High-precision determination of the changing isotopic composition of atmospheric N_2O from 1990 to 2002

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[1] High-precision nitrous oxide (N_2O) concentration and isotope ratio measurements have been carried out on archived air samples from the Antarctic station Neumayer covering the period 1990–2002. The results show that the increase in the N_2O mixing ratio over this period is accompanied by a significant decrease in the heavy isotope content. The temporal isotope trends amount to (-0.040 ± 0.003)‰/yr for $\delta^{15}N$ (the average of both nitrogen positions) and (-0.021 ± 0.003)‰/yr for $\delta^{18}O$. The individual trends for the terminal (position 1) and central (position 2) nitrogen atoms within the N_2O molecule are (-0.064 ± 0.016)‰/yr for $^1\delta^{15}N$ and (-0.014 ± 0.016)‰/yr for $^2\delta^{15}N$. The average ^{15}N and ^{18}O trends compare well with recent results from measurements on air extracted from polar firn and ice, confirming earlier estimates that isotopically depleted N_2O, mainly from soil emissions, is responsible for a large fraction of the observed N_2O increase in the atmosphere. The position-dependent ^{15}N determinations show a strong difference between the two positions. This is in disagreement with the firn and ice core data, which imply similar fractionations at both positions.

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1. Introduction

[2] Measurements of the isotopic composition of atmospheric constituents can help to investigate their global and regional budgets. This is due to the fact that trace gases emitted from different sources usually have slightly different isotopic compositions, which are characteristic for the respective sources. Also sink processes of atmospheric species are often accompanied by isotope fractionation. For the greenhouse gas N_2O, the main sources are bacterial nitrification and denitrification processes in soils and aquatic systems, and the only significant sink is destruction in the stratosphere by UV radiation and reaction with electronically excited oxygen atoms $O(^1D)$ [*Intergovernmental Panel on Climate Change (IPCC)*, 2001]. It is known that emissions from soils are generally depleted in the heavy isotopes relative to tropospheric N_2O, whereas emissions of N_2O from oceans are much closer in their isotopic composition to tropospheric N_2O and can even be slightly enriched [*Kim and Craig*, 1990; *Kim and Craig*, 1993; *Naqvi et al.*, 1998; *Pérez et al.*, 2000; *Popp et al.*, 2002; *Yoshida et al.*, 1984; *Yoshida and Toyoda*, 2000] (see *Gros et al.* [2004] for a recent overview of isotope signatures of N_2O sources). The isotope fractionation effects in the stratospheric sink processes have been extensively investigated in laboratory experiments [e.g., *Kaiser et al.*, 2002a, 2002b, 2003b], and a number of studies have precisely determined the isotopic composition of N_2O in the stratosphere [*Griffith et al.*, 2000; *Park et al.*, 2004; *Rahn and Wahlen*, 1997; *Röckmann et al.*, 2001a; *Toyoda et al.*, 2004; *Yoshida and Toyoda*, 2000]. Although discrepancies still remain between optical absorption measurements [*Griffith et al.*, 2000] and mass spectrometric measurements on stratospheric air samples (all other studies), the stratospheric measurements confirm and refine the picture of the global N_2O isotope budget first proposed by *Kim and Craig* [1993]: The heavy isotopologues of N_2O are strongly enriched in the stratosphere and via stratosphere-troposphere exchange this leads to a significant isotope enrichment of tropospheric N_2O relative to its sources at the Earth's surface. From the perspective of tropospheric N_2O, in a steady-state situation the isotopically depleted soil emissions are balanced by a flux of enriched N_2O from the stratosphere.

[3] Now that this general picture is firmly established and has yielded interesting information, particularly on the stratospheric N_2O removal processes, the question is whether N_2O isotope measurements can indeed be used to constrain its global budget. The main difficulty in studies on the global cycling of N_2O arises from its long atmospheric lifetime of about 120 years [*IPCC*, 2001]. As a consequence, N_2O is

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almost well mixed in the troposphere with a globally averaged mixing ratio of about 319 ppb (1 ppb = 10^{-9} mole N$_2$O per mole dry air) in 2004. Annual source fluxes are only a small fraction of the tropospheric inventory so that spatial and temporal gradients are small. This principal hurdle applies to both mixing ratio and isotopic composition of N$_2$O. High precision techniques for concentration measurements are available and show a seasonal cycle between 0.5 and 1.1 ppb in the Northern Hemisphere [*Levin et al.*, 2002; *Liao et al.*, 2004], an interhemispheric gradient of about 0.8 ppb and an annual increase of (0.8 ± 0.2) ppb/a [*IPCC*, 2001]. Given these small concentration variations, exceedingly small changes in the isotopic composition of N$_2$O are expected. First quantitative estimates about the temporal isotope trends of N$_2$O came from global modeling studies and suggested a rate of change of −0.03‰/a for δ^{15}N and δ^{18}O [*Rahn and Wahlen*, 2000]. This is at the low end of the uncertainty of state of the art analytical techniques, and therefore it had not been possible to detect a change in the isotopic composition of N$_2$O in recent atmospheric air samples directly. On the other hand, precisely quantifying temporal isotope trends in the atmosphere is a prerequisite for any meaningful attempt to constrain a changing global trace gas budget using isotopes.

[4] The first experimental evidence for a changing isotopic composition of N$_2$O has recently come from two studies that used air trapped in polar firn [*Röckmann et al.*, 2003a] and firn and ice [*Sowers et al.*, 2002] to estimate temporal N$_2$O isotope trends in the atmosphere. In the present paper we now, for the first time, present high-precision measurements of the isotopic composition of N$_2$O on actual air samples collected at the German Antarctic research station Neumayer, spanning the period from 1990 to 2002. We establish precise temporal trends for the average ^{15}N content and the ^{18}O content of N$_2$O, which are in good agreement with the firn air results. We also distinguish the ^{15}N fractionations at the two positions in the molecule, but the individual ^{15}N trends are not as well constrained as their mean and do not agree well with the earlier firn air results.

2. Experiment

[5] Regular air sampling for trace gas analysis at the German Antarctic research station Neumayer (71°S, 8°W), run by the Alfred Wegener Institute for Polar Research (AWI, Bremerhaven), had been started already in the early 1980s. Large volume air samples (∼1500 L) compressed into 10-liter high-pressure cylinders were regularly collected (every 2 to 4 weeks). After shipment to the University of Heidelberg they were analyzed for a number of long-lived atmospheric constituents such as CH$_4$, N$_2$O, SF$_6$, as well as the isotopic composition of CH$_4$. Since 1990, a selection of these well-characterized air samples has been stored in Heidelberg to establish an air archive for later analysis. Twenty-three of those archived air samples spanning the period from March 1990 to November 2002 have now been selected for isotopic analysis based on their N$_2$O mixing ratio (determined by gas chromatography with electron capture detector (GC-ECD) [*Schmidt et al.*, 2001]). They were analyzed at the Max-Planck Institute für Kernphysik (Heidelberg) for their ^{15}N-N$_2$O and ^{18}O-N$_2$O isotopic

composition, using a high-precision continuous-flow isotope ratio mass spectrometry (CF-IRMS) method [*Röckmann et al.*, 2003b]. The analytical technique has been continuously improved since the first applications to measurements of stratospheric N$_2$O [*Röckmann et al.*, 2001a] and N$_2$O trapped in firn air [*Röckmann et al.*, 2003a]. When enough air is available so that multiple measurements can be carried out on a single sample, which is clearly the case for the large volume samples from the University of Heidelberg air archive, the precision has now reached a level comparable to the best traditional offline isotope techniques for N$_2$O [*Kaiser et al.*, 2003a]. Thus it is possible now to investigate the minute changes in the isotope content of tropospheric N$_2$O. For details about the analytical method, we refer to *Röckmann et al.* [2003b]; here we only describe the principle of the technique, as well as important improvements made over the last year. Isotope data are reported in the common δ-notation, where, for example, δ^{15}N denotes the relative difference in ‰ of the ^{15}N/^{14}N ratio of a sample with respect to a specified reference material. To distinguish ^{15}N at the individual positions, we denote the terminal N atom as locant 1 ($^1\delta^{15}$N) and the central N atom as locant 2 ($^2\delta^{15}$N).

[6] From a high-pressure cylinder, equipped with a pressure regulator, the air samples are injected into a He carrier gas stream via a mass flow controller at a flow rate of 50 ml/min for the desired time. For the measurements presented here we used an injection time of about 400 s, corresponding to 333 ml of air for a single measurement. We note that this is not the limit for an isotope analysis but an amount that is necessary to obtain the highest possible precision. After removal of CO$_2$ over Ascarite, N$_2$O is condensed in a preconcentration trap at liquid nitrogen temperature. The sample is subsequently flushed from this trap into a focus trap at the head of the gas chromatographic column at the GC flow rate of about 2 ml/min. From there it is released onto the column for separation from condensable interferences, before it is transferred to the isotope ratio mass spectrometer via an open split interface [*Röckmann et al.*, 2003b]. To prevent interferences from compounds that have very long retention times, the column is split into a precolumn and an analytical column, with the precolumn being backflushed after each measurement as soon as the N$_2$O peak has been detected in the mass spectrometer.

[7] For the measurements presented here, we have used two different isotope ratio mass spectrometers. In 2003, the whole set of samples was analyzed on a ThermoFinnigan Delta plus XL instrument, and in 2004 18 of the samples were analyzed again on a new ThermoFinnigan Delta plus XP instrument. On the conventional Delta plus XL, only three collectors can be monitored simultaneously. Therefore for full isotopic characterization of N$_2$O, including the position-resolved ^{15}N measurements, two separate measurements have to be made, one on the N$_2$O$^+$ ions at m/z 44, 45, and 46 and one on the NO$^+$ ions at m/z 30 and 31, as described by *Brenninkmeijer and Röckmann* [1999] and *Röckmann et al.* [2003b]. The advantage of the new Delta plus XP instrument is that all five masses are monitored simultaneously; thus only one sample injection is required. This saves time (each single analysis takes about 20 min) and sample and also reduces the statistical error in the measurements, since now all signals are recorded at the

same time under the same mass spectrometer conditions. The latter was particularly important for the position-resolved measurements. On both instruments, the ratio of NO^+ fragment ions to N_2O^+ parent ions is only about 18%; thus the peaks for the fragment ions are much smaller and the precision is less. It was not possible to obtain a statistically robust trend using the Delta plus XL measurements in 2003, which may also be related to nonlinearity effects in the mass spectrometer. Thus the trends derived for the position-resolved ^{15}N fractionations reported below are from the new measurements with the Delta plus XP instrument. The amount of gas used (333 ml) is twice as much as initially used in routine analyses [*Röckmann et al.*, 2003b]. On the basis of linearity tests carried out then we had concluded that larger sample sizes than 167 ml would not lead to significantly improved precision. Measurements with the new setup show, however, that 1σ reproducibilities of ±0.06‰ for $\delta^{15}N$ and ±0.09‰ for $\delta^{18}O$ for a single measurement are routinely obtained on 333 ml sample volumes; this is about twice as good as quoted before by *Röckmann et al.* [2003b] for 167 ml of air.

[8] In the second set of measurements with the Delta plus XP instrument we have also been able to circumvent the nonlinearity problem for the fragment ion analysis. As we know the N_2O mixing ratio, we individually adjusted the injection time of the samples. For example, the injection time for our reference air sample with a nominal mixing ratio of 319 ppb on the SIO98 scale [*Prinn et al.*, 2000] is 400 s; thus the injection time for a sample with a mixing ratio of 310 ppb was set to 411.6 s to yield the same peak area. Using this simple adjustment, peak areas of sample and reference gas were always within 0.5% and a nonlinearity correction is not necessary. However, this procedure may introduce a small bias for the concentration measurements. When the sample admission valve is opened at the beginning of each measurement, the mass flow controller establishes the desired flow rate only after a certain stabilization period. As this stabilization bias is always similar in absolute terms, it will affect samples with different admission times differently, which could artificially attenuate the concentration differences. Although this was not tested systematically, this effect may be responsible for the slightly smaller temporal N_2O trend derived from the Delta plus XP measurements (see below), where the adjustment of admission times was performed, and therefore the Delta plus XL data are used for the mass spectrometric determination of the N_2O mixing ratios.

[9] Since plenty of air is available for the samples analyzed here, we have conducted in each measurement series 10 to 35 individual analyses for each sample, thus gaining further precision from statistics. They are carried out in packs of five analyses of a sample, bracketed by five analyses of our reference gas cylinder. For each sample measurement, the raw delta value is calculated relative to the mean of the reference air packs that precede and follow the sample measurement. The final delta value assigned to an air sample is the mean of all analyses of that sample, i.e., of 10 to 45 measurements carried out on multiple days and different mass spectrometers. Few obvious outliers have been removed before averaging.

[10] For isotope measurements on N_2O, no international reference material is available. To specify the ^{15}N and [18]O content of an N_2O sample versus atmospheric N_2 and V-SMOW, we have carefully calibrated our mass spectrometer reference gas as well as the reference air sample using offline preparation and conversion techniques [*Kaiser et al.*, 2003a]. This calibration for the [18]O and the average ^{15}N content using well-established methods yielded $\delta^{15}N = 6.69‰$ vs. atmospheric N_2 and $\delta^{18}O = 44.61‰$ versus V-SMOW for our reference air sample. The calibration of the intramolecular distribution in N_2O is not straightforward. Results of a mass spectrometric calibration method using mixtures of isotopically labeled N_2O isotopologues [*Kaiser et al.*, 2003c] yield a strong difference of the ^{15}N content at both positions in the molecule. The values of $^1\delta^{15}N = -23.6‰$ and $^2\delta^{15}N = 36.9‰$ for our pure N_2O running gas translate to $^1\delta^{15}N = -16.2‰$ and $^2\delta^{15}N = 29.6‰$ for our reference air sample containing clean tropospheric air. This is in clear contrast to the only other available calibration by *Toyoda and Yoshida* [1999], which showed only a small difference between the ^{15}N content at the two positions for tropospheric N_2O, $(^2\delta^{15}N - {}^1\delta^{15}N)/^1\delta^{15}N = 18.7‰$, compared to our value of $(^2\delta^{15}N - {}^1\delta^{15}N)/^1\delta^{15}N = 46.5‰$. Since this discrepancy is not resolved at present, we show the position-dependent ^{15}N values on both scales for easy comparison with existing measurements.

3. Results

[11] Figure 1 shows the results for the N_2O mixing ratio, which is obtained from the combined peak area of all isotopologues in comparison with the GC-ECD analyses performed at the University of Heidelberg, on the SIO98 scale [*Prinn et al.*, 2000]. The GC-ECD technique was used to calibrate the reference air cylinder that is used for the IRMS measurements. Applying a linear fit to the Delta Plus XL IRMS measurements, we derive a temporal trend of (0.75 ± 0.08) ppb/yr. All errors reported for the trends are 2σ. Note that the scatter in the data also includes natural (in particular seasonal) variability, as we had chosen samples from the respective maxima and minima of the seasonal cycles. The results are in very good agreement to the GC-ECD results of the University of Heidelberg measurements that yield a trend of 0.77 ± 0.06 ppb/yr and with the presently accepted trend of 0.74 ppb/yr from *IPCC* [2001]. The trend derived from the Delta Plus XP measurements is slightly smaller, (0.70 ± 0.08) ppb/yr, possibly affected by reasons discussed above, but still agrees with the other trends within the uncertainty. The mean difference between the Delta Plus XL (IRMS) and GC-ECD measurements is -0.13 ± 0.49 ppb; thus the CF-IRMS isotope technique yields as a byproduct also precise concentration data.

[12] Figure 2 shows the raw data of the isotope ratio measurements, i.e., the $^{45}\delta$, $^{46}\delta$, and $^{31}\delta$ values, relative to N_2O from our reference air cylinder, which was filled with dried ambient air at the Schauinsland observatory in the Black Forest in southern Germany in 2001. As noted before, every point on these plots is the average of 10 to 35 measurements from a sample cylinder. The error bars show the standard error of the mean. The results from the two mass spectrometers are in good agreement, although for some points the respective error bars do not overlap.
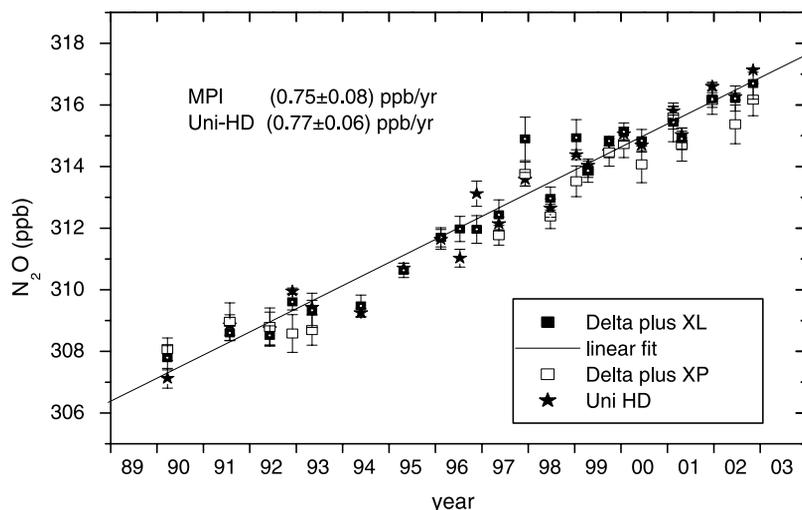
Figure 1. N₂O mixing ratios of the air samples from the University of Heidelberg air archive collected at Neumayer station, Antarctica. The black squares are the results from the isotope ratio mass spectrometer measurements, using the ThermoFinnigan Delta plus XL (open symbols) and the Delta plus XP instruments (solid symbols). Stars denote measurements made at the University of Heidelberg by gas chromatography followed by electron capture detection (GC-ECD).

Nevertheless, the average difference between the two measurements is (0.01 ± 0.04)‰ for $^{45}\delta$ and (0.02 ± 0.04)‰ for $^{46}\delta$, and for the following evaluation all measurements are combined to yield one single number for the isotopic composition of each sample. Clear linear trends are evident for $^{45}\delta$ and $^{46}\delta$ over the 13-year time span covered by the archived air samples. For $^{31}\delta$, a linear trend is barely detectable because of the reduced precision for the fragment analysis, but the trend can a priori be assumed to be linear since for the long-lived trace gas N₂O it must qualitatively follow the other trends. Nevertheless, for $^{31}\delta$ the magnitude of the trend is only poorly constrained.

[13] The atomic delta values can be calculated from the molecular delta values using the known isotopic composition of the reference gas and accounting for a small oxygen isotope anomaly of $\Delta^{17}O = 0.9$‰ that has been established for atmospheric N₂O [*Kaiser et al.*, 2003a; *Röckmann et al.*, 2001b]. The results for $\delta^{15}N$ and $\delta^{18}O$ are shown in Figure 3. As these isotopologues represent the majority of the ions that contribute to the m/z = 45 and m/z = 46 beams in the mass spectrometer, they show the same degree of scatter and have error bars of the same size. Consequently, for $\delta^{15}N$ and $\delta^{18}O$ we find clear linear trends that are similar to those found for the molecular ions. From the linear fits to the data we conclude that $\delta^{15}N$ has been decreasing over the considered time period by (-0.040 ± 0.003)‰/yr, and $\delta^{18}O$ by (-0.021 ± 0.003)‰/yr.

[14] The results for the position-resolved ^{15}N isotopic composition are shown in Figure 4. Given the reduced analytical precision for the fragment ion measurements, the errors of the position-dependent ^{15}N data are larger than for the average ^{15}N content. The intramolecular ^{15}N distribution is mainly derived from the fragment ion analysis, after accounting for the scrambling in the ion source [*Brenninkmeijer and Röckmann*, 1999; *Röckmann et al.*, 2003b]. Thus as seen in the $^{31}\delta$ raw data, the linear trends for the ^{15}N content at the individual positions are less constrained than for the average ^{15}N content. We derive
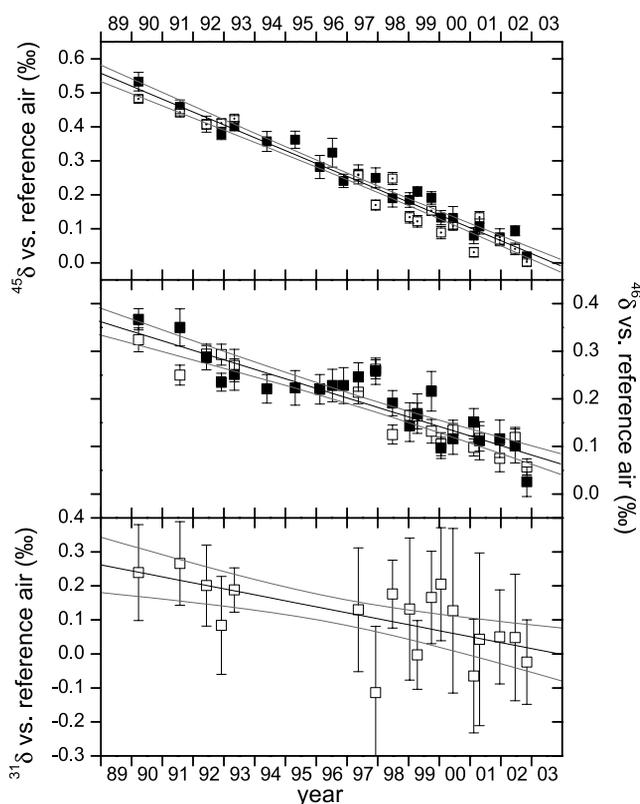

Figure 2. Raw mass spectrometer results ($^{45}\delta$(N₂O), $^{46}\delta$(N₂O), $^{31}\delta$(N₂O) versus our laboratory reference air sample) for the Antarctic air samples from the University of Heidelberg air archive. Solid symbols are measurements with the Delta plus XL instrument; open symbols are measurements with the Delta plus XP instrument. Clear linear trends are evident for $^{45}\delta$ and $^{46}\delta$, whereas a linear trend is not well established for $^{31}\delta$ due to the larger measurement errors. Black solid lines are linear least squares fits, and grey dotted lines show the 95% confidence intervals.
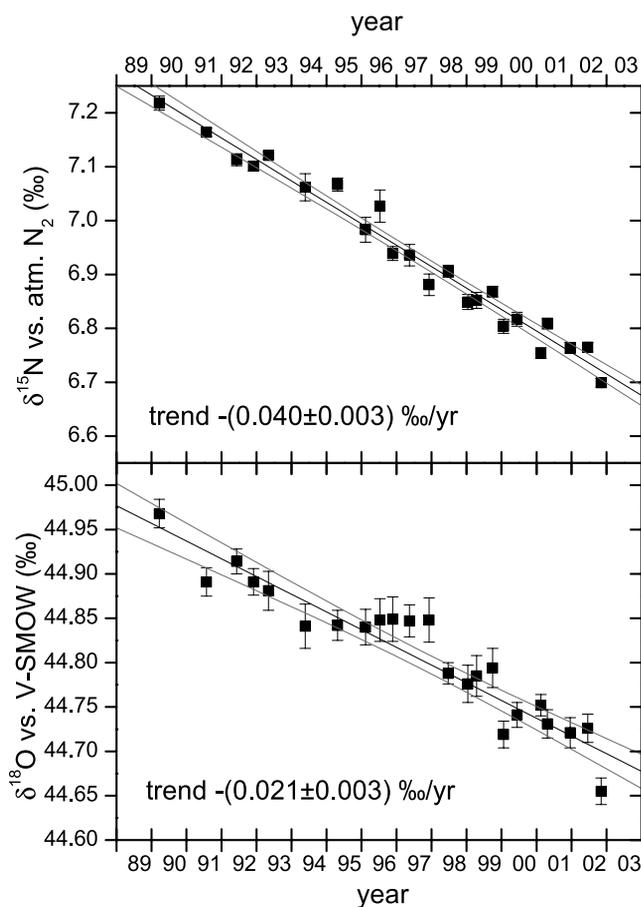
atmosphere using the preindustrial values derived from the ice core measurements. This scenario was taken as input for a firn air diffusion model. The resulting isotope profiles in the firn fit their data qualitatively, although the errors are large and the ^{18}O shift produced by the model is larger than found in the firn air measurements. This is because in this study the firn air isotope measurements were not used to further constrain the model, but the main constraint came from the total changes since preindustrial times derived from the ice core measurements. The respective recent isotope trends in the atmosphere can be obtained directly from the atmospheric scenario in Figure 2 of *Sowers et al.* [2002]. The δ^{15}N and δ^{18}O trends derived from our new direct atmospheric measurements are in very good agreement with the results from the firn air study by *Röckmann et*
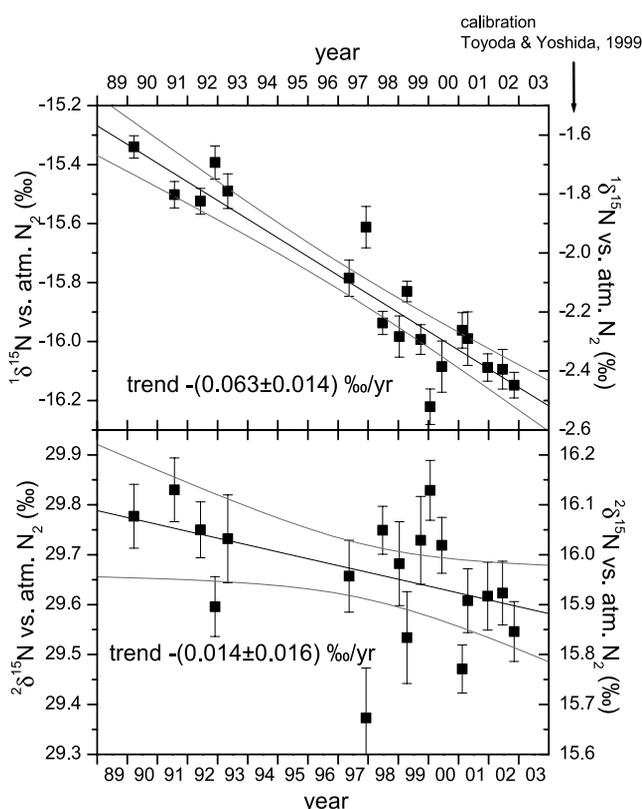
Figure 3. δ^{15}N and δ^{18}O in N$_2$O for the Antarctic air samples from the University of Heidelberg air archive. Black solid lines are linear least squares fits, and grey dotted lines show the 95% confidence intervals. The high δ^{18}O value at the end of 1997 is likely an artefact (perhaps due to isotopic alteration during sample storage) and most probably not an atmospheric signal.

trends of (-0.063 ± 0.014)‰/yr for $^1\delta^{15}$N and (-0.014 ± 0.016)‰/yr for $^2\delta^{15}$N.

4. Discussion

[15] These measurements on Antarctic surface air samples represent the first extended record of high-precision isotope measurements on atmospheric background N$_2$O. In Table 1 the results are compared to two recent studies that derived N$_2$O isotope trends from firn air and ice core measurements. *Röckmann et al.* [2003a] used a forward firn air diffusion model that calculates concentration and isotope profiles in the firn based on input scenarios for the atmospheric evolution [*Rommelaere et al.*, 1997]. The input scenarios had a prescribed shape based on the model results from *Rahn and Wahlen* [2000]. The isotope profiles measured in firn air were used to constrain the total magnitude of the isotope change since preindustrial times, and the recent temporal isotope trends were obtained directly from the selected atmospheric scenarios. *Sowers et al.* [2002] constructed a single atmospheric scenario for N$_2$O and its isotopic composition based on a two-box model of the

Figure 4. $^1\delta^{15}$N and $^2\delta^{15}$N in N$_2$O for the Antarctic air samples from the University of Heidelberg air archive. Black solid lines are linear least squares fits, and grey dotted lines show the 95% confidence intervals. Intramolecular ^{15}N results are only available for the analyses with the Delta plus XP machine, and in this data set the samples between 1994 and 1996 were not analyzed, so they are missing in Figure 4. Some of the variability, in particular the obvious outliers, can be ascribed to the larger scatter in the fragment ion measurements (Figure 2), since the values are shifted in opposite directions for $^1\delta^{15}$N and $^2\delta^{15}$N, whereas δ^{15}N shows no deviation (see Figure 3). There is still an unresolved discrepancy between the two existing calibrations for the absolute intramolecular distribution of ^{15}N in N$_2$O. Thus we show on the left ordinate our results on the *Kaiser et al.* [2003c] scale. The right ordinate shows a conversion to the calibration by *Toyoda and Yoshida* [1999].

Table 1. Comparison of the Temporal Trends Derived From the Antarctic Air Samples With Those From Recent Firn Air Measurements[a]

Isotope Signature	Air Samples (‰/yr) This Work 1990–2002	Firn Air (‰/yr) [Röckmann et al., 2003a] 1994–1998	Firn air (‰/yr) [Sowers et al., 2002] 1990–1995
$\delta^{15}N$	−(0.040 ± 0.003)	−0.038 to −0.046	−0.025[b]
$\delta^{18}O$	−(0.021 ± 0.003)	−0.021 to −0.031	−0.043[b]
$^1\delta^{15}N$	−(0.063 ± 0.014)	−0.035 to −0.049	n/m
$^2\delta^{15}N$	−(0.014 ± 0.016)	−0.039 to −0.049	n/m

[a]Note that the trends derived from the firn air are derived from averages over slightly different periods since the firn air sampling for those studies was in 1998/1999 and 1995, respectively.

[b]Trends are obtained from the atmospheric history of $\delta^{15}N$ and $\delta^{18}O$ calculated with the two-box model from *Sowers et al.* [2002] as displayed in their Figure 2 (data have been digitized from the figure). Note that those scenarios were primarily constrained by ice core measurements. Here n/m is not measured.

al. [2003a], which shows that the constraints imposed by the firn air profiles were adequate to deduce the temporal isotope trends of atmospheric N$_2$O in the recent past. Though the absolute error ranges reported in both studies are similar, we report here robust 2 σ errors, whereas in the firn air study the range of isotope trends was more loosely quantified: An atmospheric isotope scenario was classified acceptable if the firn model results matched the measurements within the 1 σ errors. Furthermore, the firn air trends were only constrained by few data points, basically the bottom air samples. Thus the present results give a more robust and tighter constraint on the temporal isotope trends. For $\delta^{15}N$ they confirm the best estimate given by *Röckmann et al.* [2003a], whereas for $\delta^{18}O$ they show that the trend is at the low end of the range reported from the firn air study.

[16] On the other hand, the isotope histories shown in Figure 2 of *Sowers et al.* [2002] are clearly different: The $\delta^{15}N$ trend is about 40% smaller and the $\delta^{18}O$ trend is a factor of 2 larger than the new high-precision results. It is important to note that *Sowers et al.* [2002] used the ice core measurements to constrain their two-box model, not the firn air measurements, thus in our Table 1 atmospheric histories derived from ice core measurements are compared with those from firn air and the new direct measurements. Apparently, the scenarios constrained by the ice core data do not lead to a realistic estimate of present isotope trends in atmospheric N$_2$O. The fact that the scenarios from the ice core data do not agree with their firn air measurements was already noted by *Sowers et al.* [2002]. The firn air results alone imply that $\delta^{15}N$ changes are almost twice as large as $\delta^{18}O$ changes, similar to our results, whereas from the ice core data much larger trends are determined for $\delta^{18}O$ than for $\delta^{15}N$. *Sowers et al.* [2002] suggest that this may indicate a "decoupling" of the $\delta^{18}O$ and $\delta^{15}N$ evolutions. This would mean that the model used to construct the scenarios, i.e., that the concentration and isotope changes since preindustrial times are due to one single "anthropogenic" N$_2$O source with a constant isotopic composition, may not be adequate. It is indeed conceivable that individual parts of a composite "anthropogenic" source with differing isotopic composition contributed differently throughout the model period so that the isotopic composition of the source was effectively not constant. If the total atmospheric N$_2$O isotope changes derived from the ice core samples by Sowers et al. are estimated correctly, this must have occurred for both, $\delta^{15}N$ and $\delta^{18}O$, but in opposite directions. For $\delta^{15}N$, the temporal trends presented here and from the firn air data [*Röckmann et al.*,

2003a; *Sowers et al.*, 2002] would indicate that the "anthropogenic" source was more depleted in the second half of the 20th century than before, since the recent trends are stronger than those required to account for the total difference since preindustrial times. Conversely, recent $\delta^{18}O$ trends would not be sufficient to explain the total depletion since preindustrial times. Thus the "anthropogenic" source would have been more depleted initially than during the second half of the 20th century.

[17] Whereas such a "decoupling of $\delta^{15}N$ and $\delta^{18}O$" [*Sowers et al.*, 2002] could certainly provide interesting information about N$_2$O source changes in the past, we believe that more precise measurements on the isotopic composition of N$_2$O from ice cores are required to confirm that this is actually the case. The experimental error in the ice core measurements from *Sowers et al.* [2002] is considerable. The six ice core samples reported in the paper span a range of 1.8‰ in $\delta^{15}N$ and 2.6‰ in $\delta^{18}O$, thus the respective total isotope change since pre-industrial times of 1.9‰ in $\delta^{15}N$ and 2.9‰ in $\delta^{18}O$ [*Sowers et al.*, 2002] is actually not well constrained, and it is hard to draw well-founded conclusions. In fact, new measurements on a small set of ice core samples from the North GRIP and Berkner Island ice cores [*Bernard et al.*, 2005] indeed show a larger total decrease since preindustrial times for $\delta^{15}N$ compared to $\delta^{18}O$, in better agreement with the firn air and direct atmospheric observations, although for those ice core measurements errors are also large.

[18] *Röckmann et al.* [2003a] determined the intramolecular distribution of ^{15}N in N$_2$O from the firn air samples. The data in Table 1 show a clear discrepancy between the Neumayer and the firn air results. Whereas the error bars for the derived temporal $^1\delta^{15}N$ trends slightly overlap, for $^2\delta^{15}N$ the trend deduced from the new measurements is significantly smaller than from the firn air measurements. Note, however, that $^1\delta^{15}N$ and $^2\delta^{15}N$ are not independent, since they are calculated from measurements of the central nitrogen atom and the sum of both. Thus they must add up to the average and it is therefore useful to compare not the absolute values but rather the relative fractionation at the two positions. The firn air results indicated similar trends at both positions, whereas the new measurements suggest a much stronger temporal trend for $^1\delta^{15}N$ than for $^2\delta^{15}N$ (although with quite large errors as discussed above). Whereas the present analyses were carried out with higher analytical precision for an individual measurement, the firn air samples from the greatest depth were much older and the observed isotope differences were larger, thus compensating

for the lack in precision. A possible source of error is the nonlinearity of the NO^+ fragment ion measurement in the mass spectrometer. In the old measurements, the nonlinearity was carefully calibrated [*Röckmann et al.*, 2003a], and in the present study the problem was circumvented by using adjusted injection times, so this effect cannot explain the difference. Although unlikely, a possible difference in the diffusion constants for $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ could bias the results in the firn air study, but no information is presently available. Given the difficulty and comparatively high errors in the fragment ion analyses to determine position-dependent $\delta^{15}N$ values, which may depend on mass spectrometer source conditions that change over time, we cannot exclude that the difference is due to systematic measurement errors. On the other hand, the difference could be an atmospheric signal, since the trends from the firn air measurements are primarily constrained by the lowest, i.e., oldest, samples and not by the isotope history of the recent years. This would be an indication for a "decoupling" of sources for the two individual ^{15}N signatures over the second half of the 20th century. However, it is unlikely that the relative trends for the individual ^{15}N positions are so different in the past decade compared to only $30-50$ years ago for a trace gas with such a long lifetime. At present the origin of the discrepancy is not understood. A new set of firn air measurements supports the previous finding that fractionations at the two positions are rather similar [*Bernard et al.*, 2005].

[19] The negative temporal isotope trends deduced from the Antarctic air samples also strengthen the results derived from the global isotope budget calculations of the firn air measurements in the work of *Röckmann et al.* [2003a]. The isotopic fingerprint derived there for the anthropogenic N_2O source indicated that primarily emissions from soils are responsible for the increase of N_2O since preindustrial times. As the new results confirm the $\delta^{15}N$ and $\delta^{18}O$ trends derived from the firn air samples, those conclusions about the nature of the "anthropogenic" source are also confirmed. *Yoshida and Toyoda* [2000] first suggested that emissions from soils should also leave an isotope signal in the intramolecular distribution of ^{15}N: They observed significant variability in the intramolecular distribution of ^{15}N close to N_2O sources and argued that N_2O emitted from soils was the end member that is depleted in $^1\delta^{15}N$ and has an enhanced difference between the positions ($^2\delta^{15}N$-$^1\delta^{15}N$), the so-called "site preference." Thus increased soil emissions should lead to lower $^1\delta^{15}N$ values and an increasing value for ($^2\delta^{15}N$-$^1\delta^{15}N$). The present data would confirm that this is indeed the case, whereas the firn air data do not support this hypothesis.

5. Conclusions

[20] The combined atmospheric concentration and isotope measurements presented here show that the increase in N_2O mixing ratio since 1990, which contributes more than 25% to the global increase since preindustrial times, is associated with a well-defined isotope signal. For $\delta^{15}N$ and $\delta^{18}O$, the isotope trends presented here are now the best-constrained temporal trends for the isotopic composition of N_2O in the last decade. Furthermore, these data are from measurements on actual air samples collected on a well-defined date, which do not require any further processing. On the other hand, firn or ice core air samples generally have broad age spectra, and concentration and isotope profiles are considerably affected by diffusion and gravitational separation. Thus the temporal trends are deduced using sophisticated modeling, and the results depend strongly on porosity and diffusivity profiles at the sampling sites. Although the present measurements only cover a comparatively short period of time, they are not subject to such additional errors. The new results are consistent with the earlier firn air results for $\delta^{15}N$ and $\delta^{18}O$, which confirms the validity of the firn air modeling approach. On the other hand, the position-dependent ^{15}N results reveal a clear discrepancy to the firn air study, which may be due to either unaccounted-for physical processes or systematic errors in the intramolecular ^{15}N measurements. The good agreement for $\delta^{15}N$ and $\delta^{18}O$ between the Neumayer and firn air studies supports the "single source" assumption at least for the past 50 years. Improved ice core N_2O isotope measurements with enhanced precision are required to investigate a possible decoupling of $\delta^{15}N$ and $\delta^{18}O$ in earlier times. We believe that there is presently no solid evidence for such a decoupling.

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