Nitrogen isotope ratio of atmospheric $N_2O$
as a key to the global cycle of $N_2O$

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An analytical system to separate $N_2O$ in the air was developed to measure the $\delta^{15}N$ value and concentration of $N_2O$. The system was designed so that $\delta^{15}N$ value and concentration of ca. 1 μmol $N_2O$ from ca. 60 l air could be measured with the accuracy of $\pm 0.2/0^o$ and $\pm 10$ ppbv, respectively. Air samples were collected at three individual sites in Japan. The average values of $\delta^{15}N$ and concentration of $N_2O$ for 32 samples with the standard deviation were $+8.1 \pm 1.0/0^o$ and $316 \pm 14$ ppbv, respectively. The diversity of the observed data was attributed to the change in the mixing ratio of air masses of different characteristics.

A discussion was made on the global cycle of $N_2O$. Bacterial reduction of $N_2O$ was proposed to be the major consuming process of $N_2O$ on the Earth's surface.

INTRODUCTION

The destruction of ozone in the stratosphere and green-house effect caused by atmospheric $N_2O$ have awakened the attention of scientists in a variety of fields (e.g., JOHNSTON, 1972; WANG et al., 1976). Yet many factors have been left unknown about the budget of $N_2O$: (1) What is the major consuming process of $N_2O$ which should compensate the great unbalance of production and consumption rates (HAHN and JUNGE, 1977)? (2) Which is the major producing process of $N_2O$, denitrification or nitrification (HAHN, 1974; YOSHINARI, 1973)? (3) Which is the major source and/or sink, land or ocean (HAHN, 1974; McELROY et al., 1976)?

Information on the nitrogen isotope ratio of atmospheric $N_2O$ would undoubtedly be useful for the elucidation of the geochemical cycle of $N_2O$. However, low concentration of $N_2O$ in the atmosphere and the lack of knowledge on the isotope fractionation in the processes of producing and consuming $N_2O$ have made it difficult to introduce isotopic information into the study of $N_2O$ cycle. There has been only a single report (MOORE, 1974) which gave some preliminary data on $\delta^{15}N$ of the atmospheric $N_2O$.

There are two ways to measure $\delta^{15}N$ for small amount of nitrogen; one is a static-operation mass spectrometer, and the other is a dynamic-operation mass spectrometer with a modified inlet system. BECKER (1982) applied a static-operation mass spectrometer to measure $\delta^{15}N$ of nitrogen with the amount as low as 1 μl STP. Some modifications of the inlet system of dynamic-operation mass spectrometer have been made to minimize dead volume for the measurement of $\delta^{15}N$ value of nitrogen of small sample size with a satisfactory accuracy: (1) use of liq. He as a cooling agent (FREYER and KOBEL, 1975), (2) use of absorbants cooled with liq. N$_2$ (WADA, 1976), and (3) use of a Toeppler pump. In this study, $\delta^{15}N$ of $N_2O$ was measured with a satisfactory accuracy by adopting the last modification.

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We report here some results on the measurement of $\delta^{15}$N of N$_2$O and our interpretation for the sources and sinks of N$_2$O on the basis of isotopic information.

**EXPERIMENTAL**

Experimental procedures are schematically illustrated in Fig. 1. Details of each procedure are as follows.

**Sampling system** The system used in this study for the collection of N$_2$O in air samples was similar to those for measuring the concentration of N$_2$O by some researchers (LAHUE et al., 1971; HAHN, 1972). The system consisted of four parts; (1) Gas flow meters to monitor the flow rate and amount of air sampled. (2) Absorbants for the contaminants which inactivate the surface of molecular sieve 5A, the absorbant for N$_2$O. Particulate matters were roughly removed by 0.45 $\mu$m Millipore filter, water vapor by ca. 500 g of Drierite (CaSO$_4$, 8 mesh) filled in polyvinyl tube of 6 m length with 16 mm diameter, and carbon dioxide by ca. 250 g of Ascarite (NaOH 92% mixed with 8% asbestos, 8-20 mesh) filled in a similar tube but the length was 3 m. (3) The absorbant for N$_2$O. Nitrous oxide was absorbed by ca. 15 g of molecular sieve 5A (1/16 inch $\phi$ pellets) of 20 cm length sustained by quartz wool in the middle of a stainless steel tube of 1/2 inch diameter and 44 cm length, to both ends of which Swagelok tube fittings were attached. Prior to sampling, this tube was heated in vacuum at 380°C for at least 10 hours. At the end of this activation procedure, the tube was cooled to room temperature and filled with dry nitrogen and capped with Swagelok caps. (4) Air pump with adjustable sucking speed.

Whole the system was connected tightly without leakage in a series in the order mentioned above. The total weight of the system was about 10 kg excluding the pump, so that the system could be operated easily in the field, where a power source for the pump was available.

**Sampling of air** Prior to the sampling, the air inside the sampling system was replaced by ambient air. Air of about 60 l was sampled in two hours through the sampling port set at about 2 m above the ground. Nitrous oxide in about 30 l of the air was fixed in a sampling tube at a flow rate of 0.5 l/min controlled by two greaseless needle-stopcocks, so that each sampling required two sampling tubes to collect a sufficient amount of N$_2$O for isotopic analyses.

**Recovery, preparation and measurement of N$_2$O**

The sampling tube in which N$_2$O was fixed was attached to a vacuum system in the laboratory. The air contained in the tube was evacuated and then the tube was heated to 250°C for an hour as a closed system in which two multi-traps cooled with liq. N$_2$ were installed.
The evolved gas condensed at liq. N$_2$ temperature was purified several times between liq. N$_2$ and dry ice-ethanol traps. Several analyses of the gas samples at this stage indicated that the condensate at liq. N$_2$ temperature after the purification was a mixture of N$_2$O, CO$_2$, H$_2$O and non-methane hydrocarbons, and completely free from any other nitrogen compounds such as N$_2$, NO, NO$_2$ and NH$_3$.

The gas mixture was circulated over heated copper (400°C) and cuprous oxide (700°C, Pt catalyst added) by the use of Toepler pump in a closed system for an hour. After quantitative reduction of N$_2$O to N$_2$ and oxidation of non-methane hydrocarbons to CO$_2$ and H$_2$O, the nitrogen gas converted from N$_2$O was purified for ten minutes by circulating in the system including traps immersed in liq. N$_2$.

The purified nitrogen gas was collected into a small constant volume (0.1 ml at the minimum) by a Toepler pump and the amount of N$_2$ was measured manometrically.

The nitrogen gas thus prepared was introduced into a mass spectrometer, Micromass 602C (VG Isotopes Ltd.), through the inlet system installed with a Toepler pump to reduce the dead volume and with a cold trap for further purification. This modification of the inlet system enabled us to measure $\delta^{15}$N of ca. 20 µl STP of N$_2$ within ± 0.2°/oo error.

Correction factors
a) Correction for the concentration of N$_2$O

The amount of air sampled was corrected for the temperature, pressure and humidity averaged over the sampling period. The concentration of N$_2$O was presented in ppbv of the dry-air.

b) Correction for $\delta^{15}$N of N$_2$O

In addition to the correction by instrumental factors such as the valve mixing, tailing and background, a further correction was necessary for the small-volume samples of N$_2$ derived from N$_2$O. The apparent increase, $\Delta$ of $\delta^{15}$N due to the residual CO and N$_2$ gasses of ca. 10$^{-4}$ Torr in the preparation and inlet systems, was inversely proportional to the sample amount in volume, $V$ (µl STP) of N$_2$ as shown below:

$$\Delta \times V = \text{const.}$$

where the constant was obtained to be + 40 ± 3 µl STP.°/oo by repeated calibrations. When $V$ is equal to 20 µl STP, a typical sample size for atmospheric N$_2$O for example, then $\Delta$ = + 2 ± 0.15°/oo, so that the corrected $\delta^{15}$N is by 2°/oo lower than the measured value.

Check of the analytical procedure

In a balloon with the volume of 10³ l, a mixture of N$_2$ – N$_2$O was blended, of which $\delta^{15}$N of N$_2$O was − 1.60 ± 0.06°/oo and N$_2$O content was 346 ppbv. The repeated analyses of this mixture made under the condition as mentioned in the previous section gave the results of − 1.67 ± 0.15°/oo for $\delta^{15}$N$_{N_2O}$ and 344 ± 10 ppbv for N$_2$O concentration, respectively. The accuracy obtained by this experiment indicates that the sampling technique, preparation and isotope ratio measurement of N$_2$O are quite satisfactory.

Results

Air samples were collected at three different sites and times: (1) 10 m above the ground level on the roof of the main building of Tokyo Institute of Technology located in the south of Tokyo Metropolis (35°35′N, 139°40′E), during the period between Sept. 30, 1979 and Jan. 22, 1980. (2) 8 m above the ground level on the roof of Otsuchi Marine Research Center, University of Tokyo located near the shore facing the Pacific Ocean in Iwate Pref. (39°20′N, 141°85′E), between July 1 and 3, 1981. (3) About 50 m above the sea level at the northern cliff of Hachijo-jima Island in the Pacific Ocean (33°10′N, 139°45′E), 300 km to the south of Tokyo on Feb. 6, 1982.

Results are summerized in Fig. 2. The average values of $\delta^{15}$N and concentration of N$_2$O with one sigma at three sites were as follows: (1) + 8.8 ± 0.9°/oo and 312 ± 13 ppbv (12 samples), (2) + 7.9 ± 0.7°/oo and 317 ± 17 ppbv (12 samples) and (3) + 7.2 ± 0.5°/oo.
and 320 ± 8 ppbv (8 samples). The average values of the total 32 samples were +8.1 ± 1.0°/oo and 316 ± 14 ppbv.

**DISCUSSION**

As shown in Fig. 2, the observed data for each sampling site were scattered beyond the experimental error. The variation of δ¹⁵N in this study was in the range from +6.6 to 10.1°/oo in contrast to the range given by Moore (1974) which is from 0 to +9.3°/oo with the average of +5.2°/oo. The range of N₂O concentrations found in this study agrees with the previous results (e.g., Goldan et al., 1978; Muramatsu et al., 1982). Several modes of variation of N₂O concentration have been reported by previous studies, i.e., diurnal variation (e.g., Matthias et al., 1979), annual variation (e.g., Pierotti and Rasmussen, 1977; Roy, 1979), secular variation (e.g., Weiss, 1981), local variation (e.g., Singh et al., 1977) and latitudinal variation (e.g., Tyson et al., 1978; Pierotti and Rasmussen, 1980).

In this study, one example of diurnal variations of δ¹⁵N value and concentration of N₂O has been interpreted in terms of air mass mixing. Further, a discussion was made on the global budget of N₂O on the basis of isotopic information.

**Mixing of air masses** Diurnal variations have been observed also in this study. The example of diurnal variation at Hachijo-jima Island is shown in Fig. 3. It can be attributed to the change in the mixing ratio of two air masses: one is the maritime tropical air mass and the other is the continental polar air mass. It was recognized from the analysis of synoptic charts during the sampling period that the variation of observed data was due to the change in mixing ratio of the two air masses caused by the frontal movement. When the continental polar air mass dominated, which is usual in the winter time in Japan, δ¹⁵N was high and concentration was low. On the contrary, when the maritime tropical air mass prevailed, the opposite occurred. The maritime tropical air mass may be characterized by lower δ¹⁵N and higher concentration and the continental polar air mass by higher δ¹⁵N and lower concentration. General trend shown in Fig. 2 can also be explained by the mixing of the air masses, except for the variation at Otsuchi where the air mass trajectory was complicated at the time of air sampling.
Some implications on the global budget of \( N_2O \) derived from nitrogen isotope ratio of tropospheric \( N_2O \)
a) A simplified model of \( N_2O \) budget

The results shown in Fig. 2 were obtained from the samples which cover most of the varieties of air masses expected. It may be reasonable to take the average of \( \delta^{15}N \) values measured (+8.1 ± 1.0/oo) as one of the parameters to elucidate the geochemical cycle of \( N_2O \). Since dissolution of \( N_2O \) in water gives only a slight enrichment of \( ^{15}N \) in the aqueous phase (less than 0.8/00 in the temperature range from 5 to 25°C; YOSHIDA et al. in preparation), the averaged value of \( \delta^{15}N \) of tropospheric \( N_2O \) (+8.1 ± 1.0/00) can be representative of that in the troposphere, land and ocean.

A simple model of geochemical cycle of \( N_2O \) is depicted in Fig. 4, neglecting some minor contributions, such as lightning and combustion as production, reaction with ozone as consumption (HAHN and JUNGE, 1977). This model consists of two sources: \( NO_3^- (R1) \) and \( NH_4^+ (R2) \), two reservoirs: troposphere, land and ocean (T) and stratosphere (S), two producing processes on the Earth's surface including the oceans: denitrification (\( NO_3^- \to N_2O; F_{R1} \)) and nitrification (\( NH_4^+ \to N_2O; F_{R2} \)), a single consuming process in the troposphere to be mentioned later which has been previously unknown (\( F_T \)), a single consuming process in the stratosphere by photolysis (\( F_S \)) and two mass transportation processes between troposphere and stratosphere (\( F_{T-S} \) and \( F_{S-T} \)).

The variation of the \( N_2O \) amount in the two reservoirs with time is expressed as follows:

\[
\frac{dT}{dt} = F_{R1} + F_{R2} + F_{S-T} - F_T - F_{T-S} \quad (1)
\]
\[
\frac{dS}{dt} = F_{T-S} - F_S + F_{S-T} \quad (2)
\]

where \( F_X \) is the annual rate of each \( X \) process, and \( T-S \) and \( S-T \) mean from troposphere to stratosphere and vice versa, respectively.

Assuming a steady state condition for the two reservoirs we obtain,

\[
F_{R1} + F_{R2} + F_{S-T} = F_T + F_{T-S} \quad (3)
\]
\[
F_{T-S} = F_S + F_{S-T} \quad (4)
\]

Substituting Eq. (4) into Eq. (3), we obtain,

\[
F_{R1} + F_{R2} = F_T + F_S \quad (5)
\]

If we assume also the steady state conditions for the heavier isotope, \( ^{15}N \), equations similar to Eqs. (4) and (5) for the heavier isotope are obtained to be,
\[ F_{T-S} = F_S + F_{S-T} \]  
\[ F_{R1} + F_{R2} = F_T + F_S \]

where the prime stands for the heavier isotope.

b) Relationship of \( \delta^{15}N \) of \( \text{N}_2\text{O} \) between troposphere and stratosphere

Dividing Eq. (4) by Eq. (4), we obtain,

\[ \frac{F_{T-S}}{F_{T-S}} = \frac{(F_S/F_S) + (F_{S-T}/F_S) \times (F_{S-T}/F_{S-T})}{1 + (F_{S-T}/F_S)} \]

(6)

Then Eq. (6) is rewritten with the introduction of \( \delta \)-notation to be,

\[ 1 + 10^{-3} \delta T = \frac{\alpha_S \times S}{1 + 10^{-3} \delta S} \]

(7)

where \( \delta T \) and \( \delta S \) are the steady state \( \delta^{15}N \) values of \( \text{N}_2\text{O} \) in two reservoirs. The \( \delta^{15}N \) value of stratospheric \( \text{N}_2\text{O}, \delta S \), can be evaluated by Eq. (8) when \( \alpha_S \) and \( F_{S-T}/F_S \) are estimated.

We adopt here ROBINSON’s estimation (1980) of \( F_{S-T} = 5.4 \times 10^7 \) ton N yr\(^{-1}\) and \( F_S = 1.0 \times 10^7 \) ton N yr\(^{-1}\). The latter estimated value, \( F_S \), is in good agreement with those estimated by other authors for the rate of photo-decomposition (e.g., JOHNSTON et al., 1979). Then, \( F_{S-T}/F_S \) can be calculated to be about 5.4.

The kinetic isotope fractionation factor, \( \alpha_S \), during photolysis of \( \text{N}_2\text{O} \) in the stratosphere is taken to be the same as the kinetic isotope fractionation factor associated with the \( \text{N}^–\text{O} \) bond rupture of \( \text{N}_2\text{O} (\text{N}_2\text{O} \rightarrow \text{N}_2) \) which can be calculated at 220°K using IR data (BEGIN and FLETCHER, 1960) of isotopic species of \( \text{N}_2\text{O} \) to be 0.895.

Inserting the values of \( F_{S-T}/F_S \) and \( \alpha_S \) into Eq. (8), we obtain,

\[ 1 + 10^{-3} \delta T = 0.984 \left(1 + 10^{-3} \delta S\right) \]

(9)

When we take \( \delta T \) of \(+8.1^{\circ}/_{\circ}0 \) as mentioned previously, then \( \delta S \) is calculated to be \(+24^{\circ}/_{\circ}0 \). This estimated value is not very far from a single observed value obtained in the stratosphere by MOORE (1974) which is \(+19.2^{\circ}/_{\circ}0 \). Since the analytical methods for measuring \( \delta^{15}N \) of \( \text{N}_2\text{O} \) are different between ours and MOORE’s, it is more reasonable to compare the numerical coefficient in Eq. (9) of 0.984 and that calculated with MOORE’s results of \( \delta T \) of \(+5.2^{\circ}/_{\circ}0 \) and \( \delta S \) of \(+19.2^{\circ}/_{\circ}0 \), which is 0.986. A good agreement is obtained, so that the following discussion on the global budget of \( \text{N}_2\text{O} \) can be made by adopting this coefficient, 0.984, as one of the parameters.

c) Some implications on processes of production and consumption

Dividing Eq. (5') by Eq. (5), we obtain,

\[ \frac{F_{R1} + F_{R2}}{F_{R1}} \times \frac{F_{R2}}{F_{R1}} = \frac{1 + \frac{F_{R2}}{F_{R1}}}{\frac{F_T}{F_{R1}} + \frac{F_S}{F_T} \times \frac{F_S}{F_S}} \]

(10)

HAHN and JUNGE (1977) estimated the total annual production rate of \( \text{N}_2\text{O} \) to be \( 1.35 \times 10^8 \) ton N yr\(^{-1}\). Since the sum of the production rates of denitrification and nitrification should be the total annual production rate in this model, \( F_{R1} + F_{R2} = 1.35 \times 10^8 \) ton N yr\(^{-1}\).
Inserting \((F_{R1} + F_{R2})\) and \(F_S\) into Eq. (5), we obtain, \(F_T\) to be \(1.25 \times 10^8\) ton N yr\(^{-1}\). Then \(F_S/F_T\) can be calculated to be \(1/12.5\).

If we assume all the processes related to the budget of \(N_2O\) in the troposphere are controlled by first order reactions, then each \((F'/F)\) value can be expressed by representative values of \(\alpha\), the kinetic isotope fractionation factor for each process, and isotope ratio as follows,

\[
\frac{F_{R1}}{F_{R1}} = \alpha_{R1} \times \left(\frac{R1}{R1}\right) \quad (11)
\]

\[
\frac{F_{R2}}{F_{R2}} = \alpha_{R2} \times \left(\frac{R2}{R2}\right) \quad (12)
\]

\[
\frac{F_T}{F_T} = \alpha_T \times \left(\frac{T}{T}\right) \quad (13)
\]

where the prime denotes \({}^{15}\)N again. Substituting \((F_S/F_T)\), Eqs. (9), (11), (12) and (13) into Eq. (10), we obtain,

\[
\frac{\alpha_{R1} \left(1 + 10^{-3} \delta R1\right) + \alpha_{R2} \left(1 + 10^{-3} \delta R2\right) \rho}{1 + \rho} = (0.926\alpha_T + 0.067) \left(1 + 10^{-3} \delta T\right) \quad (14)
\]

where \(\rho\) denotes the \(F_{R2}/F_{R1}\) ratio and \(\delta R1\) and \(\delta R2\) are the averages of \(\delta^{15}\)N of the source \(NO_3^-\) and \(NH_4^+\) respectively.

Both of the average values of \(\delta^{15}\)N of nitrate and ammonium found in a variety of natural environment appear to be around \(+60/00\) (WADA, personal communication). As has been pointed out by several authors (e.g., BLACKMER and BREMNER, 1977), denitrification process gives large depletion of \({}^{15}\)N in the product among other nitrogen-bearing reactions. We adopt a value of 0.97 for \(\alpha_{R1}\) (\(NO_3^- \rightarrow N_2O\); YOSHIDA et al. in preparation).

We do not have enough experimental results concerning the kinetic isotope effect during nitrification (\(NH_4^+ \rightarrow N_2O\)). However, there is an experimental fact that \(^{15}\)N is enriched in the product, \(N_2O\) \((\pm 28/00\) compared with the source \(NH_4^+\)) during aerobic incubation of a surface soil (WADA, personal communication)*. We adopt a value 1.028 for \(\alpha_{R2}\) on the basis of WADA’s result. Then Eq. (14) turns out to be,

\[
0.97 + 1.028\rho \frac{1 + \rho}{1 + \rho} = 1.002 (0.926\alpha_T + 0.067) \quad (15)
\]

When \(\rho\), the contribution ratio of nitrification to denitrification is estimated, then \(\alpha_T\), the kinetic isotope fractionation factor for the previously unknown consumption process in the troposphere can be evaluated by Eq. (15). The estimated \(\alpha_T\) value may be a key to the unknown consumption process. If we find out, on the other hand, the major unknown consuming process and estimate \(\alpha_T\), then \(\rho\) can be evaluated.

Microbiological studies have clarified that a variety of nitrate reducing bacteria utilize \(N_2O\) as a terminal electron acceptor as well as nitrate and nitrite. Significantly high reducing activity of soils and sediments for \(N_2O\) comparable to that for nitrate was found in a field along with a watershed using \(^{15}\)N labelled \(N_2O\) as a tracer (YOSHIDA et al., in preparation), which strongly suggests that \(N_2O\) reduction is one of the major consuming processes of \(N_2O\).

The kinetic isotope fractionation factor during \(N_2O\) reduction was measured and concluded to be close to unity in natural environment (YOSHIDA et al., in preparation). When we substitute unity for \(\alpha_T\) in Eq. (15), we obtain \(\rho\), the contribution ratio of nitrification to denitrification, to be 0.76. This high value is in good agreement with recent evidences,

* : This experiment involved many obscure factors, and \(\alpha_{R2}\) given there may not well reflect the true value of \(\alpha_{R2}\); however, we take WADA’s result in this study, since there have been no other experimental values of \(\alpha_{R2}\) reported so far. Experiments on the kinetic nitrogen isotope fractionation factor during nitrification (\(NH_4^+ \rightarrow N_2O\)) using pure culture of Nitrosomonas europaea are now proceeding in our laboratory.
suggesting that nitrification plays an important role in producing N₂O (e.g., ELKINS et al., 1978; LIPSCHULTZ et al., 1981).

CONCLUSION

Nitrogen isotope ratio of atmospheric N₂O was measured with a satisfactory accuracy to be used as a key to the global cycle of N₂O. Nitrous oxide was found in the isotopic disequilibrium with other nitrogen bearing compounds and in a steady-state on the balance between production and consumption from the isotopic point of view.

Some important implications were deduced from the discussion on the nitrogen isotope ratio of N₂O. One is the nitrogen isotope heterogeneity in the atmosphere: N₂O in the maritime air is more depleted in ¹⁵N than in the terrestrial surface air; N₂O in the stratosphere is more enriched in ¹⁵N than in the troposphere. Second is the importance of two processes involved in the N₂O cycle: nitrification as producing process and reduction of N₂O as consuming process.

Taking into account the prematurity of the model of N₂O budget proposed in this study, we need more observations on nitrogen isotope ratio of N₂O in the troposphere, stratosphere and oceans, together with the strict examinations of the parameters used in this study.

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