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## Interannual variability in tropospheric nitrous oxide

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[1] Observations of tropospheric N<sub>2</sub>O mixing ratio show significant variability on interannual timescales (0.2 ppb, 1 standard deviation). We found that interannual variability in N<sub>2</sub>O is weakly correlated with that in CFC-12 and SF<sub>6</sub> for the northern extratropics and more strongly correlated for the southern extratropics, suggesting that interannual variability in all these species is influenced by large-scale atmospheric circulation changes and, for SF<sub>6</sub> in particular, interhemispheric transport. N<sub>2</sub>O interannual variability was not, however, correlated with polar lower stratospheric temperature, which is used as a proxy for stratosphere-to-troposphere transport in the extratropics. This suggests that stratosphere-to-troposphere transport is not a dominant factor in year-to-year variations in N<sub>2</sub>O growth rate. Instead, we found strong correlations of N<sub>2</sub>O interannual variability with the Multivariate ENSO Index. The climate variables, precipitation, soil moisture, and temperature were also found to be significantly correlated with N<sub>2</sub>O interannual variability, suggesting that climate-driven changes in soil N<sub>2</sub>O flux may be important for variations in N<sub>2</sub>O growth rate. **Citation:** Thompson, R. L., et al. (2013), Interannual variability in tropospheric nitrous oxide, *Geophys. Res. Lett.*, 40, 4426–4431, doi:10.1002/grl.50721.

### 1. Introduction

[2] Nitrous oxide (N<sub>2</sub>O) is now the third most important long-lived anthropogenic greenhouse gas. N<sub>2</sub>O is also an important ozone-depleting substance (ODS), as it reacts with O(<sup>1</sup>D) to produce NO in the stratosphere, and currently the ozone-depleting potential-weighted emissions of N<sub>2</sub>O are considered the largest of any ODS [Ravishankara et al.,

2009]. The atmospheric mixing ratio of N<sub>2</sub>O has been increasing strongly since the preindustrial era largely as the result of human activities, namely the increasing input of reactive nitrogen into ecosystems (predominantly by N fertilizer use), which accelerates denitrification rates and enhances N<sub>2</sub>O emissions from soils and coastal waters to the atmosphere [Syakila and Kroeze, 2011].

[3] Atmospheric observations of N<sub>2</sub>O began in the early 1970s and have revealed a steady quasi-linear increase in concentrations since then [Prinn et al., 1990]. Superimposed on this long-term trend are seasonal and interannual variations. The seasonal variability in N<sub>2</sub>O mixing ratio is determined by the combined effect of transport and surface fluxes. Of particular importance is stratosphere-to-troposphere transport (STT), which brings air with a low N<sub>2</sub>O mixing ratio from the stratosphere into the troposphere. STT has a maximum in spring in the Northern Hemisphere and is particularly important in defining the seasonal cycle in middle to high latitudes [Ishijima et al., 2010; Nevison et al., 2004; Nevison et al., 2007; Nevison et al., 2011]. The interannual variability in N<sub>2</sub>O mixing ratio has only been investigated in a few studies [Ishijima et al., 2009; Nevison et al., 2007; Nevison et al., 2011], which has partly been due to the limited availability of long-term measurements of N<sub>2</sub>O precise enough to be used for this purpose. In the late 1990s and early 2000s, measurements of N<sub>2</sub>O began at a number of new sites and provide measurements precise enough to be used for such a study. Previous investigations have pointed to an important role of STT in N<sub>2</sub>O interannual variability [Nevison et al., 2007; Nevison et al., 2011]. This is based on the observed correlation between anomalies in N<sub>2</sub>O minima at middle- to high-latitude sites and anomalies in polar lower stratospheric temperature (PLST), which is used as a proxy for the strength of the Brewer-Dobson circulation and STT [Huck et al., 2005; Waugh et al., 1999].

[4] Here we examine tropospheric N<sub>2</sub>O from 1996 to 2009 to better understand the importance of atmospheric transport and surface flux variability on N<sub>2</sub>O interannual variability. We exploit a data set encompassing 30 flask and 6 in situ sites (see Table S1 in the supporting information) and utilize observations of two other atmospheric trace gases, CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>) and SF<sub>6</sub>, which are useful tracers for atmospheric transport and have been previously used in investigating seasonal variability in N<sub>2</sub>O [Nevison et al., 2007].

### 2. Observations and Model

[5] Approximately weekly N<sub>2</sub>O measurements from discrete air samples (flasks) are used from the NOAA CCGG (Carbon Cycle Greenhouse Gases group) (E. Dlugokencky et al., in preparation, 2013) and the Commonwealth Scientific and Industrial Research Organisation (CSIRO)

Additional supporting information may be found in the online version of this article.

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[Francey *et al.*, 2003] global networks. In situ measurements are used from AGAGE (Advanced Global Atmospheric Gases Experiment) [Prinn *et al.*, 2000] and NIES (National Institute for Environmental Studies) sites [Tohjima *et al.*, 2000] (see Table S1 in the supporting information). For AGAGE sites, the data are available at 40 min intervals while for NIES sites, the data are available as daily averages. Flask and in situ measurements are made using gas chromatographs fitted with electron capture detectors (GC-ECD) and are reported as dry air mole fractions ( $\text{nmol mol}^{-1}$ , abbreviated ppb). NOAA and CSIRO data are reported on the NOAA-2006A scale [Hall *et al.*, 2007], while AGAGE and NIES data are reported on the SIO-1998 and NIES scales, respectively. AGAGE data were adjusted to the NOAA-2006A scale by comparing measurements at sites where AGAGE and NOAA operate in parallel, while NIES data were adjusted based on the results of intercomparisons of standards ( $\Delta\chi = 0.6$  ppb, Y. Tohjima, personal communication, 2012). There is some concern that there may be a calibration shift between CCGG  $\text{N}_2\text{O}$  data collected before and after 2001. For this reason, we run our analyses twice, first using all available sites and, second, using a subset of sites (“core” sites), which excludes CCGG sites and sites with large data gaps ( $>6$  months) (see Table S1). CFC-12 and  $\text{SF}_6$  measurements are from flasks in the NOAA HATS (Halocarbons and other Atmospheric Trace Species) network and in situ instruments in the AGAGE network. Both measurements are made using GC-ECD and presented as dry air mole fractions ( $\text{pmol mol}^{-1}$ , abbreviated ppt). CFC-12 measurements are reported monthly on the NOAA-2008 (HATS) and SIO-2005 (AGAGE) scales and  $\text{SF}_6$  measurements on the NOAA-2006 (HATS) and SIO-2005 (AGAGE) scales.

[6] Interannual variability (IAV) was calculated for  $\text{N}_2\text{O}$  at each site used in this study by first subtracting the multiannual trend, fitted as a second-order polynomial, and then applying a low-pass Butterworth filter (fourth order) to the residuals to filter seasonal and higher-frequency signals. Two passes of the filter (forward and reverse) were applied to correct for any phase distortion. This method was chosen preferentially over methods that involve fitting a seasonal cycle to the data (e.g., based on harmonic curves) since at many sites the seasonality has small amplitude and/or is irregular. Our definition of IAV is the component of the signal with periodicities longer than 12 months and is closely correlated with the growth rate. The Butterworth filter has been used previously to examine IAV in atmospheric species, e.g., in the studies of Ishijima *et al.* [2009] and Nakazawa *et al.* [1997]. Both methods, however, were tested and gave consistent results. The same method was applied to CFC-12 and  $\text{SF}_6$ , but for CFC-12 a third-order polynomial was used to fit the multiannual trend.

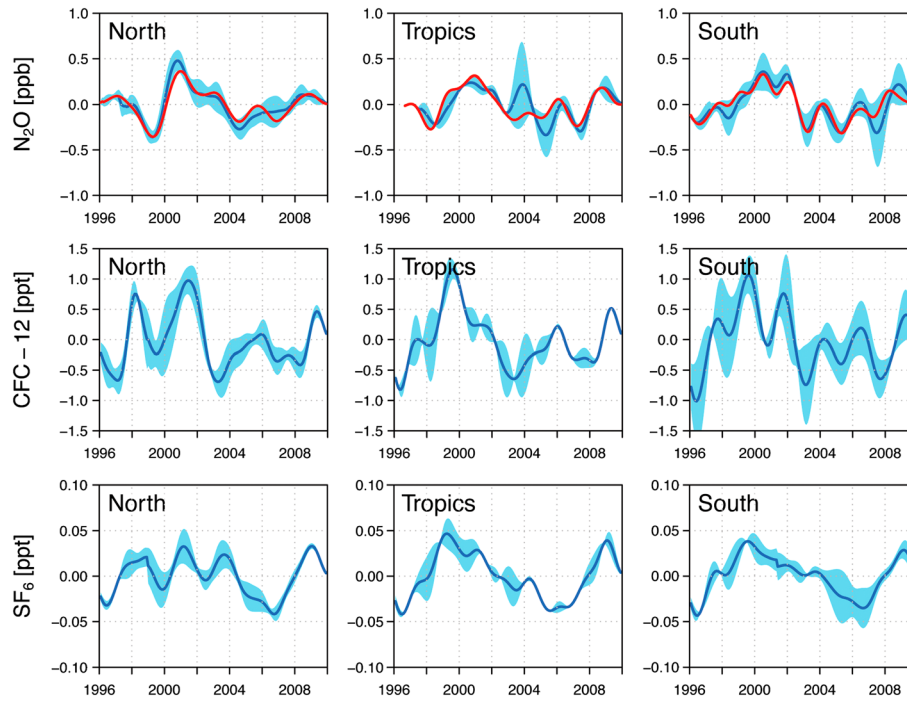
[7] Atmospheric simulations of  $\text{N}_2\text{O}$  were performed using the Laboratoire de Météorologie Dynamique general circulation model (LMDz, version 4) [Hourdin *et al.*, 2006], which includes  $\text{N}_2\text{O}$  photolysis and oxidation reactions in the stratosphere and has an  $\text{N}_2\text{O}$  lifetime of approximately 120 years which is within the range of recent estimates of  $131 \pm 10$  years [Prather *et al.*, 2012]. LMDz has a horizontal resolution of  $3.75^\circ$  longitude  $\times$   $2.5^\circ$  latitude and 19 hybrid pressure levels up to 3 hPa. Modeled transport was nudged to European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-40 wind fields at 6-hourly intervals. The model was run with climatological monthly

$\text{N}_2\text{O}$  emission estimates comprising natural and agricultural soil fluxes, ocean fluxes, as well as biomass burning and anthropogenic (nonagricultural) emissions (for details see the supporting information).

### 3. Results and Discussion

[8] IAV in  $\text{N}_2\text{O}$ , CFC-12, and  $\text{SF}_6$  is shown for the tropics and the northern and southern extratropics from 1996 to 2009 (Figure 1). The standard deviation of  $\text{N}_2\text{O}$  IAV is approximately 0.2 ppb and is significant compared to the variability across all sites used within each region (for details see Table S2).  $\text{N}_2\text{O}$  IAV is weakly correlated with CFC-12 IAV in the northern extratropics, more strongly correlated in the southern extratropics, and uncorrelated in the tropics (see Table 1). CFC-12, like  $\text{N}_2\text{O}$ , is only lost by photochemical reactions in the stratosphere and has a similar lifetime to  $\text{N}_2\text{O}$  (108 years [Rigby *et al.*, 2012]). This, and given that there is little seasonal and interannual variability in CFC-12 emissions, means that it is a pertinent tracer for the influence of STT. The fact that IAV in  $\text{N}_2\text{O}$  and CFC-12 is only weakly correlated in the northern extratropics suggests that STT is not the dominant factor in  $\text{N}_2\text{O}$  variability at these latitudes. IAV in  $\text{N}_2\text{O}$  and  $\text{SF}_6$  is also only weakly correlated in the northern extratropics but is more strongly correlated in the tropics and southern extratropics.  $\text{SF}_6$  is a very long-lived species (lifetime of 3200 years [Ravishankara *et al.*, 1993]) with no loss in the stratosphere, making variations in the tropospheric mixing ratio less sensitive to STT than, e.g.,  $\text{N}_2\text{O}$  or CFC-12. In addition, its emissions have little seasonal or interannual variability, making it a useful tracer for tropospheric transport. Emissions of  $\text{SF}_6$  are predominantly in the Northern Hemisphere and  $\text{SF}_6$  has a strong north-south concentration gradient. Therefore, the correlation of IAV in  $\text{N}_2\text{O}$  with that of  $\text{SF}_6$  in the southern extratropics likely results from variations in interhemispheric transport.

[9] Anomalies in  $\text{N}_2\text{O}$  seasonal minima at a number of middle- and high-latitude sites are correlated with anomalies in PLST (used as a proxy for STT) as shown by Nevison *et al.* [2011]. However, we also find substantial variability in the  $\text{N}_2\text{O}$  maxima, which is not correlated with variability in the  $\text{N}_2\text{O}$  minima and cannot be explained by STT alone. Comparing  $\text{N}_2\text{O}$  IAV (which is sensitive to anomalies in both the maxima and minima) in the northern (southern) extratropics with Arctic (Antarctic) PLST, we find no significant correlation (see Table S3). This indicates that STT alone cannot explain the observed IAV in  $\text{N}_2\text{O}$  in the middle to high latitudes. Another test for the influence of STT is to look at the magnitude of this effect. Following Nevison *et al.* [2007], we estimate the change in tropospheric  $\text{N}_2\text{O}$  mixing ratio from variations in STT on interannual timescales. Assuming annually balanced upward and downward air mass fluxes, a  $\text{N}_2\text{O}$  cross-tropopause gradient of 20 ppb, and a net global downward flux of between  $4 \times 10^9$  and  $11.6 \times 10^9 \text{ kg s}^{-1}$  (median of  $5.9 \times 10^9 \text{ kg s}^{-1}$ ,  $n=3$ ) [Gottelman *et al.*, 1997; Schoeberl, 2004] with a 20% interannual variation (this number is very uncertain [Schoeberl, 2004]) results in a range of  $0.5\text{--}1.4 \text{ yr}^{-1}$  interannual variation in the tropospheric mass of  $\text{N}_2\text{O}$ . This equates to  $0.11\text{--}0.32$  ppb IAV in the  $\text{N}_2\text{O}$  tropospheric mixing ratio, of which only the upper limit (i.e., 0.32 ppb) would have about the right magnitude to explain the observed IAV.



**Figure 1.** IAV of  $\text{N}_2\text{O}$ , CFC-12, and  $\text{SF}_6$  shown for northern (North) and southern (South) extratropical and tropical regions. The solid blue curve is the mean and the shaded blue area is the standard deviation of IAV calculated at all sites. For  $\text{N}_2\text{O}$ , the red line shows the mean value of IAV calculated using the core sites only (see also Table S1).

[10] Examining the latitudinal pattern of  $\text{N}_2\text{O}$  IAV, we find that there is a strong tropical and subtropical signal that is closely in phase across hemispheres and which is negatively correlated with the Multivariate ENSO Index (MEI) (<http://www.esrl.noaa.gov/psd/enso/mei/>) such that negative  $\text{N}_2\text{O}$  anomalies coincide with El Niño conditions (see Figure 2). A correlation of  $\text{N}_2\text{O}$  IAV with ENSO has been previously detected in long-term  $\text{N}_2\text{O}$  shipboard measurements in the northern and western Pacific [Ishijima *et al.*, 2009] and from in situ measurements at Samoa [Nevison *et al.*, 2007]. We find the strongest correlation with a lag time of between 7 and 9 months in the tropics ( $R = -0.61$ ) and southern extratropics ( $R = -0.59$ ), and between 9 and 11 months in the northern extratropics ( $R = -0.67$ , see Table 1). In the tropics, CFC-12 IAV (at Samoa) is also correlated with ENSO ( $R = -0.41$ ). Changes in interhemispheric transport, which is affected by ENSO-driven changes in circulation, has been suggested as a mechanism for this correlation and has been observed for other species at Samoa (e.g., methane and methylchloroform) [Hartley and Black, 1995; Prinn *et al.*, 1992]. For  $\text{N}_2\text{O}$  the IAV is closely in phase for both hemispheres; however, if changes in interhemispheric

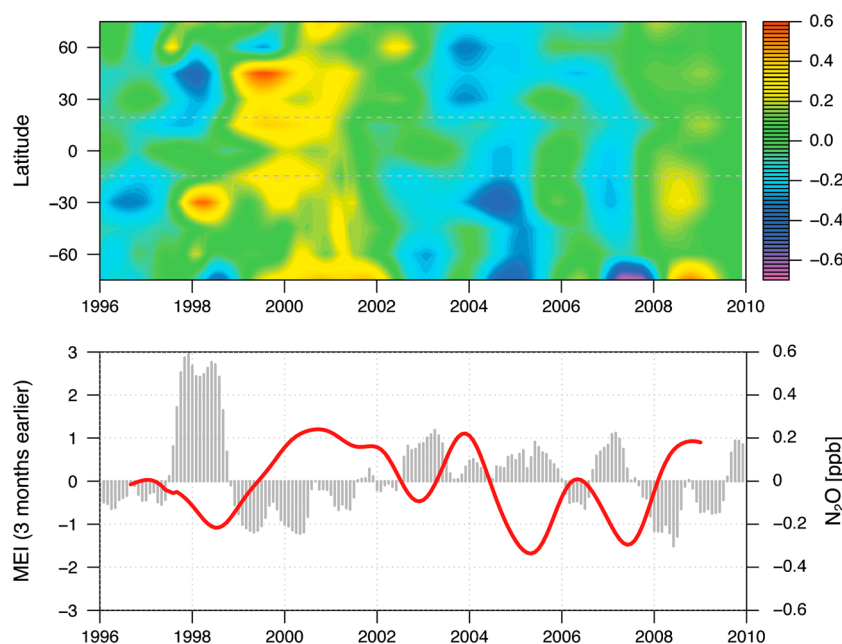
transport were mainly responsible for the IAV, then the signal in each hemisphere should be out of phase [Steele *et al.*, 1992]. Also, for species with strong biogenic sources, such as  $\text{N}_2\text{O}$ , this correlation may be partly due to variability in the emissions related to ENSO-driven climate changes. We examine the influence of tropospheric transport and emission variability on  $\text{N}_2\text{O}$  IAV in the following paragraphs.

[11] The transport influence on tropospheric  $\text{N}_2\text{O}$  variability was modeled using LMDz, and time series for each site were extracted from the 4-D simulated  $\text{N}_2\text{O}$  mixing ratios and analyzed in the same way as the observations (see section above). IAV at different sites were then averaged in five geographical regions (see Table S2). Our model (which does not account for IAV in  $\text{N}_2\text{O}$  emissions) captures about 40% of the observed variation in IAV in extratropical regions and none in the tropics (see Figure 3). Simulations using IAV in the emissions (not shown) did not perform better owing to large uncertainties in the emission variability. The model-observation difference for all regions may be partly due to model transport errors, but on the basis of comparisons with CFC-12, for which the agreement is much better ( $R = 0.57$  for the northern extratropics and  $R = 0.47$  for the

**Table 1.** Correlation of  $\text{N}_2\text{O}$  IAV With That of the Trace Gases, CFC-12 and  $\text{SF}_6$ , and With MEI<sup>a</sup>

Region	Correlation With Tracer Gases		Correlation With MEI	
	CFC-12	$\text{SF}_6$	Months of Highest Correlation	Correlation Coefficient
Northern extratropics	0.37	0.35	9–11	−0.67
Tropics	(0.25)	0.51	7–9	−0.61
Southern extratropics	0.68	0.67	7–9	−0.59

<sup>a</sup>All correlations were significant at the 0.05 level, except the correlation of  $\text{N}_2\text{O}$  with CFC-12 in the tropics, which is, therefore, shown in parentheses. The correlation with MEI is shown for the lag times (in months) that gave the highest correlation. The negative correlation means that El Niño events are correlated with negative  $\text{N}_2\text{O}$  anomalies.



**Figure 2.** (top) IAV of  $\text{N}_2\text{O}$  (ppb) interpolated with latitude and time. Data were calculated using a bivariate linear interpolation ( $15^\circ$  spatial and monthly temporal resolution) of the IAV calculated for each of the 36 sites. The dashed gray lines indicate the latitudinal extent of the stations used in the calculation of the tropical signal. (bottom) MEI shown at monthly resolution with a 3 month lag (gray bars) with the tropical  $\text{N}_2\text{O}$  IAV signal (red line).

tropics, see Table S4), this error is likely to be much less important than the influence of IAV in the emissions. The model-observation comparison suggests that the influence of tropospheric transport is important for  $\text{N}_2\text{O}$  IAV in the extratropics; however, it appears to be less important in the tropics.

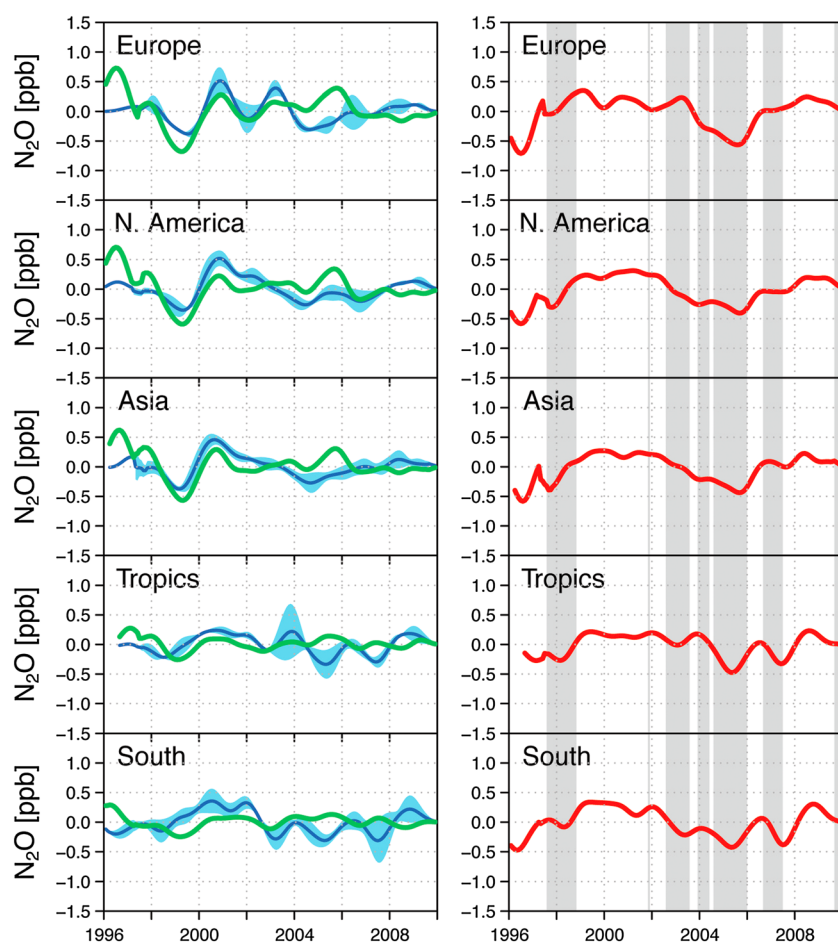
[12] Figure 3 shows the IAV in tropospheric  $\text{N}_2\text{O}$  mixing ratios attributed to changes in  $\text{N}_2\text{O}$  emissions (i.e., the observed IAV minus the simulated IAV due to the influence of transport). Denitrification (and to a lesser extent nitrification) in soils is the primary source of  $\text{N}_2\text{O}$ . These processes are known to be very sensitive to soil moisture and temperature, precipitation, soil type, soil pH, and nitrogen substrate availability [Davidson, 1993; Skiba and Smith, 2000; Smith *et al.*, 1998]. We performed an analysis of variance and a correlation analysis of  $\text{N}_2\text{O}$  IAV with the independent variables: soil moisture and temperature, and precipitation (ECMWF ERA-Interim, for details see supporting information), which vary substantially on annual timescales. ERA-Interim soil moisture has been previously evaluated against in situ data (correlation of 0.63 for 2008 to 2010) [Albergel *et al.*, 2012]. The analyses were performed on  $\text{N}_2\text{O}$  IAV data with and without the correction for the influence of transport. Due to potential errors in the modeled transport, we refer only to regions where both analyses gave consistent results (see Tables S5 and S6). For Europe, soil temperature and precipitation were positively correlated with  $\text{N}_2\text{O}$  IAV. With the correction for the influence of transport, soil moisture was also positively correlated, and the correlation coefficients increased for all variables. For the tropics, the correlation was calculated with the independent variables for South America, Africa, and Asia, separately. In contrast to Europe,  $\text{N}_2\text{O}$  IAV was negatively correlated with temperature, a result that is consistent with that of Ishijima *et al.* [2009] who found a negative correlation between  $\text{N}_2\text{O}$  IAV

and soil temperature in the Northern Hemisphere.  $\text{N}_2\text{O}$  IAV in the tropics was positively correlated with soil moisture (also consistent with Ishijima *et al.* [2009]). The opposing signs of correlation with soil moisture and temperature in the tropics may be a reflection of the fact that anomalies in soil moisture and temperature are often negatively correlated.

[13] A number of extreme climatic events are associated with significant changes in  $\text{N}_2\text{O}$  mixing ratio. The European drought in 2003 produced a strong negative soil moisture anomaly, which coincides with the onset of a significant decrease in  $\text{N}_2\text{O}$  over Europe, which is not observed in either North America or Asia (see Figure S4). In summer 2003, a persistent high-pressure system led to stable conditions and longer air mass residence times over Europe [Solberg *et al.*, 2008]. Thus, if no change in surface emissions is assumed, transport alone would result in increased  $\text{N}_2\text{O}$  mixing ratio, while the opposite is observed. Sustained periods of low soil moisture in 2005 and in the first half of 2007 in Asia and South America also coincide with negative  $\text{N}_2\text{O}$  anomalies in the tropical signal, while above average soil water content in 2003 and 2008 in Asia and Africa coincides with positive  $\text{N}_2\text{O}$  anomalies. The years 2005 and 2007 (first half only) are associated with El Niño, which typically brings drier and warmer conditions to South America, Southeast Asia, and South Africa, especially during the Northern Hemisphere winter, whereas 2003 was nearly neutral, and the second half of 2007 and 2008 were La Niña years, which brings generally cooler and wetter conditions to the same regions [Trenberth *et al.*, 1998].

[14] Interannual variability in  $\text{N}_2\text{O}$  soil emissions has been previously linked to variations in soil moisture and precipitation, particularly in the tropics [Potter *et al.*, 1996; Werner *et al.*, 2007], and in soil temperature, particularly in temperate regions [Potter *et al.*, 1996]. Low soil moisture limits the production of  $\text{N}_2\text{O}$  via denitrification [Bouwman, 1998] and may





**Figure 3.** (left) Comparison of observed (blue) and modeled (green) IAV in atmospheric  $\text{N}_2\text{O}$  for different regions. (right) Difference between the observed and modeled IAV, i.e., corrected for the influence of transport. The gray shading indicates El Niño conditions ( $\text{MEI} > 0.2$ ) with a 3 month lag.

reduce the availability of reactive nitrogen in soil by slowing the remineralization of organic matter [Borken and Matzner, 2009; Potter *et al.*, 1996]. This is opposite to the effect of temperature, which increases the rates of both. The effect of soil temperature and moisture on remineralization rates could be important in areas with little to no N fertilizer input, such as in tropical and subtropical forests, where the background  $\text{N}_2\text{O}$  source is still very large, while their effect on denitrification rates impacts  $\text{N}_2\text{O}$  emissions even in areas that have unlimited reactive nitrogen availability. In this study, we do not investigate correlations between atmospheric  $\text{N}_2\text{O}$  IAV and ocean  $\text{N}_2\text{O}$  fluxes, as from the atmospheric observations alone it is not possible to disentangle fluxes from ocean and land. ENSO influences upwelling in the Tropical Eastern Pacific and, hence, the supply of nutrient- and  $\text{N}_2\text{O}$ -rich water from below the mixed layer [Behrenfeld *et al.*, 2006]. Nevison *et al.* [2007] also propose that  $\text{N}_2\text{O}$  IAV in the tropics may be influenced by changes in ocean  $\text{N}_2\text{O}$  flux affected by ENSO. However, the magnitude of the change in  $\text{N}_2\text{O}$  flux, and the corresponding possible change in tropospheric  $\text{N}_2\text{O}$  mixing ratio, is largely unknown.

#### 4. Conclusions

[15] Our analysis shows significant variations in tropospheric  $\text{N}_2\text{O}$  on interannual timescales (0.2 ppb, 1 standard

deviation). Comparisons of  $\text{N}_2\text{O}$ ,  $\text{CFC-12}$ , and  $\text{SF}_6$  IAV show a weak correlation in the northern extratropics and a stronger correlation in the southern extratropics. The correlation of  $\text{N}_2\text{O}$  with  $\text{SF}_6$  IAV in the southern extratropics is likely due to variations in interhemispheric transport, but for  $\text{CFC-12}$  other circulation changes may be at play as  $\text{CFC-12}$  has only a very weak interhemispheric gradient. We also compared  $\text{N}_2\text{O}$  IAV with PLST (used as a proxy for STT) and found no correlation, indicating that STT is unlikely to be an important factor for year-to-year variations in tropospheric  $\text{N}_2\text{O}$  mixing ratio. On the other hand,  $\text{N}_2\text{O}$  IAV is strongly correlated with MEI, with El Niño being associated with negative  $\text{N}_2\text{O}$  anomalies and vice versa for La Niña. The meteorological parameters, precipitation, soil moisture, and temperature were found to be significant variables for explaining tropospheric  $\text{N}_2\text{O}$  IAV, suggesting that this is modulated by climate-driven changes in soil  $\text{N}_2\text{O}$  emissions. For a more complete understanding of the role climate plays in  $\text{N}_2\text{O}$  IAV, however, more high-quality atmospheric measurements in the tropics would be needed as well as atmospheric inversions to retrieve spatially and temporally resolved  $\text{N}_2\text{O}$  emissions.

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