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The distribution of nitrous oxide (N_2O) in the global atmosphere and the Pacific Ocean

By HANWANT B. SINGH, LOUIS J. SALAS, and HISAO SHIGEISHI, *SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025, U.S.A.*

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ABSTRACT

Our atmospheric measurements around the globe show that nitrous oxide (N_2O) is uniformly distributed and has an average concentration of 311 ± 2.6 p.p.b. This small atmospheric variability of N_2O suggests an N_2O residence time of greater than 20 years. Our atmospheric N_2O measurements over a 3-year period starting from November 1975 can be interpreted to mean an essentially unchanging background of N_2O. Oceanic data from the Pacific between 46° N and 40° S show a significant surface super-saturation (average surface saturation = 133%) and an average flux of 36×10^{-14} g $(N_2O)/cm^2$ s can be calculated. This oceanic flux when extrapolated to global waters suggests an oceanic N_2O source of 20 to 30 $Mt(N_2O)$/year (13 to 19 Mt(N)/year)*.

1. Introduction

Nitrous oxide (N_2O) has received attention from atmospheric scientists in recent years because of the hypothesis that continued use of nitrogen fertilizers can increase the atmospheric abundance of N_2O, therby causing a depletion in the stratospheric ozone (McElroy et al., 1976; Crutzen 1976; Liu et al., 1977). Estimates of the depletion of stratospheric ozone by N_2O are dependent on two important factors: (1) the residence time of N_2O in the atmosphere; and (2) the nature of its sources. Stratospheric ozone depletion estimates increase when the residence time is longer (Johnston, 1977), and when soil is a major source of N_2O (McElroy et al., 1976). The atmospheric residence time of N_2O is unknown, and widely varying estimates of 2 to 150 years have been suggested. Reliable long-term N_2O atmospheric data are currently unavailable, and no agreement exists on whether the N_2O atmospheric levels have been steadily increasing, decreasing, or have remained unchanged (Ellsaesser, 1977). Both the ocean and the soil have been identified as possible sources of N_2O, but their net contribution to the atmospheric burden of N_2O is a matter of considerable uncertainty. Oceans, for example, have been considered both significant sources of N_2O (Hahn, 1974) and net sinks (McElroy et al., 1976). The current study provides global measurements of N_2O in the atmosphere and the Pacific Ocean and complements these with several short-term field experiments conducted over the last 3 years in California. Our limited data support the view that the residence time of N_2O is long (> 20 years), its temporal and spatial distribution is uniform, and the oceans are most likely a significant source of N_2O.

2. Experimental procedure

N_2O was measured by electron capture gas chromatography with direct injections of 5 ml of air. Because extremely high precision was sought, every analysis of a sample was followed by the analysis of a standard. This technique led to a precision of within 0.3% (σ_p) under relatively ideal conditions. Under nonideal conditions the precision was still better than 0.5%. All N_2O data were corrected for variation in relative humidity (RH) and are reported at a constant RH of 50% and at 25 °C. All water samples were analyzed within an hour or two of collection. The analysis on N_2O in seawater was conducted by quickly

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* Mt = Million metric tons (10^{12} g).

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enclosing a 25 ml volume of seawater and an equal volume of ultra-pure air in all glass syringe of 100 ml volume. The rapidity with which samples were transferred ensured minimal temperature change and N_2O loss during sample transfer. Once in the syringe the equilibrium was allowed to completion in 15 to 30 min. This also allowed the water to achieve the room temperature which was carefully recorded. N_2O was analyzed in the air, the corresponding equilibrium concentration of N_2O in seawater was determined from solubility data (Junge et al., 1971; Singh et al., 1978) at the room temperature, and the two were added to obtain the N_2O concentration in seawater. Replicate analysis of water samples suggested a precision of better than 5%. Details of these techniques have already been presented (Singh et al., 1977; 1978).

The short-term field studies in California were conducted with the help of a mobile environmental laboratory. All monitoring with this laboratory was performed in an in-situ mode. Additional global air samples were collected between 64° N and 40° S. These data were then complemented with limited numbers of air samples from the South Pole. Fig. 1 shows the sampling locations and periods for the two field trips that were made to acquire global air samples. Trip 1 was exclusively an air sampling operation in which air samples were collected in specially constructed stainless steel (SS) and glass vessels. Specific attention was given to geographic and meteorological conditions to obtain the cleanest possible air samples. In both types of vessels the samples were pressurized to a maximum of 40 p.s.i. (typically 30 to 40 p.s.i.) with the help of an all stainless steel compression pump. These were subsequently analyzed for N_2O. Stability tests have been made, and it appears that N_2O is stable in these vessels over a period of at least 3 years. Trip 2 was conducted on board a U.S. Coast Guard ship, Burton Island (BI), that sailed from Oakland, California, to Wellington, New Zealand (Fig. 1). Two Perkin Elmer 3920 GCs were installed on board the BI for on site analysis. Multiple manifolds were installed to sample air under the cleanest possible conditions. When such conditions did not exist, sampling was terminated. In addition, air samples were also collected in SS vessels on Trip 2. All seawater

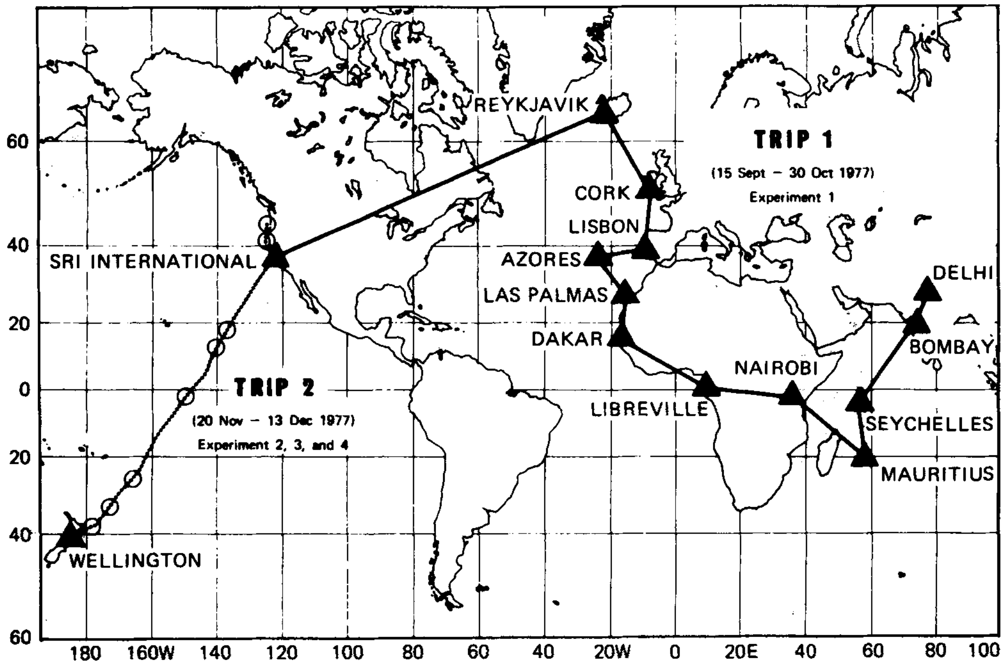

Fig. 1. Map showing the sampling locations for the four experiments. The open circles indicate the deep sea water (0 to 300 m) sampling sites.

sampling and analysis (0 to 300 m depth) was conducted on board the BI.

3. Atmospheric N_2O measurements

Fig. 2 shows the global distribution of N_2O from data obtained from Trip 1 and Trip 2. The northern hemisphere (NH) average background concentration of 311 ± 2.3 p.p.b. (p.p.b. = 10^{-9} v/v), the southern hemisphere (SH) average background concentration of 311 ± 2.8 p.p.b, and the global average of 311 ± 2.6 p.p.b. are scarcely different from each other. Thus, it appears that N_2O is highly uniformly distributed, and the standard deviation of the global variability is 0.8% (σ_t). Because part of this variability is due to the precision of our measurements ($\sigma_p = 0.4\%$) and to the small variability of about 0.2% (σ_{RH}) associated with the RH corrections, a net atmospheric variability of 0.7% (σ_a) can be calculated ($\sigma_a^2 = \sigma_t^2 - \sigma_p^2 - \sigma_{RH}^2$). Using the approximate statistical derivation of Junge (1974), an atmospheric residence time of 20 years ($\tau_{N_2O} = 14/\sigma_a$) can be calculated.

We have been conducting N_2O measurements since 1975 and have also retained air samples since September 1975. Meanwhile, we have conducted a number of short-term studies to measure N_2O background in various seasons on the West Coast of the United States. Our measurements between November 1975 and August 1978 show no systematic average increase in N_2O. However, the precision of our early measurements was not very high because of infrequent calibrations (Fig. 3). To alleviate this deficiency we carried the air samples collected by us in September 1975 and compared them with in-situ air samples between 24° N and 35° S on Trip 2 (November, 1977). Table 1 shows a comparison of replicate analysis of air samples from 1975 and 1977. The average N_2O concentration of air samples from September 1975 was found to be 312.3 ± 0.81 p.p.b.; in the in-situ samples of November–December 1977, it was 311.8 ± 1.14 p.p.b. These averages are statistically indistinguishable. It thus appears that any change in the atmospheric abundance of N_2O since 1975 has been well within the atmospheric variabilities of N_2O.

4. Pacific seawater measurements

Pacific seawater N_2O measurements are of considerable interest because preliminary data from this region collected by Craig and Gordon (1963) led McElroy et al. (1976) to propose the possibility of oceans as a sink for N_2O. The Pacific data of Craig and Gordon were preliminary because the measurement sensitivity was inadequate, and samples from various depths had to be lumped together. Rasmussen et al. (1976) have reported measurements from the eastern tropical

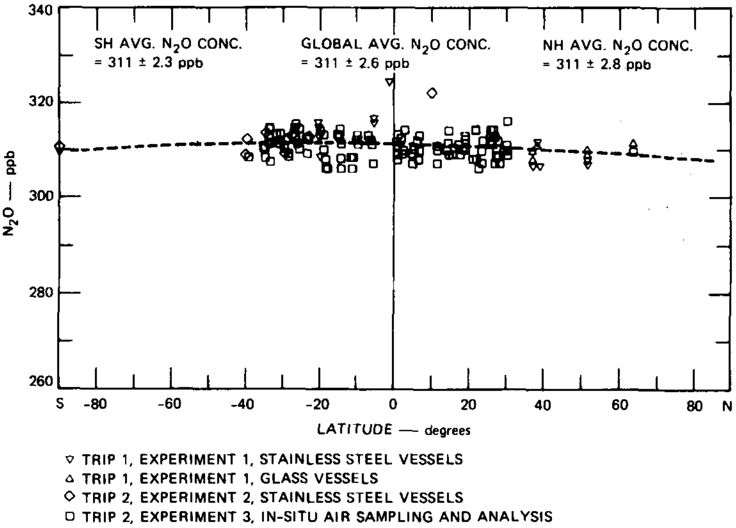

Fig. 2. Global distribution of N_2O.

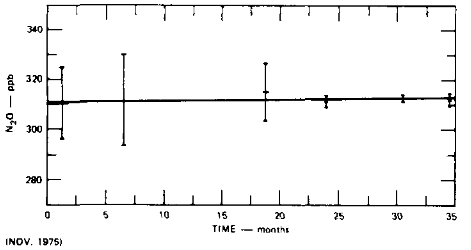

Fig. 3. Growth of N_2O with time.

Table 1. *Ambient* N_2O *concentrations* (*p.p.b.*) *in 1975 and 1977*

Latitude	September 1975	November–December 1977
24° N	312	310
18° N	311	312
14° N	313	313
4° N	312	311
1° N	313	312
4° S	313	312
15° S	313	313
25° S	312	310
30° S	313	313
35° S	311	312
Average concentration (±σ)	312.3 ± 0.81	311.8 ± 1.14

Pacific (31° N to 11° S), but their results may be low (Hahn and Junge, 1977) because of the use of incorrectly published solubility data (Junge et al., 1971). Here we provide a much wider coverage (46° N to 40° S) of N_2O data from the North and South Pacific. To the extent that the Pacific Ocean is representive of world oceans in terms of microbial activity (McElroy et al., 1976), our data tend to remedy some of past deficiencies in available oceanic N_2O data.

Replicate seawater samples from the Pacific Ocean from 45° N to 40° S were analyzed during Trip 2. A total of 16 paired surface seawater samples (0 to 3 m) were analyzed. In eight instances, N_2O analyses were conducted up to 300 m at 50 m intervals. In a majority of cases, replicate samples indicated concentration differences that were within 5%. Occasionally a greater difference of 15% was encountered. In all cases the concentrations were averaged. There were also some instances when only a single sample could be analyzed. Such situations occurred largely due to unfavorable weather conditions resulting in unsafe working conditions. The variation of surface seawater N_2O concentrations, percentage supersaturation, and seawater temperature with latitude is shown in Fig. 4. It is clear from Fig. 4 that in all instances an N_2O supersaturation is observed. The average surface N_2O concentration is found to be 0.38 μg/l and the average surface saturation is 133%, with a maximum of 190% near the equator.

Using a stagnant film diffusion model earlier employed by Hahn and Junge (1977), we calculated the flux of N_2O from the Pacific Ocean. Detailed calculations are shown elsewhere (Singh et al., 1978), but a stagnant film thickness of 60 μm, as recommended by Hahn and Junge (1977), was used. The variation of calculated flux with lattitude is also shown in Fig. 4. An average N_2O flux of 36×10^{-14} g/cm² s was calculated.

Fig. 5 shows the variability of N_2O in Pacific seawater between 0 and 300 m at 50 m intervals. The maximum N_2O concentration below the top mixed layer was 1 to 7 times the surface N_2O concentration. The most intensive synthesis of N_2O was near the equator. Near the southern midlatitudes, the supersaturation was found to be marginal. The average variability of N_2O saturation between 200 and 300 m depth with latitude is also shown in Fig. 4.

5. Results and discussion

The atmospheric distribution of N_2O is found to be uniform around the globe with an average global concentration of 311 p.p.b. A number of investigators have recently reported N_2O concentrations that vary from 290 to 330 p.p.b. and have been summarized by Liu et al. (1977). This is largely due to the unavailability of primary standards at this time. A ±6% uncertainty in the absolute concentration of N_2O currently exists. Some of this uncertainty (between 0 to 2%) can be attributed to the manner of reporting data. We have reported our data at 50% RH and 25 °C while some have reported data at 0% RH and yet others have made no RH correction (Rasmussen et al., 1976). However, the most important aspects of atmospheric measurements rest on the variability or relative concentrations of N_2O rather than its absolute value.

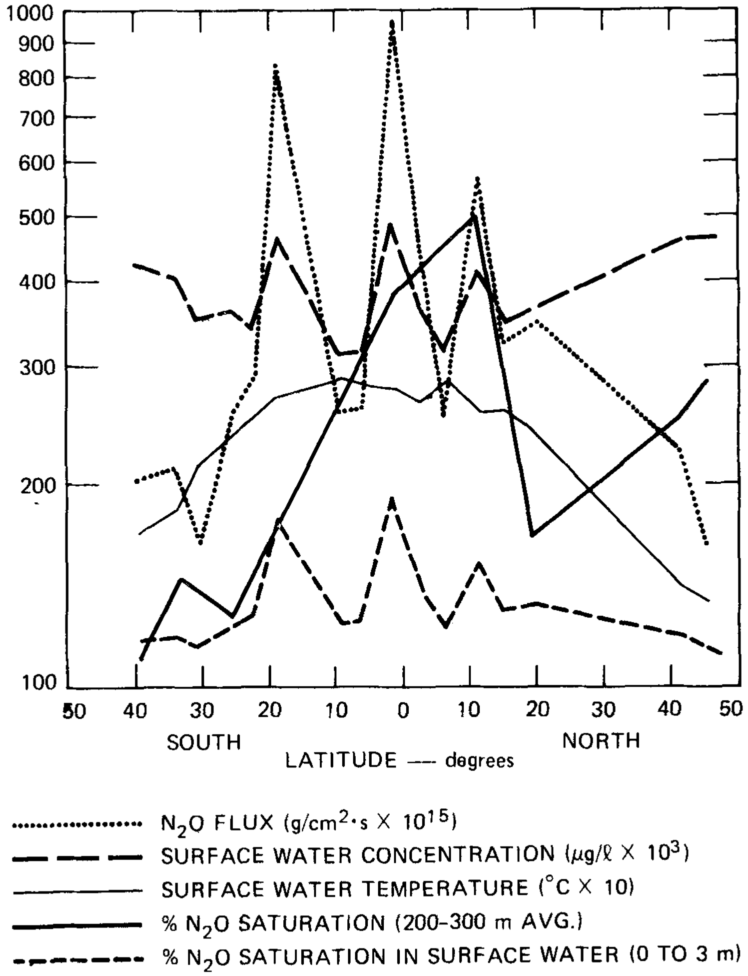

Fig. 4. N_2O supersaturation in the Pacific Ocean (46° N-40° S).

The small atmospheric variability of N_2O (σ_a = 0.7%) suggest a τ_{N_2O} of greater than 20 years. The τ_{N_2O} is higher than 20 for two major reasons: (1) all our data were collected within 15 m of sea level and can be expected to show a larger σ_a because of the close proximity of the oceanic source; and (2) the atmospheric variabilities are approaching the precision of the analysis and the true σ_a is probably less than 0.7%. In our opinion, the past estimates of τ_{N_2O} of 2 to 10 years (Hahn and Junge, 1977) are derived from measurements of less precision that result in the calculation of a large σ_a and a short τ_{N_2O}.

Our data collected over a period of about 3 years, while limited, suggest an unchanging background of N_2O. There appears little doubt that during this period (1975–1978) the change in N_2O concentrations has been less than the atmospheric variability of N_2O. This is in disagreement with the upper limit of a 4% projected increase in N_2O abundance during this time due to nitrogen fertilizer application (Crutzen, 1976). It thus appears that the lower limits of projected N_2O increases, which suggest essentially no change during this period, are more likely to be reliable (Crutzen, 1976; Hahn and Junge, 1977).

Based on our measurements in the Pacific we obtain an average N_2O flux of 36 × 10^{-14} g/cm^2 s and an average saturation of surface water of 133%. Hahn (1974) reported a saturation of 123%

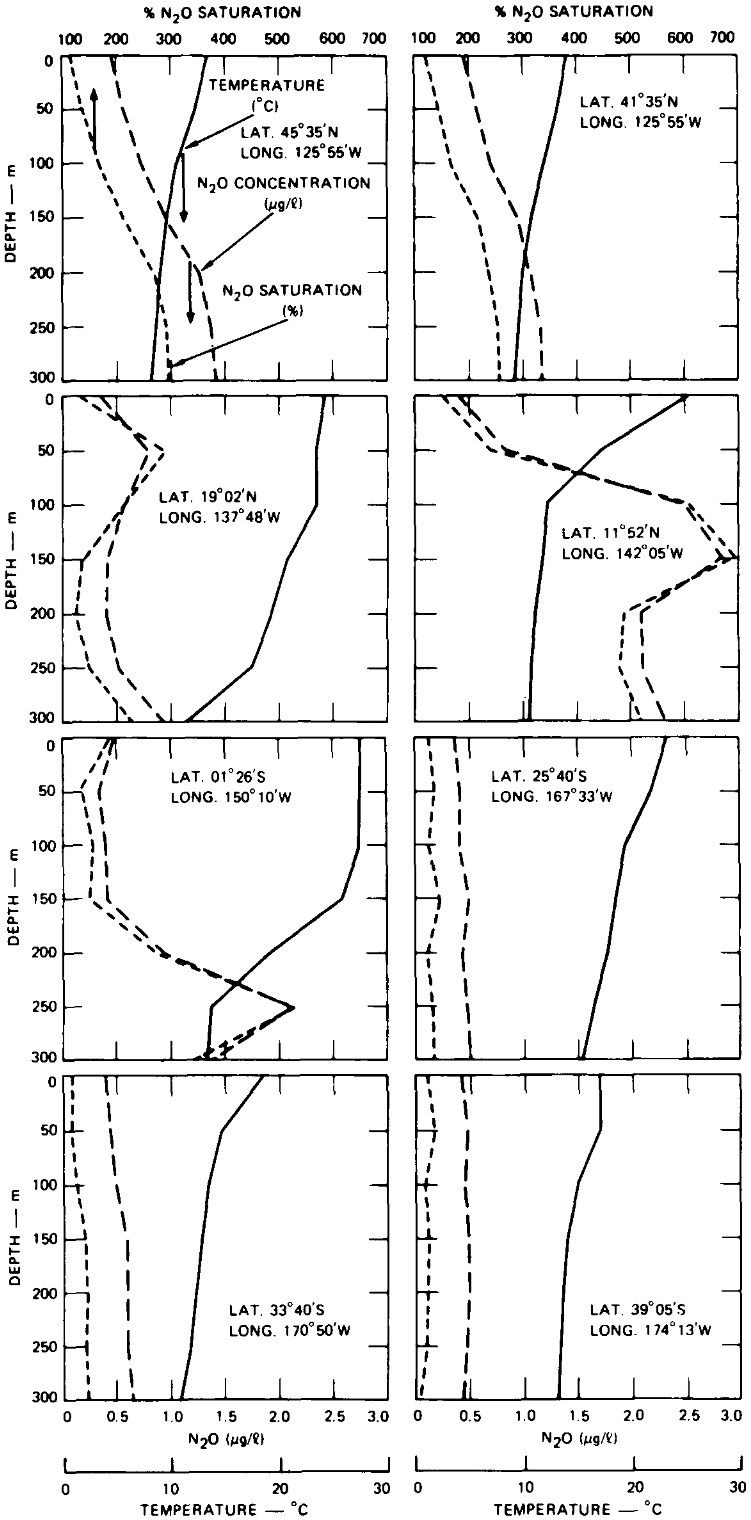

Fig. 5. Distribution of N_2O in the Pacific.

in the Atlantic between 38° N and 50° N. This can be compared with a 118% saturation measured by us between 41° N and 46° N. Comparison of data between the Pacific and Atlantic (Hahn, 1974) would suggest that our measured N_2O saturation of 133% is reasonably representative of global waters between 45° N and 45° S. Additional data are required to make this generalization, but based on currently available information this assumption does not seem to be unreasonable. In the rest of the world ocean body we assume an average saturation of 115% based on Hahn's measurements. Using the average 133% saturation for the 74% of the seawater between 45° N and 45° S, and 115% for the remaining ocean surface, a net N_2O exchange of 30 Mt(N_2O)/yr can be calculated. This estimate of oceanic N_2O flux is less than half of the best estimates of 70 Mt(N_2O)/yr derived by Hahn and Junge (1977).

We wish to further add, that this flux estimate is critically dependent on the film thickness used in the film model. While we have used a film thickness of 60 μm for comparative purposes (Hahn and Junge, 1977), the possibility that this film thickness is as high as 90 μm can not be ruled out. Therefore, our estimated oceanic flux would be between 20 and 30 Mt(N_2O)/yr. This source alone allows a turnover time of 75 to 110 years for atmospheric N_2O. Despite the uncertainties, our findings support the conclusion that oceans are most likely a net source of N_2O. This is in agreement with the findings of Junge et al., (1971) and Hahn (1974) but in disagreement with the assertions of McElroy et al. (1976) who extrapolated the Pacific N_2O measurements of Craig and Gordon (1963) to world oceans to conclude that oceans are probably net sinks of N_2O.

The high N_2O synthesis in equatorial waters is not surprising because microbial activity is known to be most pronounced in the warm equatorial regions. What is surprising, however, is the amount of N_2O synthesis in the region of the Pacific Ocean where oxygen content is typically 4 to 5 ml/l, or an order of magnitude higher than required for efficient denitrification (Hahn and Junge, 1977). This high O_2 content could, however, lead to efficient nitrification processes. It would thus appear that either nitrification processes play a more important role in N_2O synthesis in the ocean than hitherto believed, or denitrification processes are poorly understood and can proceed under conditions that are significantly different from anoxic.

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РАСПРЕДЕЛЕНИЕ ЗАКИСИ АЗОТА (N_2O) В ГЛОБАЛЬНОЙ АТМОСФЕРЕ И В ТИХОМ ОКЕАНЕ

Измерения в атмосфере вокруг земного шара показывают, что закись азота (N_2O) распределена однородно со средней концентрацией 311 ± 2,6 ррб. Из малой изменчивости N_2O в атмосфере следует, что время жизни N_2O в атмосфере больше 20 лет. Данные измерений содержания N_2O в атмосфере за трехлетний период, начиная с ноября 1975 г., указывают на существенно неизменное фоновое содержание N_2O. Данные по ее содержанию в Тихом океане между 46° с.ш. и 40° ю.ш. указывают на значительное пересыщение поверхностных вод (среднее насыщение равно 133%), откуда можно вычислить средний поток $36 \cdot 10^{-14} \cdot$г $(N_2O)/$см^2 с. Если этот поток проэкстраполировать на все океанские воды, то получится океанический источник N_2O мощностью от 20 до 30 Мт (N_2O)/год.