A reassessment of the global isotopic budget of atmospheric nitrous oxide

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Abstract. A simple box model is developed which accounts for the natural and anthropogenic sources and sinks of tropospheric nitrous oxide. Stable isotopic terms are included as well to investigate what additional insight they might provide concerning the overall picture of the global nitrous oxide budget. It is seen that fractionation associated with ultraviolet photolysis in the stratosphere plays a key role in balancing the isotopic budget. It is also noted that increased production due to human influence should have a unique isotopic signature which should provide observable differences between preindustrial air trapped in polar firm or ice and modern air. This build-up of isotopically light, anthropogenic nitrous oxide can be thought of as an N\textsubscript{2}O "Suess effect" and should be observable in time series measurements of clean baseline atmospheric samples. High-precision records of such changes could lead to a better estimate of the preindustrial N\textsubscript{2}O isotopic signature as well as provide insight into the pathways of the anthropogenic sources.

1. Introduction

Recent theoretical and experimental results have provided enough new information on the stable isotopic signature of nitrous oxide to warrant a reexamination of the global isotopic budget. Measurement of \textsuperscript{15}N and \textsuperscript{18}O depletion in N\textsubscript{2}O emitted from terrestrial sources [Casciotti et al., 1997; Pérez et al., this issue] have extended the range of values observed by Kim and Craig [1993]. New measurements in ocean surface waters [Yoshinari et al., 1997; Dore et al., 1998] fall within the range of the general trends observed by Kim and Craig [1990] in the Pacific Ocean although some variation is observed in the Arabian Sea [Yoshinari et al., 1997; Naqvi et al., 1998]. In addition, trends in the relationship between concentration and the isotopic signature of N\textsubscript{2}O in the stratosphere have resulted in the determination of fractionation factors for both \textsuperscript{15}N and \textsuperscript{18}O during stratospheric loss processes [Rahn and Wahlen, 1997]. The source of these enrichments has been qualitatively explained by Yung and Miller [1997] as being attributable to zero point energy differences between the various isotopic species which result in a wavelength dependence of the fractionation factors. Wavelength dependent fractionation has recently been verified in the laboratory [Rahn et al., 1998], although the magnitude is approximately double that predicted by Yung and Miller [1997]. A simple box model is here developed which includes these recent findings and can be used to investigate this effect on the global isotopic budget of N\textsubscript{2}O.

2. Model

A simple one-box model of the atmosphere is adopted to represent the various components of the nitrous oxide cycle as it is currently understood. The change in concentration with respect to time is defined as

\[
\frac{dC}{dt} = \frac{\sum m_i^*}{N} \frac{C}{\tau}
\]

where C is the column integrated atmospheric N\textsubscript{2}O concentration, the \(m_i\) terms are the various annual molar source terms, \(N\) is the molar volume of the atmosphere, and \(\tau\) is the atmospheric lifetime with respect to stratospheric destruction. Letting (1) approximate the concentration of the abundant isotopic species and letting the asterisk represent isotopic substitution, (1) can be written for the less abundant isotopic species as

\[
\frac{dC^*}{dt} = \frac{\sum m_i^*}{N} \frac{C^*}{\tau}
\]

which can be rewritten in terms of the heavy to light isotope ratios, \(R\), as

\[
\frac{dC^*}{dt} = \frac{\sum R_i m_i^*}{N} \frac{\alpha^*_t RC}{\tau}
\]

where \(\alpha^*_t\) is the ratio of the heavy to light time constants with respect to stratospheric destruction. For simplicity, the source terms are restricted to the major natural terrestrial and oceanic sources, \(m_{\text{nat}}\) and \(m_{\text{act}}\), and the total anthropogenic source, \(m_{\text{an}}\).

Model constraints are applied sequentially in order of decreasing confidence. The increase of nitrous oxide in the atmosphere is tightly constrained by modern time series measurements of concentration [e.g., Weiss, 1981; Rasmussen and Kahlil, 1986; Prinn et al., 1990; Butler et al., 1998] with a
January 1998 global average of 313±1 ppb (R. Weiss, personal communication, 1999). Preindustrial and early twentieth century concentrations are known, with less precision, from measurements of N₂O in polar ice and firm [Pearman et al., 1986; Kahlil and Rasmussen, 1988; Etheridge et al., 1988; Zardini et al., 1989; Leuenberger and Siegenthaler, 1992; Machida et al., 1995; Battle et al., 1996]. The Intergovernmental Panel on Climate Change (hereafter IPCC95) [Houghton et al., 1995], in assessing this information, recommends a preindustrial concentration of 275 ppb with an estimated error of +5 to -15 ppb. The model is also constrained by independent estimates of the atmospheric lifetime which range from 110 to 166 years [e.g., Prinn et al., 1990; Kahlil and Rasmussen, 1992; Minschwaner et al., 1993] with an IPCC95 recommended lifetime of 120 ± 30 years.

Assuming IPCC95 values for lifetime and preindustrial concentration requires a preindustrial N₂O source of approximately 11.0 Mt N yr⁻¹ which falls within their estimated range of 6-12 Mt N yr⁻¹. The natural source term is then separated into its oceanic and terrestrial components in the same proportions as IPCC95, 67% or 7.3 Mt N yr⁻¹ for terrestrial sources and 33% or 3.7 Mt N yr⁻¹ for the oceanic source. These flux terms are also well within the range of values estimated by the IPCC95 for the individual sources. It is assumed that the preindustrial source is entirely natural and that the strength of this source has remained unchanged until present. The annual anthropogenic source is fit to an exponential growth function

\[ m_{an} = m_r e^{g(t-t_0)} \]

with \( m_r \), the anthropogenic source strength at time \( t_0 \), and \( g \) the exponential rate of increase. The anthropogenic growth terms, \( m_r \) and \( g \), are then iteratively adjusted until the increase in tropospheric concentration is in reasonable agreement with observations.

The fractionation factors for the loss processes, \( \alpha_{N} = 0.9855 \) and \( \alpha_{O} = 0.9871 \), are taken from the relationships derived by Rahn and Wahlen [1997] from N₂O samples collected in the lower stratosphere. It should be pointed out that these fractionation factors are observed fractionation factors.

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**Figure 1.** A plot of \( \delta^{15}N \) versus \( \delta^{18}O \) with highlighted fields representing the range of data found in surface oceans (gray field) and terrestrial systems (textured field). Symbols representing the work of various authors are defined in the legend. The oceanic results shown from Kim and Craig [1990] are the measured values in the top 1000 m of the subtropical Pacific Ocean. The symbols representing Yoshinari et al. [1997] are the near surface averages of their data from the Indian Ocean and Arabian Sea. Also from the Arabian Sea is the near surface average of Naqvi et al. [1998]. The subtropical North Pacific end member value proposed by Dore et al. [1998] is also shown. In the terrestrial field, the open circles associated with the data of Pérez et al. [this issue] and Casciotti et al. [1997] are proportional to the relative magnitude of the flux for each of the points. Terrestrial data of Kim and Craig [1993] have no concurrent flux results. The open square is the commonly reported average value of tropospheric N₂O. The \( \delta^{15}N \) and \( \delta^{18}O \) values are referenced to atmospheric N₂ and O₂, respectively.
Figure 2. Evolution of the modeled tropospheric N₂O concentration overlying data from south polar ice (open triangles) [Machida et al., 1995] (adjusted as per Battle et al., [1996]); and south polar firn (open circles) [Battle et al., 1996]. Modern south polar air measurements [Butler et al., 1998] show good agreement with firn results but are omitted for clarity. Modeled increase defined by the black line is described in the text.

3. Results

The evolution of the modeled tropospheric concentration is shown in Figure 2 with data from polar ice [Machida et al., 1995], polar firn [Battle et al., 1996], and polar air [Butler et al., 1998] plotted for reference. Although a case can be made for a more stepwise increase in concentration due to climatic perturbations and human influenced changes in combustion rates and fertilizer production rates, etc., an exponential rise rate of 2.5% per year fits observations quite well and serves the purpose of this exercise.

Rather than imposing the requirement that vectors from within each source field of Figure 1 pass through the tropospheric average, the model requires only that the flux from each source be represented by a single dual-isotope value. Assuming an initial value for the oceanic source as described above, a solution for the terrestrial source which falls within the bounds of the observed terrestrial field (Figure 1) should be considered valid. Ideally, this value would be the flux-weighted average of some infinite number of measurements from all terrestrial N₂O emitting environments.

To determine if a balance of the tropospheric isotopic signature can be achieved with reasonable assumptions about the various source terms, we examine two scenarios. In the first case, we assume an isotopically depleted ocean with values of δ¹⁵N = 5%o and δ¹⁸O = 15%o as proposed by Kim and Craig [1993] in an early attempt to examine the global N₂O isotopic budget. These values are near the low end of the values observed in open ocean surface waters [Kim and Craig, 1990; Yoshinari et al., 1997] and agree well with the end-member value proposed by Dore et al. [1998]. In Figure 3 we see that the isotopic signature of the natural and anthropogenic terrestrial sources falls well within the range of observed values and very near the flux weighted average of the data from Pérez et al. [this issue] and Casciotti [1997]. (The data of Kim and Craig [1993] are not included in this average as there are no concurrent flux values reported with these measurements.) The time evolution of this system is also shown graphically in Figure 4. We note that the isotopic difference which include the combined effects of photolysis, photoxidation, and mixing. The implications of this distinction are discussed in Section 4.

The isotopic signature of the various sources are defined as follows: observations of δ¹⁵N and δ¹⁸O in surface oceans [Kim and Craig, 1990; Yoshinari et al., 1997; Naqvi et al., 1998; Dore et al., 1998] are less variable than from terrestrial sources (Figure 1), so the model is initiated with an assumed value for the oceanic source, and we then solve for the isotopic signature of the terrestrial component. The anthropogenic source is divided into separate terrestrial and industrial terms weighted as being 75 and 25% of the total anthropogenic flux in accordance with IPCC95 estimates. The anthropogenic terrestrial contribution is assumed to have an isotopic signature equal to that of the natural terrestrial component. Isotopic data for N₂O produced during industrial processes is wanting; however, Thiemens and Trogler [1991] present evidence that adipic acid production yields N₂O slightly depleted or equal to ¹⁸O of atmospheric O₂. We also note that ¹⁵N in coal ranges from -2.5 to 6.3%o, relative to and roughly in the range of atmospheric N₂ [Rigby and Batts, 1986; and references therein]. We therefore assume the industrial source to have isotopic values equal to atmospheric N₂ and O₂ and test for sensitivity to this assumption below. Solutions for the isotopic signature of the anthropogenic and terrestrial sources are found by forcing the 1983 tropospheric values through the often reported values of δ¹⁵N = 7.0%o and δ¹⁸O = 20.7%o from Kim and Craig [1990].
Figure 3. Model solutions for $\delta^{15}N$ and $\delta^{18}O$ overlain on the fields outlining the observed values in Figure 1. The filled circle in the surface ocean field represents the depleted ocean scenario, and the corresponding filled diamond in the terrestrial field represents the solution for that scenario. Likewise, the white circle and diamond represent the enriched ocean scenario and corresponding solution. The open circle in the terrestrial field is the flux weighted average of the data from Pérez et al. [this issue] and Casciotti et al. [1997], and the open square is again the tropospheric average.

between the preindustrial and modern troposphere is computed to be $-1.6\%o$ for $\delta^{15}N$ and $-1.8\%o$ for $\delta^{18}O$.

In the second case we assume an isotopically enriched oceanic source and assign oceanic isotope values of $10\%o$ for $\delta^{15}N$ and $30\%o$ for $\delta^{18}O$, equal to values near the high end of the near surface water values shown in Figure 1. In this case, we see in Figure 3 that the required balance from terrestrial and anthropogenic sources still falls within the range of the observed values for $\delta^{15}N$ and $\delta^{18}O$ values. The time evolution for this scenario is also shown in Figure 4 and indicates that the difference between preindustrial and modern values is now $-1.9\%o$ for $\delta^{15}N$ and $-2.4\%o$ for $\delta^{18}O$.

4. Discussion

The model described herein is a simple mass balance model constructed to demonstrate that the global isotopic budget of $N_2O$ can be readily accounted for within the framework of the IPCC95 recommended budget. The model differs from previous attempts to construct a global isotopic balance [Kim and Craig, 1993; Naqvi et al., 1998] in that it does not define the terrestrial isotopic signature at the outset, a source which the literature shows to have extreme variation (Figure 1), but rather solves for the isotopic signature of the terrestrial source to determine if there are acceptable solutions. Furthermore, loss processes are accounted for by incorporating the atmospheric lifetime and the observed stratospheric fractionation factor: no assumptions are required for magnitude of cross tropopause mass flux or average stratospheric isotopic values. While more thorough models incorporating the individual fractionation factors for nitrification/denitrification sources, the inorganic substrate isotopic composition, cross tropopause mass transport, etc., can be employed, the information required to complete such analyses is not available at this time. Furthermore, a more complicated model containing additional input parameters requires more assumptions which may mask real deviations from acceptable solutions.

The temporal isotope trends in the model solutions are not an unprecedented phenomena and can be thought of as analogous to the Suess effect which has been observed in measurements of $\delta^{13}C$ and $\Delta^{14}C$ of atmospheric CO$_2$. A temporal decrease of the order of $-0.02\%o$ per year in the observed value of $\delta^{13}CO_2$ in the troposphere results from the release during combustion of isotopically light organic material. In the case of nitrous oxide, the effect is the result of the increase in the isotopically light terrestrial component brought on by fertilization and agricultural processes. The model predicted trend for present day $\delta^{15}N$ in both scenarios is $-0.03\%o$. 
which is of the order of the current 813CO2 trend. We recall that the assumption has been made that the isotopic signature of the industrial contribution to the anthropogenic source is equal to that of atmospheric N2 and O2. If we test for sensitivity by allowing the industrial contribution of 15N to vary from $-10$ to $+10\%$, the temporal gradient shifts to $0.04\%$ per year and $0.02\%$ per year respectively with similar differentials for 18O. Anecdotal evidence suggests that increased atmospheric deposition of inorganic nitrogen in terrestrial systems has been accompanied by a decrease in the 15N:14N ratio taken up by plants [Högberg, 1991; Högberg et al., 1992; Poulson et al., 1995]. If such a trend does indeed exist, it would also serve to increase the gradient proposed here for the N2O isotopic trend.

In this model we have used the lower stratosphere data of Rahn and Wahlen [1997] to represent the isotopic fractionation incurred during stratospheric loss processes. These, however, are the observed fractionation factors which are the combined result of stratospheric destruction as well as intratraspheric and cross-tropopause mixing. More realistically, the model should be constrained by effective fractionation factors which account solely for isotopic selectivity determined by loss processes. Effective fractionation factors can be reduced by a factor of 2 in a purely eddy-diffusive regime [Eriksson, 1965; Rahn and Wahlen, 1998]. Injection of unmodified tropospheric air by midlatitude cross-tropopause transport could also serve to alter the isotopic content of stratospheric N2O. In either case, the mixing would serve to dilute the fractionation imparted by the loss processes. The extent to which the observed fractionation factors represent the effective fractionation factors could potentially have a significant influence on model results. It may also prove to be a very useful tracer of midlatitude cross-tropopause transport and/or intratraspheric mixing. Determining the agreement between these two parameters will require more detailed laboratory analyses of the loss processes as well as a significant modeling effort.

The capacity of the ocean to act as a buffer and to smooth out temporal trends in the tropospheric isotopic signature of N2O must also be considered. Nitrous oxide dissolved in the ocean mixed layer exchanges with the atmosphere on a timescale of $-3$ weeks [Nevison et al., 1995]. This rapid turnover effectively increases the size of the troposphere by the depth of the mixed layer, or by $-1\%$. Associated with this exchange will be an equilibrium fractionation which has been measured by Inoue and Mook [1994] to be about $-0.7\%$ and $-1.1\%$ for 15N and 18O, respectively, the heavy isotopes being preferentially taken up in solution. The total ocean N2O inventory is estimated to be $-2/3$ of the atmospheric inventory [Houghton et al., 1991]. If we assume the annual average global mixed layer to have a depth of 200 m then at most, 6% of the occe-

### Table 1. The $\delta^{15}N$ and $\delta^{18}O$ in Tropospheric N2O

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sampling date</th>
<th>Number of Samples</th>
<th>$\delta^{15}N$</th>
<th>$\delta^{18}O$</th>
<th>Sampling Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moore [1974]</td>
<td>prior to 1974</td>
<td>26</td>
<td>5.2±2.0</td>
<td>NM</td>
<td>continental</td>
</tr>
<tr>
<td>Yoshida and Matsuo [1983]</td>
<td>Oct. 1979 to Jan. 1980</td>
<td>12</td>
<td>8.8±0.9</td>
<td>NM</td>
<td>urban</td>
</tr>
<tr>
<td>Yoshida and Matsuo [1983]</td>
<td>July 1981</td>
<td>17</td>
<td>7.9±0.7</td>
<td>NM</td>
<td>coastal</td>
</tr>
<tr>
<td>Yoshida and Matsuo [1983]</td>
<td>Feb. 1982</td>
<td>8</td>
<td>7.2±0.5</td>
<td>NM</td>
<td>marine</td>
</tr>
<tr>
<td>Yoshida et al. [1984]</td>
<td>Nov. 1982 to Jan. 1983</td>
<td>16</td>
<td>7.2±1.1</td>
<td>NM</td>
<td>marine</td>
</tr>
<tr>
<td>Kim and Craig [1990]</td>
<td>April 1983 to Aug. 1985</td>
<td>5</td>
<td>7±1.1</td>
<td>20.7±0.7</td>
<td>marine</td>
</tr>
<tr>
<td>Cliff and Thiemens [1997]</td>
<td>Sept. 1994 to March 1995</td>
<td>13</td>
<td></td>
<td>18.4±0.7</td>
<td>continental</td>
</tr>
<tr>
<td>Cliff and Thiemens [1997]</td>
<td>Sept. 1995</td>
<td>5</td>
<td></td>
<td>16.8±0.6</td>
<td>urban</td>
</tr>
<tr>
<td>Cliff and Thiemens [1997]</td>
<td>Aug. 1996</td>
<td>8</td>
<td></td>
<td>18.9±0.5</td>
<td>continental</td>
</tr>
<tr>
<td>Dore et al. [1998]</td>
<td>1996</td>
<td>NA</td>
<td></td>
<td>7.3 †</td>
<td>20.3 †</td>
</tr>
<tr>
<td>Pérez et al. [this issue]</td>
<td>1995-1998</td>
<td>4</td>
<td>6.3±1.3</td>
<td>21±0.7</td>
<td>continental</td>
</tr>
</tbody>
</table>

*Here NA, sample number not available; NM, not measured.

† $\delta^{15}N$ and $\delta^{18}O$ reported relative to atmospheric N2 and O2, respectively, in units of per mil

† values estimated from original plot
5. Conclusion

The model presented herein serves to demonstrate that the stable isotopic budget of nitrous oxide can easily be accounted for within the constraints of the IPCC95 recommended budget. In all cases, the fractionation associated with destruction in the stratosphere plays a key role in the isotopic balance. While we cannot preclude the existence of novel new sources and sinks, we maintain that the data thus far collected for $\delta^{15}N$ and $\delta^{18}O$ do not require alteration of our current understanding of the $N_2O$ budget. We also suggest that there may exist a temporal trend in the isotopic signature which is due to increased emission of isotopically light $N_2O$ associated with agricultural processes. Current analytical precision (≥0.1%) would require systematic observations for several years to detect the trends proposed here, but efforts are currently underway to improve precision and may prove fruitful in the near future. Changes in the balance between oceanic and soil sources during glacial and interglacial periods may result in similar shifts which should be observable in air trapped in polar ice cores. For instance, in glacial times sequestration of $^{18}O$ in polar ice caps would lead to the expectation that the oceanic $N_2O$ source would become increasingly enriched in $^{18}O$ and that precipitation available for reaction in an enriched source. Such predictions must of course be tempered by the realization that atmospheric and source environment temperatures can have profound effects on production rates as well as fractionation factors. Detection and analysis...
of such trends will be challenging but should eventually prove useful in our efforts to unravel the details of the nitrous oxide budget.

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References


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