Modeling the Seasonal cycle of N$_2$O

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Abstract

[1] In this paper, we have found the seasonal cycle in the sources of nitrous oxide (N₂O) by comparing N₂O output from the Califormia Institute of Technology - Jet Propulsion Laboratory two dimensional (2-D) model with the observations. In order to confirm the seasonal signal in the observations, we applied the multitaper method for spectrum analysis. Then, we chose the data, which are over 99 % significance to compare with the Caltech/JPL 2-D model. We adjusted the boundary condition of the 2-D model to represent the seasonal cycle of the surface N₂O sources, biomass burning, soil and ocean. The model has similar features as the observations. There is a seasonal cycle for the ocean in the Southern Hemisphere. In the tropic region, there is a seasonal cycle similar to that from biomass burning of CH₄. However, the distance between the two peaks in the seasonal cycle of biomass burning of CH₄ should be lengthened, such that one is in January and one is in December instead of in the February and September.
1. Introduction

[2] The sources of nitrous oxide (N$_2$O) are from the microbes in nitrification and denitrification processes as well as the anthropogenic activities. As the nitrogen cycle has been perturbed by human activities, the concentration of N$_2$O in the terrestrial atmosphere is increasing since the industrial revolution and has a value of 320 ppbv (nmol/mol).

[3] The sink of N$_2$O is mainly from the UV photolysis in the stratosphere

\[ \text{N}_2\text{O} + \text{h}_\nu \rightarrow \text{N}_2 + \text{O}(^1\text{D}) \] (1)

A smaller loss occurs from the (photo-oxidation) reaction with O($^1\text{D}$)

\[ \text{N}_2\text{O} + \text{h}_\nu \rightarrow 2\text{NO} \] (2a)

\[ \rightarrow \text{N}_2 + \text{O}_2 \] (2b)

[4] The seasonal cycle of N$_2$O in the stratosphere is possibly due to the Brewer-Dobson circulation. The seasonal cycle in the stratosphere is different from the one in the troposphere, because the seasonal cycle in the troposphere is due to the mixing in the spring of N$_2$O-poor stratospheric air with N$_2$O-rich tropospheric air.

[5] Besides the seasonal cycle from dynamical transport in the atmosphere, there are seasonal cycles from the sources of N$_2$O at the surface. However, there is still considerable uncertainty in the magnitude, distribution and relative importance of the various surface sources, both natural and anthropogenic, of N$_2$O [Bouwman et al, 1995]. Studying the seasonal cycle of the trace species, we can get the information of its sources, sinks, and transport process in the atmosphere.

[6] In this paper, we will investigate the seasonal cycle in the sources by comparing the seasonal cycles of the N$_2$O between 2-D model simulation and the observations.
2. Data and Analysis

2.1 Observation data

[7] We obtained the N2O observation data by four different programs: National Oceanic and Atmospheric Administration - Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) Global Cooperative Air Sampling Network (GCASN), NOAA-CMDL Chromatograph for Atmosphere Trace Species (CATS), NOAA-CMDL Radiatively Important Trace Species (RITS), and the Advanced Global Atmospheric Gases Experiment (AGAGE) Global Trace Gas Monitoring Network. The GCASN data are divided into two separate data sets. The first set contains the data before 1996 and the second set contains the data after 1996. The RITS data are from 1988 to 1999 and the CATS data are from 2000 to 2004 [Elkins et al., 2002]. The AGAGE data are divided into three sets, which contains data from 1978 to 1986, from 1985 to 1996, and from 1996 to 2003 respectively. The locations of the stations in each program are shown in Table 1.

[8] We applied the multitaper (MTM) [Ghil et al., 2002] to investigate the existence of the seasonal cycle. MTM reduces the variance of spectral estimates by using a small set of tapers. It yields a better and more stable estimate than single-taper methods. The parameters of the MTM analysis must be chosen to give a good compromise between the required frequency resolution for resolving distinct signals and the benefit of reduced variance; we chose the resolution to be 2 and the number of tapers to be 3 [Ghil et al., 2002, Liao et al., 2004].

[9] There is a harmonic with a period of 12 months for some stations. Some are over the 99% significance level. Therefore they have a strong signal of the seasonal cycle. Although some stations do not have the harmonics with a period of 12 months, the seasonal cycle of South Pole in CATS data is over 99% significance level. The data sets in the four programs are summarized in the Table 2. We want to use the seasonal cycle in the observations to compare with the seasonal cycle from 2-D model. Therefore, we only need to consider the stations, which are over 99% statistical significance. Because there are a lot of missing data in RITS and GCASN pre1996, we will mainly focus on GCASN post1996, AGAGE 96-03, and CATS.

[10] We used the three data sets to calculate the seasonal cycle. First, we used a 4th order polynomial fitting to repair the missing data. We compared the difference between the 4th order polynomial and the 5th order polynomial, but there is no large difference, and we used the 4th...
order polynomial in all subsequent work [Liao. et al., 2004]. Second we detrended the data by the 4th order polynomial fitting, then we calculated the seasonal cycle

\[ S_i = \frac{\sum K_{in}}{n} \]  

(3)

\( S_i \) is the seasonal value, where \( i \) is the index for the month. \( K_{in} \) is the concentration of \( \text{N}_2\text{O} \) in each month, where \( n \) is the number for the month appearing in the data of one station. The standard errors of the means, \( \sigma \), for each of the 12 months were then determined by calculating the standard deviation of the seasonal values in each month. The procedure of data analysis is shown in Figure 1. The seasonal cycle of the observation data is shown in Figure 2.

2.2 Surface \( \text{N}_2\text{O} \) sources in 2-D model

[11] We then used the model to understand the \( \text{N}_2\text{O} \) sources, so we obtained the surface \( \text{N}_2\text{O} \) sources for driving the 2-D model from the Global Emission Inventory Activities (GEIA). The data are the total emission in one year. There are nine types of sources in the data. A latitude profile of the 9 sources is shown in Figure 3.

[12] The nine sources are: soil, animal excreta, post-forest clearing soil, ocean, industry, fossil fuel burning, biofuel burning, agriculture, biomass burning. The two main sources are soil and ocean, which have emissions of 7.5 and 3.6 Tg N in one year respectively. The \( \text{N}_2\text{O} \) emissions from ocean is mainly in the southern hemisphere (SH), while the emissions from soil is mainly in the tropic region.

[14] We converted the dimension of the data from the total emission (Ton N yr\(^{-1}\)) into the flux (molecues cm\(^{-2}\)s\(^{-1}\)), and got an average in the 12 months surface sources. Then we used the surface sources to drive the 2-D model and found that there is a seasonal cycle in the northern hemisphere (NH), however, there is no seasonal cycle in the tropic regions and the SH. It is because the seasonal cycle in the NH is related to the circulation in the stratosphere, so the 2-D model can produce a seasonal cycle in the NH with the averaged surface sources. However the seasonal cycle in the tropic regions and in the SH should be due to the seasonal cycle in the surface sources. Therefore, we made a seasonal surface sources for the 2-D model.
[15] We added a seasonal cycle to three sources: soil, biomass burning, and ocean. The emission of methane (CH₄) from biomass burning is similar to the emission of N₂O from biomass burning, and biomass burning is known as one of the seasonal sources of CH₄. Therefore, there should have a seasonal cycle in the biomass burning of N₂O. The precipitation induces the emission of N₂O in soil [Jaegle et al., 2004], so the seasonal cycle of N₂O from soil should relate to the seasonal cycle from precipitation. N₂O Emission from biomass burning and soil are mainly in the tropic area. It is observed that the seasonal cycle of N₂O in the SH should be related to the seasonal cycle of emission of N₂O in ocean [Nevison, 2005].

[16] We used the seasonal cycle of biomass burning in CH₄, which is shown in Figure 4a. The seasonal cycle is obtained by averaging the seasonal cycle between the latitude 20°N and 20°S, then the seasonal cycle is interpolated between the minimum and the second peak, and the first peak and the minimum are shifted by one month backward. The corrected seasonal cycle is shown in Figure 4b. The N₂O seasonal cycle of ocean is obtained in Nevison’s paper [Nevison, 2005], which is shown in Figure 5a, and the maximum is shifted by one month backward. The corrected seasonal cycle of ocean is shown in figure 5b. For the precipitation, we obtained the seasonal cycle in the National Centers for Environmental Prediction (NCEP) precipitation data. The seasonal cycle in precipitation is similar to the modified seasonal cycle in biomass burning between 20°N and 20°S. Therefore, we added the seasonal cycle of biomass burning on the precipitation between 20°N and 20°S to amplify the signal in the tropic region. Finally, we redistributed the emission of N₂O in biomass burning by distributing the total amount of N₂O in biomass burning in the shape of seasonal cycle and latitude profile of biomass burning of CH₄. For soil source, we redistributed the total amount of N₂O in soil in the shape of seasonal cycle and latitude profile of precipitation. For the Ocean, we redistributed the ocean emission in three regions: using the seasonal cycle of ocean and the latitude profile of N₂O emission of ocean in the region below 20°S, using the seasonal cycle of biomass burning in CH₄ and the latitude profile of N₂O emission of ocean between 20°N and 20°S, and using an average value of N₂O emission over 20°N in the region over 20°N. It is because we want to see the seasonal signal in the tropic region and the southern hemisphere. The surface sources are made by adding the three seasonal sources with the other 6 averaging sources.
3. Results and Discussion

3.1 Observations

[16] For the observations, the result is shown in Figure 2 and Table 3 is a brief summary of Figure 2. In the NH, there are three stations. For the first two stations, Alert (ALT) and Barrow (BRW), they have positive values before June and in December, while others are the negative values. They have peaks before May with amplitude about 0.4 ppbv. They both have minima in September with amplitudes of -0.6 ppbv. However, ALT has the peak in February while BRW has the peak in April. The third station in the NH is Mace Head (MAH), it has positive values before May and after November, which a peak is in March with an amplitude of 0.2 ppbv. The minimum is in August with an amplitude of -0.4 ppbv. It shows that the peak shifts forward and the minimum shifts backward while decreasing the latitude in the NH. Also, the amplitude is reduced when latitude decreases.

[17] In the tropic region, there are two stations, Cape Kumukahi (KUM) and Cape Matatula (SMO). They both have positive values before April and after November. KUM has a peak in March with an amplitude of 0.25 ppbv, and a minimum in July with an amplitude of -0.3 ppbv. SMO has a peak in January with an amplitude of 0.3 ppbv. SMO has a region with low amplitudes from May to September with a mean of -0.15 ppbv. There are two minima at June and September with amplitudes of -0.2 ppbv. It shows that the peak before May shifts backward when latitude decreases.

[18] In the SH, there are two stations, Cape Grim (CGO) and South Pole (SPO). They both have positive values before February and after August. SPO has a peak in October with an amplitude of 0.2 ppbv and it has amplitudes about 0.05 ppbv before February. For SPO, April, May and June have similar amplitudes of -0.15 ppbv. SMO has a peak in December with an amplitude of 0.2 ppbv, while the minimum is in May with an amplitude of -0.2 ppbv.

[19] For the seasonal cycle from the observations, we found that the peaks around March shift forward and the minima shift backward when decreasing the latitude in the NH. Besides, the amplitudes also decrease when latitude decreases. In the tropic region, both the peaks and the minima shift backward when latitude decreases. In the SH, although January and February of the South Pole have positive values, they just have a magnitude about 0.05 ppbv. From the Figure 2f and 2g, we found that the troughs are wider in the SH.
3.2 model run

[20] The 2-D model output is shown in Figure 6. It is the model data at height equal to 1 kilometer, and we used the same method of real data to obtain the seasonal cycle. Seasonal cycle in some latitudes has been extracted to Figure 7 (dotted line) to compare with the observations. Table 4 is a brief summary of the model result. In the NH, The model result has similar features as the observations. The model has nearly the same place of peaks and minima in the observations. However, the model has a larger amplitude than the observations about 0.2 ppbv. Besides, at 82°N, the minima of model has a back shift of one month relative to the observations while the peak of model shifts forward for one month.

[21] In the tropic region, the model has similar amplitudes and features as the observations. However, at 19°N, the minimum of model shifts one month forward relative to the observations and the amplitude of the peak in the model is larger than the observations by 0.1 ppbv.

[22] In the SH, we extracted the seasonal cycle in two latitudes of the model result, 41°S and 90°S. At 41°S, the peak of the model shifts two months backward relative to the observations. There is a larger difference in amplitude between the model and the observations from November to December and from January to February. At 90°S, the model has similar amplitudes and features as the observations, however, the peak from the model shifts one month backward relative to the observations.

[23] For the NH, we simply input an average data to the 2-D model, so it may have difference between the observations and the model in the NH. In the tropic region, the seasonal cycle of the model data has similar amplitudes with that in the observations. However, the amplitude is weaker around December in the model data than the seasonal cycle of real data by about 0.1 ppbv.

[24] Except the NH, we found similar strength of the seasonal signal in the tropic region and the SH. The peak and minima of seasonal cycle from 2-D model match with the seasonal cycle in observation. However, in the region of November and December, the model gave a general smaller value.
4. Conclusion

[25] we have used the MTM spectrum analysis to find the significance of the seasonal cycle from the observations in NH, SH and tropic region. We then adjusted the surface sources from sources data. As a result, the 2-D model can simulate the main feature in the seasonal cycle in the observations. However, the simulated amplitude is somewhat larger in the NH, and smaller in the region of November and December in the SH. For the difference in the NH, It maybe due to some of the approximation in the Caltech/JPL 2-D model, there is no consideration in the dynamics in troposphere. Although the 2-D model is not one to one correspondence between the boundary condition and the data generated by model at surface. It has a strong relation between them. In order to be more consistent for the November and December of tropic region, we can try to decrease the slope of the seasonal cycle in tropic from October to December. Besides working on this forward method, we can try to do an inversion method on the real data in order to find out the distribution of sources initially.
References


Figure Captions
Figure 1: Results of AGAGE data at Mace Head (53°N, 10°W). (a) Raw data (Solid) and 4th order polynomial trend (Dotted). (b) Residue between the data and the polynomial fit. (c) Seasonal Cycle. (d) Estimate of the power spectrum by multitaper method. The dashed lines represent the median, 90%, 95%, 99% confidence of significant deviation above the mean from low level to high level respectively.

Figure 2: Results of AGAGE, CATS, GCASN. The solid line is the seasonal cycle. Shaded area represents the estimate error of the seasonal cycle. (a) GCASN, Alert in Alaska (82°N, 62°W) (b) CATS, Barrow (71°N, 157°W) (c) AGAGE, Mace Head (53°N, 10°W) (d) GCASN, Cape Kumukahi (19°N, 155°W) (e) AGAGE, Cape Matatula (14°S, 171°W) (f) AGAGE, Cape Grim (41°S, 145°E) (g) CATS, South Pole (90°S, 102°W)

Figure 3: N₂O (Ton Nyr⁻¹) for the nine sources from GEIA. (a) Soil (b) Animal excreta (c) Post-forest clearing soil (d) Ocean (e) Industry (f) Fossil fuel burning (g) Biofuel burning (h) Agriculture (i) Biomass burning.

Figure 4: The seasonal cycle of biomass burning of CH₄ obtained by averaging the seasonal cycle between 20°N to 20°S. (a) Seasonal cycle of biomass burning of CH₄ (b) The modified seasonal cycle of biomass burning from Figure 4a

Figure 5: The seasonal cycle of ocean obtained from Nevison’s paper. (a) Seasonal cycle of Ocean (b) The modified seasonal cycle of ocean from Figure 5a

Figure 6: The seasonal cycle of N₂O from the Caltech/JPL 2-D model at z=1km

Figure 7: Both the model result and the observations. The solid line is the seasonal cycle in the observations. The dotted line is the seasonal cycle from the model at the same latitude. Shaded area represents the estimate error of the seasonal cycle. (a) GCASN, Alert in Alaska (82°N, 62°W) (b) CATS, Barrow (71°N, 157°W) (c) AGAGE, Mace Head (53°N, 10°W) (d) GCASN, Cape Kumukahi (19°N, 155°W) (e) AGAGE, Cape Matatula (14°S, 171°W) (f) AGAGE, Cape Grim (41°S, 145°E) (g) CATS, South Pole (90°S, 102°W)
Table 1. The locations of stations in each programs

<table>
<thead>
<tr>
<th>Program (number of stations)</th>
<th>Stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCASN (8)</td>
<td>Alert (82°N, 62°W), Barrow (71°N,157°W), Niwot Ridge (40°N, 106°W),</td>
</tr>
<tr>
<td></td>
<td>Cape Kumukahi (19°N, 155°W), Mauna Loa (19°N,156°W),</td>
</tr>
<tr>
<td></td>
<td>Cape Matatula (14°S,171°W), Cape Grim (40°S, 145°E), South Pole (90°S,102°W)</td>
</tr>
<tr>
<td>CATS (5)</td>
<td>Barrow (71°N, 157°W), Niwot Ridge (40°N, 106°W), Mauna Loa (19°N, 156°W),</td>
</tr>
<tr>
<td></td>
<td>Cape Matatula (14°S,171°W), South Pole (90°S,102°W).</td>
</tr>
<tr>
<td>AGAGE (5)</td>
<td>Mace Head (53°N, 10°W), Trinidad Head (45°N, 124°W), Ragged point (13°N, 59°W),</td>
</tr>
<tr>
<td></td>
<td>Cape matatula (14°S,171°W), Cape Grim (41°S, 145°E).</td>
</tr>
<tr>
<td>RITS (5)</td>
<td>Barrow (71°N,157°W), Niwot Ridge (40°N,106°W), Mauna Loa (19°N, 156°W),</td>
</tr>
<tr>
<td></td>
<td>Cape Matatula (14°S,171°W), South Pole (90°S,102°W).</td>
</tr>
</tbody>
</table>

CATS data are obtained from (ftp://ftp.cmdl.noaa.gov/hats/n2o/insituGCs/CATS/ global/ insitu_global_N2O). GCASN data are available at (ftp://ftp.cmdl.noaa.gov/hats/n2o/flasks/).

Table 2. Conclusion of the MTM spectrum for the observation data sets

<table>
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<tr>
<th>Data</th>
<th>above 99%</th>
<th>below 99%</th>
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<tbody>
<tr>
<td>GCASN pre1996</td>
<td>82,71,19,-40</td>
<td>40,-14,-90</td>
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<tr>
<td>GCASN post1996</td>
<td>82,71,19(Cape Kumakahi)</td>
<td>40,19(Mauna Loa),-14,40,-90</td>
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<tr>
<td>AGAGE 78-86</td>
<td>none</td>
<td>53,45,13,-14,-41</td>
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<td>AGAGE 85-96</td>
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<td>53,45,13,-14,-41</td>
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<td>AGAGE 96-03</td>
<td>53,-14,-41</td>
<td>45,13</td>
</tr>
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<td>CATS</td>
<td>71,40,-90</td>
<td>19,-14</td>
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<td>RITS</td>
<td>71,40,-90</td>
<td>19,-14</td>
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</table>
Table 3. Conclusion of the observation data (refer to Figure 2)

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Positive months</th>
<th>Maximum point month (amplitude)</th>
<th>Minimum point month (amplitude)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82N (GCASN)</td>
<td>1 - 6, 12</td>
<td>Feb (0.4)</td>
<td>Sep (-0.6)</td>
</tr>
<tr>
<td>71N (CATS)</td>
<td>1 - 6, 12</td>
<td>Apr (0.4)</td>
<td>Sep (-0.6)</td>
</tr>
<tr>
<td>53N (AGAGE)</td>
<td>1 - 5, 11-12</td>
<td>Mar (0.2)</td>
<td>Aug (-0.4)</td>
</tr>
<tr>
<td>19N (GCASN)</td>
<td>1 - 4, 11 - 12</td>
<td>Mar (0.25)</td>
<td>Jul (-0.3)</td>
</tr>
<tr>
<td>14S (AGAGE)</td>
<td>1 - 4, 11 - 12</td>
<td>Jan (0.3)</td>
<td>Jun (-0.2), Sep (-0.2); May to Sep has low amplitude with mean -0.15</td>
</tr>
<tr>
<td>41S (AGAGE)</td>
<td>1 - 2, 8 - 12</td>
<td>Dec (0.2)</td>
<td>May (-0.2)</td>
</tr>
<tr>
<td>90S (CATS)</td>
<td>1 - 2, 8 - 12</td>
<td>Oct (0.2)</td>
<td>between Apr, May and Jun (-0.15)</td>
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</table>

Table 4. Conclusion of the Model data (refer to Figure 6)

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Positive months</th>
<th>Maximum point month (amplitude)</th>
<th>Minimum point month (amplitude)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82N</td>
<td>1 - 6</td>
<td>around Mar and Apr (0.65)</td>
<td>Aug (-0.75)</td>
</tr>
<tr>
<td>71N</td>
<td>1 - 6</td>
<td>Apr (0.66)</td>
<td>Aug (-0.73)</td>
</tr>
<tr>
<td>53N</td>
<td>1 - 6, 12</td>
<td>Apr (0.4),</td>
<td>Aug (-0.5)</td>
</tr>
<tr>
<td>19N</td>
<td>1 - 5, 12</td>
<td>Mar (0.3)</td>
<td>Aug (-0.3)</td>
</tr>
<tr>
<td>14S</td>
<td>1 - 4, 11 - 12</td>
<td>around Feb and Mar (0.28)</td>
<td>Jul (-0.23)</td>
</tr>
<tr>
<td>41S</td>
<td>1 - 2, 8 - 12</td>
<td>Sep (0.2)</td>
<td>May (-0.15)</td>
</tr>
<tr>
<td>90S</td>
<td>8 - 12</td>
<td>Sep (0.15)</td>
<td>between Apr to Jun around -0.1</td>
</tr>
</tbody>
</table>
Figure 3
Figure 6
Figure 7
Color Figure Caption

Figure 8: Plots of the N₂O seasonal surfaces sources a) sources from soil b) sources from ocean c) sources from biomass burning d) The sum of the three seasonal sources

Figure 9: Plots of the seasonal cycle varies with the altitudes at different latitudes
a) latitude from 80°S to 70°S b) latitude from 50°S to 40°S c) latitude from 20°S to 20°N d) latitude from 40°N to 50°N e) latitude from 70°N to 80°N

Figure 10: Contour plots of the seasonal cycle from the observations of three stations
a) CATS b) GCASN c) AGAGE

Figure 11: Contour plot of the seasonal cycle of the model result at z = 1km
Figure 8

(c)

(b)

(d)
Figure 9
Figure 10

a)

b)
Figure 11