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Analysis of Sources and Sinks of Atmospheric Nitrous Oxide (N<sub>2</sub>O)

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There are major unanswered questions about the sources of atmospheric nitrous oxide. Recent assessments of N<sub>2</sub>O sources are diverging rather than converging. Here I use a simple model to place constraints on the relative sizes of N<sub>2</sub>O sources in the northern and southern hemispheres (NH and SH). Using measurements of the rate of temporal increase of atmospheric nitrous oxide (N<sub>2</sub>O) concentrations and observations of their cross-equator differences, I calculate the total sources of N<sub>2</sub>O for the (NH and SH). The NH source  $\Phi_N$  must exceed the SH source  $\Phi_S$ ; their ratio  $R (= \Phi_N/\Phi_S)$  is between 1.7 and 2.4 for the case where the NH concentration is 1 ppb higher than that in the SH. When the NH concentration is 0.75 ppb higher,  $R$  is between 1.5 and 1.9. These values of  $R$  increase by about 50% when more rapid loss to the NH stratosphere is introduced. Slightly wider ranges of  $R$  are calculated for certain choices of parameters. For these calculations I have used a two-box model which permits an array of assumptions to be tested; a range of values is employed for interhemispheric exchange times and for removal times due to stratospheric destruction of N<sub>2</sub>O. In addition to the common case of no uptake of atmospheric N<sub>2</sub>O by soils, I have tested the model sensitivity to two hypothesized nonzero soil sinks. Relatively small soil sinks would decrease the atmospheric residence time of N<sub>2</sub>O to values below those that are calculated from stratospheric removal alone.

## 1. INTRODUCTION

Nitrous oxide is an important trace gas in the atmosphere because it is an effective greenhouse gas and because it is the major source of stratospheric NO, which is important in ozone-layer chemistry. Its discovery and early views on its behavior are reviewed by *Bates and Hays* [1967]. Reactions that produce NO from N<sub>2</sub>O in the stratosphere and other reactions that destroy N<sub>2</sub>O and their rates are discussed by *Johnston et al.* [1979]. Evidence that N<sub>2</sub>O does release far more NO into the stratosphere than any other source was provided by *Jackman et al.* [1980]. As a greenhouse gas, N<sub>2</sub>O functions through several absorption bands in the wavelength region 7.7  $\mu\text{m}$  to 17  $\mu\text{m}$  [*Ramanathan et al.*, 1985]. In the past century the atmospheric concentrations of several greenhouse gases have increased, including CO<sub>2</sub>, CH<sub>4</sub>, chlorofluorocarbons, N<sub>2</sub>O, and tropospheric ozone. Of the enhanced greenhouse effect (radiative forcing) due to these increases to date, N<sub>2</sub>O increases have contributed 2 to 3%; depending on future concentrations, the contribution from N<sub>2</sub>O could increase to about 10% [*Dickinson and Cicerone*, 1986].

Measurements show that N<sub>2</sub>O is increasing in the global atmosphere. *Weiss* [1981] and *Weiss et al.* [1981] showed that the 1978 concentration in the northern hemisphere was 300 ppb and that the average annual increase between 1976 and 1980 was about 0.6 ppb (parts per billion by volume in dry air) per year, or about 0.2% per year. These data are from several stations spanning the globe and from several extended oceanic cruises. *Weiss* [1981] also showed that an annual increase of 0.65 ppb could be inferred for the period 1961-1978 from other data. More recent data (R. F. Weiss, private communication, 1988) shows that through 1987 the average annual increase

was about 0.7 ppb and that the average excess in the northern hemisphere relative to the southern hemisphere of 0.8 ppb reported by *Weiss* [1981], persists. Analysis of an independent data set from Oregon and Tasmania (1979-1982) showed possibly larger annual increases of 0.2 to 0.4% per year, an interhemispheric difference similar to that of *Weiss* [1981], and evidence for seasonal cycles [*Khalil and Rasmussen*, 1983]. Data from an extended ship cruise (50°N to 40°S) in 1987 have shown an excess of N<sub>2</sub>O in the northern hemisphere of about 1.0 ppb [*Butler et al.*, 1989].

Current knowledge indicates that N<sub>2</sub>O is a very long-lived gas once in the atmosphere. It is thought to be inert in the troposphere; photolysis (producing O(<sup>1</sup>D) and N<sub>2</sub>) and attack by O(<sup>1</sup>D) (producing NO) in the stratosphere are the removal mechanisms. If these processes are the only removal mechanisms, then the atmospheric residence time  $\tau_R$  for N<sub>2</sub>O is over 100 years. Calculated lifetimes are somewhat sensitive to several factors including the photoabsorption cross section for O<sub>2</sub>,  $\sigma(\text{O}_2)$ , in the Herzberg continuum wavelength region. Using early (larger) values for  $\sigma(\text{O}_2)$  *Johnston et al.* [1979] and *Golombek and Prinn* [1986] found  $\tau_R$  to be 180 years and 182 years, respectively. *Mahlman et al.* [1986] also deduced a 180-year value in their three-dimensional (3D) model but values between 100 and 130 years when they compared modeled N<sub>2</sub>O stratospheric distributions with measurements of stratospheric N<sub>2</sub>O. In their studies, *Mahlman et al.* concluded that measured and modeled N<sub>2</sub>O distributions imply faster photochemical destruction of stratospheric N<sub>2</sub>O than one calculates from then current photochemical and solar irradiance data. One possible way to increase these destruction rates is to employ lower photoabsorption cross sections for O<sub>2</sub> such as those of *Johnston et al.* [1984] but this has not yet been done in a 3D model. Using the one-dimensional (1D) model of *Cicerone et al.* [1983], I have calculated  $\tau_R = 150$  years for N<sub>2</sub>O with these smaller O<sub>2</sub> cross sections. Thus the exact value of  $\tau_R$  for N<sub>2</sub>O is not yet clear; it probably lies between 100 and 150 years if stratospheric destruction is the only sink. With  $\tau_R$  as large as 150 years, the observed annual increase of 0.7 ppb/year implies that the

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present annual source of  $N_2O$  is about 25% larger than the natural steady state source (see, for example, Keller *et al.*, [1986] and Cicerone [1987]).

Are human perturbations to the cycling of nitrogen through Earth's soils, oceans and atmosphere (see, for example, Delwiche [1981]) responsible for increasing atmospheric  $N_2O$ ? This important question has not yet been answered, although human causes are likely. Attempts to construct an accurate ledger of  $N_2O$  sources have not yet succeeded; the proposed  $N_2O$  sources do not sum to the total of the atmospheric sink rates plus the observed annual increase. Recent attempts to construct balanced  $N_2O$  budgets [Keller *et al.*, 1986; Gammon *et al.*, 1986; Hao *et al.*, 1987] have been undercut by newer measurements that indicate a much smaller (if any)  $N_2O$  source from combustion processes. Specifically, it has been shown that artifact  $N_2O$  is produced in sample flasks when air samples are rich in moisture, NO or  $NO_2$  and  $SO_2$  [Muzio and Kramlich, 1988; Linak *et al.*, 1989]. Thus earlier experiments with samples from power-plant exhaust gases and laboratory combustors that suggested significant sources of  $N_2O$  from combustion are probably in error, including the studies by Pierotti and Rasmussen [1976], Weiss and Craig [1978], and Hao *et al.* [1987]. It is also possible because of this experimental artifact that less  $N_2O$  is released during biomass burning than has been estimated to date.

There is now a 15- or 20-year history of uncertainty in  $N_2O$  source sizes, identities, and  $\tau_R$  [Liu *et al.*, 1977]. It is this continuing uncertainty that prompts me to seek simple and useful constraints on some of these quantities.

In this study, I examine the implications of atmospheric  $N_2O$  data for the distribution of  $N_2O$  sources between hemispheres. I use a two-box model that is more complicated than Weiss's [1981] one-box model but still simple enough to allow analysis of several factors. From simple considerations, Weiss concluded that northern hemispheric (NH) sources must dominate. Khalil and Rasmussen [1983] adopted a specified distribution of sources (31% oceanic, 46% "land-based" and 23% human activities") and calculated rates of  $N_2O$  growth, north-south concentration differences (for a specified value each for  $\ell$  and  $\tau_\ell$ , defined below). Recently, Butler *et al.* [1989] have used a two-box model to deduce north-south source differences, given north-south differences in concentrations; see section 4. Analysis by Levy *et al.* [1979, 1982] with three-dimensional global transport models that assumed mostly continental sources (and hence, mostly NH) calculated slightly larger  $N_2O$  concentrations in the SH than the NH, i.e., the opposite of what has been measured. The Levy *et al.* work prompted me to try a simpler approach to test the implications of several variables that could not be varied in their 3D model. Finally, I include consideration of another  $N_2O$  sink, consumption of atmospheric  $N_2O$  by soils, as discussed below. For a gas such as  $N_2O$  for which the only presently identified sinks lead us to estimate  $\tau_R$  as long as 150 years or so, the possibility of other sinks is important to examine.

## 2. THE MODEL and INPUT DATA

For an atmospheric species like  $N_2O$  whose atmospheric residence time  $\tau_R \gg \tau_e$  (the time for exchange between hemispheres), we expect significant interhemispheric ex-

change.  $N_2O$  concentrations are measurably higher in the northern hemisphere than in the southern hemisphere, from 0.8 ppb [Weiss, 1981] to 1.0 ppb [Butler *et al.*, 1989], and within each hemisphere  $N_2O$  is relatively well mixed, at least at the surface. Consequently, a two-box model can be used to obtain estimates of differences between northern and southern sources and of interhemispheric transport; shortcomings to this approach are discussed later.

Let  $N$  equal the total amount of  $N_2O$  in the northern hemisphere as a function of time,  $t$ , and let  $S$  equal the total amount of  $N_2O$  in the southern hemisphere. Then

$$\frac{dN}{dt} = \Phi_N - \Phi_{N-S} - N(\ell_N + D_N) \quad (1)$$

$$\frac{dS}{dt} = \Phi_S + \Phi_{N-S} - S(\ell_S + D_S) \quad (2)$$

where  $\Phi_N$  is the total annual (gross) surface source of  $N_2O$  for the atmosphere of the northern hemisphere and  $\Phi_S$  is the same but for the southern hemisphere. Also,  $\Phi_{N-S} = (N-S)/\tau_e$ ,  $\ell_N$  and  $\ell_S$  are the rates of loss of  $N_2O$  from each hemisphere due to stratospheric processes, and  $D_N$  and  $D_S$  are the rates of loss of atmospheric  $N_2O$  in each hemisphere due to uptake by soils. In the calculations described below, I employ a range of values for  $\ell_N$  and  $\ell_S$ . For many of the cases I take  $\ell_N = \ell_S$ , but because there is some evidence from models that  $\ell_N$  exceeds  $\ell_S$  [Levy *et al.*, 1982] I also study this case. I use the following units: for  $N$  and  $S$ , moles of  $N_2O$ ; for  $\Phi_N$ ,  $\Phi_S$  and  $\Phi_{N-S}$ , moles per year. Destruction rates for  $N_2O$ , that is  $\ell_N$ ,  $\ell_S$ ,  $D_N$ , and  $D_S$ , are expressed as inverse time constants for the respective processes.

Solutions of (1) and (2) for  $\Phi_N$  and  $\Phi_S$  can be obtained algebraically after measured values are inserted for  $N$ ,  $S$ ,  $dN/dt$ , and  $dS/dt$  and estimates are used for  $\ell_N$ ,  $\ell_S$ ,  $D_N$ , and  $D_S$ . Two different interhemispheric gradients ( $N/S$  values) are examined: ( $N, S$ ) values are proportional to (305 ppb, 304 ppb) respectively in one case, similar to measurements by Butler *et al.* [1989] and 305 ppb, 304.25 ppb, similar to the 0.8 ppb difference from Weiss [1981]. For  $N/S = 305/304$ , ( $N, S$ ) = (2.7906, 2.7815)  $\times 10^{13}$  mol of  $N_2O$ . For  $N/S = 305/304.25$ , ( $N, S$ ) = (2.7906, 2.7837)  $\times 10^{13}$  mol. For this study the exact  $N_2O$  concentrations, for example, 305 ppb in the northern hemisphere, are not of concern; the difference between hemispheres is the key factor. Again, the exact number of moles for  $N$  and  $S$  is quite insignificant but the difference  $N - S$  is important.

The rates of change in the two hemispheres,  $dN/dt$ , are taken to be equal:  $dN/dt = dS/dt = 6.55 \times 10^{10}$  mol/year, based on a measured 0.7 ppb/year rate of increase [Weiss, 1981; R. F. Weiss, private communication, 1988] in each hemisphere. Four different rates of  $N_2O$  consumption in the stratosphere are treated here:  $1/\ell = 100, 125, 150, \text{ and } 180$  years, where  $\ell = (\ell_N + \ell_S)/2$ . I adopt this range of values for  $1/\ell$  because stratospheric removal rates are somewhat uncertain as discussed above, and to illustrate the effects of differing  $\ell$  values. In addition to these cases where the atmospheric residence time due to stratospheric removal,  $1/\ell$ , is set at 100, 125, 150, and 180 years and  $\ell_N = \ell_S$ , I have also modeled the case of these same four values of  $1/\ell$  but with  $\ell_N = 1.6 \ell_S$ .

In principle, there could be faster loss of  $N_2O$  from the NH troposphere to the NH stratosphere (followed by destruction) than occurs in the SH because NH topography leads to stronger planetary wave activity and because of a stronger polar vortex in the SH. Stated differently, subsidence from the NH stratosphere delivers more  $N_2O$ -poor air on an annual basis than in the SH. Three-dimensional model results from *Mahlman et al.* [1986] can be interpreted to show that the relationship  $\ell_N = 1.8 \ell_S$  deduced from *Mahlman et al.* [1980] is too large, although it seems clear that  $\ell_N \geq \ell_S$ . It will be seen below that the relationship  $\ell_N = 1.6 \ell_S$  illustrates a point clearly. Similarly, each of three values is employed for  $\tau_e$ : 0.8, 1.0, and 1.5 years. A value of  $\tau_e = 1.1$  years was found to be optimum for three-dimensional transport modeling of  $CCl_2F_2$ ,  $CCl_3F$ , and  $^{85}Kr$  [*Prather et al.*, 1987; *Jacob et al.*, 1987].

For the soil sink rates,  $D_N$  and  $D_S$  in (1) and (2), I have adopted three values each. The first pair is  $D_N = 0 = D_S$ ; uptake of atmospheric  $N_2O$  by soils is commonly neglected in the construction of budgets. There have been far more observations of soil emissions of  $N_2O$  than of soil uptake [*Keller et al.*, 1986; *Matson and Vitousek*, 1987; *Parton et al.*, 1988], and the fluxes of  $N_2O$  into soils measured to date are smaller than the fluxes leaving the soil. Accordingly, I assume in one case that soil uptake is completely negligible.

But there is some evidence for nonzero soil sinks in some regions and under certain conditions. *Ryden* [1981] observed a significant rate of  $N_2O$  uptake by an English grassland, especially when soils were wet, nitrate-poor and relatively warm. *Ryden* observed weekly averaged fluxes into the soil of order  $4 \times 10^9$  molecules of  $N_2O/cm^2$  s for most of a 3-month period. *Keller et al.* [1986] measured  $N_2O$  fluxes at the soil-air interface at several sites in Central and South America during the dry season. The great majority of their observations were of  $N_2O$  emissions, but some sites displayed  $N_2O$  uptake. The wettest site took up  $N_2O$  on 70% of the trials; uptake rates of order  $10^9$  molecules/ $cm^2$  s were common although averaged fluxes were from the soil to the atmosphere. *Matson and Vitousek* [1987] have observed mostly emissions in several studies, but smaller fluxes to the soil of order  $10^9/cm^2$  s were observed 10% to 20% of the time in Costa Rica. Fluxes less than  $10^9/cm^2$  s present some difficulties in field studies; see discussion below. *Elkins et al.* [1978] also reported some activity of aquatic sinks of atmospheric  $N_2O$ . In all these cases, microbial reduction of  $N_2O$  to  $N_2$  is suspected to occur. Thus while the net contribution of soils to the hemispherically, annually averaged  $N_2O$  sources,  $\Phi_N$  and  $\Phi_S$ , is positive I include soil sinks,  $D_N$  and  $D_S$ , to account for hemispheric differences.

I have included nonzero soil sinks in the present calculations because sinks have been observed occasionally in field measurements but also to illustrate how relatively small surface sinks could affect the atmospheric residence time of  $N_2O$ , given that the only other  $N_2O$  sinks are in the stratosphere. Two pairs of nonzero  $D_N$  and  $D_S$  values are used  $D_N = (1/780 \text{ years})$ ,  $D_S = D_N/2.1$ , and  $D_N = (1/390 \text{ years})$ ,  $D_S = D_N/2.1$ . These rather odd and particular numbers were selected as follows. The land area in the northern hemisphere is 2.1 times as large as that in the southern hemisphere (exclusion of ice-covered land

would increase this ratio to about 2.5). Here I assume for simplicity that soil sink activity is the same for all land area. With  $D_N = 2.1 D_S$  and  $D_N = (1/780 \text{ years})$ , the total global sink is  $1.5 \times 10^{12}$  g N/year or  $5.4 \times 10^{10}$  mol  $N_2O$  per year. For the case  $D_N = (1/390 \text{ years})$ , the total global sink is  $3 \times 10^{12}$  g N/year or  $1.07 \times 10^{11}$  mol  $N_2O$ /year. Note that an  $N_2O$  consumption rate of  $5 \times 10^8$  molecules/ $cm^2$  s by all land surfaces at all times would give a 500-year atmospheric residence time. This uniform consumption rate for  $N_2O$  is used here only to illustrate magnitudes; it is clear from field experiments that the world's soils are a net source of  $N_2O$ . The case above,  $D_N = (1/780 \text{ years}) = 2.1 D_S$ , would give  $\tau_R = 1170$  years; the corresponding averaged uptake rate by all land surfaces would be  $2.1 \times 10^8$  molecules  $N_2O/cm^2$  s. Oceanic surface waters are generally oversaturated with respect to  $N_2O$ , but limited areas can be slightly undersaturated, at least seasonally [*Butler et al.*, 1989]. I do not account for this potential surface sink specifically here, but the present formalism can include it.

### 3. RESULTS and DISCUSSION

Equations (1) and (2) were solved for 96 distinct cases. With 1 ppb more  $N_2O$  in the northern hemisphere than in the southern hemisphere,  $N/S = 305/304$ , four values of  $\ell$ , three values of  $\tau_e$ , and three values for  $D_N$  were used, for a total of 36 combinations. Because  $D_S = D_N/2.1$  it was necessary only to specify  $D_N$ . Also, for the case of 0.75 ppb more  $N_2O$  in the northern hemisphere than the southern hemisphere, the corresponding 36 combinations of  $\ell$ ,  $\tau_e$  and  $D_i$  were treated. For these first 72 cases,  $\ell_N = \ell_S$ , and as always,  $\ell = (\ell_N + \ell_S)/2$ .

Results for the larger of the north-south gradients are shown in Table 1. The upper third of Table 1 is for  $\tau_e = 0.8$  years, the middle third for  $\tau_e = 1.0$  years, and the lowest third for  $\tau_e = 1.5$  years. Focusing on the middle third,  $\tau_e = 1.0$  years, we find that for  $1/\ell = 180$  years,  $\Phi_N$  and  $\Phi_S$  are 3.12 and 1.29 (units of  $10^{11}$  mol/year), respectively, and their ratio  $R$  is 2.41, for the case  $D_N = D_S = 0$ .  $R$  values for these three values of  $\tau_e$  and with zero soil sinks are also graphed in Figure 1. The next column to the right in Table 1 is for  $D_N = (1/780 \text{ years}) = 2.1 D_S$ , for which  $\Phi_N$  and  $\Phi_S$  are 3.47 and 1.46 (both times  $10^{11}$  mol/year) and  $R = 2.38$ . The right-hand column under each value of  $1/\ell$  is for  $D_N$  and  $D_S$  twice as large as the previous case.

Several patterns are seen in the results of Table 1. First, in all cases,  $R$  is greater than 1.4. It is only for the case of slow interhemispheric exchange,  $\tau_e = 1.5$  years, that  $R$  is less than 1.7. For  $\tau_e = 1.0$  year and 0.8 year,  $1.7 < R < 3.1$ . For slow interhemispheric exchange the effect of increasing the hypothesized soil sink is to increase the ratio  $\Phi_N/\Phi_S$ . But for  $\tau_e = 0.8$  years,  $R$  actually decreases from 2.66 for  $D_i = 0$  to 2.55 for the largest  $D_N$  and  $D_S$  when  $1/\ell = 150$  years, and  $R$  decreases from 3.14 to 2.89 for  $1/\ell = 180$  years. This is due to two factors: fast interhemispheric exchange decreases the time of exposure of northern hemispheric  $N_2O$  to the soil sink in the northern hemisphere, and slow stratospheric removal ( $1/\ell = 150$  or 180 years) causes  $\Phi_i$  to depend more strongly on  $D_i$ , i.e.  $\Phi_N/\Phi_S$  regresses toward the ratio of  $D_N/D_S$ , which is 2.1, as each  $D_i$  increases.

TABLE 1. Total Annual Source of Atmospheric N<sub>2</sub>O for the Northern Hemisphere ( $\Phi_N$ ) and the Southern Hemisphere ( $\Phi_S$ ), and the Ratio  $R = \Phi_N/\Phi_S$  for Northern Hemisphere N<sub>2</sub>O Concentration of 305 ppb and Southern Hemisphere Concentration of 304 ppb.

	$\ell^{-1} = 100$ Years			$\ell^{-1} = 125$ Years			$\ell^{-1} = 150$ Years			$\ell^{-1} = 180$ Years		
	$D_N = D_N = D_N =$ (1/780) (1/390) (1/390) Years) Years) Years)		$D = 0$	$D_N = D_N = D_N =$ (1/780) (1/390) (1/390) Years) Years) Years)		$D = 0$	$D_N = D_N = D_N =$ (1/780) (1/390) (1/390) Years) Years) Years)		$D = 0$	$D_N = D_N = D_N =$ (1/780) (1/390) (1/390) Years) Years) Years)		$D = 0$
	$\Phi_N$	$\Phi_S$		$R$	$\Phi_N$		$\Phi_S$	$R$		$\Phi_N$	$\Phi_S$	
	4.58	4.94	5.30	4.02	4.38	4.74	3.65	4.01	4.37	3.34	3.70	4.06
	2.30	2.47	2.64	1.74	1.91	2.08	1.37	1.54	1.71	1.06	1.23	1.40
	1.99	2.00	2.01	2.31	2.29	2.28	2.66	2.60	2.55	3.14	3.00	2.89
	4.36	4.71	5.07	3.80	4.15	4.51	3.42	3.78	4.14	3.12	3.47	3.83
	2.53	2.70	2.86	1.97	2.14	2.31	1.60	1.77	1.94	1.29	1.46	1.63
	1.72	1.75	1.77	1.93	1.94	1.95	2.14	2.14	2.14	2.41	2.38	2.35
	4.05	4.41	4.77	3.49	3.85	4.21	3.12	3.48	3.84	2.81	3.17	3.53
	2.83	3.00	3.17	2.27	2.44	2.61	1.90	2.07	2.24	1.59	1.76	1.93
	1.43	1.47	1.50	1.54	1.58	1.61	1.64	1.68	1.71	1.76	1.80	1.83

Units of  $\Phi_N$  and  $\Phi_S$  are  $10^{11}$  mol/year;  $10^{11}$  mol of N<sub>2</sub>O =  $4.4 \times 10^{12}$  g N<sub>2</sub>O or  $2.8 \times 10^{12}$  g N as N<sub>2</sub>O. For all cases,  $\ell_N = \ell_S$ .

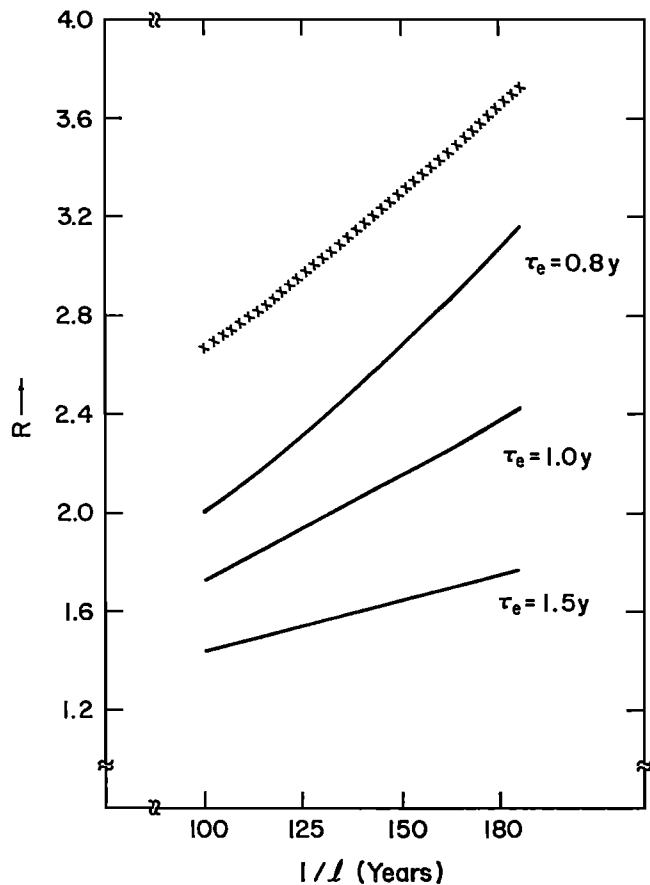


Fig. 1. Calculated values of  $R$ , i.e. the ratio of the N<sub>2</sub>O sources  $\Phi_N/\Phi_S$ , as a function of  $1/\ell$ , the inverse of the rate of stratospheric destruction of N<sub>2</sub>O. Solid curves are for  $\ell_N = \ell_S$ . All results here are for a 1 ppb excess of N<sub>2</sub>O in the NH over the SH and for the case of no soil sinks. The upper curve, graphed as crosses, is for  $\ell_N = 1.6\ell_S$ . It illustrates the effect of faster loss to the stratosphere in the NH.

Table 2 presents the results for 36 cases where the northern hemisphere concentration of N<sub>2</sub>O is only 0.75 ppb greater than that in the southern hemisphere. The source ratio  $R$  that is required to maintain this smaller gradient is less for each combination in Table 2 than for the corresponding case in Table 1. In Figure 2, graphs of these results appear for the case  $D_N = D_S = 0$ . In Table 2,  $1.31 < R < 2.29$ , although for a central case ( $\tau_e = 1.0$  year,  $1/\ell = 125$  years)  $R$  is about 1.6. Clearly, other north-south gradients would lead to different results; differences less than 0.75 ppb would imply a more uniform distribution of N<sub>2</sub>O sources with latitude, i.e.,  $R$  closer to unity.

The variable  $\Phi_{N-S}$ , the annual transfer rate (mol/year) of N<sub>2</sub>O from northern hemisphere to southern hemisphere, is a diagnostic variable in this calculation:  $\Phi_{N-S} = (N - S)/\tau_e$ . For the cases of Table 1,  $\Phi_{N-S} = (1.14, 0.91, \text{ and } 0.61) \times 10^{11}$  mol/year for  $\tau_e = 0.8, 1.0, \text{ and } 1.5$  years, respectively. For Table 2, where  $N/S = 305/304.25$ ,  $\Phi_{N-S} = (0.86, 0.69, \text{ and } 0.46) \times 10^{11}$  mol/year for  $\tau_e = 0.8, 1.0, \text{ and } 1.5$  years, respectively.

Even though the two nonzero soil sinks that are assumed here appear to be relatively small, their inclusion does affect the atmospheric residence time of N<sub>2</sub>O. With

TABLE 2. Total Annual Source of Atmospheric N<sub>2</sub>O for the Northern Hemisphere (Φ<sub>N</sub> and the Southern Hemisphere (Φ<sub>S</sub>), and the Ratio R = Φ<sub>N</sub>/Φ<sub>S</sub> but for Northern Hemispheric N<sub>2</sub>O Concentration of 305 ppb and Southern Hemispheric Concentration of 304.25 ppb

	ℓ <sup>-1</sup> = 100 years			ℓ <sup>-1</sup> = 125 years			ℓ <sup>-1</sup> = 150 years			ℓ <sup>-1</sup> = 180 years		
	D = 0	D <sub>N</sub> = (1/780 Years)	D <sub>N</sub> = (1/390 Years)	D = 0	D <sub>N</sub> = (1/790 Years)	D <sub>N</sub> = (1/390 Years)	D = 0	D <sub>N</sub> = (1/790 Years)	D <sub>N</sub> = (1/390 Years)	D = 0	D <sub>N</sub> = (1/790 Years)	D <sub>N</sub> = (1/390 Years)
	Φ <sub>N</sub>	4.31	4.66	5.02	3.75	4.11	4.46	3.38	3.74	4.09	3.07	3.42
Φ <sub>S</sub>	2.58	2.75	2.92	2.02	2.19	2.36	1.65	1.82	1.99	1.34	1.51	1.68
R	1.67	1.70	1.72	1.86	1.88	1.89	2.05	2.05	2.06	2.29	2.27	2.25
τ <sub>e</sub> = 0.8 Years	4.14	4.49	4.85	3.58	3.93	4.29	3.20	3.56	3.92	2.90	3.25	3.61
Φ <sub>S</sub>	2.75	2.92	3.09	2.19	2.36	2.53	1.82	1.99	2.16	1.51	1.68	1.85
R	1.50	1.54	1.57	1.63	1.67	1.70	1.76	1.79	1.81	1.92	1.93	1.95
τ <sub>e</sub> = 0.8 Years	3.91	4.26	4.62	3.35	3.70	4.06	2.98	3.33	3.69	2.66	3.02	3.38
Φ <sub>S</sub>	2.98	3.15	3.32	2.42	2.59	2.76	2.05	2.22	2.39	1.74	1.91	2.08
R	1.31	1.35	1.39	1.38	1.43	1.47	1.45	1.50	1.54	1.53	1.58	1.62

Units of Φ<sub>N</sub> and Φ<sub>S</sub> are 10<sup>11</sup> mol/year; 10<sup>11</sup> mol of N<sub>2</sub>O = 4.4 × 10<sup>12</sup> g N<sub>2</sub>O or 2.8 × 10<sup>12</sup> g N as N<sub>2</sub>O. For all cases, ℓ<sub>N</sub> = ℓ<sub>S</sub>.

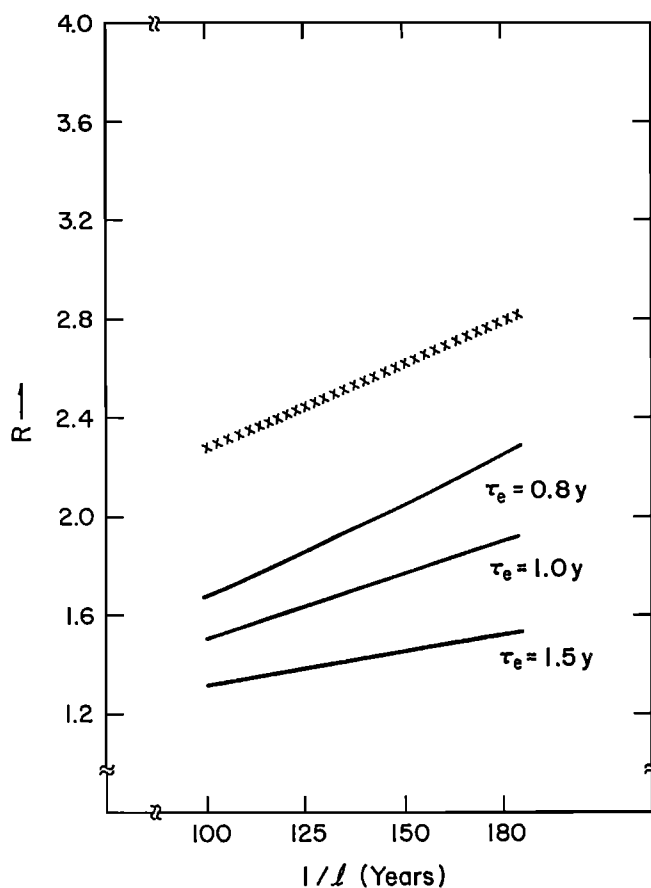


Fig. 2. Same as Figure 1 except for 0.75 ppb more N<sub>2</sub>O in the NH than the SH.

D<sub>N</sub> = (1/782 years) τ<sub>R</sub> = 91 years (100), 112 years (125), 131 years (150), and 155 years (180); numbers in parentheses are corresponding values of 1/ℓ (years) that would determine τ<sub>R</sub> if D<sub>N</sub> = 0 = D<sub>S</sub>. For the doubled soil sink rates, D<sub>N</sub> = (1/390 years), τ<sub>R</sub> = 84 years (100), 101 years (125), 117 years (150), and 135 (180) years. These reduced τ<sub>R</sub> values were deduced by adding Φ<sub>N</sub> and Φ<sub>S</sub> for each ℓ value, then subtracting the measured annual N<sub>2</sub>O increase (1.33 × 10<sup>11</sup> mol) and dividing the result into the total N<sub>2</sub>O burden of the atmosphere (5.57 × 10<sup>13</sup> mol).

If soil sinks are actually consuming atmospheric N<sub>2</sub>O as hypothesized here and τ<sub>R</sub> is thus, say, 117 years instead of 150 years; then we must identify steady state sources for N<sub>2</sub>O that are proportionally larger, for instance, 4.8 × 10<sup>11</sup> mol/year instead of 3.7 × 10<sup>11</sup> mol/year.

In the remaining 24 cases (of the total 96) for which (1) and (2) were solved, the stratospheric loss of N<sub>2</sub>O was assumed to be more rapid for N<sub>2</sub>O in the NH relative to the SH. In particular ℓ<sub>N</sub> was taken as ℓ<sub>N</sub> = 1.6ℓ<sub>S</sub>, where as before ℓ = (ℓ<sub>N</sub> + ℓ<sub>S</sub>)/2 and four values of ℓ were investigated: (1/ℓ) = 100, 125, 150, and 180 years. There is evidence for greater vertical exchange between the troposphere and stratosphere in the northern hemisphere [Mahlman et al., 1980; Levy et al., 1982] but the relative amounts are probably not as high as 1.8 as inferred from Mahlman et al. [1980] according to J. D. Mahlman (private communication, 1989). To illustrate the effect of this, I selected ℓ<sub>N</sub> = 1.6 ℓ<sub>S</sub>.

Figures 1 and 2 display (as curves defined by crosses) the source ratios  $R$  for values of  $1/\ell = 100, 125, 150,$  and  $180$  years, where  $\ell_N = 1.6\ell_S$  and  $\ell = (\ell_N + \ell_S)/2$ . Figure 1 is for the case of a 1 ppb north-south difference in  $N_2O$  mixing ratio and Figure 2 applies for a 0.75 ppb difference. For clarity of presentation, only the cases  $\tau_e = 1.0$  year are shown in these figures. Compared to the respective solid curves for  $\tau_e = 1.0$  year in Figures 1 and 2 which are for  $\ell_N = \ell_S$ , the  $R$  values for  $\ell_N = 1.6\ell_S$  are more than 50% higher. This should not be surprising; to maintain the same concentration gradient across the equator requires a higher ratio of northern hemispheric to southern hemispheric sources when there are larger sinks in the NH than the SH.

#### 4. CONCLUSION

I have solved simplified equations for mass conservation of atmospheric  $N_2O$  subject to the constraints of measured temporal increases and cross-equator differences, for a range of other related parameters including the time required for interhemispheric exchange, stratospheric destruction rates, the rates of consumption of atmospheric  $N_2O$  by soils, and possible north-south differences in  $N_2O$  loss rates. A two-box model was used; the total  $N_2O$  sources for each hemisphere, northern and southern were computed. For all choices of parameters, NH sources dominate:  $\Phi_N/\Phi_S$  lies between 1.4 and 5.2 for an  $N_2O$  concentration that is 1 ppb higher in the NH than in the SH (see Table 1), and between 1.3 and 3.5 for an  $N_2O$  concentration that is 0.75 ppb higher in the NH than in the SH (see Table 2). The most likely values are about 2.0 and 1.6 for the 1 ppb difference and the 0.75 ppb difference, respectively; these  $R$  values obtain when  $\tau_e = 1$  year,  $1/\ell = 130$  years,  $\ell_N = \ell_S$  and when no soil sinks are hypothesized. These values rise to 3.0 and 2.4, respectively, for the same two cases but with  $\ell_N = 1.6\ell_S$ . Butler *et al.* [1989] have calculated that SH sources contribute 33% to 38% of the total global source if the north-south concentration difference  $d$  is 1.1 ppb for  $\tau_R$  values of 150 and 100 years, respectively, and 42% to 44% if  $-d = 0.5$  ppb. They adopted a single value for  $\tau_e$ , 1.1 years, no differences between hemispheres for stratospheric removal, and zero soil sinks.

When an hypothesized soil sink is introduced,  $\Phi_N/\Phi_S$  ratios increase somewhat, and atmospheric residence times for  $N_2O$  become shorter. Soil sinks of the type assumed here could reduce  $\tau_R$  by as much as 20% from the value with only stratospheric destruction.

The present approach illustrates how the conclusions depend on several parameters, and how two processes, faster  $N_2O$  loss to the NH stratosphere and assumed soil sink activity, each increase calculated  $R$  values, but it cannot resolve spatial differences within hemispheres without adding more boxes or temporal variations on seasonal (or shorter) time scales. More sophisticated analyses are needed with larger data sets. For example, Prinn and colleagues are introducing a multibox approach that deduces large tropical sources of  $N_2O$  [Prinn *et al.*, Atmospheric trends and emissions of nitrous oxide deduced from ten years of ALE-GAGE data, submitted to Journal of Geophysical Research, 1989], which if correct is an important finding. To reach such conclusions will require accurate differences between  $N_2O$  concentrations

at different latitudes; the present calculations are sensitive only to hemispheric differences. In deducing concentration gradients with latitude, seasonal cycles may have to be recognized [Khalil and Rasmussen, 1983]. Vertical gradients also contain information, even though they are known to be very small in the troposphere. Three-dimensional transport models such as those by Mahlman *et al.* [1986] will be increasingly valuable as the data base grows. As they studies progress, it may become clear that there was as much or more  $N_2O$  in the SH than the NH before there were significant anthropogenic sources, as Weiss [1981] suggested.

Stable isotopes of nitrogen ( $^{15}N$ ) and oxygen ( $^{17}O$  and  $^{18}O$ ), when measured in ratio to the major isotopes ( $^{14}N$  and  $^{16}O$ ), could provide good indicators of which  $N_2O$  sources are dominant, as well as evidence of soil uptake. Such studies should be undertaken.

Field studies to quantify the sizes of soil sinks for atmospheric  $N_2O$  are certainly needed, but they are difficult. First, small concentration changes must be measured. For a typical closed chamber (volume = 7  $\ell$ , height = 9 cm), a flux to the soil of  $3 \times 10^8/cm^2$  s will decrease the  $N_2O$  concentration by only 3 ppb after 30 min. Another particular problem is that leaks can mask  $N_2O$  losses to soils in closed-chamber experiments. When ambient air (with  $N_2O$  present at 305 to 310 ppb) enters a typical closed chamber at a rate of  $3 cm^3/s$  an  $N_2O$  loss of the order of  $3 \times 10^8/cm^2$  s can be masked. The removal of, say, 50  $cm^3$  of air from such chambers in syringe sampling also forces external air into the chamber but is less of a problem. It is possible that in some field experiments to date, when  $N_2O$  sources near zero were reported, small sinks may have been operating in reality.

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