

Nitrous oxide production in the tropical Atlantic Ocean

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Abstract—Atmospheric and oceanic nitrous oxide (N_2O) measurements were carried out in 1986 in the tropical Atlantic ($5^\circ - 12^\circ N$, $20^\circ - 22^\circ W$). The average N_2O concentration in the air was 311 ± 6 ppb. Surface waters were found to be supersaturated (123–132%). The N_2O production in highly supersaturated deep waters enabled us to estimate the oceanic source of atmospheric N_2O to $11.3 \text{ ml m}^{-2} \text{ y}^{-1}$. The eddy diffusion coefficient in the upper thermocline is estimated to be $0.2 \text{ cm}^2 \text{ s}^{-1}$ to support the vertical transport of N_2O from the deep layers to the sea surface. The chemical environment (oxygen – nitrate) indicates that the nitrification is the most probable process of N_2O formation, but in certain cases assimilatory nitrate reduction may be an additional cause.

INTRODUCTION

In recent years, nitrous oxide (N_2O) has received attention from scientists owing to interest generated by the major role this trace gas appears to play in controlling the abundance of stratospheric ozone (CRUTZEN, 1976; WEISS and CRAIG, 1976). Recently interest has grown because of its direct or indirect role in global warming, as with methane (WANG *et al.*, 1976; DONNER and RAMANATHAN, 1980; WANG and MÖLNAR, 1985). The atmospheric concentrations of the two trace gases have been increasing in the last few decades (WEISS and CRAIG, 1976; WEISS, 1981a; KHALIL and RASMUSSEN, 1983; PEARMAN *et al.*, 1986) owing to increased anthropogenic input (fossil fuel combustion and fertilizer use). It is believed that their contribution to global warming could amount to as much as one-third of that of CO_2 (RAMANATHAN *et al.*, 1985). WEISS (1981a) calculated the greenhouse effect due to N_2O alone is 10–15% that of CO_2 .

Both the soil and the aquatic environment have been identified as possible sources of N_2O . Most studies of dissolved N_2O in the aquatic environments have taken place in the open ocean (CRAIG and GORDON, 1963; JUNGE and HAHN, 1971; HAHN, 1973, 1974, 1975; YOSHINARI, 1976; WEISS, 1978; ELKINS *et al.*, 1978; SINGH *et al.*, 1979; COHEN and GORDON, 1978, 1979; PIEROTTI and RASMUSSEN, 1980; HASHIMOTO *et al.*, 1983; CODISPOTI and CHRISTENSEN, 1985; CLINE *et al.*, 1987). Other workers have described the distribution of N_2O in estuaries, rivers and lakes (MCELROY *et al.*, 1978; CICERONE *et al.*, 1978a; LEMON and LEMON, 1981; KNOWLES *et al.*, 1981; WAHLEN and YOSHINARI, 1985; DE

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ANGELIS and GORDON, 1985; BUTLER *et al.*, 1987). Mostly, surface observations show that N_2O is present in concentrations in excess of saturation with respect to the atmosphere at the temperature and salinity conditions observed. Consequently, the aquatic systems, open ocean or freshwaters, act as a source for atmospheric N_2O . Undersaturation of N_2O in surface waters is rare (ELKINS *et al.*, 1978).

In subsurface and deep waters, in general, N_2O is negatively correlated with oxygen and positively correlated with nitrate. HAHN (1974) was the first to point out the inverse correlation between N_2O and O_2 in the deep ocean. This inverse relationship was later confirmed (YOSHINARI, 1976; COHEN and GORDON, 1978; ELKINS *et al.*, 1978; CLINE *et al.*, 1987) in areas of the ocean where O_2 was higher than 0.4–0.5 ml l^{-1} . JUNGE and HAHN (1971) and later HAHN (1974) suggested that N_2O is generated by denitrification. YOSHINARI (1976), COHEN and GORDON (1978, 1979) and ELKINS *et al.* (1978), on the basis of the linear relationship between the excess N_2O in the water and the apparent oxygen utilization (AOU), suggested that nitrification was a more likely source. Although PIEROTTI and RASMUSSEN (1980) claimed that N_2O also can be produced during denitrification under non-anoxic conditions ($O_2 = 0.1$ – 0.3 ml l^{-1}), it is clear today that N_2O arises principally from nitrification as shown recently by the data of CLINE *et al.* (1987) in the tropical Pacific. For COHEN and GORDON (1978) and ELKINS *et al.* (1978) there is no doubt that denitrification acts only as a sink for N_2O in the ocean. Further measurements of the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ isotopic composition of N_2O (YOSHIDA *et al.*, 1984; WAHLEN and YOSHINARI, 1985; YOSHIDA, 1988), along the lines of BENDER and GRANDE's (1987) study on the isotopic composition of O_2 , could lead to an indication of the contribution by the different production mechanisms.

Recently CLINE *et al.* (1987) showed how climatic events, such as the El Niño phenomenon, could change the flux of N_2O to the atmosphere. Their study, which confirms the previous conclusions of PIEROTTI and RASMUSSEN (1980), shows the role of the upwelling process on the supersaturation degree of N_2O in the surface waters, and thus the role of the oceans in the global N_2O cycle and the role of N_2O in the global nitrogen cycle. The possibility that N_2O may be a valuable tracer in locating areas of upwelling in the ocean makes it even more interesting to continue taking measurements of N_2O throughout the marine environment. DE ANGELIS and GORDON (1985) and BUTLER *et al.* (1987) reported high concentrations of N_2O in incoming seawater in estuaries in association with recently upwelling waters.

The purpose of our investigation is to contribute to the evaluation of marine processes in regulating the N_2O cycle within the ocean. Our study involves measurements of gas concentrations (O_2 , N_2 , N_2O) and physico-chemical characteristics (temperature, salinity, nutrients) in the northeastern tropical Atlantic.

METHODS

Analytical method for N_2O

The measurement technique for N_2O is derived from that of WEISS *et al.* (1981), employing ultrasonic phaseshift gas chromatography. As with early techniques using thermal conductivity gas chromatography (SWINNERTON *et al.*, 1962; CRAIG and GORDON, 1963; HAHN, 1974), the ultrasonic technique requires enrichment of samples, but this detector type has the advantage of being non-specific and can therefore be employed for the determination of other gases such as argon (OUDOT and MONTEL, 1987). Today most

laboratories use electron-capture gas chromatography (RASMUSSEN *et al.*, 1976; COHEN, 1977; WEISS, 1981b; CICERONE *et al.*, 1978b; SINGH *et al.*, 1979; ELKINS, 1980; LEMON and LEMON, 1981; CLINE *et al.*, 1987) which offers extremely high sensitivity and does not require enrichment, contrary to helium ionization gas chromatography (YOSHINARI, 1976).

Water samples were drawn from 5 liter Niskin bottles into 550 ml volumetric flasks to which was added 0.5 ml of a saturated HgCl_2 solution. The analyses of the samples were performed without delay after collection, but the use of HgCl_2 as a preservative was justified on account of the duration of the analyses (the last sample was generally run 6 h after the first one). The apparatus for collecting dissolved N_2O in seawater samples is shown schematically in Fig. 1 and is derived from the work of YOSHINARI (1976) and COHEN (1977).

The extraction of dissolved N_2O is carried out in the sampling flask after removing a small volume in order to allow a gas dispersion tube to be introduced. A correction is made for the quantity of the atmospheric N_2O in the small head space reserved above the liquid in the flask and carried with dissolved gases stripped by the helium flow. The helium, spread in tiny bubbles at a flow rate of 120 ml min^{-1} , removes the dissolved gases from the sample in 15 min while the sample is stirred magnetically. Water vapor and CO_2 are removed in P_4O_{10} and Ascarite columns, while all the other gases pass through a 6.35 mm o.d. stainless steel tube (length 25 cm) packed with a 13X Molecular Sieve. During the collection of N_2O , the Molecular Sieve trap is immersed in an ice-water bath. After 15 min, N_2O adsorbed on the Molecular Sieve is transferred to the gas chromatograph by switching the 6-port rotary valve B and immediately heating the trap to 250°C

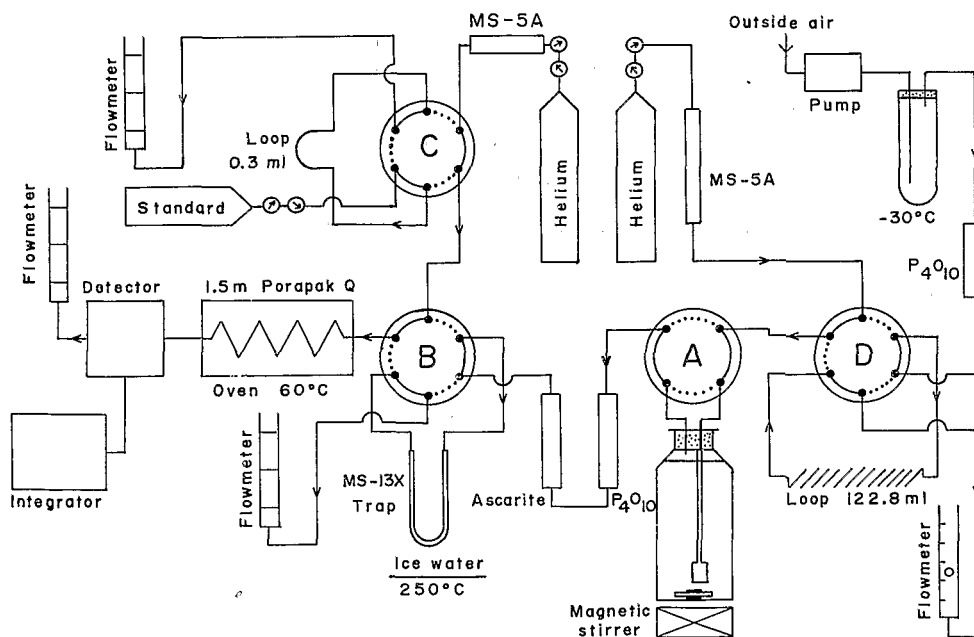


Fig. 1. Gas chromatographic apparatus for the measurement of N_2O in seawater (valve A) and in air (valve D).

with an electrically heated aluminium block. The carrier gas, helium at a flow rate of 50 ml min^{-1} , sweeps N_2O and small amounts of oxygen and nitrogen into the chromatographic column made of 1.5 m stainless-steel tube (6.35 mm o.d.) and packed with Porapak Q held at 60°C in the oven of the chromatograph. The N_2O retention time is about 6 min. At the end of integration of the peak, the heating of the trap is stopped and the valve B turned back to its original position.

The detector is a Tacor model U-90 ultrasonic phase-shift detector, identical to that employed by WEISS *et al.* (1981). The detector cell is operated with a back pressure of 0.7 bar above ambient. The detector output was integrated by a Hewlett-Packard model 3380 S integrator.

Routine calibration of the output signal of the detector is by injection of a commercial standard gas mixing containing 225 ± 6 ppb N_2O in helium (prepared by Air Liquide, France) via a gas sampling valve C with a 0.3 ml sample loop. In the absence of a more accurate standard gas related to a definite scale (e.g. Scripps' standard), the standardization of the measurements is checked against the analysis of tropospheric air.

The air analysis is done by carrying an air sample, taken in a nylon tubing loop (volume = 122.8 ml) via a sampling valve D, on the Molecular Sieve trap, by the same procedure used for seawater analysis. The stripping time is reduced to 10 min. Replicate analysis of air samples in the land laboratory indicates a precision of about $\pm 3\%$, i.e. ± 9 ppb.

The oceanic N_2O values are compared to the expected equilibrium concentrations from N_2O solubility in seawater (WEISS and PRICE, 1980) and average air content of 300 ppb that is the current partial pressure of N_2O in dry air (WEISS *et al.*, 1981).

Measuring equilibrated seawater in the land laboratory produced a supersaturation of 8% and the standard error of four replicates of that water was about 4%.

Temperature, salinity, dissolved gases and nutrients

Temperature and salinity were routinely determined with a Neil-Brown CTD system.

Dissolved O_2 was titrated according to the Winkler method with a precision of 0.1% (OUDOT *et al.*, 1988). The apparent oxygen utilization (AOU) was calculated from the oxygen solubility given by WEISS' (1970) polynomial relationship.

Dissolved molecular nitrogen was measured by gas chromatography according to the method described in OUDOT (1982). The precision of the results is 0.4%. The solubility of nitrogen was calculated by WEISS' (1970) polynomial relationship.

The nutrient analyses (nitrate) were performed using an Auto-Analyzer Technicon II according to the method of WOOD *et al.* (1967). The analytical precision was about 1%.

Site of measurements and sampling

The hydrological and chemical data presented in this paper come from the PIRAL cruise (June–August 1986) carried out aboard the R.V. *Noroit* (France) in the northeastern tropical Atlantic (Fig. 2). The N_2O measurements, in air and seawater, were taken at three sites during three time series of observations: the first, over a 12-day period, in the north equatorial convergence zone (4° – 6°N , 17° – 20°W), the second (8 days) and the third (10 days) in the Guinea Dome area, respectively, at the exact center of the dome ($11^\circ50'\text{N}$, 22°W) and then at a short distance away from it (12°N , 21°W). The thermal domes are well known because of the associated enhanced primary production.

The seawater samples were taken with a rosette (General Oceanics) of 12 Niskin PVC

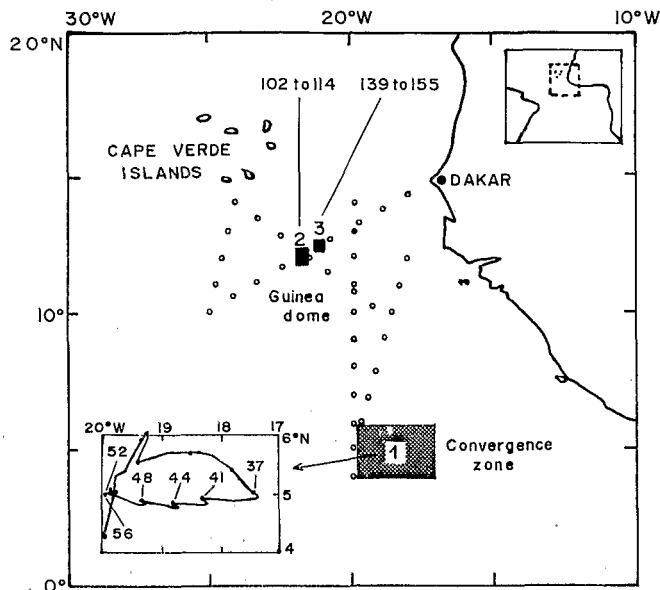


Fig. 2. Locations of stations in the convergence zone (37-56) and in the Guinea Dome area (102-114 and 139-155) during PIRAL cruise (June-August 1986).

5 liter bottles associated with the Neil-Brown CTD system. The sampling for oceanic N_2O was made from 0 to 500 m at 07.30 h (local time), six times at the first site, four and five times at the second and third ones. For dissolved gases solubilities to be calculated, temperature and salinity were measured when the bottles were closed as the CTD probe came up (elimination of the effects of the internal waves).

The air for tropospheric N_2O measurement was pumped at about 5 m above sea level and dried successively on a cold trap at $-30^\circ C$ and on P_4O_{10} column before injection into the sampling loop (Fig. 1).

All analytical measurements, on seawater as well as on air, were performed immediately after collection of samples.

RESULTS

N_2O concentrations in air

The average N_2O concentrations in dry air are, respectively, 318 ± 9 , 308 ± 2 and 308 ± 9 ppb (ppb = 10^{-9} v/v) at the three sites (Table 1). The combined average is 311 ± 6 ppb.

By comparing our average tropospheric value with those of other laboratories we can judge the validity of the calibration of our measurements. The range of atmospheric N_2O concentrations reported in the literature is wide because they depend on different calibrations, and concentrations are calculated either in wet air or in dry air. The most reproducible results are probably those of WEISS (1978) and WEISS *et al.* (1981), who reported a mean value of 299.7 ppb (in dry air) along a 34,000 km ship's track extending in both hemispheres during 1977-1978 and a mean tropospheric dry air mole fraction of N_2O in the northern hemisphere as of 1 January 1978 fixed at 300.2 ± 0.6 ppb. The

Table 1. Atmospheric N₂O measurements

1st Site 5°N, 17° to 20°W			2nd Site 11°50N, 22°W			3rd Site 12°N, 21°W		
Sta. no.	Date (1986)	N ₂ O (ppb)	Sta. no.	Date (1986)	N ₂ O (ppb)	Sta. no.	Date (1986)	N ₂ O (ppb)
37	28 Jun.	331	102	19 Jul.	309	139	03 Aug.	309
41	29 Jun.	318	106	20 Jul.	306	143	04 Aug.	312
44	30 Jun.	313	110	21 Jul.	309	147	05 Aug.	310
48	01 Jul.	315	114	22 Jul.	306	151	06 Aug.	293
52	02 Jul.	304				155	07 Aug.	315
56	03 Jul.	325						
Mean		318	Mean		308	Mean		308
S.D.		± 9	S.D.		± 2	S.D.		± 9

atmospheric measurements conducted by Young and Cline in the North Pacific in April 1979 indicate a value of 297 ± 4 ppb (CLINE *et al.*, 1987). KHALIL and RASMUSSEN (1983) reviewed current studies on the increase in N₂O: the observed rates of increase range from 0.2 to 0.4% (y)⁻¹. Taking as a reference the value (300 ppb) of WEISS *et al.* (1981) in 1978, our measurements made 8 years later should be within the range 305–310 ppb expected from the annual increase. Lately, KHALIL and RASMUSSEN (1988) measured a concentration of 310 ppb during January 1986 over the western Atlantic Ocean. Our combined average (311 ± 6 ppb) is in fair agreement with the work of other laboratories and adds some confidence to our standardization.

N₂O concentrations in surface water

In Table 2 we report the average N₂O concentrations in the surface mixed layer and also N₂O saturations. In all instances a supersaturation of N₂O is observed, ranging from 112 to 136%. Thus it has been verified that the ocean is a source of N₂O to the atmosphere. From our results we cannot distinguish significant differences between the average saturations at each site and we retain a combined average saturation of $126 \pm 8\%$ for surface oceanic water in an eastern tropical area (5°–12°N, 20°–22°W) during the summer season.

At first sight, such an average saturation is in agreement with previous measurements in similar areas. ELKINS *et al.* (1978) reported that surface waters in the central tropical Pacific are, on average, supersaturated with respect to the atmosphere by $25 \pm 10\%$. PIEROTTI and RASMUSSEN (1980) in the eastern tropical Pacific, for the same latitude band (5°–12°N) as ours, found an average N₂O saturation of $123 \pm 15\%$. Nevertheless these measurements depend largely on chosen solubilities and partial pressure of N₂O in dry air and they probably need to be revised.

According to the last research work (WEISS, personal communication), outside of the equatorial belt, where, because of upwelling, supersaturation of N₂O might reach about 30%, the surface water should be generally nearer equilibrium with respect to the atmosphere. In roughly the same region as ours, WEISS (personal communication) reports that N₂O data from TTO/TAS indicate lower supersaturation, about 3–7%. But it is not impossible that the PIRAL data, taken in summer and nearer the African coast, are larger than those of Weiss. Our measurements of oceanic CO₂ show a summer increase in the partial pressure of CO₂ in the surface layer in the Guinea Dome area (OUDOT and ANDRIE, 1986; OUDOT *et al.*, 1987).

Table 2. Average N₂O in the surface mixed layer

Sta. no.	Position	Depth (m)	Temp. (°C)	N ₂ O conc. (μl l ⁻¹)	N ₂ O sat. (%)	ΔN ₂ O (μl l ⁻¹)
37	4°59N, 17°24W	30	27.31	0.156	124	0.030
41	4°55N, 18°19W	50	27.15	0.141	112	0.015
44	4°50N, 18°50W	55	27.26	0.143	113	0.016
48	4°52N, 19°22W	35	27.48	0.167	132	0.040
52	5°01N, 19°56W	30	27.25	0.163	129	0.037
56	5°01N, 19°57W	30	27.26	0.157	125	0.031
Mean		38	27.29	0.155	123	0.028
S.D.		± 11	± 0.11	± 0.011	± 8	± 0.011
102	11°50N, 22°01W	15	26.45	0.155	120	0.026
106	11°52N, 22°05W	20	26.43	0.170	133	0.042
110	11°50N, 22°00W	10	26.82	0.159	125	0.032
114	11°50N, 22°01W	12	26.85	0.157	124	0.030
Mean		14	26.64	0.160	126	0.033
S.D.		± 4	± 0.23	± 0.007	± 5	± 0.007
139	11°59N, 21°01W	24	27.36	0.170	136	0.045
143	12°00N, 21°00W	25	27.36	0.161	129	0.036
147	12°00N, 21°00W	22	27.17	0.155	123	0.029
151	12°01N, 21°01W	25	27.31	0.169	135	0.044
155	11°58N, 21°01W	25	27.20	0.171	136	0.045
Mean		24	27.28	0.165	132	0.040
S.D.		± 1	± 0.09	± 0.007	± 6	± 0.007

N₂O saturation (%) is the N₂O saturation relative to an average atmospheric concentration of 300 ppb (v/v) in dry air.

ΔN₂O is the apparent N₂O production defined by YOSHINARI (1976) as ΔN₂O = N₂O concentration measured - N₂O concentration in equilibrium with the atmosphere (average N₂O of 300 ppb) at T and S observed.

Vertical profiles of N₂O

In almost all the marine environments where N₂O measurements have been made, its distribution appears to be inversely correlated with that of dissolved oxygen (HAHN, 1974, 1975; YOSHINARI, 1976; ELKINS *et al.*, 1978; COHEN and GORDON, 1979; CLINE *et al.*, 1987). Our observations in all three locations (Figs 3-5) confirm such distributions: we observed typical vertical profiles of N₂O in comparison with the oxygen and nitrate ones. In Fig. 3, the N₂O profile is roughly a mirror image of the O₂ profile. The lower the O₂ concentration at depth, the higher the N₂O concentration. At 11°50N, 22°W (Fig. 4), where the O₂ concentration is the lowest (approximately 1.0 ml l⁻¹), the N₂O saturation exceeds 700% at a depth of 60 m. Such large supersaturations of N₂O are not exceptional, and PIEROTTI and RASMUSSEN (1980) reported a saturation level exceeding 1000% at 75 m in the eastern tropical Pacific Ocean.

Nitrous oxide concentrations are supersaturated at all depths, with saturation values ranging from about 120-130% at the surface to 350-500% on average below the thermocline (Figs 3-5).

The distribution pattern for N₂O is quite similar from one site to the other: N₂O concentration increases rapidly from the bottom of the mixed layer to the depth of the subsurface O₂ minimum and then remains relatively constant down to the maximum sampling depth (500 m). Nevertheless, a particular feature occurs at the end of the observations period at 12°N, 21°W: a small N₂O maximum appears at the top of the thermocline, at the level of the subsurface O₂ maximum (Fig. 5). This feature, the

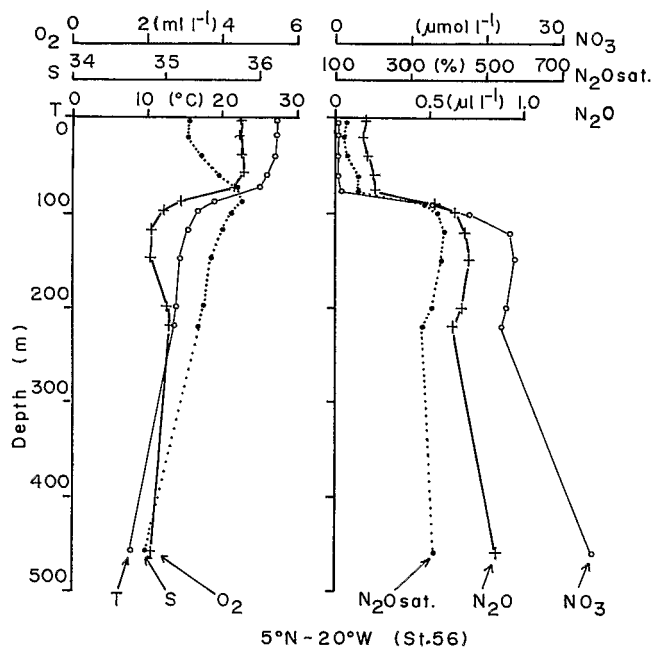


Fig. 3. Vertical profiles of temperature (T), salinity (S), oxygen (O₂), nitrous oxide (N₂O), nitrous oxide saturation (N₂O sat.) and nitrate (NO₃) in the convergence zone.

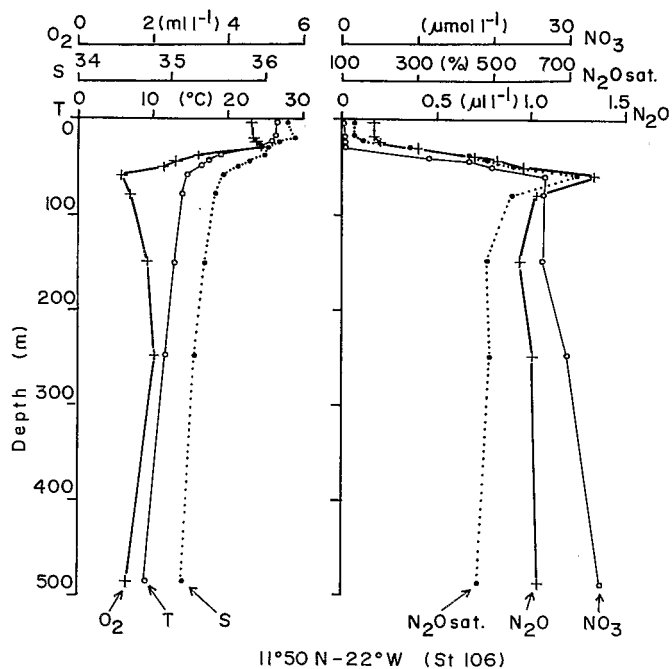


Fig. 4. Vertical profiles of temperature (T), salinity (S), oxygen (O₂), nitrous oxide (N₂O), nitrous oxide saturation (N₂O sat.) and nitrate (NO₃) at the exact center of the Guinea Dome.

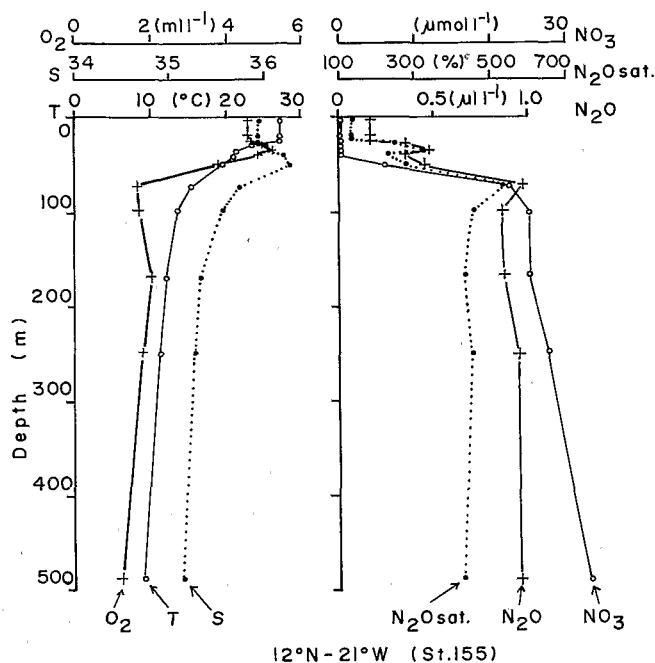


Fig. 5. Vertical profiles of temperature (T), salinity (S), oxygen (O_2), nitrous oxide (N_2O), nitrous oxide saturation (N_2O sat.) and nitrate (NO_3) a short distance from the center of the Guinea Dome.

possible origin of which will be discussed later, was found on three successive occasions (Stas 147, 151 and 155).

Apparent O_2 utilization and N_2O

Following the approach of several investigators, we used the negative correlation between dissolved O_2 and N_2O to plot the apparent production of nitrous oxide ΔN_2O (YOSHINARI, 1976) vs the apparent oxygen utilization, AOU. ΔN_2O and AOU are computed from respective solubilities by the following equations:

$$\Delta N_2O = N_2O - N_2O^* \quad (1)$$

$$AOU = O_2^* - O_2 \quad (2)$$

in which N_2O^* and O_2^* are the expected equilibrium concentrations as previously noted in the paragraph describing methods.

At $5^\circ N$ (Fig. 6), a linear trend between ΔN_2O and AOU is observed for all the groups of points, except those corresponding to the 500 m level. The slope of the regression line, which means the ratio of N_2O production to O_2 consumption $\Delta N_2O/AOU$ (" N_2O oxidative ratio", COHEN and GORDON, 1979), is $0.129 \mu l ml^{-1}$ (Table 3). To the north, in the Guinea Dome areas, the situation is more complicated, because the $\Delta N_2O/AOU$ ratio changes with depth (Fig. 7) and, moreover, at the top of the thermocline we observe a N_2O production without O_2 consumption (Figs 7 and 8). In the Guinea Dome area, the N_2O oxidative ratios for the different groups of samples vary from 0.160 to

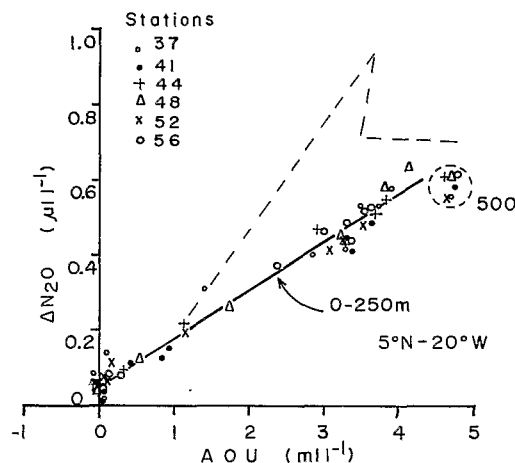


Fig. 6. Plot of apparent N_2O production (ΔN_2O) vs apparent oxygen utilization (AOU) for all stations in the convergence zone. The equation of the regression line fitted to the 0-250 m data is given in Table 3. The dashed line shows ΔN_2O calculated by equation (3) reported in ELKINS *et al.* (1978).

Table 3. Regression equations of ΔN_2O ($\mu l l^{-1}$) vs AO U ($ml l^{-1}$) for the three sites

Location	Depth range (m)	Regression equation	<i>r</i>	<i>n</i>
5°N, 17°-20°W	0-250	$\Delta N_2O = (0.129 \pm 0.003) AO U + 0.047$	0.989	63
11°50N, 22°W	0-20/40-70	$\Delta N_2O = (0.219 \pm 0.004) AO U + 0.049$	0.996	22
	0-20/150-250	$\Delta N_2O = (0.160 \pm 0.003) AO U + 0.044$	0.996	22
12°N, 21°W	0-20/50-250	$\Delta N_2O = (0.162 \pm 0.003) AO U + 0.052$	0.993	43

At 11°50N and 12°N, the samples within the upper part of the thermocline (20-40 or 50 m) are not included.

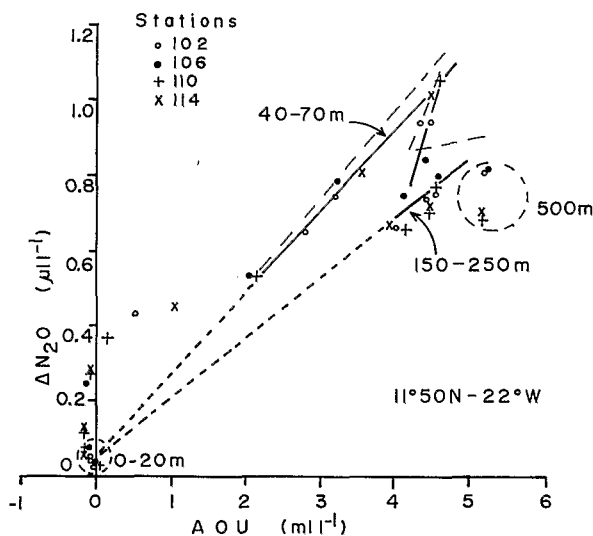


Fig. 7. Plot of apparent N_2O production (ΔN_2O) vs apparent oxygen utilization (AOU) for all stations at the exact center of the Guinea Dome. The regression lines fitted to the 40-70 m data and the 150-250 m data are forced through the surface data (0-20 m); the equations of regression lines are given in Table 3. Note the 20-40 m data apart from the regression lines. The long-dashed line shows ΔN_2O calculated by equation (3) reported in ELKINS *et al.* (1978).

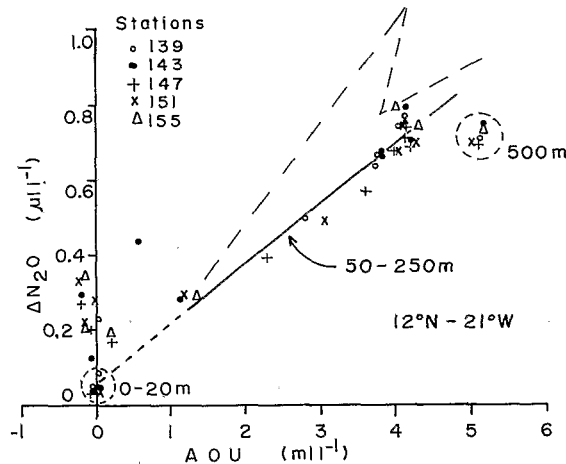


Fig. 8. Plot of apparent N_2O production (ΔN_2O) vs apparent oxygen utilization (AOU) for all stations a short distance from the center of the Guinea Dome. The regression line fitted to the 50–250 m data is forced through the surface data (0–20 m); the equation of the regression line is given in Table 3. Note the 20–50 m data apart from the regression line. The long-dashed line shows ΔN_2O calculated by equation (3) reported in ELKINS *et al.* (1978).

$0.219 \mu\text{l ml}^{-1}$ (Table 3): at $11^{\circ}50N$, i.e. the exact center of the dome, the $\Delta N_2O/AOU$ ratio is largest in the layer of the smallest O_2 concentrations (Fig. 7). These variations of the $\Delta N_2O/AOU$ ratio are not surprising if we remember that the dome area is a biologically active region, where the primary production is enhanced with respect to the surrounding area (VOITURIEZ and DANDONNEAU, 1974). The observations of ELKINS *et al.* (1978) in the tropical central Pacific showed a ratio equal to about $0.36 \mu\text{l ml}^{-1}$ in the "active" regions against $0.17 \mu\text{l ml}^{-1}$ elsewhere. Our results are in the range of the values reported in other works: the $\Delta N_2O/AOU$ ratios of COHEN and GORDON (1979) for different marine regions vary from 0.076 to $0.218 \mu\text{l ml}^{-1}$, and CLINE *et al.* (1987) measured 0.085 and $0.186 \mu\text{l ml}^{-1}$ on both sides of the Pacific Equatorial Undercurrent (150–200 m).

ELKINS *et al.* (1978) discussed the differences in the slopes of the linear regressions of ΔN_2O vs AOU. Various factors may explain these variations: differences in the composition of organic material to be oxidized; differences in the yield for production of N_2O ; mixing of different water masses; additional sources of N_2O in "active" regions associated with assimilatory reduction of nitrate. They considered that ΔN_2O might be an increasing function of temperature:

$$\Delta N_2O = (0.18 + 0.0277 T) AOU - 0.46 \quad (3)$$

with ΔN_2O and AOU measured in $\mu\text{g l}^{-1}$ and ml l^{-1} and T in $^{\circ}\text{C}$. As did CLINE *et al.* (1987), we calculated ΔN_2O from this regression function. As the latter authors observed, we find that equation (3) (dashed lines in Figs 6–8) does not fit our observations in the layer of the rapid increase of N_2O concentrations except at $11^{\circ}50N$ (Fig. 7). Only in the exact center of the dome is the yield for production of N_2O consistent with temperature sensitivity as described by ELKINS *et al.* (1978). Thus, this relationship of temperature dependence may be only applicable in the biologically active region, which is in complete contradiction with the results of Elkins and co-workers,

according to whom the equation (3) provides an excellent fit to all the data except results from the "active" region.

N₂O production and nitrate

As a consequence of the relationship between ΔN_2O and AOU, there follows, of course, a positive correlation between N_2O production and nitrate concentration, since nitrate regeneration is linearly related to O_2 consumption (REDFIELD *et al.*, 1963). This relation is illustrated in Figs 9–11. The ratio of N_2O formation to nitrate formation varies according to the site of observations and the depth. Expressed as a percentage on an atom-N basis, the values of this ratio range from 0.18 to 0.36% (Figs 9–11). COHEN and GORDON (1979) found that the ratio of N_2O to nitrate production calculated from the REDFIELD *et al.* (1963) plankton model varied from 0.13 to 0.37% in different marine environments. YOSHINARI (1973), in the Sargasso Sea, estimated N_2O production to be only 0.12% of nitrate formation.

In the Guinea Dome area (Figs 10 and 11) we observe some samples that do not fit the regression line of ΔN_2O vs NO_3 . For these samples, located at the top of the thermocline, a production of N_2O occurs without the appearance of nitrate. This feature is most apparent at 12°N (Fig. 11) for depths less than 50 m. At this level the process responsible for N_2O production is undoubtedly different from what happens at a deeper level and which leads to nitrate regeneration. This process sometimes leads to the creation of a secondary upper maximum of N_2O .

Secondary upper N₂O maximum

A secondary upper N_2O maximum was found in the last three successive days of continuous observations in the Guinea Dome area (Fig. 12: Stas 147, 151 and 155). It is located at 30–35 m depth in the upper layer of the thermocline and corresponds to the level of the subsurface O_2 maximum. Moreover, together with the small N_2O maximum there appears a small N_2 maximum (Stas 151–155).

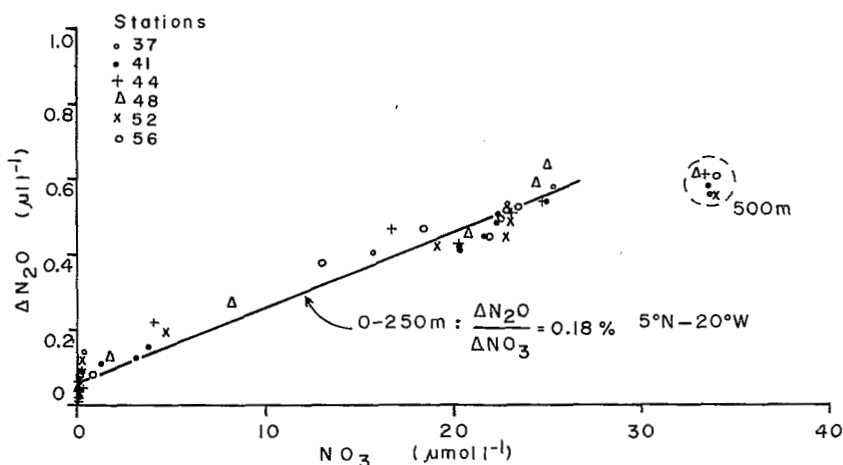


Fig. 9. Plot of apparent N_2O production (ΔN_2O) vs nitrate concentration (NO_3) for all stations in the convergence zone. The slope regression line fitted to the 0–250 m data ($r = 0.986$ for $n = 62$) shows the apparent ratio of N_2O to nitrate production.

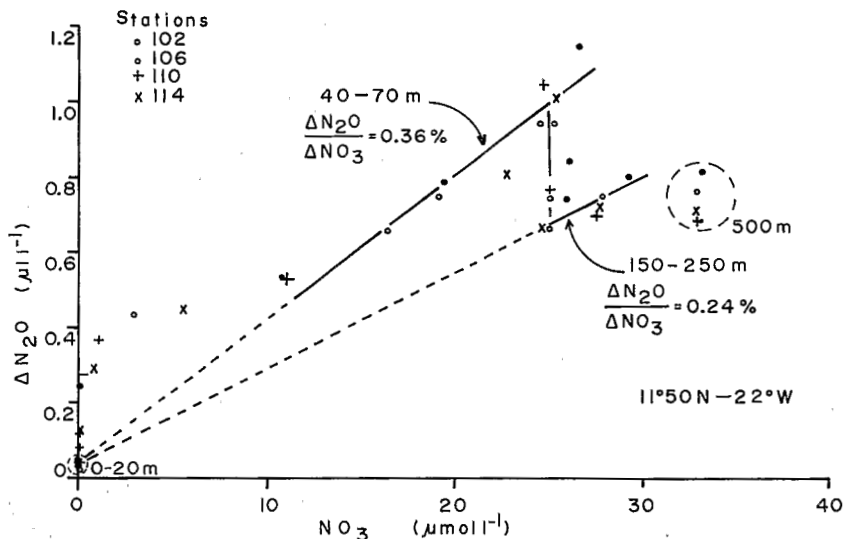


Fig. 10. Plot of apparent N_2O production (ΔN_2O) vs nitrate concentration (NO_3) for all stations at the exact center of the Guinea Dome. The regression lines fitted to the 40-70 m data and 150-250 m data are forced through the surface data (0-20 m): the slopes of these regression lines show the apparent ratio of N_2O to nitrate production. Note the 20-40 m data apart from the regression lines. In the 150-250 m range the ratio is identical to that in the 50-250 m range a short distance from the center of the Guinea Dome (Fig. 11).

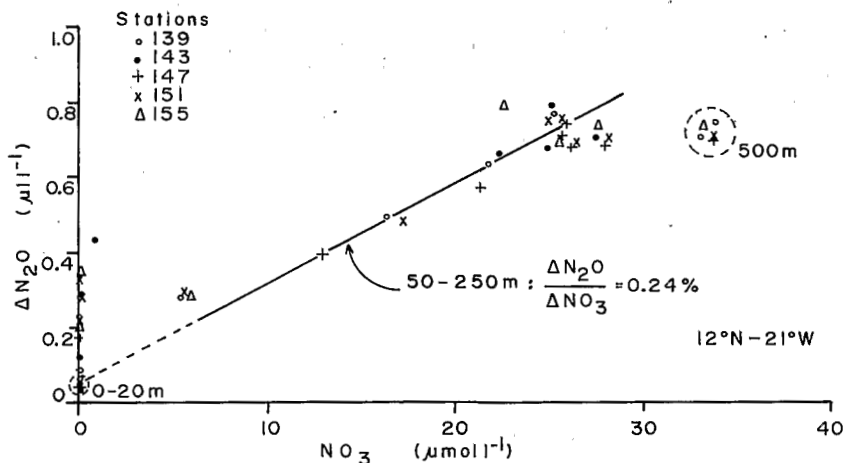


Fig. 11. Plot of apparent N_2O production (ΔN_2O) vs nitrate concentration (NO_3) for all stations a short distance from the center of the Guinea Dome. The regression line fitted to the 50-250 m data is forced through the surface data (0-20 m): the slope of the regression line shows the apparent ratio of N_2O to nitrate production. Note the 20-50 m data apart from the regression line.

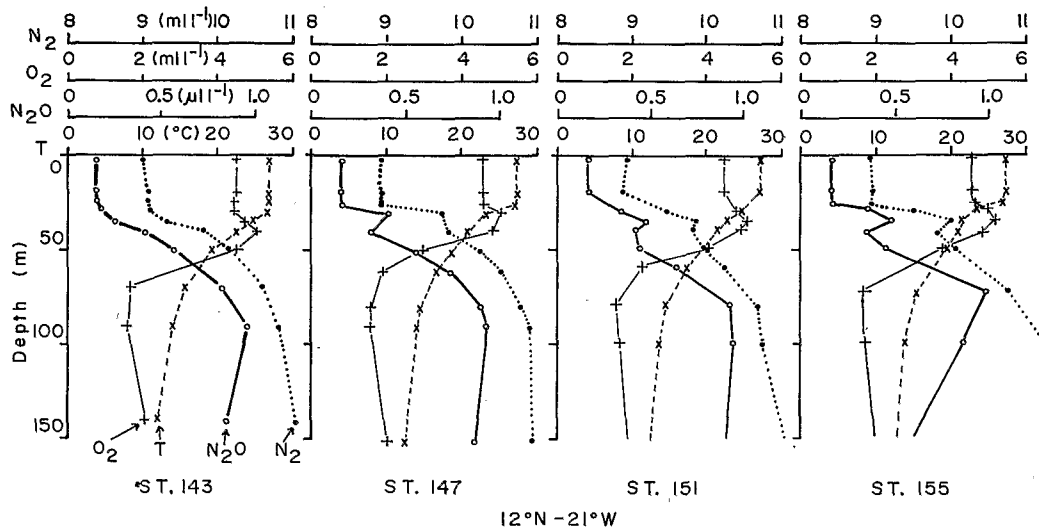


Fig. 12. Vertical profiles of temperature (T), nitrous oxide (N_2O), oxygen (O_2) and molecular nitrogen (N_2) for stations a short distance from the center of the Guinea Dome. Note the appearance of a small N_2O maximum from Sta. 147 and a small N_2 maximum from Sta. 151.

DISCUSSION

Nitrification, denitrification and assimilatory nitrate reduction

The actual mechanism by which N_2O is produced in specific ecosystems is a subject of current debate. HAHN and JUNGE (1977) have suggested that three processes are apt to produce N_2O in the oceans: nitrification, denitrification and assimilatory nitrate reduction. Our results exhibit two of the three mechanisms of N_2O formation.

The first (nitrification) is the main source of N_2O in the open ocean. Through nitrification, the ammonium ion is oxidized step-wise to nitrite and nitrate by microbially mediated reactions and a small amount of N_2O is released into the water column. The amount of N_2O released is, in general, proportional to the amount of O_2 consumed, i.e. the AOU. YOSHINARI (1976) was the first to suggest that nitrification was a major source of N_2O in the Atlantic Ocean. The inverse correlation between N_2O and O_2 in the water column was, for Yoshinari, proof that production of N_2O is closely related to biological activity in the sea. The linear relationship between excess N_2O in the water (ΔN_2O) and AOU, confirmed on several occasions (COHEN and GORDON, 1978; ELKINS *et al.*, 1978; CLINE *et al.*, 1987, this study), is the main argument in support of nitrification. The linear relationship between ΔN_2O and nitrate concentration could be a further illustration of nitrification. Our results show that for any given value of AOU, the concentration of N_2O is spatially variable (Figs 6–8). It is the same for the ratio of N_2O to nitrate production (Figs 9–11). These variations of the N_2O yield may represent some differences in biological activity in the water column (ELKINS *et al.*, 1978). The Guinea Dome area is well known as an area of enhanced primary production, and it is not surprising that the $\Delta N_2O/AOU$ and $\Delta N_2O/\Delta NO_3$ ratios are higher here than in the oligotrophic convergence zone at $5^\circ N$. A different composition of organic material to be oxidized and

a different yield for production of N_2O (ELKINS *et al.*, 1978) may be at the origin of the increase of the $\Delta N_2O/AOU$ ratio in the dome area. CLINE *et al.* (1987) remind us that the N_2O production rate increases when concentrations of O_2 decrease, which is what happens in the exact center of the dome. On the other hand, N_2O being an intermediary step in nitrate regeneration from ammonia and organic nitrogen, the N_2O concentration depends on equilibrium between the production rate of N_2O from ammonia and the oxidation rate of N_2O into nitrite then nitrate. Thus the excess N_2O proportion (percentage of nitrate production) can be more or less high according to the state of progress of the nitrification process. A high excess N_2O proportion can be synonymous with a young water mass in which the oxidation of organic nitrogen (or ammonia) is at an early step, while a low ΔN_2O proportion corresponds with an older water mass in which the oxidation is nearly at the final step (nitrate). Measurements of helium 3-tritium (ANDRIE and OUDOT, in preparation) give us information about the "age" of water masses: the "age" of the layer of maximum N_2O concentrations at $5^\circ N$, $11^\circ 50' N$ and $12^\circ N$ is estimated at 20, 12 and 17 years, respectively, where the ratio of N_2O to nitrate production is 0.18, 0.36 and 0.24%.

The second process, denitrification or dissimilatory nitrate reduction, has little chance of occurring here, because the O_2 concentrations are significantly above the required conditions ($O_2 < 0.1 \text{ ml l}^{-1}$) for the appearance of denitrification (CODISPOTI and CHRISTENSEN, 1985). The smallest O_2 concentration, observed at $11^\circ 50' N$, is 0.86 ml l^{-1} .

The last process, assimilatory nitrate reduction, seems to us to be the explanation for the large N_2O anomalies and the secondary upper N_2O maximum at the top of the thermocline. This process, proposed by several investigators (HAHN, 1975; ELKINS *et al.*, 1978; PIEROTTI and RASMUSSEN, 1980), has never been really demonstrated. It has been principally put forward to explain the high surface concentrations of N_2O in the waters of upwelling areas, since nitrate is the major source of nitrogen primary productivity in regions of upwelling. The fact that we found the upper N_2O anomalies at the top of the thermocline only in the Guinea Dome area, a zone where nitrate in the euphotic layer is elevated and thus primary productivity enhanced, and not in the convergence region, which is less rich, argues in favor of assimilatory nitrate reduction.

Another exciting feature is the small N_2 maximum sometimes observed (Fig. 12) at the same depth as the upper N_2O maximum. Within oxygenated waters, no biological process is known to create a detectable change in N_2 concentrations (SCRANTON, 1983). Several physical processes (air injection and temperature change after gas equilibration), in the absence of biological activity, can create significant gaseous saturation anomalies (KESTER, 1975) but never to the extent that inversions occur in the vertical distribution of these gases. Thus we cannot explain the occurrence of such an anomaly of N_2 distributions which occurred several times in succession.

N_2O exchange across the air-sea interface and vertical diffusion of N_2O

The N_2O exchange across the air-sea interface is governed by the equation:

$$F(N_2O)_{\text{atm}} = V_t \times (N_2O - N_2O^*) , \quad (4)$$

where $F(N_2O)_{\text{atm}}$ is the N_2O flux across the air-sea interface, V_t the transfer velocity and N_2O and N_2O^* the average surface concentration and the equilibrium concentration. The transfer velocity is an empirical function of wind speed and temperature through the Schmidt number, Sc , dependency (LISS and MERLIVAT, 1986). V_t varies with the kind of

gas through its molecular diffusivity D (Sc is the ratio of the kinematic viscosity of the water to the molecular diffusivity of the gas). The N_2O transfer velocity is derived from that computed for CO_2 (OUDOT and ANDRIE, 1989) according to the equation:

$$\frac{V_t(N_2O)}{V_t(CO_2)} = \frac{D(N_2O)^{1/2}}{D(CO_2)^{1/2}}, \quad (5)$$

where $D(N_2O)$ and $D(CO_2)$ are the molecular diffusivity of N_2O and CO_2 . Between 25 and 30°C, $D(N_2O)/D(CO_2) = 1.27$ (BROECKER and PENG, 1974). For an average wind speed of 5.1 m s⁻¹, the CO_2 transfer velocity was estimated at 1.6 ± 1.3 m d⁻¹ (OUDOT and ANDRIE, 1989). The N_2O transfer velocity corresponding to this wind speed is 1.8 ± 1.5 m d⁻¹. The measured N_2O saturation anomaly is 0.028 ± 0.011 μl l⁻¹ (Table 2: ΔN_2O). The N_2O flux escaping into the atmosphere across the air-sea interface, which is generated by N_2O supersaturation, should be equal to 18.4 ± 22.5 ml m⁻² y⁻¹.

Assuming a steady state of N_2O distribution, the N_2O escape into the atmosphere ("air-sea" flux) must be balanced by the N_2O production in the underlying layers corrected by its biochemical consumption in oxygen-deficient and anoxic waters and a possible assimilatory N_2O consumption in nitrate-starved surface waters. Such oxygen-depleted conditions not being observed in the eastern tropical Atlantic, transport across the air-sea interface and photosynthetic N_2O assimilation in the mixed layer, if it exists, must balance N_2O production in the surface column.

JENKINS (1982) estimated the oxygen utilization rate (OUR) by associating the idea of "age" of a water mass with AOU. In the same way we have evaluated the rate of N_2O production by using the data of helium 3-tritium collected during the PIRAL cruise (ANDRIE and OUDOT, in preparation). Figure 13 shows apparent N_2O production vs "age" for Sta. 56 (5°N, 20°W): the slope of the regression line ($r = 0.98$ for $n = 11$) is an average rate of N_2O production (0.027 ± 0.002 μl l⁻¹ y⁻¹) over about 420 m.

Assuming this rate remains constant over the thickness of the water column (80–500 m), the N_2O flux, called "age" flux, is 0.027 ± 0.002 μl l⁻¹ y⁻¹ × 420 m = 11.3 ± 0.8 ml m⁻² y⁻¹.

Most of the investigators who have studied N_2O distribution within the ocean have estimated N_2O production in the ocean and the N_2O flux escaping into the atmosphere. CLINE *et al.* (1987), by means of eddy coefficients, evaluated the average flux of N_2O into the mixed layer in the equatorial Pacific at 7.4 ± 5.7 ml m⁻² y⁻¹ in an abnormal year (1982–1983 El Niño event) without upwelling. Other estimates of the annual global flux of N_2O from the ocean to the atmosphere were previously reported: ELKINS *et al.* (1978), using data from surface ocean waters between latitudes ±20° in the central Pacific, gave a marine source for atmospheric N_2O of 7×10^6 tons N y⁻¹, i.e. 15.3 ml m⁻² y⁻¹, by dividing by the whole ocean surface (366×10^{12} m²); COHEN and GORDON (1979), from the ratio of N_2O to nitrate production during nitrate regeneration and estimates of the overall regeneration of nitrate in the ocean, concluded that the oceanic source of atmospheric N_2O ranged from 6 to 16×10^{12} g N_2O y⁻¹, i.e. $8.3 - 22.2$ ml m⁻² y⁻¹; PIROTTI and RASMUSSEN (1980) conducted measurements in coastal and equatorial upwelling regions of the Pacific Ocean, and calculated an average flux of N_2O of 80 ml m⁻² y⁻¹. Our estimates, 18.4 ± 22.5 ml m⁻² y⁻¹ for the "air-sea" flux and 11.3 ± 0.8 ml m⁻² y⁻¹ for the "age" flux, representative of non-upwelling areas, agree well with the measurements of ELKINS *et al.* (1978), that encompassed oligotrophic areas of the subtropical Pacific.

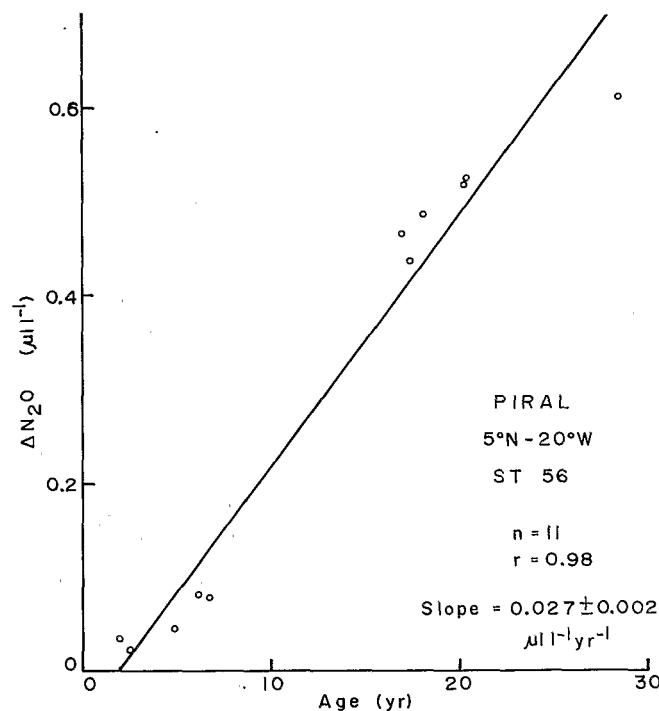


Fig. 13. Plot of apparent N_2O production (ΔN_2O) vs the "age" determined by the helium 3-tritium method (ANDRIE and OUDOT, in preparation) for a station in the convergence zone. The slope of the regression line fitted to the data shows the apparent rate of N_2O production.

Nevertheless, there needs to be some discussion of the difference between our flux estimates. Firstly the "age" flux, referring to a water column of only 420 m, is probably underestimated. Another possible explanation is the recognition that the two different methods measure different "average" quantities. The "age" method, a long-term integrated production estimate, is really needed for global flux calculations. The air-sea exchange flux is extremely sensitive to short-term changes at the sea surface and in the thermocline structure; it is characterized by high-frequency and high-amplitude variations. Moreover, the "air-sea" method is dependent upon uncertainties about determinations of absolute supersaturations and transfer velocity. To obtain an accurate picture of the gradient flux it is necessary to make numerous local measurements of the N_2O gradient and wind speed over a long period of time. The "age" method probably gives a better measure for a global flux. The "age" flux of $11.3 \text{ ml m}^{-2} \text{ y}^{-1}$, i.e. 0.18 Tmol y^{-1} , corresponds better to the WEISS' (personal communication) estimation of 0.1 Tmol y^{-1} than the "air-sea" flux, which would reach 0.3 Tmol y^{-1} . Nevertheless, our "age" flux has to be considered with caution when speaking about global flux, because there is no evidence for no N_2O consumption in the mixed layer and the PIRAL station is not representative of the whole ocean. The conservative behavior of N_2O in well-oxygenated waters never has been demonstrated in the literature, and it seems to some authors (CLINE and WEISS, personal communications) that phytoplankton may well possess the capability of assimilating N_2O in the absence of nitrate and ammonium ions, which is just the case in oligotrophic tropical areas.

In the convergence zone (5°N), the flux of N₂O into the mixed layer, supported by the N₂O production in the underlying layers, depends on the N₂O gradient and the local eddy diffusivity:

$$F(\text{N}_2\text{O})_{\text{ml}} = K_z \times \frac{d\text{N}_2\text{O}}{dz}, \quad (6)$$

where $F(\text{N}_2\text{O})_{\text{ml}}$ is the N₂O flux across the base of the mixed layer, K_z is the eddy diffusion coefficient and $d\text{N}_2\text{O}/dz$ the N₂O gradient corresponding to the thermocline. Assuming $F(\text{N}_2\text{O})_{\text{ml}}$ identical with the "age" flux (11.3 ml m⁻² y⁻¹) and taking the N₂O gradient as equal to 0.018 ml m⁻⁴ (Fig. 3), K_z would be 0.20 cm² s⁻¹. This value is consistent with what is known of eddy diffusivity at the top of the thermocline in tropical areas through the radioactive or stable tracer distributions (ROETHER *et al.*, 1970; ROTH and OSTLUND, 1972; PENG *et al.*, 1974; KING and DEVOL, 1979). The independent estimate of K_z , based on the surface heat flux of HANEY (1971) (in CLINE *et al.*, 1987), would have led in the case of PIRAL (5°N, 20°W) to a result of 0.17 cm² s⁻¹. The agreement between these different values is acceptable and suggests that the N₂O saturation of surface waters is related to turbulent fluxes across the base of the mixed layer, as noted by CLINE *et al.* (1987).

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