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Nitrogen-15 and Oxygen-18 Characteristics of Nitrous Oxide: A Global Perspective

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The global budget of N₂O shows a significant imbalance between the known rate of destruction in the stratosphere and the estimated rates of natural and anthropogenic production in soils and the ocean. Measurements of the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios in two major tropospheric sources of N₂O, tropical rain forest soils and fertilized soils, show that soil N₂O from a tropical rain forest in Costa Rica and from sugar-cane fields in Maui is strongly depleted in both ¹⁵N and ¹⁸O relative to mean tropospheric N₂O. A major source of heavy N₂O, enriched in both ¹⁵N and ¹⁸O, must therefore be present to balance the light N₂O from soils. One such source is the back-mixing flux of N₂O from the stratosphere, which is enriched in ¹⁵N and ¹⁸O by photolysis and chemistry. However these return fluxes of ¹⁵N and ¹⁸O are so great that a large oceanic flux of N₂O is required to balance the heavy isotope-enriched stratospheric flux. All these effects will be reflected in climatically related isotopic variations in trapped N₂O in polar ice cores.

Nitrous oxide (N₂O) is an active atmospheric trace gas (tropospheric mixing ratio = 310 ppbv) that is currently increasing in concentration at a rate of ~0.25% per year (1). Various sources both natural and anthropogenic have been identified, but the relative importance of these sources has not yet been established, although it seems clear that tropical forest soils are the primary single source (2, 3). The atmospheric residence time of N₂O relative to destruction by stratospheric pho-

tolysis and chemistry is ~150 years, but known and estimated inputs to the atmosphere are only about half of the flux required to balance the calculated destruction rate (4), and reasons for the imbalance are unknown.

Characterization of tropospheric and dissolved oceanic N₂O by the two isotope ratios ¹⁵N/¹⁴N and ¹⁸O/¹⁶O provides important constraints on the geochemistry and sources of this gas (5). In this report we extend this approach to a study of N₂O in tropical rain forest soils (6) and in stratospheric air. The ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios were measured by injecting molecular N₂O directly into the dual-inlet, triple-collecting mass spectrometer

SAMSON and simultaneously measuring masses 44, 45, and 46 for the ¹⁵N/¹⁴N and ¹⁸O/¹⁶O isotope ratios (7).

Soil-gas samples were collected from natural soils in the rain forest of Costa Rica (8, 9) and from fertilizer-treated soils of sugar-cane fields on the island of Maui (10). Air samples were withdrawn from existing soil-flux measurement chambers (11) and returned to La Jolla where the N₂O-air mixing ratios were determined by ECD gas chromatography, and the isotope ratios were measured. Table 1 shows that quasi-duplicate samples at one Maui site and at one of the Costa Rican sites agree quite well for both the measured N₂O mixing ratios and the end-member isotopic δ values of the soil N₂O (12).

Figure 1 shows the soil-N₂O isotopic data and the δ values of tropospheric N₂O (5). Although the isotopic values from different soil sites show rather large variations, they are uniformly depleted in the heavy isotopes and isotopically lighter than the tropospheric air and oceanic samples in all cases. On Maui N₂O from the abundant rainfall site is enriched in the heavy isotopes of both N and O relative to N₂O from the dry-side soil. This effect may be due to denitrification in the wet soils, as nitrification in dry soils generally produces isotopically light N₂O (13, 14).

These data show that the isotopic ratios of N₂O emitted from soils in both the natural and fertilized states are significantly depleted in ¹⁵N and ¹⁸O relative to tropospheric N₂O. Thus there must also exist sources of N₂O enriched in the heavy isotopes to balance the input fluxes of light soil-gas N₂O.

One such heavy tropospheric source is the N₂O produced by nitrification in deep ocean water (5): these data are also plotted in Fig. 1. The heavy isotope enrichments in these waters increase with depth, but the deep-water production is not a significant tropospheric source. In contrast to these heavy isotope-enriched samples, the δ values of near-surface dissolved N₂O are quite similar to those of tropospheric N₂O but are slightly depleted in ¹⁵N and ¹⁸O. It is possible that in some oceanic areas of strong regional upwelling such as the Equatorial Eastern Pacific (15) and the northwest Indian Ocean (16), N₂O brought to the surface may have been produced by denitrification (17) and that N₂O produced in this way may be enriched in ¹⁵N (18), and perhaps in ¹⁸O, relative to values for tropospheric air. However the δ values of dissolved N₂O in shallow depths (surface to depths of ~800 m) are quite similar to those of tropospheric N₂O [(5), Fig. 1], so that there is a strong buffering effect of subsurface N₂O

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on the isotopic ratios in tropospheric N_2O . It is evident from Fig. 1 that, given the present data for the isotopic composition of N_2O produced by tropical soils, there must exist another tropospheric source that is enriched in both ^{15}N and ^{18}O relative to the tropospheric values. The only candidate for such a source appears to be the feedback of stratospheric N_2O , which is enriched in both ^{15}N and ^{18}O by photolysis and photochemical reactions.

The measured $\delta^{15}N$ and $\delta^{18}O$ values in N_2O from a high-latitude profile of stratospheric air (19) are indeed highly enriched in both heavy isotopes relative to values of N_2O in tropospheric air (Table 1). Moreover the isotopic data lie on a smooth mixing curve with the δ values of tropospheric N_2O . These data therefore demonstrate that the soil-gas input of ^{15}N -depleted and ^{18}O -depleted N_2O must be at least partially balanced by the return flux into the troposphere of stratospheric N_2O enriched in both heavy isotopes.

The return flux of air from the stratosphere to the troposphere has been evaluated in several ways. Newell (20) estimated this flux as 2.4 Mt/s (1 Mt = 10^9 kg) of air brought down in mid-latitudes through the folded tropopause. More recently, Holton (21) calculated the global balances of upward mass and N_2O fluxes through the tropical tropopause, and the compensating downward fluxes in the extratropical regions, on the basis of dynamics of eddy dissipation above the 100-mbar level. The upward flux of N_2O into the stratosphere, based on the integrated air flux and a tropospheric mixing ratio of 300 ppbv, is 60.5 MtN/y. The downward flux from the stratosphere is obtained by subtract-

ing the destruction rate in the stratosphere (10.5 MtN/y): This flux is then 50 MtN/y, corresponding to a mean mixing ratio in the source region of the downward flux (~ 16 km) of ~ 245 ppbv.

In Fig. 2 we show the approximate isotopic signature of N_2O from this source region interpolated on the curve between the two measured stratospheric samples and the mean value of tropospheric air: $\delta^{15}N = +15$ per mil and $\delta^{18}O = +30.7$ per mil. The vector from this point to a crudely estimated mean soil-gas isotopic composition is also shown. There are two points to be noted:

The steady-state tropospheric isotopic flux balance is:

$$\sum J_i \Delta_i + F_{st} \Delta_{st} = 0 \quad (1)$$

where $\Delta_i = (\delta_i - \delta_t)$, subscript i refers to a tropospheric source (soil-gas, oceanic production, and so forth), and subscript t denotes the tropospheric isotope ratios. Similarly $\Delta_{st} = (\delta_{st} - \delta_t)$, where the subscript st refers to an isotope ratio in N_2O at the source level for the stratospheric return flux. J is a tropospheric source, F is a mass flux of N_2O , and Eq. 1 describes the mass balance for either heavy isotope. The $F\Delta$ and $J\Delta$ terms are thus isotopic flux terms [with units of (megatons of N per mil) per year (MtN%/y)]. From the Δ_{st} values for the estimated stratospheric and tropospheric δ values we see that the $F\Delta$ terms are approximately +400 and +500 MtN%/y, respectively,

for ^{15}N and ^{18}O . These terms are exceedingly large compared to the $J\Delta$ terms for soil gas, which from the adopted mean values (Fig. 2), and setting $J \approx 4$ MtN/y (4), are only -80 and -40 MtN%/y for ^{15}N and ^{18}O , too small to balance the $F\Delta$ terms by factors of 5 and 12, respectively. Indeed in order to obtain approximate isotopic mass balances with soil gases for the most negative global mean isotopic δ values for N and O shown in Fig. 1 (approximately -25 and 0), soil-gas source functions of 12.5 and 24 MtN/y are required. Such fluxes are certainly conceivable, but it seems improbable that we have underestimated the soil source term by such large factors (5).

However, there is yet another problem with balancing the stratospheric return flux by the soil-gas emission of N_2O : In Fig. 2 the vector between the mean isotopic composition of the stratospheric return flux and the mean soil-gas composition (or indeed to any possible soil-gas composition based on these data) does not intersect the isotopic composition of mean tropospheric air (thus the difference in the two isotopic flux results found in the preceding paragraph). No matter how large the soil-gas source terms may be, a third component is required to account for the isotopic composition of tropospheric N_2O . In Fig. 2 we have chosen the source composition of the oceanic near-surface production as this third component, with values of $\delta^{15}N \approx +5$ per mil and $\delta^{18}O \approx +15$ per mil (deliberately estimated as somewhat more extreme than the mea-

Table 1. Nitrogen and oxygen isotope ratios of soil-gas N_2O (end-members) and stratospheric N_2O , as δ values (per mil) relative to atmospheric N_2 and O_2 . Average marine tropospheric N_2O [from (5)] is also shown. For Maui samples, W sample is from the wet side and D samples are from the dry side of the island. Location of stratospheric samples is given as height.

Location	Date	N_2O (ppb)	$\delta^{15}N$	$\delta^{18}O$
<i>Soil-gas N_2O</i>				
Maui - W*	12/5/91	670	0.1	19.2
- D1*	12/6/91	1100	-25.0	10.8
- D2*	12/6/91	1220	-22.1	11.0
Costa Rica -JA	11/25/91	1270	-22.5	3.6
-CE1	11/27/91	1340	-7.1	12.3
-CE2	11/27/91	1100	-7.8	9.8
<i>Stratospheric N_2O (68°N)</i>				
12.8 km	1/10/88	284	12.8	29.1
17.8 km	2/10/88	182	21.1	35.0
Av. trop. N_2O	4/83-5/83	~ 303	7.0	20.7

*Two samples from the same chamber of nearby chambers, combined for the isotope analysis.

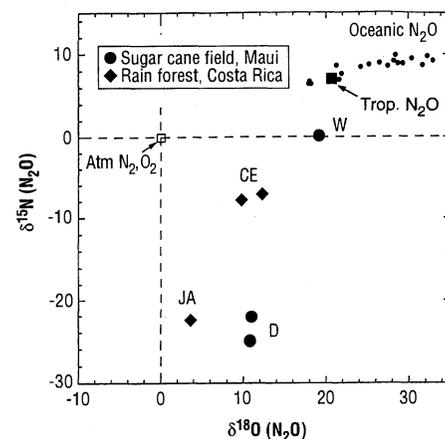


Fig. 1. $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios (as δ values relative to atmospheric N_2 and O_2) in N_2O from soil gases on Maui and in a Costa Rican rain forest, compared with the isotopic composition of tropospheric N_2O (5). Also shown are the isotopic data on dissolved N_2O in the oceans (5): In these data the δ values for both N and O increase with depth to the bottom (~ 4000 m), and the near-subsurface waters (surface to ~ 800 m) are slightly lower in $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios than tropospheric N_2O . W, CE, JA, and D delineate data from several sites (Table 1, 8, 10).

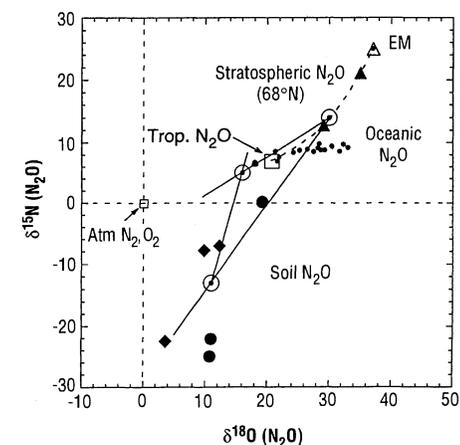


Fig. 2. Isotopic composition of stratospheric N_2O compared to tropospheric N_2O , soil gases, and oceanic N_2O (5). The three vectors connect the estimated mean source values (circled points) for the three major steady-state input fluxes: the stratospheric return flux, the input of soil gases, and the near-subsurface oceanic production (5). EM: the estimated stratospheric end-member (that is, the maximum isotopic enrichments in stratospheric N_2O).

sured data). Thus the isotopic differences from tropospheric N_2O are -2 per mil and -5.7 per mil, and with the conventional value for the oceanic J source term of ~ 2 MtN/y (5) the isotopic flux terms are respectively -4 and -11 MtN‰/y for N and O. These isotopic fluxes are therefore too small by factors of 100 and 50 to balance the isotopic stratospheric return fluxes.

Although we have analyzed only a limited number of soil gases, these are presumably representative of N_2O from tropical rain forests and fertilized soils. It is doubtful, therefore, that we can look to a vastly different mean soil-gas isotopic composition to solve the isotopic mass balance problem. However, two more reasonable possibilities exist. First, the stratospheric profile we have analyzed is from $68^\circ N$ and may therefore not be representative of the mean stratospheric return flux. This problem can readily be investigated by studying more profiles to see if there is less enrichment (or more mixing) in the return-flux stratospheric N_2O . This would decrease the isotopic flux terms, although the vector would still not pass through mean tropospheric N_2O .

The second possibility is that the tropospheric fluxes to and from the ocean are large, so that as suggested above, the oceanic production of light N_2O in the near-subsurface waters buffers the tropospheric composition by balancing the stratospheric return flux of the isotopic species. For example, if the atmospheric residence time, relative to the flux into the sea, can be assumed to be similar to that for CO_2 [$\tau_{atm} \sim 7$ years (22)] then the flux into and out of the sea that is relevant for the isotopic flux balances is ~ 200 MtN/y, the $J\Delta$ terms for ^{15}N and ^{18}O (assuming the mean source marked in Fig. 2) become -400 and -1100 MtN‰/y respectively, and the balances are achieved. (The differences between these numbers are due to the fact that neither mixing vector from the other two sources to the assumed oceanic source passes through the tropospheric N_2O point. However, in this case the composition of the oceanic subsurface source is known only in the crudest approximation at present: We need not despair at the imbalances.)

In general, resolution of the magnitude of the soil-gas and oceanic source fluxes from the isotopic data is difficult when the isotopic balance is made within the troposphere. The soil-gas (and anthropogenic) terms are essentially small differences between two large numbers. What is needed is a careful evaluation of the isotopic removal fluxes in the stratosphere by photolysis and chemistry: that is, one needs the isotopic fractionation

factors and concentrations over the altitude range in which the destruction of N_2O takes place. In this case the stratospheric flux terms in and out of the troposphere are not involved, and the continental and oceanic terms can be directly compared with the much smaller isotopic removal flux terms. It is important also to establish the isotopic composition of the N_2O produced in the upper regions of the oceans and to continue to study stratospheric profiles from more representative geographical sites.

The N_2O mixing ratio in trapped gases in ice cores has fluctuated drastically in glacial epochs, by as much as 30% in times of maximum glaciation (23). This drop was presumably caused by the decrease in exposed soil areas in the Northern Hemisphere, but other sources may change as well. The decreased mixing ratios should be reflected in increases in the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of tropospheric air because of the decreased input of isotopically light soil- N_2O . At present we are able to see only dimly, and with only the least understanding, the broad picture of interaction of soils, oceanic subsurface and surface waters, stratospheric fluxes, and photolysis rates that determine the secular changes in the tropospheric concentration of N_2O (24).

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- The atmospheric reservoir of N_2O is ~ 1500 Tg of nitrogen (TgN), so that the stratospheric destruction rate corresponds to a steady-state input flux of ~ 10 MtN/y (megatons of N per year). Current estimates for the major sources, summarized in (1), are ~ 4 MtN/y from forest soils (75% tropical forests and 25% temperate forests), 2 MtN/y from oceanic production, and 1.3 MtN/y from anthropogenic sources (fertilizer: 1, combustion: 0.2, biomass burning: 0.1). All these estimates are subject to large and poorly known uncertainties, but at face value the figures indicate that the total estimated source strength (~ 7.3 MtN/y) amounts to $\sim 50\%$ of the destruction rate (10 MtN/y) plus the atmospheric increase rate of ~ 4 MtN/y. Despite the large uncertainties, there is general agreement (1) that the sources and sinks cannot be brought into agreement.
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- The Costa Rica samples were collected at La Selva Biological Station ($10^\circ 26' N$, $84^\circ 00' W$), at two sites: the Jaguar soils (JA) and La Selva soils (CE). At both these sites the soils are moist and the forest is mature old growth that has been undisturbed in historical times (8). The JA site is a highly weathered, relatively infertile, clay-accumulating soil (technically an ultisol) on Pleistocene lava. The CE site, on a middle terrace of the Puerto Viejo River, is a younger, more fertile soil without a horizon of accumulation (technically an inceptisol).
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- The Maui samples were collected at two young sugar-cane fields, one on the wet side (W) and one on the dry side (D) of the island. Urea used as the fertilizer in both fields is introduced intensively through the irrigation lines during the first year of growth.
- Soil-air samples of ~ 28 l were collected from the soil-flux measurement chambers in pre-evacuated 27-l aluminum cylinders. From the flux chambers, with ~ 10 l of head space over the soils, air was slowly drawn into the cylinder (flow rate ~ 120 ml/min) while ambient air was fed into the chamber at the top to maintain the ambient pressure. When the cylinder pressure was approximately atmospheric, a small battery-operated pump brought the cylinder up to 2 to 3 psi over ambient. The Maui samples had relatively low concentrations of N_2O , and two cylinders collected from the same chamber in series, or from nearby chambers, were combined into a single sample during N_2O purification. In the laboratory, after measurement of the N_2O mixing ratios, N_2O was separated at liquid nitrogen temperature after removal of most of the CO_2 by passage through an Ascarite column. The N_2O was further purified by a preparatory GC system with a Porapak Q column.
- The soil-gas samples contained ambient atmospheric N_2O (~ 310 ppbv) together with the N_2O that had diffused from the soil. The end-member compositions of the soil N_2O are calculated from the air and soil-gas N_2O concentrations and the known isotopic composition of tropospheric N_2O .
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