Effect of local and regional sources on the isotopic composition of nitrous oxide in the tropical free troposphere and tropopause layer

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[1] Measurements and models of the spatiotemporal variability of surface N2O mixing ratios and isotopic compositions are increasingly used to constrain the global N2O budget. However, large variability observed on the small spatial scales of soil chambers and shipboard sampling, which appears to be very sensitive to local environmental conditions, has made extrapolation to the global scale difficult. In this study, we present measurements of the isotopic composition of N2O (δ15Nbulk, δ15Nis, δ15Nbs, and δ18O) from whole-air samples collected at altitudes of 0.5 to 19 km by the NASA DC-8 and WB-57 aircraft during the Costa Rica-Aura Validation Experiment (CR-AVE) and the Tropical Composition, Cloud and Climate Coupling Experiment (TC4) campaigns in January–February 2006 and July–August 2007, respectively. The vertical profiles of isotopic composition showed predictable, repeating patterns consistent with the influence of a surface source at lower altitudes and the influence of stratospheric photochemistry in the lower stratosphere. Their correlations with marine tracers at lower altitudes are consistent with a predominantly oceanic source, although a soil source cannot be ruled out. Measurements in a combustion plume revealed a strong depletion in 15N at the central nitrogen atom (i.e., low δ15Nis values), providing new information on N2O isotopic compositions from combustion. This new data set demonstrates that a coherent picture of the isotopic composition of tropospheric N2O is possible at currently attainable precisions and that its variations from 0.5 km to the lower stratosphere are a useful tool in investigating the sources and distributions of this important greenhouse gas.

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1. Introduction

[2] Nitrous oxide, N2O, is an important greenhouse gas with a tropospheric mixing ratio that has risen from a pre-industrial level of ~270 ppbv to current levels of ~320 ppbv [e.g., MacFarling-Meure et al., 2006], revealing an imbalance between the N2O sources and sinks of ~5 TgN yr−1 [Forster et al., 2007]. The magnitudes of the particular processes that contribute to this imbalance (and how these may change as climate changes and as a side-effect of CO2 mitigation strategies) have large uncertainties [e.g., Forster et al., 2007]. Atmospheric N2O originates predominantly at Earth’s surface as a product or by-product of microbial nitrification and denitrification in water and in both natural and agricultural soils, and is emitted to the atmosphere by air-sea and air-soil exchange. These processes yield N2O with oxygen and nitrogen isotopic compositions that depend on the isotopic composition of the N and O reservoirs from which it is produced as well as isotope effects associated with the micro-biogeochemistry of N2O production and consumption. The only major N2O sink is destruction by photolysis and reaction with O(1D) in the stratosphere, which enriches the remaining N2O in the heavy isotopes 15N and 18O [e.g., Kim and Craig, 1993]. Since the sources and sinks of atmospheric N2O determine its isotopic composition, isotope measurements can provide additional constraints on the N2O budget beyond those based on measurements of N2O mixing ratios alone.
[e.g., Kim and Craig, 1993; Toyoda et al., 2002; Park et al., 2004].

[5] So far, however, the large variability in N₂O isotopic compositions measured in and above soils [e.g., Pérez et al., 2000, 2001] and the oceans [e.g., Popp et al., 2002; Toyoda et al., 2002] has precluded a “bottom up” approach to simultaneously balancing the global N₂O concentration and isotope budgets. Isotopic compositions of emitted N₂O appear to depend sensitively on small-scale variations in many environmental parameters such as soil texture, soil water content, and substrate isotopic composition (e.g., nitrates), as well as the relative amounts of N₂O production (during nitrification and denitrification) and consumption (e.g., during denitrification under anaerobic conditions). Indeed, apportioning the relative amounts of N₂O production and consumption in the soils before emission to the atmosphere is one of the goals of using isotope measurements at the field scale [e.g., Bol et al., 2003; Pérez et al., 2006]; knowledge of how the magnitudes of these processes change with environmental variables could be used to adjust agricultural parameters, such as soil water content during fertilization, in order to mitigate the release of N₂O to the atmosphere and to better predict effective mitigation strategies as mean surface temperatures rise [e.g., Fujinuma and Balster, 2009; Baggs, 2008]. However, this large variability has also meant that a “bottom up” approach to balancing the regional, hemispheric, and global budgets is unlikely to be sufficiently constrained.

[4] A “top-down” approach via inverse modeling of N₂O measurements [Hirsch et al., 2006; Huang et al., 2008] has also been underconstrained, at least apart from box model studies of the long-term increase in N₂O concentrations and the concurrent depletion in its heavy isotopes that have been measured in air from firm and ice cores [Rahn and Wahlen, 2000; Sowers et al., 2002; Röckmann et al., 2003; Bernard et al., 2006; Ishijima et al., 2007]. Due to its long atmospheric lifetime of 120 years, N₂O (and hence its isotopic composition) has commonly been assumed to be well-mixed and thus was expected to show little variation in the troposphere, leaving inverse models underconstrained. Recently, however, time series analyses [Nevison et al., 2005, 2007; Jiang et al., 2007] of nearly continuous high-precision N₂O mixing ratio measurements at the surface have revealed detectable seasonal cycles and interannual variations in N₂O concentrations, and new N₂O isotope measurements on archived air samples from the surface at Cape Grim, Tasmania reveal the same [Park et al., 2005, 2008], demonstrating that a top-down approach using these data sets might ultimately help constrain the magnitudes of different sources. Further information on the isotopic compositions of N₂O emitted from the oceans and soils and the degree to which they may affect regional and hemispheric N₂O isotopic compositions are greatly needed to proceed, however, as there is a dearth of observations.

[5] Here, we report measurements of the ¹⁸O and ¹⁵N isotopic compositions (including site-specific ¹⁵N) of N₂O in whole air samples collected from 0.5 km to the lower stratosphere in the tropics. The N₂O isotope altitude profiles obtained in both January and July in different years show a persistent pattern that, based on our initial analysis, appears to reflect the influence at lower altitudes of N₂O most likely from the ocean, transitioning at high altitudes in the lower stratosphere to the influence of stratospheric photochemistry. Although the variations are small, they are detectable at current measurement precisions using Continuous-Flow Isotope Ratio Mass Spectrometry (CF-IRMS) and serve as the basis for hypotheses regarding the sources that control the isotopic composition of tropospheric nitrous oxide that we put forth here to be tested by future measurements and analyses. As such, these measurements, combined with future vertical profiles in different regions and with increased measurement precision, may finally succeed in allowing isotopes to be used in a “top down” approach to constrain the magnitude and distribution of anthropogenic and natural N₂O sources.

2. Methods

[6] Whole air samples were collected from the WB-57 aircraft in January and February 2006 during the Costa Rica-Aura Validation Experiment (CR-AVE) and from the WB-57 and DC-8 aircraft in July and August 2007 during the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), both NASA missions based in San Jose, Costa Rica (9.99°N, 84.21°W). The University of Miami (UM) whole air sampler (WAS) [Flocke et al., 1999], which flew on the WB-57, included 50 1.5-L electropolished stainless steel canisters equipped with automated metal valves. The evacuated canisters were pressurized to 40 psi using a 4-stage bellows pump in flight. The University of California, Irvine (UCI) whole air sampler [Colman et al., 2001], which flew on the DC-8, used a stainless-steel bellows pump to pressurize 2-L stainless steel canisters to 40 psi. The canisters were equipped with stainless steel bellows valves and were evacuated and then filled with ~20 Torr of water vapor prior to the flights. Samples were collected in the planetary boundary layer, the free troposphere, and into the tropical tropopause layer (or “TTL,” defined here as the region between ~12–20 km [Toon et al., 2010], which includes the tropical lower stratosphere). Most of the WB-57 samples selected for isotopic analysis (see below) were collected between ~10 and 20 km, and those selected from among the DC-8 samples were collected between ~0.5 and 11.5 km. For reference, the cold-point tropopause was located on average at ~16.5 km during TC4 and ~17.5 km during CR-AVE. Most of the samples selected for isotopic analysis were collected between ~1°S and 10°N, but 25 of the samples were collected between ~20 and 30°N on two similar WB-57 transit flights (one for TC4 and one for CR-AVE) between Costa Rica and Houston, Texas. Sample selection was based largely on obtaining representative latitude and altitude distributions from both missions and on what samples were still available for analysis (i.e., those which had not been “recycled” to collect additional samples for trace gas analyses), with the exception of the plume samples which were selected because they were of interest based on the tracer mixing ratios.

[7] After sample collection, the WB-57 and the DC-8 whole air samples were first measured for numerous trace gas mixing ratios at UM and UCI, respectively, by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). For the WB-57 WAS samples, measurements that are relevant for this study are mixing ratios of N₂O, ethane.
(C₂H₆), propane (C₃H₈), benzene (C₆H₆), and tetrachloroethylene (C₂Cl₄). In particular, N₂O mixing ratio measurements were made using an HP5890 II+ series GC fitted with an electron capture detector (ECD) relative to a 314 ppbv N₂O secondary standard of whole air calibrated against a National Institute of Standards and Technology (NIST) reference gas, Standard Reference Material #2608 with an N₂O mixing ratio of 300 nmol/mol ± 1%. The average uncertainty (2σ) for the N₂O mixing ratio data is less than 0.7 ± 1% [Hurst et al., 2000]. Hydrocarbon species were measured by GC with flame ionization detection (GC-FID) with limits of detection (LOD) of about 2 ppt. C₂Cl₄ was measured with GC mass spectrometry (GC-MS) with LOD of better than 0.1 pptv. For the DC-8 samples, measurements that are relevant for this study include mixing ratios of methyl iodide (CH₃I), methyl nitrate (CH₃ONO₂), and ethyl nitrate (C₂H₅ONO₂), ethyne and benzene. CH₁₃, CH₂ONO₂, and C₂H₂ONO₂ were measured by GC–ECD with LODs of 0.01, 0.02, and 0.02 pptv, respectively. Ethyne and benzene were measured by GC-FID, both with LODs of 3 pptv. Our analyses of the DC-8 samples also included correlations of the N₂O isotope measurements with in situ measurements of carbon monoxide (CO) and methane (CH₄) mixing ratios from a tunable diode laser instrument, DACOM [Sachse et al., 1987, 1991]; measurements were made at 1 Hz with 0.1% precision and were averaged over the whole air canister sampling interval to compare with the whole air sample measurements. N₂O mixing ratio measurements sometimes made using the DACOM instrument are not available for these flights, nor were N₂O mixing ratios for the DC-8 samples measured at UCI. Since the ratio of the m/z 44 peak area of N₂O (measured on the IRMS at University of California at Berkeley UCB)) to the sample pressure is proportional to the N₂O mixing ratio, we attempted to retrieve an N₂O mixing ratio from the IRMS data and the sample pressure at the time of the isotope analyses. However, because the pressure measurements during sample transfer from the canister to the IRMS flask (see below) were intended only as a housekeeping measure and not as an accurate absolute pressure measurement independent of the gaseous composition, a convection-enhanced pirani gauge that was not calibrated for samples of widely varying water content was used, and our attempt to retrieve a proxy for the N₂O mixing ratio of the sample was therefore not successful.

After these and other trace gas mixing ratio measurements at UM and UCI, a total of 125 samples were selected for isotopic analysis and shipped to UCB. The isotopic composition of N₂O in the whole air samples was measured at UCB by CF-IRMS on a Finnigan MAT-252 IRMS coupled with preconcentration (PreCon) and gas chromatography (GC) devices – i.e., “PreCon/GC/CF-IRMS.” Prior to the isotope measurements, the CR-AVE whole-air samples were archived in 1.5-L Pyrex flasks; aliquots for the isotope measurements were taken from these archival flasks by expansion into evacuated 100–200mL measurement flasks. The TC4 samples were not archived; 100 ml aliquots for isotopic analysis were taken directly from the sample canisters.

N₂O isotopic compositions are reported here as δ-values in “per mil” (‰), which is the part per thousand difference of the isotope ratio of the sample relative to a standard: δ = 1000 (R/Rstandard − 1), where R = ¹⁵N/¹⁴N or ¹⁸O/¹⁶O and the subscript ‘standard’ refers to an international reference material, which is air–N₂ for ¹⁵N and Vienna Standard Mean Ocean Water (VSMOW) for ¹⁸O. Two types of nitrogen isotopic compositions are reported: (1) δ¹⁵Nbulk, which is the ¹⁵N isotope composition averaged over the two nitrogen atom sites in N₂O, and (2) δ¹⁵Nα and δ¹⁵Nβ, which represent the “site-specific” isotopic compositions – i.e., the ¹⁵N isotopic composition at the central nitrogen atom (the “α” site) and the ¹⁵N isotopic composition at the terminal nitrogen atom (the “β” site), respectively. In addition, we report the ‘Site Preference’ (SP) of the α-site relative to the β-site (SP = δ¹⁵Nα/δ¹⁵Nβ − 1), a form of the site-specific isotopic composition that is now frequently used, particularly in ecological studies in which it may be useful in discriminating between different production mechanisms [e.g., Bol et al., 2003, Staka et al., 2006, Pérez et al., 2006]. While some studies have used an alternative definition of SP as simply the difference between δ¹⁵Nα and δ¹⁵Nβ values (i.e., SP = δ¹⁵Nα − δ¹⁵Nβ), a difference between truncated ratios is not a mathematically rigorous quantity [Gros et al., 2003]. However, for the small values of SP usually encountered, the two expressions are equivalent [see, e.g., Toyoda et al., 2004].

Since the details of the isotopic measurements have been described elsewhere [Park et al., 2004], only a brief overview is given here. Two aliquots are required to determine the site-specific isotopic composition of N₂O using the MAT-252 IRMS, one for δ¹⁵Nbulk and δ¹⁸O, and a second for δ¹⁸O and δ¹⁵N. To determine δ¹⁵Nbulk and δ¹⁸O values, m/z 44, 45, and 46 (which correspond to isotopologues of N₂O⁺) are measured and compared with a standard for the first aliquot. To determine δ¹⁵Nbulk, the NO⁺ fragment ion at m/z 30 and 31 is measured and compared with a standard for the second aliquot and the degree of ‘scrambling’ – i.e., the fraction of NO⁺ in the sample that included the β N-atom—is taken into account; the ‘scrambling factor’ measured for our Finnigan MAT-252 is 8.04% [see Kaiser et al., 2004], which is similar to that measured for other 252 series instruments [e.g., Toyoda and Yoshida, 1999]. The measured values for δ¹⁵Nbulk and δ¹⁸O are then used to calculate δ¹⁵N and δ¹⁸O, which in turn is combined with δ¹⁸O to calculate SP.

Although for several years there had been controversy regarding how to convert δ¹⁸O to δ¹⁵N IRMS measurements onto the international air–N₂ scale [e.g., Toyoda and Yoshida, 1999; Yoshida and Toyoda, 2000; Kaiser et al., 2004; Park et al., 2004; Westley et al., 2007], Griffith et al. [2009] recently determined the SP of tropospheric N₂O using a Fourier Transform infrared spectroscopic technique which is independent of mass spectrometric measurements, yielding values that are in agreement with the Yoshida and Toyoda [2000] air–N₂ scale. Thus, we report δ¹⁸O and δ¹⁵N values on the Yoshida and Toyoda [2000] scale using tropospheric N₂O as a ‘transfer standard’ given the SP value of tropospheric N₂O from Yoshida and Toyoda [2000] of 18.7‰, the value of δ¹⁵Nbulk of tropospheric N₂O measured at UCB of 6.2‰, and the measured site-specific isotopic composition relative to tropospheric N₂O at UCB to effect the conversion.

The 1σ measurement precisions are ~0.2‰ for δ¹⁵Nbulk, ~0.3‰ for δ¹⁸O, ~0.8‰ for δ¹⁵N, and ~0.9‰ for δ¹⁸O, determined by repeated measurements of different volumes of tropospheric air collected at UCB and runs of...
of the measurements reported here are estimated to be 1\% for $\delta^{15}N_{\text{bulk}}$ and $\delta^{18}O$ and 4\% for $\delta^{15}N$ and $\delta^{15}N^{15}$ based on a comparison of the average isotopic composition of tropospheric N$_2$O reported by different groups, including ours, which show a range of differences of these magnitudes [Yoshida and Toyoda, 2000; Kaiser et al., 2003; Griffith et al., 2009]. Laboratory intercomparisons should improve the relative accuracies, and the implications of any future laboratory intercomparisons for the measurements reported here will be published when available.

3. Results and Discussion

[13] Figure 1 shows the latitude and altitude distribution of the 125 samples from CR-AVE and TC4 measured for N$_2$O isotopic compositions. Measured values for $\delta^{15}N_{\text{bulk}}$, $\delta^{15}N$, and $\delta^{18}O$ are represented by the color scaling shown in the legends and are also given in Tables S1, S2, and S3.

As expected, the isotopic variability is small, with a range in $\delta$-values for each equivalent to ~4 times the corresponding 1$\sigma$ measurement precision, as is evident in the range of the legend. In the following sections, we examine both the averaged vertical profiles for the different aircraft and missions as well as unaveraged portions of particular flights that show interesting correlations with marine and combustion tracers. We focus on the tropical measurements (<11°N) but include the subtropical points between 20° and 29°N in Figure 1 and the supplementary data files for completeness.

3.1. Averaged Vertical Profiles in the Tropics

[14] Figure 2 shows the results for averaging the tropical data (i.e., <11°N) in 1-km altitude bins, parsed and color-coded by aircraft (WB-57 and DC-8) and campaign (CR-AVE and TC4). The error-bars shown are the 1$\sigma$ standard deviation of the average of the data for that altitude bin (solid bars) or, for the few bins for which there is only a single datum, the measurement precision (dotted bars); the number of samples per altitude bin is also indicated in Figure 2a in the corresponding color. For comparison, the gray shading in each panel shows the ±1$\sigma$ ($N = 288$ for $\delta^{15}N_{\text{bulk}}$ and $\delta^{18}O$ and $N = 239$ for $\delta^{15}N^{15}$) variability in measured tropospheric N$_2$O isotopic compositions in air sampled on the UCB campus (37.87°N, 122.26°W) between September 2001 and November 2006. (Note that the shaded ranges therefore include small trends and are thus larger than the day-to-day variability of tropospheric N$_2$O isotopic composition, which is similar to the measurement precision, suggesting no major influence from local sources. Furthermore, the meridional gradients between UCB and the tropics are expected to be well within these ranges [Kaiser et al., 2003].)

[15] For $\delta^{15}N_{\text{bulk}}$, the average values and variability for the tropical profiles shown in Figure 2a fall within the range of those measured at the surface at midlatitudes at UCB. The largest deviation appears in the lower stratosphere, where average $\delta^{15}N_{\text{bulk}}$ values increase; this is shown more clearly in Figure 3 in which the measurements are binned into 0.5 km rather than 1 km ranges and then averaged. The

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a 1% N$_2$O-in-air laboratory standard [see, e.g., Park et al., 2004; Kaiser et al., 2003]. The precision is limited by instrumental noise, sample size, and the number of measurements for a given sample. In addition, the site-specific precisions are limited by the fact that two different aliquots are required for our MAT-252 since it is not possible to fit ion collectors for simultaneous measurements of m/z 30, 31, 44, 45, and 46 into the detection region. Of the 125 samples in this data set, 27 were measured in duplicate and showed repeatability that was similar to the precision. The accuracy

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Figure 1. Whole air samples analyzed for the isotopic composition of N$_2$O for the CR-AVE and TC4 missions. Symbols show sampling location given by altitude (y axis) vs latitude (x axis) for the CR-AVE WB-57 samples (squares), TC4 WB-57 samples (circles), and TC4 DC-8 samples (triangles), color-scaled by the isotopic composition of N$_2$O: (a) $\delta^{15}N_{\text{bulk}}$, (b) $\delta^{15}N$, and (c) $\delta^{18}O$. Aircraft landings in Costa Rica occurred at 10°N, while other descents occur as dives on various flights, as noted in the text.

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1Auxiliary materials are available in the HTML. doi:10.1029/2009JD013117.
increase in the $^{15}\text{N}/^{14}\text{N}$ ratio in N$_2$O with altitude is due primarily to the photolysis of N$_2$O in the stratosphere, which preferentially dissociates the $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ isotopologue with a smaller contribution from photo-oxidation of N$_2$O by reaction with O($^1\text{D}$) [e.g., Blake et al., 2003; Johnson et al., 2001; Kaiser et al., 2002a; Yung and Miller, 1997]. As the N$_2$O mixing ratios decrease with altitude in the stratosphere, the $\delta^{15}\text{N}_{\text{bulk}}$ values increase, as expected based on previous stratospheric measurements [e.g., Toyoda et al., 2001; Röckmann et al., 2001; Park et al., 2004, Kaiser et al., 2006].

When the $\delta^{15}\text{N}_{\text{bulk}}$ and N$_2$O values for individual samples are plotted in a Rayleigh isotope fractionation format in Figure 4 (i.e., as ln(1+ $\delta^{15}\text{N}_{\text{bulk}}$/1000) vs ln([N$_2$O]/[N$_2$O]$_0$)), where [N$_2$O]$_0$ is the N$_2$O mixing ratio for air entering the stratosphere) apparent fractionation constants, $\varepsilon_{\text{app}}$, of $-21 \pm 7$‰ and $-19 \pm 7$‰ are obtained for CR-AVE and TC4, respectively, from the slope of the fit line as determined by the Williamson-York method which considers uncertainty in both the x- and y-data [Cantrell, 2008, and references therein]. While the correlations are statistically significant ($R = -0.527$, $P < 0.03$ and $R = -0.610$, $P < 0.03$ for CR-AVE and TC4, respectively), the uncertainties are large since the N$_2$O mixing ratios decrease by only $\sim$4 to 8 ppbv and the $\delta^{15}\text{N}_{\text{bulk}}$ values increase by only $\sim$0.5‰ in the lowest 2 km of the stratosphere, which are intrinsically small and are close to the isotope measurement precision of $\pm 0.2$‰. Nevertheless, these values for $\varepsilon_{\text{app}}$ are within the
range of −14 to −19‰ obtained in the stratosphere for N$_2$O mixing ratios > 200 ppbv at 18°N [Kaiser et al., 2006], midlatitudes [e.g., Toyoda et al., 2001; Röckmann et al., 2001], and high latitudes [e.g., Park et al., 2004]. As discussed in the previous studies, these values for $\varepsilon_{\text{app}}$ are at least a factor of two smaller than the fractionation constant expected in an isolated system – that is, one in which chemistry alone is acting to alter the isotopic composition and not transport or mixing of air of different isotopic compositions. For example, a value of −34.7‰ is expected based on broadband photolysis of N$_2$O at room temperature in the laboratory and a 10% contribution from N$_2$O oxidation by O(1D) [Kaiser et al., 2002a; Röckmann et al., 2001]; transport and mixing decrease the slope of the Rayleigh fractionation line, yielding a value for $\varepsilon_{\text{app}}$ that is necessarily smaller than that for an isolated system.

[17] This isotope fractionation cannot be due to in situ photochemistry occurring in the tropics, as shown by a simple Rayleigh model analysis given in the appendix. Rather, as shown previously using measurements of the mixing ratios of a number of trace gas species below ~23 km, photochemically aged stratospheric air from midlatitudes must be transported and mixed isentropically into the tropical upwelling region [e.g., Avallone and Prather, 1996; Boering et al., 1996; Volk et al., 1996]; it is this mixing in of older midlatitude air rather than in situ N$_2$O destruction in the tropics that results in the decreasing N$_2$O mixing ratio and increasing $^{15}$N enrichment with altitude above the tropical tropopause in Figure 3. In subsequent work, we will attempt to quantify this in-mixing of midlatitude air as a function of altitude and compare it with previous estimates based on the tracer mixing ratio models noted above since such a number is of interest for stratospheric dynamics, mean ages, and residence times and how these may or may not be changing over time [e.g., Engel et al., 2009; Austin and Li, 2006]. Finally, we note that an increase in $\delta^{18}$O above the tropopause (e.g., Figure 2c) is not as clear as for $\delta^{15}$N$_{\text{bulk}}$ and not apparent at all in $\delta^{15}$N$^a$ (e.g., Figure 2b); this difference with respect to $\delta^{15}$N$_{\text{bulk}}$ is likely due to a fractionation

![Figure 3](image1.png)  
**Figure 3.** Vertical profiles of the mixing ratio (open symbols) and $\delta^{15}$N$_{\text{bulk}}$ (closed symbols) of N$_2$O, averaged into 0.5 km bins for samples collected at latitudes < 11°N and altitudes > 15 km for (a) CR-AVE and (b) TC4.

![Figure 4](image2.png)  
**Figure 4.** Individual measurements of $\delta^{15}$N$_{\text{bulk}}$ of N$_2$O for samples from the tropical lower stratosphere (<11°N and (a) > 17 km for CR-AVE and (b) > 16 km for TC4) are shown here plotted in a Rayleigh isotope fractionation format, i.e., as ln(1 + $\delta^{15}$N$_{\text{bulk}}$/1000) vs ln([N$_2$O]/[N$_2$O]$_o$), where [N$_2$O]$_o$ is the N$_2$O mixing ratio for air entering the stratosphere, taken to be the average of the N$_2$O mixing ratios measured below the cutoff altitude, 319.4 ± 0.9 and 320.7 ± 0.4 for CR-AVE and TC4, respectively.
constant for $\delta^{18}$O that is smaller than that for $\delta^{15}$N_{bulk} by 10% and to a measurement precision that is 4 times larger for $\delta^{15}$N than for $\delta^{15}$N_{bulk} so that stratospheric enrichments may be masked by noise in this data set.

For $\delta^{15}$N, the averaged tropical profiles in Figure 2 show a remarkably consistent pattern between the CR-AVE and TC4 missions. At the lowest altitudes, $N_2O$ is relatively depleted in $^{15}N$, and is outside the ±1σ range observed on average at the surface at UCB (gray shaded area). Values for $\delta^{18}$O then increase up to ~8 or 9 km and then generally decrease up to the tropopause. Such repeatability between the two missions suggests that the profiles are determined by an interplay of similar processes. One possibility is that the drivers underlying this profile pattern are analogous to those for other species that exhibit a common “inverse C"-shaped altitude profile that is determined by convection of surface air combined with chemistry and/or mixing [e.g., Prather and Jacob, 1997]. For $\delta^{18}$O, an inverse C pattern could result from a source of $N_2O$ that is depleted in $^{18}O$ relative to the free troposphere at the surface, either from soils or the ocean. Tropical convection takes this near-surface $N_2O$ and deposits it at altitudes up to 10 to 14 km, thus leading to a decrease in $\delta^{18}$O values at these higher altitudes influenced by convective outflow. In between these altitudes, the air may be more characteristic of background tropical and/or midlatitude air, with higher values of $\delta^{18}$O; the further from the surface source, the more it resembles background air (i.e., $\delta^{18}$O increases with altitude) until convective outflow of surface air at higher altitudes begins to turn the profile back around toward lower $\delta^{18}$O values. The vertical profiles for $\delta^{15}$N_{bulk} and $\delta^{15}$N_{N2O} (Figures 2a and 2b) do not show such a pattern.

Comparing these characteristics of the vertical profiles for $\delta^{18}$O, $\delta^{15}$N_{bulk}, and $\delta^{15}$N_{N2O} with the range of isotopic compositions measured to date in soils and the ocean suggests that the source that may be influencing the lower altitudes may be more similar in isotopic composition to an ocean source than to a soil source, although a mixture of the two is suspected. In the absence of more comprehensive data, in particular since both the Eastern Tropical North Pacific Ocean and the Central America and tropical soils are thought to be significant sources of $N_2O$ [e.g., Cohen and Gordon, 1978; Nevison et al., 1995; Matson and Vitousek, 1990]. For example, the isotopic composition of $N_2O$ in the subtropical North Pacific gyre was measured by Popp et al. [2002] and indicates that $N_2O$ transferred from ocean to air should be slightly depleted in bulk $N$ and slightly more so in $^{18}O$ relative to the background troposphere; they suggest a range for the ocean source of 3.5 to 5.5‰ for $\delta^{15}$N_{bulk} and 35.5 to 41.5‰ for $\delta^{18}$O. Different ranges for the isotopic composition of emitted $N_2O$ have been measured in other ocean regions [e.g., Toyoda et al., 2002]; in the absence of more comprehensive ocean measurements and an understanding of what controls them, the ranges relevant for this study will remain uncertain. In contrast, while there is great variability in measurements of the isotopic composition of $N_2O$ emitted from soils, in general it is significantly more so in bulk $^{15}N$ than in $^{18}O$. For example, the emission weighted isotope signature from unfertilized Costa Rican tropical rain forest soil $\delta^{15}$N_{bulk} = $-26 \pm 2.5$‰ and $\delta^{18}$O = $26 \pm 6$‰ [Pérez et al., 2000]. If a soil source of $N_2O$ were the dominant factor determining the lower $\delta^{15}$N values in the lower altitudes of the vertical profile, then a signal in $\delta^{15}$N_{bulk} would be expected to be even stronger and yet such behavior appears to be absent, as noted above. Furthermore, although measurements of the site-specific isotopic composition of oceanic $N_2O$ are even more rare than $\delta^{15}$N_{bulk} and $\delta^{18}$O, Toyoda et al. [2002] have shown ocean profiles in which $\delta^{15}$N_{N2O} values are high and $\delta^{15}$N_{N2O} are low relative to background tropospheric air; as a result, $\delta^{15}$N_{bulk} values would be more similar to tropospheric air than either $\delta^{15}$N or $\delta^{18}$O since it is the average of the two. Such a source could also be consistent with the observations since $\delta^{18}$O appears to be higher below 5 km, although such a pattern is arguably in the noise of the measurements. Overall, these characteristics of ocean $N_2O$ isotopic compositions seem more similar to the trends and differences in the averaged profiles shown here than to a soil source, assuming the averaged profiles are indeed representative of regional profiles in general.

3.2. Correlations Between $N_2O$ Isotopic Compositions and Surface Tracer Mixing Ratios

Examining unaveraged measurements from the flight of 08 August 2007 for the TC4 mission may provide further insight into the possible influence of a surface source on the isotopic composition of $N_2O$ in the tropical profiles. The DC–8 flight on this date included 3 distinct segments: a dive over the Pacific Ocean into the boundary layer, followed by an 11.5 km cruise and then a dive over the Colombian jungle. Particularly striking are the significant negative correlations between measurements of $\delta^{15}$N of $N_2O$ and the measured mixing ratios of methyl iodide (CH$_3$I), methyl nitrate (CH$_3$ONO$_2$), and ethyl nitrate (C$_2$H$_5$ONO$_2$), which are all tracers of marine convection, shown in Figure 5. While the correlations between $\delta^{15}$N and the marine tracers for all 3 flight segments included together were significant (P < 0.04 for each marine tracer), inspection of the individual flight segments shows that the negative correlation is largely due to the Pacific dive. For the Pacific dive data, R = $-0.737$ and P < 0.03 for CH$_3$ONO$_2$ (Figure 5a), R = $-0.726$ and P < 0.03 C$_2$H$_5$ONO$_2$ (Figure 5b), and R = $-0.714$ and P < 0.04 for CH$_3$I (Figure 5c) whereas the 2 other flight segments do not show statistically significant correlations (P > 0.15 for all). That these tracers of marine convection show a strong anti-correlation with $\delta^{15}$N, especially during the dive over the ocean, suggests that $N_2O$ from the ocean may be influencing $\delta^{15}$N of $N_2O$ in the tropical profiles from both CR-AVE and TC4. Unfortunately, as noted above, the $N_2O$ mixing ratios for these samples were not measured and, therefore, a Keeling plot analysis (in which the y-intercept of a plot of isotopic composition versus the reciprocal of the mixing ratio yields an estimate of the isotopic composition of the "undiluted" source [Keeling, 1958]) is impossible. Rather, the correlation with the marine tracers is only suggestive of an ocean link for the source, or at least one of the sources, influencing the decrease in $\delta^{15}$O values toward the surface in the profiles shown here. For $\delta^{15}$N_{bulk} and $\delta^{15}$N_{N2O}, the individual data points show no significant correlation with the marine tracers (see Figures S1 and S2).

For samples from the descent over the Colombian jungle, $\delta^{18}$O is significantly anti-correlated with the surface
tracers CO (P < 0.02) and ethyne (P < 0.01), which is consistent with either a soil or an ocean source since both are depleted in 18O relative to background tropospheric N2O; see Figure S3. (We note that only 1 whole air sample from an altitude of 1.5 km for the jungle dive into the boundary layer was still available for isotopic analysis and it did not display the highly elevated isoprene mixing ratios of many of the other boundary layer samples taken at the bottom of the dive.) For $\delta^{15}N_{bulk}$, no significant correlation with surface tracers was observed (P > 0.15 for all), analogous to the lack of $\delta^{15}N_{bulk}$‐marine tracer correlations for the ocean dive (Figure S1). Interestingly, however, there were significant positive correlations between $\delta^{15}N_a$ and the surface tracers CH4 (P < 0.01), ethyne (P < 0.03), and benzene (P < 0.01) in the jungle dive (Figure S2). Such a positive correlation is not expected for a soil source of N2O. There are two interesting possibilities that might yield such positive correlations based on details of the flight. One is that the N2O isotopic composition still reflects an ocean source (which is more likely to be enriched in $^{15}N$ at the α‐position); back trajectory calculations by M. R. Schoeberl, P. A. Newman, and L. R. Lait (available through the NASA/ARC Earth Science Project Office Archive at http://espoarchive.nasa.gov [see also Schoeberl and Sparling, 1995]) suggest that the samples at 500 mbar pressure and lower altitudes had been over the Atlantic within 2 to 7 days of the flight. Another possibility is based on observations by the DC‐8 whole air sampler scientist that at the bottom of the Colombian jungle dive there were a surprising number of swampy areas as well as cattle. Both are potential sources of N2O enriched in $^{15}N$ at the α position relative to a soil source and, most likely, the background troposphere as well since in both systems N2O may be reduced to N2 during denitrification [Boontanon et al., 2000; Mahimairaja et al., 1995] which can cause $^{15}N$ accumulation in the remaining N2O at the α position [e.g., Toyoda et al., 2005]. Given these two apparently plausible scenarios, it is unclear whether the positive correlations between $\delta^{15}N$ and the surface tracers are rather local (as might be expected from cows and swamps) or more regional in nature (an ocean source, or a mixture of ocean and soil sources).

In summary, the significant correlations observed between $\delta^{18}O$ and marine tracers from a dive over the Pacific Ocean suggest the influence of an ocean source on the N2O isotopic composition in the lower tropical troposphere, while the correlations between $\delta^{18}O$ and $\delta^{15}N_a$ and other surface tracers are consistent with the influence of either a continental and/or oceanic source. While more measurements are clearly needed to test the hypotheses put forth in this section, this new data set provides new constraints and points to specific needs for the further characterization of the isotopic composition of the various possible surface sources.

### 3.3. Isotopic Composition in a Combustion Plume

Another flight yielding interesting correlations between the measured N2O isotopic compositions and other atmospheric tracers was the WB‐57 flight of 05 August 2007 from the TC4 mission. Samples from this flight yielded several measurements of site‐specific N2O isotopologues that showed a large deviation (4σ) from the average tropospheric values and a striking correlation with greatly
enhanced mixing ratios of several tracers indicative of industrial combustion or biomass burning processes but only slightly enhanced N$_2$O mixing ratios of up to ~1 ppbv. The (unaveraged) altitude profiles for measurements of ethane, propane, benzene, and tetrachloroethylene are shown in Figure 6a. The plume, encountered at altitudes between 14 and 15 km is clearly visible. Trajectory-based convective influence calculations provided by L. Pfister (Pfister et al., 2001, 2010) suggest that these samples were likely affected by convection within one day of the sampling, and that this convection was at least partially over Central America, near Panama City, Panama.

Figure 6b shows the anti-correlation between $\delta^{15}$N$_{\text{bulk}}$, $\delta^{15}$N$^\alpha$, Site Preference (see text): circles; and $\delta^{18}$O: diamonds.

4. Conclusions

[25] We have demonstrated that the isotopic composition of nitrous oxide varies throughout the tropical troposphere with an average vertical structure in $\delta^{18}$O, discernible at current measurement precision, but that is not observed in the $\delta^{15}$N measurements – characteristics that are at least consistent with the influence of an oceanic source of N$_2$O on a regional scale, or perhaps a mixture of ocean and soil sources. This hypothesis is supported by correlations observed between $\delta^{18}$O of N$_2$O and tracers of marine convection, which are particularly strong during a dive over the Pacific Ocean. In addition, we have further demonstrated the dramatic effect of an industrial or biomass burning plume on the site-specific isotopic composition of N$_2$O. The hypotheses put forth here regarding the sources of N$_2$O and the extent of their regional and hemispheric influence on tropospheric profiles will require additional measurements to test them. On the other hand, we note that it is somewhat surprising that the variations in observed N$_2$O isotopic compositions and their coherent patterns with respect to altitude and the mixing ratios of a number of surface tracers is large enough to at least formulate the hypotheses put forth here. Nevertheless, the variations in the measurements of the isotopic composition of tropospheric N$_2$O reported here are small compared to the measurement precision – the range of measured isotopic compositions is only about 4σ – suggesting that improvements in analytical techniques (and/or using the more time-consuming dual inlet IRMS technique of Kaiser et al. [2003] or much larger samples sizes for many replicate CF-IRMS measurements on the same sample) would be useful, allowing more information to be extracted from the data. Ultimately, these measurements are “proof-of-
Appendix A

[26] Using the $\delta^{15}N_{\text{bulk}}$ measurements (shown in Figure 3), we can calculate a lower limit for the vertical ascent rate in the tropical lower stratosphere (TLS) during CR-AVE assuming no in-mixing of midlatitude air based on Rayleigh fractionation in an isolated system – i.e., by calculating how long it would take to enrich $N_2O$ from the average $\delta^{15}N_{\text{bulk}}$ value observed at 17.25 km to that observed at 19.25 km based on the in situ destruction rate of $N_2O$. Using the fractionation constant of $\sim 34.7\%$ noted above and a 70-year lifetime for $N_2O$ with respect to photolysis yields an ascent rate of 0.063 mm s$^{-1}$ (or 0.17 km/month), which implies that, if there were no in-mixing of midlatitude air, the air at 19.25 km would require 12 months to ascend to that altitude from 17.25 km in order to obtain the observed enrichment. In contrast, annually averaged vertical ascent rates in the TLS derived from observations of the propagation of annual cycles in CO$_2$ [Boering et al., 1996] and water vapor [e.g., Mote et al., 1996] and from radiative calculations [e.g., Eluszkiewicz et al., 1996; Rosenlof, 1995] are $\sim 0.2$ mm s$^{-1}$ ($\sim 0.5$ km/month) and are even larger ($\sim 0.35$ mm s$^{-1}$ = 0.88 km/month) during northern winter when the CR-AVE samples were collected, indicating that the transit time for air from $\sim$17 to 19 km is on average 4 months, not 12 months, the value yielded by a Rayleigh model for an isolated lower stratosphere. Using temperature-dependent rather than room temperature photolysis fractionation constants, which gives an expected fractionation constant of $\sim 48$ to $\sim 51\%$ for the lower tropical stratosphere [Kaiser et al., 2002a, 2002b], decreases that transit time to $\sim$9 months, a time scale that is still more than a factor of two larger than the generally accepted ascent time scales noted above. Thus there is simply not enough time using a closed-system Rayleigh model to enrich tropical $N_2O$ in $^{15}N$ to the extent observed by in situ photochemistry occurring in the tropics. Therefore, photochemically processed air that is isotopically enriched in $^{15}N$ must have mixed into the tropics, a conclusion that is consistent with the current understanding of the chemical composition of the TLS and the time scales for transport of older, midlatitude air into the tropics.

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