, *Meteor Forschungsergeb. B*, *6*, 1–11, 1971.

Khalil, M.A.K., and R.A. Rasmussen, The global sources of nitrous oxide, *J. Geophys. Res.*, *97*, 14,651–14,660, 1992.

Kim, K.-R., and H. Craig, Two-isotope characterization of N_2O in the Pacific Ocean and constraints on its origin in deep water, *Nature*, *347*, 58–61, 1990.

Lal, S., P.K. Patra, S. Venkataramani, and M.M. Sarin, Distribution of nitrous oxide and methane in the Arabian Sea, *Curr. Sci.*, *71*, 894–899, 1996.

Law, C.S., and N.J.P. Owens, Significant flux of atmospheric nitrous oxide from the northwest Indian Ocean, *Nature*, *346*, 826–828, 1990.

Lilley, M.D., M.A. de Angelis, and L.I. Gordon, CH_4, H_2, CO, N_2O in submarine hydrothermal vent waters, *Nature*, *300*, 48–50, 1982.

Mantoura, R.F.C., C.S. Law, N.J.P. Owens, P.H. Burkill, E.M.S. Woodward, R.J.M. Howland, and C.A. Llewellyn, Nitrogen biogeochemical cycling in the northwestern Indian Ocean, *Deep Sea Res., Part II*, *40*, 651–671, 1993.

Menard, H.W., and S.M. Smith, Hypsometry of the ocean basin provinces, *J. Geophys. Res.*, *71*, 4305–4325, 1966.

Naqvi, S.W.A., and R.J. Noronha, Nitrous oxide in the Arabian Sea, *Deep Sea Res., Part A*, *38*, 871–890, 1991.

Naqvi, S.W.A., T. Yoshinari, D.A. Jayakumar, M.A.A. Altabet, P.V. Narvekar, A.H. Devol, J.A. Brandes, and L.A. Codispoti, Budgetary and biogeochemical implications of N_2O isotope signatures in the Arabian Sea, *Nature*, *394*, 462–464, 1998.

Nevison, C.D., R.F. Weiss, and D.J. Erickson III, Global oceanic emissions of nitrous oxide, *J. Geophys. Res.*, *100*, 15,809–15,820, 1995.

Polzin, K.L., J.M. Toole, J.R. Ledwell, and R.W. Schmitt, Spatial variability of turbulent mixing in the abyssal ocean, *Science*, *276*, 93–96, 1997.

Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1995, The Science of Climate Change, Contribution of Working Group I to the Second Assessment of the Intergovernmental Panel on Climate Change*, edited by J.T. Houghton et al., pp. 86–103, Cambridge Univ. Press, New York, 1996.

Rahmstorf, S., Decadal variability of the thermohaline ocean circulation, in *Beyond El Niño: Decadal Variability in the Climate System*, edited by A. Navarra, in press, Springer-Verlag, New York, 1998.

Sarmiento, J.L., T.M.C. Hughes, R.J. Stouffer, and S. Manabe, Simulated response of the ocean carbon cycle to anthropogenic climate warming, *Nature*, *393*, 245–249, 1998.

Schmitz, W.J., Jr., On the interbasin-scale thermohaline circulation, *Rev. Geophys.*, *33*, 151–173, 1995.

Seitzinger, S.P., Denitrification in aquatic sediments, in *Denitrification in Soil and Sediment*, edited by N.P. Revsbech and J. Sörensen, pp. 301–321, Plenum, New York, 1990.

Tréguer, P., D.M. Nelson, A.J. Van Bennekom, D.J. DeMaster, A. Leynaert, and B. Quéguiner, The silica balance in the world ocean: A reestimate, *Science*, *268*, 375–379, 1995.

Usui, T., I. Koike, and N. Ogura, Vertical profiles of nitrous oxide and dissolved oxygen in marine sediments, *Mar. Chem.*, *59*, 253–270, 1998.

Weiss, R.F., Changing global concentrations of atmospheric nitrous oxide, in *International Symposium on Global Cycles of Atmospheric Greenhouse Gases*, pp. 78–80, Tohoku Univ., Sendai, Japan, 1994.

Weiss, R.F., and B.A. Price, Nitrous oxide solubility in water and seawater, *Mar. Chem.*, *8*, 347–359, 1980.

Wolgast, D.M., A.F. Carlucci, and J.E. Bauer, Nitrate respiration associated with detrital aggregates in aerobic bottom waters of the abyssal NE Pacific, *Deep Sea Res., Part II*, *45*, 881–892, 1998.

Yoshida, N., H. Morimoto, M. Hirano, I. Koike, S. Matsuo, E. Wada, T. Saino, and A. Hattori, Nitrification rates and ^{15}N abundances of N_2O and NO_3^- in the western North Pacific, *Nature*, *342*, 895–897, 1989.

Yoshinari, T., Nitrous oxide in the sea, *Mar. Chem.*, *4*, 189–202, 1976.

Yoshinari, T., M.A. Altabet, S.W.A. Naqvi, L. Codispoti, A. Jayakumar, M. Kuhland, and A. Devol, Nitrogen and oxygen isotopic composition of N_2O from suboxic waters of the eastern tropical North Pacific and the Arabian Sea – Measurements by continuous-flow isotope-ratio monitoring, *Mar. Chem.*, *56*, 253–264, 1997.

You, Y., Dianeutral mixing, transformation and transport of deep water of the Indian Ocean, *Deep Sea Res., Part I*, *46*, 109–148, 1999.

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