

Nitrous oxide measurements in the eastern tropical Pacific Ocean

By DAVID PIEROTTI and R. A. RASMUSSEN, *Atmospheric Trace Gas Laboratory, Environmental Science Department, Oregon Graduate Center, Beaverton, Oregon 97005, U.S.A.*

(Manuscript received June 26, 1978; in final form April 12, 1979)

ABSTRACT

In March 1976 the first N_2O measurements were made in the sea water and marine air of the eastern tropical Pacific Ocean during a cruise from San Diego, California, to San Martín, Peru. Continuous measurements of N_2O in the marine atmosphere were made throughout the duration of the cruise. The tropospheric mixing ratio was 332 ± 9 p.p.b. v/v N_2O . The concentration of N_2O in the marine air appeared to show a direct relationship to the N_2O concentration in the surface sea water, with the highest N_2O mixing ratios over regions which were highly supersaturated, off the coasts of Baja California and Peru, and in the equatorial upwelling region. The surface sea water samples were generally supersaturated with N_2O , with an average saturation of 145% relative to the marine atmosphere. The average flux of N_2O from the surface sea water into the atmosphere was 0.5×10^{-12} g N_2O cm^{-2} s^{-1} . Only one surface sea water sample showed significant undersaturation; the other 28 surface water samples were approximately saturated or supersaturated. Water samples were also collected down to depths of 300 m during seven hydrocast stations. The stations showed two distinct distribution patterns for N_2O concentration versus depth for the region between the surface and 300 m. At five of the seven stations the N_2O concentration increased rapidly from the surface to a depth of 100 m, and then remained relatively constant down to the maximum depth of 300 m. At the other two stations the N_2O concentration showed the same rapid increase between the surface and 75–100 m, but then the N_2O concentration decreased in the next 50–75 m until the concentration of N_2O at 150 m was lower than that found at the surface. At these two stations the water from 150 m to 300 m was just saturated or undersaturated with N_2O with respect to the atmosphere. These two stations were located in the oxygen-deficient region off the coast of Mexico, which suggests that the low N_2O concentrations below the thermocline may be due to denitrification. However, stations in the oxygen-deficient region off the coast of Peru showed considerable N_2O supersaturation at all depths. Recent results indicate that the role of N_2O in the nitrogen cycle of the ocean may be more complex than has previously been suggested.

1. Introduction

There is considerable uncertainty at the present time over the role of the oceans in the global cycle of nitrous oxide. The estimates of the flux of N_2O between the ocean and the atmosphere range from a net global marine production of 135 Mt N_2O year^{-1} (1 Mt = 10^{12} g) (Hahn, 1974) to a net sink of 40 Mt N_2O year^{-1} in the oceans (McElroy *et al.*, 1976). In order to help reduce the uncertainty about the role of the oceans, we measured N_2O concentrations in the marine air and sea water of the eastern tropical Pacific Ocean (ETPO) during

a cruise of the R.V. *Alpha Helix* from San Diego, California, to San Martín, Peru, in March 1976 (Fig. 1).

Extensive N_2O measurements in the northern Atlantic Ocean had shown that the surface sea water was generally supersaturated (Hahn, 1974; Yoshinari, 1976) which pointed to the North Atlantic as a significant source of N_2O . The only N_2O measurements ever made in the Pacific Ocean (Craig and Gordon, 1963) had indicated that some regions of the Pacific might be sinks for nitrous oxide. However, Craig and Gordon's data cannot be applied to estimates of the sea $\leftrightarrow$ air flux, since

they combined water samples from many different depths of the ocean into three groups, and the two groups which showed N_2O undersaturation were from average depths of 600 m and 4000 m. Since only the concentration of N_2O in surface water samples is relevant to calculations of the sea ↔ air flux, their results could only be considered evidence that the Pacific Ocean might possibly behave differently from the Atlantic with regard to the global cycle of nitrous oxide.

We made continuous measurements of N_2O in the marine atmosphere throughout the duration of the cruise (Fig. 2). We also measured the N_2O concentration in 65 sea water samples collected during seven hydro-cast stations (Fig. 3) extending from the surface down to a depth of 300 m, and in 22 samples collected in the sea surface water layer during the course of the cruise.

2. Analytical methods

The analyses of N_2O were carried out using a Perkin-Elmer 3920 gas chromatograph equipped with an electron capture detector, which was operated at 350 °C. Both the atmospheric and sea water samples were analyzed for N_2O on a 2 m × 3 mm (o.d.) column packed with Porasil B. The details of the method for the atmospheric analyses are given in Rasmussen et al. (1976).

The sea water samples were analyzed using the multiple phase-equilibration method of McAuliffe (1971). A 100 ml glass syringe is flushed several times with helium until a blank run on the gas chromatograph shows no contaminant peaks. The helium used in the analyses is purified prior to use by passage through a trap of Molecular Sieve 5 Å. Then 50 ml of sea water are taken into the syringe, making sure that no outside air is introduced along with the sea water. After this, 50 ml of purified helium are added, and the syringe is capped by closing a Luer-Lok fitting. The syringe is then shaken vigorously for 5–10 min in order to establish equilibrium between the phases. Finally, 40–45 ml of the helium is passed through the sampling lines of the gas chromatograph to flush them out before a measured volume is injected onto the column for analysis. We used a 1 ml sample for our analyses of N_2O on the Porasil B column. Any helium remaining in the syringe is then discharged, and 50 ml of fresh helium are added. The equi-

libration process is repeated as many times as required for a specific analysis. We normally performed two to four equilibrations per sample for the N_2O analyses. If any water is lost during an analysis, then a correspondingly smaller amount of helium is added for the succeeding equilibration steps, i.e., only the ratio of the volume of the gas phase to the volume of the liquid phase must be kept constant.

The mathematics of the analysis is quite simple. A plot of the log of the concentration (i.e., peak height or peak area) versus the number of the equilibration produces a straight line. The negative slope of the line is the log of the distribution coefficient (or Henry's Law Constant) plus one. The intercept of the line is the product of the initial concentration of the compound and the distribution coefficient. The details of the method are given by McAuliffe (1971).

The precision of the multiple phase-equilibration method for analyses of N_2O in sea water was approximately $\pm 2\%$ during the *Alpha Helix* cruise. We have now improved our analytical technique for making measurements of dissolved gases in sea water, so that a precision of better than $\pm 1\%$ is possible for N_2O .

The nutrient analyses for NO_3 , NO_2 , NH_4 , SiO_4 , and PO_4 listed in Table 1 for the hydro-cast stations were performed by Roger Shepard of Duke University Marine Laboratory using a photometric autoanalyzer on board the ship. The temperature profiles at the stations were obtained using an expendable bathythermograph (XBT) with the help of Jane Kogelschatz of Duke.

3. Results

The discussion of the results of the nitrous oxide measurements made during the cruise will be divided into two sections, atmospheric measurements and sea water measurements. Since the marine air concentration is obviously important in determining the expected equilibrium concentration of N_2O in the surface sea water, the atmospheric measurements of N_2O will be discussed first.

3.1. Atmospheric measurements

The map of the cruise track is shown in Fig. 1, and the results of the atmospheric N_2O measurements are shown in Fig. 2. The N_2O concentration

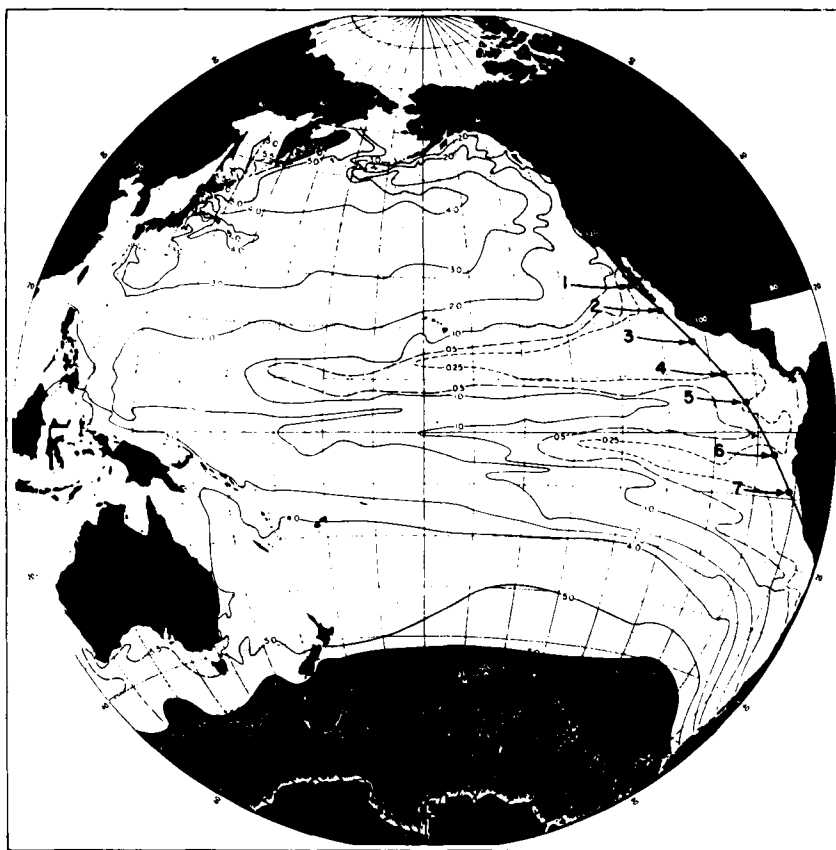


Fig. 1. Cruise track of the *Alpha Helix* from San Diego, California, to San Martin, Peru. The locations of the hydrocast stations are shown, numbered as in Table 2. The oxygen concentrations (in ml/l) on the $\delta_T = 125$ cl/ton surface, which is at a depth of 300–500 m in this region, are also shown. (Figure from Reid, 1965.)

in the marine atmosphere was quite uniform throughout the cruise: based upon 212 hourly averages representing more than 1200 individual measurements, the mixing ratio of N_2O was 332 ± 9 p.p.b. v/v, a relative standard deviation of only 2.8% of the mean. This is a very homogeneous distribution in view of the fact that the cruise covered a period of 15 days and a distance of more than 4000 miles, traversing both hemispheres in an area of the ocean believed to be a significant source of N_2O , and encountering several different synoptic wind systems.

The mean concentration for the cruise, 332 p.p.b. v/v N_2O , agrees closely with the mixing ratio of 331 ± 3 p.p.b. v/v N_2O which our laboratory measured in 40 air samples collected during seven high-altitude aircraft flights made over Montana

during the same time period, the first three weeks in March 1976. In addition, 20 discrete air samples we collected during the *Alpha Helix* cruise and analyzed in our laboratory at home had a concentration of 331 ± 6 p.p.b. v/v N_2O . These two sets of measurements had relative standard deviations of 0.9% and 1.8%, respectively.

We also made continuous measurements of N_2O at a site in the north-western United States for a period of a year, beginning in June 1976. The results from the summer of 1976 (Pierotti et al., 1978a) showed a very stable tropospheric N_2O level of 328.5 ± 1.5 p.p.b. v/v, a relative standard deviation of less than 0.5%.

There are several possible reasons for the greater variability observed in atmospheric N_2O levels during the *Alpha Helix* cruise. First of all, since

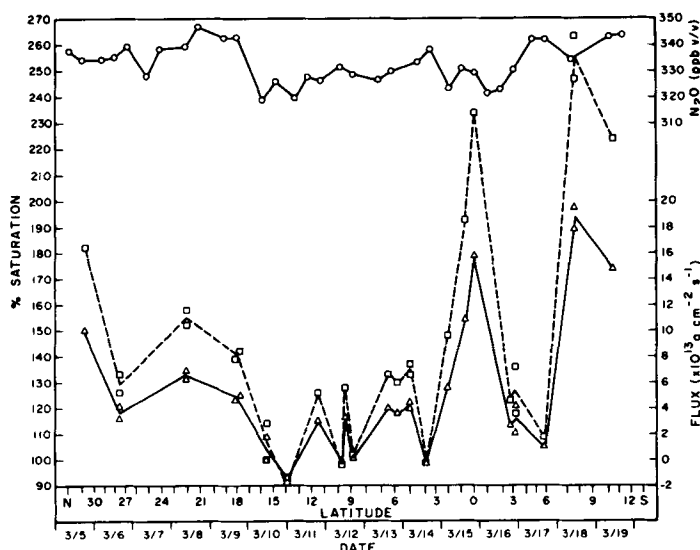


Fig. 2. Results of the surface air and sea water measurements of N_2O during the *Alpha Helix* cruise. The mixing ratio of N_2O in the marine air (in p.p.b. v/v) is shown at the top (○). The measurements of N_2O in the surface sea water are shown in the other two plots. The degree of saturation of the surface water with N_2O , relative to a marine atmospheric concentration of 330 p.p.b. v/v, is shown (in % saturation) by (□). The flux of N_2O from the sea into the atmosphere ($\times 10^{-13} \text{ g cm}^{-2} \text{ s}^{-1}$), calculated using the stagnant film model, as described in the text, is shown by (Δ).

these measurements were made on whole air samples, varying water vapor pressure in the atmosphere undoubtedly contributed to the apparent variability of atmospheric N_2O . Since all of our measurements up to this time had been made on samples collected in the upper troposphere and lower stratosphere, where the water vapor pressure is vanishingly small, we had not anticipated this difficulty. However, the vapor pressure of H_2O during the cruise was $16.5 \pm_{4.1}^{5.2}$ mmHg, which corresponds to an H_2O mixing ratio of $2.2 \pm_{0.6}^{0.7}\%$, so the variations in water vapor pressure contributed at most one-quarter of the variability observed in the N_2O level. Since there was condensation of water vapor in the air sampling lines upon entering the cooler laboratory, the actual effect of variations in H_2O vapor pressure would be somewhat less.

Another reason for the variability of N_2O in the marine air can be seen in Fig. 2, where we have shown the relative saturation and flux of N_2O from the surface sea water during the cruise. There appears to be direct relationship between the N_2O concentration in the surface sea water and the marine atmosphere. The general features of the N_2O concentration in the air and surface sea water

agree over most of the cruise track, with the highest atmospheric N_2O levels occurring in the upwelling regions off the coasts of Mexico and Peru, where the highest dissolved N_2O concentrations were observed, and the lowest N_2O concentrations in the marine air occurring in the regions where the surface water was only slightly supersaturated and even undersaturated, in a few cases. This indicates that parts of the eastern tropical Pacific, specifically the upwelling regions off Mexico and Peru, are very strong sources of N_2O to the atmosphere. We shall return to this point in the discussion of the sea water measurements.

Another factor which may have contributed to the low N_2O concentrations observed during the middle of the cruise is the possible effect of desert surfaces as a sink for N_2O . We have observed significantly lower levels of N_2O in dust clouds over the eastern Sahara (Pierotti et al., 1978b), and Junge et al. (1971) found that air masses associated with the northwest trade winds and originating in North Africa had abnormally low levels of N_2O during a cruise from 10°S to 60°N along the 30°W meridian. Although the very lowest N_2O levels we observed during the cruise were associated with the northeast trade winds, it is

uncertain if the air masses we measured were of Saharan origin, so we cannot attribute the low nitrous oxide levels to removal by desert surfaces, although it remains a possibility.

The concentrations of N_2O which we have measured in the troposphere compare quite favorably with other recent measurements. Yoshinari (1976) obtained an average mixing ratio of 328 ± 5 p.p.b. v/v N_2O in 20 air samples collected over the Atlantic Ocean and Caribbean Sea in March and April 1972. Goldan et al. (1978) obtained a ground level N_2O mixing ratio of 326 ± 5 p.p.b. v/v from 75 measurements made during a six-month period in 1976–77. Cicerone et al. (1978) found a tropospheric concentration of 330 ± 3 p.p.b. v/v N_2O in 47 samples collected and analyzed between August 1976 and September 1977. Finally, recent measurements by Weiss (1978) and Singh et al. (1977) have also shown an extremely homogeneous distribution of nitrous oxide in the troposphere, although their absolute concentrations are approximately 10% and 5% lower, respectively, than those reported above, reflecting a systematic difference in absolute calibration standards.

The spatial and temporal variations in the tropospheric concentration of N_2O observed by our laboratory and the other laboratories making measurements would seem to indicate that the tropospheric distribution of N_2O is considerably less variable than has been reported in the past (Schütz et al., 1970; Junge et al., 1971; Hahn, 1975). This difference is most likely the result of simpler analytical techniques and greater precision in recent measurements. The greater uniformity in the tropospheric distribution of N_2O observed in most recent measurements is significant in view of the current uncertainties with regard to the sources and sinks of N_2O . Junge (1974) has proposed that the time and space variations of tropospheric constituents should be inversely proportional to their tropospheric residence times. He obtained an empirical relationship from the available data on tropospheric gases:

$$(\text{Tropospheric Residence Time}) \times (\text{Relative Standard Deviation}) = 0.14 \text{ Years}$$

Applying this formula, the best recent measurements indicate that the tropospheric lifetime of N_2O is probably longer than 30 years. However, a recent paper by Levy et al. (1979) has shown that even with a uniform global source of N_2O and

destruction only by photolysis in the stratosphere (with a lifetime of 150 years), temporal relative standard deviations of 0.2–0.8% and spatial variations of as much as 1% are to be expected in the troposphere. Therefore, the Junge relationship breaks down for long-lived trace gases such as N_2O , and we cannot expect to learn anything more about the atmospheric lifetime of N_2O through improvements in the analytical techniques. However, we can set a lower limit for the N_2O lifetime of approximately 30 years. Assuming an atmospheric burden of 2400 Mt N_2O (equal to 330 p.p.b. v/v N_2O in the troposphere), this would set an upper limit on the global net production of approximately 80 Mt N_2O year⁻¹, only about 40% of the amount estimated by Hahn and Junge (1977) for the total global source: 210 Mt N_2O year⁻¹.

3.2. Sea water measurements

The course of the R.V. *Alpha Helix* from San Diego, California, to San Martin, Peru, is shown in Fig. 1, along with the dissolved oxygen concentrations (in ml/l) occurring at depths of 300–500 m in this area of the ocean ($\delta_T = 125$ cl ton⁻¹ surface) (Reid, 1965). The locations of the seven hydro-cast stations are also shown in Fig. 1.

Virtually the entire cruise was over a region of the ocean which displays extremely low oxygen concentrations from a depth of around 100 m down to almost 900 m (Codispoti, 1973). These waters are nearly anoxic, and they have displayed characteristics which indicate that they are the site of considerable denitrification (Fiadero and Strickland, 1968; Goering, 1968; Thomas, 1966). Estimates of the total amount of denitrification for the oxygen-deficient zone north of the equator in the ETPO range from 10 to 230 Mt N year⁻¹ (Richard, 1971; Cline and Richards, 1972; Goering et al., 1973; Codispoti and Richards, 1976), far larger than the total estimated rate of denitrification from such well-known anoxic environments as the Black Sea and the Cariaco Trench. This means that the eastern tropical North Pacific and the corresponding zone in the South Pacific are a major factor in the oceanic budget of combined nitrogen. Therefore, the concentration of nitrous oxide in the sea water of this area is of considerable interest with regard to the nitrogen cycle in the ocean and the global budget of N_2O .

Although the earliest measurements of N_2O in sea water were made by Craig and Gordon (1963)

in the Pacific Ocean, they had to combine their 28 samples into three groups in order to have enough N_2O for analysis, so the results they obtained were severely limited. Since that time Junge, Hahn, and coworkers have made extensive measurements of nitrous oxide in and over the northern Atlantic Ocean (Junge et al., 1971; Junge and Hahn, 1971; Hahn, 1974, 1975). They found considerable supersaturation of N_2O in the surface waters of the Atlantic Ocean, with the supersaturation decreasing with increasing latitude. From these results they have concluded that the oceans are a large source of N_2O . However, no detailed measurements of N_2O had been made in the marine air and sea water of the Pacific Ocean. In order to remedy this omission we participated in the *Alpha Helix* cruise from San Diego to San Martin, Peru. The measure-

ments in the marine air, reported above, showed a very homogeneous distribution of N_2O , with a concentration of 332 ± 9 p.p.b. v/v. The sea water measurements of N_2O were also extremely interesting, providing a picture of the distribution of N_2O in waters where upwelling and extensive denitrification are taking place.

Direct estimates of the flux of nitrous oxide from the ocean into the atmosphere can be made using the N_2O concentrations which we measured in the surface water samples. Table 1 lists the N_2O data for all 29 samples collected in the surface water layer during the course of the cruise. The data and location of the samples are in columns 1–3, the surface water temperature in column 4, the N_2O concentration (in $\mu g/l$) in column 5, the percent saturation of the surface water (relative to a marine

Table 1. *Alpha Helix* cruise surface water samples

Date	Latitude	Longitude	Temperature (°C)	[N_2O] $\mu g/l$	Percent saturation	Flux
March 5	30°40' N	116°27' W	15.0	0.74	182	10.00
6	27°33' N	114°57.6' W	15.2	0.51	126	3.17
6	27°33' N	114°57.6' W	15.2	0.54	133	4.07
8	22°01' N	109°4.9' W	21.9	0.52	158	6.90
8	22°01' N	109°4.9' W	21.9	0.50	152	6.18
9	18°05' N	105°25' W	25.0	0.42	139	4.66
9	17°42' N	104°59' W	25.8	0.42	142	5.04
10	15°36.9' N	103°10.7' W	27.7	0.28	100	0.00
10	15°36.9' N	103°19.7' W	27.7	0.32	114	1.69
10	13°50' N	101°06' W	27.2	0.25	88	−1.46
11	11°35' N	99°27' W	28.8	0.34	126	3.06
12	9°45' N	97°40' W	26.8	0.28	98	−0.21
12	9°32.6' N	97°26.1' W	26.4	0.37	128	3.26
12	8°48' N	96°42' W	27.2	0.29	102	0.21
13	6°33' N	94°35' W	27.2	0.38	133	3.98
13	5°50' N	94°00' W	27.2	0.37	130	3.56
13–14	5°09' N	93°22.7' W	29.2	0.37	137	4.40
13–14	5°09' N	93°22.7' W	29.2	0.36	133	3.96
14	3°55' N	91°42' W	28.7	0.27	99	−0.09
14	2°12' N	90°48' W	28.8	0.40	148	5.64
15	0°42' N	89°07' W	26.0	0.56	193	10.93
15	Equator	88°30' W	26.0	0.68	234	15.79
16	2°40' S	86°15' W	27.0	0.35	123	2.70
16	3°13.4' S	85°25.1' W	27.4	0.38	136	4.20
16	3°13.4' S	85°25.1' W	27.4	0.33	118	2.10
17	5°42' S	83°37' W	26.6	0.31	109	1.03
18	7°40' S	81°26.2' W	25.8	0.78	264	19.56
18	7°40' S	81°26.2' W	25.8	0.73	247	17.95
19	10°30' S	79°15' W	21.8	0.74	224	14.83

Percent saturation is the N_2O saturation of the surface water relative to an atmospheric concentration of 330 p.p.b. v/v.

air concentration of 330 p.p.b. v/v N_2O) has been calculated in column 6, and the flux of N_2O from the sea to the air ($\times 10^{-13} \text{ g cm}^{-2} \text{ s}^{-1}$) has been calculated in column 7. These last two quantities are also shown in Fig. 2 along with the atmospheric N_2O concentrations.

Of the 29 surface water samples, only one shows significant undersaturation, while four other samples are approximately saturated, and a fifth shows a supersaturation of less than 10%, an amount which could be accounted for by physical processes such as bubble injection in surface waters or the mixing of water masses of different temperatures. However, the other 23 surface water samples show levels of N_2O which can only be accounted for by production of nitrous oxide in the sea water.

The flux of a gas between the ocean and the atmosphere can be calculated using the stagnant film model (Broecker and Peng, 1974), where the flux is given by the formula:

$$\text{Flux} = \frac{D}{Z} (C^w - P \times \alpha(T, S))$$

where C^w is the concentration of the gas in sea water, P is the partial pressure of the gas in the atmosphere, $\alpha(T, S)$ is the solubility of the gas in sea water, and Z is the film thickness. The solubility coefficient $\alpha(T, S)$ was calculated using the data of Weiss and Price (1979). The molecular diffusion rates for N_2O and the value for the film thickness (60μ) were taken from Broecker and Peng (1974).

Assuming a marine air mixing ratio of 330 p.p.b. v/v N_2O , and a salinity of 35.0‰, we used the calculated solubility coefficients and the stagnant film model to estimate the N_2O saturation values and the flux of N_2O from the ocean to the atmosphere for each of the 29 surface water samples (Table 1, Fig. 2). As we mentioned above, only one surface water sample showed significant undersaturation, and 23 of the samples showed significant supersaturations which could not be accounted for by physical processes. The average saturation for all 29 samples was 145%, with some samples showing greater than 200% saturation. Therefore, this region of the ocean is clearly a source of nitrous oxide to the atmosphere.

We calculated the flux of N_2O for each surface water sample (Table 1). The flux values ranged from $-1.46 \times 10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$ to $+19.56 \times$

$10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$. The average flux from the surface sea water into the atmosphere for all 29 samples was $5.42 \times 10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$.

These flux values are of the same order as those reported by Hahn (1975) for the northeast Atlantic Ocean, $2.2\text{--}4.7 \times 10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$, with a maximum flux of $12.5 \times 10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$ calculated for the tropical latitudes of the North Atlantic from the data obtained on the *Meteor* cruise of April 1969.

Assuming that our average flux of $5.42 \times 10^{-13} \text{ g N}_2\text{O cm}^{-2} \text{ s}^{-1}$ from the ocean to the atmosphere is representative of the entire oxygen-deficient region of the eastern tropical North Pacific, we obtain a net flux of approximately 1.2 Mt N_2O year $^{-1}$ from this area of the ocean. Including the oxygen-minimum region of the eastern tropical South Pacific would give us an estimated flux of more than 2 Mt N_2O year $^{-1}$ for the entire region of low oxygen concentration in the ETPO. These N_2O flux estimates are reasonable in relation to the denitrification rate of $\sim 20 \text{ Mt N year}^{-1}$ calculated by Codispoti and Richards (1976) for the eastern tropical North Pacific, since the $\text{N}_2\text{O}/\text{N}_2$ ratio in denitrification products is commonly 0.05–0.1 in soil denitrification studies (CAST, 1976).

If we apply our average flux to the entire world ocean surface of $360.8 \times 10^6 \text{ km}^2$, we obtain a global marine production of $61.7 \text{ Mt N}_2\text{O year}^{-1}$, less than half of Hahn's (1974) estimate of 135 Mt $\text{N}_2\text{O year}^{-1}$. Although our specific flux values are similar to those measured by Hahn in the Atlantic Ocean, the discrepancy between our global flux estimates results from Hahn's choice of flux values in calculating the global oceanic flux of N_2O to the atmosphere. He averaged the flux values obtained at each latitude, assuming that these averages are representative of the flux at that latitude for the entire ocean surface. However, his samples were not evenly distributed over the ocean: he had seven samples collected from 0.6°N to 59.9°N during the Atlantic cruise of 1969, twenty samples collected on the Iceland–Faroe Ridge (from 62°N to 65.5°N) in 1970, and fifteen samples collected from 38.5°N to 48.5°N in the eastern Atlantic in 1971. By weighting his data in order to give each latitude proper weight according to the relative ocean surface area in each latitudinal belt, Hahn has given inordinate importance to five samples collected from 0.6°N to 36.6°N during the 1969 cruise, when the analytical procedure they were

using was much less precise than on later cruises (Hahn, 1974). These five samples, and particularly the two samples collected at 0.6°N and 10.3°N , are responsible for the average N_2O saturation of 180% for the North Atlantic surface water which Hahn (1974) used in calculating his total flux estimates for the North Atlantic and his global marine net production.

Furthermore, the sample from 10.3°N , which showed by far the highest N_2O saturation (293%) of all Hahn's samples, was not taken from the surface water, but at a depth of 25 m. The use of a sample from a depth of 25 m in calculating air $\leftrightarrow$ sea flux, even when the surface water is reasonably well mixed to that depth, is highly questionable in view of the variability of biological activity near the surface, particularly in the sea surface film layer (Williams, 1967; Goering and Menzel, 1965).

Finally, Hahn (1974) used a value for the film thickness of $28\ \mu$ in making his global estimates, while we used a film thickness of $60\ \mu$ in making our flux calculations.

Recently, Hahn and Junge (1977) recalculated their global flux estimates using film thicknesses of $40\text{--}60\ \mu$, but still using the N_2O data from the 1969 cruise, including the result from 10.3°N . They now estimate a global marine net production of $45\text{--}120\ \text{Mt}\ \text{N}_2\text{O}\ \text{year}^{-1}$, with a most likely value of $75\ \text{Mt}\ \text{N}_2\text{O}\ \text{year}^{-1}$. This is fairly close to our extrapolation of the average flux values from the ETPO, which gave us a global marine production of $61.7\ \text{Mt}\ \text{N}_2\text{O}\ \text{year}^{-1}$. The results of the analyses on the 65 samples collected during the seven hydro-cast stations are given in Table 2. Columns 1 and 2 give the water temperature and the depth (in meters) at which the sample was collected, columns 3–7 give the data on the nutrients (in $\mu\text{M/l}$), column 8 gives the N_2O concentration (in $\mu\text{g/l}$), columns 9 and 10 give the location and column 11 gives the date of the station. The results for N_2O , NO_2 , NO_3 , and temperature have been plotted against depth, in Fig. 3 for the seven stations.

An examination of Fig. 3 shows two distinct distribution patterns for N_2O among the seven stations. At stations No. 1, 4, 5, 6, and 7 the N_2O concentration increases rapidly from the surface down to a depth of 100 m, and then remains relatively constant down to the maximum depth of 300 m. Stations No. 2 and 3 show the same rapid increase in the N_2O concentration between the surface and 75–100 m, but then the N_2O concentration shows a corresponding decrease in the next

50–75 m, until the concentration of N_2O at 150 m is actually lower than that found at the surface. In fact, at stations No. 2 and 3 the water samples are either just saturated or undersaturated with N_2O below a depth of 150 m. The N_2O equilibrium values shown in Fig. 3 were obtained by assuming that the water at each depth was in equilibrium with an atmosphere containing 330 p.p.b. v/v N_2O at the ambient water temperature and a salinity of 35.0‰. We assumed a salinity of 35.0‰ for all of our solubility calculations, since the solubility of N_2O is not very sensitive to changes in salinity (it changes by less than 1% for variations in the salinity between 34.0‰ and 36.0‰), and we did not have concurrent salinity measurements for the water samples.

The behavior of N_2O at stations No. 2 and 3 indicates that different levels of the same water column can have drastically different roles in the N_2O cycle. At both stations the upper 100 m of the water column, from the bottom of the thermocline to the surface, acts as a source of nitrous oxide. The water in this region is consistently supersaturated, with some of the saturation levels exceeding 1000%, including the highest dissolved N_2O concentration we measured during the entire cruise, at 75 m at station No. 3. However, the water column beneath the thermocline appears to be a sink for N_2O . Although we do not have concurrent measurements of dissolved O_2 for our sea water samples, stations No. 2 and 3 are in the core of a well-defined oxygen-deficient zone (Fig. 1) (Codispoti, 1973), where the oxygen concentration is less than 0.2 ml/l from a depth of ~ 100 m down to almost 900 m. This suggests that the low N_2O concentrations below 100 m at stations No. 2 and 3 are the result of denitrification. The behavior of N_2O at stations No. 2 and 3 is similar to the primary nitrite maximum, examples of which can be seen at stations No. 4 and 5 (and which is indicated by the high NO_2 value at 50 m at station No. 3). The primary nitrite maximum is associated with the thermocline, and is generally attributed to the accumulation of nitrite produced as an intermediate in bacterial nitrification and assimilatory nitrate reduction by phytoplankton (Wada and Hattori, 1971; Hattori and Wada, 1971). It is likely that the distribution of N_2O at stations No. 2 and 3 can be attributed to the same processes, and is accumulating in the thermocline due to the restriction which it poses upon vertical circulation.

However, the N_2O distribution found at stations

Table 2. *Hydro-cast Stations for Alpha Helix cruise*

St. No.	Temp. (°C)	Depth	NO ₃	PO ₄	SiO ₄	NO ₂	NH ₄	[N ₂ O] µg/l	Lat.	Long.	Date
1	15.2	0	0.00	0.46	1.94	0.06	0.24	0.51, 0.54	27°33' N	114°57.6' W	March 6, 1976
	11.6	50	12.45	1.44	13.31	0.15	0.67	1.01, 1.04			
	11.1	100	22.43	2.19	29.08	0.07	0.22	2.03			
	10.7	150	23.84	2.68	37.57	0.06	0.22	2.35			
	10.1	200	24.24	2.87	42.29	0.06	0.28	2.34			
	9.9	225	23.05	2.95	44.37	0.05	0.34	2.16			
	9.8	250	25.25	2.98	44.93	0.05	0.28	2.19			
	9.6	275	25.75	3.00	47.58	0.05	0.42	2.09			
	9.6	290	26.35	3.02	49.09	0.05	0.28	2.16			
	9.6	300	26.35	3.03	50.03	0.05	0.21	2.19			
2	21.9	0						0.52, 0.50	22°01' N	109°4.9' W	March 8, 1976
	17.9	50						0.71			
	12.9	100						2.78			
	12.3	150						0.43			
	11.9	175						0.43			
3	27.7	0	0.03	0.45	1.29	0.07	0.30	0.28, 0.32	15°36.9' N	103°10.7' W	March 10, 1976
	27.6	10	0.04	0.45	1.24	0.06	0.28	0.31			
	27.5	25	0.07	0.46	1.24	0.08	0.26	0.44			
	25.6	50	13.36	1.52	6.15	2.02	0.31	1.89			
	18.1	75						5.08			
	14.8	100						2.11			
	12.6	150						0.23			
	11.9	200						0.60			
	11.1	250						0.18			
	10.3	300						0.12			
4	26.4	0	1.34	0.51	3.0	0.13	0.30	0.37	9°32.6' N	97°26.1' W	March 12, 1976
	26.4	10	1.43	0.54	3.0	0.13	0.45	0.37			
	26.3	25	3.35	0.66	3.6	0.17	0.33	0.44			
	24.9	50	14.74	1.67	8.9	1.04	0.30	1.85			
	15.8	75	27.91	2.48	21.9	1.69	0.27	4.06			
	13.4	100	32.04	2.52	25.6	0.10	0.27	3.53			
	12.2	150	31.75	2.46	28.2	0.10	0.26	3.27			
	11.6	200	32.15	2.52	30.2	0.09	0.27	3.03			
	10.9	250	32.35	2.55	32.2	0.09	0.27	2.54			
	10.3	300	32.44	2.70	36.8	0.09	0.27	2.36			

5	29.2	0	0.37	0.42	1.65	0.10	0.35	0.37, 0.36	5°09'N	93°22.7'W	March 13-14, 1976
	27.8	10	0.47	0.43	1.85	0.10	0.33	0.40			
	27.1	25	2.69	0.60	2.80	0.14	0.29	0.53			
	23.3	50	4.15	0.77	3.20	0.19	0.35	0.58			
	16.0	75	5.88	0.88	3.20	0.21	0.52	1.22			
	13.7	100	21.45	1.90	15.16	0.59	0.35	2.40			
	13.1	150	41.20	2.22	19.61	0.29	0.31	2.78			
	12.8	200	28.88	2.37	21.51	0.15	0.27	3.03			
	12.4	250	27.66	2.35	22.26	0.09	0.28	2.74			
	11.9	300	28.66	2.39	24.01	0.08	0.28	2.74			
6	27.4	0	1.69	0.79	4.40	0.11	0.71	0.38, 0.33	3°13.4'S	85°25.1'W	March 16, 1976
	27.3	10	1.64	0.54	2.34	0.11	0.34	0.34			
	26.8	25	2.84	0.67	3.22	0.14	0.55	0.49			
	18.2	50	13.23	1.70	8.30	1.32	1.17	1.85			
	14.7	75	15.93	1.94	16.66	1.12	1.35	2.07			
	13.9	100	21.97	1.94	17.59	0.14	0.21	2.56			
	13.3	150	19.96	1.97	19.98	0.07	0.20	2.28			
	13.1	200	22.14	2.13	22.28	0.06	0.18	2.01			
	12.7	250	23.71	2.41	25.30	0.00	0.19	3.84			
	12.1	300	20.53	2.68	30.09	0.07	0.18	3.42			
7	25.8	0	0.97	0.64	2.04	0.11	0.33	0.78, 0.73	7°40'S	81°26.2'W	March 18, 1976
	25.7	10	0.16	0.51	2.42	0.09	0.23	0.91			
	23.3	25	0.40	0.64	3.78	0.14	0.97	1.50			
	15.4	50	22.33	2.40	16.97	0.19	0.20	2.41			
	13.8	100	25.03	2.41	21.24	0.14	0.20	3.51			
	13.6	150	23.73	2.47	22.55	0.12	0.17	4.39			
	13.2	200	22.29	2.24	24.73	0.09	0.18	3.95			
	12.8	200-250	23.32	2.55	28.37	0.23	0.18	3.92			
	12.5	250	22.81	2.56	28.66	0.30	0.19	3.59			
	12.0	300	24.78	2.61	29.24	0.10	0.19	4.47			

All concentrations $\mu\text{M/l}$, except N_2O , which is $\mu\text{g/l}$.

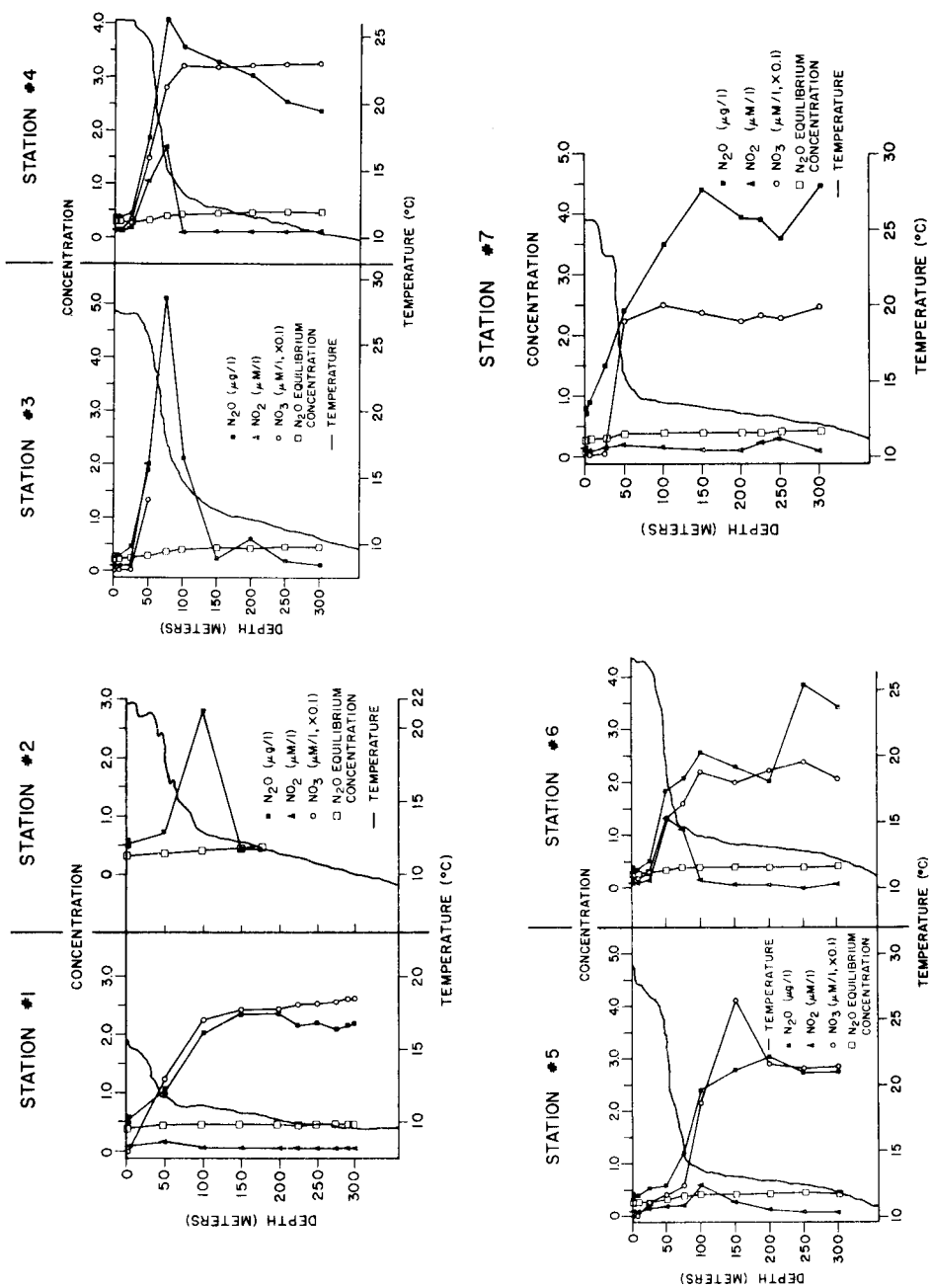


Fig. 3. Results of the measurements of N_2O , NO_2 , and NO_3 from the seven hydro-cast stations. The N_2O concentration (in $\mu\text{g/l}$) is shown versus the depth (in meters) by (■). The concentration of NO_2 (in $\mu\text{M/l}$) is shown by (▲), and the concentration of NO_3 (in $\mu\text{M/l}$) is shown by (○). The calculated equilibrium concentration of N_2O at all depths was obtained using the stagnant film model and assuming an atmospheric concentration of 330 p.p.v. v/v N_2O . It is shown by (□). The water temperature (in $^{\circ}\text{C}$) is shown by the solid line.

No. 1, 4, 5, 6, and 7 cannot be explained in this manner. The N_2O concentrations which we measured below the thermocline are clear evidence of *in situ* production of nitrous oxide throughout the water column. The N_2O concentrations are considerably supersaturated at all depths, with values ranging from $\sim 140\%$ at the surface to more than 1000% saturation in the intermediate waters below the thermocline.

4. Discussion

The first extensive measurements of nitrous oxide in the ocean were made by Junge, Hahn and coworkers (Junge et al., 1971; Hahn, 1974, 1975), who found the surface waters of the northern Atlantic Ocean to be supersaturated, with the degree of saturation decreasing with increasing latitude. They also found that there was an inverse relationship between N_2O and O_2 concentrations, with the highest N_2O concentrations occurring in the oxygen-minimum layer (Hahn, 1974, 1975). Consequently, Hahn concluded that denitrification was the source of excess N_2O in the oceans, despite the fact that the dissolved oxygen concentrations were always quite high. Yoshinari (1976) made a number of measurements of N_2O in the western Atlantic and the Caribbean Sea, finding results similar to Hahn and Junge. However, he found that there was a linear relationship between the excess N_2O concentration ($N_2O(\text{obs}) - N_2O(\text{sat})$) and the apparent oxygen utilization (AOU), which suggests that the rate of N_2O production is proportional to the rate of oxygen utilization. This led him to conclude that N_2O may be formed by the oxidation of organic amines, i.e., nitrification.

The measurements reported here were the first detailed measurements of nitrous oxide in the Pacific Ocean. The results for this area (the ETPO) are important in view of the role it is believed to play in the global nitrogen cycle (Cline and Kaplan, 1975; Codispoti and Richards, 1976; Richards, 1971; Cline and Richards, 1972; Goering et al., 1973; Richards and Broenkow, 1971). The surface water in this region is generally supersaturated with N_2O , particularly in areas of upwelling. The intermediate waters show two distinct patterns, with five of the stations showing large N_2O supersaturations throughout the water column, and two stations showing a nitrous oxide

maximum at 75–100 m, and then decreasing rapidly in the next 50–75 m until the N_2O concentration at 150 m and below is lower than that found at the surface. These two stations were located in the oxygen-deficient zone off the coast of Mexico (Codispoti, 1973), which points to denitrification in the intermediate waters as a sink for N_2O . However, other stations (Nos. 6 and 7) located in the oxygen-deficient region off the coast of Peru, where denitrification is known to take place (Carlucci and Schubert, 1969; Dugdale et al., 1977), showed considerable supersaturation throughout the water column.

More recent measurements in the same region by Cohen and Gordon (1978) and Elkins et al. (1978) show similar results. Cohen and Gordon, making measurements in the oxygen-deficient region off the coast of Mexico, found that the stations fit into two groups, one with a broad N_2O minimum below the thermocline, and a second group which showed significant supersaturation for N_2O throughout the entire water column. The stations displaying the N_2O minimum were in the heart of the oxygen-deficient region, and had "near-zero oxygen concentrations and well-developed secondary nitrite maxima". The stations which showed supersaturation for N_2O throughout the water column, while showing slightly higher oxygen concentrations than those in the other group, were still in the oxygen-deficient region, and had very low oxygen concentrations, less than ~ 0.25 ml/l. Elkins et al. made measurements off the coast of Peru, finding "the observed concentration of N_2O is undersaturated with respect to the atmosphere between 150 and 250 m, a region in which the oxygen concentrations lie below 0.1 ml/l". However, they also found large supersaturations of N_2O at 100 and 300 m, where the dissolved oxygen concentration was only ~ 0.25 ml/l.

Furthermore, Cohen (1978) has reported results from Saanich Inlet, an anoxic basin in British Columbia. His measurements show that the anoxic, sulfate-reducing deep waters of the inlet contain essentially no nitrous oxide. This is unequivocal proof that N_2O is consumed by denitrification in a totally anoxic environment. However, Cohen also found N_2O saturation values of almost 200% only a few meters above the anoxic zone, with oxygen concentrations of less than ~ 0.5 ml/l.

The pattern which seems to be emerging from these results suggests that the role of N_2O in the

nitrogen cycle in the oceans is not a simple one. It appears as though nitrous oxide is probably produced by any of three different processes, depending upon the chemical and biological conditions, and is consumed by one of these processes, denitrification, under totally anoxic conditions.

Hahn and Junge (1977) have suggested that three processes are likely candidates for N_2O production in the oceans: (1) nitrification (ammonia oxidation), (2) assimilatory nitrate reduction (nitrate uptake), and (3) dissimilatory nitrate reduction (denitrification).

The evidence that nitrification is a significant source of N_2O in the oceans is mostly indirect. Yoshinari (1976) was the first to suggest that nitrification was a major source of nitrous oxide in the Atlantic Ocean on the basis of a linear relationship between the excess N_2O in the water (ΔN_2O) and the apparent oxygen utilization (AOU). Subsequently, Cohen and Gordon (1978) and Elkins *et al.* (1978) have also obtained similar plots for ΔN_2O versus AOU. The association of an N_2O maximum with the primary nitrite maximum, which is often attributed to bacterial nitrification, supports the view that nitrification may be a major source of N_2O . However, the relationship between ΔN_2O and AOU does not prove that nitrification is the process responsible for N_2O production in these waters. AOU is a measure of the total biological oxygen utilization in the water since it left the surface, where it was presumably in equilibrium with the atmosphere. Since oxidation of ammonia or organic amines accounts for an extremely small part of the total biological oxygen demand, the ΔN_2O :AOU plots actually demonstrate a relationship between nitrous oxide production and total non-photosynthetic biological activity in the water since it left the surface. In fact, the results of Elkins *et al.* (1978) for the Pacific Ocean show a much larger value for ΔN_2O for any given value of AOU than the results of Yoshinari (1976) for the Atlantic Ocean, which implies that different processes may be responsible for nitrous oxide production in the different regions of the ocean. Therefore, while there is considerable evidence which suggests that bacterial nitrification in the ocean is a major source of N_2O , it is not conclusive.

Assimilatory nitrate reduction (nitrate uptake) was originally suggested as a possible source of N_2O by Hahn and Junge (1977) on the basis of the similarity of the biochemical pathways involved in

dissimilatory (denitrification) and assimilatory nitrate reduction. However, recent experimental evidence indicates that nitrate uptake may be a very intense source of N_2O in regions of upwelling (this paper; Elkins *et al.*, 1978; Weiss, 1978). We found the highest surface concentrations of N_2O in the waters of upwelling areas off the coast of Baja California and Peru, and in the equatorial upwelling region. Elkins *et al.* (1978) also found the highest N_2O concentrations "in an intense feature associated most probably with upwelling in the north tropical divergence zone", and the "largest surface concentrations were observed in the zone of high productivity associated with the equatorial upwelling". Weiss (1978), making measurements in the eastern tropical Pacific, the Atlantic Ocean, the Arabian Sea, and the Indian Ocean, has also found that nitrous oxide is an outstanding indicator of local upwelling. Since nitrate uptake is the major source of nitrogen primary productivity in upwelling regions (Dugdale and Goering, 1967), assimilatory nitrate reduction is clearly implicated as a very intense source of N_2O . Therefore, regions of upwelling may represent localized but very strong sources of N_2O . Since the eastern tropical Pacific is a region of upwelling and very high productivity, it is clearly not typical of the ocean with respect to nitrous oxide production, and the flux of N_2O from this region is probably near the upper limit for the marine production of nitrous oxide. This is true even if denitrification in the intermediate waters of the region is a sink for N_2O , since they are isolated from the atmosphere by the surface mixed layer, which is consistently supersaturated with N_2O .

The role of denitrification (dissimilatory nitrate reduction) is currently the most controversial aspect of the nitrous oxide cycle in the ocean. It was originally believed that denitrification was the major source of N_2O in the oceans (Hahn, 1974), analogous to the nitrogen cycle in soils (Wijler and Delwiche, 1954; Payne, 1973). However, the recent results from the eastern tropical Pacific (Cohen and Gordon, 1978; Elkins *et al.*, 1978) and Saanich Inlet (Cohen, 1978) indicate that denitrification under anoxic conditions acts as a net sink for N_2O . Cohen and Gordon (1978) have concluded from this that denitrification acts only as a sink in the ocean, and therefore there is no relationship between the production of N_2O and N_2 in the ocean.

We do not believe that the data support this simplistic view of the role of denitrification in the

nitrous oxide cycle of the ocean. It appears, rather, that N_2O is both produced and consumed by denitrification in sea water, with the net effect of these processes depending upon a number of factors, particularly the oxygen concentration in the water. Under virtually anoxic conditions ($O_2 < 0.1$ ml/l) it is apparent that whatever N_2O is formed by denitrification is subsequently reduced to N_2 , and thus these waters act as a net sink for N_2O . That N_2O is being formed very rapidly under these conditions was shown by Elkins et al. (1978), who incubated samples from the oxygen minimum region ($O_2 < 0.1$ ml/l) in the presence of acetylene, which has been shown to inhibit the reduction of N_2O to N_2 by denitrifying organisms (Yoshinari and Knowles, 1976). In one sample the N_2O concentration had increased from 1.3 to 4.3 $\mu\text{g/l}$ within an hour after the application of C_2H_2 , and the N_2O concentration reached 191 $\mu\text{g/l}$ after 18 days, indicating that 30% of the starting concentration of NO_3 had accumulated as N_2O .

Under slightly higher oxygen concentrations ($O_2 \cong 0.1$ – 0.3 ml/l) nitrous oxide may be the major product of denitrification, and under these conditions denitrification will act as a net source of N_2O . It has been shown that denitrification proceeds at these higher oxygen concentrations (Goering, 1968), although at a slightly diminished rate. Furthermore, Wijler and Delwiche (1954) found that while the rate of denitrification decreased by a factor of 3–10 in going from anoxic conditions to oxygen concentrations of 1–3%, the denitrification products changed from 100% N_2 under anoxic conditions to 68–83% N_2O under 1–3% O_2 . Therefore, there is evidence to support the hypothesis that nitrous oxide will be produced by denitrification under oxygen-deficient, but not anoxic, conditions.

It appears as though the role of the secondary nitrite maximum in marine denitrification may have produced some of the confusion. Because they could not measure the other products of denitrification (N_2 , N_2O), oceanographers seized upon NO_2 in the oxygen-minimum layer as the sign that denitrification was taking place (Thomas, 1966; Goering, 1968; Fiadero and Strickland, 1968; Wooster et al., 1965; Cline and Richards, 1972). However, it has been shown that secondary NO_2 concentrations in excess of 0.1 μM occur only at oxygen concentrations below ~ 0.02 ml/l (Fiadero and Strickland, 1968; Cline and Richards, 1972).

Since it is known that denitrification can occur at O_2 concentrations of 0.2 ml/l (Goering, 1968) or greater (Payne, 1973, 1976), and that considerable nitrate reduction is evident in waters containing more than 0.2 ml/l O_2 (Cline and Richards, 1972), we are apparently seeing the result of nitrite instability at oxygen concentrations greater than ~ 0.05 ml/l rather than an absence of denitrification at these oxygen concentrations.

Further support comes from the measurements by Packard et al. (1978) of nitrate reductase (NR) activity in the subsurface waters of the Peru Current. Nitrate reductase is the enzyme which catalyzes the reduction of NO_3 to NO_2 , the first step in denitrification. They found that NR activity "was independent of *in situ* O_2 within the low levels observed", between 0.09–0.27 ml/l O_2 . They also found that NR activity "could not be predicted from the NO_2 concentration". They found samples with low NR activity and high NO_2 concentrations, and others with high NR activity and low NO_2 concentrations. Therefore, the secondary nitrite maximum is not a good indicator of active denitrification, and may be a relic of denitrification which only survives under anoxic conditions. In the presence of oxygen, NO_2 may be re-oxidized to NO_3 by nitrate reductase or some other enzyme present in the ocean, although this is purely speculative. All of the data obtained thus far on the concentration of nitrous oxide in the oceans point to them as a source of N_2O to the atmosphere. There are virtually no measurements showing undersaturation of N_2O in surface sea water, even in regions where it appears as though the intermediate waters are undersaturated (or even devoid of N_2O , such as the deep waters of Saanich Inlet). If denitrification in the anoxic intermediate waters of the ETPO is a net sink for N_2O , they will still not act as a sink for atmospheric N_2O , since they are shielded from the atmosphere by the surface water layer, which is consistently supersaturated with nitrous oxide. Therefore, the estimate by McElroy et al. (1976) that the oceans might be a sink of 40 Mt N_2O year⁻¹ is untenable. None of the evidence supports any sink for N_2O in the oceans, let alone one of this magnitude. Indeed, Elkins et al. (1978) now estimate a global marine source of ~ 7 Mt N_2O year⁻¹ on the basis of their experimental data.

The extrapolation of our average flux values from the ETPO yields a global marine production of 61.7 Mt N_2O year⁻¹. However, we believe that

this estimate of the net production of N_2O from the oceans is more properly an upper limit, for several reasons. First of all, Richards (1971) has concluded "that denitrification in the eastern tropical Pacific is a major factor in the oceanic budget of combined nitrogen". Therefore, the ETPO is extremely active biologically, and is not typical of the nitrogen metabolism rate in the oceans. Furthermore, the high N_2O supersaturations associated with upwelling regions (stations No. 1, 6, and 7, for example) point to nitrate uptake by phytoplankton as a significant source of N_2O . Since a number of our surface water samples were collected in regions of upwelling, and the ETPO is a region of considerably above average productivity, it is likely that the production of nitrous oxide is much more vigorous along our cruise track (Fig. 1) than it is throughout the rest of the oceans, on the average.

Therefore, we estimate the upper limit for the net marine production of N_2O is approximately 60 Mt N_2O year⁻¹. We previously calculated an upper limit for the global net production of N_2O (based upon a minimum 30-year atmospheric lifetime) of approximately 80 Mt year⁻¹. However, the uncertainties in both of these numbers (a factor of five in the global net production, and a factor of ten in the marine source strength) are so great that it is fruitless to attempt to draw any conclusions from them.

The only way to determine the role of the oceans in the global N_2O cycle, and the role of N_2O in the global nitrogen cycle is to continue making

measurements of nitrous oxide throughout the marine environment. The possibility that N_2O may be valuable as a tracer in locating areas of upwelling in the ocean provides yet another reason to continue this research. While the measurement of N_2O in the ocean was begun with the intention of determining their impact upon atmospheric N_2O levels, it may turn out to be more important as a tool for studying the nitrogen cycle in the oceans. Since nitrogen is the limiting nutrient for primary productivity in large parts of the ocean, this is a subject of considerable importance to our understanding of the oceans, and the impingement of mankind upon them.

5. Acknowledgements

We would like to thank Roger Shepard and Jane Kogelschatz of Duke Marine Laboratory, Ted Packard of Bigelow Marine Laboratory, and the crew and support personnel of the R.V. *Alpha Helix* for their advice and assistance in carrying out our research. We would particularly like to thank Walter Garey for his encouragement to our participation in this cruise. They were of invaluable help in assuring the success of our efforts. We would also like to thank Jim Elkins of Harvard for supplying us with his program to calculate N_2O solubilities in sea water.

This research was supported in part by grants from the National Science Foundation, National Aeronautics and Space Administration, and the Manufacturing Chemists Association.

REFERENCES

- Broecker, W. S. and Peng, T. H. 1974. Gas exchange rates between air and sea. *Tellus* 26, 21–35.
- Carlucci, A. F. and Schubert, H. R. 1969. Nitrate reduction in sea-water of the deep nitrite maximum off Peru. *Limnol Oceanogr.* 14, 187–193.
- Council for Agricultural Science and Technology (CAST) 1976. Report No. 53, January 19. 33 pp.
- Cicerone, R. J., Shetter, J. D., Stedman, D. H., Kelly, T. J. and Liu, S. C. 1978. Atmospheric N_2O : Measurements to determine its sources, sinks, and variations. *J. Geophys. Res.* 83, 3042–3050.
- Cline, J. D. and Kaplan, I. R. 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. *Marine Chem.* 3, 271–299.
- Cline, J. R. and Richards, F. A. 1972. Oxygen deficient conditions and nitrate reduction in the eastern tropical North Pacific Ocean. *Limnol. Oceanogr.* 17, 885–899.
- Codispoti, L. A. 1973. Denitrification in the eastern tropical North Pacific Ocean. Ph.D. Thesis, University of Washington. 118 pp.
- Codispoti, L. A. and Richards, F. A. 1976. An analysis of the horizontal regime of denitrification in the eastern tropical North Pacific. *Limnol. Oceanogr.* 21, 379–388.
- Cohen, Y. 1978. Consumption of dissolved nitrous oxide in an anoxic basin. Saanich Inlet, British Columbia. *Nature* 272, 235–237.
- Cohen, Y. and Gordon, L. I. 1978. Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: Evidence for its consumption during denitrification and possible mechanisms for its production. *Deep-Sea Res.* 25, 509/524.

- Craig, H. and Gordon, L. I. 1963. Nitrous oxide in the ocean and the marine atmosphere. *Geochim. et Cosmochim. Acta* 27, 959–955.
- Dugdale, R. C. and Goering, J. J. 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnol. Oceanogr.* 12, 196–206.
- Dugdale, R. C., Goering, J. J., Barber, R. T., Smith, R. L. and Packard, T. T. 1977. Denitrification and hydrogen sulfide in the Peru upwelling region during 1976. *Deep-Sea Res.* 24, 601–608.
- Elkins, J. W., Wofsy, S. C., McElroy, M. B., Kolb, C. E. and Kaplan, W. A. 1978. Aquatic sources and sinks for nitrous oxide. *Nature* 275, 602–606.
- Fiadero, M. and Strickland, J. D. H. 1968. Nitrate reduction and the occurrence of a deep nitrite maximum in the ocean off the west coast of South America. *J. Marine Res.* 26, 187–201.
- Goering, J. J. 1968. Denitrification in the oxygen minimum layer of the eastern tropical Pacific Ocean. *Deep-Sea Res.* 15, 157–164.
- Goering, J. J., Richards, F. A., Codispoti, L. A. and Dugdale, R. C. 1973. Biogeochemical budgets. In *Proceedings of symposium on hydrogeochemistry and biogeochemistry* (ed. E. Ingerson), Vol. II: Biogeochemistry. Washington, D.C.: Clarke Co.
- Goering, J. J. and Menzel, D. W. 1965. The nutrient chemistry of the sea surface. *Deep-Sea Res.* 12, 839–843.
- Goldan, P. D., Bush, Y. A., Fehsenfeld, F. C., Albritton, D. L., Crutzen, P. J., Schmeltekopf, A. L. and Ferguson, E. E. 1978. Tropospheric N_2O mixing ratio measurements. *J. Geophys. Res.* 83, 935–939.
- Hahn, J. 1974. The North Atlantic Ocean as a source of atmospheric N_2O . *Tellus* 26, 160–168.
- Hahn, J. 1975. N_2O measurements in the Northeast Atlantic Ocean. *Meteor. Forschungsergebnisse, Reihe A* 16, 1–14.
- Hahn, J. and Junge, C. 1977. Atmospheric nitrous oxide: A critical review. *Z. Naturforsch.* 32a, 190–214.
- Hattori, A. and Wada, E. 1971. Nitrite distribution and its regulating processes in the equatorial Pacific Ocean. *Deep-Sea Res.* 18, 557–568.
- Junge, C. and Hahn, J. 1971. N_2O measurements in the North Atlantic. *J. Geophys. Res.* 76, 143–146.
- Junge, C., Bockholt, B., Schütz, K. and Beck, R. 1971. N_2O measurements in air and sea water over the Atlantic. *Meteor. Forschungsergebnisse, Reihe B* 6, 1–11.
- Junge, C. 1974. Residence time and variability of tropospheric trace gases. *Tellus* 26, 477–488.
- Levy, H., Mahlman, J. D. and Moxim, W. J. 1979. A preliminary report on the numerical simulation of the three-dimensional structure and variability of atmospheric N_2O . Submitted to *Geophys. Res. Lett.*
- McAuliffe, C. 1971. GC determination of solutes by multiple phase equilibrium. *Chem. Tech.*, January, 46–51.
- McElroy, M. B., Elkins, J. W., Wofsy, S. C. and Yung, Y. L. 1976. Sources and sinks for atmospheric N_2O . *Rev. Geophys. Space Phys.* 14, 143–150.
- Packard, T. T., Dugdale, R. C., Goering, J. J. and Barber, R. T. 1978. Nitrate reductase activity in the subsurface waters of the Peru Current. *J. Marine Res.* 36.
- Payne, W. J. 1973. Reduction of nitrogenous oxides by microorganisms. *Bacteriol. Rev.* 37, 409–452.
- Payne, W. J. 1976. Denitrification. *Trends in Biochem. Sci.* 1, 220–222.
- Pierotti, D., Rasmussen, R. A. and Chatfield, R. 1978a. Continuous measurements of nitrous oxide in the troposphere. *Nature* 274, 574–576.
- Pierotti, D., Rasmussen, L. E. and Rasmussen, R. A. 1978b. The Sahara as a possible sink for trace gases. *Geophys. Res. Lett.* 5, 1001–1004.
- Rasmussen, R. A., Krasnec, J. and Pierotti, D. 1976. N_2O analysis in the atmosphere via electron capture-gas chromatography. *Geophys. Res. Lett.* 3, 615–618.
- Reid, J. L. 1965. *Intermediate waters of the Pacific Ocean*. Baltimore: Johns Hopkins Press. 85 pp.
- Richards, F. A. 1971. Comments on the effects of denitrification on the budget of combined nitrogen in the ocean. *Extrait de la mer* 9, 68–77.
- Richards, F. A. and Broenkow, W. W. 1971. Chemical changes, including nitrate reduction, in Darwin Bay, Galapagos Archipelago, over a two-month period, 1969. *Limnol. Oceanogr.* 16, 758–765.
- Schütz, K., Junge, C., Beck, R. and Albrecht, B. 1970. Studies of Atmospheric N_2O . *J. Geophys. Res.* 75, 2230–2246.
- Singh, H. B., Salas, L. J., Shigeishi, H. and Crawford, A. 1977. Urban-nonurban relationships of halocarbons, SF_6 , N_2O , and other atmospheric trace constituents. *Atmos. Environ.* 11, 819–828.
- Thomas, W. H. 1966. On denitrification in the north-eastern tropical Pacific Ocean. *Deep-Sea Res.* 13, 1109–1114.
- Wada, E. and Hattori, A. 1971. Nitrite metabolism in the euphotic layer of the central North Pacific Ocean. *Limnol. Oceanogr.* 16, 766–772.
- Weiss, R. F. and Price, B. A. 1979. Manuscript in preparation.
- Weiss, R. F. 1978. Nitrous oxide in the surface water and marine atmosphere of the North Atlantic and Indian Oceans. Paper presented at the Fall AGU meeting, San Francisco, December 4–8.
- Wijler, J. and Delwiche, C. C. 1954. Investigations on the denitrifying process in soil. *Plant and Soil* 5, 155–169.
- Williams, P. M. 1967. Sea surface chemistry: organic carbon and organic and inorganic nitrogen and phosphorus in surface films and subsurface waters. *Deep-Sea Res.* 14, 791–800.
- Wooster, W. S., Chow, T. J. and Barrett, I. 1965. Nitrite distribution in Peru Current waters. *J. Marine Res.* 23, 210–221.
- Yoshinari, T. 1976. Nitrous oxide in the sea. *Marine Chem.* 4, 189–202.
- Yoshinari, T. and Knowles, R. 1976. Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. *Biochem. Biophys. Res. Comm.* 69, 705–710.

ИЗМЕРЕНИЯ ЗАКИСИ АЗОТА В ВОСТОЧНОЙ ТРОПИЧЕСКОЙ ЧАСТИ ТИХОГО ОКЕАНА

В марте 1976 г. во время рейса из Сан-Диего, Калифорния в Сан Мартин, Перу были выполнены первые измерения N_2O в морской воде и в воздухе в восточной тропической части Тихого океана. Непрерывные измерения N_2O в атмосфере над морем производились в течение всего рейса. Тропосферное отношение смеси N_2O было $(332 \pm 9) \times 10^{-9}$. Представляется, что концентрация N_2O в морском воздухе указывает на прямую связь с концентрацией N_2O в поверхностных водах с наибольшими отношениями смеси N_2O над областями, которые были сильно перенасыщены-вблизи берегов Калифорнийского залива и Перу и в области экваториального апвеллинга. Пробы поверхностных морских вод были обычно перенасыщены N_2O со средним насыщением в 145 % относительно атмосферы над морем. Средний поток N_2O из поверхностных вод в атмосферу был $0,5 \times 10^{-12}$ г N_2O см $^{-2}$ с $^{-1}$. Только одна проба воды имела значительное недосыщение; 28 других проб были приблизительно насыщены или перенасыщены. Пробы воды отбирались также до глубин 300 м во время

7 станций с вертикальными разрезами. Станции показали два различных типа распределений концентрации N_2O с глубиной. На 5 из 7 станций концентрация N_2O быстро росла от поверхности до 100 м, а затем оставалась сравнительно постоянной до максимальной глубины 300 м. На двух других станциях концентрация N_2O имела тот же быстрый рост от поверхности до 75–100 м, но затем она уменьшалась в следующих 50–75 м, так что концентрация N_2O на 150 м была ниже, чем на поверхности. На этих двух станциях вода от 150 до 300 м была близка к насыщению или недосыщена по отношению к атмосфере. Эти две станции были в области с недостатком кислорода вблизи Мексики, из чего можно сделать вывод, что низкие концентрации N_2O под термоклином могут быть из-за денитрификации. Однако станции в области с недостатком кислорода вблизи Перу выявили значительное перенасыщение N_2O на всех глубинах. Недавние результаты указывают на то, что роль N_2O в азотном цикле в океане может быть более сложной, чем это предполагалось ранее.